

**Fundamental Study on Carrier Transport in
Si Nanowire MOSFETs
with Smooth Nanowire Surfaces**

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Abstract

This thesis studied the fabrication process of Si nanowires (NWs) with smooth surface and the carrier transport in Si NW MOSFETs with a diameter about 10 nm and below, which are aimed for future building block devices in Si LSIs. Si planar MOSFETs have been miniaturized extremely and their gate length has reached below 50 nm, which causes severe short-channel effects (SCEs), and further scaling may become very difficult due to SCEs. Si NW MOSFETs are expected to be used in an ultrascaled LSI technology with the gate length of 10 nm and below because they have superior control on SCEs thanks to their very small channel dimension and three-dimensional gate structures, which improve electrostatic controllability.

However, carrier transport characteristics in Si NWs have not been fully clarified yet, and there are several factors that hamper the understanding of the carrier transport in Si NWs. In NWs, quantum confinement effect (QCE) modifies electronic band structures and density of states (DOS), which strongly affect on carrier transport. However, the physical understanding and anisotropy of QCE on holes in Si NWs are insufficient. To investigate the inherent nature of the carrier transport in NWs, the control of the surface roughness and width fluctuation is indispensable, because surface roughness can limit the carrier mobility in ultrathin Si NWs and the width fluctuation might induce localization of carriers, which can cause unintentional Coulomb blockade. However, the surface-smoothing process of Si NWs has not been well established.

In this thesis, three important and fundamental issues for realizing the application of Si NW MOSFETs for LSIs are studied: fundamental comprehension of QCE on holes, formation technique of very smooth Si NWs, and one-dimensional carrier transport characteristics in smoothed Si NWs.

In Chapter 2, QCE on holes in Si NWs is theoretically investigated. To focus on the anisotropy of the band structure, hole states in rectangular-shaped NWs with various aspect ratios and transport orientations of [001], [110], [111], and [112] are calculated. By using a nearest neighbor $sp^3d^5s^*$ tight binding model, the relationship between the band structure and p orbital states is analyzed. The orientation dependence of the hole effective mass (m^*) is $[111] < [110] < [112] < [001]$ in square NWs. However, the band structure and m^* in [110] Si NWs exhibit strong anisotropy with respect to the confinement directions. m^* of [110] NWs rapidly increases as the width along $[1\bar{1}0]$ increases, whereas it is insensitive

to confinement in the $[001]$ direction. On the other hand, m^* of $[111]$ NWs does not show notable confinement anisotropy. From these observations, $[111]$ NWs with any aspect ratios and $[110]$ NWs with thin $[1\bar{1}0]$ width and wider $[001]$ width are desirable for high-performance hole transport. These anisotropic behaviors are explained from the character of p orbitals that form subbands.

In Chapter 3, fabrication process of thin Si NWs is established with a top-down method using electron-beam lithography (EBL), RIE, and sacrificial oxidation on (110) silicon-on-insulator (SOI) substrates, focusing on the suppression of structural fluctuations that can arise in patterning processes. Hydrogen silsesquioxane (HSQ) resist, which is a high-resolution negative tone EBL resist with small line-edge roughness, and Cl_2 -based inductively-coupled-plasma (ICP) RIE at a low bias-rf power are used to realize reliable pattern transfer to SOI. After the sacrificial oxidation, Si NWs down to $6\text{ nm} \times 9\text{ nm}$ are successfully fabricated in $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ directions, and width fluctuations are suppressed below 2–3 nm.

To realize further reduction of width fluctuations and surface roughness of Si NWs, surface-smoothing processes are investigated in Chapters 4 and 5.

In Chapter 4, hydrogen chloride (HCl) gas etching is studied for Si surface smoothing. It is found that HCl gas etching at atmospheric pressure and 1050°C can flatten the bare Si(100) surface down to 0.08 nm in RMS roughness with a low etching rate $< 10\text{ nm/min}$. However, strong surface-pattern dependence of the etching rate (loading effect) is observed, which can lead to the loss of etching controllability for nanostructures. Through experiments and thermochemical calculation, SiCl_2 diffusion in the gas phase is identified as the rate-limiting step. The loading effect is attributed to the pattern-dependent diffusion of SiCl_2 , which is confirmed by gas diffusion simulation. From these observations, the methodology to weaken the loading effect is discussed.

In Chapter 5, hydrogen annealing is studied for Si surface smoothing. In low-temperature ($\leq 850^\circ\text{C}$) hydrogen annealing, surface preparation to reduce surface contaminations, in particular, trace surface oxygen, is a key. It is found that the surface oxidation caused by the ultra-pure water rinse after HF-based wet cleaning results in failure in surface flattening by hydrogen annealing. In this thesis, HF-based cleaning followed by rinse in low-pH solution (HCl) is proposed as an effective surface preparation for hydrogen annealing. In addition to this, the hydrogen flow rate and pressure are optimized from the viewpoint of contamination control in hydrogen ambient. As a result, simultaneous atomic-level flattening of Si(100), (110), and (111) bulk surfaces is realized at a low-temperature of 810°C by a short-time (2 min) annealing at 75 Torr, which are well-designed annealing conditions for the flattening of Si NWs.

In Chapter 6, hydrogen annealing developed in Chapter 5 is applied to Si NWs with various sizes and wire axes of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$. It is found that hydrogen annealing can smoothen width fluctuations and surface roughness, but NWs with small diameter break during annealing via surface atom diffusion. The minimum diameter of

survived NWs is about 10, 18, 21, 23 nm for $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs, respectively. These threshold diameters are smaller than previous reports on hydrogen annealing at a comparable temperature. This improvement probably originates from the lower surface diffusion coefficient of Si atoms at higher hydrogen pressure. The diameter of NWs with a short length (140 nm) decreased via diffusion of Si atoms on NWs to anchors, and its speed was $\langle 100 \rangle > \langle 111 \rangle \gtrsim \langle 112 \rangle > \langle 110 \rangle$, which is the reverse order of wire stability. This result suggests that strong anisotropy in surface self-diffusion of Si atoms exists on the NW surface and that the speed of diffusion is strongly correlated with the wire instability.

In Chapter 7, gate-all-around Si NW MOSFETs are fabricated by applying surface-smoothing hydrogen annealing, and their transport properties are characterized. The effective hole mobility of thin Si NWs with different orientations was characterized from NW PMOSFETs with parallel 750 NWs at room temperature. In Si NWs in $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ with a diameter of 11–13 nm, hole mobilities are about 90–120 $\text{cm}^2/\text{V}\cdot\text{s}$ at the surface carrier density of $1 \times 10^{13} \text{ cm}^{-2}$. Hole mobility degradation was observed in thinner $\langle 110 \rangle$ NWs down to 7 nm and the mobility decreases from $\sim 110 \text{ cm}^2/\text{V}\cdot\text{s}$ to $\sim 80 \text{ cm}^2/\text{V}\cdot\text{s}$ as the NW diameter decreases from 15 nm to 7 nm. These mobilities are, however, still comparable to or higher than bulk MOSFET's universal hole mobility on (100), which offers promising prospects of Si NW MOSFETs in ultrascaled technologies. In a NW MOSFET with a single NW channel which can operate as both NMOSFET and PMOSFET, oscillation is observed in transconductance characteristics (g_m – V_G). The oscillation is modeled by the modulation of the carrier scattering rate by one-dimensional density of states. The calculated g_m oscillation based on the band structure obtained by the tight-binding method (reproducing the actual cross-sectional shape of NWs characterized by transmission electron microscopy) shows very good agreement with experiments, and the spacing of the oscillation corresponds to the subband splitting. This result indicates that subband structures in Si NWs are observable through g_m and that they are well predicted by theoretical band structure calculation.

In Chapter 8, conclusions and the suggestion of future work are given.

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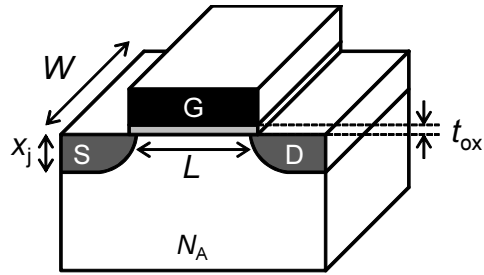
Chapter 1

Introduction

1.1 Background

The progress of electronic technology has always transformed and enriched our lives. It goes without saying that the advent of transistors has opened the immense possibility of solid-state electronics. A particular emphasis should be placed on the invention of a semiconductor integrated circuit by J. Kilby and R. Noyce in 1958. A tiny but sophisticated “stone” made of silicon (Si) has brought us an easy access to complicated information and signal processing at high speed, which had previously required very large and specialized installations. Now that a wide variety of devices involved with home appliances, industrial machines, transportation, finance, medical care, communications, energy consumption, and securities etc., as well as obvious computers, receive the full benefit of integrated circuits and significantly improved their efficiency and effectiveness, integrated circuits are indispensable to modern society. With prospective demand rises in developing countries, need of higher performance and efficiency in information processing is growing more and more, and the further performance improvement of integrated circuits is highly expected in the future.

Over the last four decades, miniaturization has been the main guiding principle of the performance improvement of integrated circuits which are based on conventional planar metal-oxide-semiconductor field-effect transistors (MOSFETs) technology. By reducing the size of planar MOSFETs vertically and horizontally and the supply voltage at the same rate, which is a “scaling rule” proposed by R. H. Dennard *et al.* in 1974 [1], higher operating speed and integration density are achievable keeping energy-consumption density unchanged. The schematic of the main concept of Dennard’s scaling theory is shown in Fig. 1.1. The miniaturization has worked effectively, and the prediction known as Moore’s law in 1965 [2], which states that the number of components (transistors) on an integration increases at an exponential rate, has been still valid at present. In fact, as the application of integrated circuits increases, the size of MOSFETs and the integration degree have been scaled explosively. In 1971, the world’s first microprocessor 4004 by Intel had 2,300 transistors and was fabricated in a 10 μm process. However, the dimension of the state-of-the-art



Parameters	Symbols	Scaling Factors
Device dimension	L, W, t_{ox}, x_j	$1/k$
Doping concentration	N_A	k
Voltage	V	$1/k$
Current	I	$1/k$
Capacitance	C	$1/k$
Delay	CV/I	$1/k$
Power dissipation	IV	$1/k^2$
Power density	IV/area	1

Figure 1.1: Dennard's scaling theory for miniaturization of planar MOSFETs [1].

processes is now below 50 nm, and the number of the transistors on a chip is in the order of a billion. In such an extremely small-scale MOSFET, several technological challenges have appeared. Accordingly, pursuing “More Moore” by further scaling of MOSFETs has faced difficult problems.

Several examples of scaling-related issues are listed here. An extremely thin gate SiO_2 insulator less than 3 nm has induced direct tunneling of gate leakage. In addition, the depletion capacitance in a polycrystalline silicon (poly-Si) gate has become nonnegligible with such a thin gate insulator, which induces the reduction of inversion charges in the channel [3]. To scale the depletion layer thickness, the doping concentration in the channel region should be increased. However, this might lead to mobility degradation owing to Coulomb scattering and surface-roughness scattering because of an increased effective transverse electric field [4]. In a small device with a high channel doping concentration, threshold voltage variation coming from a random number and position of dopant atoms becomes obvious (random dopant fluctuation: RDF) [5]. Otherwise, it is impossible to increase the channel doping indefinitely because of the breakdown of p - n junctions. From the viewpoint of fabrication process, the formation of ultrashallow source/drain regions with steep dopant profiles is a challenge. Moreover, the scaling theory requires the reduction of supply and threshold voltages. Meanwhile, it is difficult to scale threshold voltage because the subthreshold slope is limited by the thermal energy. From these difficulties, the ideal scaling has not been performed, which induced short-channel effects. As a result, several problems have appeared including the roll-off/variation of threshold voltage with the gate length [1, 6, 7], the degradation of subthreshold swing [8], and drain-induced barrier lowering [9]. These problems arise from inadequate electrostatic controllability by the gate to get rid of the effect of source and drain. Increased leakage current and resulting static power consumption are severe problems in large-scale integrations (LSI) since they cause significant heat generation and operation failure even when the circuit is inactive.

1.2 Technology Boosters for More Moore in MOSFETs

To overcome the difficulties related to device scaling, several novel technologies have been introduced to MOSFETs. These technologies are called as “technology boosters” and contribute to the enhancement of device performance outside a simple scaling.

For instance, SiO_2 as a gate insulator has been replaced with dielectric materials with higher dielectric constant κ . These high- κ gate dielectrics can increase gate capacitance while keeping enough thickness to suppress direct electron tunneling through the gate insulator. Hf-based oxide materials (HfO_2 and HfSiO_x , for example) are typically used at present. High- κ materials, however, are incompatible with poly-Si gate because of the charge interaction between them [10], and it causes Fermi level pinning (threshold voltage

pinning) and increased carrier scattering (mobility degradation). These problems can be alleviated by using metal gates and thus high- κ technology is used with metal gates. Metal gates can also resolve the poly-Si depletion problem.

To obtain high on/off ratio ($I_{\text{ON}}/I_{\text{OFF}}$) of drain current, high channel mobility is favorable. To improve channel mobility, strained-Si technology has been adopted. Appropriate strain induces the split of energies of valleys or bands with light effective mass m^* from those with heavy m^* . As a result, electrons and holes occupy the bands with light m^* rather than heavy m^* , which reduces averaged conductivity mass. In addition, the energy splitting of bands can reduce carrier scattering between different bands (interband or intervalley scattering) [11]. From these effects, strained-Si exhibits higher mobility than unstrained Si.

These new techniques have already been applied to planar Si MOSFETs in LSIs (first mass production of strained-Si: 90 nm in 2004 [12], high- κ /metal gate: 45 nm in 2008 [13], both from Intel). These technologies can alleviate short-channel effects and have helped scaling in recent years, but they do not provide fundamental solutions of short-channel effects. For this reason, it is expected that planar MOSFETs do not meet performance demands at 14 nm node and beyond (Fig. 1.2) [14]. Therefore, new device structures that can suppress short-channel effects are required.

The main idea to suppress short-channel effects is using (1) thin Si body with two-dimensional and three-dimensional structures to fully deplete the Si channel and (2) multiple gate structure [15]. In thin Si body, it is hard for electric field lines from source and drain to penetrate through, and thus source and drain give less effect on the channel. Multiple gate helps to improve this effect and also contributes to terminate electric field lines from source and drain. Before now, many types of thin body and multigate devices have been proposed. Some examples are shown in Fig. 1.3: (a) ultra thin body (UTB) single gate MOSFET [UTB SOI (silicon-on-insulator) MOSFET], (b) double gate SOI MOSFET (XMOS) [16], (c) trigate MOSFET or DELTA (fully-DEpleted-Lean-channel TrAnsistor) [17], (d) FinFET [18], and (e) surrounding gate or gate-all-around MOSFET [19, 20]. The difference between DELTA (trigate) and FinFET was originally the use of hard mask to eliminate the top-face channel, but recently FinFET has included trigate geometries. In these structures, channel doping is no longer necessary because the depletion layer thickness is restricted by the Si body thickness. Consequently, problems related to channel doping, RDF in particular, are suppressed, which contributes to the reduction of variability. Among these proposed structures, trigate MOSFETs combined with high- κ /metal gate and strained-Si technologies on bulk Si substrate were practically adopted in 22 nm process by Intel in 2012 [21]. To step into extremely-scaled technologies about 10 nm and below, however, further suppression of short-channel effects will be necessary.

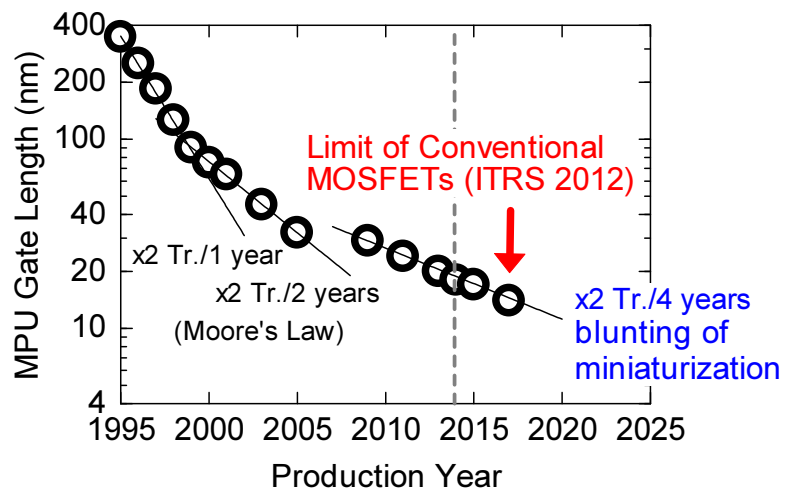


Figure 1.2: Past and future trends of gate length of planar MOSFETs in micro processing unit (MPU) from International Technology Roadmap for Semiconductors 2001–2012 [14].

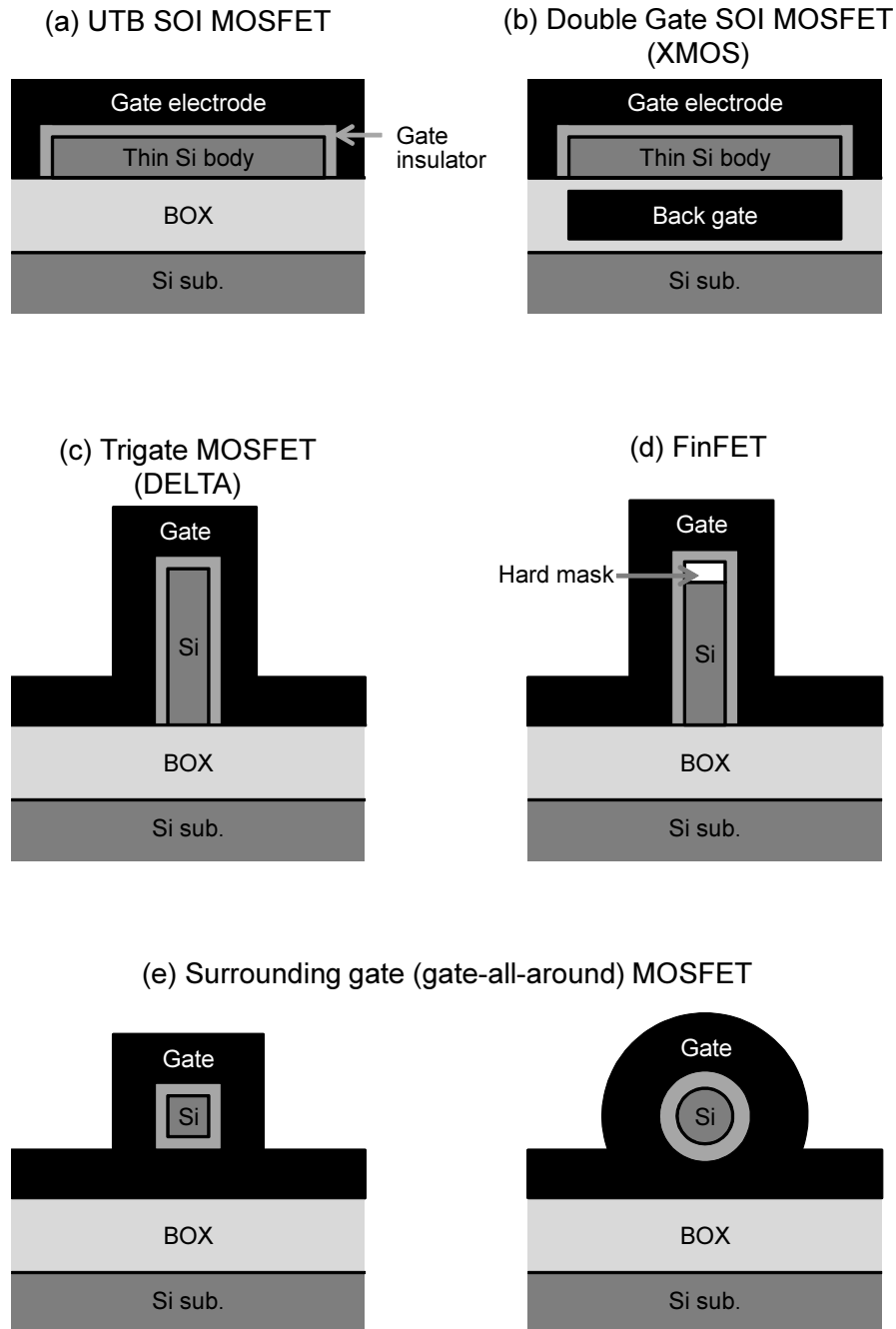


Figure 1.3: Schematics of representative examples of SOI and multigate MOSFETs for ultra-scaled LSI technologies. These figures illustrate in the cross-sectional plane perpendicular to the channel direction.

1.3 Si Nanowire MOSFETs for Extremely-Scaled LSI Technologies

1.3.1 Device Concept

As a new structure to suppress short-channel effects in ultra-short channel devices, Si nanowire (NW) MOSFETs have been proposed. This device is descended from three-dimensional trigate and gate-all-around MOSFETs. In Si NW MOSFETs, extremely thin wire-shaped Si channel with nanoscale diameters, typically several to tens nm, is used and the channel is fully or partially surrounded by the gate to realize further improvement of immunity to short-channel effects. A schematic image of Si NW MOSFETs is shown in Fig. 1.4.

In the last decade, many successful fabrication studies of NW MOSFETs with ultrashort channel length of about and sub 10 nm have been reported [22–28], and a NW MOSFET with a diameter down to 3 nm was also reported [29]. These studies have already demonstrated superior short channel performance. For example, a 10-nm-thick NW PMOSFET with 5-nm gate length exhibits nearly ideal subthreshold slope of 65 mV/decade with high $I_{\text{ON}}/I_{\text{OFF}}$ over 10^5 [22]. However, because of the nanoscopic dimension of NWs, quantum effect might affect carrier transport properties in very thin Si NWs. From this viewpoint, the carrier transport in Si NWs has not been fully understood.

1.3.2 Quantum Confinement Effect

When the cross-sectional size of nanowires becomes comparable to the quantum-mechanical wavelength of carriers, whose situation happens in Si NWs with a diameter of about 10 nm and below, the transverse motion of carriers is restricted. This is called quantum confinement effect (QCE). QCE alters the electronic state in Si NWs from that in bulk. To understand the carrier transport in Si NWs, the comprehension of QCE is important.

By QCE, the wavefunction of carriers becomes standing wave in the confinement plane. For each different confined wave mode, free carrier motion is possible along the NW. This results in the split of the band structure into subbands. Assume that the motion of electrons in parallel (z -axis) and perpendicular (x - and y -axes) directions is separable and that it can be treated by a simple effective mass theory with effective masses of m_x^* , m_y^* , and m_z^* . If the confinement potential at NW surfaces is assumed to be infinitely high, the wavefunction $\psi(x, y, z)$, quantum-confinement energy ε , and the subband structures $E(k)$ in a rectangular

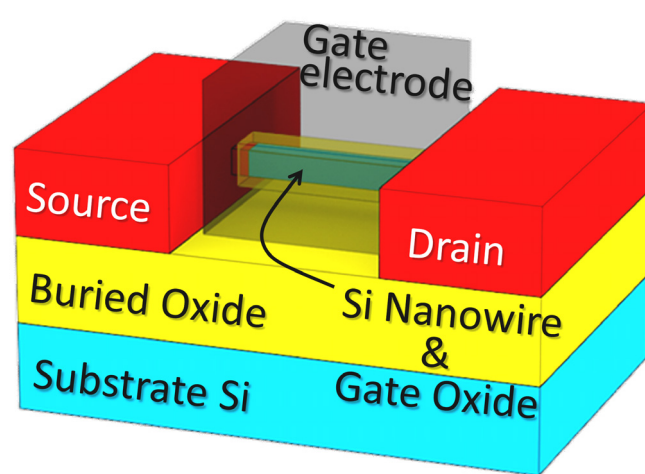


Figure 1.4: Schematic structure of Si NW MOSFETs.

NW with the widths of w_x and w_y and the length of L are given by [30]

$$\psi(x, y, z) = \frac{2}{\sqrt{w_x w_y}} \frac{1}{\sqrt{L}} \sin \frac{\pi n_x x}{w_x} \sin \frac{\pi n_y y}{w_y} \exp(ikz), \quad (1.1)$$

$$\varepsilon_{n_x, n_y} = \frac{\pi^2 \hbar^2}{2} \left(\frac{n_x^2}{m_x^* w_x^2} + \frac{n_y^2}{m_y^* w_y^2} \right), \quad (1.2)$$

$$E_{n_x, n_y}(k) = \frac{\hbar^2 (k - k_{0z})^2}{2m_z^*} + \varepsilon_{n_x, n_y}. \quad (1.3)$$

Here, n_x and n_y are quantum numbers that discriminate different modes in x and y directions, respectively, and k_{0z} is the wave number of band minima (or maxima) where QCE is considered. As can be seen in Eq. (1.2), the energy splitting depends on the wire size and m^* . Since Si has anisotropy in effective masses of electrons and holes, the band structure of Si NWs is expected to be strongly dependent on the transport and confinement directions as well as the NW size. In addition to the subband splitting, the density of states [DOS, $N(E)$] is modulated by QCE. DOS of bulk Si is proportional to $\sqrt{E}$, but that of NWs is proportional to $1/\sqrt{E}$ [30]

$$N(E) = \sum_{n_x, n_y} \frac{g_{\text{spin}}}{2\pi\hbar} \sqrt{\frac{2m_z^*}{E - \varepsilon_{n_x, n_y}}} \quad (g_{\text{spin}}: \text{spin degeneracy}). \quad (1.4)$$

DOS of NWs has singular points which go infinity at the bottom of each subband, which is characteristics unique to one-dimensional electronic structures.

To obtain subband structures in Si NWs, multiple valleys and their anisotropic effective masses should be taken into account. Here one example is given: the conduction band structure in a [001]-oriented square cross-sectional NWs (elongated to z -axis). Fig. 1.5(a) shows the 1st Brillouin zone of Si and its important symmetry points and axes. Here, a_0 is the lattice constant of bulk Si (5.431 Å) [31]. The conduction band minima of Si are six equivalent valleys located on six Δ axes at positions of $\pm 85\%$ from Γ to X, as indicated in Fig. 1.5(b). Each valley is approximated by spheroid elongated to Δ with transverse and longitudinal effective masses (m_t^* and m_l^*) of $m_t^* = 0.19m_0$ and $m_l^* = 0.92m_0$, respectively [Fig. 1.5(c)] [31]. The valleys at $\pm k_z$ have heavy $m^* = m_l^*$ along the NW (z -axis) and have light $m^* = m_t^*$ in the confinement (x - y) plane. This small confinement m^* leads to larger energy shift. From these observations, one can say that the subbands originating from $\pm k_z$ bulk valleys become heavy (m_l^*) and they are located at off- Γ positions in one-dimensional k -space in the NW. On the contrary, the valleys at $\pm k_x$ and $\pm k_y$ have light $m^* = m_t^*$ along the NW, while the confinement effective mass has two components of light and heavy $m^* = m_l^*, m_t^*$. The heavy component of confinement m^* makes quantum-confinement energy shift small. Accordingly, $\pm k_x$ and $\pm k_y$ valleys constitute four-fold subbands with small subband splitting at Γ and their transport mass is small (m_t^*). The energy of the first subband at Γ is lower than that at off- Γ and thus the conduction band minimum in the NW has light effective mass $m_t^* = 0.19m_0$. Since the averaged conductivity effective mass in bulk

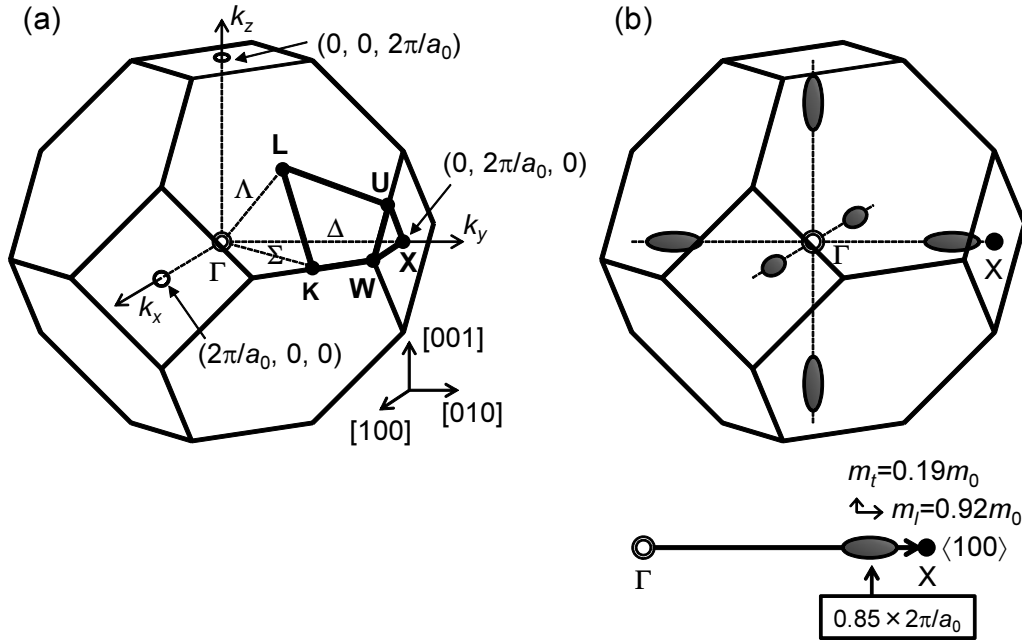


Figure 1.5: (a) Reciprocal space of diamond-type structure (face-centered cubic Bravais lattice) and its important symmetry points and axes. (b) Schematic of energy contour around the conduction band minima of bulk Si. Conduction band valleys are approximated by equivalent six spheroids located at positions of $\pm 85\%$ from Γ to X . The transverse and longitudinal effective masses are $0.19m_0$ and $0.92m_0$, respectively. a_0 is the lattice constant ($5.431 \text{ \AA}$).

Si is $3m_t^*m_l^*/(2m_l^* + m_t^*) = 0.26m_0$, the effective mass of Si NWs can become smaller than that in bulk if subband splitting is large enough compared to the thermal fluctuation of carriers. By using Eq. (1.2), Eq. (1.3), and Eq. (1.4), the band structure and the density of states of a 5.3-nm-thick square [001] Si NW was calculated and they were compared with the result of more detailed calculation with a $sp^3d^5s^*$ tight-binding model [32] in Fig. 1.6 (The calculation method by the tight-binding model is described in Chapter 2 and Appendix A). The agreement of general features of the band structure described above is good between the simple effective-mass approach and detailed tight-binding, although there exist differences in detailed structures such as small lift of degeneracy, subband energies at high-energy regions, and precise value of transport effective masses. In NWs in other orientations, similar understanding is still valid by applying a unitary transform of effective mass tensor into NWs' principal axes [33].

To understand the QCE-induced band structure change in Si NWs, many theoretical studies have been performed [33–43]. As a general rule, the conduction band structure can be understood from the energy dispersion of bulk Si. By considering the nonparabolic nature of energy dispersion in the bulk conduction band, detailed size and orientation dependences of effective mass and the deviation of energy level from a simple effective mass equation are explainable [42, 44].

On the other hand, QCE in the valence band is more complex and simple picture which is used for electrons is not available. The valence band is formed by bonding p -orbital states. Resulting from the three characters of p orbitals (p_x , p_y , and p_z), the valence band in bulk Si has three different components. At the valence band maximum (VBM), there are light hole (LH) and heavy hole (HH). LH has small effective mass with weak anisotropy in energy dispersion, whereas HH has large effective mass and exhibits strongly anisotropic dispersion. Energy dispersions of LH and HH in Si are shown in Fig. 1.7(a) and (b), respectively. Owing to the spin-orbit coupling, the last component among the three is separated from VBM by 45 meV [31]. This band is referred to as split-off hole (SOH). SOH has small effective mass and weak anisotropy. The dispersion is shown in Fig. 1.7(c). Since the energy splitting by spin-orbit coupling is small, SOH also plays a role in hole transport. In NWs, QCE mixes up these states together and thus these bulk states cannot be treated separately. This is obvious from the fact that theoretical calculations of the valence band of Si NWs have reported that VBM has generally small effective mass [35, 36, 38, 39, 45], while simple single-band treatment predicts that VBM becomes heavy band due to its small confinement energy. Hence, easy but physically proper interpretation of QCE on holes in Si NWs is demanded, whereas this is still missing.

1.3.3 Carrier Transport in Si Nanowires

The carrier transport characteristics in Si NW MOSFETs is expected to be different from that of bulk planar MOSFETs. First of all, QCE strongly affects the carrier transport

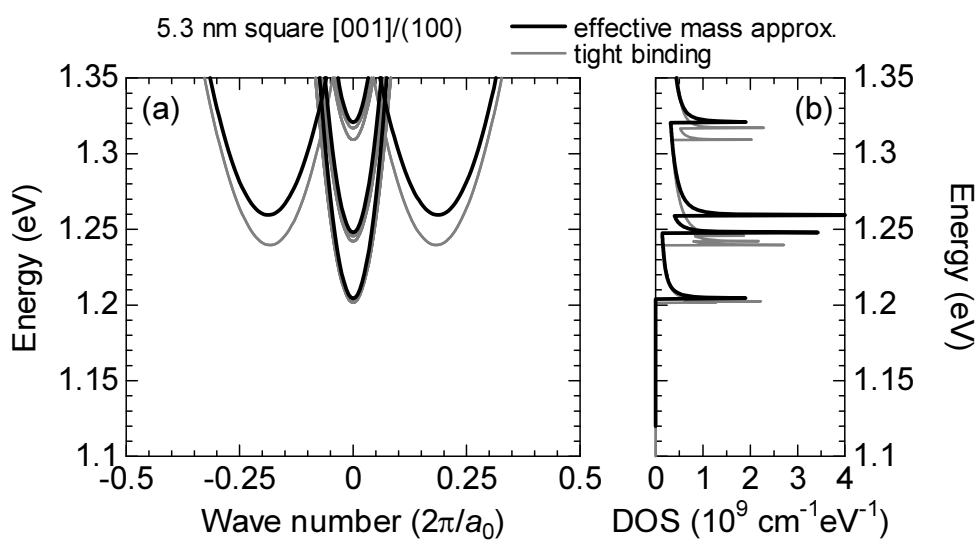


Figure 1.6: Conduction band structure (a) and density of states (DOS) (b) of a 5.3-nm-thick square cross-sectional [001]/(100) Si NW calculated by simple effective mass approximation (black) and $sp^3d^5s^*$ tight-binding method (gray).

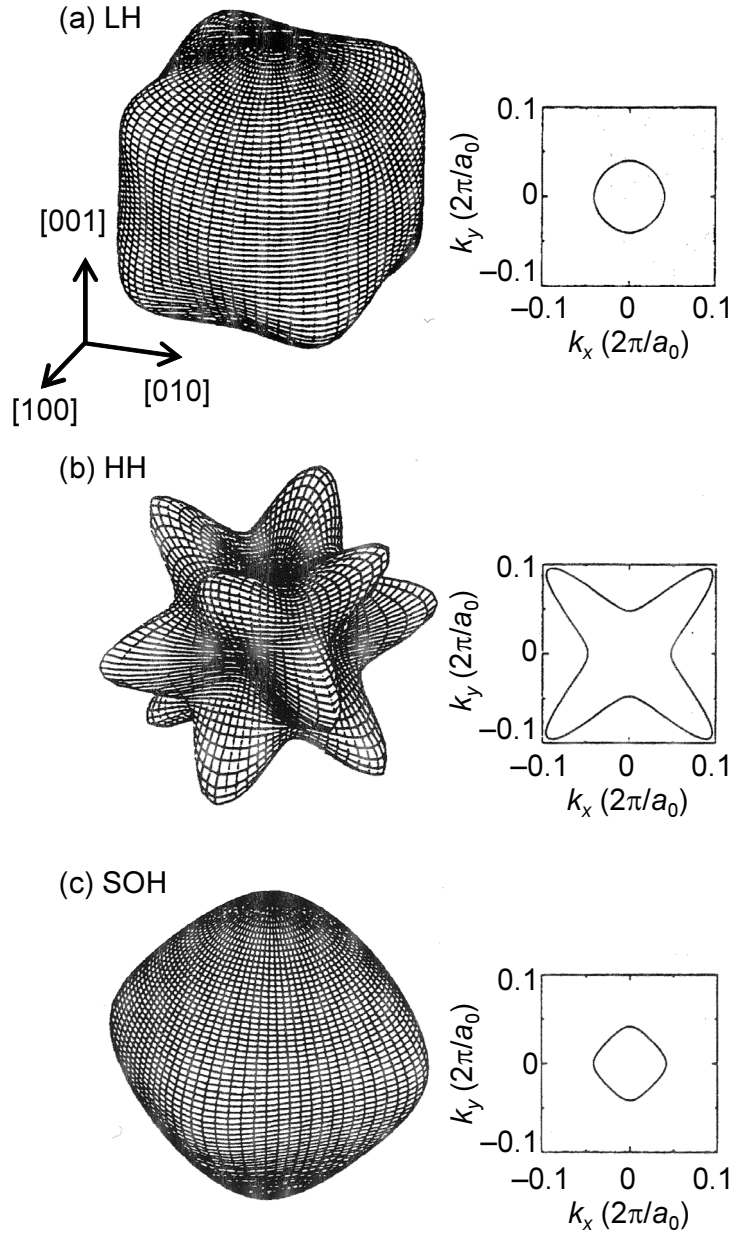


Figure 1.7: Energy contour plots (40 meV from each band edge) of (a) light hole, (b) heavy hole, and (c) split-off hole in bulk Si, reproduced from Ref. 46.

through the modification of the electronic states. For example, the transport effective mass m^* is related to carrier mobility μ in diffusive transport and carrier injection velocity v_{inj} in ballistic transport as $\mu \propto 1/m^*$ and $v_{\text{inj}} \propto 1/\sqrt{m^*}$. The energy splitting modulates carrier scattering because intervalley scattering, which strongly affects electron mobility of bulk Si at room temperature [46], might be reduced with sufficiently large subband splitting.

Secondly, one-dimensional k space can also modifies carrier scattering. Considering the case of elastic scattering and sufficiently large subband splitting in very thin NWs, the electron at k_z can be scattered only to the state at $-k_z$, while there are vast amount of destinations in two-dimensional or three-dimensional $\mathbf{k}$ spaces, which can contributes to the reduction of scattering rate [47]. On the other hand, more detailed theoretical calculations of carrier scattering rates and mobility found significant decrease in carrier mobility in thin quantum wires [48–50]. In a tiny space, the overlap of wavefunctions between initial and final states in scattering (form factor) increases [46], and it takes over the effect of reduction in final k states available in the scattering [50, 51]. Therefore, the scattering rate increases. Several recent theoretical studies, however, suggest that phonon-limited hole mobility in thin (3–10 nm) [110] and [111] Si NWs increases as the diameter decreases thanks to a significant valence band modification (light-band/heavy-band splitting) [52–54]. An experimental study also reported hole mobility improvement in thinner [110] NWs (10 nm $\times$ 9 nm and 4 nm $\times$ 9 nm) compared to NWs with larger widths, although this study also report re-degradation in much thinner NWs [55].

Finally, one-dimensional oscillating DOS and subband structures are expected to affect the transport properties of NW MOSFETs. As increasing the gate voltage, carriers are induced and the Fermi level (E_F) in the NW channel increases and subbands are filled subsequently. When E_F passes over the bottom of subbands, DOS around E_F suddenly increases. Since the carrier scattering rate is proportional to available DOS at final states, this sudden increase results in the sudden decrease in the mobility. Therefore, carrier mobility can show oscillation with the change of gate voltage [56, 57]. In addition, the rapid change of DOS might cause the oscillation of gate capacitance resulting from steep increase of carrier density when E_F passes by the bottom of subbands [58–60]. These mobility and capacitance oscillation can be observed through the oscillation of transconductance g_m because it is proportional to the mobility and gate capacitance. Since these oscillatory features reflect the nature of one-dimensional electronic states, the experimental observation of these phenomena helps with understanding of subband structures. However, different oscillation can happen from the nonideality in NWs. The width fluctuation along the wire length causes subband energy fluctuation along the channel. Carriers can localize in pockets of the energy (Fig. 1.8). These pockets are equivalent to quantum dots and therefore Coulomb blockade oscillation can happen in NWs [61]. So far, experimental current and transconductance oscillation have been reported in Si NW MOSFETs from many groups [56, 62–66]. These studies attribute the oscillation to one-dimensional electronic states, but do not mention the effect of width fluctuation. Therefore, further analysis and experimental

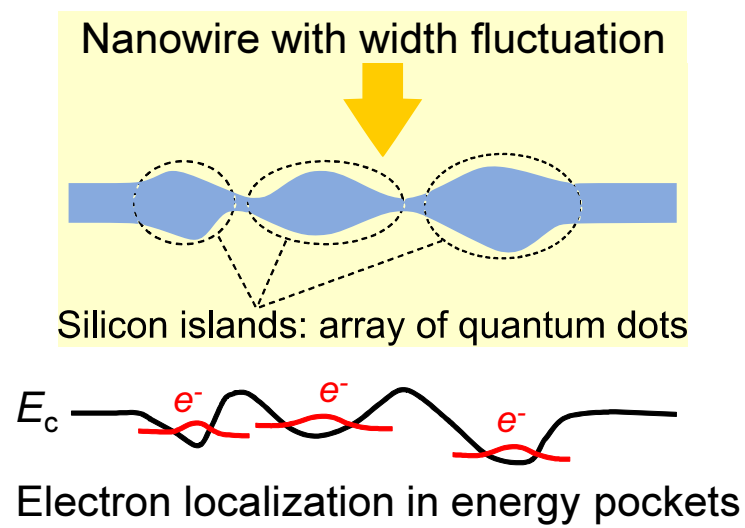


Figure 1.8: Illustration of width fluctuation in Si NWs and resulting electron localization effect.

study are necessary to determine the origin of oscillations.

1.3.4 Key Issues in Nanowire MOSFETs

As described above, QCE gives significant effects on carrier transport in Si NWs. As stated in Sec. 1.3.2, QCE on holes is less easy to understand than that on electrons and fundamental comprehension of QCE in NWs with various orientations and confinement directions is missing. Since NW MOSFETs will be used in complimentary logic, the understanding of hole transport, as well as electron transport, is important.

The experimental observation of carrier transport unique to one-dimensional electronic states such as mobility degradation/improvement by modified band structures and current/conductance oscillations is also an important issue. Carrier mobility is a fundamental transport parameter and the investigation of carrier mobility in NWs with various confinement conditions such as different sizes and orientations is essential for designing NW MOSFET devices with high transport performance. Experimental determination of carrier mobility of NWs has been reported so far, and several studies have reported carrier mobility in (sub-)10-nm NWs [28, 55, 67–73]. However, the reported mobilities vary largely, and thus further investigation is necessary. In addition, if the subband structure affected by QCE is understood by current oscillation behaviors, it helps the understanding of the relationship between subband structures and transport performance such as mobility. To observe such phenomena, however, structural fluctuations of NWs such as width fluctuations and surface roughness should be minimized because they might hinder the one-dimensional transport through Coulomb blockade and surface roughness scattering. Surface roughness scattering may become more severe in narrower NWs than phonon scattering [53, 57]. Experimental studies on mobility in NWs also suggest that mobility in thin NWs is limited by surface roughness [74] especially in [110] NW pFETs [28, 75], which is expected to exhibit potentially-high hole mobility [53, 54]. Several methods to flatten width fluctuations and surface roughness of NWs have been proposed so far: hydrogen etching [76], hydrogen annealing [27, 77, 78], active oxidation [79], and basic solution etching [80]. However, the behavior of these techniques has not been well understood and further investigation is required.

1.4 Purpose and Outline of This Thesis

In this thesis, three important and fundamental issues for realizing the application of Si NW MOSFETs to LSIs are studied: fundamental comprehension of QCE on holes, formation technique of very smooth Si NWs, and one-dimensional carrier transport characteristics in smoothed Si NWs.

In Chapter 2, QCE in the valence band in Si NWs is theoretically investigated. To focus on the anisotropy of the band structure, hole states in rectangular-shaped NWs with

various aspect ratios and transport orientations of $[001]$, $[110]$, $[111]$, and $[112]$ are calculated. From the results, NW structures promising for p-channel FET devices are proposed. In addition, physical understanding of anisotropic behavior of band structures is given from the viewpoint of p orbitals which constitute hole states.

In Chapter 3, fabrication process of thin Si NWs is established with a top-down method using electron-beam lithography, reactive ion etching, and sacrificial oxidation, focusing on the suppression of structural fluctuations that can arise in patterning processes. Si NWs are fabricated on a (110) SOI substrate and in orientations of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$. Si NWs down to $6\text{ nm} \times 9\text{ nm}$ are successfully fabricated and width fluctuations are suppressed below 2–3 nm.

To realize further reduction of width fluctuations and surface roughness, investigation of surface-smoothing process is performed. In Chapter 4, hydrogen chloride (HCl) gas etching is studied as a surface smoothing process. It is found that HCl gas at atmospheric pressure and around 1050°C can flatten the surface of bare Si, but that it shows strong surface pattern dependence of the etching rate, which can lose controllability in the etching of nanostructures. From the elaborate investigation of etching-limiting process, the origin of the etching-pattern dependence is figured out and the strategy to avoid pattern-dependent etching is suggested. In Chapter 5, hydrogen annealing is studied for Si surface smoothing. In low-temperature annealing which is applicable for nanowire annealing, surface preparation is important to avoid the failure in annealing caused by surface contamination, in particular, trace surface oxygen. From the speculation of initial oxidation of Si surface, hydrogen fluoride wet treatment and subsequent rinse in low-pH solution are proposed as an effective surface preparation for hydrogen annealing. Then, simultaneous smoothing of Si(100), (110), and (111) bulk surfaces is established with a low-temperature and short-time annealing conditions which are compatible with NWs.

In Chapter 6, hydrogen annealing is applied to Si NWs along $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ and its capability to flatten width fluctuations and surface roughness is investigated. In addition, the orientation dependence of stability and shape deformation of NWs in hydrogen annealing is studied. In this study, NWs with smaller diameters are successfully smoothed compared to previous reports, and the reason is discussed from the viewpoint of hydrogen pressure.

In Chapter 7, gate-all-around Si NW MOSFETs smoothed by hydrogen annealing is fabricated and their transport properties are characterized. From the low-temperature characteristics of single-NW-channel devices, current and transconductance oscillation behaviors and its relationship to theoretically calculated one-dimensional electronic states are examined. In addition, hole mobility in Si NWs with different orientations is experimentally extracted from multiple-nanowire-channel PMOSFETs with wire orientations of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$.

In Chapter 8, conclusions of this thesis and suggestion of future work are given.

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Chapter 2

Theoretical Investigation of Orientation-Dependent Quantum Confinement Effect on Holes in Si Nanowires

2.1 Introduction

Carrier transport characteristics in semiconductors are significantly affected by their electronic band structures. Thus, sufficient understanding of the band structure of Si nanowires (NWs) is essential to predict the device performance of Si NW MOSFETs. As mentioned in the introductory chapter 1, the band structure of Si NWs is modulated from that of bulk Si crystal because of the quantum confinement effect (QCE). General feature of conduction band (CB) in Si NWs is explainable by a simple effective mass approximation (EMA). However, as the size of NWs decreases, EMA overestimates confinement-induced energy shifts and change of effective mass from bulk values appears. These features can be explained from the nonparabolicity of CB valleys in bulk Si at higher kinetic energies [1–4], and more importantly, the bulk E - $\mathbf{k}$ dispersion in the three-dimensional $\mathbf{k}$ space itself is sufficient to explain QCE on electrons. These facts indicate that the single-band picture can be a good approximation for electron states of Si NWs and that the interaction between equivalent six CB valleys is small. However, when similar discussion based on the bulk E - $\mathbf{k}$ dispersions is applied to the valence band (VB) of Si NWs treating heavy hole (HH) and light-hole (LH) dispersion independently, it may derive inaccurate results in thin NWs below 10 nm [5]. Simple interpretation seems unavailable for VB.

To investigate QCE on holes in Si NWs, many theoretical studies have been reported, and they have obtained some common results. For example, [001] Si NWs exhibit large hole effective mass at VB maximum (VBM) and [110] and [111] NWs show small mass [5–8]. The light effective mass subbands are separated from heavy ones in small NWs, and thus

high transport performance in the ballistic-transport regime is expected in [110] and [111] NWs [5, 6, 9]. In addition, in the diffusive (scattering-limited) transport regime, hole mobility in [110] and [111] NWs can become higher than that in bulk Si [9–12]. The same tendency of orientation-dependent effective mass is also reported for other diamond- and zincblende-type semiconductor NWs such as Ge [6], InP [13, 14], and InAs [14]. However, the origin of this property is still unclear even though the physical understanding of this result is essential to discuss the transport performance of Si NWs. Moreover, these results are obtained mainly in NWs with highly-symmetric cross-sectional shapes such as circle and square. To understand the profound physics of QCE on holes, the study on anisotropic nature in rectangular NWs is important. However, limited studies on rectangular Si NWs have been performed so far [15, 16].

This study attempted to understand the behavior of QCE on holes in Si NWs comprehensively by theoretical calculation. To investigate the effects of quantum-confinement conditions such as width, height, and orientation of NWs, the author calculated the VB structure and hole effective mass of rectangular cross-sectional Si NWs with a wide range of the aspect ratio. In addition, atomic-like-orbital-decomposed wavefunction was calculated because p orbitals may contribute to the anisotropy in QCE on holes. From the calculation, it is found that the main properties of the subbands such as effective mass and quantization energy are clearly attributed to the character of p orbitals which constitute the state of the subband.

2.2 Calculation Method of Valence Band Structures

2.2.1 $sp^3d^5s^*$ Tight-Binding Method

There are several useful methods to calculate the detailed electronic state of Si NWs. They are classified into two groups, a first-principles method and an empirical method. The first-principles method, which is typified by the density functional theory, calculates the electronic state of a new material without using any empirical assumptions. Therefore, it is useful to predict the electronic state of unknown and novel materials and structures. However, the first-principles calculation is significantly computationally demanding especially when the unit cell of the target structure is large, which is the case of NWs. The empirical method calculates the electronic state of materials using some empirically-determined parameters and approximations. Therefore, this method involves arbitrariness to some extent. However, by using an appropriate model and parameters, the electronic state of Si can be calculated accurately.

Major empirical calculation techniques for the calculation of NWs include a tight-binding approximation and a $\mathbf{k} \cdot \mathbf{p}$ method. In the tight-binding method, the wavefunction is described by a linear combination of atomic orbitals bound to each atom and the calculation is based on the interactions between orbitals in the potential formed by atomic nuclei. This

method is suitable for nanostructures owing to its atomistic formulation. Moreover, the information of atomic orbitals which contribute to the states can be easily analyzed thanks to the atomic-orbital basis, which makes it easier to analyze properties of the VB of Si NWs since hole states in Si NWs are strongly affected by the anisotropy of p orbitals. The $\mathbf{k} \cdot \mathbf{p}$ method calculates the band structure around a given wave number point $\mathbf{k}$ by considering the perturbation from interactions between different bands. This method gives good results around the given $\mathbf{k}$ point, but it cannot calculate the band structure in the whole first Brillouin zone, while the tight-binding method can. For these reasons, this study used the tight-binding method.

This study employed the nearest-neighbor $sp^3d^5s^*$ tight-binding method [17–19], which describes the VB states of Si with keeping a clear view of electronic structures. This method considers one s orbital, three p orbitals $\{p_x, p_y, p_z\}$, five d orbitals $\{d_{yz}, d_{zx}, d_{xy}, d_{3z^2-r^2}, d_{x^2-y^2}\}$, and one excited s^* orbital. The coordinate axes of x , y , and z are fixed to the $[100]$, $[010]$, and $[001]$ directions, respectively. The effect of spin-orbit (SO) coupling [20] is included in this study. To distinguish up-spin and down-spin states for each atomic orbital, twice the number of atomic orbitals are necessary, *i.e.* the orbital set becomes $\mathcal{B} = \{s, p_x, p_y, p_z, d_{yz}, d_{zx}, d_{xy}, d_{3z^2-r^2}, d_{x^2-y^2}, s^*\} \otimes \{\uparrow, \downarrow\}$. The calculation with SO coupling produces more accurate results deservingly, whereas it should be noted that the VB structure and effective mass of thin (< 5 nm) NWs are not very sensitive to the SO interaction. Surface dangling bonds were passivated by sp^3 hybridization scheme [21], which brings a situation similar to hydrogen termination. The $sp^3d^5s^*$ parameter set of Si was taken from Ref. 19. The detailed formulation of the tight-binding method including SO coupling and the surface treatment is given in Appendix A.

2.2.2 Calculated Nanowire Structures

To capture the effects of quantum confinement, square and rectangular cross-sectional Si NWs were calculated in this study. The results of rectangular NWs give us information about the anisotropy of quantization effect in different crystal orientations. The axial orientation and two side faces were determined as $[001]/(100)/(010)$, $[110]/(001)/(\bar{1}\bar{1}0)$, $[111]/(11\bar{2})/(\bar{1}10)$, and $[112]/(11\bar{1})/(\bar{1}10)$. The detailed crystal structures and geometry settings are illustrated by ball-stick images in Fig. 2.1. In the square case, the height and width were varied from 1 nm to 13 nm. In the rectangular case, the height was kept constant at 2 nm while the width was varied from 1 nm to 13 nm. In our calculation, the effect of strain, relaxation, and surface reconstruction were neglected. The bonds between Si atoms were assumed to be ideal sp^3 bonds, and the bond length was set at 2.352 Å, the same value as in bulk Si (the lattice constant of bulk Si is $a_0 = 5.431$ Å [22]).

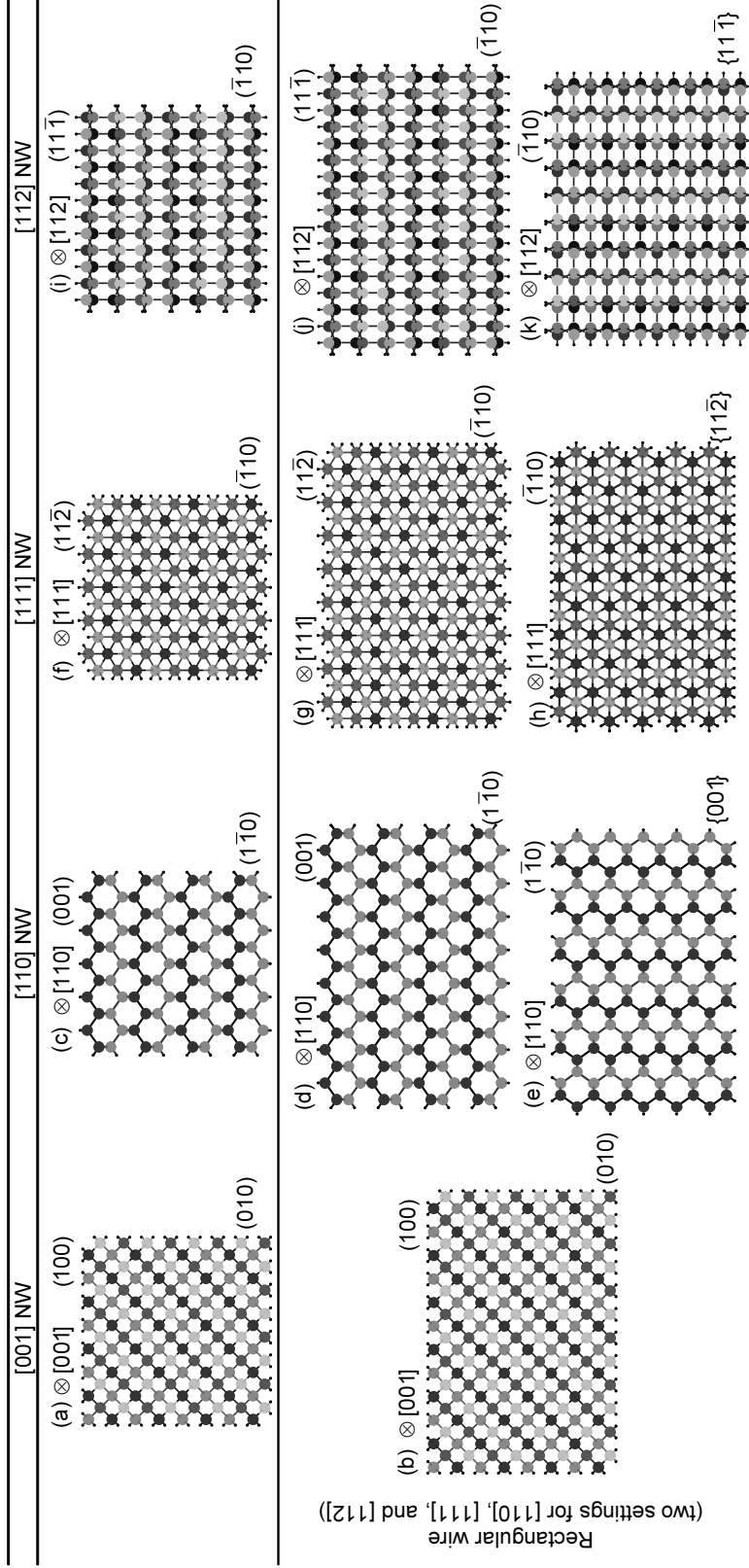


Figure 2.1: Ball-stick structures of calculated Si NWs. This figure illustrates NWs with the height of approximately 2 nm. Surface bonds with small black balls indicate the passivated sp^3 bonds. Each figure illustrates (a) [001] square, (b) [001] rectangular, (c) [110] square, (d) [110]/(001) rectangular, (e) [110]/(110) rectangular, (f) [111] square, (g) [111]/(112) rectangular, (h) [111]/(110) rectangular, (i) [112] square, (j) [112]/(111) rectangular, and (k) [112]/(110) rectangular NWs.

2.2.3 Analysis of Contribution of Atomic Orbitals from Tight-Binding Wavefunction

As briefly mentioned above, the tight-binding wave function with a wave number vector $\mathbf{k}$, $\Psi(\mathbf{k})$, is expressed as a linear combination of Bloch sums $\Phi_{\alpha m}(\mathbf{k})$ of atomic-like orbitals (labeled $m \in \mathcal{B}$) centered at an equivalent atom position (labeled α) over N unit cells constituting the NW:

$$\Phi_{\alpha m}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_l e^{i\mathbf{k} \cdot (\mathbf{R}_\alpha + l\mathbf{T})} \phi_m(\mathbf{r} - \mathbf{R}_\alpha - l\mathbf{T}), \quad (2.1)$$

$$\Psi(\mathbf{k}) = \sum_\alpha \sum_m c_{\alpha m}(\mathbf{k}) \Phi_{\alpha m}(\mathbf{k}), \quad (2.2)$$

where ϕ_m is the wave function of Si's Löwdin orbital [23] of m , $\mathbf{R}_\alpha$ is a direct vector to the Si atom labeled α , $\mathbf{T}$ is the translation vector of the NW crystal. By diagonalizing the tight-binding Hamiltonian matrix at a given $\mathbf{k}$, energy levels, E , and superposition coefficient of each Bloch sum, $[c_{\alpha m}]$, are obtained as eigenvalues and eigenvectors, respectively. From the obtained coefficient vector corresponding to a certain state, the author defines the degree of contribution of atomic orbitals, which represents how much the orbital is involved in this state. For example, the degree of contribution from the p_x orbital is defined by $\sum_\alpha \sum_{\sigma=\uparrow, \downarrow} |c_{\alpha p_x^\sigma}|^2$, where p_x^σ indicates the p_x orbital with the spin state of σ . The cases of the other orbitals are defined in the same way. By calculating the contribution of each orbital, the author investigated the relationship between the character of wave function and properties of the VB structure. It is a great strength of the tight-binding method that these analyses can be performed straightforward.

2.3 Results

2.3.1 [001] Nanowires

In the $sp^3d^5s^*$ tight-binding method, the state space of VBM of bulk Si (heavy, light, and split-off holes) is built by the orbital set of $\{p_x, p_y, p_z, d_{yz}, d_{zx}, d_{xy}\} \otimes \{\uparrow, \downarrow\}$ [19]. It was found that this result holds true in NWs because the incorporation of s , $d_{3z^2-r^2}$, $d_{x^2-y^2}$, and s^* components by quantum confinement is very small. Therefore, the degree of contribution is calculated only for these six characters of p and d orbitals. To emphasize the fact that the directionality of these orbitals is elongated along the three axes of NWs' geometry ($[100]/[010]/[001]$), $p_x, p_y, p_z, d_{yz}, d_{zx}$, and d_{xy} are denoted as $p_{100}, p_{010}, p_{001}, d_{100}, d_{010}$, and d_{001} , respectively. These notations of p and d orbitals are generalized down to the orbitals with the directionality in $[lmn]$ as

$$p_{lmn} \equiv (lp_x + mp_y + np_z) / \sqrt{l^2 + m^2 + n^2}, \quad (2.3)$$

$$d_{lmn} \equiv (ld_{yz} + md_{zx} + nd_{xy}) / \sqrt{l^2 + m^2 + n^2}. \quad (2.4)$$

In addition, p_{lmn} and d_{lmn} are put into the single denotation $|lmn\rangle$ in this thesis because they are classified into the same symmetry character when they are arranged in a diamond-type lattice.

Figure 2.2 shows the hole effective mass and contribution of each atomic orbital at VBM in square cross-sectional [001] Si NWs as a function of the width. Hole effective mass of [001] NWs takes a minimum at a width of 2 nm and increases as the width departs from the minimum point. The contribution of atomic orbitals exhibits a characteristic change responding to the change in the effective mass. It is clearly observed that the p_{001} orbital, which is the main component of VBM, makes a maximum contribution when the effective mass becomes minimum and its fraction decreases as the effective mass increases. The width dependence of composition of the d_{001} orbital, whose symmetry character is the same as p_{001} , is similar to that of p_{001} , whereas the magnitude of contribution from d_{001} is less than about one fifth of that from p_{001} . From this result, one may say that $|001\rangle$ is actually the p_{001} orbital. This holds also true for $|100\rangle$, $|010\rangle$, and other orbital characters of $|lmn\rangle$ defined for NWs in other orientations that appear later in this section. The degree of contribution from p_{100} and p_{010} orbitals exhibits the minimum at the minimum point of the effective mass and increases with the increase in the effective mass, which is an opposite change to the case of the p_{001} orbital. In summary, a hole state with a larger fraction of p orbital along the transport direction and smaller along the confinement directions exhibits smaller effective mass.

Figure 2.3 shows the width dependence of hole effective mass and degree of contribution of p and d orbitals at VBM in rectangular [001] Si NWs. The height of NWs ($h_{[100]}$) is kept at 2.0 nm and the width ($w_{[010]}$) is variable. It is clearly observed that the effective mass takes minimum when the NW has a square cross section and becomes heavier rapidly when $w_{[010]}$ increases or decreases from 2 nm. This increase in the effective mass is easily understood from the variation of energy dispersion (Fig. 2.4). Only in the square case, the dispersion curve has a “small hill” at VBM, which gives smaller effective mass in square NWs. However, the energy range of this small hill is mere approximately 30 meV and thus the inherent nature of the top subband is considered as the band with heavy effective mass.

In rectangular NWs, the contribution from p_{001} exhibits maximum in the square case and decreases with the increase in the effective mass when the width is varied. This correspondence between the effective mass and the degree of contribution from p_{001} is the same as the case in square NWs. In addition, the contribution from p_{100} and p_{010} changes significantly by the change of the width in rectangular NWs. First, in the case of $h_{[100]} = w_{[010]}$, the contribution from the p_{100} and p_{010} orbitals is equal. However, in the case of $h_{[100]} < w_{[010]}$, the contribution from the p orbital along the width direction (p_{010}) increases and that from the p orbital along the height direction (p_{100}) decreases, and vice versa in the case of $h_{[100]} > w_{[010]}$. In other words, the p orbital parallel to the wider surface mixes into the VBM state with large amount in rectangular cross-sectional NWs, and thus the fraction of p_{001} decreases. Although above results are obtained for a very thin (2.0 nm) NW, similar

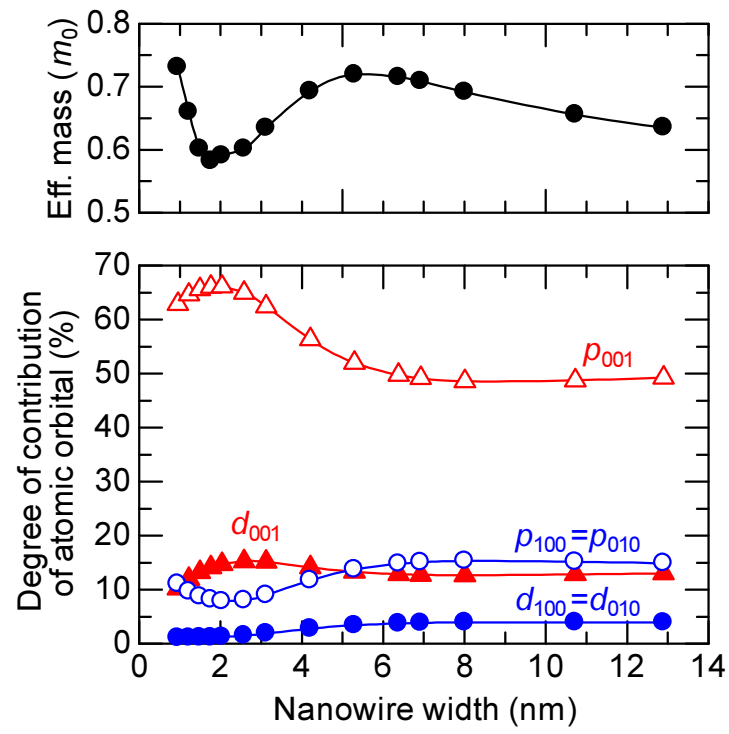


Figure 2.2: Hole effective mass and degree of contribution of atomic orbitals at VBM in square cross-sectional [001] Si NWs.

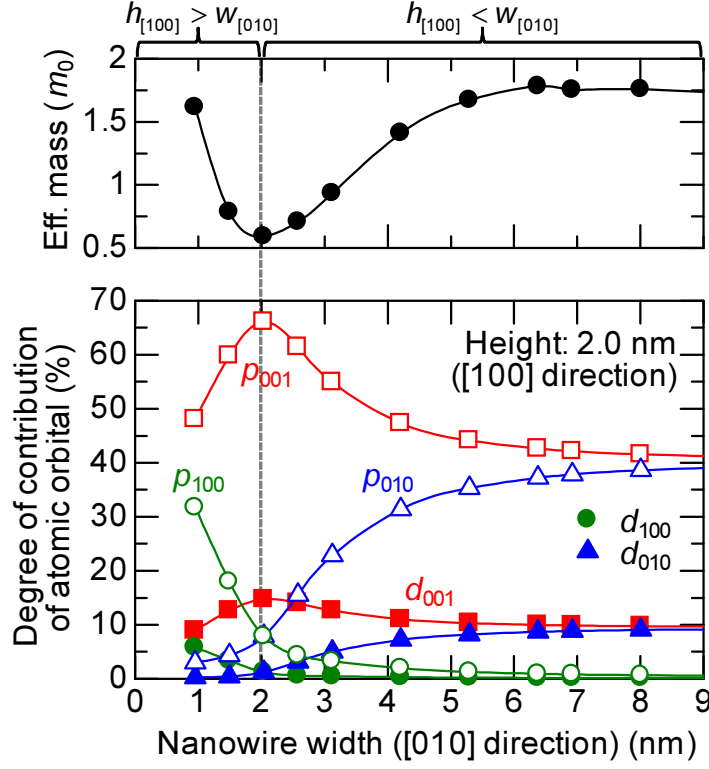


Figure 2.3: Hole effective mass and degree of contribution of atomic orbitals at VBM in rectangular cross-sectional $[001]$ Si NWs. The height ($h_{[100]}$) is kept at 2 nm and the width ($w_{[010]}$) is varied.

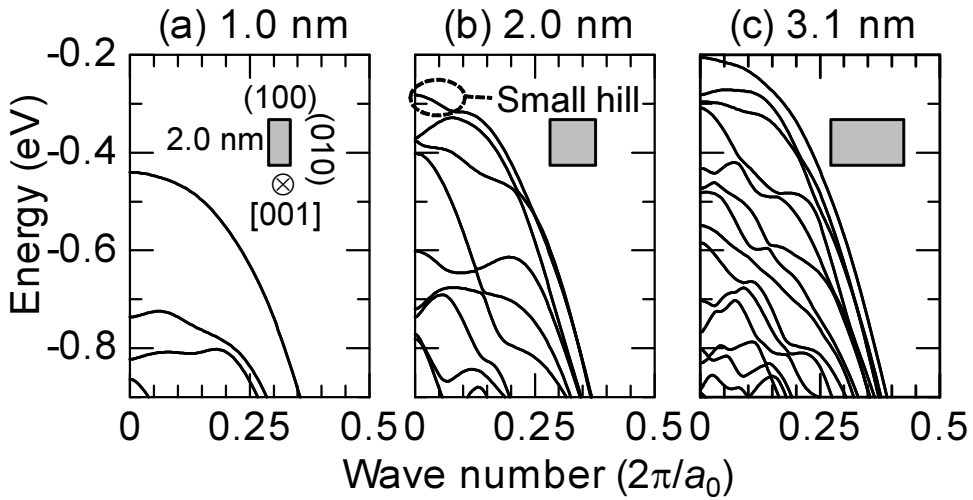


Figure 2.4: Valence band structure of 2.0-nm-high rectangular cross-sectional $[001]$ NWs, where the width is (a) 1.0 nm, (b) 2.0 nm, and (c) 3.1 nm. The energy is referenced from VBM of bulk Si. Inset rectangles indicate the cross-sectional shape of calculated NWs.

results were observed for 4.2-nm-high [001] NWs.

As mentioned above, the energy dispersion of the band structure in [001] Si NWs has a small hill and it seemed to have heavier effective mass at deeper energy. To evaluate these nonparabolic nature of the band structure, an averaged effective mass (m_{avg}^*) which is defined as the hole-density-weighted mean was calculated by the equation of

$$\frac{1}{m_{\text{avg}}^*} = \frac{\sum_n \int \frac{1}{m^*(k)} [1 - f_0(E_n(k) - E_F)] dk}{\sum_n \int [1 - f_0(E_n(k) - E_F)] dk}, \quad (2.5)$$

$$\frac{1}{m^*(k)} = \frac{1}{\hbar^2} \frac{d^2 E_n(k)}{dk^2}, \quad (2.6)$$

where n is the number that distinguishes each subband, $E_n(k)$ is the energy dispersion of the subband n , f_0 the Fermi-Dirac distribution, E_F the Fermi level. The integration is performed in the first Brillouin zone. In the calculation, the nondegenerate case was assumed ($E_F = 0.3$ eV above the bulk VBM) and the temperature was set at 300 K. Since the calculation of m_{avg}^* requires full E - k dispersion, this requires much longer computation time than the calculation of the effective mass at VBM. Therefore, m_{avg}^* was calculated for NWs with small cross-sectional sizes ($\lesssim 6$ nm). The averaged effective mass of square- and rectangular-shaped [001] NWs is shown in Fig. 2.5. In the square NWs, m_{avg}^* is larger than m^* at VBM. Its value is almost equal to $1.2m_0$ at larger sizes and slightly decreases with the NW size. Because the height of the “small hill” at VBM is few tens of millielectron volts, the warped nature of the first subband at deeper energies makes m_{avg}^* heavier. At smaller sizes, the height of the small hill increases, and the effect of heavy warped m^* dispersions at deep energies becomes small. Although VBM m^* slightly increases in NWs with the width < 2 nm, the effect of the hill-height increase is stronger than the change of VBM m^* and thus m_{avg}^* becomes smaller as the NW size decreases. In the rectangular NWs with the height of 2.0 nm, m_{avg}^* takes the minimum at the width of 2.0 nm and increases as the width increases or decreases, which reflects the width dependence of the effective mass at VBM (disappearance of the small hill) since the first subband is separated from the second in energy. In fact, the calculation of hole occupation in each subband revealed that about 80% or more holes exist at the first subband within the range of the NW width in this figure.

2.3.2 [110] Nanowires

In respect to [110]/(001)/(1 $\bar{1}$ 0) NWs, the p_x and p_y orbitals are unsuitable basis for atomic orbital analyses because they swap each other by symmetry operations which the crystal has. Hence p_{110} and $p_{1\bar{1}0}$ were used as the basis for p orbital analyses, where p_{110} and $p_{1\bar{1}0}$ are p orbitals along the [110] (transport) direction and the [1 $\bar{1}$ 0] (width or height) direction, respectively. At the same time, d_{110} and $d_{1\bar{1}0}$ are used for d orbitals. These four

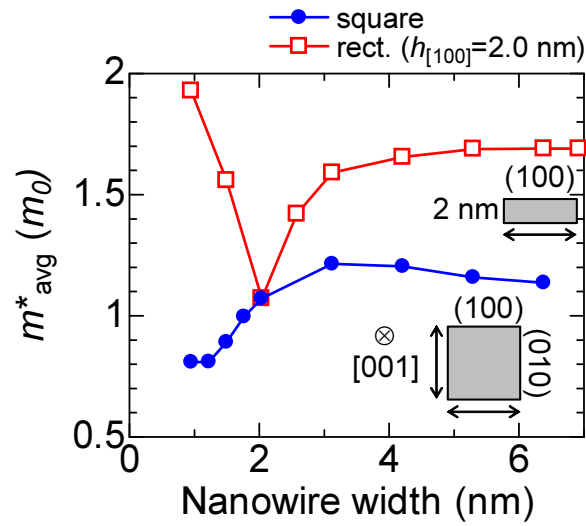


Figure 2.5: Width dependence of averaged effective mass m_{avg}^* in [001] square and rectangular NWs (nondegenerate, temperature: 300 K).

orbitals plus p_{001} and d_{001} form the orthonormal basis set for atomic orbital analyses. In practice, after constructing and diagonalizing the Hamiltonian matrix in the regular basis $\mathcal{B}$, unitary transform was performed into the new basis set, and the degree of contribution was calculated.

Figure 2.6 describes the width dependence of hole effective mass and contribution of each atomic orbital at VBM in square [110] Si NWs. The light-hole effective mass of bulk Si calculated by the same tight-binding method (w/ and w/o SO coupling) is also plotted in the figure. It is found that [110] NWs exhibit small effective mass close to that of bulk's light hole. In addition, the effective mass obtained in our calculation shows good agreement with first-principles calculations [7, 8]. From wave function analyses, it is revealed that the hole state at VBM in square NWs is well described by p_{110} , which is parallel to the transport direction.

Next, the results of rectangular NWs are described. There are two settings of geometry for rectangular cross-sectional [110] NWs: [110]/(001) [Fig. 2.1(d)] and [110]/(1 $\bar{1}$ 0) [Fig. 2.1(e)]. The width dependences of hole effective mass and the degree of contribution of atomic orbitals at VBM in 2.0-nm-high rectangular [110]/(001) Si NWs are plotted in Fig. 2.7. In the [110]/(001) geometry, the height and width directions are along [001] ($h_{[001]}$) and [1 $\bar{1}$ 0] ($w_{[1\bar{1}0]}$), respectively. In the case $w_{[1\bar{1}0]} \lesssim 4$ nm, the effective mass is as small as that in square [110] NWs. In the case $w_{[1\bar{1}0]} \gtrsim 4$ nm, however, the effective mass of the top subband increases with the width. The orbital analysis reveals that this variation of effective mass by the variation of $w_{[1\bar{1}0]}$ accompanies the variation of the main character of wave function from $|110\rangle$ to $|1\bar{1}0\rangle$.

This change of the effective mass and the character of wave function is due to the change in ordering of subbands that have different characteristics. Calculated band structure of 2.0-nm-high rectangular [110]/(001) Si NWs is shown in Fig. 2.8. The band structure of [110] NWs contains three different types of subbands — one with small effective mass (L band), another with large effective mass (H band), and the third with a shape like the right half of 'M' letter (M band). When $w_{[1\bar{1}0]} \lesssim 4$ nm, the L band forms VBM and the H band is located far below the top L band. The H band, however, increases its energy as the width increases and finally comes over the top L band, which results in the increase in effective mass at VBM. From atomic orbital analyses and the band structure, the character of the L and H bands is identified as $|110\rangle$ and $|1\bar{1}0\rangle$, respectively. The author performed additional wave function calculation for lower-energy states and confirmed that the M band has a character of $|001\rangle$. In fact, the formation of L , M , and H bands in [110] NWs is commonly observed by many theoretical calculations of not only Si NWs [5, 7, 8, 15, 16, 24–26] but also other diamond- and zincblende-type semiconductor NWs such as Ge [27, 28] and InP [13]. Of these studies, Leu *et al.* [24] conducted atomic orbital analyses and identified that the main component of the L and M band states is the p orbital with a character of p_{110} and p_{001} , respectively, by density functional theory. This agrees with our tight-binding results.

On the other hand, the situation is different in [110]/(1 $\bar{1}$ 0) rectangular NWs. In 1.9-

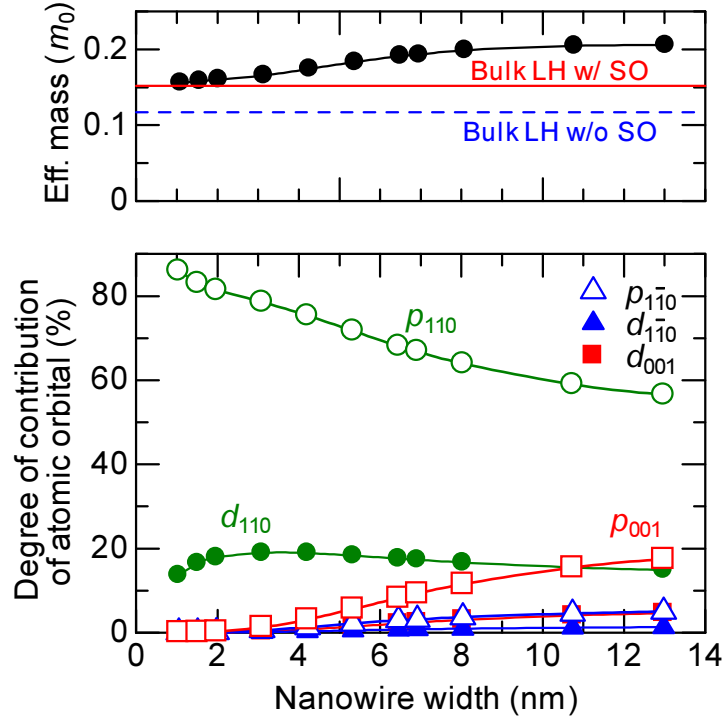


Figure 2.6: Hole effective mass and degree of contribution of atomic orbitals at VBM in square cross-sectional $[110]$ Si NWs.

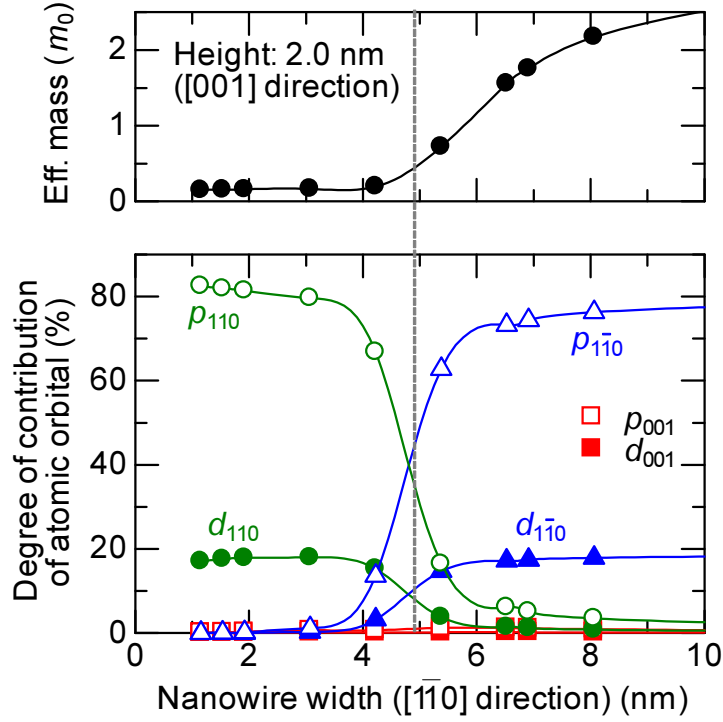


Figure 2.7: Hole effective mass and degree of contribution of atomic orbitals at VBM in rectangular cross-sectional $[110]/(001)$ Si NWs. The height along $[001]$ is kept at 2.0 nm and the width along $[1\bar{1}0]$ is varied.

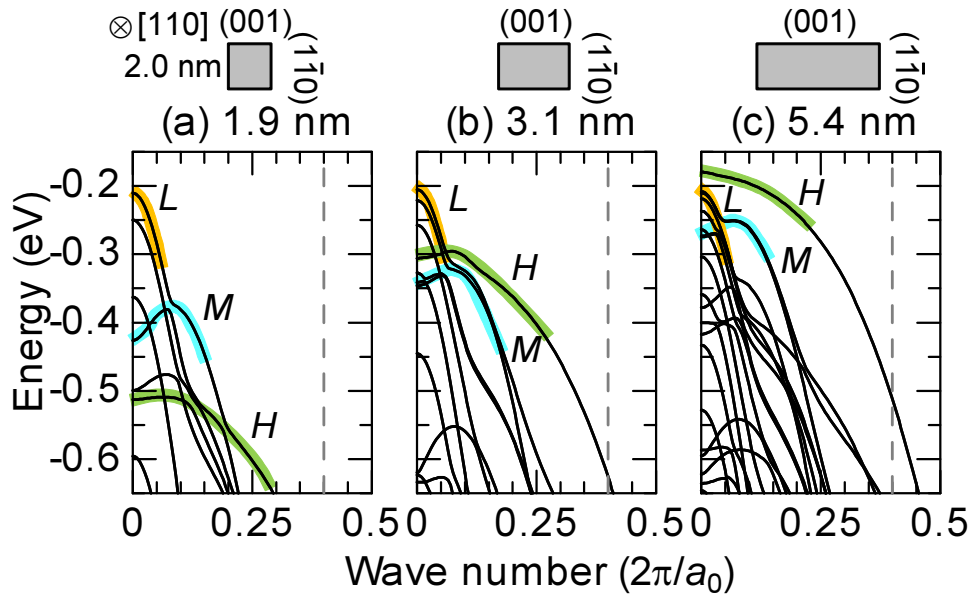


Figure 2.8: Valence band structure of 2.0-nm-high rectangular cross-sectional [110]/(001) NWs with widths of (a) 1.9 nm (square case), (b) 3.1 nm, and (c) 5.4 nm. The energy is referenced from VBM of bulk Si. Rectangles above each plot indicates the cross-sectional shape of calculated NWs. Band structure contains three different types of subbands: small effective mass subband (L band), half-M-shaped subband (M band), and large effective mass subband (H band). The gray dashed line indicates the position of $k = 0.4 \times 2\pi/a_0$, where the energy level of the topmost H band is analyzed in Fig. 2.9.

nm-thick $[110]/(1\bar{1}0)$ NWs with a width of 1–13 nm ($w_{[001]}$), the L band forms the topmost band at VBM and thus both hole effective mass and the mixture fraction of atomic orbitals almost maintain the value obtained in the 2 nm square $[110]$ NW. In addition, it is found that the energy of the H band is insensitive to the variation of $w_{[001]}$. The energy level of the topmost H band at $k = 0.4 \times (2\pi/a_0)$ in both 1.9-nm-thick $[110]/(1\bar{1}0)$ NWs and 2-nm-thick $[110]/(001)$ NWs are plotted as a function of the width ($w_{[001]}$ or $w_{[1\bar{1}0]}$) in Fig. 2.9. The energy level of H band is strongly dependent on the strength of $[1\bar{1}0]$ confinement but less susceptible to $[001]$ confinement. The origin of this anisotropic nature of the H band will be discussed in Section 2.4.2.

Here it should be noted that the results for $[110]/(001)$ NWs do not necessarily imply that the H band always has higher energy in sufficiently wide $[110]/(001)$ NWs. Actually, the band ordering depends on the NWs' height and the detailed crystal symmetry, and there are some cases that the energy of the H band does not exceed that of the L band. However, even in those cases, the difference of the energy level between the L and H bands is very small and comparable to the thermal energy at room temperature. What is essential is that the energy level of the L and H bands can become very close and the both bands may be involved in the hole transport.

The averaged effective mass (m_{avg}^*) of square and rectangular $[110]$ Si NWs was calculated and shown in Fig. 2.10. In the case of square NWs, m_{avg}^* and m^* of the first subband at VBM are comparable when the size is smaller than 3 nm. However, the m_{avg}^* gradually increases with the NW size and it reaches $0.5m_0$ at the width of 6.5 nm. This increase in m_{avg}^* regardless of size-independent and small VBM m^* is due to the increase in the energy of H and M bands at larger sizes. In rectangular $[110]$ NWs with the height of 2 nm, it is noticeable that the width dependence of m_{avg}^* is very similar to that of VBM m^* , *i.e.*, m_{avg}^* of $[110]/(1\bar{1}0)$ is small regardless of the NW width and it significantly increases with the width in $[110]/(001)$ NWs. These behaviors seem a direct consequence of the energy separation between the L band and the H band. Therefore, understanding of the behavior of these characteristic subbands is important to grasp the details of the quantum-confinement-induced change in m_{avg}^* in $[110]$ NWs.

2.3.3 $[111]$ Nanowires

For $[111]$ NWs, the set of p_x , p_y , p_z , and corresponding d orbitals are unsuitable for the basis of atomic orbital analyses. Thus, the author determined new p and d orbitals as $\{p_{111}, p_{11\bar{2}}, p_{1\bar{1}0}, d_{111}, d_{11\bar{2}}, d_{1\bar{1}0}\}$, whose directionality is along three axes of the NWs' geometry (length, height, and width direction).

Figure 2.11 shows the width dependences of hole effective mass and contribution of each atomic orbital at VBM in square cross-sectional $[111]$ Si NWs. The effective mass of $[111]$ NWs is very small and very close to that of bulk light hole, and the wave function of the topmost subband at the Γ point is almost pure state of $|111\rangle$, which is directed to the

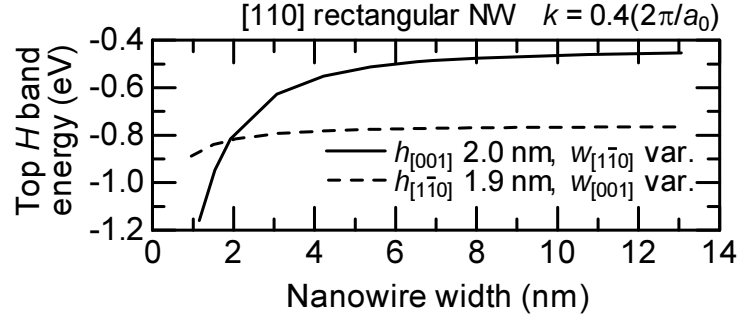


Figure 2.9: The energy level of the highest heavy (H) band in [110] rectangular cross-sectional Si NWs at $k = 0.4 \times 2\pi/a_0$. The energy is referenced from the band edge of bulk. Solid: [110]/(001) NWs with constant [001] height ($h_{[001]} = 2.0 \text{ nm}$) and varying $[1\bar{1}0]$ widths ($w_{[1\bar{1}0]}$); dashed: [110]/($1\bar{1}0$) NWs with constant $[1\bar{1}0]$ height ($h_{[1\bar{1}0]} = 1.9 \text{ nm}$) and varying [001] widths ($w_{[001]}$).

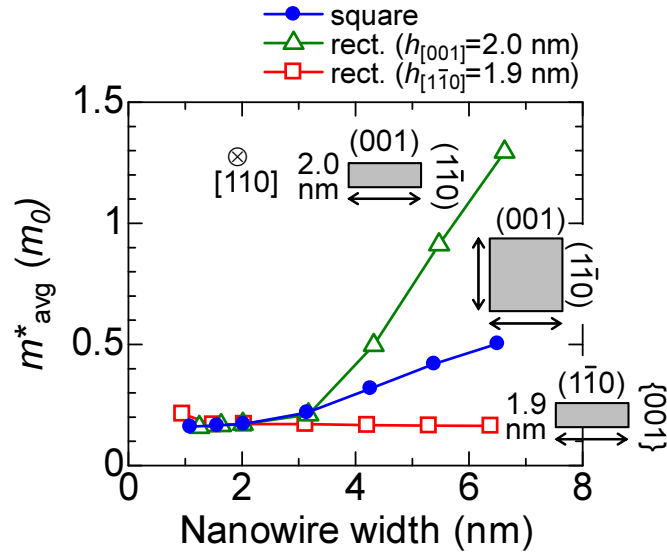


Figure 2.10: Width dependence of averaged effective mass m^*_{avg} in square [110], rectangular [110]/(001), and rectangular [110]/($1\bar{1}0$) NWs (nondegenerate, temperature: 300 K).

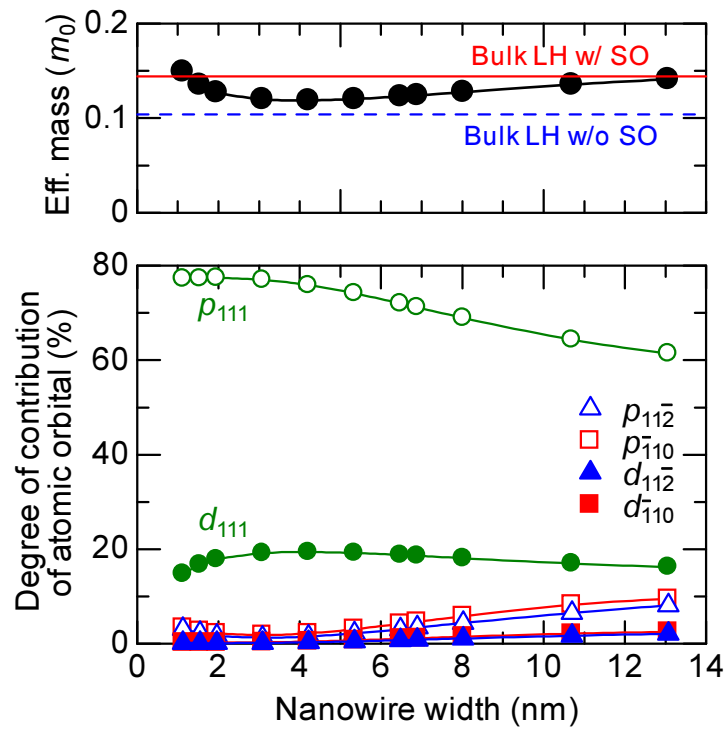


Figure 2.11: Hole effective mass and degree of contribution of atomic orbitals at VBM in square cross-sectional $[111]$ Si NWs.

transport orientation. The effective masses of [111] Si NWs obtained by our calculation well agree with those by other theoretical studies [7, 8, 29]. The band structure of square [111] Si NWs is shown in Fig. 2.12. It is clearly observed that upper subbands around the zone center generally have small effective mass (L' band), and upper subbands distant from the zone center have large effective mass (H' band). To investigate the character of wave function of an H' subband, atomic orbital analyses were performed for the H' state with the highest energy at $k = 0.2 \times 2\pi/a_0$, and the result for square NWs is shown in Fig. 2.13(a). As the plot indicates, H' subbands are formed by orbitals along confinement directions, the mixture of $|11\bar{2})$ and $|\bar{1}10)$. Leu *et al.* [24] have found by a first-principles calculation that the top heavy band in hexagonal cross-sectional [111] Si NWs has pure character of $p_{\bar{1}10}$, not a mixture of $p_{\bar{1}10}$ and $p_{11\bar{2}}$. This discrepancy may be due to the difference of cross-sectional shape and symmetry. It should be mentioned that the general shape of the VB structure of [111] NWs is common in diamond- and zincblende-type semiconductors such as Si, [5, 7, 8, 24, 29] Ge, [27, 29] InP, [13] and GaAs [30]. In particular, Ref. 30 states about GaAs NWs that the wave function of the states with small effective mass has its characteristic extension along the transport direction and that of the states with large effective mass has extension in the transverse direction. This observation is consistent with our results.

The author calculated the band structure and effective mass of rectangular cross-sectional [111]/(11 $\bar{2}$) (2-nm-high) and [111]/($\bar{1}10$) (1.9-nm-high) NWs by varying a width from 1 nm to 13 nm. From this calculation, it was found that in every case the L' subband appeared as the top band at the zone center and as a result the effective mass at VBM was almost constant. In addition, the energy level of the H' bands increases as the width increases though the height is kept constant, but the energy of the H' band does not exceed that of the L' band. The amount of the energy shift is almost isotropic (Fig. 2.14, which describes the energy level of the top H' band at $k = 0.2 \times 2\pi/a_0$ in the both rectangular structures). This feature of H' band in [111] NWs is quite different from that of H band in [110] NWs.

The orbital analysis for rectangular NWs revealed that the top L' subband remained almost pure $|111)$ state but that the composition of the orbital of the top H' band was dependent on the geometry of NWs. Figs. 2.13(b) and (c) show the width dependence of the composition of atomic orbitals of the topmost H' subband at $k = 0.2 \times 2\pi/a_0$ in rectangular [111] NWs. In square cross-sectional NWs, the top H' band is composed of the mixture of $|11\bar{2})$ and $|\bar{1}10)$, as discussed above. In rectangular NWs, however, the mixing of $|11\bar{2})$ and $|\bar{1}10)$ is dissolved and the top heavy subband is formed by almost single character of $\{p, d\}$ orbitals along the direction of the wider side. Here let me take 2-nm-high [111]/(11 $\bar{2}$) NWs as an example [see Fig. 2.13(b)]. When the width (along $[\bar{1}10]$) is larger than the height (along $[11\bar{2}]$), the topmost H' subband becomes almost pure $|\bar{1}10)$ state. It should be emphasized that this result does not say that H' subbands with single $|11\bar{2})$ character and the mixed state of $|11\bar{2})$ and $|\bar{1}10)$ disappeared. These states form

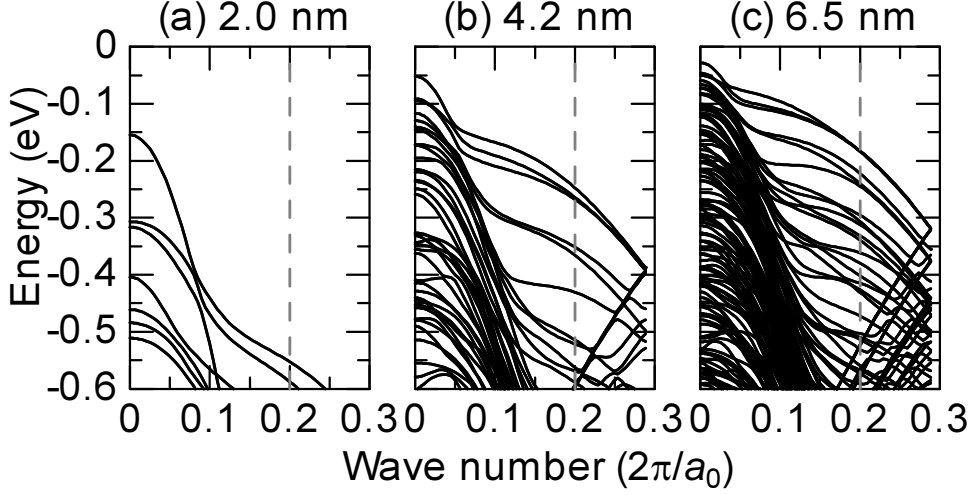


Figure 2.12: Valence band structure of square cross-sectional [111] Si NWs, where the width is (a) 2.0 nm, (b) 4.2 nm, and (c) 6.5 nm. The energy is referenced from VBM of bulk Si. The boundaries of the first Brillouin zone are located at $\pm 2\pi/\sqrt{12}a_0$. The gray dashed line indicates the position of $k = 0.2 \times 2\pi/a_0$, where the atomic-orbital analysis of the top heavy band is conducted for square and rectangular [111] NWs in Fig. 2.13. For rectangular [111] NWs, the analysis of the energy levels of the top heavy band is performed at this wave number, which is shown in Fig. 2.14.

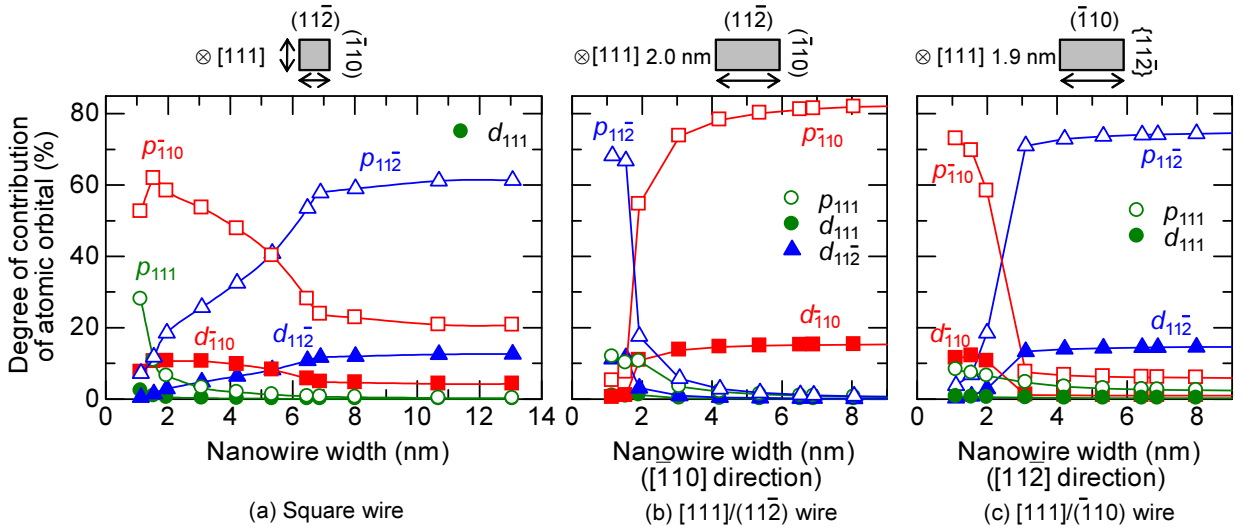


Figure 2.13: Degree of atomic orbital contribution of the topmost hole state at $k = 0.2 \times 2\pi/a_0$ in (a) square cross-sectional [111], (b) 2.0-nm-high rectangular cross-sectional [111]/(112), and (c) 1.9-nm-high rectangular cross-sectional [111]/(110) Si NWs.

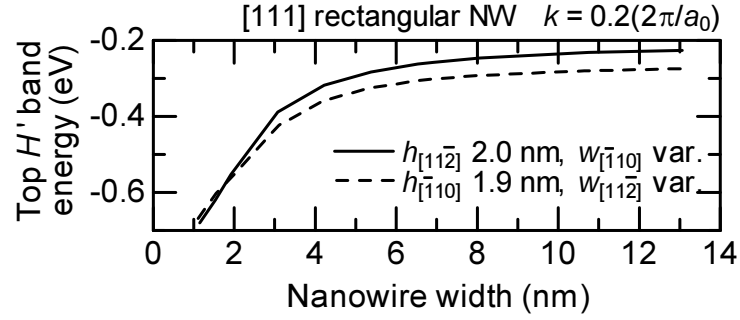


Figure 2.14: The energy level of the highest heavy (H') band in [111] rectangular cross-sectional Si NWs at $k = 0.2 \times 2\pi/a_0$. The energy is referenced from the band edge of bulk. Solid: [111]/(11 $\bar{2}$) NWs with constant [11 $\bar{2}$] height ($h_{[11\bar{2}]} = 2.0 \text{ nm}$) and varying [$\bar{1}10$] widths ($w_{[\bar{1}10]}$); dashed: [111]/($\bar{1}10$) NWs with constant [$\bar{1}10$] height ($h_{[\bar{1}10]} = 1.9 \text{ nm}$) and varying [11 $\bar{2}$] widths ($w_{[11\bar{2}]}$).

other lower-energy H' subbands existing below the top $|\bar{1}10\rangle$ band.

To evaluate whether the small VBM effective mass in $[111]$ NWs truly leads to better hole transport characteristics or not, the averaged effective mass m_{avg}^* was calculated and shown in Fig. 2.15. In 2-nm-high rectangular NWs, m_{avg}^* is very small ($0.13\text{--}0.19m_0$) within the range of the width ($\sim 1\text{--}\sim 6$ nm) thanks to large energy separation between the L' and H' subbands and good parabolicity of the VBM L' band. In addition, the increase in m_{avg}^* of square NWs with the width is mild. m_{avg}^* is $0.28m_0$ even in the 6.5 nm-nm-thick square NW. This is the smallest among square NWs with the similar size in other orientations. The reason of this small m_{avg}^* is attributed to (1) the smallest VBM m^* with a good parabolicity and (2) relatively large energy splitting between top light and heavy subbands especially compared to $[110]$ NWs, which have the second smallest VBM m^* in this study. Therefore, high hole transport performance is expected in $[111]$ NWs.

2.3.4 $[112]$ Nanowires

Finally, the calculation result of $[112]$ oriented NWs is given. In the case of $[112]$ NWs, the basis set for atomic orbital analyses was defined as $\{p_{112}, p_{11\bar{1}}, p_{\bar{1}10}, d_{112}, d_{11\bar{1}}, d_{\bar{1}10}\}$.

Figure 2.16 shows the width dependence of hole effective mass at VBM and contribution of each atomic orbital at VBM in square and rectangular cross-sectional $[112]$ Si NWs. First of all, the author focuses on the VBM m^* . In square NWs [Fig. 2.16(a)], VBM m^* is about $0.25\text{--}0.26m_0$ regardless of the NW size. This value is consistent with the previous tight-binding report on a 3 nm circular NW ($0.26m_0$) [6]. This VBM m^* is heavier than that of $[110]$ and $[111]$ NWs and also heavier than $[112]$ bulk LH calculated by $sp^3d^5s^*$ tight binding ($0.154m_0$ with SO and $0.113m_0$ w/o SO). Although VBM m^* does not show the size dependence, m_{avg}^* in square NWs (circles in Fig. 2.17) gradually increases with the width and reaches $0.58m_0$ at the width of 7 nm. This m_{avg}^* value is smaller than m_{avg}^* in square $[001]$ NWs but is larger than m_{avg}^* in square $[111]$ and $[110]$ NWs. In rectangular NWs with the height of 2.1 nm both on $(11\bar{1})$ [Fig. 2.16(b)] and $(\bar{1}10)$ [Fig. 2.16(c)], the VBM m^* does not show significant dependences both on the substrate face and width. However, the width dependence of m_{avg}^* shows small confinement anisotropy. From the width dependence of m_{avg}^* shown in Fig. 2.17, it can be seen that the increase in m_{avg}^* with width is faster in 2.1-nm-thick $[112]/(11\bar{1})$ NWs than in $[112]/(\bar{1}10)$. In other words, m_{avg}^* is more sensitive to $|\bar{1}10\rangle$ confinement. To find out the reason of these complex size dependences of the averaged effective mass, the band structure should be characterized carefully.

The band structure of 2.1-nm-thick square $[112]$ Si NW is shown in Fig. 2.18(a). As is the case with $[110]$ and $[111]$ NWs, the topmost subband has light effective mass (denoted as L'') and there exist subbands with heavier mass at deeper energies (denoted as H''). In addition to them, an M-shaped subband exists near VBM as indicated by M'' . As the NW size increases, the energy splitting of M'' and H'' bands from L'' bands diminishes and they mixes with the top L'' band. Therefore, m_{avg}^* becomes heavier in larger square NWs.

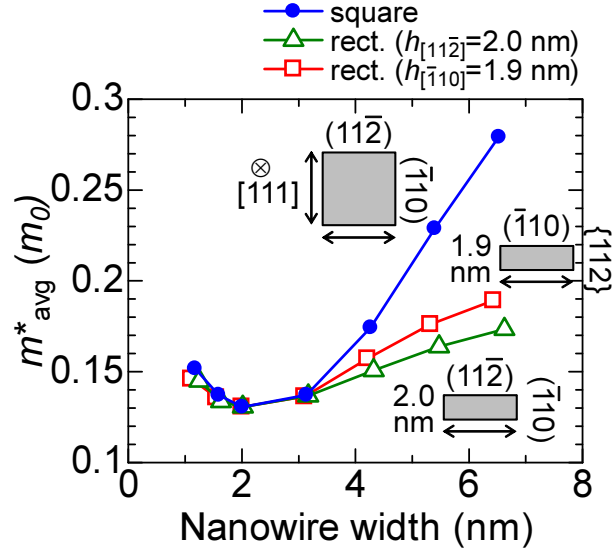


Figure 2.15: Width dependence of averaged effective mass m_{avg}^* in square $[111]$, rectangular $[111]/(11\bar{2})$, and rectangular $[111]/(\bar{1}10)$ NWs (nondegenerate, temperature: 300 K).

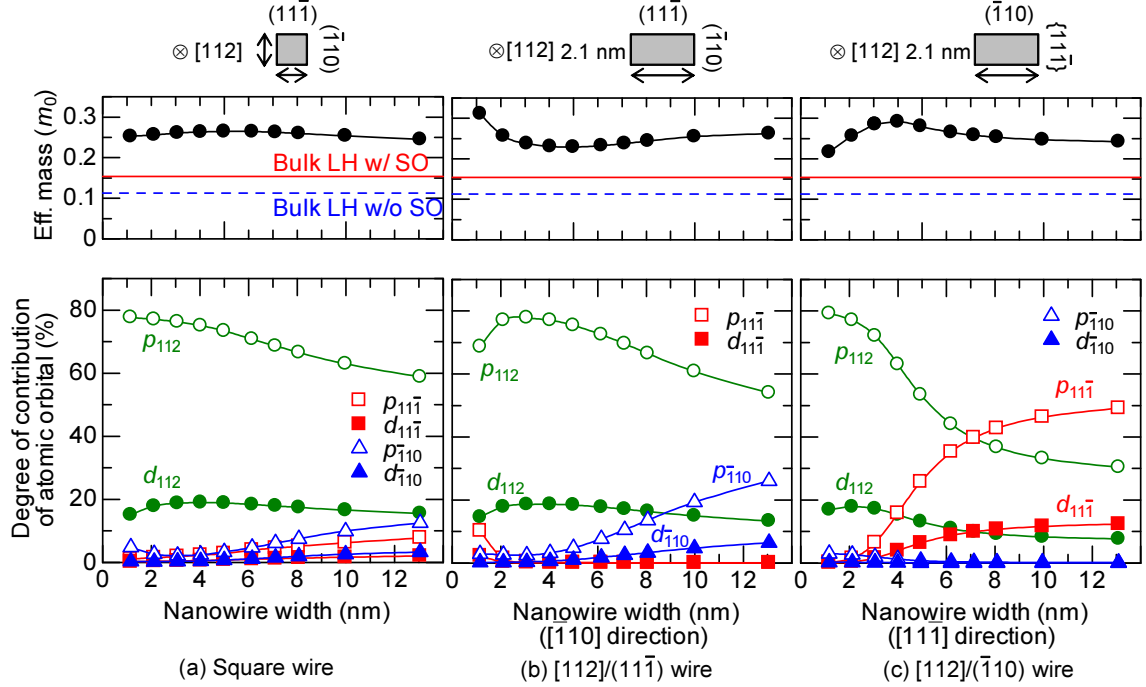


Figure 2.16: VBM effective mass and degree of atomic orbital contribution of the corresponding hole state at $k = 0$ in (a) square cross-sectional $[112]$, (b) 2.1-nm-high rectangular cross-sectional $[112]/(11\bar{1})$, and (c) 2.1-nm-high rectangular cross-sectional $[112]/(\bar{1}10)$ Si NWs.

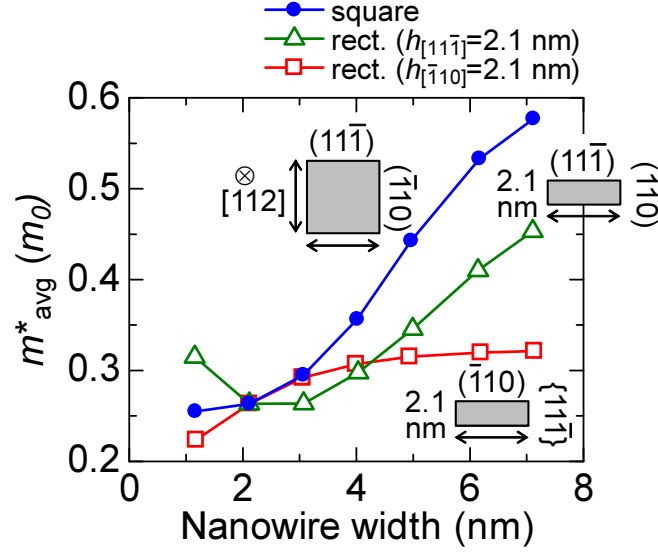


Figure 2.17: Width dependence of averaged effective mass m_{avg}^* in square $[112]$, rectangular $[112]/(11\bar{1})$, and rectangular $[112]/(\bar{1}10)$ NWs (nondegenerate, temperature: 300 K).

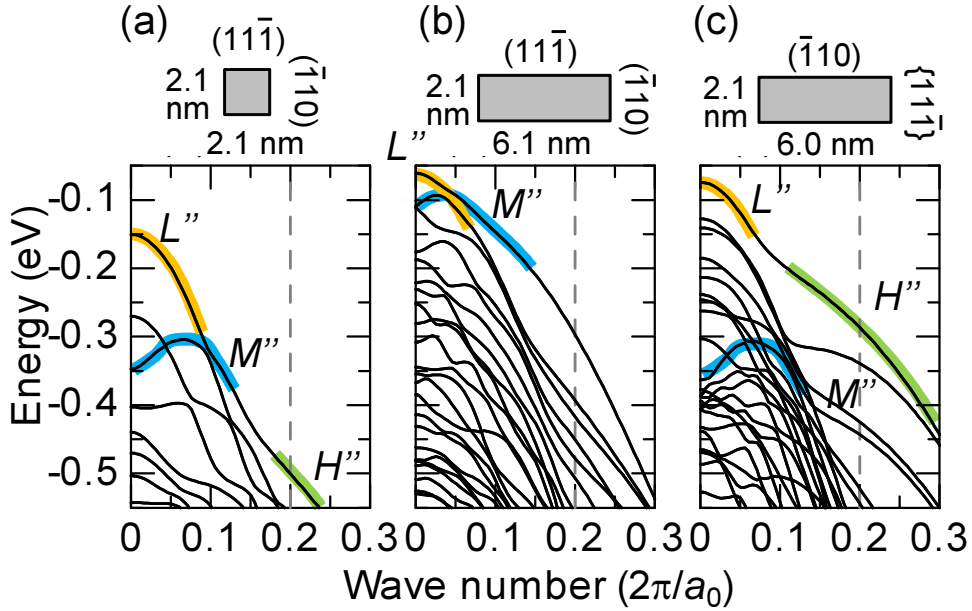


Figure 2.18: Valence band structure of (a) 2.1-nm square cross-sectional $[112]$ Si NW, (b) 2.1-nm-high and 6.1-nm-wide $[112]/(11\bar{1})$ Si NW, 2.1-nm-high and 6.0-nm-wide $[112]/(\bar{1}10)$ Si NW. The energy is referenced from VBM of bulk Si. The boundaries of the first Brillouin zone are located at $\pm 2\pi/\sqrt{6}a_0$. The gray dashed line indicates the position of $k = 0.2 \times 2\pi/a_0$.

In rectangular $[112]$ NWs with the height of 2 nm, this M'' band behaves anisotropically. Figs. 2.18(b) and (c) show band structures of rectangular NWs with 2 nm by 6 nm geometry on $(11\bar{1})$ and $(\bar{1}10)$, respectively. The increase in the width along $[\bar{1}10]$ pushes up the energy of the M'' . As a result, M'' approaches VBM. This does not change the VBM m^* but increases m_{avg}^* because m_{avg}^* is affected by the dispersion at slightly deeper energies from VBM. On the other hand, the approach of M'' to VBM is not seen when the $[11\bar{1}]$ width increases. Although the energy of H'' band increases, it is still separated from the top L'' and thus m_{avg}^* does not increase. Like this, the anisotropic behavior in m_{avg}^* can be attributed to the anisotropy in the M'' subband.

Here the author looks into the contribution of atomic orbitals in the topmost states at Γ and off- Γ ($k = 0.2 \times 2\pi/a_0$). First, the results of orbital analyses in square $[112]$ NWs at Γ and off- Γ are shown in Fig. 2.16(a) and Fig. 2.19(a), respectively. At $k = 0$, the orbital component at VBM is mainly $|112\rangle$ with slightly mixed $|11\bar{1}\rangle$ and $|\bar{1}10\rangle$. The orbital component at off- Γ position is almost composed of $|11\bar{1}\rangle$ and $|\bar{1}10\rangle$, whose directionalities are perpendicular to the NW. Next, the contribution of atomic orbitals in 2.1-nm-thick rectangular $[112]/(11\bar{1})$ NWs at Γ and off- Γ are shown in Fig. 2.16(b) and Fig. 2.19(b), respectively. At Γ , the slight increase in $|\bar{1}10\rangle$ composition and decrease in $|11\bar{2}\rangle$ composition were observed as the $[\bar{1}10]$ width increases [Fig. 2.16(b)]. However, this change of composition does not accompany a significant change in VBM m^* . At off- Γ , the increase in $[\bar{1}10]$ width induces a significant increase of $|\bar{1}10\rangle$ component and the component of the other orbitals diminish. Since the heavy band state at $k = 0.2 \times 2\pi/a_0$ seems extended from the M'' state as can be seen in Fig. 2.18(b), the M'' subband in $[112]$ NWs probably originates from $|\bar{1}10\rangle$. Actually, the orbital component of M'' around Γ was calculated and found to be the mixed state of $|112\rangle$ and $|\bar{1}10\rangle$. Therefore, M'' may not be a pure state from $|\bar{1}10\rangle$, but it can be said that M'' is affected by $|\bar{1}10\rangle$. Finally, the contribution of atomic orbitals in 2.1-nm-thick rectangular $[112]/(\bar{1}10)$ NWs at Γ and off- Γ are shown in Fig. 2.16(c) and Fig. 2.19(c), respectively. At Γ , strong mixing of $|11\bar{1}\rangle$ into $|112\rangle$ is observed as $[11\bar{1}]$ width increases. However, as mentioned above, both m^* at VBM and m_{avg}^* are almost unchanged. The hole states in $[112]$ NWs are complicated. The off- Γ state is mainly formed by $|11\bar{1}\rangle$ at large widths, but there still exist small $|112\rangle$ and $|\bar{1}10\rangle$.

2.3.5 Brief Summary of Orientation Dependence of Hole Effective Mass

The calculation results are briefly summarized in this section. The width dependences of m_{avg}^* of $[001]$, $[110]$, $[111]$, and $[112]$ square NWs are summarized in Fig. 2.20. The orientation dependence of m_{avg}^* in NWs is $[111] < [110] < [112] < [001]$ within the width (W) range of 1–6 nm. m_{avg}^* of $[001]$ NWs is much heavier compared to that NWs in the other orientations. At $W \leq 2$ nm, m_{avg}^* of $[110]$ NWs is almost comparable to that of $[111]$ NWs. However, m_{avg}^* of $[110]$ NWs increases faster than that of $[111]$ NWs. The transport

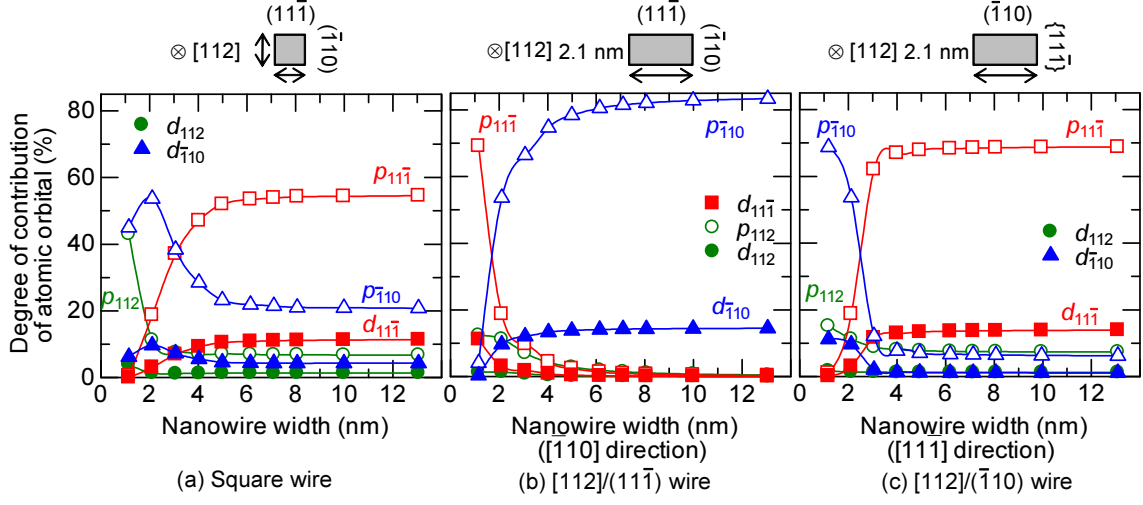


Figure 2.19: Degree of atomic orbital contribution of the topmost hole state at off- Γ ($k = 0.2 \times 2\pi/a_0$) in (a) square cross-sectional [112], (b) 2.1-nm-high rectangular cross-sectional [112]/(111̄), and (c) 2.1-nm-high rectangular cross-sectional [112]/(110) Si NWs.

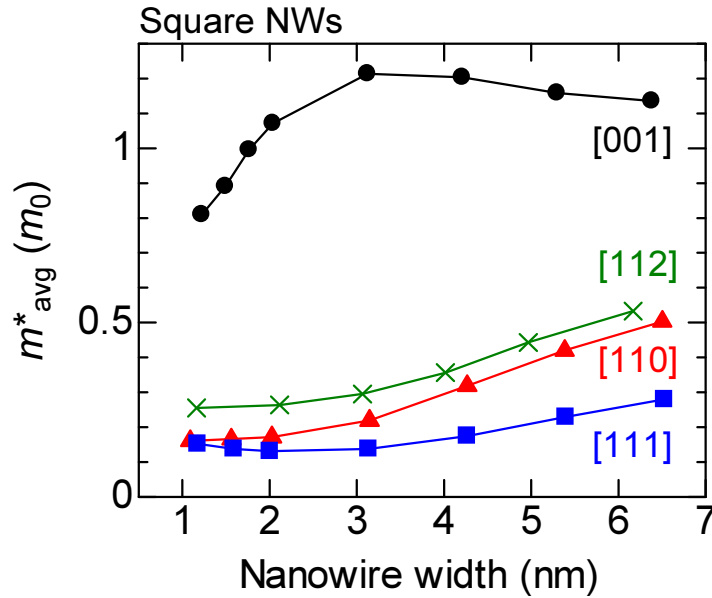


Figure 2.20: Summary of width dependences of averaged hole effective mass m^*_{avg} in square [001], [110], [111], and [112] NWs. The data are the same as in Figs. 2.5, 2.10, 2.15, and 2.17.

and confinement orientation dependence of m_{avg}^* is summarized in Fig. 2.21. [001] NWs do not have confinement-direction anisotropy due to the crystal symmetry. [110] NWs show strong confinement-direction anisotropy, and [112] NWs show weak anisotropy. [111] NWs do not show the anisotropy. [111] NWs with any aspect ratios and [110] NWs with thin width in $[1\bar{1}0]$ have small m_{avg}^* , and thus high hole transport performance is expected in these NW structures.

2.4 Discussion

2.4.1 Relationship between Transport Effective Mass and Character of Atomic Orbitals

First, the anisotropy in transport effective mass in NWs will be given. In Sec. 2.3, it was found that a subband with large amount of a p component oriented to the transport direction has small transport effective mass and one with a large contribution from p orbital perpendicular to the transport direction has large transport effective mass, which is a common result to [001], [110], and [111] NWs. In [112] NWs, the situation seems slightly different in rectangular cases, but it looks true in square cases. This observation about the relationship of the orientation between p orbitals and the transport direction is not hard to be understood instinctively; the effective mass of the hole state formed by p orbitals parallel to the transport direction is lighter and that by p orbitals perpendicular to the transport direction is heavier. Actually, this relationship can be found also in bulk Si. Thus, it is possible to state that the hole states in Si NWs can be understood from the hole states in bulk Si. However, what is important is the wavefunction, not the energy dispersion. To comprehend these results and the relationship between the effective mass and the orbital component in the wavefunction more deeply, the essential physics of the effective mass should be reviewed from the viewpoint of the inter-orbital interactions.

The calculation of NWs presented in this study includes the effect of SO coupling, but the calculation without SO coupling was also performed and it was confirmed that the general shape of the band structure and the effective mass are not very sensitive to SO coupling. This insensitivity to SO coupling is due to the relatively small SO splitting energy of bulk Si (45 meV in experimental [22] and 47 meV in the $sp^3d^5s^*$ tight-binding fitting [19]) compared to the quantum-confinement energy, which is the geometric effect. Because of the quantum confinement, hole states in Si NWs are reconstructed by mixing up bulk LH, HH, and SOH states. Therefore, direct comparison between the wave function components of NWs and $sp^3d^5s^*$ -SO bulk does not work well because the bulk model with SO treats heavy/light and split-off holes as separated off, and thus comparison with the bulk model without SO, which treats three p states equivalently, is more meaningful. For this reason, the author uses nearest-neighbor sp^3 tight-binding model without SO coupling in the discussion of inter-orbital interactions [31]. s^* and d orbitals are neglected for a clear

NW axis		NW shape	m_{avg}^* (2 nm × 2 nm → 6 nm × 2 nm) comments
[001]			$1.1m_0$ (heavy) → $\sim 1.7m_0$ (very heavy) <u>increase</u> with W
[110]			$0.17m_0$ (light) → $0.16m_0$ (light) <u>almost unchanged</u>
			$0.17m_0$ (light) → $\sim 1.1m_0$ (heavy) <u>rapid and significant increase</u> with W
[111]			$0.13m_0$ (light) → $0.18m_0$ (light) <u>very slow increase</u> with H
			$0.13m_0$ (light) → $0.17m_0$ (light) <u>very slow increase</u> with W
[112]			$0.26m_0$ (light) → $0.32m_0$ (medium) <u>slow increase</u> with H
			$0.26m_0$ (light) → $0.40m_0$ (medium) <u>increase</u> with W (faster than in vertically-long case)

Figure 2.21: Brief summary of the NW shape and orientation dependence of averaged hole effective mass m_{avg}^* in rectangular [001], [110], [111], and [112] NWs.

view of explanation.

Theoretical Background of Effective Mass from Microscopic Inter-Orbital Interactions

Second-order $\mathbf{k} \cdot \mathbf{p}$ perturbation gives an analytical expression of the energy dispersion around the wave number vector $\mathbf{k} = \mathbf{0}$ as [32]

$$E_n(\mathbf{k}) = E_n(\mathbf{0}) + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar^2}{m_0^2} \sum_{\alpha, \beta \in \{x, y, z\}} k_\alpha k_\beta \sum_{j \neq n} \frac{\langle n | p_\alpha | j \rangle \langle j | p_\beta | n \rangle}{E_n(\mathbf{0}) - E_j(\mathbf{0})}, \quad (2.7)$$

where $|n\rangle$ is the eigenstate of the band n at $\mathbf{k} = \mathbf{0}$, $\mathbf{p}$ is the momentum operator. In this equation, the third term on the right hand side (RHS) represents the interaction between different bands, and this term determines the effective mass. If the total interband interaction is strong, the effective mass becomes small. Conversely, if the interaction is weak or missing, the effective mass becomes heavy. This is a result for a complete basis set. With an incomplete basis set, an additional term for incompleteness correction is necessary to reproduce an exact effective mass [33]. However, the importance of the interband interactions is still essential. Therefore, the author focuses on the interband interaction term here. The general second-order expression of the energy dispersion around the Γ point for a degenerate case including the incompleteness correction is given by [33]

$$E_{n,i}(\mathbf{k}) = E_n(\mathbf{0}) + \langle n, i | \mathbf{k} \cdot \nabla_{\mathbf{k}} H(\mathbf{0}) | n, i \rangle + \frac{1}{2} \sum_{\alpha, \beta \in \{x, y, z\}} k_\alpha k_\beta \langle n, i | \frac{\partial^2 H(\mathbf{0})}{\partial k_\alpha \partial k_\beta} | n, i \rangle + \sum_{j \neq n} \frac{\langle n, i | \mathbf{k} \cdot \nabla_{\mathbf{k}} H(\mathbf{0}) | j \rangle \langle j | \mathbf{k} \cdot \nabla_{\mathbf{k}} H(\mathbf{0}) | n, i \rangle}{E_n(\mathbf{0}) - E_j(\mathbf{0})}, \quad (2.8)$$

where $H(\mathbf{k})$ is the Hamiltonian, $\nabla_{\mathbf{k}} H(\mathbf{0})$ is the $\mathbf{k}$ -space gradient of Hamiltonian at $\mathbf{k} = \mathbf{0}$, $|n, i\rangle$ is one of the eigenstates in the degenerate eigenstate set $\{|n, 1\rangle, |n, 2\rangle, \dots, |n, \nu\rangle\}$ (ν : degeneracy) which can diagonalize the second-order perturbation Hamiltonian matrix $[H'']_{rs}$:

$$[H'']_{rs} = \frac{1}{2} \sum_{\alpha, \beta \in \{x, y, z\}} k_\alpha k_\beta \langle n, r | \frac{\partial^2 H(\mathbf{0})}{\partial k_\alpha \partial k_\beta} | n, s \rangle + \sum_{j \neq n} \frac{\langle n, r | \mathbf{k} \cdot \nabla_{\mathbf{k}} H(\mathbf{0}) | j \rangle \langle j | \mathbf{k} \cdot \nabla_{\mathbf{k}} H(\mathbf{0}) | n, s \rangle}{E_n(\mathbf{0}) - E_j(\mathbf{0})}. \quad (2.9)$$

The first term on RHS in Eq. (2.8) is the unperturbed energy, the second is the first-order perturbation which becomes zero at VBM, and the third is the correction for incomplete basis set. The fourth term represents the interband interaction, which is practically the same as the second term on RHS in Eq. (2.7). A tight-binding model describes the interband interactions as the inter-orbital interactions between the orbitals that form the band states. Within the two-center approximation [see Eq. (A.12) in Appendix A], the tight-binding Hamiltonian matrix element between two neighboring atoms (a_1 and a_2) and orbitals at respective atoms (o_1 and o_2) is given by

$$\tilde{H}_{a_1 o_1, a_2 o_2}(\mathbf{k}) = e^{i\mathbf{k} \cdot \mathbf{R}_{1,2}} V_{a_1 o_1, a_2 o_2}, \quad (2.10)$$

where $\mathbf{R}_{1,2}$ is the vector from a_1 to a_2 and $V_{a_1o_1,a_2o_2}$ the two-center interaction matrix element. Accordingly, the expression of $\mathbf{k} \cdot \nabla_{\mathbf{k}} H(\mathbf{0})$ is given by the sum of

$$\mathbf{k} \cdot \nabla_{\mathbf{k}} \tilde{H}_{a_1o_1,a_2o_2}(\mathbf{0}) = i(\mathbf{k} \cdot \mathbf{R}_{1,2})V_{a_1o_1,a_2o_2} \equiv iI_{a_1o_1,a_2o_2} \quad (2.11)$$

about all the neighboring atoms.

The bulk Si's eigenstates at Γ point in sp^3 tight-binding are [31]

$$\mathcal{B}^{\pm} = \{|s^+\rangle, |p_x^+\rangle, |p_y^+\rangle, |p_z^+\rangle, |s^-\rangle, |p_x^-\rangle, |p_y^-\rangle, |p_z^-\rangle\}, \quad (2.12)$$

$$|s^{\pm}\rangle = (|s^a\rangle \mp |s^c\rangle) / \sqrt{2}, \quad (2.13)$$

$$|p_{\alpha}^{\pm}\rangle = (\pm|p_{\alpha}^a\rangle + |p_{\alpha}^c\rangle) / \sqrt{2} \quad (\alpha = x, y, z). \quad (2.14)$$

Superscripts (a,c) represent the anion and cation sites, respectively, and the ket means the Bloch sum on each orbital [see Eq. (2.1) and Appendix A]. The states with the superscript ‘−’ are bonding configuration (VB) and those with ‘+’ are antibonding configuration (CB). The relationship between these eigenstates and the band structure is depicted in Fig. 2.22. Table 2.1 shows the linear combinations of p -orbital states which describe light hole (LH), heavy hole 1 (HH1), and heavy hole 2 (HH2), where $m_{\text{HH1}}^* \geq m_{\text{HH2}}^*$, obtained by diagonalizing Eq. (2.9) in [001], [110], and [111] directions. The definition of the p -orbital directionality such as $|p_{110}^-\rangle$ is the same as in Eq. (2.3). The possible inter-orbital interactions are also shown. In the following part, the relationship between inter-orbital interactions and the hole effective mass in bulk Si are explained at first, and then the discussion is applied to the NW states.

Effective Mass and Orbital Interactions along [110] Direction

Along the [110] direction, three distinct hole states in bulk Si are formed by $|p_{110}^-\rangle$, $|p_{1\bar{1}0}^-\rangle$, and $|p_{001}^-\rangle$. First of all, $|p_{110}^-\rangle$ has strong inter-orbital interactions and thus becomes LH. Fig. 2.23 shows the schematic of inter-orbit interactions [corresponding to $I_{a_1o_1,a_2o_2}$ in Eq (2.11)] between p_{110} at an anion site (numbered as 0) and neighboring four (a) s , (b) p_{110} , (c) $p_{1\bar{1}0}$, and (d) p_{001} orbitals at nearest-neighbor cation sites (numbered as 1, 2, 3, and 4). Note that p_{110} at the position 0 is the orbital from VB, and that s and p orbitals at the position 1–4 are those from CB. $sp\sigma(> 0)$, $pp\sigma(> 0)$, and $pp\pi(< 0)$ written in the figure correspond to two-center integrals of σ bond between s and p , σ bond between p and p , and π bond between p and p orbitals, respectively [18]. The atomic-orbital configurations of these two-center interactions are illustrated in Fig. 2.24(a)–(c). The cases in which inter-orbital interactions cancel out by $+/-$ phase of the electron cloud are also shown in Fig. 2.24(d). p_{110} has σ interactions with s [Fig. 2.23(a) and Fig. 2.24(a)], and σ and π interaction with p_{001} [Fig. 2.23(d) and Fig. 2.24(b) and (c)]. There is no interaction with $p_{1\bar{1}0}$ [Fig. 2.23(c)] because the interaction vanishes owing to the phase of $+/-$ of the electron cloud of p orbital [Fig. 2.24(d)]. The interaction with p_{110} vanishes due to the symmetry [Fig. 2.23(b)]. The same interactions exist with respect to $|p^- \rangle$ states located at anion sites, and the sum of

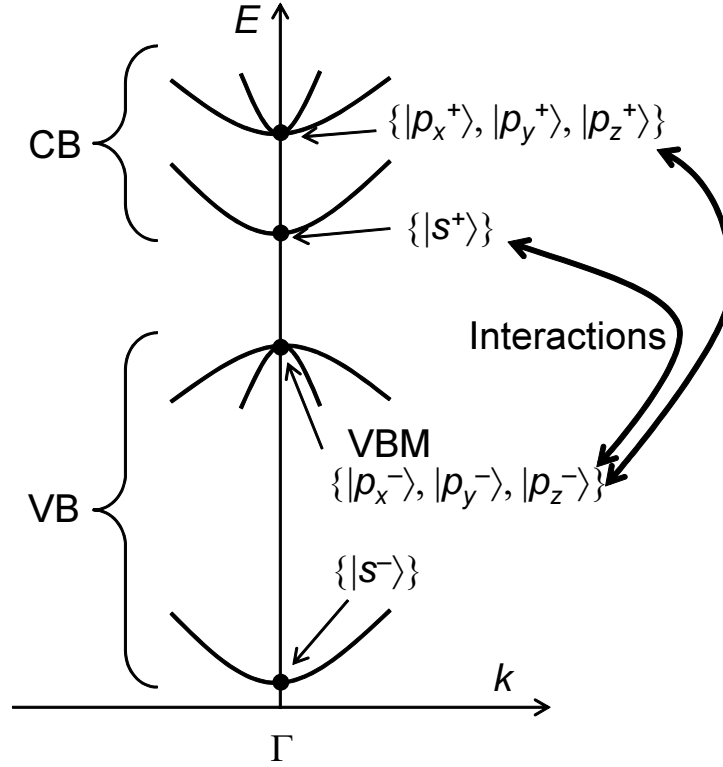


Figure 2.22: Eigenstates of band structure at Γ in bulk Si.

Table 2.1: Eigenstates of light and heavy holes along $[001]$, $[110]$, and $[111]$ in bulk Si in sp^3 tight-binding scheme without spin-orbit coupling. The conduction band states that interact with each hole state are also shown. The definition of the p -orbital directionality is the same as in Eq. (2.3).

		LH	HH1	HH2	
[001]	valence state	$ p_{001}^- \rangle$	$ p_{100}^- \rangle$	$ p_{010}^- \rangle$	(HH1&2 degenerate)
	interaction with	$ s^+ \rangle$	$ p_{010}^+ \rangle$	$ p_{100}^+ \rangle$	
		(strong)	(weak)		
[110]	valence state	$ p_{110}^- \rangle$	$ p_{1\bar{1}0}^- \rangle$	$ p_{001}^- \rangle$	$(m_{\text{HH1}}^* > m_{\text{HH2}}^*)$
	interaction with	$ s^+ \rangle, p_{001}^+ \rangle$	—	$ p_{110}^+ \rangle$	
		(strong)		(weak)	
[111]	valence state	$ p_{111}^- \rangle$	$ p_{11\bar{2}}^- \rangle$	$ p_{1\bar{1}0}^- \rangle$	(HH1&2 degenerate)
	interaction with	$ s^+ \rangle, p_{111}^+ \rangle$	$ p_{11\bar{2}}^+ \rangle$	$ p_{110}^+ \rangle$	
		(strong)	(weak)		

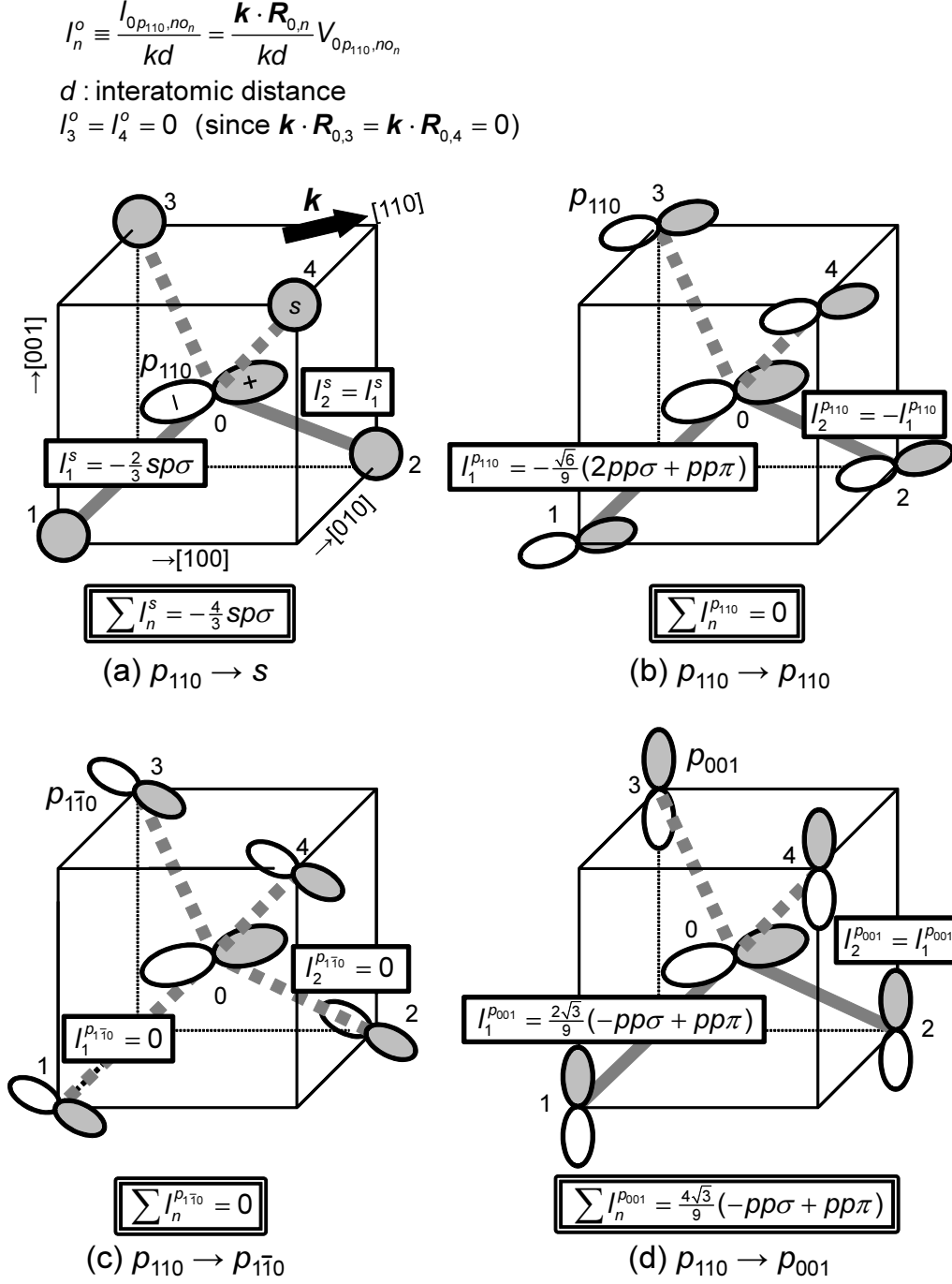


Figure 2.23: Inter-orbital interactions [corresponding to Eq (2.11)] between $|p_{110}^- \rangle$ ($[110]$ LH) and other orbital states in conduction (a) $|s^+ \rangle$, (b) $|p_{110}^+ \rangle$, (c) $|p_{\bar{1}\bar{1}0}^+ \rangle$, and (d) $|p_{001}^+ \rangle$ states in $[110]$ direction. p_{110} in $|p_{110}^- \rangle$ is placed at an anion site (numbered as 0) and neighboring s and p orbitals in conduction band states are placed at cation sites (numbered as 1, 2, 3, and 4). It is obvious that $|p_{110}^- \rangle$ has strong interactions with s and p orbitals, which results in light effective mass.

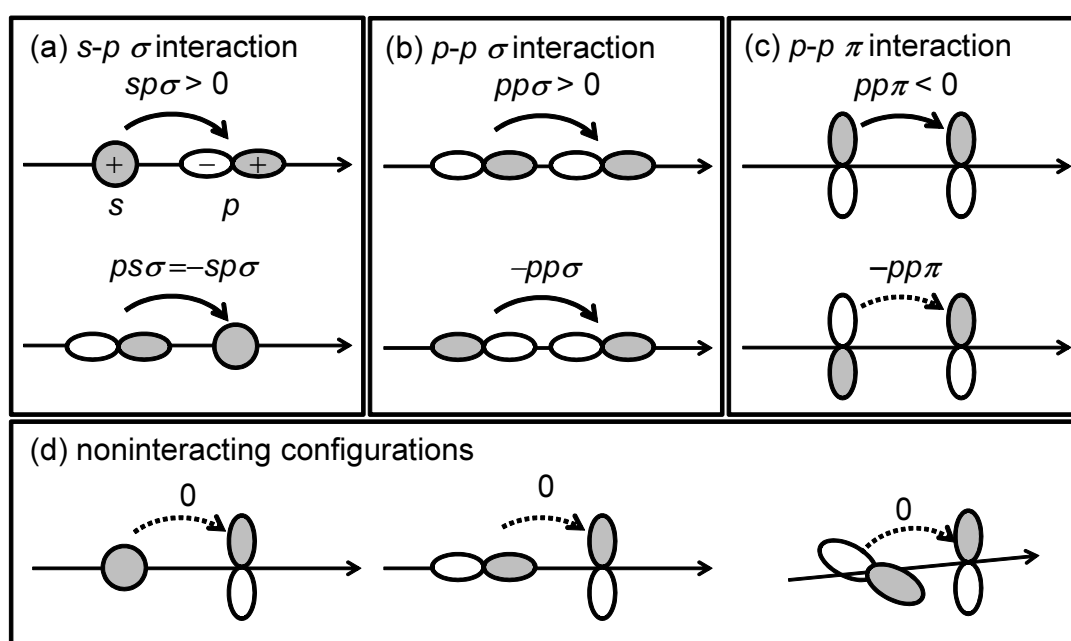


Figure 2.24: Configurations of two-center orbital interactions of s and p orbitals: (a) σ interaction between s and p , (b) σ interaction between p and p , and (c) π interaction between p and p . The cases in which inter-orbital interactions cancel out by $+/ -$ phase of the electron cloud are listed in (d).

the total interactions at anion and cation sites does not cancel out when the interaction between the valence band states $\{|p^-\rangle\}$ and the conduction band states $\{|s^+\rangle\}, \{|p^+\rangle\}$ are considered.

Secondly, $|p_{\bar{1}\bar{1}0}^-\rangle$ cannot interact with any other orbitals in $[110]$ and thus it forms HH1 with a very heavy effective mass. This poor neighboring inter-orbital interaction is understandable from the schematic image (Fig. 2.25) of interaction of $p_{\bar{1}\bar{1}0}$ with the conduction band states.

Finally, $|p_{001}^-\rangle$ has a weak interaction with $|p_{\bar{1}\bar{1}0}^-\rangle$, which is practically the same configuration as Fig. 2.23(d). Therefore, this state forms HH2, but the effective mass is not very heavy compared to HH1.

Since this interpretation of the effective mass in bulk Si is based on microscopic structures, the author speculate that the relationship between the character of orbitals and the effective mass holds true in $[110]$ NWs. In fact, the L and H bands are formed by bonding p_{110} and $p_{\bar{1}\bar{1}0}$ states, respectively. In addition, the author should point out that the effective mass of L band is very close to the bulk LH mass as shown in Fig. 2.6. This fact indicates that the understanding of effective mass by microscopic inter-atomic interactions is properly valid in NWs, and L and H bands in NWs probably stem from bulk LH and HH1 in $[110]$, respectively. The reason of the formation of ‘M’-shaped dispersion by p_{001} has not been clarified yet. However, the effective mass of the M band is heavier than the L band but lighter than H band, which is the same as in the bulk Si.

Effective Mass and Orbital Interactions along $[111]$ Direction

Along $[111]$ the bulk hole states are composed of $|p_{111}^-\rangle$, $|p_{\bar{1}\bar{1}\bar{2}}^-\rangle$, and $|p_{\bar{1}\bar{1}0}^-\rangle$. $|p_{111}^-\rangle$ strongly interacts with $|s^+\rangle$ and $|p_{111}^+\rangle$ and therefore it becomes LH. The strength of the interaction with s is the same as that of $[110]$ LH, but the interaction with p is slightly stronger than that of $[110]$ LH. This is the reason why bulk LH m^* along $[111]$ is lighter than that along $[110]$. Considering the fact that m^* of the L' band in $[111]$ NWs is very close to bulk LH m^* (Fig. 2.11), the discussion about m^* from microscopic interactions is convincing also in $[111]$ NWs.

The bulk HH along $[111]$ is doubly degenerate and formed by $|p_{\bar{1}\bar{1}\bar{2}}^-\rangle$ and $|p_{\bar{1}\bar{1}0}^-\rangle$. They interact with $|p_{112}^+\rangle$ and $|p_{\bar{1}\bar{1}0}^+\rangle$, respectively, and the strength of the interactions is smaller than that of bulk $[110]$ HH2, which results in a heavier m^* than $[110]$ HH2. In $[111]$ NWs, the H' band in square NWs is formed by the mixed state of $p_{11\bar{2}}$ and $p_{\bar{1}\bar{1}0}$ [Fig. 2.13(a)]. In addition, these two orbital components split off in rectangular NWs [Figs. 2.13(b) and (c)] and they independently form H' bands again. These behaviors of the H' band in NWs can be attributed to the degenerate bulk $[111]$ HH formed by $|p_{\bar{1}\bar{1}\bar{2}}^-\rangle$ and $|p_{\bar{1}\bar{1}0}^-\rangle$.

$$I_n^o \equiv \frac{I_{0p_{1\bar{1}0},no_n}}{kd} = \frac{\mathbf{k} \cdot \mathbf{R}_{0,n}}{kd} V_{0p_{1\bar{1}0},no_n}$$

d : interatomic distance

$$I_3^o = I_4^o = 0 \quad (\text{since } \mathbf{k} \cdot \mathbf{R}_{0,3} = \mathbf{k} \cdot \mathbf{R}_{0,4} = 0)$$

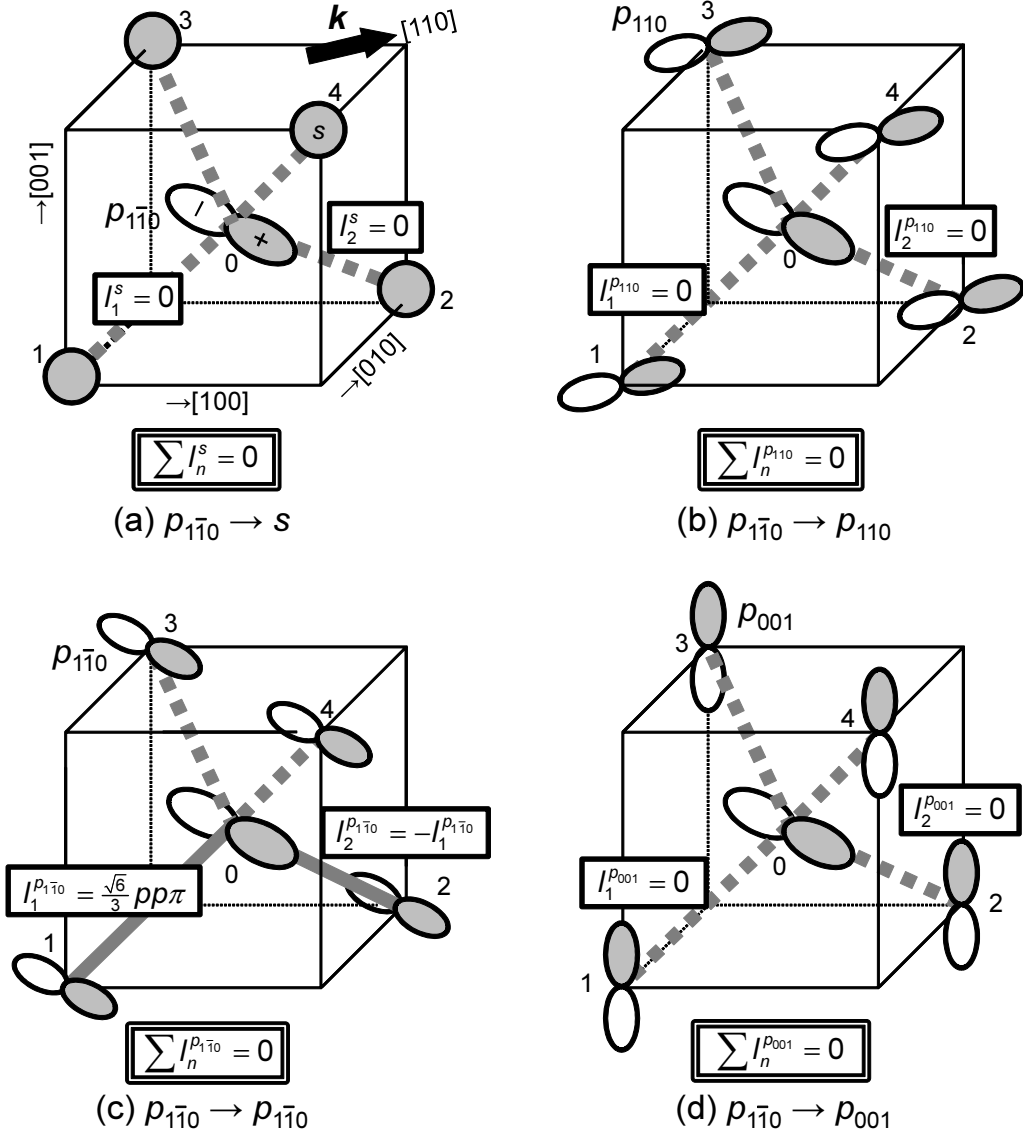


Figure 2.25: Inter-orbital interactions [corresponding to Eq (2.11)] between $|p_{1\bar{1}0}^- \rangle$ ([110] **HH1**) and other orbital states in conduction (a) $|s^+ \rangle$, (b) $|p_{110}^+ \rangle$, (c) $|p_{1\bar{1}0}^+ \rangle$, and (d) $|p_{001}^+ \rangle$ states in [110] direction. $p_{1\bar{1}0}$ in $|p_{1\bar{1}0}^- \rangle$ is placed at an anion site (numbered as 0) and neighboring s and p orbitals in conduction band states are placed at cation sites (numbered as 1, 2, 3, and 4). It can be understood that $|p_{1\bar{1}0}^- \rangle$ does not interact with other orbitals, which results in significantly heavy effective mass.

Effective Mass and Orbital Interactions along [001] Direction

The bulk LH along [001] is formed by $|p_{001}^- \rangle$. The bulk HH is doubly degenerate and formed by $\{|p_{010}^- \rangle, |p_{001}^- \rangle\}$. The discrimination of LH and HH along [001] is based on the fact that the LH state interacts with only s orbitals ($|p_{001}^- \rangle \leftrightarrow |s^+ \rangle$) and the HH with only p orbitals ($|p_{100}^- \rangle \leftrightarrow |p_{010}^+ \rangle, |p_{010}^- \rangle \leftrightarrow |p_{100}^+ \rangle$). It is true that the p - s interaction is stronger than p - p , but the difference is small. For this reason, the [001] LH is heavy compared to LH in other orientations, and the [001] HH is not very heavy (in the sp^3 tight-binding theory, m^* of [001] HH and that of [110] HH2 are the same).¹

In NWs, the trend that the VBM state with higher p_{001} contribution has smaller transport effective mass was observed (Fig. 2.2). This may be due to the LH character of p_{001} with respect to the inter-orbital interactions. However, perpendicular p states are strongly mixed to p_{001} in the VBM state in [001] NWs. The origin of this mixing should be further studied, but the author points out that p_{001} , p_{100} , and p_{010} are very symmetric with each other so that they can possibly mix up easily under a quantum confinement.

Effective Mass in [112] Direction

In the [110], [111], and [001] directions at VBM of bulk Si, the hole states were clearly described by principal axes that were used in the orbital-contribution calculation in NWs in these directions. However, in the [112] direction, the hole states are complicated even in bulk Si. One of the HH states in the [112] direction in bulk can easily be identified: $|p_{110}^- \rangle$. However, LH and the other HH are formed by the combination of $|p_{112}^- \rangle$ and $|p_{11\bar{1}}^- \rangle$. The mixing between them can be separated by diagonalizing Eq. (2.9) within the space $\{|p_{112}^- \rangle, |p_{11\bar{1}}^- \rangle\}$. With this procedure, LH is found to be formed by $|p_{112}^- \rangle$ in large part with a small contribution of $|p_{11\bar{1}}^- \rangle$. On the contrary, the other HH is mainly formed by $|p_{11\bar{1}}^- \rangle$. Although the analytical form of the effective mass is available by the diagonalization, the expressions are very complicated and it is difficult to find out physical meaning. Therefore, a straightforward discussion which is applied to [110], [111], and [001] NWs might be invalid to explain the relationship between the orbital and conductivity mass, and thus L'' band in [112] NWs is hard to be understood.

In general, the orbital composition of L'' in [112] NWs is dominated by p_{112} . This is the case in square NWs [Fig. 2.16(a)] and rectangular NWs with a wider $[\bar{1}10]$ width than a $[11\bar{1}]$ width [Fig. 2.16(b)]. The VBM effective mass in these structures is about $0.25m_0$. This value is larger than bulk LH m^* in [112], as shown in Fig. 2.16. This discrepancy might be attributed to the difference of wavefunction between NWs and the bulk. However, the contribution of $p_{11\bar{1}}$ significantly increases as the $[11\bar{1}]$ width increases keeping the $[\bar{1}10]$ width constant at 2.1 nm [Fig. 2.16(c)]. Despite this orbital-component change, VBM m^* remains constant. Therefore, the discussion about L'' needs further analyses. However,

¹In the $sp^3d^5s^*$ model without spin-orbit coupling, the interactions of the LH state with s^* and $d_{3r^2-z^2}$ are added, but the situation does not change very much.

relatively heavy m^* of M'' band, which is formed by $p_{\bar{1}10}$, can be attributed to the bulk HH formed by $|p_{\bar{1}10}^- \rangle$.

2.4.2 Relationship between Energy Shift by Quantum Confinement and Character of Atomic Orbitals

Next, the author considers the shift of energy levels by quantum confinement. Neophytou *et al.* have pointed out that the energy levels of subbands with large transport effective mass in both [110] and [111] NWs are more susceptible to the variation of the dimension than that of subbands with small transport effective mass [15, 16]. They explain that this difference of quantization energy is due to the anisotropy of the bulk heavy-hole $E-\mathbf{k}$ dispersion. In this thesis, this phenomenon is explained from a viewpoint of the character of wavefunction using inter-orbital interactions which were intensively discussed in the previous section.

[110] NWs

In [110] NWs, the p_{110} state has strong inter-orbital interactions toward the transport direction, but it has small interactions toward the confinement direction. In particular, the interaction along the $[1\bar{1}0]$ direction is extremely small. This is because the inter-orbital interaction with respect to p_{110} along the $[1\bar{1}0]$ direction is equivalent to the interaction with respect to $p_{1\bar{1}0}$ along the [110] direction, which is illustrated in Fig. 2.25, owing to the symmetry. On the other hand, $p_{1\bar{1}0}$ has very strong interactions along the $[1\bar{1}0]$ direction to the same extent as p_{110} has along [110] (Fig. 2.23). In the context of bulk Si, the p_{110} and $p_{1\bar{1}0}$ states form HH1 and LH along $[1\bar{1}0]$, respectively, as schematized in Fig. 2.26. Like this, the same wavefunction can become both LH and HH in different $\mathbf{k}$ directions. Hence the explanation of QCE that treats HH and LH separately may be not appropriate.

As the relationship between the transport effective mass and the magnitude of inter-orbital interactions along the transport direction indicates, it is expected that the larger interactions toward the confinement direction results in the smaller confinement effective mass. In other words, the energy level of a subband with larger interactions along the confinement direction shifts more easily by quantum confinement. As a result, the energy level of $|110\rangle$ states (L band) in [110] NWs is insensitive to $[1\bar{1}0]$ confinement but that of $|1\bar{1}0\rangle$ states (H band) is significantly sensitive to $[1\bar{1}0]$ confinement. For the [001] confinement, it is expected that the amount of the energy shifts in L and H bands is small and comparable because the p_{110} and $p_{1\bar{1}0}$ look symmetric with respect to the [001] confinement axis and they both correspond to the HH in [001] (superposition of p_{100} and p_{010}). When taken together, the energy shift of the L band is less susceptible to the strength of both $[1\bar{1}0]$ and [001] confinement (but note that the energy shift is larger for [001] confinement than that for $[1\bar{1}0]$ due to the extremely small inter-orbital interaction in $[1\bar{1}0]$). On the other hand, H band has strong anisotropy, that is, the energy shift is expected to be large for $[1\bar{1}0]$ confinement but small for [001] confinement. It follows from what has been discussed

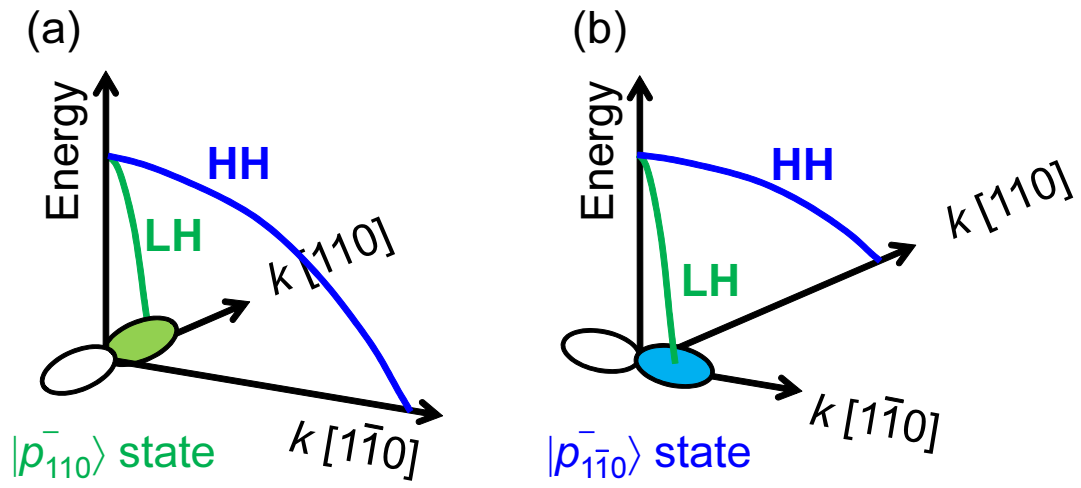


Figure 2.26: Schematic of anisotropic hole states of bulk Si in $[110]$ and $[1\bar{1}0]$ formed by (a) $|p_{110}^- \rangle$ and (b) $|p_{1\bar{1}0}^- \rangle$. A single wavefunction can form both LH and HH in different directions.

thus far that the difference of quantum-confinement-induced energy shift between the L subband and H subband is expected to be dominated by $[1\bar{1}0]$ confinement. In square (or circular) cross-sectional NWs, the L subband has smaller energy shift than the H subband, and thus the L subband comes to VBM. In rectangular $[110]/(1\bar{1}0)$ NWs with a constant height of 2 nm, a large amount of the energy shift is introduced to the H band by strong $[1\bar{1}0]$ confinement but the shift of the L band induced by both side faces is very small. For this reason, the energy of the H subband is far below the L subband and the topmost subband always becomes the L subband, as mentioned in Section 2.3.2. For rectangular $[110]/(001)$ NWs with a varying $[1\bar{1}0]$ -oriented width, the energy position of the L band hardly varies by the variation of $(1\bar{1}0)$ thickness while that of the H band easily moves (see Figs. 2.8 and 2.9). In the situation that the $[1\bar{1}0]$ width becomes sufficiently wide, the energy levels of the L and H bands become comparable because the confinement effective mass of these bands along $[001]$ is expected to be similar. This is the case observed in calculation of 2-nm-thick $[110]/(001)$ Si NWs. Again the author should stress that whether the interchange of L and H bands occurs or not depends on the calculation condition such as the thickness and detailed arrangement of atoms, and therefore the interchange itself is not an essential issue. What is important is that the energy level of the top L band and H band can become very close in rectangular $[110]/(001)$ NWs but cannot in $[110]/(1\bar{1}0)$ NWs due to the anisotropic behavior of the H band.

[111] NWs

A similar discussion holds validity for $[111]$ NWs. In square cross-sectional $[111]$ NWs, p_{111} exhibits small inter-orbital interactions toward the confinement directions and $\{p_{11\bar{2}}, p_{\bar{1}10}\}$ do large. This indicates that the energy level of $|111\rangle$ states (L' band) is much smaller than that of $\{|11\bar{2}\rangle, |\bar{1}10\rangle\}$ states (H' band). This is what is observed in Ref. 16 and why the L' band dominates around VBM in thin NWs. The nearly isotropic behavior of the VB structures due to both $[11\bar{2}]$ and $[\bar{1}10]$ confinement may originate from the fact that the H' band is formed by both $p_{11\bar{2}}$ and $p_{\bar{1}10}$. When the aspect ratio is about unity, the both orbitals couple together and form the top H' band. This coupling may be due to double degeneracy of the heavy hole states along the $[111]$ direction in bulk Si. However, when the width is larger than the height, the coupling is dissolved and the orbital parallel to the width direction forms the top H' band because that orbital has large interaction, *i.e.*, light confinement effective mass along the width direction. The reason why the energy of H' hardly comes close to that of L' may be attributed to the following two facts. First of all, p orbitals of L' and H' bands are not symmetric. Secondly, the inter-orbital interactions of $p_{11\bar{2}}$ along $[\bar{1}10]$ and those of $p_{\bar{1}10}$ along $[11\bar{2}]$ (H' band) are the same, but they are larger than interactions of p_{111} (L' band) along the two confinement directions, $[\bar{1}10]$ and $[11\bar{2}]$. In other words, H' has lighter confinement masses than L' , unlike in $[110]$ NWs. Therefore, the confinement-induced energy shift is always smaller in L' than in H' .

[001] NWs

Although the hole states of [001] NWs are complex compared with other orientations, discussions based on the atomic orbital are partially still valid. For example, as the width of NWs becomes larger under a constant height, the amount of contribution from p orbitals along the width direction increases, as seen in Fig. 2.3. This is probably because the p -orbital state along the weaker confinement direction has smaller energy shift. It should be also pointed out that the VBM state of [001] NWs has larger energy shift than that of [110] and [111] NWs (see Figs. 2.4 and 2.8). This may be due to the stronger inter-orbital interaction of p_{001} along the confinement directions and the incorporation of transverse p states to the VBM state of [001] NWs.

[112] NWs

In [112] NWs, the weak anisotropy of the behavior of the M'' band has to be discussed. M'' is formed by $p_{\bar{1}10}$. Unlike p_{112} and $p_{11\bar{1}}$ states, which can couple together in bulk hole states in [112], the hole state formed by $p_{\bar{1}10}$ may be affected by quantum confinement solely because $p_{\bar{1}10}$ is separated from the other two orbitals with respect to the inter-orbital interactions along [112], as discussed in the previous section. The orbital interaction of $p_{\bar{1}10}$ is very strong along $[\bar{1}10]$ (corresponding to $[\bar{1}10]$ LH) but is very weak along $[11\bar{1}]$ (corresponding to $[11\bar{1}]$ HH). This anisotropic strength of the interaction induces the confinement anisotropy of M'' band; sensitive to the $[\bar{1}10]$ confinement but insensitive to the $[11\bar{1}]$ confinement. Therefore, M'' band approaches VBM quickly only when the $[\bar{1}10]$ width increases.

2.5 Summary

To investigate the effects of quantum confinement on hole states in Si NWs, the valence band structure, hole effective mass, and wavefunction of hole states of [001], [110], [111], and [112] oriented rectangular cross-sectional Si NWs have been studied using an $sp^3d^5s^*$ -SO tight-binding method. In general, VBM is formed by a subband with light effective mass and subbands with heavier mass are located at deeper energies. This energy separation expands as the cross-sectional size of NWs decreases, and thus the averaged effective mass, which considers the distribution of holes owing to the thermal energies, is smaller in thinner NWs. The averaged effective mass is orientation dependent: $m_{[111]}^* < m_{[110]}^* < m_{[112]}^* < m_{[001]}^*$. [111] NWs with rectangular cross-section do not exhibit anisotropy in the band structure regarding the confinement directions and their m^* remains small in any aspect ratio considered in this study. On the other hand, [110] NWs exhibit strong anisotropy. When the width along [001] is larger than that along $[\bar{1}10]$, heavy subbands are separated from the top light subband. When the width along $[\bar{1}10]$ is larger than that along [001], however, the heavy subbands rapidly approach the top light subband, which increases the averaged effective mass. [001] NWs do not show anisotropy because of the symmetry in the

crystal structures, but the effective mass is dependent on the cross-sectional aspect ratio in rectangular NWs; the mass is the smallest in square NWs and it increases as the shape deviates from square. $[112]$ NWs exhibit weak anisotropy. The averaged effective mass increases with the $[\bar{1}10]$ width while it does not happen when the $[11\bar{1}]$ width increases. These behaviors of band structures are understandable from the viewpoint of inter-orbital interactions between nearest-neighbor atoms. In terms of application to p-channel FET devices, $[111]$ NWs with any cross-sectional aspect ratios and $[110]$ NWs with thin $[1\bar{1}0]$ width and wider $[001]$ width are promising thanks to their small effective mass with large energy separation between light and heavy subbands.

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Chapter 3

Fabrication Method of Si Nanowires by Top-Down Process

3.1 Introduction

The fabrication method of Si nanowires (NWs) can be classified into two groups, bottom-up and top-down approaches. In the bottom-up approach, NWs are synthesized by crystal growth techniques such as vapor-liquid-solid (VLS) growth method [1, 2]. The crystal growth is generally cost-effective and vast numbers of NWs can be grown at once. However, the assembly techniques are necessary to fabricate NW devices unless a vertical device structure [3] is adopted. In addition, the control of the crystallographic orientation of NWs is not easy [4, 5]. The top-down approach, which is based on lithography and reactive ion etching (RIE) techniques, can be used for the fabrication of NW FET devices more easily because the control of size, position, and crystallographic orientation is relatively easy. In addition, the top-down approach is highly compatible with CMOS LSI processes. As lithography techniques to fabricate Si NWs, state-of-the-art optical lithography and electron-beam lithography (EBL) can be utilized. The optical lithography is a high-throughput process, but it is usually combined with other techniques such as resist trimming [6, 7] and side-wall patterning [8] to fabricate thin NW structures with a few-nm to few-dozens-of-nm scale owing to its insufficient resolution originating from the limitation of light wavelength. This method is useful for mass production of NW devices. On the other hand, EBL is a low-throughput process. However, nm-scale structures can be fabricated directly with high flexibility by EBL, and thus EBL is one of the most suitable methods for fundamental research of nanoscopic devices. In fact, EBL has been employed for fabrication of NWs with sub-10-nm cross-sectional sizes [9], which exhibit quantum effect at room temperature, by usually combining with thermal oxidation for further reduction of NW size. In this study, the author used EBL and RIE for NW definition. In the following sections, key points in the fabrication process are discussed and the overall process sequence is given. Furthermore, the structures of fabricated NWs are characterized.

3.2 Fabrication Procedure

3.2.1 Electron-Beam Lithography

The EBL system used in this study is JBX-6300SA (JEOL Ltd.), which is a vector-scanned spot-beam exposure system. To realize fine structures, high acceleration voltage of 100 kV and small beam current of 100 pA were used. In the formation of NW patterns by EBL, the line-edge roughness of resist patterns should be minimized because the irregular resist patterns are directly transferred to Si NWs by subsequent dry etching. There exist two main factors that cause line-edge roughness in EBL, the size of aggregates in resist polymers and the accuracy of pattern stitching in the exposure system.

If the size of aggregates in a resist polymer is large at pattern edges (lightly-exposed area), the line-edge roughness is limited by the size of polymer aggregates as shown in Fig. 3.1 [10]. Therefore, if the size of aggregates is larger, the amplitude of line-edge roughness becomes larger. Several common electron-beam sensitive resist materials such as ZEP-520A (ZEON Corp.) and PMMA [poly(methyl methacrylate)] are known to have large aggregate size (about 30 nm in ZEP) [10], and thus they are not promising for NW patterning. As an electron-beam resist with small aggregate size (~ 10 nm), hydrogen silsesquioxane (HSQ) is known [11]. HSQ has a negative tone, high resolution, and high durability against dry etching. Therefore, HSQ is useful for patterning of Si NW structures and in fact it has been used in several groups in the fabrication of Si NW MOSFETs [9, 12, 13]. In this study, HSQ was used for NW patterning. However, HSQ has two disadvantages. The first disadvantage is that the sensitivity of HSQ is low and it requires high electron dose. It requires long time to leave large-area HSQ films, which is required for source and drain pad regions to be protected in the following RIE process. Therefore, hybrid lithography technique [14, 15], which defines pad patterns and NW patterns separately by two-step lithography, was adopted. The author used ZEP-520A resist to define the source and drain pads because of its low required electron dose and small exposure area thanks to positive tone of the resist. The detailed description of the hybrid exposure is given in Sec. 3.2.3. The second disadvantage of HSQ is fast time-dependent variation of sensitivity after spin coating [16] even within 1 hour [17]. This feature is crucial in long-time exposures since NW widths may vary with time. Fortunately, this time-dependent behavior is known to be avoidable by capping the HSQ surface by a conductive film. The author used Espacer 300HX-02 (aqueous solution of a conductive polymer produced by Showa Denko) as a top coating, which is reported to be very effective to stabilize HSQ [18]. High stability of exposure of NW patterns over 11 hours after HSQ coating was confirmed under the optimized EBL conditions (50-nm-thick HSQ, $1800 \mu\text{C}/\text{cm}^2$) with Espacer. Figure 3.2 shows the dependence of nanowire-pattern width of 20 nm-, 28 nm-, and 40 nm-wide HSQ on the time after spin-coating of HSQ. The sample was kept in vacuum (in the exposure chamber) during waiting for the exposure. The time-dependent behavior is successfully suppressed, and

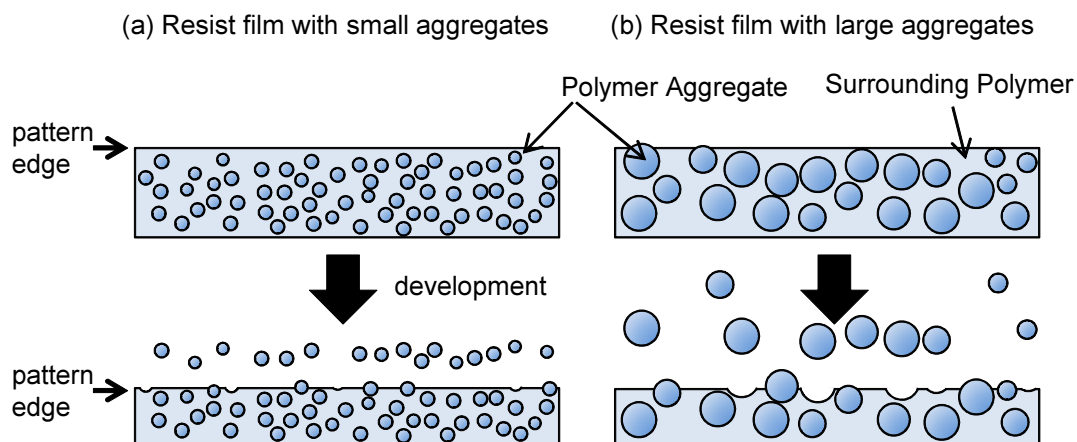


Figure 3.1: Line-edge roughness of the resist induced by (a) small and (b) large polymer aggregates.

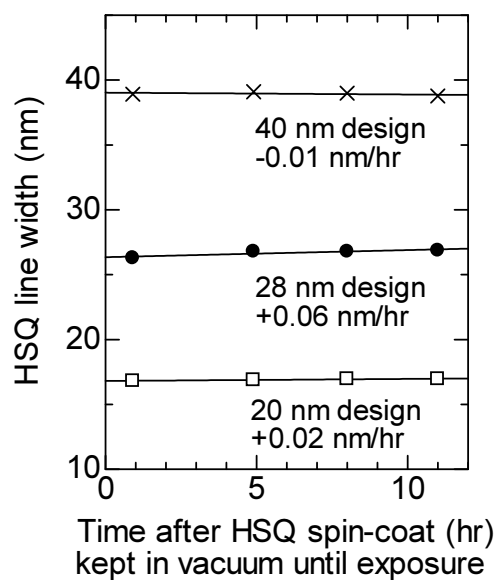


Figure 3.2: Vacuum-stored-time dependency of HSQ line width designed as 20, 28, and 40 nm in EBL at $1800 \mu\text{C}/\text{cm}^2$. 40-nm-thick Espacer 300HX-02 was used as a protective top coating and HSQ thickness was 50 nm.

the variation of line widths is less than 1 nm (the accuracy of line-width measurements).

As mentioned above, the stitching of patterns is another important factor which influences on line-edge roughness of NWs. JBX-6300SA divides exposure patterns into 250-nm-square blocks and vector scan of electron beam is performed in sequence for each block. In this exposure method, misalignment of patterns between neighboring blocks induced by the slight oscillation of the sample stage and statistical errors and accuracy in beam deflection become a problem in the exposure of very small NWs. To avoid this field-stitching error, a quarter of the necessary dose was exposed four times overwriting the same patterns. By this method, errors are averaged and thus smooth resist patterns can be obtained. Figure 3.3 shows NW patterns fabricated (a) with and (b) without the overlap exposure. Without the overlap exposure, the stitching error of NW patterns is obvious at intervals of about 250 nm. On the other hand, the stitching error is successfully suppressed with the overlap exposure.

3.2.2 Reactive Ion Etching

After developing the resist pattern by electron-beam lithography, the pattern should be transferred to the Si layer to fabricate Si NWs by RIE. To transfer the resist pattern to Si NWs successfully, corrosion and erosion of the resist should be suppressed since the deterioration of the resist pattern may lead to the roughness of Si NWs. Therefore, an appropriate reaction gas which reacts with Si but does not with HSQ should be chosen. The author tried Si etching with HSQ mask by CF_4 based capacitively coupled plasma RIE at first, but the selectivity of Si/HSQ was very poor and NW pattern could not be transferred to Si [Fig. 3.4(b)]. Electron-irradiated HSQ has a structure like SiO_x [11] and thus the etching mechanism of HSQ is considered to be the same as that of SiO_2 . In general, SiO_2 is easily etched by (hydro)fluorocarbon gases such as CF_4 because Si atoms in SiO_2 can react with F and vaporize as SiF_4 and O atoms can react with C and then vaporize as CO. Therefore, carbon-containing halogen gases should be avoided for Si etching with HSQ masks to realize high Si/HSQ selectivity, and thus Cl_2 [11] or HBr [19, 20] based chemistry (sometimes with O_2) is generally used because of its highly selective Si etching against SiO_2 [21, 22]. In this study, Cl_2 gas was used for Si/HSQ selective etching. Figure 3.4(c) shows a Si NW pattern etched by Cl_2 -based ICP-RIE (under still unoptimized conditions). Compared to CF_4 -based RIE [Fig. 3.4(b)], successful pattern transfer was achieved.

In addition to the chemical reactions, physical sputtering by energetic ions in plasma can deteriorate the shape of HSQ resist. SiO_2 is known to be chemically nonreactive to chlorine but etched by sputtering if the ion energy is above sputtering threshold (~ 50 eV) [23]. Therefore, the ion energy should be low enough to ensure high Si/HSQ selectivity. In this study, inductively-coupled-plasma reactive ion etching (ICP-RIE) system was employed to control the ion density and the ion energy independently, and the bias rf power was reduced to minimize oxide etching. Figure 3.5 depicts the etching rates of crystalline Si(100) and

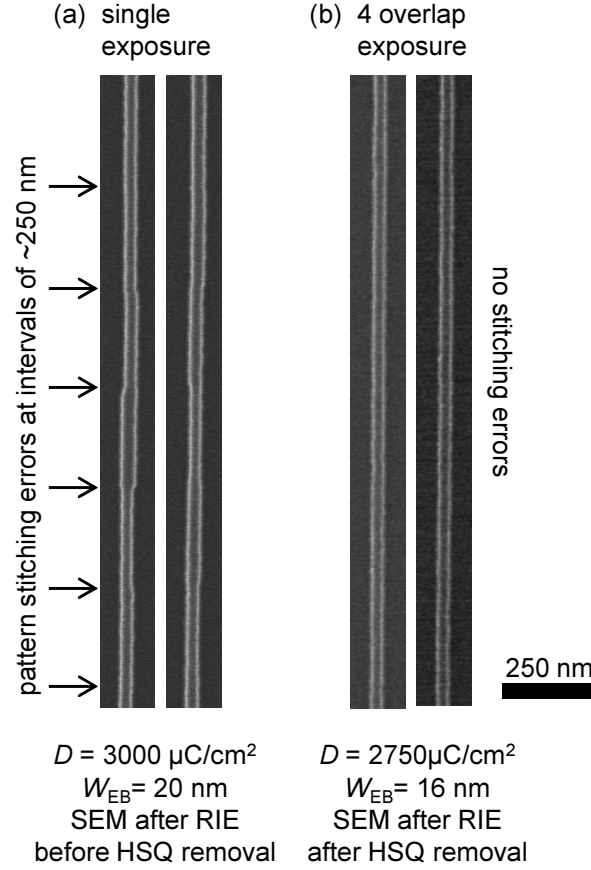


Figure 3.3: Effect of overlap exposure: (a) single exposure and (b) 4-times overlap exposure. By using the overlap exposure, the stitching errors of patterns between exposure fields were suppressed. Although the conditions of EB lithography are slightly different [design width and EB dose were 20 nm and $3000 \mu\text{C}/\text{cm}^2$ in (a) and 16 nm and $2750 \mu\text{C}/\text{cm}^2$ in (b), respectively], which are not fully optimized conditions, these differences are nonessential in stitching errors.

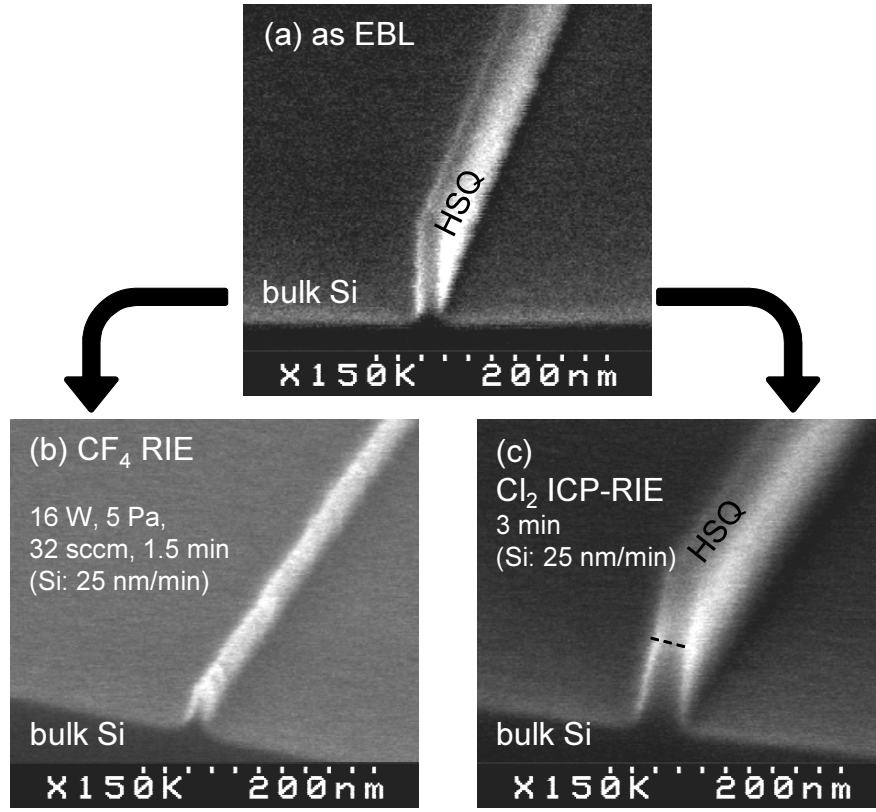


Figure 3.4: SEM images of test structure of HSQ NW pattern (110-nm-thick, 20-nm-wide, $3800\mu C/cm^2$: not fully optimized conditions) on bulk Si (a) as EBL, (b) etched by CF_4 -based parallel-plate RIE, and (c) etched by Cl_2 -based ICP-RIE (not optimized). After CF_4 RIE, The HSQ pattern disappeared owing to the poor etching selectivity, and thus the pattern transfer to Si failed, whereas it was successful with Cl_2 ICP-RIE.

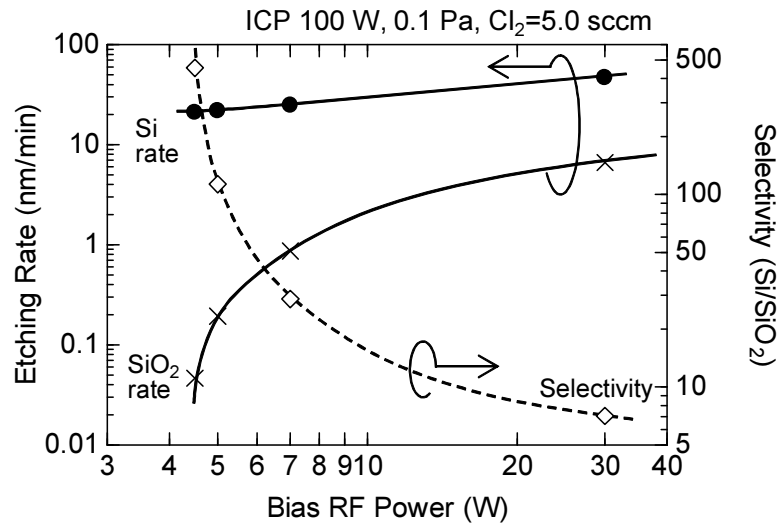


Figure 3.5: Bias power dependence of etching rates of Si(100) and thermally-grown SiO₂ and selectivity (Si/SiO₂). Lines are guides for eyes.

thermally-grown SiO_2 and the selectivity of Si over SiO_2 as a function of bias rf power. The ICP power was kept at 100 W and a low pressure of 0.1 Pa was used. The etching rate of Si does not show strong dependence on bias power, but the etching rate of thermal SiO_2 rapidly decreases with bias rf power. Since HSQ is not as resistant as thermal SiO_2 , the etching rate of HSQ is faster than that of thermal oxide. However, by using a low bias-power condition, a good selectivity ~ 6 was obtained (Fig. 3.6) at bias rf power = 5 W.

3.2.3 Details of Fabrication Process

In this section, the detailed fabrication method of Si NWs is described. The starting material is silicon-on-insulator (SOI) substrate. In this study, SOI substrates with different surface orientations of (100) and (110) were used. Both substrates have a lightly-boron-doped p-type top Si layer and 200-nm-thick buried oxide. The detailed specifications of SOI substrates are summarized in Table 3.1. First, SOI substrates were thinned down by sacrificial thermal oxidation. After thinning down, 10-nm-thick thermal oxide was grown. As stated above, the hybrid lithography technique [14] was used to define Si NW patterns. Figure 3.7 shows the hybrid lithography process adopted in this study. First, an isolated space of resist was written by EBL using 110-nm-thick ZEP at EB dose of $180 \mu\text{C}/\text{cm}^2$ [Fig. 3.7(a)]. The complete recipe of the EB lithography of this step is given in Table 3.2. Next, the thermal oxide layer exposed in the resist trench was etched by buffered HF (10 nm+8 nm overetching) and subsequently ZEP was stripped by N-methylpyrrolidone (NMP) and subsequent SC-1 cleaning (28% NH_4OH : 30% H_2O_2 : $\text{H}_2\text{O} \simeq 0.25 : 1 : 5$, 65°C , 10 min) [Fig. 3.7(b)]. Here, the gap of SiO_2 films defines the length of Si NWs, and the areas covered by SiO_2 supporting pads of NWs (source and drain of NW MOSFETs). After that, NW patterns were exposed across the SiO_2 aperture like bridges by 50-nm-thick HSQ (manufactured by Dow Corning) [Fig. 3.7(c)]. The complete recipe of the EB lithography for NW patterning is shown in Table 3.3. After HSQ EBL, pattern transfer to the Si layer was performed by Cl_2 ICP-RIE using HSQ and SiO_2 films as etching masks [Fig. 3.7(d)]. The ICP power, pressure, and the flow rate of Cl_2 gas were 100 W, 0.1 Pa, and 5.0 sccm, respectively. First, the etching was performed with the bias power of 7 W for 30 s to remove surface oxide and then the bias power was decreased to 4.5 W to realize Si/HSQ selective main etching. The etching rate of Si was about 22 nm/min at 4.5 W. The etching was performed with the overetching thickness of 100% of the SOI film thickness. After removing HSQ by 1-min etching with 0.5 % HF and subsequent chemical cleaning, the surface of Si NWs was slightly oxidized by a few nm in Si thickness in 10% O_2/N_2 ambient at 1000°C to remove a superficial layer that was exposed to and damaged by chlorine plasma.

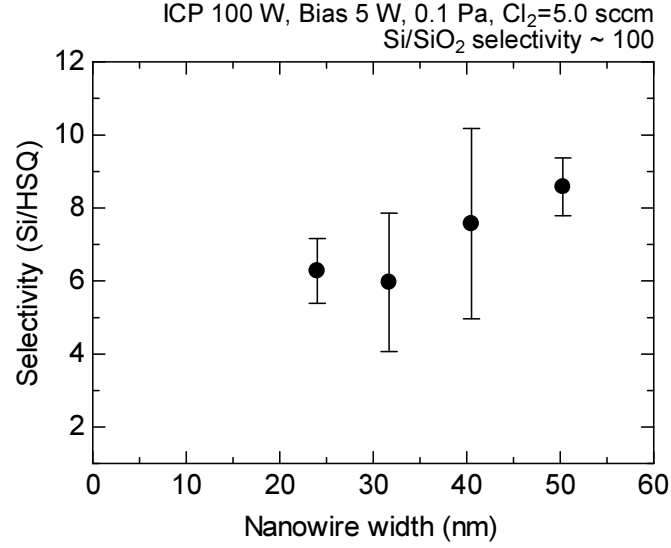


Figure 3.6: NW width dependence of etching selective ratio of Si over HSQ in optimized Cl₂-based ICP-RIE.

Table 3.1: Specifications of SOI substrates used in this thesis.

	(110)SOI	(100)SOI
Si thickness	100 nm	110 nm
BOX thickness	200 nm	200 nm
conductivity type	p-type	p-type
dopant	boron (B)	boron (B)
resistivity	13.5–22.5 $\Omega \cdot \text{cm}$	5–50 $\Omega \cdot \text{cm}$
dopant concentration	5×10^{14} – $2 \times 10^{15} \text{ cm}^{-3}$	3×10^{14} – $3 \times 10^{15} \text{ cm}^{-3}$

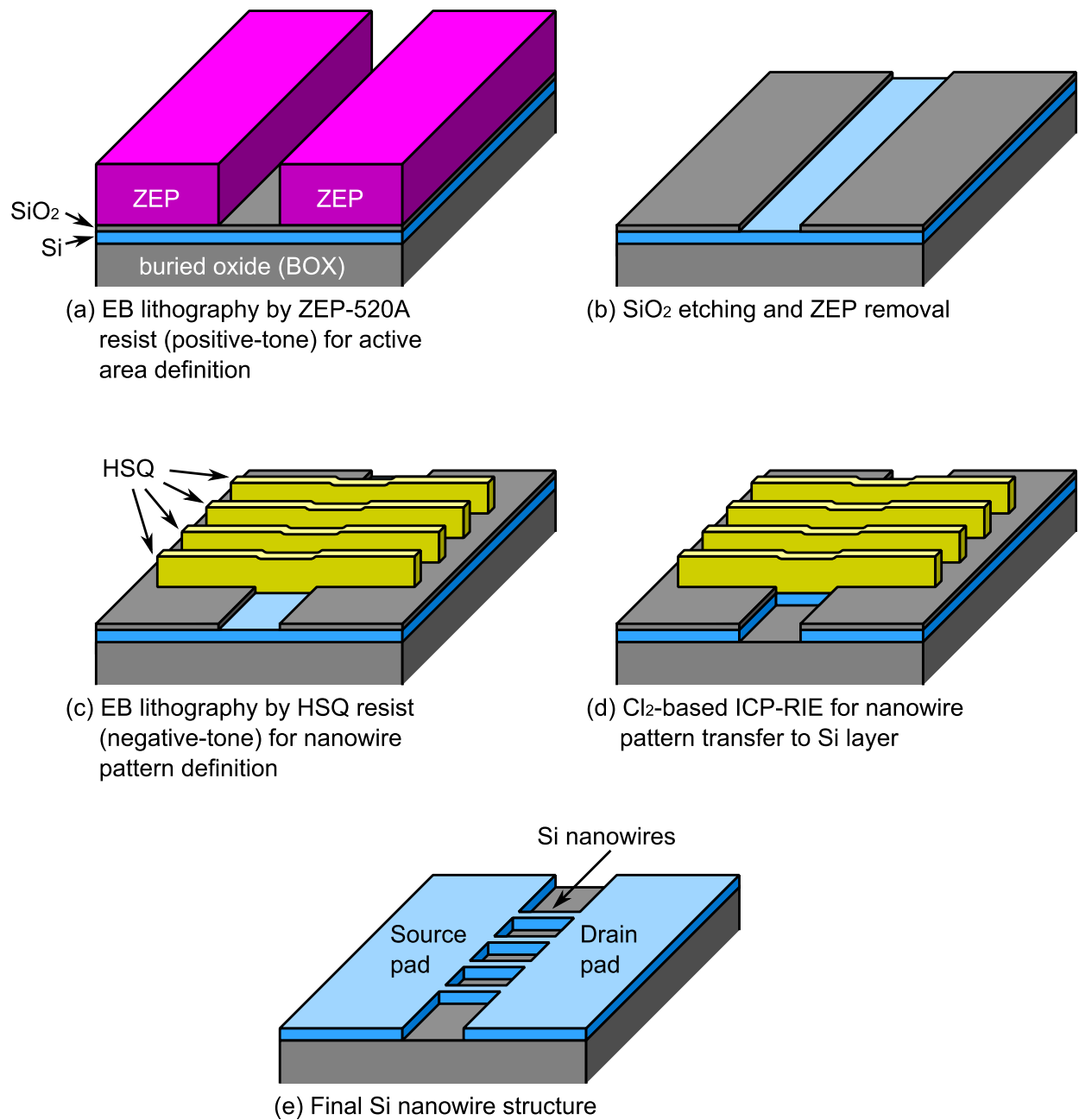


Figure 3.7: Hybrid lithography process to fabricate Si NW patterns.

Table 3.2: Recipe of EB lithography with ZEP-520A resist for active area definition

Process	Chemicals / Tools	Conditions
1 UV/O ₃ cleaning		RT, 36 min
2 dehydration bake	hot plate	160°C, 5 min
3 HMDS prime	HMDS vapor	140°C, 30 sec
4 resist spin-coat	ZEP-520A-7 : anisole = 1 : 1	1800 rpm, 60 sec (110 nm)
5 soft bake	hot plate	160°C, 3 min
6 EB exposure	JBX-6300SA	100 kV, 100 pA, 1800 $\mu\text{C}/\text{cm}^2$
7 development	n-amyl acetate (ZEP-N50)	23°C, 2 min
8 rinse	isopropyl alcohol	RT, 30 sec
9 N ₂ dry		

Table 3.3: Recipe of EB lithography with HSQ resist for NW patterning

Process	Chemicals / Tools	Conditions
1 dehydration bake	hotplate	120°C , 5 min
2 HMDS prime	HMDS vapor	140°C, 2 min
3 resist spin-coat	3%HSQ/MIBK	6000 rpm, 60 sec (50 nm)
4 soft bake	hotplate	150°C, 2 min
5 Spacer spin-coat	Spacer 300HX-02	1500 rpm, 60 sec (40 nm)
6 soft bake	hotplate	100°C, 1 min
7 EB exposure	JBX-6300SA	100 kV, 100 pA, 1800 $\mu\text{C}/\text{cm}^2$
8 Spacer removal	ultrapure water	RT, 1.5 min (paddle)
9 N ₂ dry		
10 post-exposure bake	hotplate	100°C, 2 min
11 development	TMAH 2.38%	23°C, 40 or 50 sec
12 rinse	ultrapure water	RT, 30 sec paddle + 10 sec flow
13 N ₂ dry		

3.3 Characterization of Nanowire Structures

In this section, the NWs fabricated by the method described above are characterized. The NWs were fabricated on SOI(110) thinned down to about 40, 27, and 19 nm with thermally-grown 10-nm-thick SiO₂ hard mask. The length of NWs designed in ZEP lithography was 100 nm, and the EB design widths for HSQ were 20–40 nm. Four different orientations of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ were designed on the same substrate. The ICP-RIE time was adjusted for different thickness samples. The sacrificial oxidation was performed for 12 min. The grown SiO₂ thicknesses were monitored on bulk Si(100), (110), and (111): 7.2, 9.9, 8.3 nm, respectively. They correspond to surface Si loss by 3.2, 4.3, 3.6 nm, respectively. After stripping the sacrificial oxide by HF, top-view scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (TEM) were performed.

3.3.1 Top-View Observation by SEM

Figure 3.8 shows $\langle 110 \rangle$ oriented Si NWs with various EB design widths formed on SOI(110) substrates with different SOI thicknesses. SEM was observed after etching the sacrificial oxide and releasing from the BOX layer. NWs look almost straight, but they have some line-edge and line-width roughnesses. The detailed evaluation of the line-width roughness will be given in Section 3.4. The length of NWs which was designed as 100 nm in EBL became 140 nm. This increase in length is probably caused by overetching of hard mask SiO₂ by BHF and sacrificial oxidation.

The width of $\langle 110 \rangle$ NWs on the SOI substrates with different thicknesses was measured from SEM (with a correction from TEM measurement) and is given in Fig. 3.9. Since the etching time (*i.e.*, the total amount of consumed HSQ thickness) is different among the samples with different SOI thicknesses, the width would vary if the shape of HSQ resist deteriorated during ICP-RIE. However, it was found that the widths of NWs with different SOI thicknesses are the same for each HSQ design width, which is thanks to high Si/HSQ selectivity. The relationship between the final width (W_{NW}) vs EB width (W_{EB}) is linear, but the slope is 1.1, not unity. The NWs with narrower W_{EB} have smaller W_{NW} . This is because the EB dose is slightly scant to produce precise critical dimension in thin patterns because of smaller proximity effect. Fig. 3.2 also indicates that narrower W_{EB} produces smaller HSQ pattern width. The width of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ NWs fabricated on SOI with different Si thicknesses was characterized and shown in Fig. 3.10. As can be seen, there is a little difference among NWs along four orientations (1–3 nm), but clear orientation dependence was not observed. Therefore, the formation of NWs in different orientations was successful.

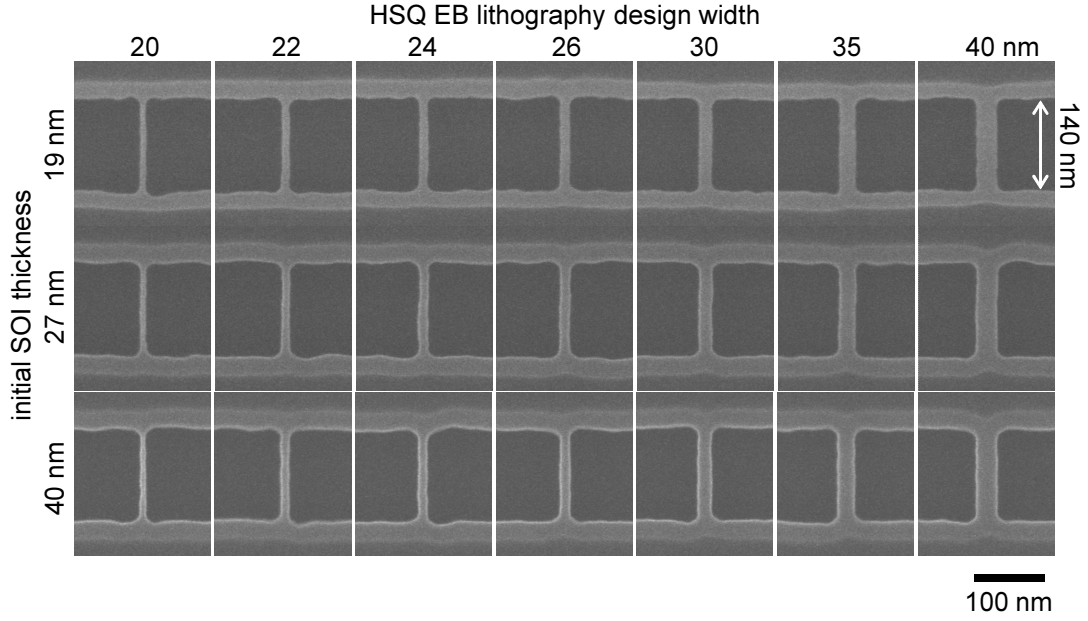


Figure 3.8: Top-view SEM images of fabricated $\langle 110 \rangle / (\langle 110 \rangle)$ Si NWs with various EBL design widths and initial SOI thicknesses. SEM was performed after removing surface sacrificial oxide and releasing NWs from BOX.

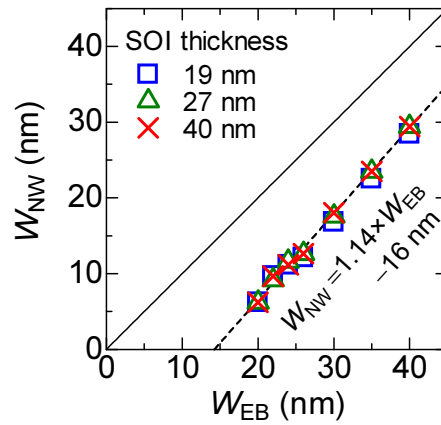


Figure 3.9: Width of $\langle 110 \rangle / (\langle 110 \rangle)$ Si NWs (W_{NW}) with various EBL design widths (W_{EB}) and initial SOI thicknesses. SEM was performed after removing surface sacrificial oxide and releasing NWs from BOX. W_{NW} is almost independent of the SOI thicknesses.

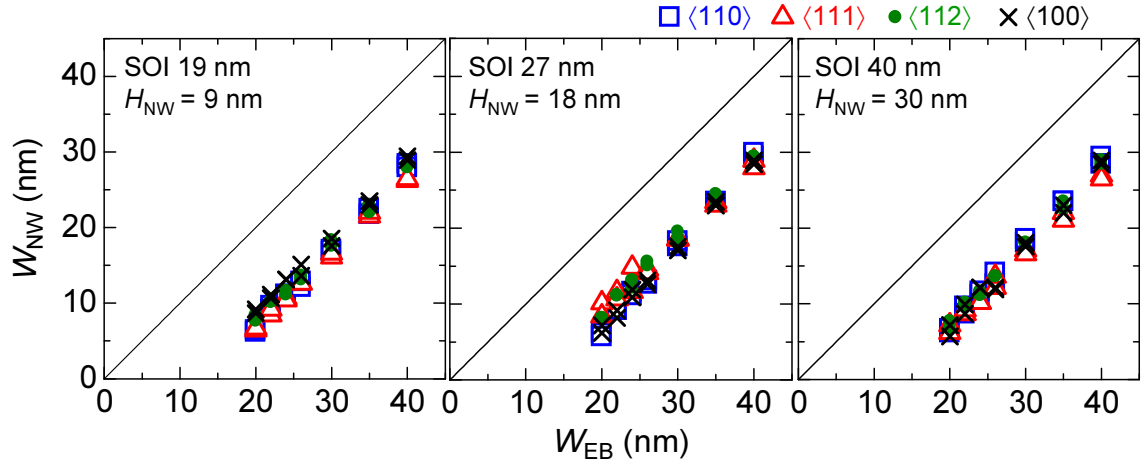


Figure 3.10: Width of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ Si NWs (W_{NW}) with various EBL design widths (W_{EB}) and initial SOI thicknesses. SEM was performed after removing surface sacrificial oxide and releasing NWs from BOX. W_{NW} is almost independent of the NW orientations.

3.3.2 Cross-Sectional Observation by TEM

Figure 3.11 shows cross-sectional high-resolution TEM (HRTEM) images of $\langle 110 \rangle$ -oriented Si NWs fabricated on SOI with different thicknesses. The thickness of TEM specimens is expected to be about 100 nm or less, which does not include SOI parts to which NWs are originally connected. The cross-sectional shape of NWs is almost rectangular with a small sidewall angle and rounded corner (radius: ~ 3 nm). Around NWs, a native oxide which grew after the removal of sacrificial oxide is observed, and its thickness is typically 1.5 nm. When the size of NWs is measured, the thickness of Si consumed by the native oxide is corrected assuming that the surfaces of all NWs are consumed by 1.5-nm-thick SiO_2 . The thickness of source and drain pads is slightly thicker by ~ 5 nm than NW heights because pad areas were initially protected by SiO_2 during chemical cleaning and sacrificial oxidation processes. Especially in NWs with small heights (9 and 18 nm), the image contrast on sidewalls does not look clear. This uncertain contrast comes from line-edge and width fluctuations. In addition, there exists surface atomic roughness on sidewalls which is probably attributed to the RIE process.

3.4 Discussion

In the SEM observation, line-edge and width fluctuations were observed. The profiles of the width fluctuation of NWs along the length determined from SEM images by edge extraction are shown in Fig. 3.12. Here, the fluctuation was defined as the deviation of the width at each position from the average (+: thicker width, -: thinner width). The extraction was performed on $\langle 110 \rangle$ NWs with a height of 18 nm (27-nm thick SOI) shown in Fig. 3.8. Since the size of 1 pixel of the SEM images corresponds to about 0.5 nm, the fluctuation below 1 nm (± 0.5 nm = ± 1 px) may be meaningless because of the detection accuracy. However, there exists the definite fluctuation of 2–3 nm along the wire axis regardless of the wire width [1–2 nm as root-mean-square (RMS) roughnesses]. This fluctuation is small, but it may be not enough in thin NWs.

Assuming that a 5-nm-thick square $\langle 110 \rangle / (110)$ NW has a ΔW -nm fluctuation in the width, the variation of the energy of the first subband in CB and VB was calculated by the $sp^3d^5s^*$ tight-binding method and shown in Fig. 3.13. When the width of the NW fluctuates along the NW length, the energy levels become position dependent, as illustrated in Fig. 1.8. For example, the fluctuation of $\Delta W = -2$ nm induces 24 meV shift in CB and 59 meV in VB, which are comparable to or higher than the thermal energy at room temperature (26 meV). Thus, these amounts of energy barriers for carriers formed in a NW by the width fluctuation may affect the carrier transport. When ΔW is within ± 1 nm, the energy fluctuation becomes below the thermal energy at room temperature, although it is difficult to mention the definite requirement of the flatness of Si NWs. From the viewpoint of variability of device operation at room temperature, a simulation study have pointed out that the

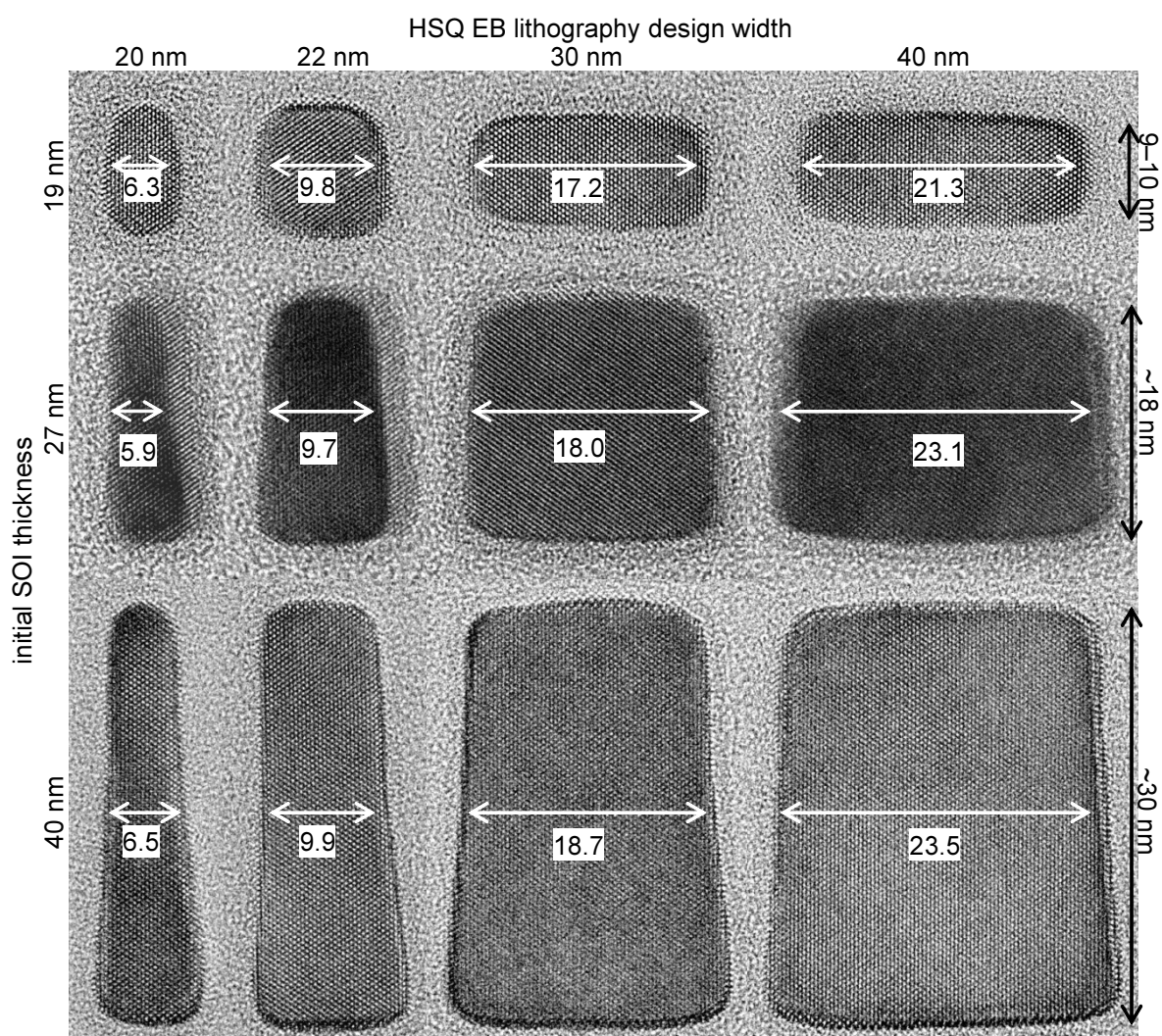


Figure 3.11: High-resolution cross-sectional TEM images of fabricated $\langle 110 \rangle / (110)$ Si NWs with various EBL design widths and initial SOI thicknesses. Native oxide was observed on the surface of NWs. The width (unit: nm) and the height were measured taking account of the Si loss by the native oxide.

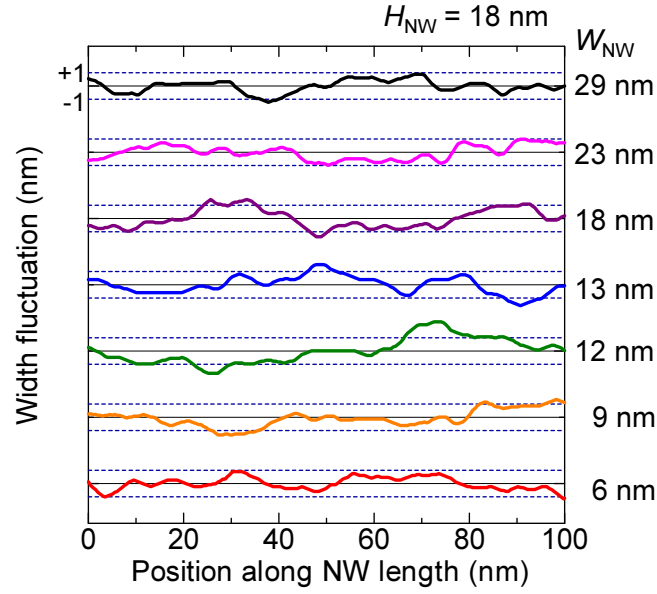


Figure 3.12: Width fluctuation along the length in fabricated $\langle 110 \rangle / (110)$ Si NWs with various widths (height: 18 nm) extracted from SEM images.

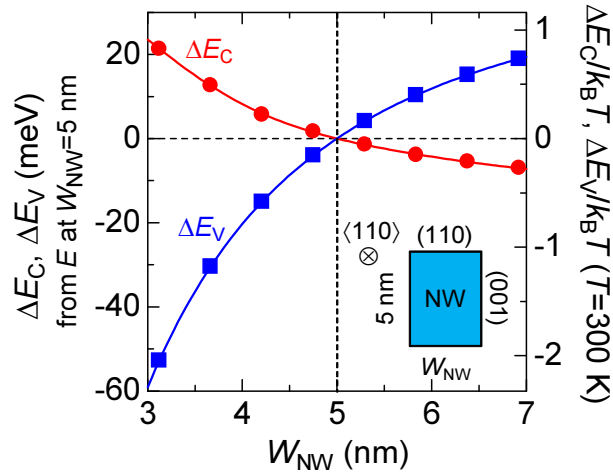


Figure 3.13: Calculated fluctuation of first subband energy in CB and VB induced by width fluctuation in 5-nm-high $\langle 110 \rangle / (110)$ Si NWs. The energy is referenced from the energy in the 5 nm $\times$ 5 nm NW. The calculation was performed by an $sp^3d^5s^*$ tight-binding method.

RMS amplitude of the line-edge roughness has to be suppressed down to $0.1 \times (\text{diameter})$ to minimize the variability of threshold voltage and mobility, for example [24]. When carrier transport properties in Si NWs are studied at low temperatures, the surface smoothness should become much more important because the thermal energy corresponding to the energy distribution of carriers also decreases at low temperatures. Since complete elimination of the width fluctuation which arises in the patterning process is difficult, post-patterning treatment is necessary for further reduction of the fluctuation.

3.5 Summary

In this chapter, a fabrication method of Si NWs was described and the shape of NWs was characterized by SEM and TEM. NWs were fabricated by a top-down process using EBL and ICP-RIE with a hybrid lithography technique on a (110) SOI substrate. To reduce the fluctuations in NWs, HSQ resist with overwriting technique was used in EBL and high-selective-ratio (Si/HSQ) ICP-RIE process was developed. NWs had almost rectangular cross-section, and the size of the smallest NWs was $6 \text{ nm} \times 9 \text{ nm}$ with small width fluctuation of 2–3 nm and atomic-level surface roughness.

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Chapter 4

Investigation of HCl Gas Etching for Si Surface Smoothing

4.1 Introduction

In this chapter, hydrogen chloride (HCl) gas etching is investigated as a surface-smoothing process of Si. HCl gas has been conventionally employed for *in situ* cleaning of the Si surface prior to Si epitaxial growth. HCl etches the Si surface without physically damaging the crystal, resulting in a clean and flat Si surface. Over the last decade, new applications of HCl etching have been proposed. The selective etching of Si-based materials such as SiGe/Si [1] and polycrystalline-Si/crystalline-Si [2] is one of the examples. The recess etching of Si was proposed for SiGe regrowth to realize the SiGe source/drain of Si MOSFETs [3–5]. This recess etching can also be applied to the growth of a strained Si layer on a relaxed thin SiGe buffer in a shallow trench isolation window to realize high-mobility strained Si channel devices [6]. In addition, defect-free thinning of a silicon-on-insulator (SOI) layer by HCl gas etching was demonstrated [7, 8], and a very smooth surface with step-terrace structures with monatomic steps with a Si thickness down to about 10 nm was obtained [7]. This surface smoothing effect may also be useful as a post-patterning flattening process of Si NWs. Moreover, the etching effect can reduce the width of Si NWs and thus very thin Si NWs with smooth surfaces might be obtained by HCl gas etching.

To apply HCl etching to NWs, low-rate etching is necessary and its kinetics should be well understood to ensure high process controllability. In addition, the etching loading effect, *i.e.*, etching rate variation depending on the etching mask pattern and Si surface exposure, should be minimized. In previous studies, the detailed etching mechanism of high-rate Si etching at high temperatures over 1100°C and high HCl concentrations over 1% was investigated [9, 10]. Although there have been several reports on the kinetics of low-rate etching [1, 4, 6, 11, 12] including the etching loading effect [1, 3, 4, 6, 12], detailed etching kinetics such as the etching-rate-limiting step and the origin of the loading effect in HCl gas etching are still unclear. Therefore, the kinetics of low-rate Si etching with HCl

gas was studied focusing on the identification of the etching-limiting step, and the strength and origin of the loading effect.

4.2 Experimental Details

HCl etching was performed in a horizontal cold-wall reactor at atmospheric pressure. A schematic image of the etching reactor is shown in Fig. 4.1. A SiC-coated graphite susceptor was heated using an inductive heating system. The process temperature was monitored by measuring the temperature of the susceptor with an optical pyrometer. The range of process temperatures in this study was 1000–1100°C. To obtain a low etching rate < 10 nm/min for nanometer-order etching, HCl gas was diluted to below 0.3% in purified H_2 gas at a flow rate of 3 slm. During the heating and cooling periods, the HCl gas flow was stopped and only H_2 gas was flowed unless otherwise specified. Owing to the cold-wall reactor and the small susceptor, fast heating and cooling were realized (about 1.5 min from room temperature to 1050°C). Before the etching experiments, the samples were cleaned in a H_2SO_4 - H_2O_2 mixture (SPM) followed by dipping in HF aqueous solution to obtain a clean hydrogen-terminated surface.

4.3 Experimental Results

4.3.1 Etching Rate of Bulk Si

First, the HCl concentration dependence of the etching rate of the Si(100) face at 1050°C was investigated. A p-type (100) SOI wafer (1–10 $\Omega \cdot \text{cm}$, 110 nm Si/200 nm buried oxide (BOX)/725 μm handle wafer) was used for this experiment. This wafer is the same as in Table 3.1. The etching rate was evaluated by measuring the difference in SOI layer thickness before and after etching by spectroscopic ellipsometry. To eliminate the etching portion during the *ex situ* wet cleaning (SPM and HF) and heating and cooling periods, three etching experiments with different etching durations were performed at various HCl concentrations, and the etching rate was determined from the slope of etched thickness vs. time plots of Fig. 4.2(a). The obtained etching rate is shown in Fig. 4.2(b). A low etching rate of < 10 nm/min was obtained owing to the low HCl concentration. The etching rate is not linear with respect to the HCl concentration but it can be fitted by a quadratic function of the concentration [dashed line in Fig. 4.2(b)].

Next, the speeds of etching of Si(100) and (110) were compared. Bare (100) and (110) SOI chips were simultaneously etched for 3 min at 1050°C and the thickness difference before and after etching was measured by spectroscopic ellipsometry. The (110) SOI wafer used in this experiment had a p-type (13.5–22.5 $\Omega \cdot \text{cm}$) 100-nm-thick Si layer and a 200-nm-thick buried oxide layer on a 625- μm -thick handle wafer (Table 3.1). Figure 4.3 shows the thicknesses of etched SOI (100) and (110) layers as a function of HCl concentration.

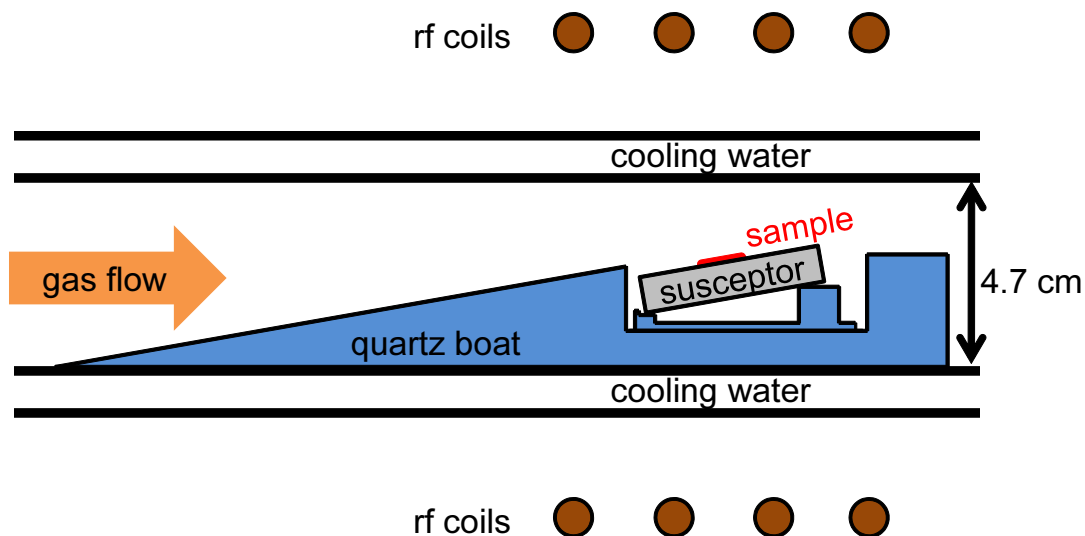


Figure 4.1: Schematic image of the HCl gas etching system.

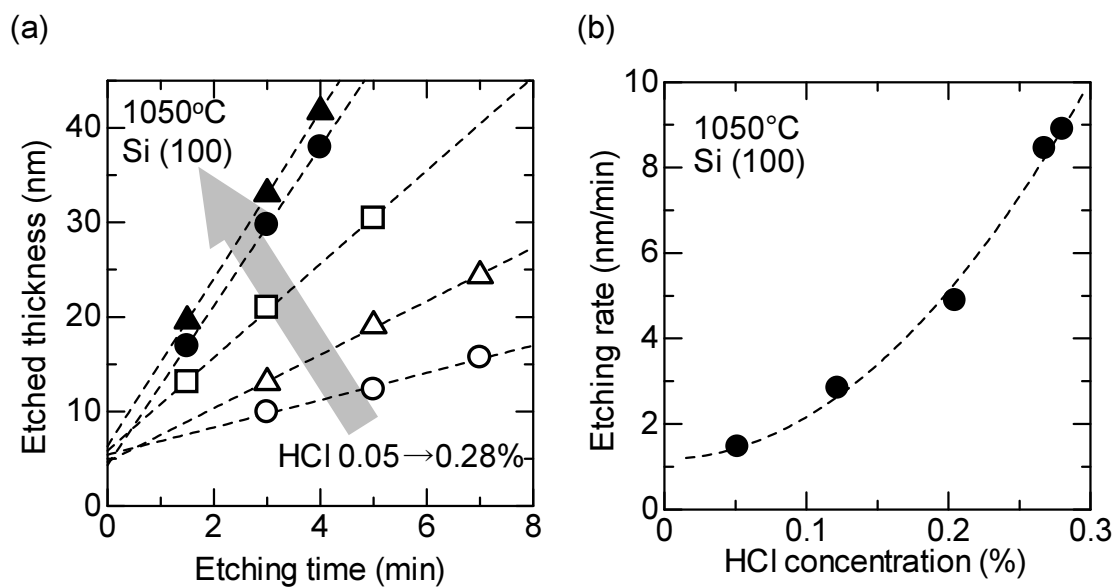


Figure 4.2: (a) Etching time dependence of etched depths of Si(100) with HCl/H₂ gas at 1050°C at various HCl concentrations in H₂ gas. (b) The rate of Si(100) etching with HCl/H₂ gas at 1050°C as a function of HCl concentration in H₂ gas which is calculated from the slopes of (a). The etching rate is not linear, but it can be fitted by a quadratic function of HCl concentration [dashed line in (b)].

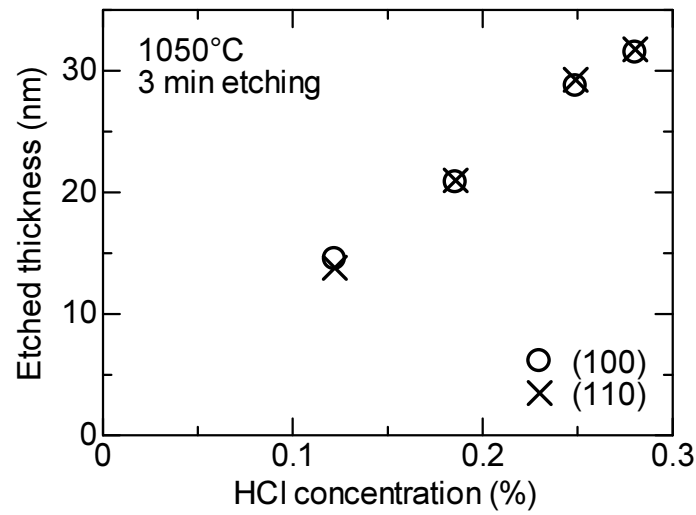


Figure 4.3: HCl concentration dependence of thicknesses of etched Si(100) and (110) for 3 min HCl etching at 1050°C. The etching depths of Si(100) and (110) are almost the same, which indicates that the flux of atoms removed from the surface is independent of the crystal face.

From this figure, the thicknesses of the etched Si(100) and (110) were found to be almost the same. This result indicates that the flux of removed atoms, *i.e.*, the number of atoms removed from the surface per unit area and time, is controlled at a constant value regardless of the crystal face under these etching conditions.

The etching temperature is also an important parameter that controls etching kinetics. The effect of the etching temperature was investigated in the temperature range of 1000–1100°C. Figure 4.4 describes the relationship between the thickness of etched SOI (100) and the etching time at different temperatures with a HCl concentration of 0.12%. Within this temperature range, the etching rate hardly depends on the temperature. The activation energy of the etching rate with the temperature is estimated to be less than 10 kcal/mole.

4.3.2 Surface Morphology of Etched Bulk Si

Here, the morphology of the Si surface after HCl gas etching is discussed. The surface morphology was investigated by a tapping-mode atomic force microscopy (AFM). Before HCl gas etching, the surfaces of Si(100) and (110) were structureless, and the RMS roughnesses were about 0.12 and 0.10 nm for Si(100) and (110), respectively. Figure 4.5 shows AFM images of the bare (100) and (110) SOI surfaces after etching with 0.12% HCl at 1050°C for 3 min. After HCl gas etching, a small RMS roughness of 0.08 nm was obtained on (100), and a step-terrace structure appeared on (110). The step height on (110) corresponded to mainly two (1–4) atomic layers, and the RMS roughness on a terrace was 0.07 nm, indicating a very smooth surface. Actually, these etching conditions are close to those used for bare SOI (100) wafer thinning and flattening reported by Thilderkvist *et al.* [7]. Therefore, the good surface morphology after etching itself is not surprising. In this study, however, the surface is etched by only about 15–20 nm. Moreover, it is confirmed that the Si(100) surface intentionally roughened by NH₃ aqueous solution [RMS as roughened: ~0.35 nm, Fig. 4.6(a)] can be smoothened by etching with 0.12% HCl gas at 1050°C for 3 min [RMS after etching: 0.08 nm, Fig. 4.6(b)]. Therefore, even such a slight surface removal by HCl etching can significantly improve surface roughness.

4.3.3 Mask-Pattern Dependent Etching Acceleration (Etching Loading Effect)

To apply HCl etching to patterned Si wafers, the behavior of loading effects should be understood for precise etching control. Therefore, the author investigated the strength of loading effects by etching a bulk Si wafer partially masked by thermally grown SiO₂.

Two types of mask/aperture stripe pattern were used to evaluate the loading effect. One had a constant aperture width of 10 μm and various mask widths of 10, 50, 100, and 500 μm . The other had the same width for the aperture and mask of 10, 50, 100, and 500 μm . Etching was performed for 3 min at 1050°C at a HCl concentration of 0.12%.

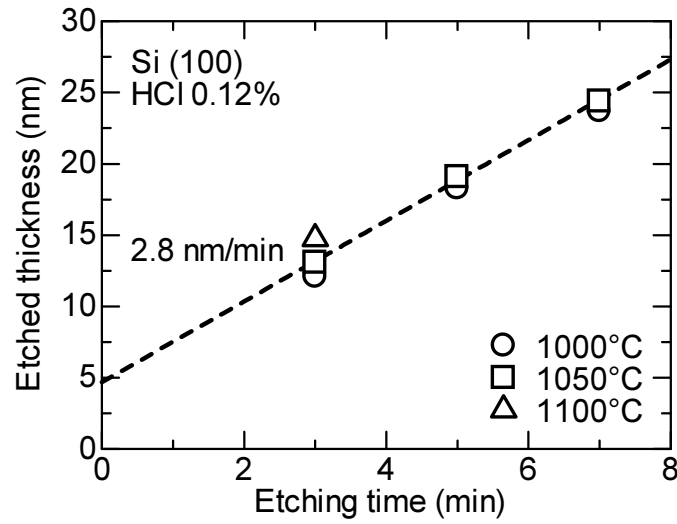


Figure 4.4: Relationship between the etched thickness of Si(100) and etching time at different etching temperatures of 1000, 1050, and 1100°C (HCl concentration = 0.12%). Etching is insensitive to temperature in this temperature range.

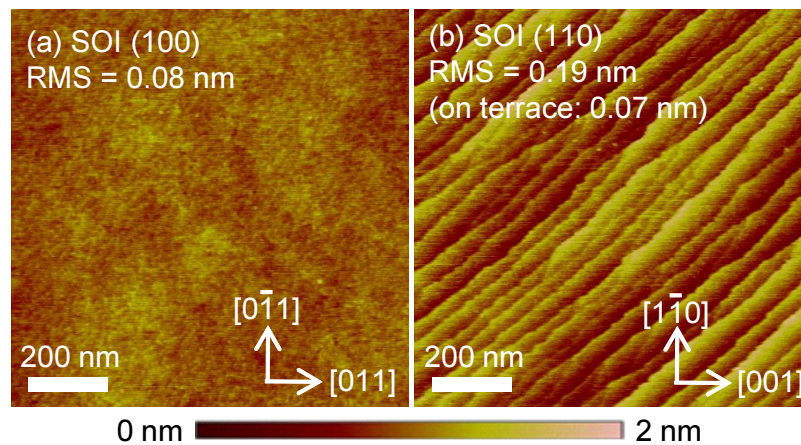


Figure 4.5: Surface morphology of bare SOI (100) and (110) surfaces etched with 0.12% HCl gas at 1050°C for 3 min measured by tapping-mode atomic force microscopy. The RMS roughnesses are very small: 0.08 nm on (100) and 0.07 nm on terraces on (110), which indicates a very smooth surface after HCl etching.

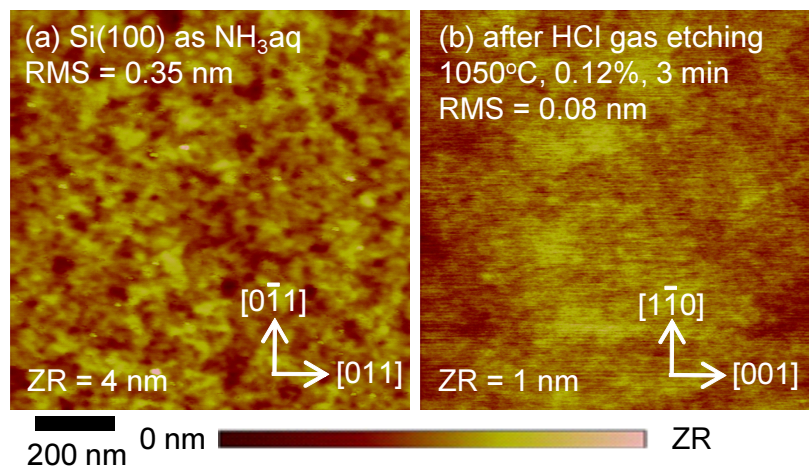


Figure 4.6: Surface morphology of bulk Si(100) intentionally roughened by NH_3aq immersion and smoothed surface by etching with 0.12% HCl gas at 1050°C for 3 min: (a) as roughened and (b) after HCl gas etching. ZR indicates the height range of each image.

Under these conditions, the surface of bare Si(100) is etched by about 20 nm and SiO₂ is hardly etched. After etching, the SiO₂ mask was selectively removed with HF solution, and the etching profile was measured using an optical profiler (Zygo NewView 7300).

The results of the etching profiles are shown in Fig. 4.7. The vertical axis corresponds to the etched depth at a Si opening area and the horizontal axis indicates the position in the aperture. The zero position on the horizontal axis corresponds to the center of the aperture. In the case of the etching of the 10- μ m-wide Si aperture [Fig. 4.7(a)], the etching rate significantly accelerated with the increase in the mask width from 10 to 500 μ m. The sample with the 10- μ m-wide aperture and 500- μ m-wide mask was etched about 30 times deeper than that with the 10- μ m-wide opening and mask. On the other hand, when the aperture has the same width as the mask [Fig. 4.7(b)], the etching depth at the center of the aperture is almost independent of the pattern width. In the latter case [Fig. 4.7(b)], an increase in the etching rate is observed only near the aperture edges, which is also observed in the former case [Fig. 4.7(a)].

The observed loading effect is too large to etch patterned Si NWs with high controllability. To determine the origin of this heavy loading effect, the author considered the etching mechanism.

4.4 Discussion on Etching Kinetics

4.4.1 Etching Limiting Process

In the 1970s, the mechanism of high-rate Si etching with HCl gas was intensively studied [9, 10, 13]. HCl gas etching involves the successive processes of (a) HCl diffusion in the gas phase from the bulk gas stream to the Si surface, (b) surface chlorination given by the reaction



(c) surface migration of SiCl₂, (d) desorption of SiCl₂, and (e) diffusion of SiCl₂ in the gas phase from the Si surface to the gas stream, as schematically illustrated in Fig. 4.8 [10]. These processes can be classified into two groups: diffusion in the gas phase [(a) and (e)] and surface reactions [(b), (c), and (d)]. Within the temperature range of this study, H and Cl atoms are not surface and thus surface bonds of Si are probably almost free [14]. Therefore, desorption of H and Cl atoms should not limit the etching rate. If one of the surface reaction processes from (b) to (d) is the etching limiting step, the loading effect should be very weak; thus, the strong loading effect observed in the experiments is not explainable. Furthermore, the activation energies of surface diffusion/desorption of SiCl₂ have already been reported. For the surface diffusion process, the reported activation energy is 32 kcal/mole on Si (111) [15], and for the surface desorption process, the activation energies are reported to be 47 [16], 59 [17], and 73 kcal/mole [18] on Si(100). These large values contradict the very small activation energy of the etching rate in this study (< 10 kcal/mole).

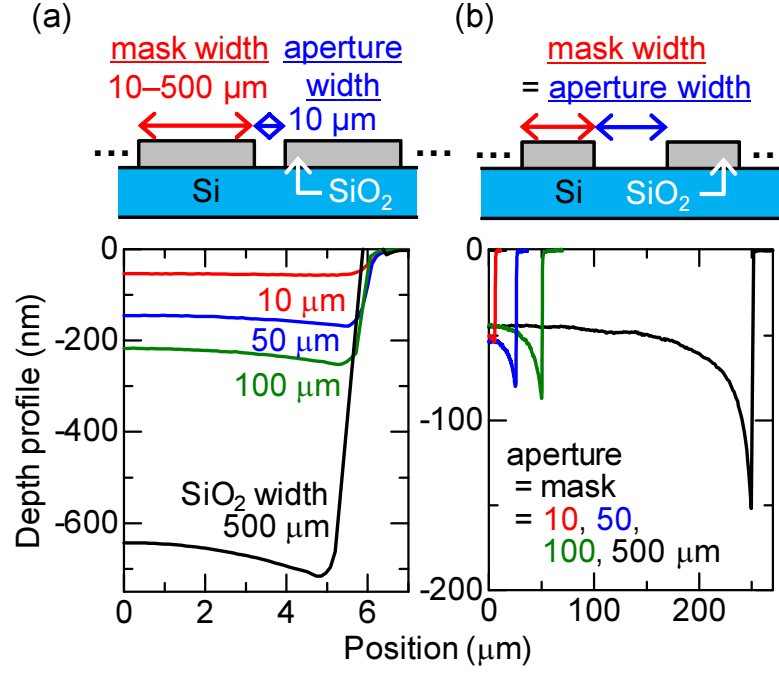


Figure 4.7: Etched depth profile of bulk Si(100) with SiO₂ line mask patterns. Position = 0 on the horizontal axis indicates the center of the aperture, and the data are symmetric with respect to the vertical axis at position = 0. (a) The SiO₂ mask width was varied from 10 to 500 μm while the aperture size was kept constant at 10 μm. (b) The SiO₂ mask and aperture had the same width from 10 to 500 μm. In both cases, etching was performed in 0.12% HCl/H₂ ambient at 1050°C for 3 min.

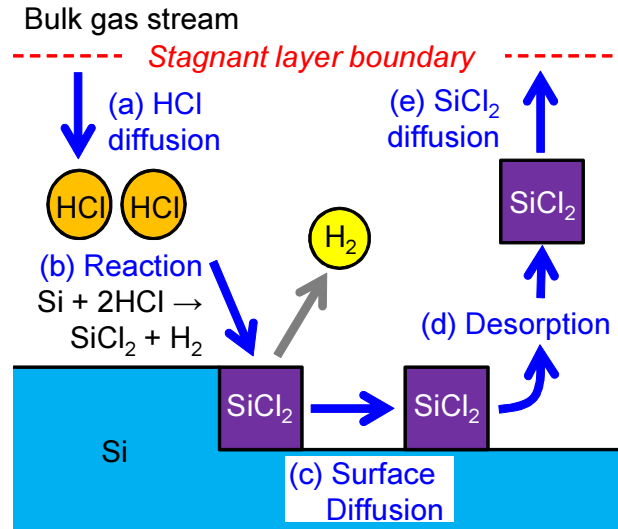


Figure 4.8: Schematics of reaction process of Si etching with HCl gas (Ref. 10).

Moreover, surface-reaction-limited etching would be crystal-orientation-dependent because surface reactions should depend on the microscopic configuration of atoms and/or bonds at the surface. From these viewpoints, the surface reaction processes should not limit the etching in the present experiment. On the other hand, because the temperature dependence of the diffusion coefficient in the gas phase is small in general [19], gas-phase-diffusion-controlled etching exhibits a small temperature dependence unless the equilibrium pressure of the diffusing species is susceptible to the temperature. In addition, gas-phase-diffusion-limited etching does not show crystal face dependence. From the above discussion, the etching under the conditions in this study should be limited by the diffusion of gas species: HCl (in-diffusion) or SiCl₂ (out-diffusion).

Van der Putte *et al.* have already discussed diffusion-limited Si etching with HCl [10]. If the in-diffusion of HCl were the dominant process, the etching rate would be proportional to the HCl flux from the bulk gas to the surface, and thus the etching rate should be proportional to the HCl concentration. However, this does not explain the experimental superlinear dependence [Fig. 4.2(b)]. In addition, the number of HCl molecules supplied to Si surface is large with respect to the etching rate. From a rough calculation of the diffusion flux of HCl molecules from the bulk gas stream to the Si surface, it was found that the etching rate would be about two orders of magnitude higher than the experimental values if all HCl molecules are consumed for etching, which is the case in the HCl-supply-limited etching. Therefore, HCl in-diffusion is not the etching limiting step. If the out-diffusion of SiCl₂ limits the etching, all the processes before the gas-phase diffusion of SiCl₂ will reach their equilibria so that the desorption of SiCl₂ is limited to keep the partial pressure of SiCl₂ (P_{SiCl_2}) immediately above the Si surface at its thermodynamical equilibrium value. For this reason, the etching rate becomes proportional to the equilibrium partial pressure of SiCl₂. It has been confirmed that HCl etching at a high rate (> 250 nm/min) at atmospheric pressure, a temperature of 1123–1323°C, and a HCl fraction $> 1\%$ is limited by SiCl₂ diffusion [10]. Although the etching rate in this study is at least two orders of magnitude smaller than that in Ref. 10 owing to the lower temperature (about 1050°C) and HCl fraction ($< 0.3\%$), our results indicate that the etching is also limited by the diffusion of SiCl₂ in the gas phase.

To confirm the hypothesis that the etching-limiting step is the out-diffusion of SiCl₂ in the gas phase, the following three propositions have to be validated. First of all, SiCl₂ is the dominant etching by-product existing in the gas phase under the conditions in this study. Secondly, the temperature dependence of the equilibrium SiCl₂ partial pressure is small. Finally, the etching rate is proportional to the equilibrium SiCl₂ partial pressure. However, it is very difficult to measure the SiCl₂ partial pressure directly in experiments. Therefore, the thermodynamical gas phase equilibria of H-Cl-Si systems were calculated under the etching conditions. Thirteen gas phase equilibrium equations for fifteen gas species [H₂, Cl₂, HCl, H, Cl, SiH, SiH₄, SiH₃Cl, SiH₂Cl₂, SiHCl₃, SiCl, SiCl₂, SiCl₃, SiCl₄, Si(g)] were simultaneously solved while keeping the total pressure at atmospheric pressure and varying

the Cl/H ratio and temperature. Equilibrium constants were taken from the NIST-JANAF thermochemical tables [20].

At first, the author confirms the first proposition. Figure 4.9 shows the HCl concentration dependence of the calculated equilibrium pressures in the H-Cl-Si system at 1050°C. Because HCl is tenuous, the pressure of monosilane SiH_4 , which might be related to Si etching with hydrogen carrier gas, is constant. To discuss the etching by HCl, the author focuses on chlorine-containing Si species. Among the chlorine-containing Si species, SiCl_2 and $\text{SiH}_{4-n}\text{Cl}_n$ ($n = 1, 2, 3$) are important and the others are negligible in this system. The amounts of these species as percentages of the total amount of chlorine-containing Si species (SiCl_n and $\text{SiH}_{4-m}\text{Cl}_m$, $n = 1, 2, 3, 4$, $m = 1, 2, 3$) are shown in Fig. 4.10. When the inlet HCl concentration is below 0.04%, the fraction of SiH_3Cl is highest. When the HCl concentration is above 0.04%, which is the case in this study, the fraction of SiCl_2 is highest. In addition, it saturates at about 70% when the HCl concentration is over 0.1%. The remaining portion (about 30%) of the chlorine-containing Si species is formed by reactions among mainly H_2 , HCl, SiH_4 , and SiCl_2 , and their diffusion speeds in the gas phase are expected to be comparable to that of SiCl_2 since diffusion coefficients in the gas phase are not significantly different among the gas species. Therefore, it would not cause a serious error even if only the diffusion of SiCl_2 is assumed to determine the etching rate although the fraction of SiCl_2 is not actually 100%.

Next, the author discusses the second proposition. Figure 4.11 shows the temperature dependence of gas equilibria of the H-Cl-Si system in the temperature range of 950–1150°C at the HCl fraction of 0.12%. As can be seen, the temperature does not change the composition significantly in this range. The activation energies of the partial pressure of SiH_mCl_n compounds were extracted in this temperature range. Here, a positive (negative) activation energy means that the equilibrium concentration of a species increases (decreases) as the temperature increases. As the equilibrium concentration of the dominant etching by-product increases on the surface, the concentration gradient in the stagnant layer increases. This results in enhanced mass transport in the stagnant layer, which leads to the enhancement of the etching rate. In the present experiments, the etching rate seems to increase slightly with the temperature. Therefore, the dominant species of the etching by-product may have a positive but very small temperature dependence. However, the increase in the etching rate was very small and the sign of the activation energy could be very small negative in case the experimental data have some errors. Therefore, species with both positive and negative activation energies are considered.

Among the chlorine-containing silicon species, SiCl_2 has the smallest positive temperature dependence. The activation energy for SiCl_2 is extracted as +3.3 kcal/mole. SiH_3Cl has the second smallest but a negative temperature dependence, −12.8 kcal/mole, but this activation energy is too large (as an absolute value) to explain the small experimentally obtained temperature dependence of the etching rate because this value corresponds to a 77% reduction in the partial pressure when the temperature rises from 1000 to 1100°C.

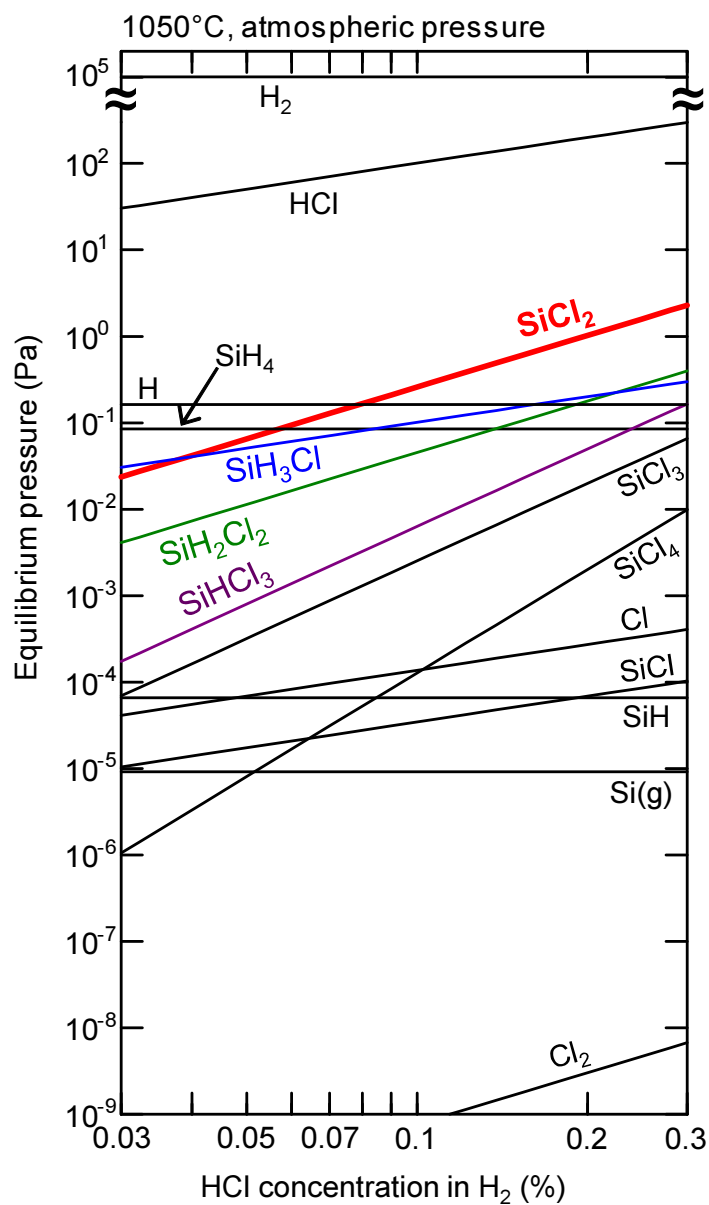


Figure 4.9: Equilibrium partial pressures of gases in H-Cl-Si system as a function of inlet HCl concentration in H_2 carrier gas at 1050°C and atmospheric pressure. The main chlorine-containing silicon species in the system is SiCl_2 , which indicates that SiCl_2 is the dominant etching by-product in the stagnant layer.

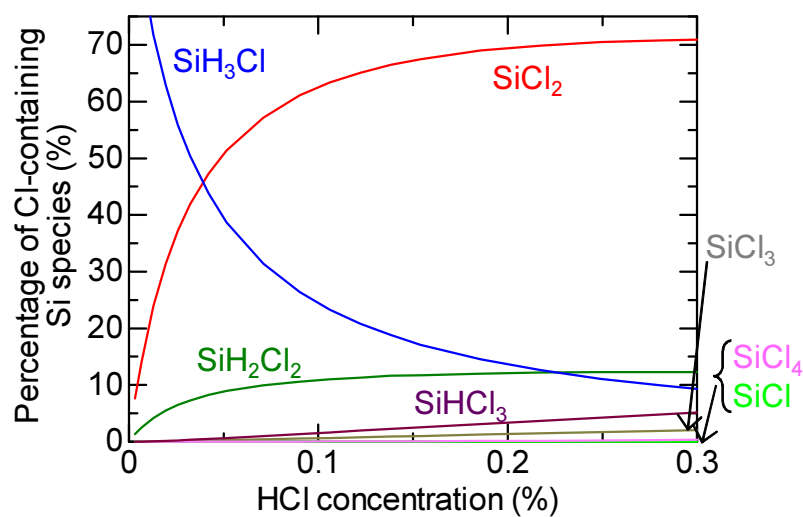


Figure 4.10: Calculated amounts as percentages of the total amount of chlorine-containing silicon species [SiCl_n ($n = 1, 2, 3, 4$) and $\text{SiH}_{4-m}\text{Cl}_m$ ($m = 1, 2, 3$)] as a function of inlet HCl concentration. In the calculation, the equilibrium H-Cl-Si gas system at 1050°C and atmospheric pressure was assumed.

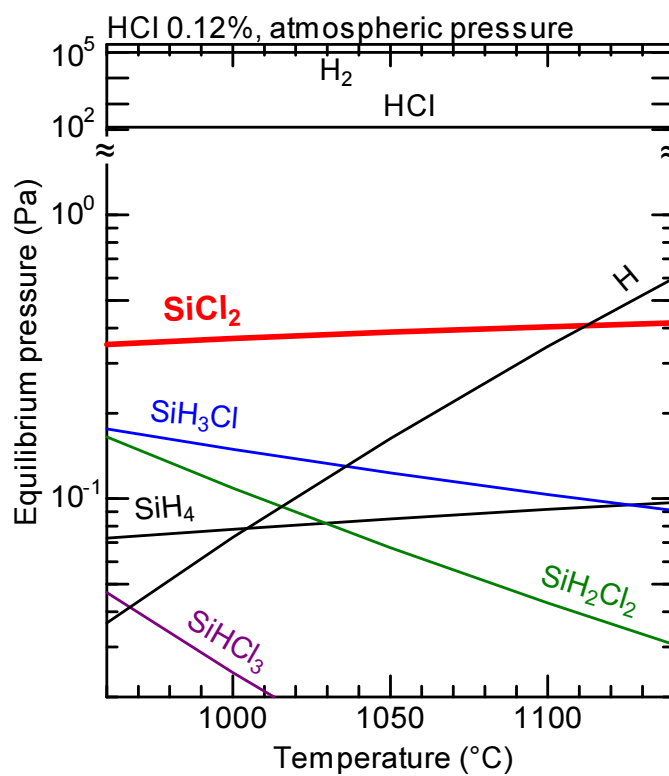


Figure 4.11: Calculated temperature dependence of equilibrium H-Cl-Si gas system at 950–1150°C. The HCl concentration is assumed to be 0.12% and the pressure is atmospheric pressure. $SiCl_2$ has a very small temperature dependence (activation energy = +3.3 kcal/mole).

Consequently, SiCl_2 can be identified to be the species whose desorption and readsorption are in balance between the Si surface and the gas phase.

Finally, the third proposition is examined. The experimental etching rate at 1050°C was replotted as a function of the calculated equilibrium SiCl_2 pressure (Fig. 4.12). A clear proportional relationship is obtained and its slope S is $S = 3.9 \text{ nm}/(\text{min}\cdot\text{Pa})$. This proportional relationship indicates that the etching is predominantly limited by SiCl_2 diffusion. In Fig. 4.12, the fitted line has a vertical intercept at an etching rate of $1.1 \text{ nm}/\text{min}$. This is probably due to the etching by H_2 gas or by residual moisture in H_2 gas. Experimentally measured etching rates of Si by H_2 without HCl were $0.8\text{--}0.9 \text{ nm}/\text{min}$ for both the (100) and (110) faces at 1050°C , which are reasonably consistent with the intercept of Fig. 4.12 and previous reports on the Si etching rate in H_2 ambient (about $1 \text{ nm}/\text{min}$) [21].

Here the diffusion length δ (the thickness of the stagnant layer) of the etching by-product SiCl_2 is calculated from the proportional relationship between the etching rate r (without etching by H_2) and the equilibrium partial pressure $p_{\text{eq}}(\text{SiCl}_2)$,

$$r = S \cdot p_{\text{eq}}(\text{SiCl}_2). \quad (4.2)$$

If mass transportation by the gas flow and the temperature nonuniformity in the diffusion domain is neglected and the partial pressure of SiCl_2 in the bulk gas is assumed to be zero, the gradient of the partial pressure of SiCl_2 $p(\text{SiCl}_2)$ toward the surface normal (y -axis) is given by (Fig. 4.13)

$$\frac{dp(\text{SiCl}_2)}{dy} = -\frac{p_{\text{eq}}(\text{SiCl}_2)}{\delta}, \quad (4.3)$$

where $p_{\text{eq}}(\text{SiCl}_2)$ is the equilibrium partial pressure of SiCl_2 immediately above the Si surface. Within the ideal gas approximation, this gradient of the pressure can be converted to the gradient of the number density (concentration) of SiCl_2 molecules, $c(\text{SiCl}_2)$, by dividing by the thermal energy $k_{\text{B}}T$. Therefore, from Fick's law, the flux of molecules caused by the diffusion in the gas phase J is expressed by

$$J = -D \frac{dc(\text{SiCl}_2)}{dy} = D \frac{p_{\text{eq}}(\text{SiCl}_2)}{\delta k_{\text{B}}T}, \quad (4.4)$$

where D is the diffusion coefficient of SiCl_2 in H_2 . On the other hand, J can be expressed in terms of the etching rate r and the atom density of bulk Si N as

$$J = rN. \quad (4.5)$$

The atom density of Si is $N = 8/a_0^3$ ($a_0 = 0.357 \text{ nm}$). By equating Eqs. (4.4) and (4.5), and by using Eq. (4.2), the relationship between δ and S is obtained as

$$\delta = \frac{D}{S \cdot N k_{\text{B}}T}. \quad (4.6)$$

At 1050°C , $D = 5.7 \times 10^{-4} \text{ m}^2/\text{s}$ [22] and thus $\delta = 9.6 \text{ mm}$. Because the amount of SiCl_2 as a percentage of all the (hydro)chlorinated silicon species is as high as 70%, as discussed

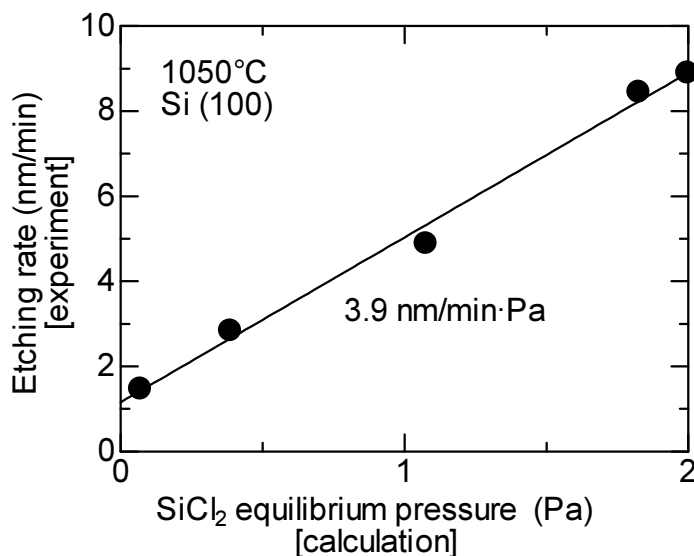


Figure 4.12: Etching rate of bare Si(100) face in Fig. 4.2 replotted as a function of calculated SiCl₂ equilibrium partial pressure at 1050°C and atmospheric pressure. The etching rate is clearly proportional to the SiCl₂ partial pressure.

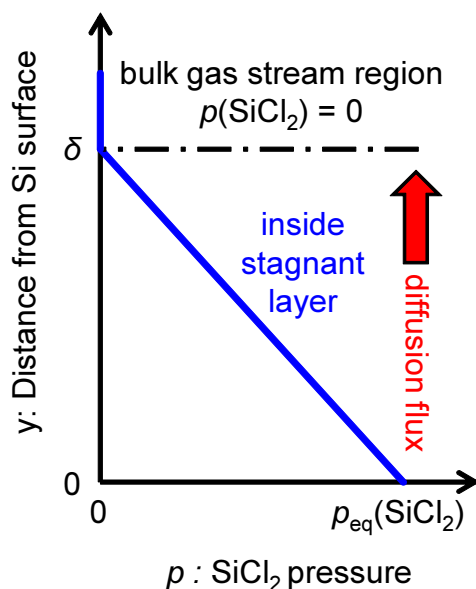


Figure 4.13: SiCl₂ distribution in stagnant layer by stationary diffusion of SiCl₂ on bare Si surface.

in Section 4.4, diffusion of all the SiH_nCl_m species should be considered if more precise prediction is necessary. However, the mechanism of etching limitation discussed in this section itself is sufficiently reliable. This is a reasonable value since this is almost half of the gap between the Si surface and the inner wall of the reactor tube (23 mm).

4.4.2 Origin of Loading Effect

The strong loading effect discussed in Section 4.3.3 is understandable, taking into account the diffusion of SiCl_2 in the gas phase. On the bare Si surface, SiCl_2 generates uniformly. As a result, the gas diffusion only proceeds vertically. However, the situation is different on the Si surface with SiO_2 mask, as schematized in Fig. 4.14. Since SiCl_2 is not generated on the oxide mask, the density of SiCl_2 immediately above the oxide is very small. SiCl_2 generated on the Si opening area next to the oxide can easily diffuse laterally and this increases the total amount of out-diffusing SiCl_2 per unit area in the opening area compared with the surface without an oxide mask. If the surface reaction processes [(b)–(d) in Fig. 4.8] are sufficiently faster than the out-diffusion of SiCl_2 , the partial pressure can retain its equilibrium value by increasing the number of molecules that are desorbed from the Si surface as SiCl_2 and thus etching is accelerated. On the mask patterns with the smaller exposed area of Si surface, the amount of SiCl_2 which diffuses laterally increases. Therefore, the etching rate increases in sparser patterns, which was observed in the experiment shown in Fig. 4.7(a).

4.5 Study of Loading Effect by Gas Diffusion Simulation

To confirm the mechanism of this loading effect, etching enhancement by SiCl_2 diffusion in the gas phase was simulated by numerically solving a stationary two-dimensional diffusion equation inside the stagnant layer. In the simulation, Si- SiO_2 aperture-mask stripe patterns with the same structure as in the experiments were assumed.

4.5.1 Simulation Method

For simplification, mass transport by the gas flow and the temperature distribution in the gas phase were neglected. The evolution of surface profiles by etching is not actually simulated but stationary profiles of the partial pressure of SiCl_2 , p , in the gas phase were calculated. In this calculation, it was assumed that the partial pressure of SiCl_2 is in equilibrium (p_{eq}) on the Si surface and that the generation of the etching product does not occur on oxide masks. These conditions were achieved mathematically by setting $p = p_{\text{eq}}$ on the Si surface and $\partial p / \partial y = 0$ on SiO_2 , where the y -axis is along the surface normal. Along the direction of the stripe width, the x -axis, a periodic boundary condition was adopted to duplicate the repeated aperture/mask stripe patterns that were used in the experiments. An illustration

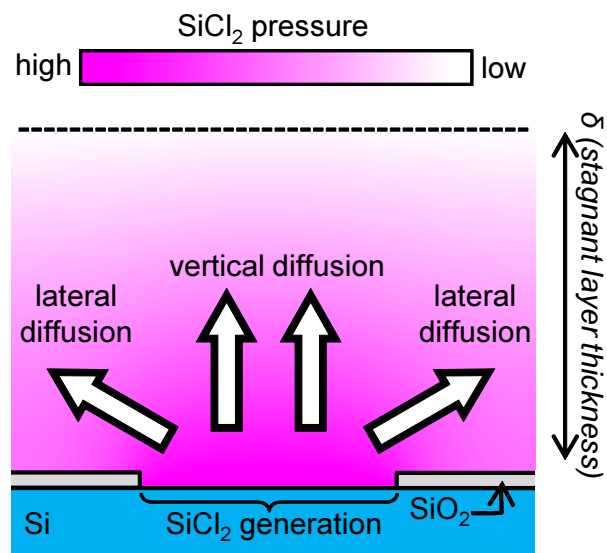


Figure 4.14: Illustration of the distribution of SiCl_2 partial pressure in stagnant layer on Si surface with SiO_2 masks.

of a simulation domain is given in Fig. 4.15. In the simulation, the stagnant layer thickness was assumed to be 9.6 mm, which was estimated from the experiments. It should be noted that the calculated results are insensitive to the stagnant layer thickness because the scale of the stripe pattern is much smaller than that of the stagnant layer thickness. From the calculated SiCl_2 distribution, the ratio of the etching rate in stripe patterns to that of bare Si was calculated by

$$\text{acceleration ratio} = \left. \frac{\partial p}{\partial y} \right|_{\text{surface}} \div \frac{p_{\text{eq}}}{\delta}, \quad (4.7)$$

where p_{eq}/δ corresponds to the gradient of the partial pressure on the bare Si surface (without any SiO_2 masks).

4.5.2 Results and Discussion

The simulation results are compared with the experimental results, as shown in Fig. 4.16. The vertical axis in this figure corresponds to the etching acceleration ratio to that without mask patterns (bare Si etching). The solid lines describe the experimental data, and the broken lines show the simulation data. Figure 4.16(a) shows data of the 10- μm -wide aperture with different mask widths, and Fig. 4.16(b) shows data of the aperture and mask with the same width. Although the acceleration ratios are slightly different from those in the experiment, the simulation well describes the trend of experimental results and reproduces the important features of the experiments. First of all, when the aperture width is constant at 10 μm [Fig. 4.16(a)], the etching rate increases with increasing mask width. Secondly, when the aperture and mask widths are the same [Fig. 4.16(b)], the etching rate is constant at the center and independent of the pattern width, but the etching rate increases at the Si aperture edges. Therefore, the author concludes that the etching loading effect in this study originates from the pattern-dependent diffusion of SiCl_2 .

Here the sources of the differences between the experiments and simulation are discussed. First of all, the etching acceleration ratio in the experiments is slightly different from that in the simulation. This may be due to the relatively short etching time in the experiments. Secondly, particularly in the case of very fast etching, the rate of the surface reaction might become unignorable, which the author totally neglected in the simulation. Actually, by scanning electron microscopy (SEM), some facets such as $\{311\}$ were observed at the aperture edges after etching (Fig. 4.17), and such facet formation might inhibit the acceleration of etching at aperture edges. Finally, the neglect of the gas flow and temperature distribution can induce some error. To improve the agreement between the experimental and simulation results, all of the above factors have to be considered.

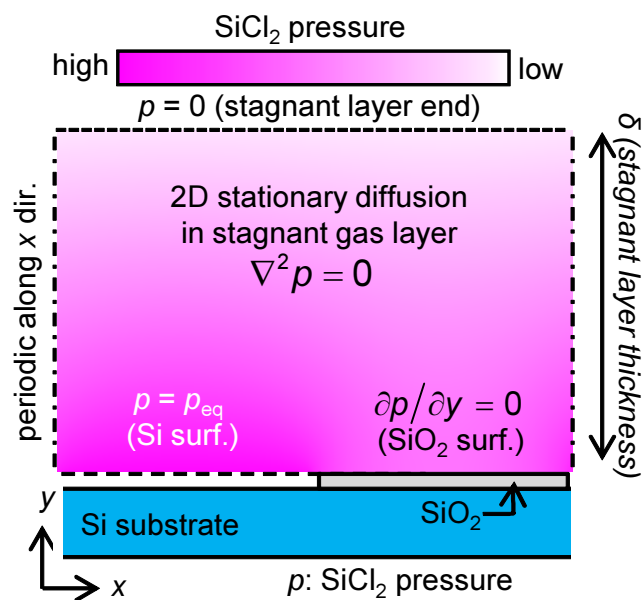


Figure 4.15: Setup of SiCl_2 two-dimensional stationary diffusion simulation in a stagnant layer.

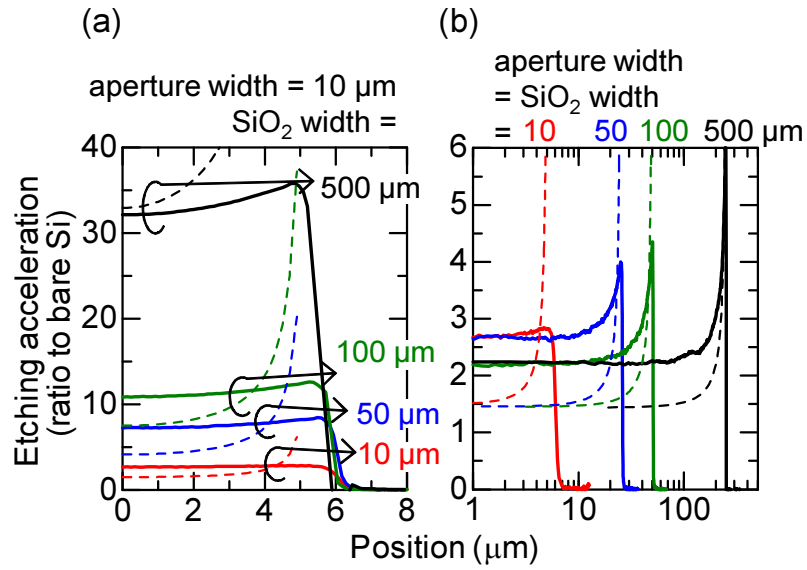


Figure 4.16: Comparison between experiments (solid lines) and simulation (broken lines) of etching loading effects showing etching rate acceleration in SiO₂ mask and aperture stripe structure. (a) The SiO₂ mask width was varied from 10 to 500 μm while the aperture size was kept constant at 10 μm. (b) The SiO₂ mask and aperture had the same width from 10 to 500 μm. Experimental data are the same as in Fig. 4.7, but the vertical axis is converted to the etching acceleration ratio with respect to bare Si, which is the etching depth in the patterned structures divided by the etching depth of bare Si. Position = 0 on the horizontal axis indicates the center of the apertures and the data are symmetric with respect to the vertical axis at position = 0.

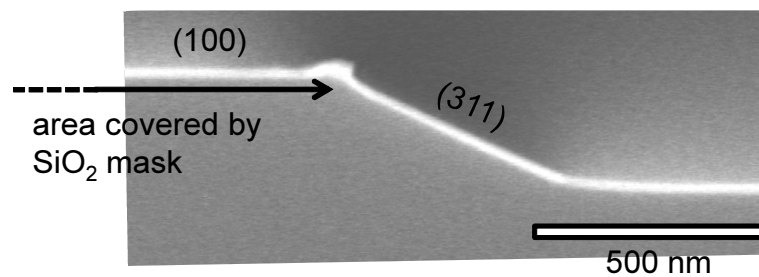


Figure 4.17: Cross-sectional SEM image of bulk Si(100) with line SiO₂ mask structures at an edge of a SiO₂ mask (aperture width = 10 μm, SiO₂ width = 100 μm) after HCl gas etching and SiO₂ removal. A {311} facet was observed.

4.6 Applicability to Nanowire Structures

Under the atmospheric-pressure conditions, the loading effect is too strong to control nanometer-scale etching of NW patterns. However, the intensive investigation verified that the limiting step of etching and loading effect is SiCl_2 diffusion in the gas phase. Since surface reactions should exhibit a weaker loading effect, it is better to perform etching in a surface-kinetics-limiting regime. To realize this type of etching, the process pressure and temperature should be reduced. The gas-phase diffusion coefficient is inversely proportional to the total pressure [19]. Therefore, the diffusion in the gas phase becomes sufficiently fast so as not to restrict the etching rate by reducing the pressure. In addition, the viscous flow at atmospheric pressure becomes a molecular flow at a low pressure in which the stagnant layer does not exist, which is used in low-pressure chemical vapor deposition (LPCVD) technique to obtain high conformity of deposited film thickness. From this viewpoint, the pressure lower than a few Torr, which are usually used in LPCVD, may be necessary to make the diffusion in the gas phase negligible. However, the activation energy of the surface reactions is much higher than that of the diffusion in the gas phase, as discussed in Section 4.4, and thus the etching at lower temperatures can be limited by the surface kinetics even if the pressure is significantly reduced. Therefore, the pressure should be selected taking the effect of the temperature into account. The reduction in the temperature is also important to keep a low etching rate because the etching rate increases when only the pressure was reduced and this may also lead to the loss of etching controllability. From above discussions, lower pressure and temperature conditions seem worth a try, although these etching experiments could not be performed in the etching system used in this study.

4.7 Summary

At atmospheric pressure and high temperatures of 1000–1100°C, slow Si etching (below 10 nm/min) with HCl/H₂ gas was achieved by reducing the HCl concentration to below 0.3%. From the dependence of the etching rate on the HCl concentration, temperature, and crystal face, and from thermochemical analysis and the nature of the loading effect, the author concludes that the out-diffusion of the etching product SiCl_2 in the stagnant layer dominates the etching rate. Because the Si surface after etching was very smooth [roughnesses of 0.08 nm for bare (100) and 0.07 nm for terraces on bare (110)], this process is useful for flattening a rough surface. However, the strong loading effect makes it difficult to apply this process to patterned wafers such as Si NWs, although the etching profile is roughly predictable by a simple diffusion simulation. As a possible countermeasure, lower-pressure and lower-temperature etching was suggested.

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Chapter 5

Hydrogen Annealing Process for Surface Smoothing of Si

5.1 Introduction

In the Si epitaxial growth technology, high-temperature (1150–1200°C) baking of Si in hydrogen ambient has been used as an *in-situ* surface cleaning process to remove surface oxide [1]. High-temperature hydrogen baking produces atomically-flat Si surface [2, 3], and the formation mechanism of atomically-flat surface is attributed to the surface migration (diffusion) of Si atoms rather than etching [4]. In the last decade or so, the heat treatment in hydrogen ambient has come to be applied to non-planar Si structures. First, the heat treatment was applied to the shape transformation of micron- and submicron-scale three-dimensional Si structures at 900–1100°C using the nature of surface migration [5–8], which is called hydrogen annealing process. Hydrogen annealing is capable of surface smoothing of sidewalls etched by reactive ion etching (RIE) [5, 7, 9] and corner rounding. In addition, the speed of surface migration, *i.e.*, the speed of transformation, is controllable by temperature and hydrogen pressure [5, 7, 8, 10, 11]. Hydrogen annealing at a lower temperature of 900°C was then applied to Si FinFETs to improve surface flatness and obtain rounded corners, which resulted in reduction of DC and low-frequency noise, fin-width reduction, and reduced gate leakage [12, 13]. Recently, hydrogen annealing has also been used to obtain smooth and rounded Si nanowires (NWs) [14–20]. In the annealing of NWs, annealing temperature should be low to avoid wire breaking caused by excess surface atom diffusion [15], and it is reported that temperatures $\leq 850^\circ\text{C}$ are favorable [15, 20, 21]. In previous studies, however, it has been reported that surface flattening of bulk Si by hydrogen annealing/baking is difficult at such low temperatures $\leq 900^\circ\text{C}$ because the removal of surface oxide becomes imperfect [3, 22]. Simultaneous atomic-level surface flattening of different crystal faces is a key to obtain smooth Si NWs since NWs are three-dimensional structures and have various facets in a single structure, whereas the report of the simultaneous flattening of different crystal faces by hydrogen annealing at low temperatures is still limited [20]. For this reason,

this chapter aims to develop the hydrogen annealing process which realizes simultaneous flattening of Si(100), (110), and (111) at a low temperature designed for the annealing of Si NWs.

5.2 Annealing System in Experiments

The annealing system used in this study has a tube-shaped SiC-coated graphite susceptor which can be heated by rf-heating. The sample is put on an SiC plate placed inside the susceptor tube and the susceptor is heated in the quartz tube under hydrogen flow (hot-wall arrangement). The annealing system does not have a load-lock chamber, which causes the exposure of the interior of the chamber to air every time the sample is loaded. To avoid the direct exposure to air, Ar gas is flowed whenever the chamber is open for sample loading. In addition, the gas is purged by pumping with a turbo molecular pump (TMP) immediately after loading the sample. The hydrogen gas is purified by a palladium diffuser. It removes the impurity content in the hydrogen gas down to less than 10 ppb. To obtain hydrogen ambient at reduced pressures, the hydrogen gas is flowed, evacuating with dry pumps during the annealing. Thanks to the rf-heating system, quick heating and cooling are realized (70 sec from room-temperature to 850 °C). The susceptor temperature is monitored by an infrared radiation thermometer (InGaAs detector, wavelength = 1.55 μm).

5.3 Surface Preparation of Si before Hydrogen Annealing

5.3.1 Importance of Surface Preparation before Hydrogen Annealing

As mentioned in Sec. 5.1, the temperature of hydrogen annealing should be low to avoid the breaking of Si NWs. However, surface contaminations such as a trace of carbon and oxygen are difficult to desorb from the surface at low temperatures [23, 24]. Therefore, the Si surface should be cleaned carefully before hydrogen annealing. In general, SPM cleaning (mixture of H_2SO_4 and H_2O_2), RCA standard clean 1 (SC-1, mixture of NH_3aq , H_2O_2 , and H_2O) and RCA standard clean 2 (SC-2, mixture of HCl , H_2O_2 , and H_2O) are used sequentially to remove organic and metal contaminations from the Si surface [25]. These peroxide-based cleaning solutions, however, oxidize the Si surface. To obtain oxygen-free Si surface, HF-based aqueous solutions are used between and after these cleaning steps. HF dissolves the silicon oxide and leaves the bare surface terminated by hydrogen atoms. These surface hydrogen atoms prevent the Si surface from oxidation (stable up to an hour [26]), and they desorb during the heating process leaving the clean Si surface. If the HF-treated surface is destroyed and oxidized partially before annealing, the oxidized area may disturb

a successful annealing. Therefore, the hydrogen-terminated Si surface obtained by the HF-based treatment must be retained as it is until immediately before the hydrogen annealing to realize low-temperature hydrogen annealing.

5.3.2 Effect of Surface Oxidation by Water Rinse after HF Wet Cleaning on Hydrogen Annealing

As the first trial in this study, the hydrogen annealing experiment was performed with the following sequence. At first, bulk Si(100) sample (boron-doped p-type, $1\text{--}10\ \Omega \cdot \text{cm}$) was cleaned by SPM, DHF (diluted HF, 0.5%), SC-1, DHF, and SC-2 sequentially. Then, the surface oxide was etched by HF/HCl solution (47% HF : 35% HCl = 1 : 100) for two minutes to obtain the hydrogen-terminated surface. HF/HCl is reported to be a better surface preparation solution than normal diluted HF [27]. Immediately after the etching, the sample was rinsed in ultra-pure water (UPW) for about two minutes. After the cleaning sequence, the sample was loaded into the annealing system within eight minutes after the HF/HCl treatment and the chamber was evacuated down to 6.6×10^{-6} Torr by the TMP. Finally, hydrogen gas was flowed at 9 slm and 20 Torr, and annealing was performed at 850°C for 30 min.

After the annealing, the surface morphology of the annealed Si sample was characterized by atomic-force microscopy (AFM). The initial surface morphology of Si surface is featureless and rough (RMS $\sim$ 0.15–0.18 nm). A typical surface morphology of Si(100) before annealing is shown in Fig. 5.1(a). Fig. 5.1(b) shows the AFM image ($1\ \mu\text{m} \times 1\ \mu\text{m}$ area) of an annealed Si(100) surface. Many hillocks were observed on the surface (density $\gtrsim 3 \times 10^{10}\ \text{cm}^{-2}$). The height of hillocks was about 2–5 nm. A possible formation mechanism of the hillocks is as follows. In hydrogen ambient at a low temperature, a trace of oxygen and moisture slightly etches Si (etching of Si with hydrogen gas is negligible at this temperature), but SiO_2 is hardly decomposed [3, 22, 28]. After the HF/HCl treatment, sample surface might be partially oxidized. During the 30-minutes annealing, Si surface might be slightly etched but the areas covered by oxide could be protected, which resulted in the hillock formation.

The main cause of surface oxidation is probably the water rinse after the HF/HCl treatment. It is reported that HF-treated Si surface is terminated by hydrogen atoms with a small amount of Si–F bonds [29–31]. The coverage of F depends on the concentration of HF: 5–38 % coverage in 0.1–50% HF in water [31]. They are very unstable and quickly replaced with hydroxyl groups to Si–OH when the surface is exposed to water even for only 10 sec [29–31]. A quantum-chemical calculation revealed that this reaction is initiated by hydroxyl ions (OH^-) in water rather than H_2O molecules [32] even though the density of OH^- is very small in water ($6 \times 10^{13}\ \text{ions/cm}^3$).

When the sample was annealed omitting the water rinse after HF/HCl and directly blowing the HF/HCl solution away with N_2 gas, the number of hillocks after the anneal-

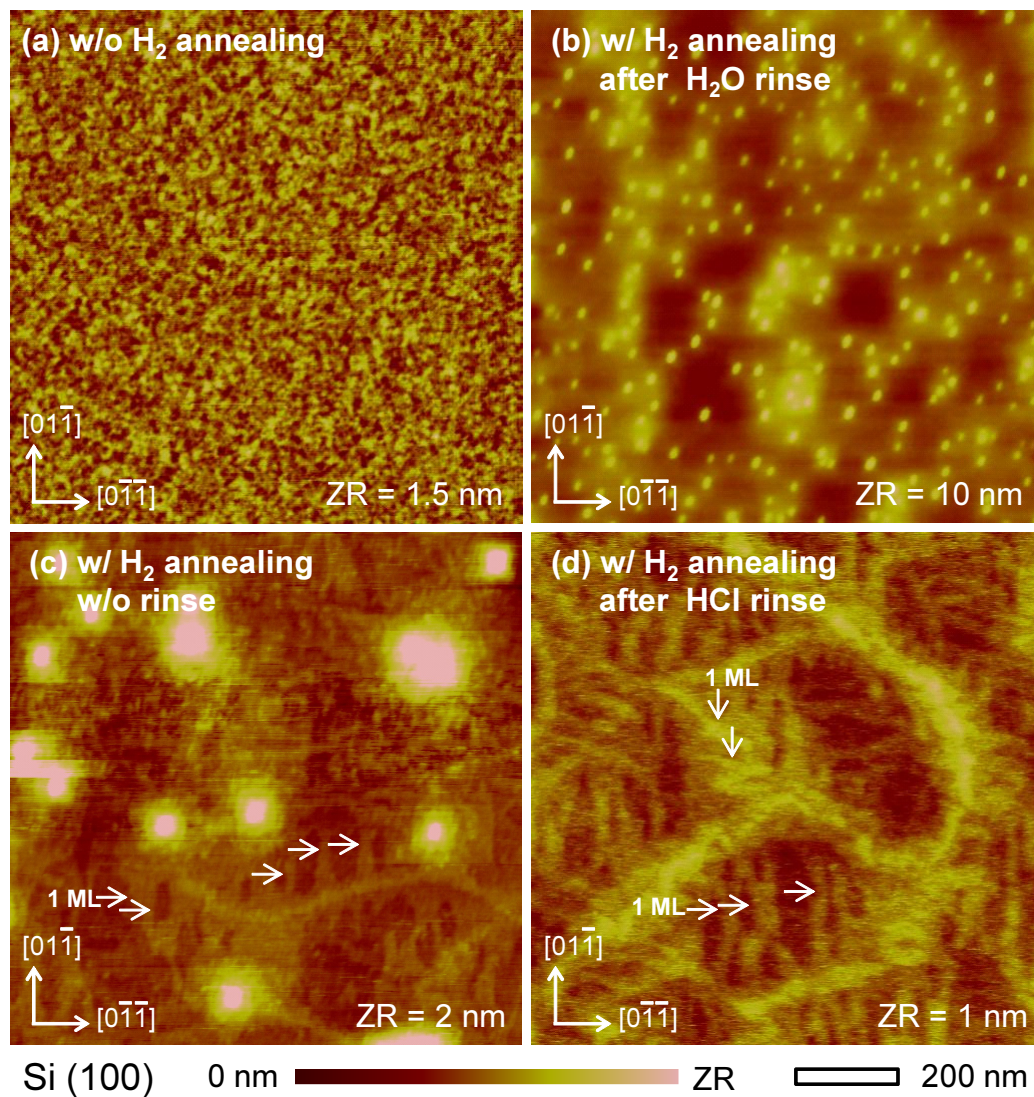


Figure 5.1: AFM images of Si(100) surfaces (a) without hydrogen annealing (as cleaned), (b) with hydrogen annealing after 2-min HF/HCl cleaning followed by $\sim$ 2-min ultrapure water rinse, (c) with hydrogen annealing after 2-min HF/HCl cleaning omitting rinse process, (d) with hydrogen annealing after 2-min HF/HCl cleaning followed by 5-sec HCl rinse. The annealing conditions are 850°C, 20 Torr, 9 slm and 30 min. ZR means the height scale of each image.

ing significantly decreased as shown in Fig. 5.1(c). Furthermore, step-terrace structures partially appeared with the step height of one monolayer (1 ML). This result certainly indicates that the exposure of the surface to water is the problem. When hydrogen annealing is applied to NW devices, however, the rinse process is indispensable for the precise control of the etching thickness of SiO_2 . Therefore, a countermeasure against the surface oxidation during the rinse process must be developed.

5.3.3 Prevention of Surface Oxidation by Rinsing in HCl Aqueous Solution: Experiments and Discussion

Considering the oxidation of Si-F sites, OH^- in a rinse liquid must be reduced. In addition, it is reported that oxidation of Si-H is preferentially initiated by OH^- rather than by H_2O [32, 33]. Therefore, utilization of a rinse liquid with a low OH^- concentration can be effective to prevent the HF-treated Si surface from oxidation. For this purpose, 35% HCl aqueous solution was adopted as the acidic rinse solution because of its compatibility with HF/HCl solution and small reactivity with Si [34]. In 35% HCl, the concentration of OH^- ions is at least 7-orders-of-magnitude smaller than in water. The Si(100) sample was cleaned in the same way as in the previous section and then surface oxide was etched with HF/HCl for 2 min. Immediately after the HF/HCl treatment, sample was rinsed in 35% HCl for 5 sec. Then hydrogen annealing was performed under the same conditions as in the previous section (9 slm, 20 Torr, 850°C, and 30 min). The sample surface after the annealing was characterized by AFM, as shown in Fig. 5.1(d). By applying the HCl rinse instead of the water rinse, the number of hillocks remarkably reduced. In this figure, the hillock was not observed on the surface. In addition, the step-terrace structure with about 1 ML step height was observed, although the global structure looks irregular.

To confirm a preventative effect of HCl rinse on surface oxidation, surface chemical analyses were performed on Si(100) treated by different rinse methods. After RCA cleaning and 2-min HF/HCl treatment of bare Si(100), three different rinse processes of water rinse (10 sec), HCl rinse (10 sec), and without rinse (direct blowing-away of HF/HCl solution) were applied individually and the surface of those samples was analyzed by X-ray photoelectron spectroscopy (XPS) and multiple-reflection attenuated-total-reflection Fourier transform infrared spectroscopy (ATR-FTIR). XPS measurement was performed with Mg K_α radiation (1253.6 eV for $K_{\alpha 1,2}$) at 130 kW (13 kV $\times$ 10 A). The take-off angle of photoelectrons was 30° from the surface normal. ATR-FTIR was measured using a Ge prism attachment with the incident angle of 60°. The p -polarized light was analyzed with the resolution of the wave number of 2 cm^{-1} . The estimated number of the light reflection on the surface is three.

From the XPS analysis, Si, C, O, and F atoms were detected but Cl atom was not observed (Si-Cl: 270.3 eV [35]). Therefore, neither HF/HCl etching nor HCl rinse leaves Cl atom on the Si surface. The XPS spectra of Si_{2p} , O_{1s} , F_{1s} , and Cl_{1s} are shown in Figs. 5.2(a),

(c), (d), and (e), respectively. The Si_{2p} spectra at higher binding energies are magnified in Fig. 5.2(b). The spectra are normalized by the area of the Si_{2p} signals (the differences in the area of the Si_{2p} signals among the different rinse methods before normalization are below 3 %). The Si_{2p} peaks of the samples treated by three processes were almost the same. However, the water-rinsed sample had a very weak skirt at higher binding energies around 102–104 eV [Fig. 5.2(b)]. This signal possibly indicates the existence of oxidized Si states on the surface. As reported in a previous report on HF-treated Si [29–31], a small amount of F atoms was detected after HF/HCl, and it disappeared by the water rinse, whereas the F peak almost remained after the HCl rinse. At the same time, O atoms increased by the water rinse but remained unchanged by the HCl rinse. Therefore, the HCl rinse seems effective not to oxidize surface Si–F bonds to Si–OH, which is inevitable in water. The number of F and O atoms detected by XPS was quantified and shown in Fig. 5.3 as a ratio to that of Si atoms. The number of O atoms which increased by the water rinse is almost the same as but slightly larger than that of F atoms which disappeared by the water rinse. This indicates the existence of the additional increase of oxygen other than the conversion of Si–F into Si–OH. This additional signal may come from the oxidation of Si–H to Si–OH and/or oxygen inserted in back bonds of Si–H, both of which arise in the initial stage of Si oxidation in water.

Figure 5.4 shows ATR-FTIR absorption spectra of stretching vibration of Si–H_n groups. The peaks around 2080, 2110, and 2140 cm^{−1} are assigned to monohydride (Si–H), dihydride (Si–H₂), and trihydride (Si–H₃), and the broad peak around 2150–2260 cm^{−1} is absorption by Si–H_n groups bounded to oxygen atoms at back bonds [36]. On the HF/HCl-treated Si(100) surface without rinsing (the solid line), the surface was terminated by Si–H₂ and Si–H₃, and the signal of back bond oxidation was not detected. However, after the sample was rinsed in water for 10 sec (the dashed line), the hydrogen-terminated structure changed. By the exposure to water, Si–H absorption slightly increased, and the broad peak around 2150–2260 cm^{−1} appeared. Therefore, the water rinse slightly destroys clean hydrogen termination and initiates surface oxidation in part. On the other hand, the FTIR absorption spectrum of the sample rinsed in HCl (the circular symbol) is almost the same as that without rinse process, and no signal from oxidized back bonds was observed. Unfortunately, the detection of a SiOH group by ATR-FTIR measurement was difficult because SiOH signal is probably very weak and overlapped by a signal from adsorbed water (FTIR measurement was performed not in vacuum).

When taken together, it can be concluded that partial oxidation of Si surface by the rinse process after HF/HCl treatment was successfully suppressed by adopting HCl as a rinse liquid, and HCl rinse is effective as a surface-preparation treatment of Si surfaces before hydrogen annealing. Finally the author discusses the thermal stability of Si–F bonds left on the surface after HCl rinse, and the effect of the dissolved oxygen (DO) in the rinse liquids. The desorption temperature of F atoms on Si surface is reported to be 820 K ($\sim 550^\circ\text{C}$) [37]. Therefore, the remained F atoms desorb during heating and they do not

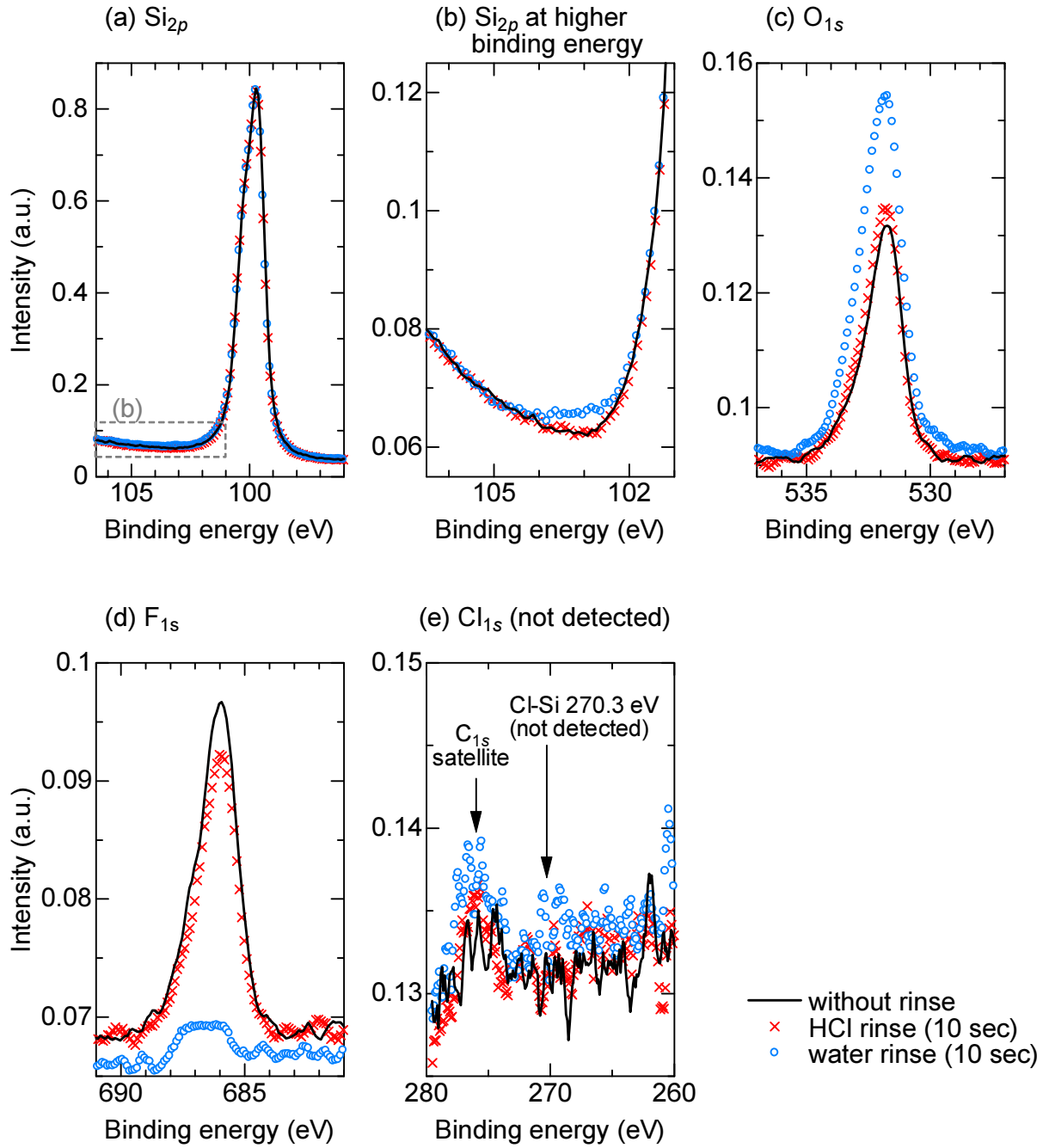


Figure 5.2: XPS spectra of (a) Si_{2p} , (b) Si_{2p} in high energy region [corresponding to inset of (a)], (c) O_{1s} , (d) F_{1s} , and (e) Cl_{1s} (not detected) on Si(100) surfaces just after 2-min HF/HCl treatment without rinse, 2-min HF/HCl followed by 10-sec HCl rinse, and 2-min HF/HCl followed by 10-sec ultra-pure water rinse. The spectra are normalized by the area of the Si_{2p} signal.

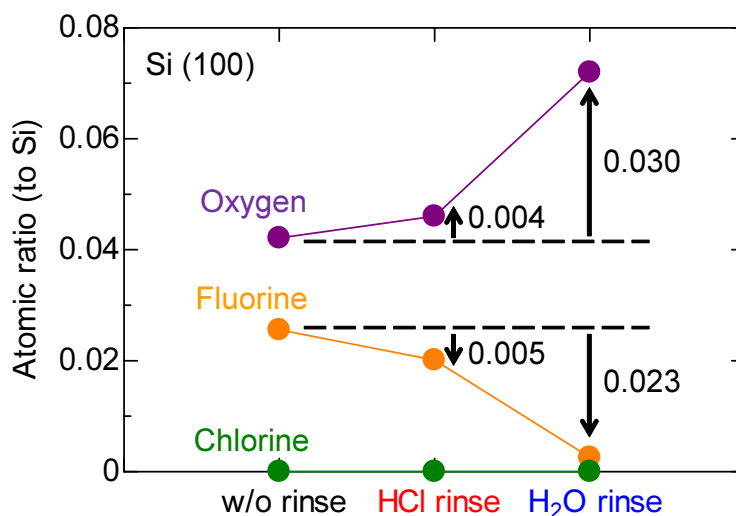


Figure 5.3: Quantification results of surface O, F, and Cl atoms (normalized by Si atom) from XPS on Si(100) surfaces just after 2-min HF/HCl treatment without rinse, 2-min HF/HCl followed by 10-sec HCl rinse, and 2-min HF/HCl followed by 10-sec ultrapure water rinse.

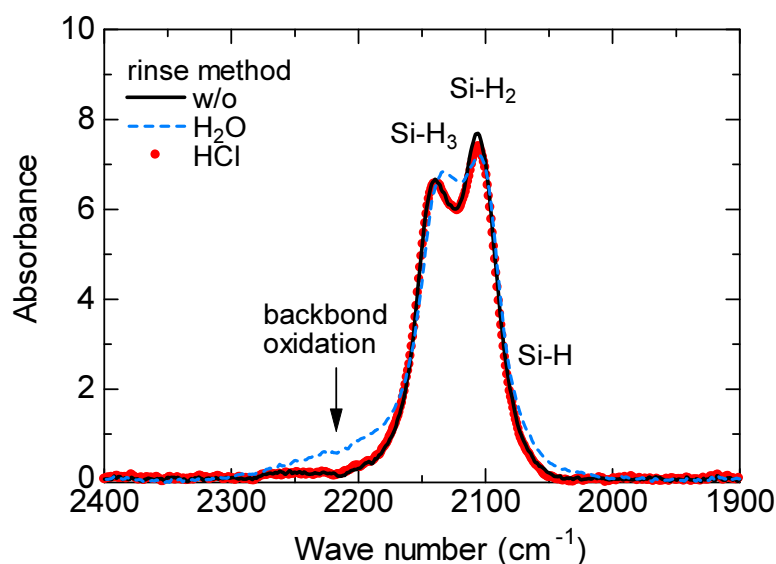


Figure 5.4: ATR-FTIR absorbance spectra of Si-H stretching vibration on Si(100) surfaces just after 2-min HF/HCl treatment without rinse, 2-min HF/HCl followed by 10-sec HCl rinse, and 2-min HF/HCl followed by 10-sec ultrapure water rinse. A Ge ATR prism was used and *p*-polarized light was detected.

affect the annealing. DO in water can initiate the oxidation of HF-treated Si surface [26]. The UPW used in this study contains about 6-ppm DO (saturation solubility: 8.5 ppm). Li *et al.* reported that immersion into water with this level of DO for 5 sec and 10 min causes surface oxidation of 0.2–0.3 Å and 1.1–1.3 Å, respectively [38]. Therefore, short-time rinse is desirable. Since the DO concentration in the HCl solution used in this study is not controlled, HCl may contain DO at saturation level (not measured). Although the solubility of oxygen in electrolyte solutions is smaller than in water owing to the salting-out effect, the salting-out effect is small in HCl and it saturates at high HCl concentrations [39, 40]. When experimental results originally up to 17% HCl are extrapolated to 35% HCl with the model in Ref. 41, the solubility of DO is estimated to be about 70% of the saturation level in the water (~ 6 ppm). If the surface oxidation mechanism by DO does not depend on pH of the rinse liquid, the effect of DO may be comparable in UPW and HCl. Therefore, short-time rinsing should be used even in HCl to avoid the possible effect of DO.

5.4 Dependence of Surface Morphology of Bulk Si on Hydrogen Flow Rate and Pressure

By adopting the HCl rinse process, the quality of hydrogen annealing improved, whereas the surface flatness is still insufficient. In this section, the author investigates the effect of the hydrogen flow rate and pressure on the surface morphology and finds out the appropriate conditions for simultaneous flattening of Si(100), (110), and (111) surfaces. Regarding the annealing temperature, 850°C is supposed to be the maximum because NW breaking is reported at temperatures above 850°C. For this reason, the temperature was kept at 850°C in this section and annealing was performed for 30 minutes, the same as in the previous sections. This section shows the importance of the purity of hydrogen gas in addition to the cleanliness of the surface.

5.4.1 Experiments

In an ideal situation, the hydrogen annealing is not presumed to be influenced by the hydrogen flow rate. In practice, however, the result of annealing is strongly dependent on the flow rate. First, hydrogen annealing was performed at a reduced flow rate of 3 slm (in the previous section, 9 slm) and the AFM image of the Si(100) surface is shown in Fig. 5.5. Other conditions were the same as in the previous section (850°C, 20 Torr, and 30 min) and rinse process was omitted after HF/HCl treatment in the surface preparation before annealing. In contradiction to the case at 9 slm [Fig. 5.1(c)], the surface was roughened and any step-terrace structures were not observed at 3 slm.

Next, hydrogen annealing at different pressures was performed. The surface morphologies of the Si(100), (110), and (111) samples ($1\ \mu\text{m} \times 1\ \mu\text{m}$) annealed at 20, 75, 150,

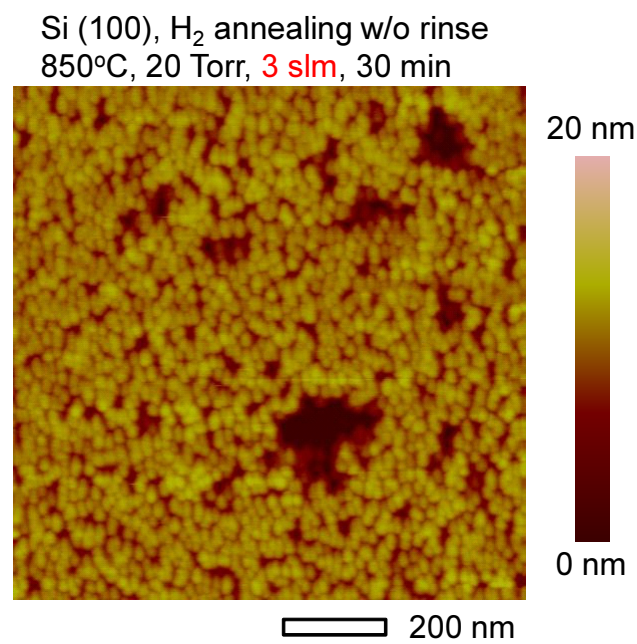


Figure 5.5: AFM image of Si(100) surface annealed in hydrogen ambient at flow rate of 3 slm. The other conditions are the same as those used in Fig. 5.1(c): 850°C, 20 Torr, 30 min, and omitting the rinse process after HF/HCl cleaning.

200, and 500 Torr are shown in Fig. 5.6. For some specific samples, additional $2\ \mu\text{m} \times 2\ \mu\text{m}$ AFM images are shown in Fig. 5.7. In these experiments, HCl rinse was performed after HF/HCl treatment and the flow rate was 9 slm (the limit of vacuum pumps) at 20 Torr and 10 slm at the higher pressures. On (100), irregular steps and narrow terraces were observed at 20 Torr [Fig. 5.6(a)], and wide terraces with one-monolayer-high steps were observed from 75 to 200 Torr [Figs. 5.6(b)–(d)]. However, large pits were observed at 500 Torr [Fig. 5.6(e)]. The morphology obtained at medium pressures probably corresponds to Si(100)(2×1 – 1×2):H structure, which is the typical structure of Si (100) after hydrogen annealing [2, 4, 9]. On (110), one-monolayer step-terrace structures with almost regular terrace widths were obtained at 75–200 Torr [Figs. 5.6(g)–(i)]. However, some hillocks were observed on the sample annealed at 20 Torr and they seemed to block the evolution of regular step lines even though the terraces were smooth [Figs. 5.6(f) and 5.7(a)]. This hindrance of annealing by hillocks was also observed on (111) at 20 Torr [Figs. 5.6(j) and 5.7(b)]. The hillocks blocked the evolution of the steps and this resulted in triangular step morphologies with hillocks at kink sites. The triangular step normals are $\langle \bar{1}\bar{1}2 \rangle$ directions, which are low-energy step lines of Si(111) [42]. At 75 Torr, no hillocks were observed and regular steps with the one-bilayer (1 BL) height appeared on (111) [Figs. 5.6(k) and 5.7(c)]. The step lines were not restricted to $\langle \bar{1}\bar{1}2 \rangle$ directions. At higher pressures up to 200 Torr, the steps showed triangular shapes and these step normals preferred $\langle \bar{1}\bar{1}2 \rangle$ directions [Figs. 5.6(l) and (m), and Fig. 5.7(d)]. In addition, these steps gathered and bunched. Unlike the result at 20 Torr, however, hillocks were not observed at the kinks of steps. These triangular and bunched steps seemed to be formed autonomously.

5.4.2 Discussion

Since good surface morphologies have already been reported even at lower pressures of 0.1–10 Torr for (100), (110), and (111) faces at 800°C in an ultrahigh-vacuum annealing system [20] and at 20 Torr for (100) at 775°C in a commercially-available industrial Si/SiGe chemical vapor deposition tool [43], the insufficient annealing capability at lower pressures is not inherent in the nature of hydrogen annealing itself. This may be also true for the detrimental effect of the reduced hydrogen flow. One possible reason of the negative effect of the lower hydrogen flow is that the impurity oxygen and moisture in hydrogen gas oxidize the surface and annealing is disturbed. Although the hydrogen gas is purified, the annealing chamber takes in a certain amount of outside gas through leakage. Typical build-up characteristics of the annealing chamber are shown in Fig. 5.8. The leakage rate is estimated to be $5.6 \times 10^{-6}\ \text{Pa}\cdot\text{m}^3/\text{s}$. Assuming that the incoming gas to the chamber is air (22% oxygen), the estimated oxygen flow to the chamber from the outside atmosphere is 6.5×10^{-7} slm. This is a very small value but not negligible. When the total pressure is 20 Torr, the partial pressure of the oxygen becomes 4.2×10^{-6} Torr in a 3-slm hydrogen flow and 1.4×10^{-6} Torr in a 9-slm flow. Since the reported critical pressure of the silicon oxide growth by a reaction

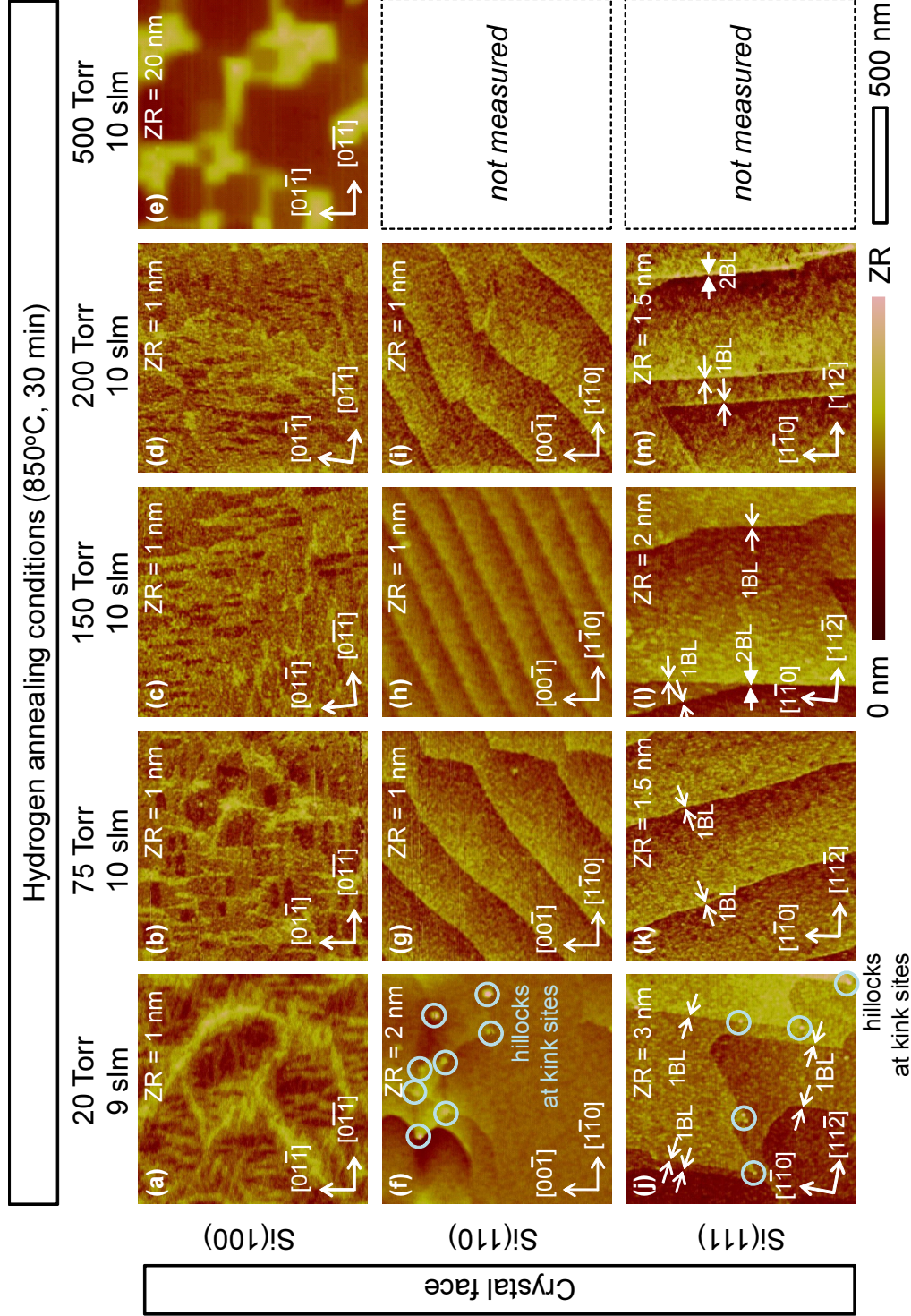


Figure 5.6: $1\ \mu\text{m} \times 1\ \mu\text{m}$ AFM images of Si(100), (110), and (111) surfaces annealed in hydrogen ambient at different pressures: 20, 75, 150, 200, and 500 Torr. The flow rate is 9 slm at 20 Torr and 10 slm otherwise. Samples are rinsed in HCl after HF/HCl cleaning and annealed at 850°C for 30 min. Roughnesses are observed on terraces, but they are probably due to the difficulties in the measurement caused by surface static charges and insufficient optimization of scan parameters, and they may be nonessential.

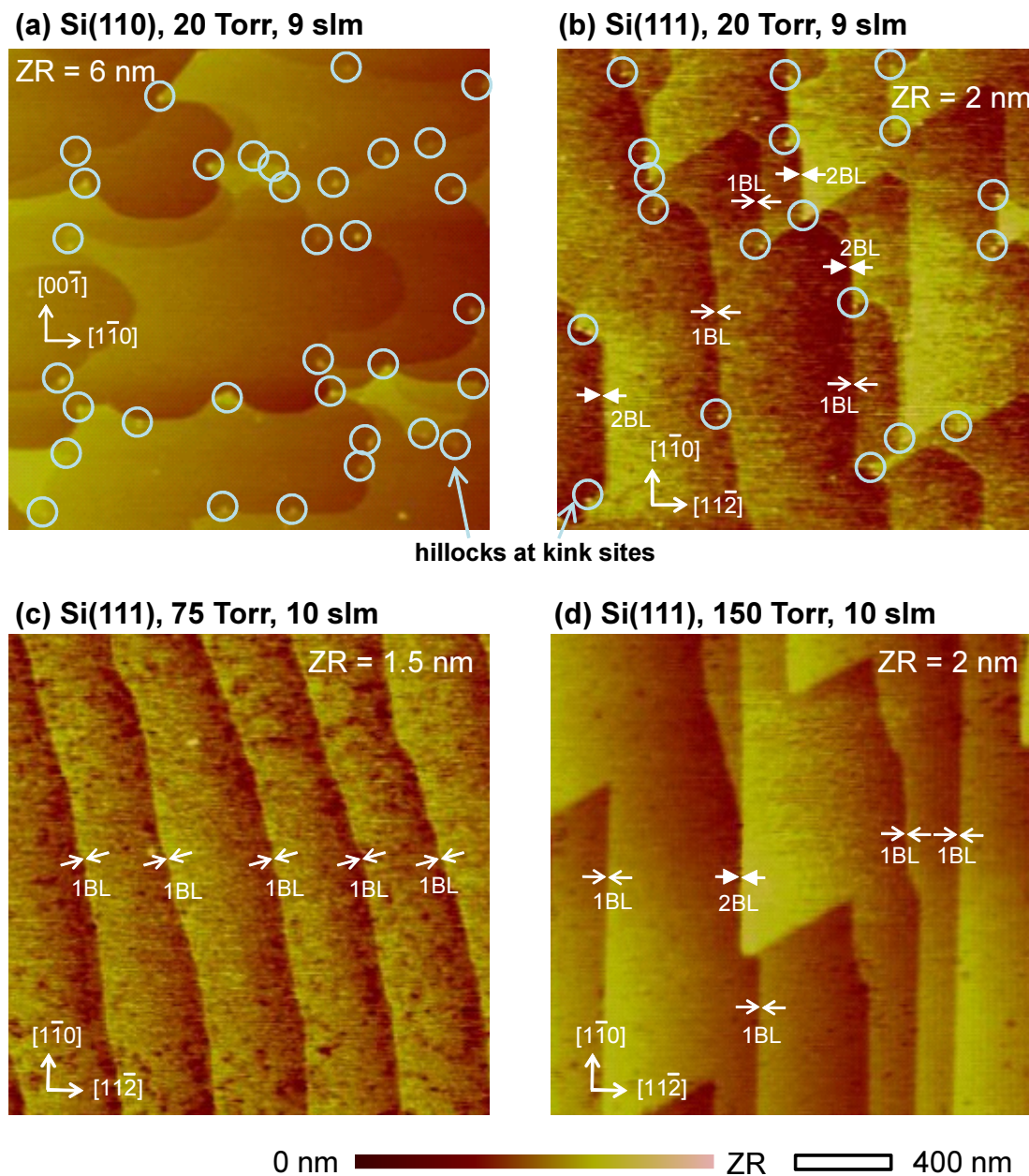


Figure 5.7: $2\ \mu\text{m} \times 2\ \mu\text{m}$ AFM images of (a) Si(110) annealed in hydrogen ambient at 20 Torr and 9 slm, (b) Si(111) annealed at 20 Torr and 9 slm, (c) Si(111) annealed at 75 Torr and 10 slm, and (d) Si(111) annealed at 150 Torr and 10 slm. Samples are rinsed in HCl after HF/HCl cleaning and annealed at 850°C for 30 min. ZR means the height scale of each image.

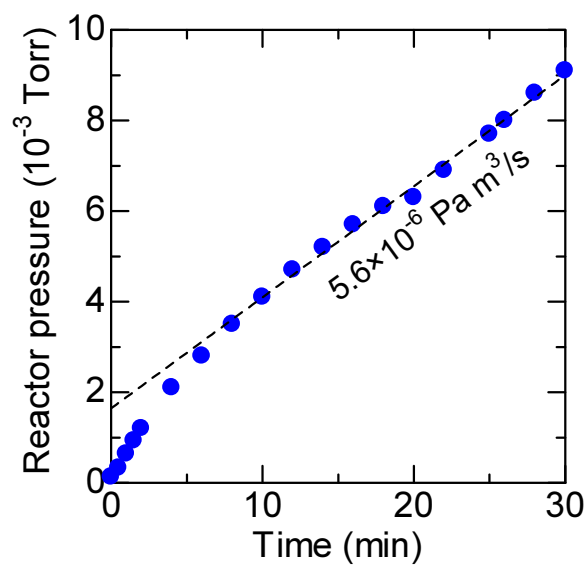


Figure 5.8: Typical build-up characteristics of the annealing chamber. The linear leakage is observed and its speed is estimated to be $5.6 \times 10^{-6} \text{ Pa} \cdot \text{m}^3/\text{s}$.

with oxygen is about 5×10^{-6} Torr [44] or 1×10^{-5} Torr [45] at 850°C , the oxygen partial pressure in a 3-slm hydrogen flow is near the threshold above which surface oxidation occurs. In addition, impurity of moisture should exist other than oxygen. The moisture impurity has a lower critical surface oxidation pressure of 1.4×10^{-6} Torr (850°C) [46] than oxygen. Moreover, outgassing from the susceptor and inner parts should exist at the beginning of heating. At a high hydrogen flow rate, these undesirable impurities are diluted and quickly flowed away. For this reason, a higher hydrogen flow rate is necessary to realize high-quality Si surfaces by hydrogen annealing.

The slightly irregular morphologies on (100) and hillocks on (110) and (111) at 20 Torr and 9 slm may be due to still insufficient hydrogen flow (9 slm), which is limited by the pumping capability of dry pumps used in this study. At higher pressures, the hydrogen flow of 10 slm was used and the higher pressure in the annealing chamber may help to prevent the leak-in of impurities. A lower impurity content in the ambient can result in desorption of the oxygen contamination rather than oxidation from the ambient [45, 46]. Thus, hillocks were not observed at higher pressures ≥ 75 Torr. The increase in the total pressure, however, accompanies with the increase in the partial pressure of impurities [24, 28]. Therefore, the annealing at too high pressures (500 Torr) could be affected by impurities. It should be noted that these impurity effects are specific to each annealing apparatus. In fact, other studies report the complete desorption of oxygen contamination by 2-min hydrogen annealing at 20 Torr at 800°C on (100) and (110), for example [43, 47]. Therefore, a very clean annealing system is desirable for the stable annealing process.

Finally the author discusses a possible reason for the formation of step bunching on (111) at higher pressure. At lower pressures, surface Si atoms may diffuse over terraces and regular step arrays can be formed unless hillocks exist on the surface. However, at higher pressure, the surface diffusion coefficient of Si atoms decreases [10]. With the reduced diffusion coefficient, Si atoms emitted from a step can migrate around the vicinity of the step and (re)incorporated to low-energy $\{\bar{1}12\}$ steps. As a result, the author speculates that $\{\bar{1}12\}$ steps hardly bend and thus they become long and straight, which finally runs into a merge of steps (step bunching formation). To confirm this bunching mechanism, however, further study on the diffusion coefficient and step stability under hydrogen-annealing conditions, for example, is necessary, which is beyond the scope of this thesis. Considering the application to NW structures, the step bunching can lead to the increase of the surface roughness. However, they are the results of long-time annealing, which is inapplicable to NWs. The bunching behavior of short-time annealing may be different because of insufficient time to equilibrate the surface kinetics, and the surface morphologies in the short-time annealing should be investigated separately.

To conclude this section, 75–200 Torr annealing can be used to flatten Si(100), (110), and (111) simultaneously thanks to suppressed effect of gas impurities. However, if enough clean annealing system is available, the limitation of the pressure probably does not exist. One thing that should be noted is the step bunching formation on (111) at higher hydrogen

pressures which may be due to lower surface-diffusion coefficient of Si atoms.

5.5 Short-Time Hydrogen Annealing for Application to Nanowires

In Secs. 5.3 and 5.4, fundamental aspects of hydrogen annealing became clear and methodologies of successful annealing were established. However, the discussed annealing conditions may be too strong to be applied to Si NWs. In this section, the annealing conditions designed for NWs are presented and tested on bulk Si substrates.

To apply hydrogen annealing to NWs, temperature should be further reduced and the annealing time has to be shortened to avoid excess surface-atom diffusion and resulting wire breaking. Therefore, the temperature was reduced to 810°C and the annealing time was shortened to 2 min, which are typical conditions for NW annealing also in previous studies [15–20]. To avoid the surface oxidation in the wet treatment, HCl rinse (10 sec) after HF/HCl treatment (2 min) was adopted. After the samples were loaded, the chamber was evacuated by TMP for 30 min (longer than above experiments) down to 2×10^{-6} Torr to improve the background of the chamber. In addition to this, a higher flow rate of hydrogen of 11 slm (the maximum of the annealing system) was used to minimize the influence of impurities. Two different pressures of 75 and 150 Torr were tested.

Figures 5.9(a), (b), and (c) show AFM images of bulk Si (100), (110), and (111) surfaces annealed at 75 Torr, respectively. Despite the short-time and lower-temperature annealing, the surfaces were successfully flattened and step-terrace structures appeared. On the (100) face [Fig. 5.9(a)], the step-terrace structure with narrow islands appeared. The step height corresponds to 1 ML. The step directions and the general morphology are similar to the result of long-time annealing at 850°C [Fig. 5.6(b)], and thus the surface structure is supposed to be the same $[(2 \times 1)-(1 \times 2):H]$ structure. The terrace widths are, however, smaller than the result of 850°C annealing, and they have variation from about 10 nm to 100 nm. The annealed (110) face [Fig. 5.9(b)] has wide terraces (about 250 nm) with 1-ML-high steps. However, there are some 1-ML-deep craters with lateral sizes of about 30–200 nm on terraces. In addition, the step lines are wounded, and the step direction has no preference. On (111) [Fig. 5.9(c)], steps with 1-BL height and 330-nm-wide terraces whose step lines are normal to $\langle \bar{1}\bar{1}2 \rangle$ appear and they exhibit triangular features with a corner angle of $\sim 60^\circ$. Around step edges, there are some islands and craters whose height or depth are the same as those of regular steps and their lateral sizes are about 20 nm to 100 nm. Since more regular step-terrace structures without craters and islands were obtained on Si(110) and (111) at 850°C, the surface diffusion of Si atoms at 810°C and 75 Torr for 2 min may be insufficient to equilibrate the bulk Si surface because of lower temperature and short annealing time. However, the terrace widths on surfaces obtained by annealing in these conditions are large enough when compared with the dimension of NWs. Therefore, hydrogen annealing under

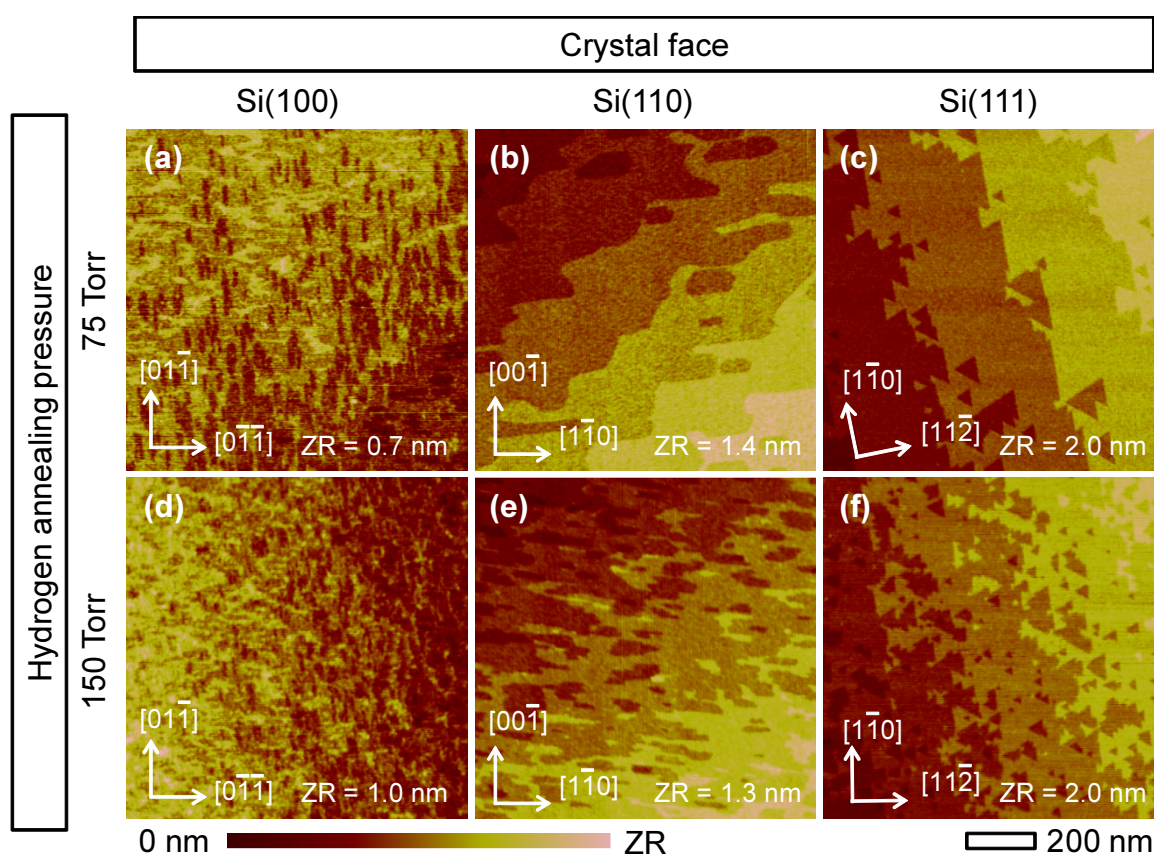


Figure 5.9: AFM images of bulk Si (a) (100), (b) (110), and (c) (111) annealed in hydrogen ambient at 75 Torr and 810°C for 2 min. The results of 150 Torr annealing with the same temperature and annealing time are shown in the lower part: (d) (100), (e) (110), and (f) (111). ZR means the height scale of each image.

the 75 Torr condition is expected to produce flat surfaces on NW structures thanks to the simultaneous flattening of various surfaces.

The surfaces of Si(100), (110), and (111) annealed at a higher pressure of 150 Torr are shown in Figs. 5.9(d), (e), and (f), respectively. They exhibit step-terrace structures and the step heights are the same as the results at 75 Torr, and simultaneous flattening is successful even at 150 Torr. However, the width of terraces on (100) is narrower, and the number of two-dimensional islands and craters on (110) and (111) faces is larger than the case of 75 Torr annealing, although the temperature and the annealing time are the same. The surfaces annealed at both 75 Torr and 150 Torr seem to be halfway through complete smoothing (equilibrium), but the speed of smoothing seems slower in the annealing at 150 Torr, which indicates a weaker driving force of surface self-diffusion of Si atoms in annealing at a higher pressure. This observation is consistent with the previous report on the pressure dependence of the diffusion coefficient [10].

5.6 Summary

As a surface-preparation prior to hydrogen annealing at low temperatures, the rinse process in HCl aqueous solution after HF-based surface cleaning was proposed instead of the water rinse to prevent surface oxidation during the rinse process, and its advantageous effect was validated by surface chemical analyses. In addition, it was found that the appropriate hydrogen flow rate and pressure is necessary to minimize the effect of impurities in the annealing ambient. Although these factors involve the system-specific problems such as the leakage in the chamber, they are not only technologically but also scientifically important. Considering above factors, surface-smoothing of Si was realized at a low temperature of 810°C with a short annealing time of 2 min on Si(100), (110) and (111) simultaneously. This annealing condition is probably applicable to Si NWs. Although the direct evaluation of the smoothness of the surface of Si NWs is difficult due to their nanoscopic and three-dimensional structure, the hydrogen annealing is promising for surface smoothing of Si NWs since the simultaneous flattening of three fundamental crystal faces of Si was verified.

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Chapter 6

Effect of Pressure and Anisotropy in Wire Stability in Hydrogen Annealing of Si Nanowires

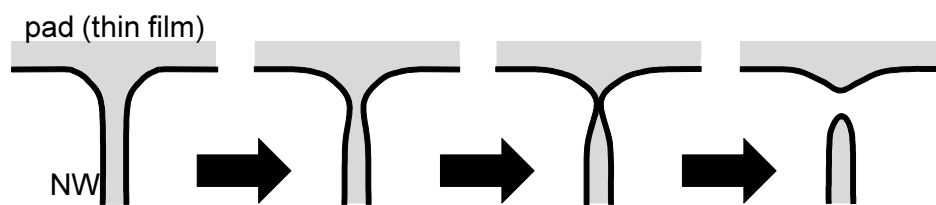
6.1 Introduction

Hydrogen annealing of Si nanowires (NWs) is one of the powerful processes to obtain smooth NW surfaces. The smoothing mechanism is the surface mass transport via migration of Si atoms, but this mass transport also leads to wire breaking. Dornel *et al.* pointed out that Si NWs anchored by Si thin films at their both ends can break at those anchor points during annealing, as illustrated in Fig. 6.1(a), and this wire breaking becomes significant at temperatures over 850°C [1]. Here, the thin films that support NWs are source and drain pads in Si NW FET devices. The mechanism of wire breaking has been explained by capillarity-driven excess surface-diffusion of Si atoms at anchor points induced by a convex curvature at anchors [1]. Therefore, the speed of surface diffusion should be reduced not to cause wire breaking, whereas surface diffusion itself is necessary to flatten NW surface.

One of the straightforward ways to reduce the diffusion coefficient is reducing annealing temperature. Temperature dependence of a diffusion coefficient (D_s) obeys an Arrhenius equation, and its activation energy (E_a) is typically a few eV. For example, Keeffe *et al.* reported $E_a = 2.3 \pm 0.1$ eV for Si surface in ultra-high vacuum, which was obtained from the surface-profile evolution of square-wave gratings fabricated on Si (001) [2]. Dornel *et al.* found that 800°C is adequately low for $\langle 110 \rangle$ -oriented Si NWs with a diameter of 40 nm when annealed for 2 minutes at 20 Torr. This motivated the author to develop the hydrogen annealing process at as low temperature as possible by applying contamination-control techniques described in Chapter 5.

Realization of flattening of Si NWs with various wire axes is also a technology of great importance because the carrier transport characteristics of Si NWs would depend on wire orientations as seen in Chapter 2. In most cases, however, hydrogen annealing has been

(a) NW breaking at anchors



(b) NW breaking by Rayleigh instability

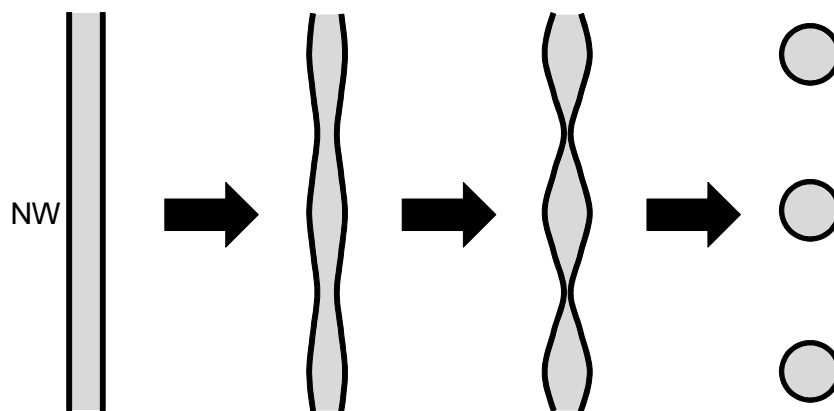


Figure 6.1: Schematics of Si NW breaking (a) at an anchor point connected to a supporting thin Si film and (b) Rayleigh instability.

applied only to $\langle 110 \rangle$ -oriented Si NWs so far. Recently, Barwicz *et al.* have investigated the annealing of NWs with various orientations of $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ as well as $\langle 110 \rangle$ [3]. They found that NWs in orientations other than $\langle 110 \rangle$ are much easier to break at anchor points. To overcome stronger instability, they masked anchors with SiN to block the surface diffusion of Si atoms toward pads, together with the adoption of low annealing temperatures, and they successfully annealed very thin and suspended NWs with diameters of ~ 20 nm and below with various orientations at 750°C and 10 Torr for 1 min. In addition, they found that annealing of Si NWs with diffusion masks fails not at anchors but by Rayleigh instability [4], as seen in other materials such as sapphire (insulator) rods [5] and copper (metal) NWs [6]. Schematic of wire breaking by the Rayleigh instability is shown in Fig. 6.1(b). $\langle 100 \rangle$ NWs are the least stable, and $\langle 111 \rangle$ and $\langle 112 \rangle$ NWs are more stable. $\langle 110 \rangle$ NWs are the most stable and never fail by Rayleigh instability. However, a methodology of applying maskless hydrogen annealing to NWs with a very small diameter and various wire orientations is in demand. In addition, the orientation dependence of wire instability in maskless annealing is also important. Although Morita and Ota demonstrated maskless hydrogen annealing of NWs along the above four orientations at 800°C and 0.1–1 Torr for 1–2 min, their NWs were relatively thick (about 50–60 nm for $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ NWs). Moreover, their NWs lay on a buried oxide layer. In this case, annealing instability is known to be relieved. [1, 7] Therefore, if NWs are suspended for gate-all-around geometry, the wire instability in maskless hydrogen annealing might be much stronger.

In previous studies, the effect of temperature on wire instability has intensively been discussed [1, 3, 8, 9]. However, they have not studied the effect of hydrogen pressure, which is expected to be another important parameter to modulate D_s . The effect of hydrogen pressure on the shape transformation rate of silicon three-dimensional structures was first reported by Sato *et al.* [10]. They found out that the deformation of rectangular-shaped Si trench by hydrogen annealing is slower at higher hydrogen pressures. Kuribayashi *et al.* [11] annealed Si trench structures in hydrogen ambient at different pressures ranging from 40 to 760 Torr and at 1000°C , and quantified D_s of Si atoms from the time-dependent evolution of the curvature at corners of trenches. According to their results, D_s decreases as hydrogen pressure P increases as $D_s \propto P^{-2.1}$.¹ As presented above, the process control by hydrogen pressure is commonly accepted in the shape-transformation process of micrometer-scale silicon structures, even though the physical mechanism has not been clarified yet. At this moment, however, the effect of the hydrogen pressure on the annealing of Si NWs is still unknown. In general, hydrogen annealing has been performed at relatively low pressures of 0.1–10 Torr for NWs with various orientations [3, 8]. On the other hand, the author developed and optimized the hydrogen annealing process at higher pressures of 75 Torr and

¹This exponent value was calculated from the values of the diffusion coefficient they gave in Ref. 11. However, they mentioned that the curvature was proportional to the hydrogen pressure. Considering the curvature is proportional to the $(\gamma D_s)^{-1/4}$ and assuming γ is independent of the pressure, where γ is the surface energy, $D_s \propto P^{-4}$, which is stronger than the dependence with the exponent of -2.1 .

150 Torr designed for Si NW smoothing in Chapter 5 (see Sec. 5.5). This difference may make the effect of hydrogen pressure on hydrogen annealing clear.

In this chapter, maskless hydrogen annealing of Si NWs was investigated to realize smoothing of thin NWs along various orientations. Then, the orientation dependence of the minimum diameters that survive hydrogen annealing without wire breaking was determined and the relationship between the orientation-dependent strength of diffusion and the instability is discussed.

6.2 Experimental Procedure

6.2.1 Formation of Si Nanowires

The NWs used in this chapter are the same as those fabricated in Section 3.3, with electron-beam lithography (EBL), Cl_2 -based inductively-coupled-plasma reactive ion etching (ICP-RIE), and sacrificial oxidation. $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ NWs were fabricated on the same lightly-boron-doped p-type (110) Si-on-insulator (SOI) wafer with the specifications given in Table 3.1, and the cross-sectional shape of fabricated NWs is rectangle. The height of Si NWs was approximately 9, 18, and 30 nm, and the width of NWs was ranging from ~ 6 nm to ~ 30 nm. The length of NWs was about 140 nm, and they were connected to dummy source and drain pads [Fig. 6.2(a)].

6.2.2 Procedure of Hydrogen Annealing

Just before annealing of NW samples, the buried oxide layer and the surface sacrificial oxide layer were etched by about 50 nm in HF/HCl (47% HF : 35% HCl = 1 : 100) mixture solution [12] and subsequently rinsed in 35% HCl for 10 sec to obtain hydrogen-terminated and suspended Si NWs [Fig. 6.2(b)]. Soon after the wet treatment, samples were loaded to the annealing furnace within a few minutes. After pumping of the chamber by a turbo-molecular pump (TMP) below 2×10^{-6} Torr to purge the gas, purified hydrogen gas was flowed at 11 slm at the pressure of 75 Torr or 150 Torr (total pressure) while the TMP was switched to dry pumps. The susceptor was heated up from room temperature to 810°C in one minute by rf heating and annealing was performed for two minutes. The heating power was immediately shut down when annealing ended and samples were cooled down. The samples with three different wire heights were annealed at the same time for reliable comparison of the results. These annealing conditions give very smooth step and terrace structures on bulk Si(100), (110), and (111), as stated in Chapter 5 (Sec. 5.5). Si NW samples after hydrogen annealing were characterized by scanning electron microscopy (SEM) and cross-sectional high-resolution transmission electron microscopy (HRTEM).

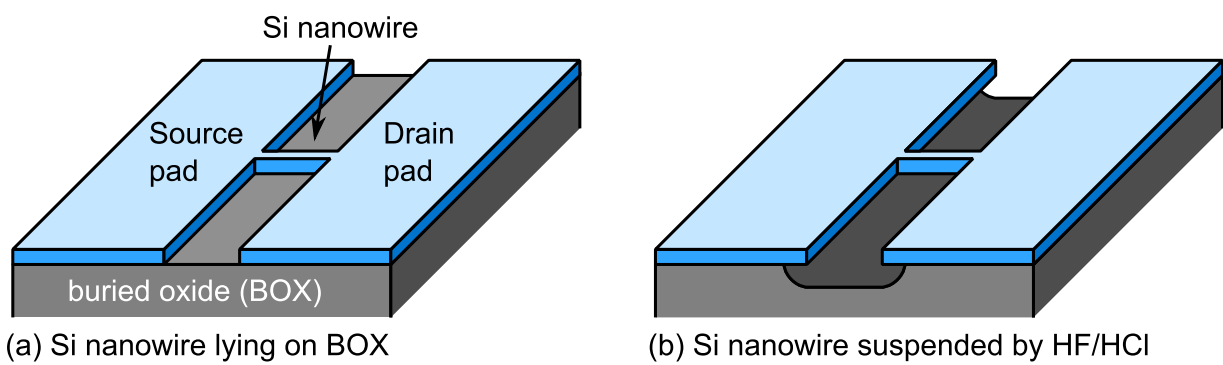


Figure 6.2: Illustration of Si NW (a) lying on buried oxide (BOX) layer and (b) released from BOX by HF/HCl wet etching.

6.3 Structural Change and Instability of Si Nanowires by Hydrogen Annealing at 75 Torr

This section presents the structural change of NWs by hydrogen annealing at 75 Torr. In addition, the breaking behavior and the minimum diameter of NWs that survive annealing are analyzed. To investigate the orientation dependence of the wire instability, the anisotropic behavior of the surface diffusion is also given.

6.3.1 NW Smoothing Effect

Figure 6.3 shows top-view SEM images of Si NWs without (upper images) and with (lower images) hydrogen annealing at 75 Torr for four different wire orientations of $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$. These NWs are almost the smallest ones that survived annealing without breaking for each orientation among the NWs with the initial height of 18 nm. The smallest size of NWs was dependent on the wire axis, and thus the initial widths of NWs in Fig. 6.3 are different for different axes; 7, 12, 19, and 23 nm for $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs, respectively. By applying hydrogen annealing, line-width roughness seems much reduced within the resolution of SEM observations.

To confirm the nanoscopic smoothing effect of hydrogen annealing, cross-sectional HRTEM was performed. The HRTEM images of $\langle 110 \rangle$ NWs without and with 75-Torr annealing are shown in Fig. 6.4. For NWs without annealing, anomalous contrast resulting from the line width fluctuation [Fig. 6.4(a)] and atomic-scale surface roughness [Fig. 6.4(b)] are evident. By applying the hydrogen annealing, the contrast of the interface became very clear, which evidences the smoothening capability of hydrogen annealing even at the relatively high pressure of 75 Torr.

6.3.2 Wire Instability Behavior

Figure 6.5 shows SEM images of annealed $\langle 100 \rangle$ NWs with different initial widths. Thicker NWs were successfully smoothened. However, necking occurred in smaller NWs and finally they broke at anchors. The instability always occurred at anchor points of NWs in this study. Because the present experiment is maskless annealing, the convex curvature at anchors induced enhanced surface diffusion and the Si atoms were lost [1]. Therefore, capillarity-driven surface self-diffusion toward source and drain can change cross-sectional size of NWs by annealing. In addition, diffusion along the circumference of NWs can change the cross-sectional shape. To analyze the change of wire size by annealing regardless of shape deformation, an effective diameter D_{eff} , a diameter of a cylinder whose cross-sectional area is the same as a given NW, was defined as a unique measure of the NW size as the following equation,

$$D_{\text{eff}} = 2\sqrt{\frac{S}{\pi}}. \quad (6.1)$$

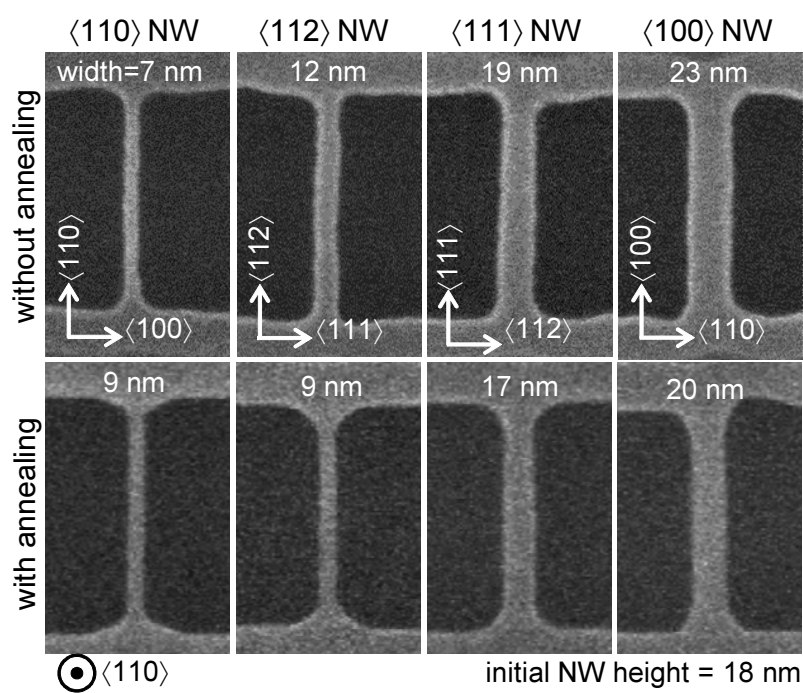


Figure 6.3: Top-view SEM images of 140-nm-long suspended Si NWs along $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ directions without (upper images) and with (lower images) hydrogen annealing at 75 Torr and 810°C for 2 min. Initial wire height was 18 nm.

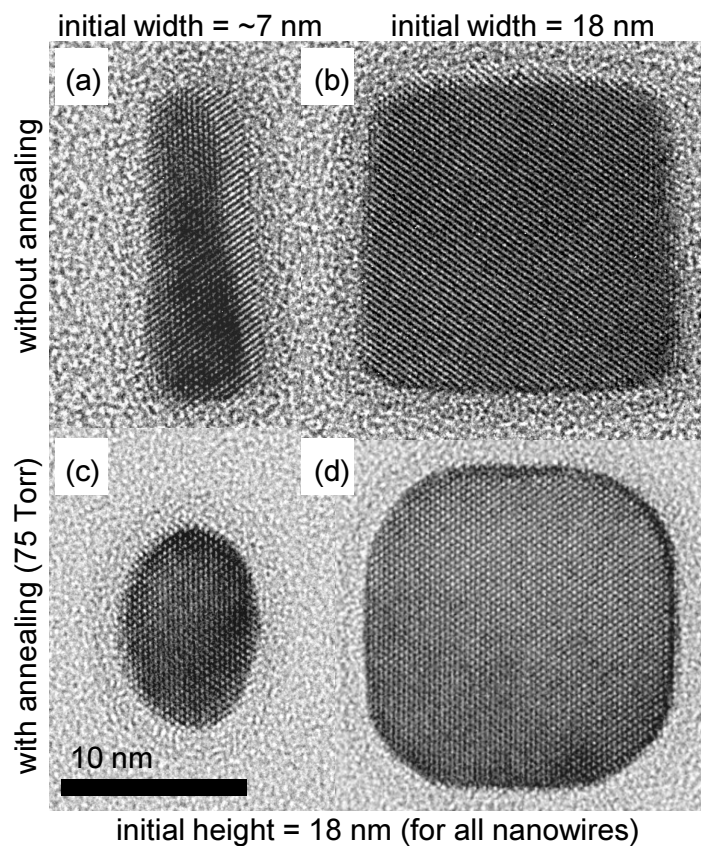


Figure 6.4: Cross-sectional high-resolution TEM (HRTEM) images of $\langle 110 \rangle$ -oriented Si NWs with initial width of (a) ~ 7 nm and (b) 18 nm without hydrogen annealing. HRTEM images of Si NWs with 75-Torr hydrogen annealing are shown in (c) and (d) for the initial width of ~ 7 nm and 18 nm, respectively. For all NWs, the initial height is 18 nm.

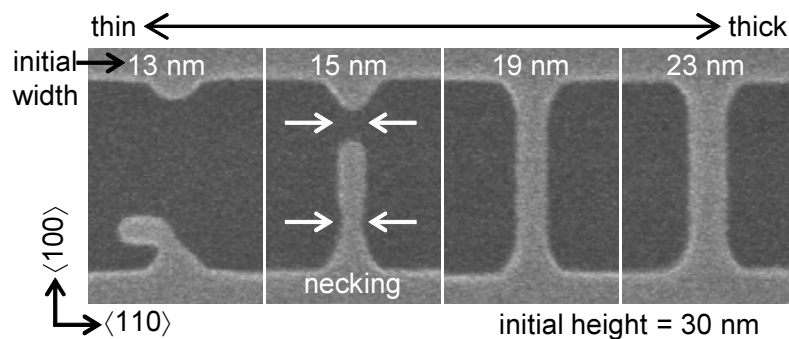


Figure 6.5: Top-view SEM images of 75-Torr hydrogen annealed 140-nm-long $\langle 100 \rangle$ Si NWs with different initial widths. In smaller NWs, severe necking and breaking occur at anchor points originating from excess surface self-diffusion.

To determine precise widths, heights, and D_{eff} of pre-annealed NWs, TEM observation was performed for $\langle 110 \rangle$ NWs. The height measured by TEM for $\langle 110 \rangle$ NWs was used also for pre-annealed $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ NWs. The widths were characterized by SEM and calibrated by TEM results of $\langle 110 \rangle$ NWs. From above widths and heights, D_{eff} of pre-annealed NWs was calculated. For annealed NWs, the cross-sectional shape and area were characterized by cross-sectional TEM for each NW. During the period of time from annealing and SEM/TEM, native oxide with a thickness of about 1–2 nm was grown on NW surface. The thickness of Si consumed by the native oxide was corrected in analyses.

Figure 6.6 describes the relationship between NW width after 75-Torr hydrogen annealing and D_{eff} before annealing for each NW orientation. The data of NWs with different initial heights are plotted on the same graph. In this figure, NWs which broke up by annealing were treated as zero width after annealing (on the vertical axis). This figure indicates that the size with which a NW runs into break is almost independent of the initial NW height. For a given orientation, initial D_{eff} , *i.e.* the cross-sectional area, determines whether a NW breaks or not within the range of aspect ratio of NWs in this study (maximum: ~ 4.4). In addition, the wire stability is clearly dependent on the wire orientation. The minimum D_{eff} (before annealing) of survived NWs is approximately 10, 18, 21, and 23 nm for $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ -oriented NWs, which shows their stability order. In Table 6.1, these values of minimum D_{eff} are compared with the results in Ref. 3, which utilized hydrogen annealing with diffusion-blocking mask at anchors and used low pressure of 10 Torr. The minimum D_{eff} in this study (at 810°C) is even smaller than that at 775°C in Ref. 3, even though diffusion mask structures are not used in this study. Thus, the stability of NWs to annealing improved in this study (strictly, wire breaking was postponed). In addition, Hashemi [9] reported successful annealing of suspended and maskless $\langle 110 \rangle$ NWs with diameters down to 13 nm at 100 Torr and 850°C, which is actually the temperature that induces severe necking in 30-nm-thick $\langle 110 \rangle$ Si NWs at anchors when the pressure is 20 Torr [1]. Although Hashemi did not mention the reason of improved stability, from above facts, the stabilizing effect of higher hydrogen pressure must be significant. The rank of stability with respect to the wire orientation is the same as that for Rayleigh instability of Si NWs obtained from the experiment of hydrogen annealing with diffusion masks [3], though the failure mechanism is different. The reason of this similar stability order is discussed in Sec. 6.5.1.

6.3.3 Anisotropy in Surface Self-Diffusion along Nanowire Axis

The strength of mass transport on the surface along the wire axis was evaluated from the change of D_{eff} by annealing. Figure 6.7 represents the comparison of D_{eff} before and after hydrogen annealing ($D_{\text{eff,before}}$ and $D_{\text{eff,after}}$, respectively). The data of different initial heights are plotted in the same figure. When $D_{\text{eff,before}}$ is small and near the threshold of wire breaking, $D_{\text{eff,after}}$ rapidly decreases as $D_{\text{eff,before}}$ decreases and finally NWs break

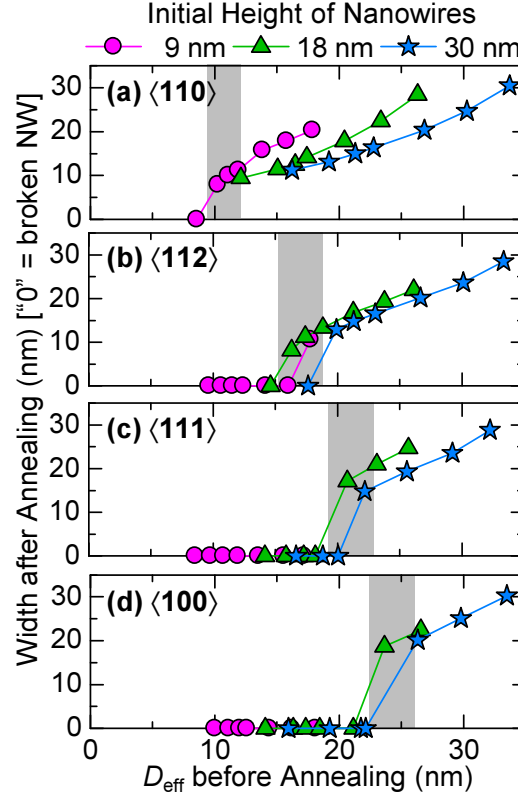


Figure 6.6: Relationship between the width of Si NWs after hydrogen annealing at 75 Torr and effective diameter [defined as Eq. (6.1)] before annealing for (a) $\langle 110 \rangle$, (b) $\langle 112 \rangle$, (c) $\langle 111 \rangle$, and (d) $\langle 100 \rangle$ oriented NWs. Results of different initial NW heights are plotted. Thin NWs which broke up during the annealing are plotted as (width) = 0 in the vertical axis. The threshold of initial effective diameter with which NWs run into break or not was indicated by gray bands.

Table 6.1: Minimum initial effective diameter with which Si nanowires survive hydrogen annealing without wire breaking (unit: nm). The data is compared with the results by Ref. 3, which utilized hydrogen annealing with diffusion-blocking mask at anchors and used low pressure of 10 Torr.

	$\langle 110 \rangle$ NW	$\langle 112 \rangle$ NW	$\langle 111 \rangle$ NW	$\langle 100 \rangle$ NW
810°C ^a	~ 10	~ 18	~ 21	~ 23
775°C ^b	~ 18	~ 27	~ 30	~ 40
850°C ^b	~ 42	~ 46	~ 50	~ 70

^a 75 Torr, 2 min, without diffusion mask (this work).

^b 10 Torr, 1 min, with diffusion mask (Ref. 3).

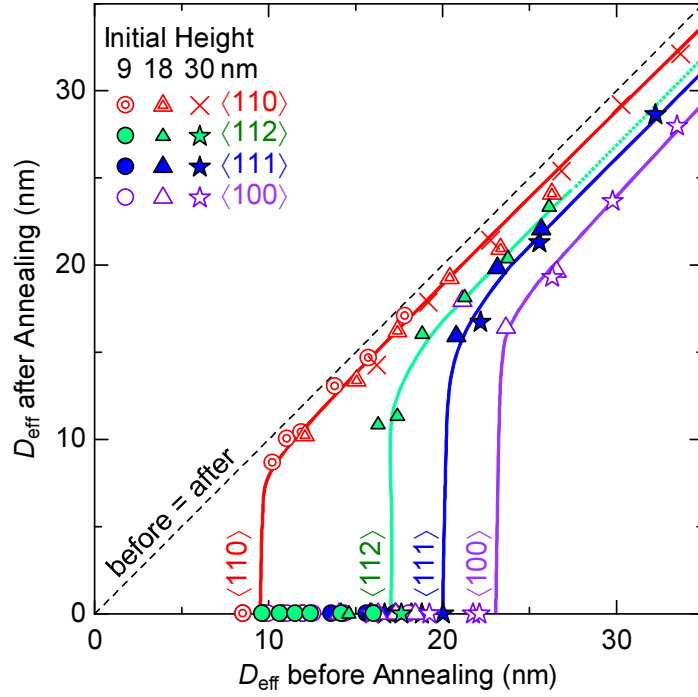


Figure 6.7: Comparison of effective diameter (D_{eff}) before and after 75-Torr annealing for $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ Si nanowires. The symbols are the measured data and the solid lines are guides to the eyes. The dashed line indicates the case where D_{eff} does not change by annealing. D_{eff} of broken wires after annealing is plotted at zero in the vertical axis. The data of three different initial heights (9, 18, 30 nm) are plotted for $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs. For $\langle 112 \rangle$ NWs, only the data of initially 18-nm-high wires is plotted since the D_{eff} of initially 9- and 30-nm-high $\langle 112 \rangle$ wires after annealing is unavailable (uncharacterized by TEM). However, the data of broken NWs are available also for initially 9- and 30-nm-high NWs (thanks to SEM).

(plotted as $D_{\text{eff,after}} = 0$). When the $D_{\text{eff,before}}$ is large enough, the $D_{\text{eff,after}}$ decreases from $D_{\text{eff,before}}$ by an almost constant value of Δ for each orientation,

$$D_{\text{eff,after}} = D_{\text{eff,before}} - \Delta. \quad (6.2)$$

The value of Δ has wire-axis dependence: $\Delta_{\langle 110 \rangle} \simeq 1$ nm, $\Delta_{\langle 112 \rangle} \simeq 3$ nm, $\Delta_{\langle 111 \rangle} \simeq 4$ nm, and $\Delta_{\langle 100 \rangle} \simeq 6$ –7 nm. Since the etching of Si with hydrogen gas is negligible at this temperature, this volume loss of NWs may be caused by out-diffusion of Si atoms toward the source and drain. Therefore, the speed of the diffusion along the wire is orientation dependent. Moreover, it should be noticed that a NW with the orientation that can easily be broken has a larger Δ value, which means that a NW with the orientation that shows faster diffusion along the wire breaks faster.

6.3.4 Anisotropy in Deformation of Cross-Sectional Shape by Circumferential Surface Diffusion

To study the speed of the surface diffusion along the circumference, the change of the width/height ratio (W/H) of NWs was calculated from cross-sectional TEM images and compared between before and after annealing. Figure 6.8 describes the relationship of the W/H ratio of NWs before and after 75-Torr annealing in the case of initially 18-nm-high NWs. The horizontal axis is the value of W/H before annealing, and the vertical axis is after annealing. Since the initial height of NW is the same, the horizontal axis is equivalent to the variation of NW width. The dashed line in Fig. 6.8 is the case where the aspect ratio does not change by annealing. As the deviation from the dotted line becomes larger, the deformation of the cross-sectional shape becomes larger. NWs along $\langle 110 \rangle$ did not break in the range of this plot, but NWs along $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ with small width, *i.e.* small initial W/H , broke. If the cross-sectional shape reaches its two-dimensional equilibrium shape of Si crystal, the W/H ratio after annealing converges on a certain value regardless of the initial W/H ratio. If the surface energy is isotropic, the converged value must be unity. If the cross-sectional shape of $\langle 111 \rangle$ and $\langle 100 \rangle$ NWs is equilibrated, the W/H ratio is expected to be about unity, taking account of the symmetry of the crystal structure. For $\langle 110 \rangle$ and $\langle 112 \rangle$ NWs, the equilibrated W/H value should depend on the surface energy anisotropy. Since the surface energy anisotropy around the $\langle 112 \rangle$ zone axis is not known under hydrogen ambient, it is difficult to mention a specific value of equilibrated W/H . However, $\langle 110 \rangle$ NWs in two-dimensional equilibrium are expected to become almost circular ($W/H = 1$) according to previous reports [1, 3].

Among the four wire orientations in Fig. 6.8, it can be found that the $\langle 110 \rangle$ NWs exhibit the smallest change in the W/H ratio (the smallest deviation from the dashed line), which means the circumferential surface diffusion on $\langle 110 \rangle$ NWs is very slow. On the other hand, the W/H value of the $\langle 100 \rangle$ NWs converged on unity after annealing irrespective of the initial aspect ratio. Therefore, the surface diffusion around the cross-section of $\langle 100 \rangle$

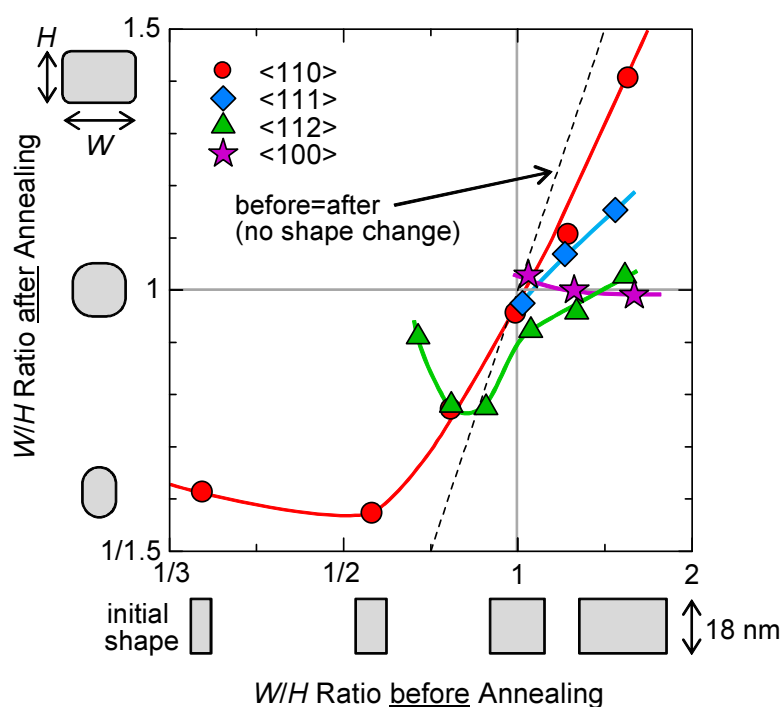


Figure 6.8: Relationship of width/height (W/H) ratio of Si NWs between before and after hydrogen annealing at 75 Torr. The height of NWs before annealing is 18 nm, and only the width before annealing was varied in this figure. The solid lines are guides to the eyes, and the dashed line describes the case where the W/H ratio does not change by annealing. $\langle 110 \rangle$ NWs did not break up even for the NWs with the smallest width in this figure (~ 7 nm). $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs with small initial widths broke by annealing. Therefore, the data for those NWs with small W/H ratios is missing.

NWs is fast enough to get to two-dimensional equilibrium within two-minutes annealing at 75 Torr. $\langle 112 \rangle$ and $\langle 111 \rangle$ NWs exhibited the speed of deformation in-between $\langle 110 \rangle$ and $\langle 100 \rangle$. As the width approaches the breaking threshold, however, the W/H ratio comes close to unity in those NWs. Thus, NWs just before breaking seem to become equilibrated in the cross-section.

To confirm how the evolution of the cross-sectional shape is different depending on the initial NW shape, the cross-sectional shape of annealed NWs whose initial shapes are vertically-long or horizontally-long are compared in Fig. 6.9. The width/height of NWs before annealing is 29 nm/18 nm for the horizontally-long structure [Fig. 6.9(a)] and 18 nm/30 nm for the vertically-long structure [Fig. 6.9(f)]. Therefore, $D_{\text{eff, before}}$ is almost the same between these two types of structures. The cross-sectional HRTEM images of NWs with the orientations of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 112 \rangle$ for each initial structure are shown, but only that of the initially horizontally-long $\langle 112 \rangle$ NW is missing since TEM was not observed for this structure. In $\langle 100 \rangle$ NWs, the cross-sectional shape of both vertically-long and horizontally-long NWs became a regular octagon after annealing. They have $\{100\}$ and $\{110\}$ facets, and $\{100\}$ facets are wider than $\{110\}$. When similar hydrogen-annealing experiments were performed on $\langle 100 \rangle$ NWs fabricated on a (100)SOI substrate, the same cross-sectional structure was obtained as shown in Fig. 6.10. In $\langle 110 \rangle$ NWs, slightly tapered sidewalls became vertical, which are $\{100\}$ facets. The corners are slightly faceted with mainly $\{111\}$ and $\{311\}$ planes. In some NWs, $\{331\}$, $\{221\}$, and $\{211\}$ facets were also observed. As mentioned before, the initial aspect ratio was almost preserved for $\langle 110 \rangle$ NWs. The cross-section of annealed $\langle 111 \rangle$ NWs is a dodecagon surrounded by six $\{110\}$ facets and six $\{211\}$ facets. The deformation of $\langle 111 \rangle$ NWs is larger than that of $\langle 110 \rangle$ NWs, but the cross-sectional shape of $\langle 111 \rangle$ NWs is not equilibrated because initially horizontally-long and vertically-long NWs became the different shapes after annealing. Hydrogen-annealed $\langle 112 \rangle$ NWs are surrounded by $\{110\}$, $\{111\}$, $\{311\}$, and $\{531\}$ facets. Facet faces appeared above are considered as the surfaces with low surface free energies. The surface free energies of facets are not able to be determined from the results of $\langle 110 \rangle$, $\langle 111 \rangle$ and $\langle 112 \rangle$ NWs. However, the relative surface free energy of $\{110\}$ facets to $\{100\}$ facets, $\gamma_{\{110\}}/\gamma_{\{100\}}$ can be determined from the cross-sectional shape of annealed $\langle 100 \rangle$ NWs. Using Wulff's theorem [13], $\gamma_{\{110\}}/\gamma_{\{100\}}$ is calculated to be 1.06 ± 0.01 , which is very close to the reported value (1.05) at 700°C [14].

6.4 Annealing at Higher Hydrogen Pressure (150 Torr)

To check the effect of the increased pressure of 150 Torr, the threshold D_{eff} where NWs survive hydrogen annealing was compared between 75 Torr and 150 Torr annealing in Table 6.2. In $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs, the minimum D_{eff} decreased by about 5 nm by

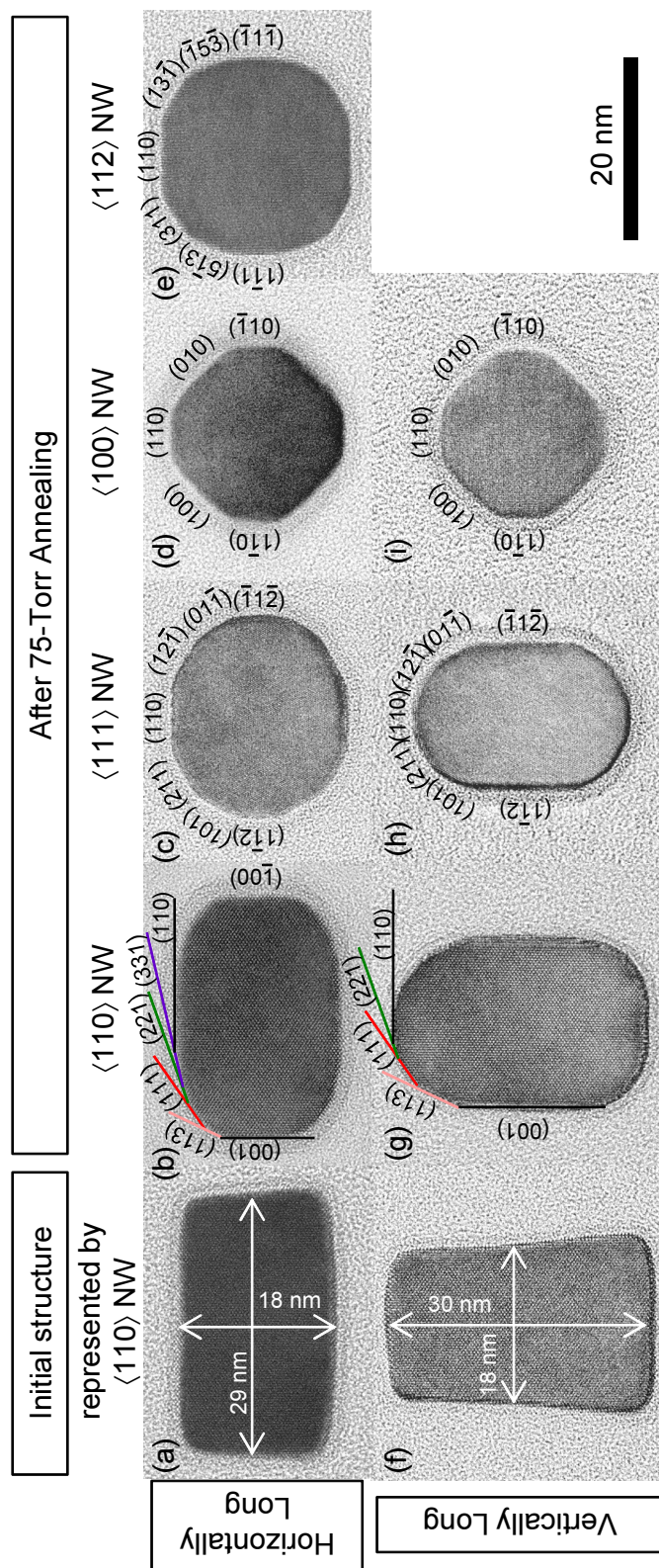


Figure 6.9: Cross-sectional high-resolution TEM images of Si NWs before and after 75-Torr hydrogen annealing. The initial structure represented by the $\langle 110 \rangle$ NW and annealed $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 112 \rangle$ NWs with initially a horizontally-long structure are shown in (a)–(e), respectively. The initial structure and annealed $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs with initially a vertically-long structure are shown in (f)–(i), respectively.

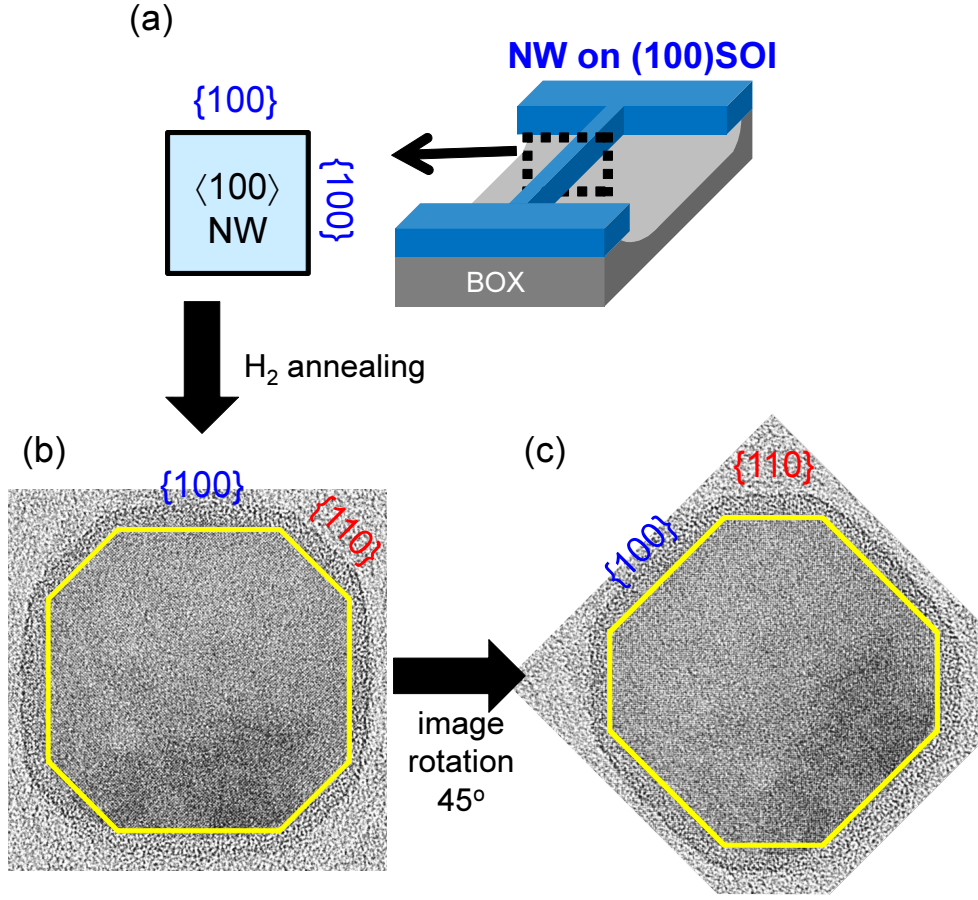


Figure 6.10: (a) Schematic image of $\langle 100 \rangle$ Si NW fabricated on (100)SOI substrate. (b) The cross-sectional HRTEM image of a $\langle 100 \rangle / (100)$ Si NW after hydrogen annealing. (c) The same image as (b) with 45° rotation. Even though the substrate face is different, the structure after hydrogen annealing is the same as that of $\langle 100 \rangle / (110)$ Si NWs shown in Figs. 6.9(d) and (i).

Table 6.2: Orientation dependence of minimum initial effective diameter with which Si nanowires survive hydrogen annealing at 75 Torr and 150 Torr (unit: nm).

	$\langle 110 \rangle$ NW	$\langle 112 \rangle$ NW	$\langle 111 \rangle$ NW	$\langle 100 \rangle$ NW
75 Torr	~ 10	~ 18	~ 21	~ 23
150 Torr	< 8	~ 14	~ 16	~ 17

increasing the hydrogen pressure from 75 Torr to 150 Torr. In $\langle 110 \rangle$ NWs, D_{eff} decreased but the specific value could not be determined because even the smallest NW survived. Like this, NWs are less easy to get broken at 150 Torr. However, this increased stability does not necessarily coincide with the flattening capability. The SEM images of Si NWs after annealing at 150 Torr are shown in Fig. 6.11. Upper images are NWs with the initial width/height of ~ 24 nm/9 nm, respectively ($D_{\text{eff}} \sim 16$ nm), and lower images are with that of ~ 24 nm/18 nm ($D_{\text{eff}} \sim 24$ nm). When the size of NWs is large, the line-edges of NWs can be smoothened. However, when the size of NWs is very small, the line-edges become rather fluctuated than smoothened except for $\langle 110 \rangle$ NWs. Therefore, higher pressure annealing does not always exhibit good smoothing effect especially in very thin Si NWs and there may exist a certain maximum pressure that can be used for NW annealing. However, $\langle 110 \rangle$ -oriented Si NWs seem exceptionally stable and 150-Torr annealing is still effective even for very thin $\langle 110 \rangle$ NWs.

6.5 Discussion

6.5.1 Orientation-Dependent Instability

In the previous section, the minimum size of NWs that survive annealing was found to be dependent not on the initial shape and aspect ratio (height and width) but on the effective diameter D_{eff} , which is determined by the cross-sectional area of NWs. When the size of NW is small enough, the cross-sectional shape of NWs can get rounded, as seen in Fig. 6.8, and it may reach its two-dimensional equilibrium in the early stage of annealing. This may be the reason why the threshold for breaking is independent of the initial shape. At the same time, loss of surface Si atoms occurs via surface diffusion, which is driven by capillarity at anchor points where NWs are supported. It was found that the speed of the loss of Si atoms is orientation-dependent and NWs break more easily when they are elongated to the orientation along which the speed of outflow of Si atoms is faster.

There exist several possibilities to explain this anisotropy in surface diffusion. The speed of mass transport by surface diffusion is mainly dependent on three factors. The first factor is the dependence of surface-diffusion coefficient on the surface and in-plane directions, because the flux of atomic transport on the surface, $\mathbf{J}$, is directly proportional to the surface diffusion coefficient as

$$\mathbf{J} = -\frac{D_s n_s}{k_B T} \nabla_s \mu, \quad (6.3)$$

where n_s is the surface density of atoms, $k_B T$ the thermal energy, ∇_s the surface gradient operator, and μ the chemical potential [15]. The second factor is the surface free energy anisotropy. As seen in Eq. (6.3), the flux of mass transport is proportional to the negated surface gradient of chemical potential of atoms. Assuming the number of atoms is conserved in the system, the chemical potential of the atoms on surface can be determined by the

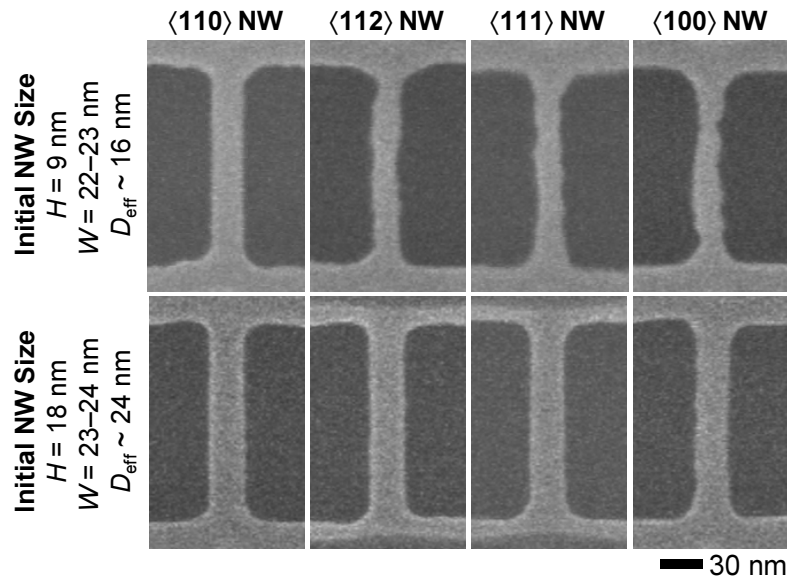


Figure 6.11: Top-view SEM images of Si NWs after annealing at 150 Torr with the orientations of $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$ and $\langle 100 \rangle$. The upper images are NWs with initial width and height of 22–23 nm and 9 nm, respectively ($D_{\text{eff}} \sim 16$ nm). NWs with this size cannot survive 75 Torr annealing except for $\langle 110 \rangle$ NWs. The lower images are thicker NWs with initial width and height of 23–24 nm and 18 nm, respectively ($D_{\text{eff}} \sim 23$ nm). 150 Torr annealing can smoothen sidewalls of thick NWs, but thin NWs were not smoothened and fluctuated except for $\langle 110 \rangle$ NWs.

surface tension, which is the product of surface free energy (more precisely, surface stiffness) and the curvature. Therefore, if the total surface energy can gain a larger profit by moving atoms from one place to another because of the surface energy anisotropy, surface atom movement is much more enhanced. The third factor, which does not directly appear in Eq. (6.3), is the crystal-face and step-direction dependences of the attachment/detachment rate of Si atoms to/from steps. Actually, the island decay on some Si faces such as (100)-(2 × 1) (640–1170°C) [16] and (111)-(7 × 7) (400–600°C) [17] in UHV is limited by the detachment of atoms from step edges. To completely elucidate the result of this study, these complex factors should be known in hydrogen ambient under the annealing condition. However, those kinds of properties including the mechanism of the modulation of diffusion coefficient and/or the surface free energy under the annealing conditions have not fully been known at this moment, although some studies have reported surface-hydrogen-induced γ decrease/change [18] and D_s decrease [19–22]. At present, the author infers some possibilities that can explain the orientation-dependent instability from the experimental results.

First, the NWs that have {111} facets on sidewalls such as $\langle 110 \rangle$ and $\langle 112 \rangle$ NWs are more stable, but the NWs that can have {111} facets crossing the wire axis such as $\langle 111 \rangle$ and $\langle 100 \rangle$ NWs are less stable. The {111} facets which can appear in Si NWs along each orientation are illustrated in Fig. 6.12. The {111} face is regarded as one of the stable facets of Si. In fact, from the equilibrium shape of Si at 700°C, (111) is known to have the lowest surface energy [14]. In addition, a theoretical study reported that the surface energy of the hydrogenated Si (111) is still lower than that of (100) and (110) [18]. Since {111} facets are observed on sidewalls of Si NWs, as shown in Fig. 6.9, {111} should be one of the stable facets even under the hydrogen-annealing condition. Therefore, the author speculates that {111} facets have a stabilizing effect and the shape evolution may be stabilized by generating {111} facets. If {111} facets intersect the axis of NWs, the mass transport would preferentially produce intersecting {111} facets and finally NWs would break up. For $\langle 100 \rangle$ NWs, the {111} facets are inclined from the perpendicular face of NW axis by 54.7°. On the other hand, the {111} facet of $\langle 111 \rangle$ NWs is completely perpendicular to the $\langle 111 \rangle$ axis. Therefore, smaller mass transport can produce {111} facets more easily in $\langle 100 \rangle$ -oriented NWs than in $\langle 111 \rangle$ NWs, which might explain very unstable behavior of $\langle 100 \rangle$ -oriented NWs.

Second, the cross-sectional shape of the NWs along the $\langle 110 \rangle$ axis showed small deformation after annealing. To deform the cross-sectional shape of $\langle 110 \rangle$ NWs significantly, Si atoms have to diffuse over {111} facets at the corners in cross-section of NWs. The author speculates that the diffusion of adatoms over {111} facets is relatively slow. It has been known from both experiments and calculation that, the energy barrier of surface adatom diffusion is larger on Si (111)-(1 × 1) (1.3 eV in experiment [23], 0.97 eV in calculation [24]) than on Si (100)(2 × 1) (0.67 eV in experiment [25] and 0.6–0.7 eV in calculation [26–28]). Here (1 × 1) reconstruction on (111) and (2 × 1) on (100) are considered since the Si surfaces after hydrogen annealing show those surface reconstructions [8]. However, hydrogenated Si

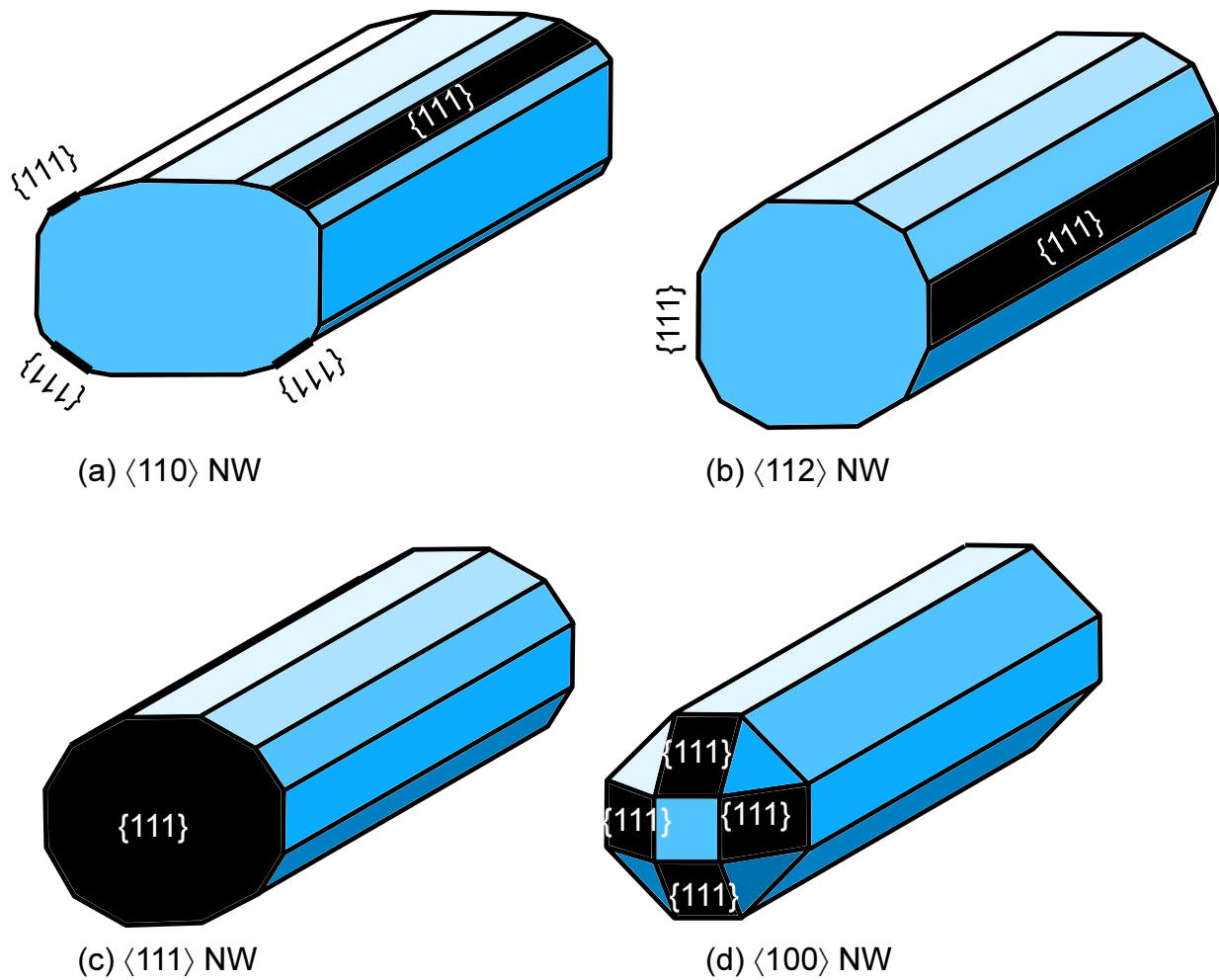


Figure 6.12: Illustrations of $\{111\}$ facets which can appear in Si NWs along (a) $\langle 110 \rangle$, (b) $\langle 112 \rangle$, (c) $\langle 111 \rangle$, and (d) $\langle 100 \rangle$ Si NWs. $\{111\}$ facets appear on sidewalls in $\langle 110 \rangle$ and $\langle 112 \rangle$ Si NWs, whereas they only intersect with $\langle 111 \rangle$ and $\langle 100 \rangle$ Si NWs.

(111)-(1 × 1) has been calculated to exhibit almost the same energy barrier of adatom diffusion (1.30 eV) as hydrogenated Si (100)-(2 × 1) (1.33 eV) [29]. Therefore, the diffusion kinetics of adatoms on hydrogenated Si surfaces have to be investigated carefully to confirm this hypothesis.

It is also noticeable that the stability to NW breaking at anchor points and the stability to failure by Rayleigh instability are in the same order with respect to the wire orientations. On the other hand, the prediction of the wire instability in maskless hydrogen annealing from the viewpoint of step direction on facets [8] does not agree with our results. Rayleigh instability occurs if the growth of a structural fluctuation in a rod by mass transport can reduce the total energy of the structure. If mass transport occurs by surface self-diffusion, the variation of the energy is determined by the total surface energy because the volume of the structure is conserved. Thus, the surface energy (and surface stiffness) plays an important role in the growth of the perturbation in Rayleigh instability [30, 31]. If the profit of the surface energy which the structure can gain by the growth of the fluctuation is larger, the surface diffusion should proceed faster [30]. Inversely, if the profit of the energy by the fluctuation growth is compensated by the increase in the surface area, the fluctuation cannot grow and thus wire structure can be stabilized. In a NW structure supported at the both ends by thin films, the connected points (anchors) are the structural perturbation from the viewpoint of the NW. In addition, since the anchors have convex curvatures, they play as atomic sinks that soak up atoms from NW surfaces. If the surface diffusion is easy to proceed with respect to the surface energy at anchor points, the NW easily runs into break due to fast surface diffusion. In this manner, there is the common physics in-between the Rayleigh instability and wire breaking at anchors. The author speculates that this is why the instability observed in this study has a similar orientation dependence to the Rayleigh instability.

6.5.2 Trade-Off between Wire Stability and Smoothing Effect in Annealing at Higher Pressures

Finally, the reason why very thin NWs cannot be smoothened enough by 150-Torr annealing is discussed. As mentioned in Sec. 6.3.3, severe wire-size reduction was observed in $\langle 100 \rangle$ -oriented NWs (Fig. 6.7). The author investigated the wire-size reduction for longer NWs ($L = 240, 540$ nm) and found that this wire-size reduction was not observed in the whole region of long NWs but appeared in the region of about 60 nm from the edge of $\langle 100 \rangle$ -oriented Si NWs for 75 Torr annealing, as shown in Figs. 6.13(a)–(c). The length of the area where the wire size was reduced can be interpreted as a kind of ‘surface diffusion length’ on NWs. For 140-nm-long NWs, the whole area of NWs was slenderized since the length of NWs is shorter than $2 \times$ (diffusion length) (note that the value of 140 nm includes the regions of anchors, 30–40 nm). In annealing at 150 Torr, however, the amount of the decrease in wire size was reduced and the length of the slenderized region at NW edges was shortened

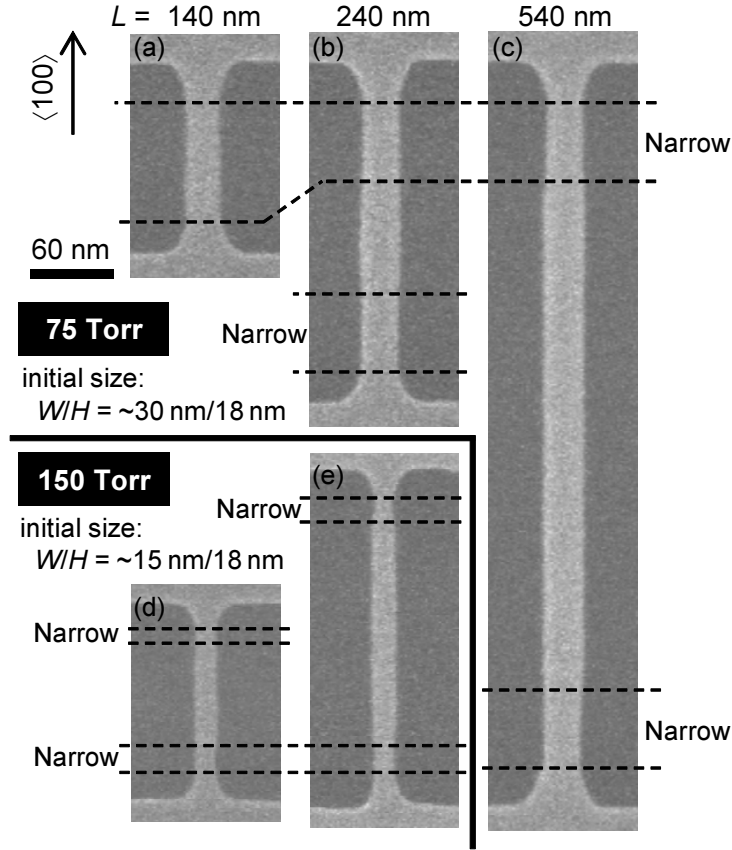


Figure 6.13: Top-view SEM images of $\langle 100 \rangle$ -oriented Si NWs with almost the same initial width ($\sim 30 \text{ nm}$) and height (18 nm) but the different wire lengths of (a) 140, (b) 240, and (c) 540 nm annealed at 75 Torr. The NWs annealed at 150 Torr with the lengths of (d) 140 and (e) 240 nm are also shown. Note that the initial size of NWs annealed at 150 Torr is smaller (width $\sim 15 \text{ nm}$, height $= 18 \text{ nm}$) than that at 75 Torr. Near the anchor points, NWs were slenderized due to out-diffusion of Si atoms toward dummy source and drain pads. The length of the slenderized region is about 60 nm and 10–20 nm for 75-Torr and 150-Torr annealing, respectively.

to about 10–20 nm [Figs. 6.13(d) and (e)]. This result evidences the reduced diffusion length at higher hydrogen pressure. To flatten Si NWs, the length in which atoms can be transported should be large enough. If the diffusion length is small compared to the scale of structural fluctuations in NWs, surface atoms might diffuse rather locally. In particular, structural fluctuations in NWs with smaller diameter correspond to larger curvature even if the amplitude of the fluctuations is same as those in thicker NWs. This larger curvature might enhance the local diffusion by which fluctuations would grow, even though the NWs with small diameter survived annealing due to a smaller diffusion coefficient.

6.6 Summary

Hydrogen annealing of Si NWs as a surface-smoothing process was studied at relatively high pressures of 75 Torr and 150 Torr to minimize excess surface diffusion of Si atoms. The annealing temperature and time were 810°C and 2 min, respectively. At 75 Torr, the surface smoothing capability and slowdown of the progress of wire breaking during annealing were compatible. The minimum diameter with which NWs survived annealing at 75 Torr was about 10, 18, 21, 23 nm for $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs, respectively. From the characterization of the cross-sectional size and shape of NWs before and after annealing, cross-sectional size of NWs was found to decrease by annealing, and the speed of volume loss was orientation dependent: $\langle 100 \rangle > \langle 111 \rangle \gtrsim \langle 112 \rangle > \langle 110 \rangle$, which is the reverse order of wire stability. This size decrease is attributed to the out-diffusion of silicon atoms on NWs toward supporting thin films. This result suggests that strong anisotropy in surface self-diffusion of Si atoms exists in NW structures and that the speed of diffusion strongly correlated with the wire stability at anchor points. At 150 Torr, wire breaking was considerably minimized and the minimum diameter was reduced to <8, 14, 16, and 17 nm for $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs, respectively. However, NWs with very small diameters (except $\langle 110 \rangle$ NWs) were not smoothened enough owing to shorter diffusion length compared to 75 Torr annealing. Therefore, 75 Torr annealing gives good results and there is a limitation of maximum pressure of hydrogen that can be utilized for NW smoothing.

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Chapter 7

Carrier Transport Properties in Si Nanowire MOSFETs with Smooth Surfaces

7.1 Introduction

It is very important to experimentally evaluate the effect of one-dimensional electronic states, which are significantly modulated by a quantum confinement effect (QCE), on carrier transport in Si nanowires (NWs). QCE induces the split of the bulk band structure into subbands in NWs. This accompanies the modulation of the density of states (DOS) in NWs, and DOS in NWs oscillates with respect to the energy because DOS at the bottom of each subband goes infinity. This nature of DOS leads to the oscillation of carrier mobility [1, 2] and gate capacitance [3–6]. The spacing of the peaks in oscillation can be interpreted as the spacing of the subbands. Therefore, if these oscillations can be observed experimentally, it can be a great clue to understand the subband structure in NWs when the experimental oscillations are compared to numerically obtained subband structures. After knowing the subband structures, optimization of NW structures (shape, size, and orientation) can be performed to obtain higher transport performance. The mobility and capacitance oscillations can be evaluated through drain current I_D oscillation and transconductance g_m oscillation in Si NW MOSFETs. To observe these oscillations induced by one-dimensional DOS, however, the width fluctuation in NWs has to be minimized not to cause another type of oscillation by Coulomb blockade [7, 8]. Although several studies have reported the oscillation of I_D and g_m in Si NWs [1, 9–13], more detailed discussion whether the observed oscillation truly originates from subband structures or from Coulomb blockade is necessary. Moreover, comparison of the experimentally obtained oscillation and the theory is still limited.

The experimental measurement of carrier mobility in very thin NWs is also one of the important issues. In a small NW with a cross-sectional size of about ten nanometers or

less, QCE might become conspicuous and the transport properties can be affected by QCE caused by its nanoscale geometry. Several studies have reported carrier mobility in (sub-)10-nm-scale NWs [14–22], but the reported mobilities vary largely, and studies on orientation dependence of mobility in NWs are limited mainly for $\langle 100 \rangle$ and $\langle 110 \rangle$. The hole mobility in $\langle 111 \rangle$ NWs, which are theoretically expected to be very suitable for hole transport (Chapter 2) and predicted to exhibit high hole mobility [23, 24], is not still well known experimentally.

In this study, Si NW MOSFETs are fabricated by applying the surface-smoothing hydrogen annealing process, which was studied in Chapters 5 and 6, and carrier transport properties in NW MOSFETs are characterized focusing on the transconductance oscillation to assess the effect of one-dimensional electronic states in NWs on carrier transport. In addition, hole mobilities in $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ Si NWs with a diameter smaller than 15 nm are experimentally extracted.

7.2 Fabrication Process of Nanowire MOSFETs

7.2.1 Device Structures

For the two purposes of this study, two different types of Si NW MOSFETs were fabricated. The first one has a single NW and both n^+ - and p^+ -implanted regions in source and drain, as illustrated in Fig. 7.1(a) (referred as dual MOSFET hereafter). This MOSFET operates as NMOS at a positive gate voltage (V_G) and PMOS at a negative V_G , and thus electron and hole transport can be observed and characterized in an identical NW [25, 26]. Therefore, the information of both conduction band and valence band of the same NW can be obtained. The dual MOSFETs are used for the observation and analysis of the g_m oscillation phenomenon. The second one is NW PMOSFETs which have parallel 750 NWs at intervals of 250 nm, as shown in Fig. 7.1(b) (referred as multi-NW MOSFET hereafter). Multi-NW MOSFETs are used for hole mobility extraction. Parallel 750 NWs are adopted to increase the gate capacitance of NWs, which is required for mobility evaluation, because the gate capacitance of a single NW is too small to be measured. For example, the gate capacitances of a single cylindrical NW with a diameter of 5 and 10 nm covered by 10-nm-thick SiO_2 are estimated to be 135 and 197 aF/ μm , respectively (depletion and inversion-layer capacitances are neglected in this calculation). 750 NWs with these structures give the capacitances of 101 and 148 fF/ μm , respectively, which are detectable by a capacitance meter. The method of mobility evaluation is described in Section 7.4.2.

A summary of the device structures of dual MOSFETs and multi-NW MOSFETs is given in Table 7.1. In both device structures, Si NWs were released from the buried oxide (BOX) to flatten the whole surfaces of Si NWs by hydrogen annealing. To form a gate electrode on suspended NWs properly, a gate-all-around geometry with polycrystalline Si (poly-Si) gate was adopted. The gate insulator was formed by thermal oxidation. To minimize the regeneration of surface roughness by gate oxidation after hydrogen annealing, oxidation

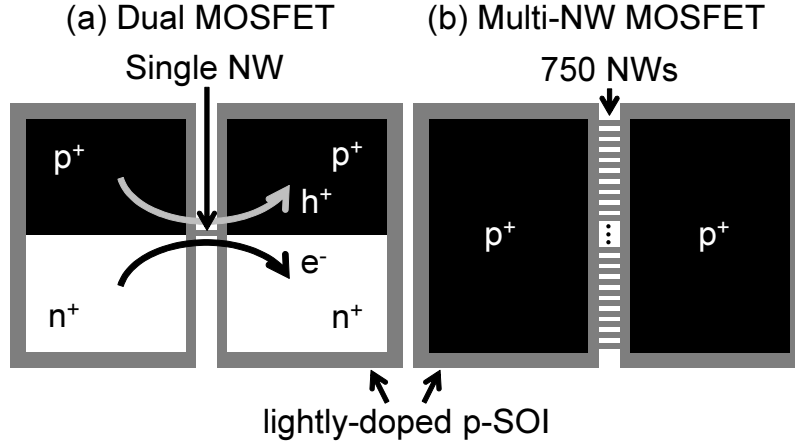


Figure 7.1: Schematic image of fabricated MOSFETs. (a) A single-NW MOSFET with both n^+ and p^+ regions in source and drain (dual MOSFET). (b) A PMOSFET with parallel 750-NW channels (multi-NW MOSFET).

Table 7.1: Summary and comparison of dual MOSFET and multi-NW MOSFET.

	Dual MOSFET	Multi-NW MOSFET
purpose	Comparative study of QCE on electrons and holes	Evaluation of hole mobility
substrate	p^- (110)SOI	p^- (110)SOI
channel type	NMOS and PMOS sharing the same single NW	PMOS only
NW orientation	$\langle 110 \rangle$ only	$\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, $\langle 100 \rangle$
number of NWs	1	750
NW length	150 nm	1, 1.25, 2 μm
gate length	5 μm	5, 5.25, 6 μm
NW diameter	5–14 nm	7–15 nm
gate geometry	gate-all-around	gate-all-around
gate stack	p^+ poly-Si/thermal SiO_2	p^+ poly-Si/thermal SiO_2
gate SiO_2 thickness	10–16 nm (average: ~ 12 nm)	7–10.5 nm
S/D SOI thickness	20 nm	13 nm

conditions were studied beforehand. This oxidation process is discussed in Section 7.2.2. For dual MOSFETs, $\langle 110 \rangle$ NW MOSFETs with various diameters from 5 nm to 14 nm were fabricated on a $\langle 110 \rangle$ silicon-on-insulator (SOI) wafer and characterized at room and low temperatures. The length of NWs is about 150 nm. For multi-NW MOSFETs, $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ NWs were fabricated on $\langle 110 \rangle$ SOI and the hole mobility of Si NWs with various sizes and orientations were evaluated. Three different devices with NW lengths of 1, 1.25, and 2 μm were fabricated for each NW width.

7.2.2 Method of Gate SiO₂ Growth by Thermal Oxidation with Minimized Surface Roughening

Si surfaces are smoothened by hydrogen annealing, but they can be roughened by thermal oxidation for the gate formation. Unconventional oxidation methods such as oxygen radical oxidation [27] and nitric-acid oxidation [28] are reported to produce atomically-flat SiO₂/Si interface, although the thickness of SiO₂ by nitric-acid oxidation is about 1 nm. Flat interfaces can be also kept when the gate insulator is deposited (SiO₂ and high- κ materials by chemical-vapor deposition and atomic-layer deposition, for example). However, ultrathin oxide induces tunnel gate leakage, which may make the capacitance measurement not easy, and unconventional oxidation techniques and deposition techniques require special experimental tools designed for those processes. This study formed SiO₂ by thermal oxidation for the gate insulator, and the oxidation conditions which can minimize the interface roughening were investigated.

The surfaces of bulk Si(100), (110), (111) samples were smoothened by hydrogen annealing under the conditions of 850°C, 75 Torr, 11 slm, and 2 min immediately before oxidation. The samples were then thermally oxidized in a vertical resistive-heating furnace at various temperatures of 800, 970, 1000, 1050, and 1100°C. At lower temperatures (800 and $\sim 970^\circ\text{C}$), the samples were oxidized in 100% O₂ ambient. At higher temperatures, diluted O₂ in N₂ (10% at 1000°C and 2.5% at 1050 and 1100°C) was used for a control of a thin oxide growth. The oxidation time was chosen to produce 7–8-nm-thick SiO₂ on Si(100). Therefore, the SiO₂ thickness (t_{ox}) on Si(110) and (111) varies with different oxidation conditions. In oxidation experiments, the oxidant gas was flowed during the heating (20°C/min) and oxidation time, and then the gas was switched to N₂ when the oxidation time ended. The furnace was slowly cooled from the oxidation temperature to 800°C at a rate of $-2.5^\circ\text{C}/\text{min}$ and then the heater was turned off. After oxidation, the SiO₂ thickness was measured by spectroscopic ellipsometry. The oxidation conditions and corresponding t_{ox} are summarized in Table 7.2. The interface roughness was evaluated by a tapping-mode atomic force microscopy (AFM) after removing SiO₂ with HF/HCl (47% HF : 35% HCl = 1 : 100) for 2–3 min and following HCl rinse for 10 sec. HF/HCl etching is expected to preserve the interface structure since HF solution at low pH does not etch Si [29].

Figure 7.2 shows the relationship between the oxidation conditions and the interface

Table 7.2: Thermal oxidation conditions and resulting SiO₂ thicknesses (t_{ox}) on Si(100), (110), and (111). The oxidation at 970°C for 0 min means that O₂ gas was flowed during the heating and then was stopped and changed to N₂ gas when the temperature reached 970°C.

Temperature (°C)	O ₂ (%)	Time (min)	t_{ox} (100) (nm)	t_{ox} (110) (nm)	t_{ox} (111) (nm)
800	100	55	7.1	11.7	10.3
~970	100	0	7.7	11.1	12.0
1000	10	14	7.6	10.6	9.0
1050	2.5	20	7.6	9.5	7.5
1100	2.5	10	8.0	9.7	7.8

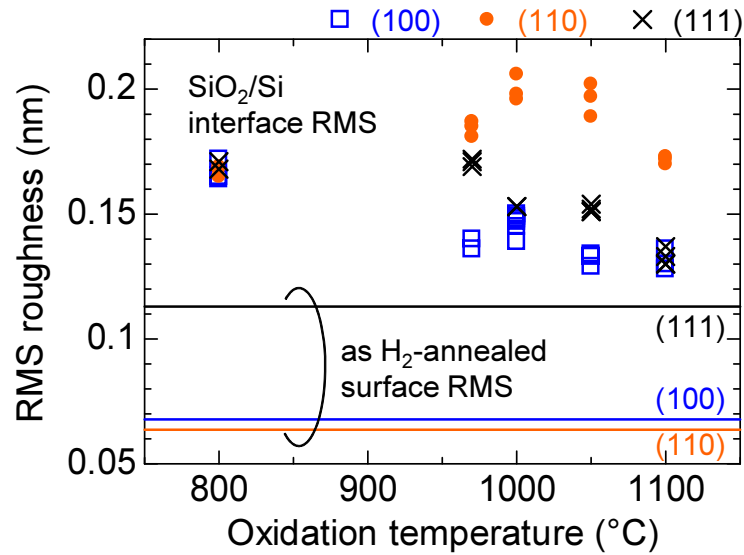


Figure 7.2: SiO₂/Si interface RMS roughness under various oxidation conditions listed in Table 7.2. This figure is plotted as a function of the oxidation temperature.

RMS roughnesses ($1\ \mu\text{m} \times 1\ \mu\text{m}$ area) of SiO_2/Si interface evaluated by AFM. Here, the oxidation temperatures are taken as a representative parameter of the oxidation conditions to make this plot. Figure 7.3 shows AFM images of Si(100), (110), and (111) surface morphologies of Si which was treated by hydrogen annealing and the interface morphologies of thermally-grown SiO_2/Si (100), (110), and (111). The smooth surfaces with monatomic steps and wide terraces obtained by hydrogen annealing were roughened by thermal oxidation.

On the (100) face, the RMS roughness at SiO_2/Si interface (0.13–0.17 nm) is much higher than that of the Si surface smoothened by hydrogen annealing (0.06–0.07 nm). The RMS roughness decreases as the oxidation temperature increases. The spatial information of the roughness is investigated from power spectral density (PSD), which can analyze the wavelength component of the surface and interface morphologies. Figure 7.4(a) shows PSD of smoothened Si(100) surface and SiO_2/Si (100) interface oxidized at 800, 1000, and 1100°C. In all the range of the frequency (or wavelength), smoother interface (lower PSD) was obtained at higher oxidation temperature.

On the (110) face, the roughness increases from 0.06–0.07 nm to 0.17 nm by 800°C oxidation, and the step-terrace structure is almost destroyed. As the oxidation temperature increases, the RMS roughness further degrades and reached ~ 0.20 nm at 1000°C. However, the RMS roughness decreases at 1100°C. The interface roughness oxidized at 1100°C is about 0.17 nm. This value is almost the same as that obtained by 800°C oxidation, but the morphology is different. The morphology of the interface oxidized at 800°C is finer than that oxidized at 1100°C. This result can be seen more clearly in PSD [Fig. 7.4(b)]. When PSD of the 800°C sample and 1100°C sample is compared, PSD is larger for the 1100°C sample in the wavelength range of about 20–50 nm, whereas the roughness component with a shorter wavelength < 20 nm is higher on the 800°C sample.

On the (111) face, the smooth terrace (initial RMS = 0.11 nm in $1\ \mu\text{m} \times 1\ \mu\text{m}$ area and 0.06 nm on a terrace) becomes rough at 800°C with fine dents and protrusions. The interface morphologies of Si(111) oxidized at higher temperatures become smoother, and dents and protrusions become wide island-like structures. This change of the interface morphologies can be observed in PSD spectra in Fig. 7.4(c). At 800°C, PSD is large in all range of the wavelength. By increasing the temperature up to 1100°C, PSD decreases down to the value of hydrogen-annealed surface in the small wavelength (≤ 10 nm) region, whereas PSD in long wavelength (> 20 nm) region is still larger than initial smooth surface probably due to islands on the terraces.

Judging from the interface flatness of different crystal faces in a comprehensive manner, 1100°C oxidation in 2.5% O_2/N_2 looks the most promising. In addition, high-temperature oxidation can minimize the stress in SiO_2 and Si NW core induced by volume expansion by oxidation because SiO_2 becomes viscous at high temperature [30]. Therefore, this study uses the 1100°C oxidation conditions for the gate oxidation process. The relatively smooth interface at 1100°C may be attributed to two factors. The first one is smaller stress at

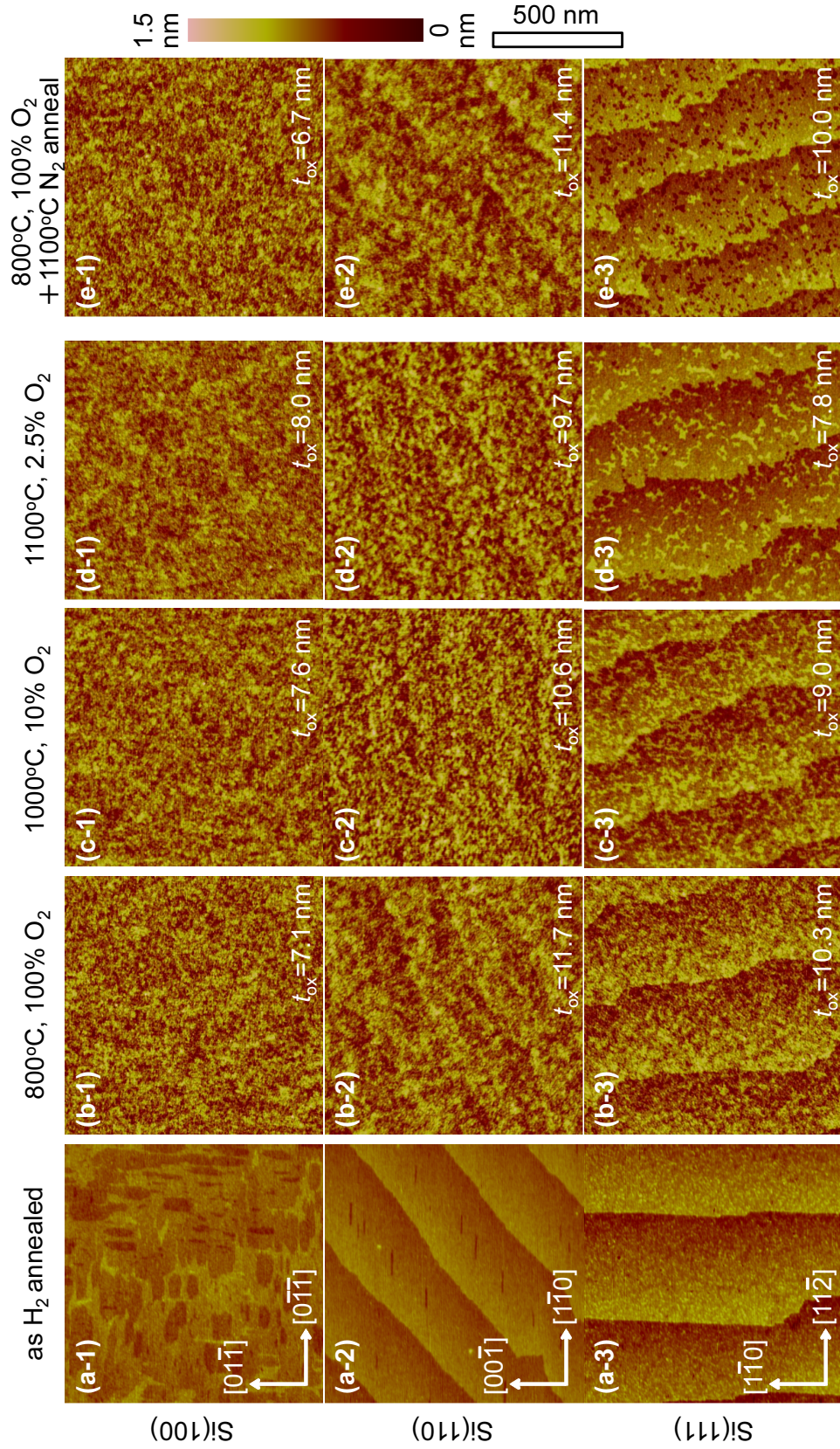


Figure 7.3: AFM images of Si(100), (110), and (111) surface morphologies after hydrogen annealing (850°C, 75 Torr, 11 s/m, and 2 min) [(a-1)–(a-3)], and interface morphologies of thermally-grown SiO₂/Si(100), (110), and (111). The thermal oxide was grown at various temperatures and O₂ percentages: 800°C in 100% O₂ [(b-1)–(b-3)], 1000°C in 10% O₂/N₂ [(c-1)–(c-3)], and 1100°C in 2.5% O₂/N₂ [(d-1)–(d-3)]. Monatomic steps and wide terraces were obtained by hydrogen annealing, but the interface roughness was generated after thermal oxidation. (e-1)–(e-3) show the interface morphologies of SiO₂/Si grown at 800°C in 100% O₂ and subsequently annealed in 100% N₂ at 1100°C for 15 min. Comparing to (b-1)–(b-3) without N₂ annealing, the interface roughness is improved.

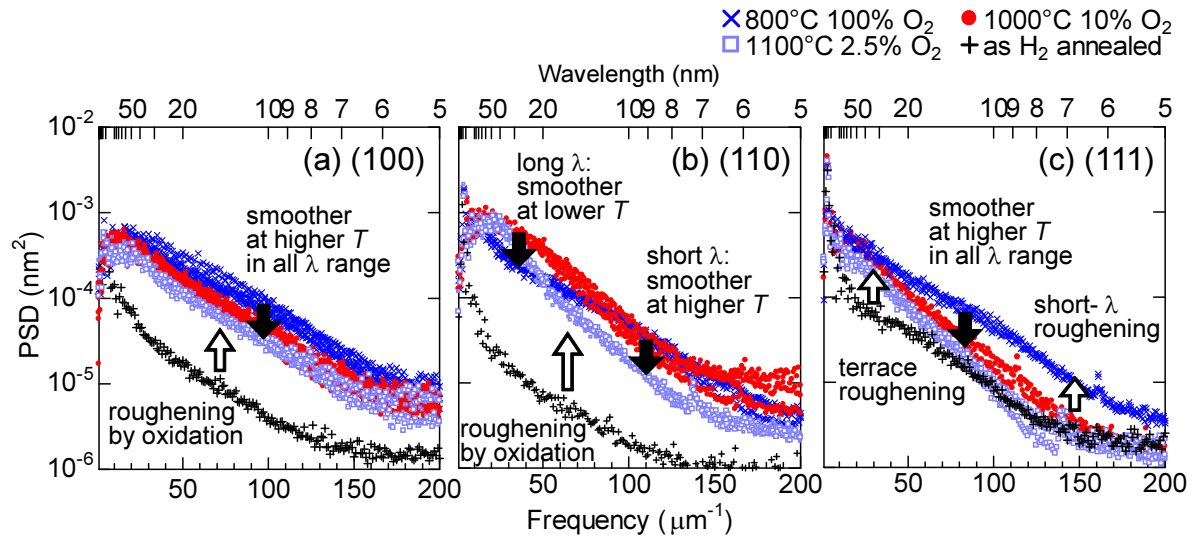


Figure 7.4: Power spectral density (PSD) of roughness profiles of Si surface after hydrogen annealing and SiO_2/Si interfaces (after oxidation) obtained by AFM with $1\ \mu\text{m} \times 1\ \mu\text{m}$ scan for (a) Si(100), (b) Si(110), and (c) Si(111). Three different oxidation conditions of 800°C in 100% O_2 , 1000°C in 10% O_2 , and 1100°C in 2.5% O_2 are compared. The thickness of SiO_2 is listed in Table 7.2.

oxide interface, which can minimize the growth of protrusions at the interface [31]. The second one is the interface smoothing effect by a thermal annealing during relatively slow oxidation at a high temperature and during the slow cooling process from 1100°C to 800°C at $-2.5^\circ\text{C}/\text{min}$ after oxidation. On Si(100), it is reported that the interface roughness can be improved by post-oxidation annealing at 900°C for 15 min in N_2 [32]. The author confirmed the effect of post-oxidation annealing at 1100°C (high-temperature condition) for 15 min in N_2 for SiO_2/Si interfaces whose oxide was grown at 800°C in pure O_2 . The AFM images are shown in Figs. 7.3(e-1)–(e-3). By this annealing, the roughness at $\text{SiO}_2/\text{Si}(100)$, (110), and (111) interfaces were improved (RMS: 0.15, 0.16, and 0.15 nm, respectively). In particular, rough protrusions are smoothed and relatively wide islands were obtained on (111).

7.2.3 Overview of Fabrication Process

An illustration of the device fabrication process is shown in Fig. 7.5. This figure represents the case of a dual MOSFET, but the main differences in a multi-NW MOSFET are the length and number of NWs and the existence of n^+ regions in source/drain. A lightly-boron-doped (5×10^{14} – $2 \times 10^{15} \text{ cm}^{-3}$) p-type (110)SOI wafer was used. The initial Si and BOX thicknesses are 100 and 200 nm, respectively. The specifications can be found in Table 3.1. First of all, the SOI thickness was reduced to about 41 nm and 33 nm for dual MOSFETs and multi-NW MOSFETs, respectively, by thermal oxidation [Fig. 7.5(b)]. Next, the device area definition and isolation were performed by Si trench formation with photolithography and Cl_2 -based ICP-RIE [Fig. 7.5(c)]. After that, 9-nm-thick thermal oxide was grown for etching mask in NW fabrication [Fig. 7.5(d)], and Si NW patterns were defined by electron-beam lithography (EBL) and Cl_2 -based ICP-RIE. The hybrid lithography technique with ZEP-520A resist and hydrogen silsesquioxane (HSQ) resist described in Chapter 3 (Section. 3.2.3) were used. After NW definition, sacrificial oxidation was performed at 1000°C for 30 min in 10% O_2/N_2 to reduce the NW size and remove the surface which was exposed to plasma. The expected thickness of surface Si consumed by this oxidation is about 5, 6.5, and 5.5 nm for Si(100), (110), and (111), respectively. Then, NWs were released from BOX by etching BOX by 110 nm with HF/HCl (47% HF : 35% HCl = 1 : 100), rinsed in 35% HCl for 10 sec, and hydrogen annealing was performed at 810°C, 75 Torr and 11 slm for 2 min for NW smoothing. Subsequently, gate oxidation was performed at 1100°C in 2.5% O_2/N_2 for 10 min and 35 min for multi-NW MOSFETs and dual MOSFETs, respectively, and undoped 210-nm-thick poly-Si was deposited by a low-pressure chemical vapor deposition (LPCVD). Shallow $^{49}\text{BF}_2^+$ ion implantation was performed to the poly-Si surface at 15 keV and $4 \times 10^{15} \text{ cm}^{-2}$. The low energy was used to prevent boron atoms from penetrating into NW channels. The range of ions is about 13 nm. After the implantation, gate patterns were defined by photolithography and Cl_2 -based ICP-RIE, and p^+ and n^+ source and drain regions (the n^+ regions are only for dual MOSFETs) were formed by $^{49}\text{BF}_2^+$ and As^+ ion

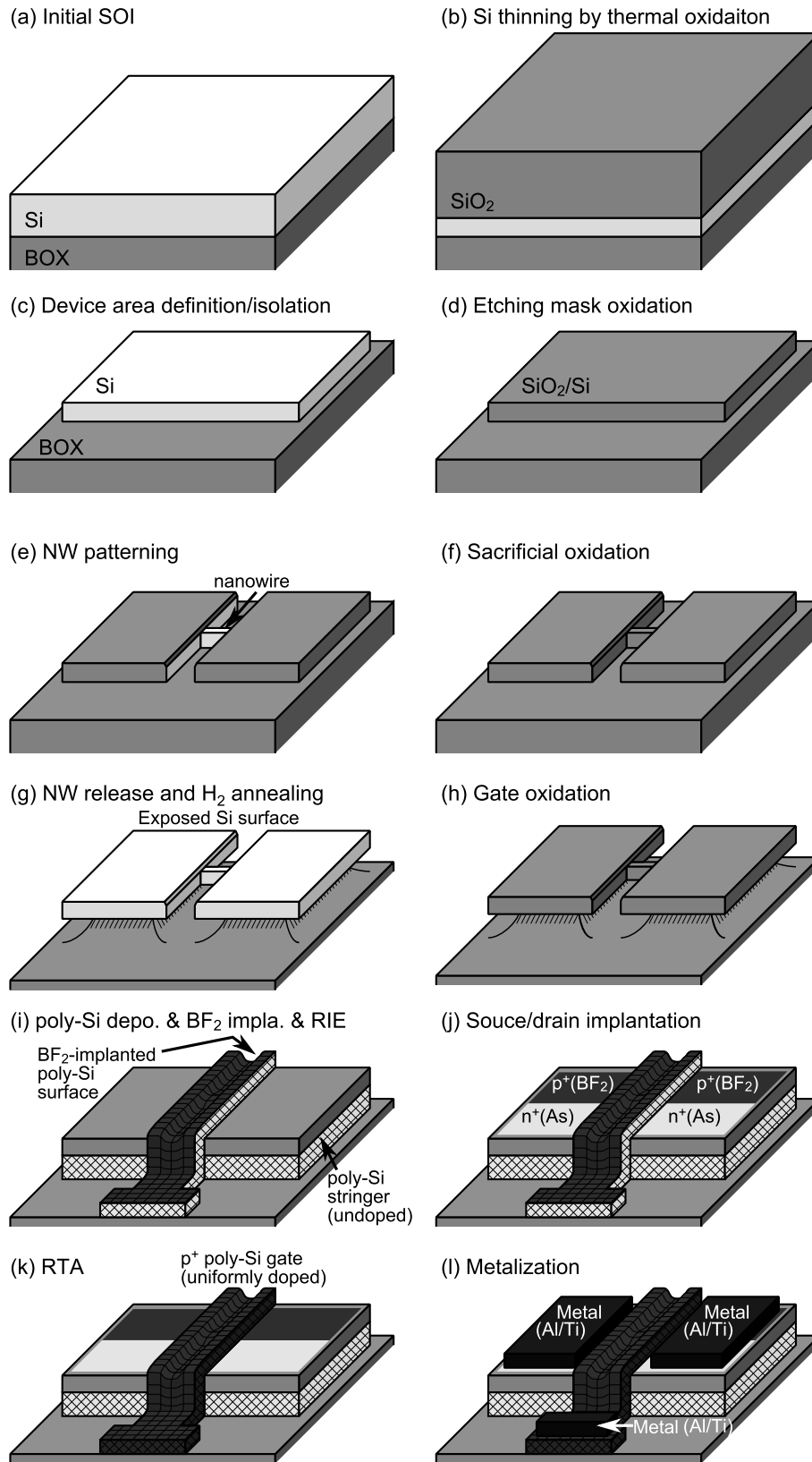


Figure 7.5: Fabrication process of Si NW MOSFETs. This figure represents the process for dual MOSFETs. The differences of the process in multi-NW MOSFETs are the length and number of NWs in NW patterning (e) and the n^+ regions in source/drain implantation (j).

implantation. At the periphery of source and drain pads, poly-Si stringers remain, but they do not affect the device operation because they are undoped. Rapid thermal annealing was performed at 1050°C for 25 sec with a SiO₂ cap to obtain uniformly-doped p⁺ poly-Si by diffusion and activation and to activate source/drain dopants. Forming gas (10% H₂/N₂) annealing was also performed at 450°C for 30 min to passivate the SiO₂/Si interface traps. Finally, the fabrication process completed with contact hole etching, Al/Ti(/Si) electrode formation, and sintering in forming gas at 350°C for 10 min. The complete process flow and details of process conditions are given in Appendix B.

Cross-sectional transmission electron microscopy (TEM) images of a fabricated dual MOSFET and multi-NW MOSFET are shown in Fig. 7.6. The gate-all-around structure was successfully implemented in both devices, and the array of multiple NWs was successfully obtained.

7.3 Effect of One-Dimensional Density of States on Electron and Hole Transport Properties

In this section, $\langle 110 \rangle$ single-NW dual MOSFETs are characterized at room temperature (RT) and low temperatures down to ~ 8 K. The devices exhibit oscillations in drain current I_D and transconductance g_m at low temperatures. Therefore, the nature of the oscillations is investigated.

7.3.1 Structure of Nanowire Channels

The expected NW structure before hydrogen annealing and subsequent gate oxidation is rectangle with a height of about 23 nm and a width of about 18–36 nm. By hydrogen annealing and gate oxidation, the corners of NWs were rounded, but the rounding effect of hydrogen annealing on $\langle 110 \rangle$ NWs is not significant as discussed in Sec. 6.3.4. Therefore, the final NW structures are nearly rectangular with rounded corners or oval. The cross-sectional shapes of the fabricated NWs were precisely determined by cross-sectional high-resolution TEM (HRTEM) measurement after electrical characterization. The width and height of NWs are plotted in Fig. 7.7(a) as a function of an effective diameter (D_{eff}) defined by

$$D_{\text{eff}} = 2\sqrt{(\text{cross-sectional area of NW})/\pi}. \quad (7.1)$$

In this figure, corresponding HRTEM images are also shown. D_{eff} of fabricated NWs are 5.1–13.5 nm, and the width and height are 4.1–19.5 and 5.7–9.0 nm, respectively. The thickness of thermally-grown gate SiO₂ (t_{ox}) was characterized and shown in Fig. 7.7(b). t_{ox} on the side faces $\{100\}$ is 10–12 nm and it does not strongly depend on the NW size. On the other hand, t_{ox} on the top and bottom faces $\{110\}$ has variation of 12.3–16.3 nm and NWs with a wider width have thicker top and bottom t_{ox} . Therefore, t_{ox} is almost conformal

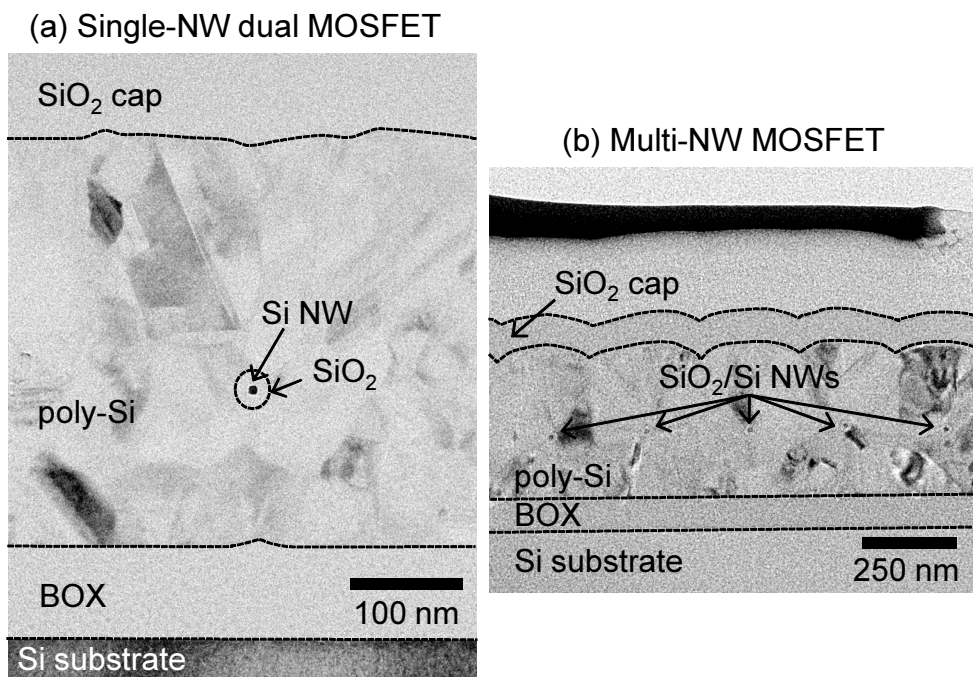


Figure 7.6: Cross-sectional TEM images of fabricated (a) dual MOSFET with the NW length of 150 nm and (b) multi-NW MOSFET with the NW length of 2 μm . The gate-all-around structure was successfully realized in both types of devices, and the NW array was implemented in the multi-NW MOSFET.

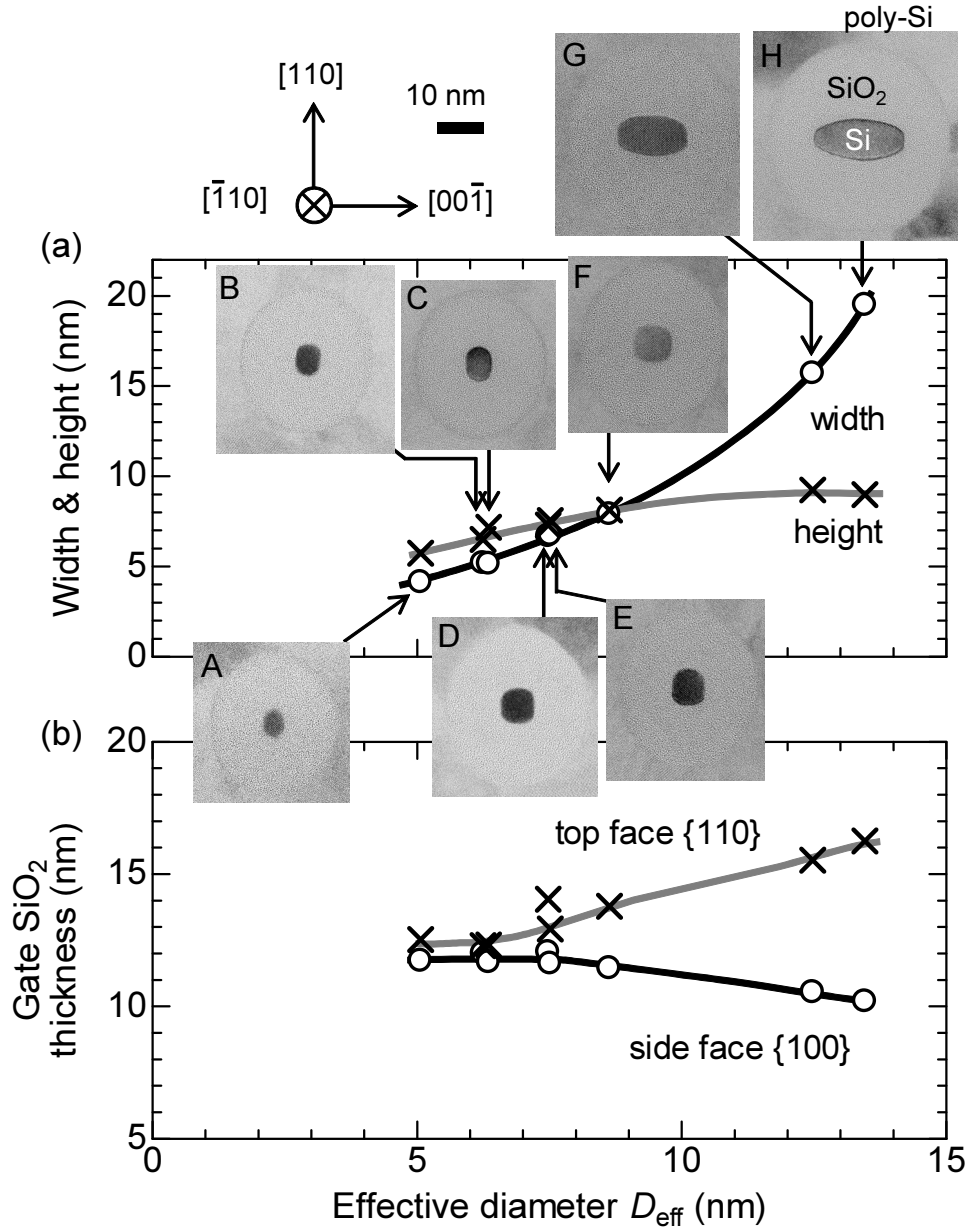


Figure 7.7: (a) Width and height of Si NWs and (b) gate SiO_2 thickness of fabricated dual MOSFETs as a function of effective diameter D_{eff} . These values were characterized by cross-sectional TEM images of eight Si NWs, and the corresponding TEM images are also shown. For each TEM image, device ID from A to H is given from small- to large- D_{eff} NWs. This device ID is referred hereafter to specify the device.

on thinner NWs but anisotropic on thicker NWs. Since t_{ox} on bulk Si(100) and (110) are 14.3 and 16.2 nm, respectively, the oxidation of top/bottom faces in thick t_{ox} of 16.3 nm in the widest NW is bulk-like. The retarded oxidation rate in thin NWs is probably due to the stress at SiO₂/Si interface induced by volume expansion of SiO₂ during oxidation [33–35]. Even though these results indicate the existence of the stress during 35-min oxidation at 1100°C, it does not directly mean that the final NW structures contain stress in NW core since the temperature was slowly cooled down from 1100°C to 800°C at $-2.5^\circ\text{C}/\text{min}$ and the stress can be relaxed to some extent. Since the doping concentration of SOI layer is 5×10^{14} – $2 \times 10^{15} \text{ cm}^{-3}$ and the volume of a NW is 3 – $20 \times 10^{-17} \text{ cm}^3$ (NW length: 150 nm), the estimated number of dopants in a NW is 0.015–0.4. Therefore, the NW channel can be regarded as almost intrinsic.

7.3.2 Device Operation at Room Temperature

At first, the device operation of fabricated single-NW dual MOSFETs was measured at RT (297–298 K). A low drain voltage $V_D = +10 \text{ mV}$ or -10 mV was used for the measurement of NMOS or PMOS operations, respectively. The NMOS and PMOS operations were observed at the gate voltages (V_G) above and below 0.5 V, respectively. Figure 7.8(a) shows I_D – V_G characteristics of NW MOSFETs whose cross-sectional size and shape were determined by TEM. I_D is normalized by V_D in the figure. The device ID listed in the legend corresponds to HRTEM images of NWs shown in Fig. 7.7. In general, I_D becomes lower and the threshold voltage V_T becomes higher in smaller NWs in both NMOS and PMOS. The transconductances $g_m = \partial I_D / \partial V_G$ of these NWs are shown in Fig. 7.8(b). g_m is shown as normalized values by V_D (g_m/V_D). At RT, any systematic oscillation in g_m is not observed except for an accidental oscillation (for example, NMOS of device F). The general property of g_m is the same in almost all the devices, showing a sharp rise near the threshold voltage and gradual decrease with the increase in the gate overdrive voltage, which is normally observed in MOSFETs because of the mobility degradation at higher transverse electric field and current limitation by the series resistance [36]. However, the PMOS operation in the smallest NW (device A, $D_{\text{eff}} = 5.1 \text{ nm}$) does not rise up near the threshold voltage. Therefore, this device seems to suffer from additional current limitation mechanisms. The $I_{\text{ON}}/I_{\text{OFF}}$ ratio is over 10^6 . The subthreshold swing (SS), which is ΔV_G that is needed to increase I_D by one magnitude ($\text{SS} = |\partial V_G / \partial (\log_{10} |I_D|)|$), was evaluated and shown in Fig. 7.9. In this figure, SS of NW MOSFETs which was not characterized by TEM is also plotted. For these NWs, D_{eff} is estimated from the relationship between EBL design width and TEM results. SS of PMOS is scattered within the range of 59–66 mV/decade (average: 62.5 mV/decade), and that of NMOS was about 61–68 mV/decade (average: 63.6 mV/decade), except two devices (SS = 81–82 mV/decade) including TEM device D. The theoretical limit of SS at the temperature T [$\text{SS}_0(T)$] is

$$\text{SS}_0(T) = (\ln 10) \frac{k_B T}{q}, \quad (7.2)$$

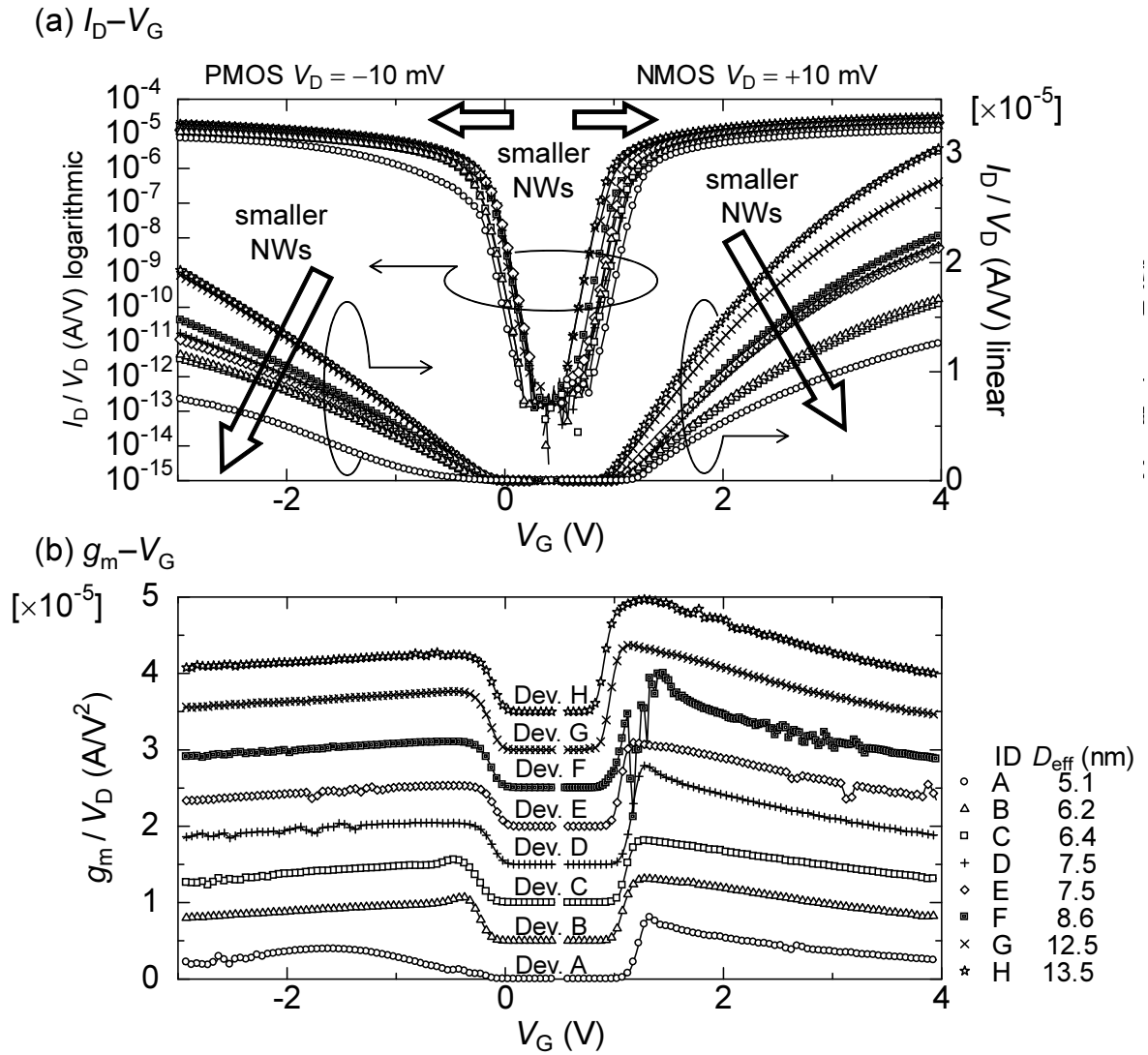


Figure 7.8: (a) $I_D/V_D - V_G$ and (b) $g_m/V_D - V_G$ characteristics of Si NW dual MOSFETs of device A–H ($D_{\text{eff}} = 5.1\text{--}13.5$ nm) at room temperature. In NMOS ($V_G > 0.5$ V) and PMOS ($V_G < 0.5$ V) operations, $V_D = +10$ mV and $V_D = -10$ mV, respectively. In (b), the plots are vertically shifted by 0.5×10^{-5} (A/V²) for each device.

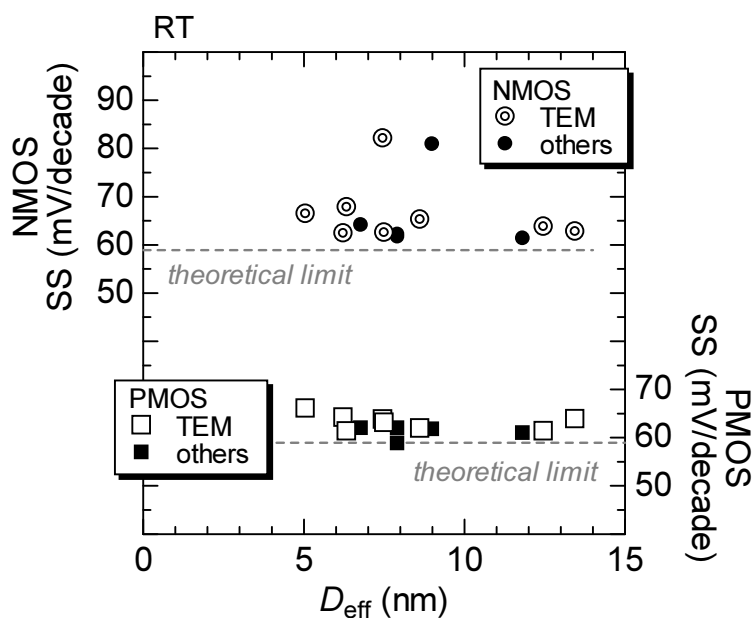


Figure 7.9: Subthreshold slope (SS) of Si NW dual MOSFETs for NMOS and PMOS at room temperature. The data of NWs whose cross-sectional shapes were characterized by TEM (TEM) and those without TEM (others) are plotted. The theoretical limit of SS at room temperature (59 mV/decade) is shown by gray dashed lines.

where k_B is the Boltzmann constant ($k_B T$: thermal energy), q the elementary charge, and $SS_0(297\text{--}298\text{ K}) = 58.9\text{--}59.1\text{ mV/decade}$. Therefore, the obtained SS values are close to the theoretical limit, which indicates good MOSFET operations.

7.3.3 Wire-Size Dependent Threshold Voltage

The threshold voltage (V_T) of NMOS and PMOS were extracted by linear fitting of $I_D/\sqrt{g_m}$ vs. V_G [36] and shown in Fig. 7.10 as a function of D_{eff} . The V_T of NWs both with and without TEM measurements are plotted in the same figure. Open symbols are for NWs with TEM, and black filled symbols are for NWs without TEM. In both NMOS and PMOS, V_T increases as D_{eff} decreases. The shift of V_T may be due to the band-edge energy shift by QCE [8, 37, 38]. As D_{eff} decreases, the energy of conduction band (CB) edge increases and the energy of valence band (VB) edge decreases. Therefore, V_T rolls up in both NMOS and PMOS, as illustrated in Fig. 7.11. To evaluate the magnitude of V_T shift, they are compared with the CB and VB edge energy shift (ΔE_C , ΔE_V) in Si NWs without strain and surface reconstruction calculated by an $sp^3d^5s^*$ tight-binding (TB) method [39]. The dangling bonds on the surface were passivated by sp^3 hybridization scheme, which gives a situation similar to hydrogen termination [40]. The calculation method of TB model is given in Appendix A. For CB, spin-orbit coupling was neglected since it does not change the CB structures very much. The calculation was performed for cross-sectional structures reproduced from TEM images. Obtained energy shifts are shown in Fig. 7.12. The absolute value of the energy shift is larger in CB than in VB, probably due to very heavy [110]-confinement (height direction, hardly changes with D_{eff}) effective mass of the VB maximum state in $\langle 110 \rangle$ Si NWs, as discussed in Chapter 2 (see Sec. 2.4.2). However, the relative shift of the CB and VB edge energies from $D_{\text{eff}} = 13.5\text{ nm}$ to $\sim 6.4\text{ nm}$ are comparable ($\sim 30\text{ meV}$). When the CB edge shifts by ΔE_C , the energy region inside the bandgap where the Fermi level E_F needs to pass through to turn on the MOSFET in the subthreshold region increases by ΔE_C . To obtain the change of E_F by ΔE_F , the gate voltage change ΔV_G of [38, 41]

$$\Delta V_G = \frac{SS}{SS_0} \Delta E_F \quad (7.3)$$

is necessary. Thus, the shift of threshold voltage ΔV_T is approximated as

$$\Delta V_T = \frac{SS}{SS_0} \Delta E_C. \quad (7.4)$$

The V_T shift in PMOS is estimated by the same procedure. $SS = 63\text{ mV/decade}$ was used for all calculations in both NMOS and PMOS. Since ΔV_T is only the variation component, the actual D_{eff} -dependent V_T is given by adding an appropriate constant V_{T0} without QCE. The V_T shifts obtained from this procedure are plotted in Fig. 7.10 as gray symbols (lines are guides for eyes). Since the V_T without QCE was not available in the experiments, the V_{T0} is set at -0.14 V and $+1.08\text{ V}$ for PMOS and NMOS, respectively, as the fit between

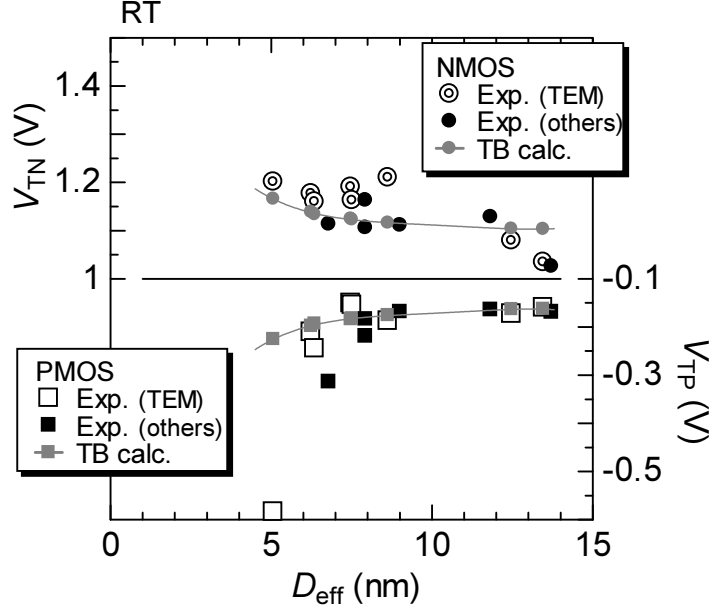


Figure 7.10: D_{eff} -dependent threshold voltage of Si NW dual MOSFETs for NMOS (V_{TN}) and PMOS (V_{TP}) at room temperature. The data of NWs whose cross sectional shapes were characterized by TEM and those without TEM (others) are plotted. In addition to the experimental results, calculated V_{T} shift is also shown. The calculation was performed by tight-binding method (TB) and the band-edge energy of Si NWs for which TEM was performed was calculated, reproducing the cross-sectional structures obtained by TEM (Fig. 7.12).

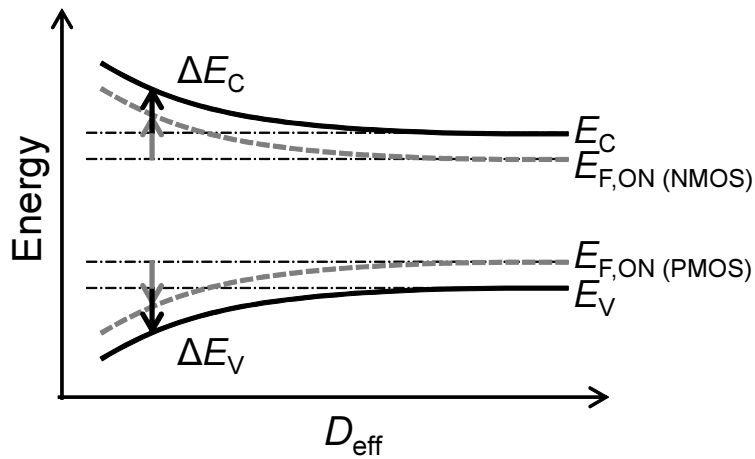


Figure 7.11: Schematic of energy shift in conduction band edge (E_{C}) and valence band edge (E_{V}). By QCE, E_{C} increases and E_{V} decreases as D_{eff} decreases. As the band edge energies shift, the Fermi levels where MOSFETs (NMOS and PMOS) turn on ($E_{\text{F,ON}}$) also change at the same pace. This results in the shift of V_{T} .

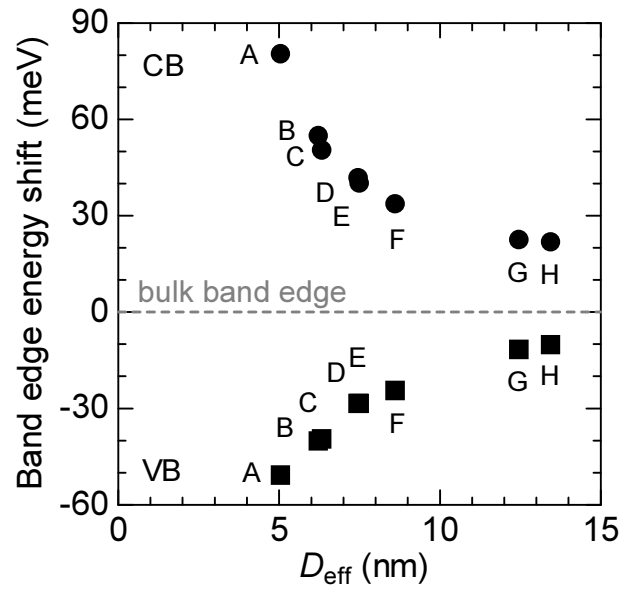


Figure 7.12: Calculated band-edge energy shift in conduction band (CB) and valence band (VB) in Si NWs of the device A–H in Fig. 7.7 obtained by tight-binding method. The calculation was performed, reproducing the cross-sectional structures obtained by TEM.

experiments and calculation looks good. In PMOS, the agreement between experiments and theoretical calculations is relatively better when it is compared to the case in NMOS, except the experimental very large PMOS V_T shift in the smallest NW (device A), which showed an unusual g_m property in Fig. 7.8(b). In NMOS, experimental V_T shift looks stronger than TB calculation. Because the actual NW structures obtained by TEM are reproduced, the TB result should match the results of TEM samples. From this viewpoint, the agreement is poor in NMOS whereas PMOS shows relatively good agreement. A previous report indicated that the size dependent bandgap of [100]-oriented Si NWs extracted from NW MOSFETs well agrees with the bandgap obtained by $sp^3d^5s^*$ TB [38]. Thus the TB results are more or less reliable. V_T can vary by fixed charges in SiO_2 and/or trapped charges at the SiO_2/Si interface [42]. The fixed charges shift V_T of NMOS and PMOS in the same amount and in the same polarity; meanwhile, the interface charges can modulate V_T of NMOS and PMOS separately because the interface state densities near CB and VB edges can be different from each other. Acceptor-like interface states are usually detected near CB edge, and negative interface charges trapped in acceptor-like states can induce positive V_T shift in NMOS. In this study, the conditions of forming gas annealing were not fully optimized for NMOS. Actually, the gate to channel capacitance of (110)SOI ultra thin body (UTB) MOSFETs fabricated on the same chip with the same gate stack was measured (Fig. 7.13) and it was found that NMOSFETs showed larger frequency dispersion of the capacitance around the threshold region than PMOSFETs, which indicates the existence of larger interface state density in NMOS than in PMOS. This is one of the possibilities of the explanation of the rapid increase in V_T in NMOS. To confirm this hypothesis, the direct measurement of interface state density in NW MOSFETs should be performed by a charge pumping method on NWs [43], for example.

7.3.4 Low Temperature Carrier Transport Properties

At RT, any notable oscillation of I_D and g_m was not observed. To observe the quantum effect, electrical measurement was performed at low temperatures down to ~ 8 K. Figures 7.14(a) and (b) show $I_D/V_D - V_G$ and $g_m/V_D - V_G$ characteristics of the device D in Fig. 7.7 ($D_{\text{eff}} = 7.5$ nm) for $-7 \leq V_G \leq 8$ V. In addition, subthreshold and near-threshold ($-1 \leq V_G \leq 2$) characteristics are magnified in Fig. 7.14(c). The subthreshold and near-threshold properties of device F ($D_{\text{eff}} = 8.6$ nm) and H ($D_{\text{eff}} = 13.5$ nm) are also shown in Figs. 7.15(a) and (b), respectively. The measurements were performed with $V_D = +10$ mV in NMOS and -10 mV in PMOS operation regions with the V_G step of 25 mV. The g_m in Fig. 7.14(b) was calculated as a least square fit of 5 V_G points (100 mV range) in the vicinity of a given V_G to reduce the noise.

In PMOS operations, I_D increased as the temperature decreased, which is typical characteristics of Si MOSFETs because phonon scattering decreases at lower temperatures, and it came to show current and transconductance oscillations. This trend was observed in all of

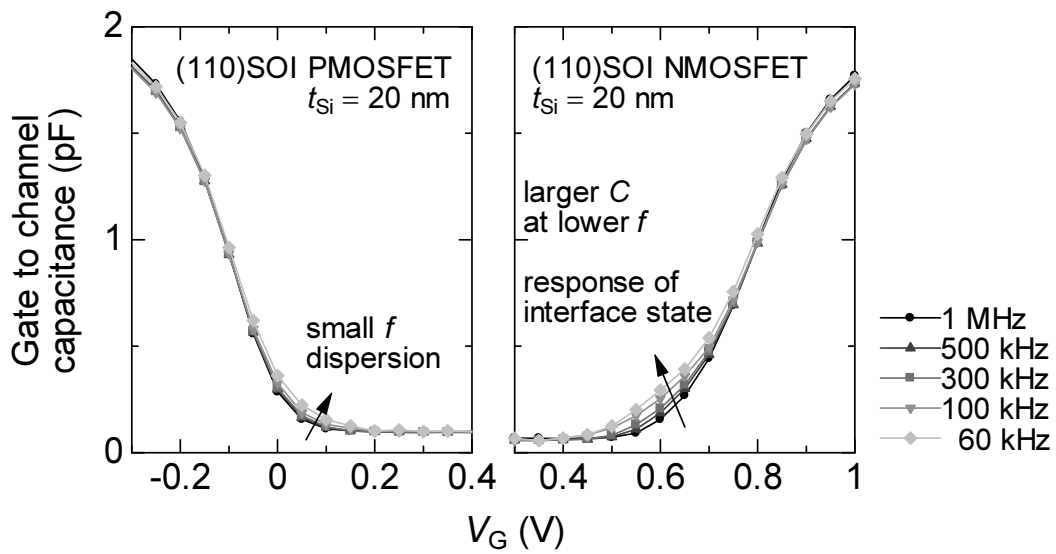


Figure 7.13: Subthreshold (in depletion and weak inversion regions) gate to channel capacitance of ultra thin body (Si thickness: 20 nm) (110)SOI PMOSFET (left) and NMOSFET (right) fabricated on the same chip as NW dual MOSFETs with the same process. The capacitance was measured at RT with different ac frequencies of 1 M, 500 k, 300 k, 100 k, and 60 kHz. The NMOSFET showed the capacitance increase in the subthreshold region with the decrease of the frequency, whereas the PMOSFET showed much weaker frequency dispersion of the gate capacitance. These results indicate that NMOS has large interface state density than PMOS.

Device D ($D_{\text{eff}} = 7.5$ nm), $V_D = \pm 10$ mV

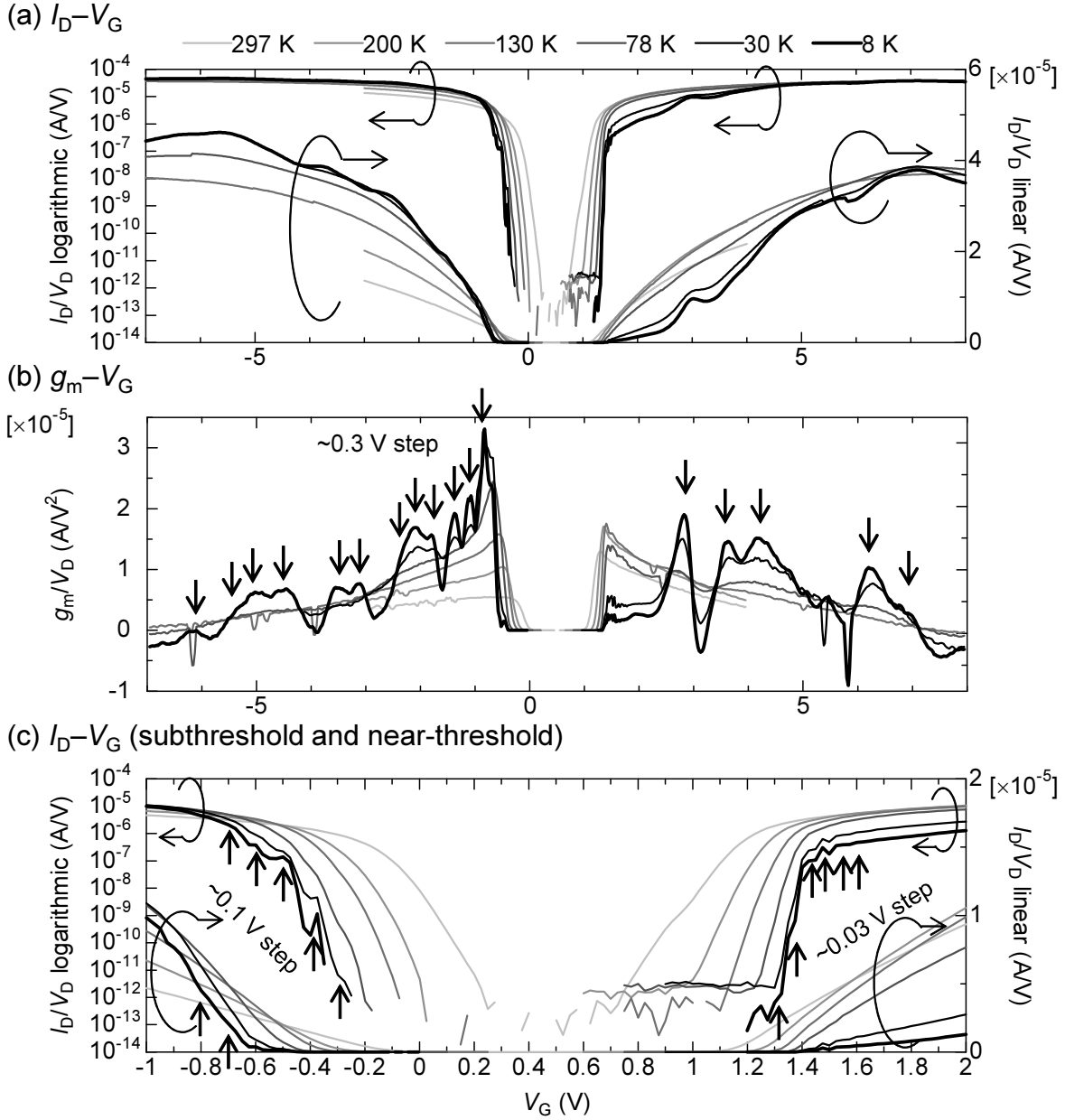


Figure 7.14: (a) $I_D/V_D - V_G$ and (b) $g_m/V_D - V_G$ characteristics of Si NW dual MOSFETs of device D ($D_{\text{eff}} = 7.5$ nm) at room temperature and low temperatures down to 8 K. In NMOS ($V_G > 0.5$ V) and PMOS ($V_G < 0.5$ V) operations, $V_D = +10$ mV and $V_D = -10$ mV, respectively. In both NMOS and PMOS, long-period oscillations in g_m were observed above threshold, and the observed peaks are indicated by arrows in (b). The $I_D/V_D - V_G$ characteristics in subthreshold and near-threshold regions are magnified in (c). Subthreshold current oscillations were observed in both NMOS and PMOS, and the observed peaks are indicated by arrows in (c). The oscillation periods in subthreshold are shorter than those above threshold.

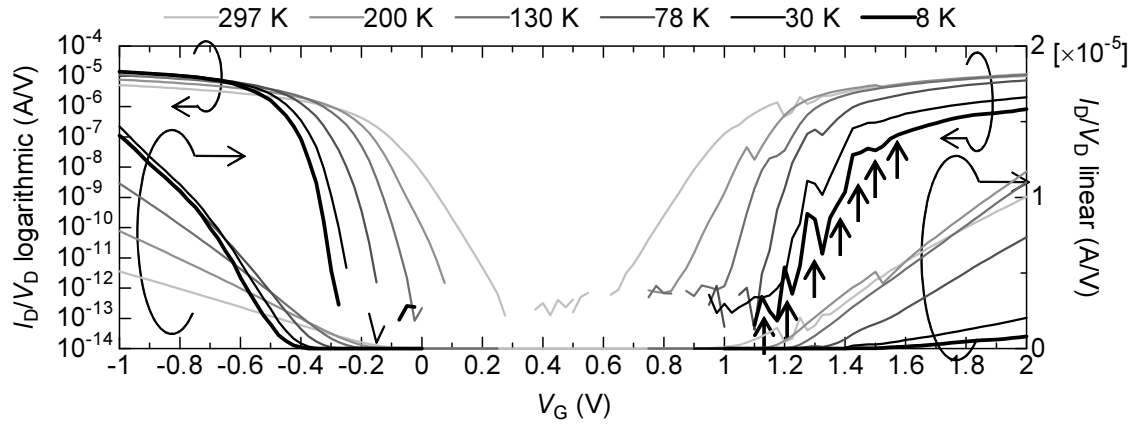
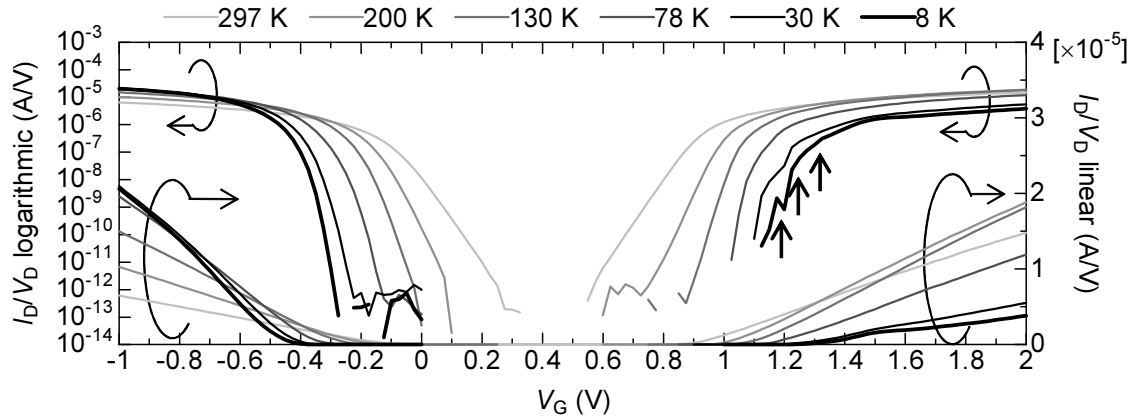
(a) Device F ($D_{\text{eff}} = 8.6$ nm), $V_D = \pm 10$ mV(b) Device H ($D_{\text{eff}} = 13.5$ nm), $V_D = \pm 10$ mV

Figure 7.15: Subthreshold and near-threshold I_D/V_D - V_G characteristics of Si NW dual MOSFETs of (a) device F ($D_{\text{eff}} = 8.6$ nm) and (b) device H ($D_{\text{eff}} = 13.5$ nm) at room temperature and low temperatures down to 8 K. In NMOS operation ($V_G > 0.5$ V) and PMOS operation ($V_G < 0.5$ V), $V_D = +10$ mV and $V_D = -10$ mV, respectively. Oscillations in subthreshold I_D were observed at 8 K in NMOS (peaks are indicated by arrows) but not observed in PMOS.

the measured NWs except for device A, which has the smallest diameter of $D_{\text{eff}} = 5.1$ nm. In PMOS of several NWs with small diameters about 6–8 nm, small oscillations of I_D and g_m were observed at 8 K in the subthreshold and near-threshold regions with an oscillation period of 0.05–0.1 V. As an example, the device D showed I_D oscillation with a period of about 0.1 V in $V_G > -0.8$ V. The observable peaks are indicated in Fig. 7.14(c). This oscillation becomes weaker at lower V_G (higher gate overdrive), and there exist NWs which do not exhibit oscillation in the subthreshold region [Figs. 7.15(a) and (b)]. Above threshold, g_m oscillation with a longer period was observed in PMOS at 8 K. For example, the device D showed the oscillation with a period of about 0.3 V [Fig. 7.14(b)]. Because the oscillation periods in subthreshold and above threshold are different, they probably have different origins.

In NMOS operations [Fig. 7.14(a)] of almost all the NWs, I_D increased from RT to 130 K, but it turned to decrease at 78 K and below. At temperatures below 30 K, the onset of I_D around V_T significantly restricted, and low I_D was observed typically in the region of $V_G < 5$ –7 V. However, at higher gate overdrives, I_D increased and finally took over I_D at higher temperatures from 130 K to RT. Therefore, I_D is restricted only at low gate overdrive. It is also noticeable that even large NWs showed the very low current region, although good PMOS operations were observed in those NWs. Similar to PMOS of several NWs, NMOS showed small I_D oscillation in subthreshold and near-threshold regions. For example, the oscillation period in the device D was about 0.03 V. However, unlike PMOS, the oscillation was observed even in the largest NW (device H) for NMOS operation although the amplitude is very weak, whereas any notable oscillation was not found in PMOS of device H [Fig. 7.15(b)]. The device F also showed the subthreshold I_D oscillation in NMOS, whereas it did not appear in PMOS. Other than the short-period oscillation at low V_G region, g_m of NMOS showed longer-period oscillations. For example, Device D showed the oscillation with spacing of one or a few volts. The peaks are indicated in Fig. 7.14(b). This long-period oscillation seems a common nature in NMOS.

7.3.5 Discussion

Origin of Oscillation in Drain Current and Transconductance

In the NMOS gate characteristics, I_D near the threshold voltage decreased at low temperatures. In general, carrier mobility increases at lower temperatures as mentioned above. Thus the observed I_D decrease in NMOS is not common operation. This restriction of I_D is not explainable by the series resistance such as contact and extension resistances because I_D increased at higher gate overdrive at the same V_D . There existed NWs which showed short-period (≤ 0.1 V) I_D oscillations in the subthreshold and near-threshold regions in both NMOS and PMOS, but there also existed NWs which showed notable oscillation only in NMOS. Because multiple subbands are not occupied in the subthreshold region, these oscillations cannot be attributed to the subband effect. The author speculates that this

oscillation may be due to the Coulomb blockade effect. Then, the origin of the Coulomb blockade should be analyzed.

Since Coulomb blockade is current transport through a quantum dot separated by tunnel junctions, quantum dots should be formed in NWs in series. It is reported that quantum dots are formed by the fluctuation of band-edge energies by the width fluctuation [7] and by electrostatic potential by ionized donors/acceptors [44] and trapped interface charges and/or fixed oxide charges [8]. As indicated in Fig. 7.12, the variation of band-edge energies of CB and VB by the change in D_{eff} are comparable when $D_{\text{eff}} > 6$ nm. Therefore, if the width fluctuation is the cause of Coulomb oscillation, similar current oscillations must be observed in both NMOS and PMOS. In several devices, this may be the case. However, the existence of several devices which showed oscillations only in NMOS and the severe current restriction in NMOS are not explainable only by the width fluctuation. Donors and acceptors do not form quantum dots in this study because Si NWs are nearly-intrinsic. Therefore, the quantum dots are probably formed by trapped charges at SiO₂/Si interface or fixed oxide charges. In the analysis of V_T shift, it is inferred that NMOS interface has higher interface trap density than PMOS. In addition, NMOS shows stronger effect of Coulomb blockade than PMOS. Hence, the author speculates that the origin of Coulomb blockade in the MOSFETs should be the fluctuation of electrostatic potential by trapped charges at SiO₂/Si interface. The I_D restriction in the wide V_G range may also be affected by Coulomb scattering from interface charges as well as Coulomb blockade. At a higher gate overdrive, large numbers of carriers can screen the potential by interface charges and thus the Coulomb blockade and Coulomb scattering can be alleviated. This may be the reason why the short-period oscillations and current restriction disappeared at high V_G in NMOS.

Although the oscillations in subthreshold and near-threshold regions are attributed to Coulomb blockade, longer-period oscillations above threshold in both NMOS and PMOS probably come from a different mechanism. These different oscillations can be related to one-dimensional subband structures. For carriers existing in an subband, the scattering rate of the carriers increases when the number of available final states increases. Therefore, when the E_F crosses upper subbands, the scattering rate of the carriers significantly increases because of the sharp rise of DOS. From this mechanism, carrier mobility can oscillate with the increase of V_G [1, 2]. To analyze this oscillation, subband structures and DOS of NWs are calculated by TB method, and the oscillation related to the carrier scattering is roughly evaluated using a simple model.

Modeling of Oscillation in Transconductance and Comparison with Experimental Results

In a relaxation time approximation, the mobility of the carriers in the subband i , μ_i , at the temperature T and the Fermi level E_F is given by [45]

$$\mu_i(T, E_F) = \frac{q}{k_B T} \frac{\int \tau(E) v^2 f_0(E, E_F, T) [1 - f_0(E, E_F, T)] dk}{\int f_0(E, E_F, T) dk}, \quad (7.5)$$

where $\tau(E)$ is the relaxation time of the carrier, v the carrier velocity, k the wave number, and f_0 the carrier distribution function in equilibrium, which is the Fermi-Dirac distribution

$$f_{FD}(E, E_F, T) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} = f_0(E, E_F, T) \quad (7.6)$$

for electrons and

$$f_0(E, E_F, T) = 1 - f_{FD}(E, E_F, T) \quad (7.7)$$

for holes. In this study, an exact carrier scattering rate $1/\tau(E)$ is not calculated, but it is assumed to be proportional to DOS $N(E)$:

$$\frac{1}{\tau(E)} \propto N(E). \quad (7.8)$$

The scattering rate by acoustic phonon and surface roughness, which are expected to be dominant carrier scattering mechanisms in Si NWs, is known to be proportional to the accessible number of final states. Thus, this approximation of the scattering rate may be quantitatively incorrect but qualitatively acceptable to describe the nature of the oscillation. The integral over k in Eq. (7.6) is transformed into the integral over E by using DOS of the subband i , $N_i(E)$, as

$$\mu_i(T, E_F) = \frac{q}{k_B T} \frac{\int \tau(E) v^2 f_0(1 - f_0) N_i(E) dE}{\int f_0 N_i(E) dE}. \quad (7.9)$$

Since the one dimensional DOS (per unit volume) is given by [46]

$$N_i(E) = \frac{g_{\text{spin}}}{\pi S} \left| \frac{\partial E_i}{\partial k} \right| = \frac{g_{\text{spin}}}{\pi \hbar S} \frac{1}{|v|}, \quad (7.10)$$

where S is the cross-sectional area of the NW, Eq. (7.9) can be rewritten as

$$\mu_i(T, E_F) = \frac{q}{k_B T} \frac{\int \tau(E) |v| f_0(1 - f_0) dE}{\int f_0(E, E_F, T) |v|^{-1} dE}. \quad (7.11)$$

By evaluating these two integrals, mobility is obtained. Here, several approximations are introduced to evaluate the integrals. The author treats the NW as a degenerate semiconductor since the focused V_G region is above threshold. At low temperatures, f_0 is regarded as a step function which becomes unity (zero) below E_F and zero (unity) over E_F for electrons (holes). In addition, the integral $\int |v|^{-1} dE$ is approximately evaluated as $(\text{const.}) \times |v|$. This is rigorous when the subband is parabolic: $\int |v|^{-1} dE = m^* |v|$. Therefore, the integral in the denominator in Eq. (7.11) is evaluated to be

$$\int f_0 |v|^{-1} dE \approx |v(E_F)|, \quad (7.12)$$

for degenerate NWs at low temperature. For the numerator of Eq. (7.9), the function $f_0(1 - f_0)/k_B T$ has large value at $E = E_F$ with the full-width at half maximum (FWHM) of about $3.5k_B T$, and $\int [f_0(1 - f_0)/k_B T] dE = 1$. $\tau(E)$ (approximated as the inverse of DOS) shows strong and rapid change when E_F crosses the subsequent subbands, whereas $|v|$ changes slowly. Therefore, the change of $|v|$ with E can be neglected within the small energy range around E_F where $f_0(1 - f_0)/k_B T$ has a large value and $|v|$ is evaluated to be $|v(E_F)|$. This gives

$$q \int \tau(E) |v| \frac{f_0(1 - f_0)}{k_B T} dE \approx q |v(E_F)| \int \tau(E) \frac{f_0(1 - f_0)}{k_B T} dE. \quad (7.13)$$

This approximation is valid only for degenerate semiconductors at low temperatures. Based on these approximations, the mobility can be expressed by

$$\mu_i(T, E_F) \approx \int \tau(E) \frac{f_0(1 - f_0)}{k_B T} dE \approx \int \frac{1}{N(E)} \frac{f_0(1 - f_0)}{k_B T} dE \equiv \langle N^{-1} \rangle(T, E_F). \quad (7.14)$$

Here, $\langle N^{-1} \rangle(T, E_F)$ is an average of “inverse” DOS. In this study, a single $\tau(E)$ is used for the all subbands. Strictly, the mobility is not the same in different subbands since the rigorous scattering rate should be subband dependent, and thus this calculation does not give a numerically correct value of the mobility. However, the author expects that the approximate amplitude, oscillation spacing, and thermal smoothing effect can be predicted in this model, and the comparison with the experimental results would be meaningful. One should note that this calculation does not give a correct result in subthreshold region because a degenerate semiconductor is assumed.

In the calculation of V_G and carrier density n , the Poisson equation was not solved, for simplicity, and approximated relationships among n , E_F , and V_G as

$$n(T, E_F) = \int f_0(E, E_F, T) N(E) dE, \quad (7.15)$$

$$V_{\text{ox}}(T, E_F) = \pm q n S / C_{\text{ox}} \quad (+ : \text{electron}, - : \text{hole}), \quad (7.16)$$

$$V_G(T, E_F) = V_{\text{ox}}(T, E_F) + E_F / q + V_0 \quad (V_0 : \text{constant for control of } V_T). \quad (7.17)$$

were used. Here, C_{ox} is the gate oxide capacitance per unit length. Then, to compare the experimentally obtained g_m and calculation results, the derivative

$$\frac{d}{dV_G}(n\mu) \approx \frac{d}{dV_G}(n \langle N^{-1} \rangle) \approx g_m \quad (7.18)$$

was calculated.

In this study, band structures and DOS were calculated by the $sp^3d^5s^*$ TB model [39] for the actual cross-sectional structures of NWs observed by TEM. The TB calculation was performed assuming that Si NWs have neither strain nor surface reconstruction, and surface dangling bonds were passivated by sp^3 hybridization scheme [40], which brings a situation similar to hydrogen termination. In the calculation, the effect of the gate voltage (gate electric field) and the drain voltage (source to drain electric field) were neglected, and a uniform potential profile was assumed inside the NWs. Spin-orbit coupling was taken into account for VB calculation. C_{ox} is approximated by the cylindrical co-axial capacitance with the D_{eff} of the NW core ($D_{\text{eff,NW}}$) and D_{eff} of SiO₂ shell ($D_{\text{eff,ox}}$) as

$$C_{\text{ox}} \approx \frac{2\pi\epsilon_{\text{ox}}\epsilon_0}{\ln(D_{\text{eff,ox}}/D_{\text{eff,NW}})}, \quad (7.19)$$

where ϵ_{ox} is the relative permittivity of SiO₂ (3.9) and ϵ_0 the vacuum permittivity. This approximation is acceptable in small- D_{eff} NWs whose SiO₂ thickness is almost conformal.

The calculated CB and VB structures with DOS of the device D ($D_{\text{eff}} = 7.5$ nm) are shown in Fig. 7.16. In this figure, the average of DOS, which is given by

$$\langle N \rangle(T, E_F) = \int N(E) \frac{f_0(1 - f_0)}{k_B T} dE \quad (7.20)$$

and the average of inverse DOS $\langle N^{-1} \rangle$ are also plotted to see the effect of the thermal fluctuation on the density of states ($T = 297, 78$, and 10 K). As a general result in $\langle 110 \rangle$ -oriented NWs, the energy spacing of subbands is much larger in CB than those in VB. This is due to much heavier confinement effective mass in VB. Note that the number of subbands in CB in the energy range shown in the plot is also large (16 without spin degeneracy) although it seems apparently small. This is due to the large degeneracy of subbands in CB: two for subbands at Γ (disregarding a slight energy split) and four ($2 \times \pm k$) for off- Γ subbands. As a result, both the amplitude and the spacing of oscillation in $\langle N \rangle$ are large. For example, the energy separation between the first and second peaks in DOS is about 18 meV, and the energy region written as “large split” corresponds to 44 meV split. These values of energy split (18 and 44 meV) correspond to FWHM of $f_0(1 - f_0)$ at 59 K and 145 K, respectively. Therefore, the first and second peaks cannot be discriminated at 78 K, but a weak oscillation in $\langle N \rangle$ and $\langle N^{-1} \rangle$ is observed even at 78 K for the “large split” region. On the other hand, small subband energy split (5–10 meV in this NW) and strongly warped nature of the band structure results in a dense DOS in VB. Therefore, much lower temperature is necessary to observe oscillation in $\langle N \rangle$, and the spacing of the peaks in g_m oscillation in VB becomes shorter than that in CB. For example, 10 meV corresponds to the FWHM of the function $f_0(1 - f_0)$ at 33 K.

The calculated $d(n\langle N^{-1} \rangle)/dV_G \propto d(n\mu)/dV_G$ and experimentally observed g_m oscillation are compared in Fig. 7.17(a) for device D ($D_{\text{eff}} = 7.5$ nm), which showed relatively weak Coulomb blockade regardless of the small D_{eff} . In CB, the drain current near V_T

Device D ($D_{\text{eff}} = 7.5 \text{ nm}$), $C_{\text{ox}} = 148 \text{ aF}/\mu\text{m}$

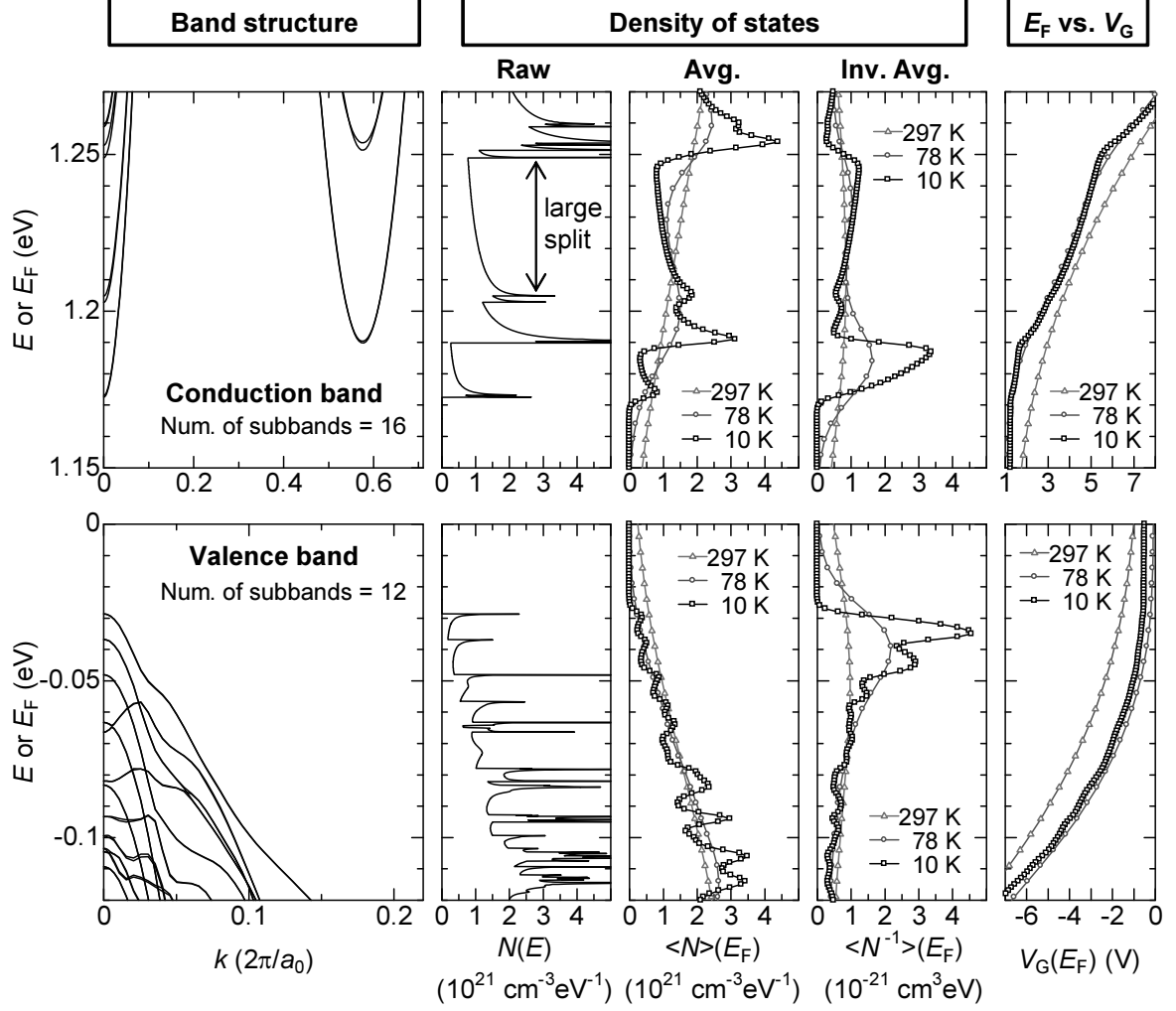


Figure 7.16: Calculated conduction band (CB) and valence band (VB) structures (left) of the Si NW in Device D ($D_{\text{eff}} = 7.5 \text{ nm}$), corresponding density of states (DOS) $N(E)$ of CB and VB (center), and E_F – V_G relationship estimated from Eqs. (7.15)–(7.17) assuming C_{ox} to be $148 \text{ aF}/\mu\text{m}$, obtained from cylindrical co-axial capacitance approximation in Eq. (7.19). For DOS, averaged DOS $\langle N \rangle$ and averaged inverse DOS $\langle N^{-1} \rangle$, defined in Eq. (7.20) and Eq. (7.14), respectively, are also shown. The calculation of averaged (inverse) DOS and V_G were performed at different temperatures of 297, 78, and 10 K.

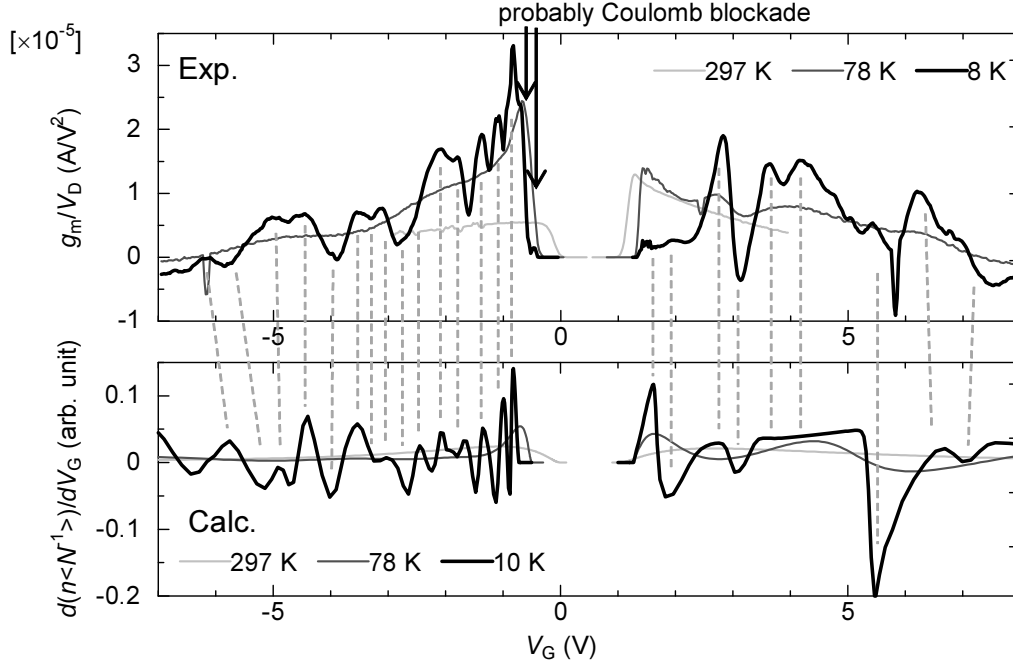
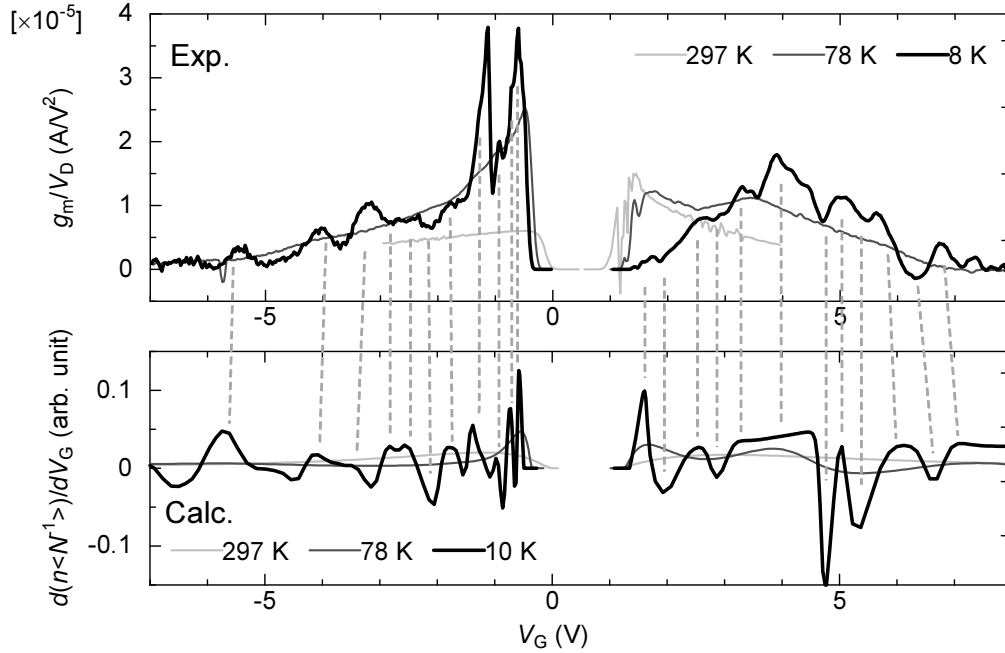
(a) Device D ($D_{\text{eff}} = 7.5$ nm), $C_{\text{ox}} = 148$ aF/ μm (b) Device F ($D_{\text{eff}} = 8.6$ nm), $C_{\text{ox}} = 160$ aF/ μm 

Figure 7.17: Comparison of experimental oscillation in g_m - V_G characteristics in Si NW dual MOSFET with calculated $d(n\langle N^{-1} \rangle)/dV_G$, which is modeled as g_m oscillation from the viewpoint of the modulation of carrier scattering rate by one-dimensional DOS, for the device D ($D_{\text{eff}} = 7.5$ nm) in (a) and F ($D_{\text{eff}} = 8.6$ nm) in (b). The temperatures in measurement are 297, 78, and 8 K, and those in calculation are 297, 78, and 10 K. V_G in calculation is artificially shifted to match the position of the first peak. The estimated correspondence relations of peaks and valleys between experiments and calculation are indicated by gray dashed lines.

slowly increases as stated above, and the first peak in g_m expected in the calculation is not clearly observed. However, long-period oscillation is well reproduced both at 78 K and 10 K, although the amplitude of the oscillation does not agree and some irreproducible peaks and valleys are observed, for example, in the V_G range of $3 \text{ V} \leq V_G \leq 5 \text{ V}$. This V_G range corresponds to $1.21 \text{ eV} \leq E_F \leq 1.24 \text{ eV}$ in Fig. 7.16 (corresponds to the region written as “large separation” in the CB DOS plot) where any peak do not exist in DOS. If the experimentally obtained peaks and valleys in this region originate from the subbands, subband structures at higher energies is partly incorrect. The assumption of the uniform electrostatic potential in the cross-section of the NW may not be a good approximation at high gate overdrive [47], and the change of the band structure by the nonuniform potential may cause the disagreement. The NW NMOSFETs fabricated in this study, however, more or less suffer from nonideal factors (current restriction behavior), and thus further study is necessary especially for CB.

In VB, the peak in experimental g_m in subthreshold and the first peak above threshold may come from Coulomb blockade as stated above. Therefore, the calculated results are compared with experimental results neglecting these two peaks. In this case, g_m oscillation with a period of about 0.3 V is well reproduced up to $V_G > -4 \text{ V}$. In particular, first three sharp peaks are reproduced very well. These sharp peaks come from top three subbands with light effective mass in VB structure as shown in Fig. 7.16. The existence and the nature of these light subbands in $\langle 110 \rangle$ NWs are intensively discussed in Chapter 2. The degeneracy of these subbands is two including spin degeneracy.¹ Since the inverse of DOS of the subband with the effective m^* is proportional to $\sqrt{E/m^*}/g$ (g : degeneracy) [48], the inverse of DOS of light- m^* bands with small degeneracy shows a rapid increase and they appear as sharp peaks in g_m . In the region of $V_G < -4 \text{ V}$, the positions of the peaks and valleys do not match strictly between the experiment and the calculation, but the general feature and spacing of the oscillation are captured. Since the device D slightly shows Coulomb blockade near the threshold, one may doubt the assignment of peaks and valleys. A similar comparison was performed for the device F ($D_{\text{eff}} = 8.6 \text{ nm}$), which does not exhibit Coulomb blockade in PMOS, and the result is shown in Fig. 7.17(b). Also in this case, the calculation predicts sharp peaks at low gate overdrive. In the experiments, the second peak seems to exist at the shoulder of the first peak, and the period of the peaks agrees with the calculation very much. However, also in this NW, the correspondence of the peak positions becomes slightly poor in $V_G < -4 \text{ V}$ for PMOS. This is probably due to the change of the band structure by the nonuniform electrostatic potential in the cross-section of the NW which is caused by gate electric field [49], as already discussed in the NMOS case. To take this effect into account, the band structure calculation by TB and potential calculation by the Poisson equation should be performed self-consistently.

In this study, the hole transport properties in sub-10-nm NWs seem to be well evalu-

¹Strictly, two spin states are split because of the spin-orbit coupling. However, this split is extremely small and not obvious in DOS.

ated. This may be thanks to well-developed smooth NW structures realized by hydrogen annealing, since strong Coulomb blockade phenomenon has been reported even in NWs with a size of ~ 10 nm [50] and ~ 7 nm [51]. The good agreement between the experiment and the calculation indicates that the detailed subband structures can be predicted by the TB model. The electron transport in NWs probably suffered from Coulomb blockade and strong Coulomb scattering in part, and the observation of oscillation peaks and valleys in the region slightly above the threshold was difficult. To observe proper electron transport properties, the interface state density should be minimized. Moreover, this study evaluated NWs with limited sizes (6–13.5 nm) and the orientation ($\langle 110 \rangle$). It is also important to study the quantum effect in NWs with much smaller sizes and various orientations. By changing sizes and orientations, band structure is significantly modulated and thus the validity of the model of subband-induced mobility modulation can be investigated more deeply. More rigorous calculation of the mobility would improve the quantitative agreement of oscillation amplitude.

Finally, the author should point out the effect of the oscillation of the gate capacitance. The gate capacitance rapidly increases at the bottom of subbands, which gives opposite effect on g_m oscillation compared to the mobility oscillation; g_m decreases at the bottom of subbands by the increase of carrier scattering. Also in the simple model used in this study, the oscillation of gate capacitance was observed as shown in Fig. 7.18, and this oscillation was taken into consideration. However, this capacitance oscillation simply originates from the quantum capacitance. In practice, the quantum-mechanical carrier distribution causes the oscillation of the depletion capacitance [2, 4], which can also contribute to the gate capacitance oscillation, and the present calculation may underestimate the oscillation of the gate capacitance. To take these effects into account, self-consistent calculation of the band structures, charge distribution, and the potential is necessary. However, the calculated peaks and valleys well agreed with the experimental ones for the first several peaks, where the capacitance oscillation is conspicuous, and the calculated oscillation is dominantly caused by the strong oscillation of $\langle N^{-1} \rangle$. Therefore, the author speculates that the oscillation of g_m observed in experiments is dominantly caused by the modulation of the scattering rate.

7.4 Hole Mobility in Si Nanowires with Different Orientations

In this section, hole mobility in Si NWs in various orientations of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ is experimentally evaluated from the fabricated multi-NW MOSFETs. The cross-sectional size of NWs is about 10 nm. After the structures of the fabricated NWs are described, the method of mobility extraction is explained. Then, the evaluated mobility is shown and the results are discussed.

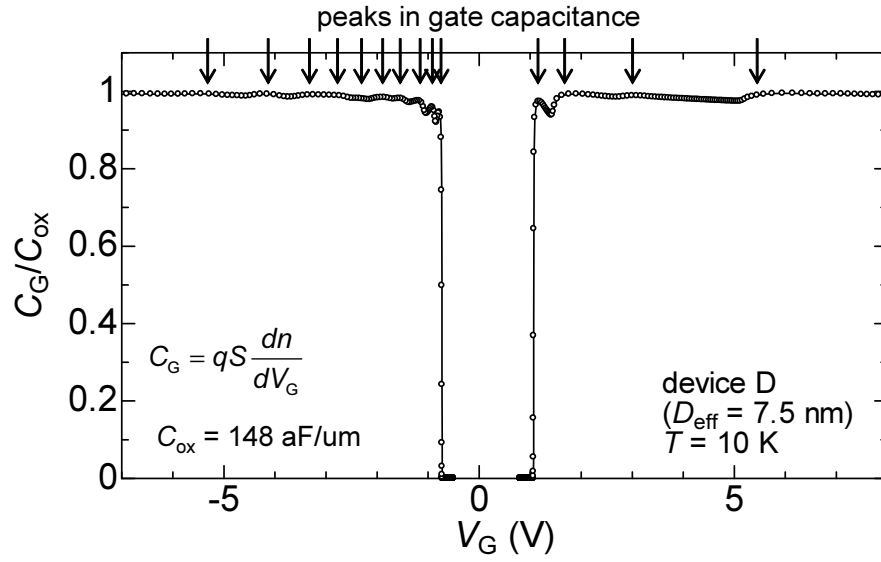


Figure 7.18: Calculated gate capacitance in device D. Oscillations of capacitance are observed due to the oscillating one-dimensional density of states in Si NWs. This calculation does not include the depletion capacitance and quantum-mechanical charge distributions in the NW, and thus the capacitance may be overestimated and the amplitude of the capacitance oscillations may be underestimated.

7.4.1 Structure of Nanowire Channels

The initial NW structures are horizontally long on (110)SOI. The estimated height and width of the NWs before hydrogen annealing are about 12 nm and 15–40 nm, respectively. NWs with small initial D_{eff} broke by hydrogen annealing owing to the instability at both ends of NWs (see Chapter 6, Sec. 6.3.2) especially for $\langle 100 \rangle$ and $\langle 111 \rangle$ NWs. The final D_{eff} of fabricated Si NWs is summarized in Table 7.3. D_{eff} was characterized by cross-sectional HRTEM for several devices, and D_{eff} of the rest devices was estimated from the relationship among TEM observation results, the design width in EBL, and scanning electron microscopy measurement results. The minimum D_{eff} of fabricated $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ NWs was about 7, 10, 12, and 14 nm, respectively. The maximum D_{eff} was about 15 nm for $\langle 110 \rangle$ NWs and about 14 nm for NWs with the other orientations.

Due to the hydrogen annealing and the gate oxidation, the cross-sectional shape of NWs got rounded and became nearly circular or oval structures. The speed of transformation in the cross-sectional shape by hydrogen annealing is orientation dependent as investigated in Chapter 6 (see Sec. 6.3.4); $\langle 110 \rangle$ NWs are slowest, $\langle 112 \rangle$ and $\langle 111 \rangle$ NWs are modest, and $\langle 100 \rangle$ NWs are fastest and easily become a symmetric shape. As a result, the cross-sectional shapes are orientation dependent. Cross-sectional HRTEM images of NW channels are shown in Fig. 7.19. For $\langle 110 \rangle$ NWs, the cross-sectional shape is almost circular and t_{ox} is almost conformal when D_{eff} is small. However, it becomes horizontally wide as D_{eff} increases (wider width before hydrogen annealing), and $\{111\}$ facets were observed at corners. In large NWs, t_{ox} is thicker (10.5 nm) on the top and bottom $\{110\}$ faces and thinner (7 nm) on the side $\{100\}$ faces, which is caused by the same reason as discussed in Sec. 7.3.1 for NW structure of dual MOSFETs. The cross-sectional structure of $\langle 111 \rangle$ NWs is almost circular, but it seems to be slightly faceted with $\{112\}$ facets. $\langle 112 \rangle$ NWs have nearly oval shapes, but $\{111\}$, $\{531\}$, $\{311\}$, and $\{110\}$ facets can be seen. These facets on $\langle 111 \rangle$ and $\langle 112 \rangle$ NWs are formed by hydrogen annealing. The cross-sectional shape of $\langle 100 \rangle$ NWs is circular. However, the anisotropy in t_{ox} was observed. t_{ox} is thicker on the $\{110\}$ faces and thinner on the $\{100\}$ faces.

The MOSFET operation of multi-NW MOSFETs is very good. Fig. 7.20 shows SS of multi-NW MOSFETs at 297 K. SS values are 60–62 mV/decade regardless of NW sizes and orientations. They are very close to the theoretical limit (59 mV/decade).

7.4.2 Mobility Extraction from Si Nanowire MOSFETs by Advanced Split C – V Method

The effective mobility μ_{eff} of planar MOSFETs is usually evaluated with a split C – V method [52] by measuring the channel resistance $R_{\text{ch}}(V_G) = V_D/I_D(V_G)$ and the gate-to-channel

Table 7.3: Effective diameters D_{eff} of NWs in fabricated multi-NW MOSFETs.

NW axis	D_{eff} (nm)
$\langle 110 \rangle$	7, 8, 9, 11, 13, 15
$\langle 112 \rangle$	10, 11, 14
$\langle 111 \rangle$	12, 14
$\langle 100 \rangle$	14

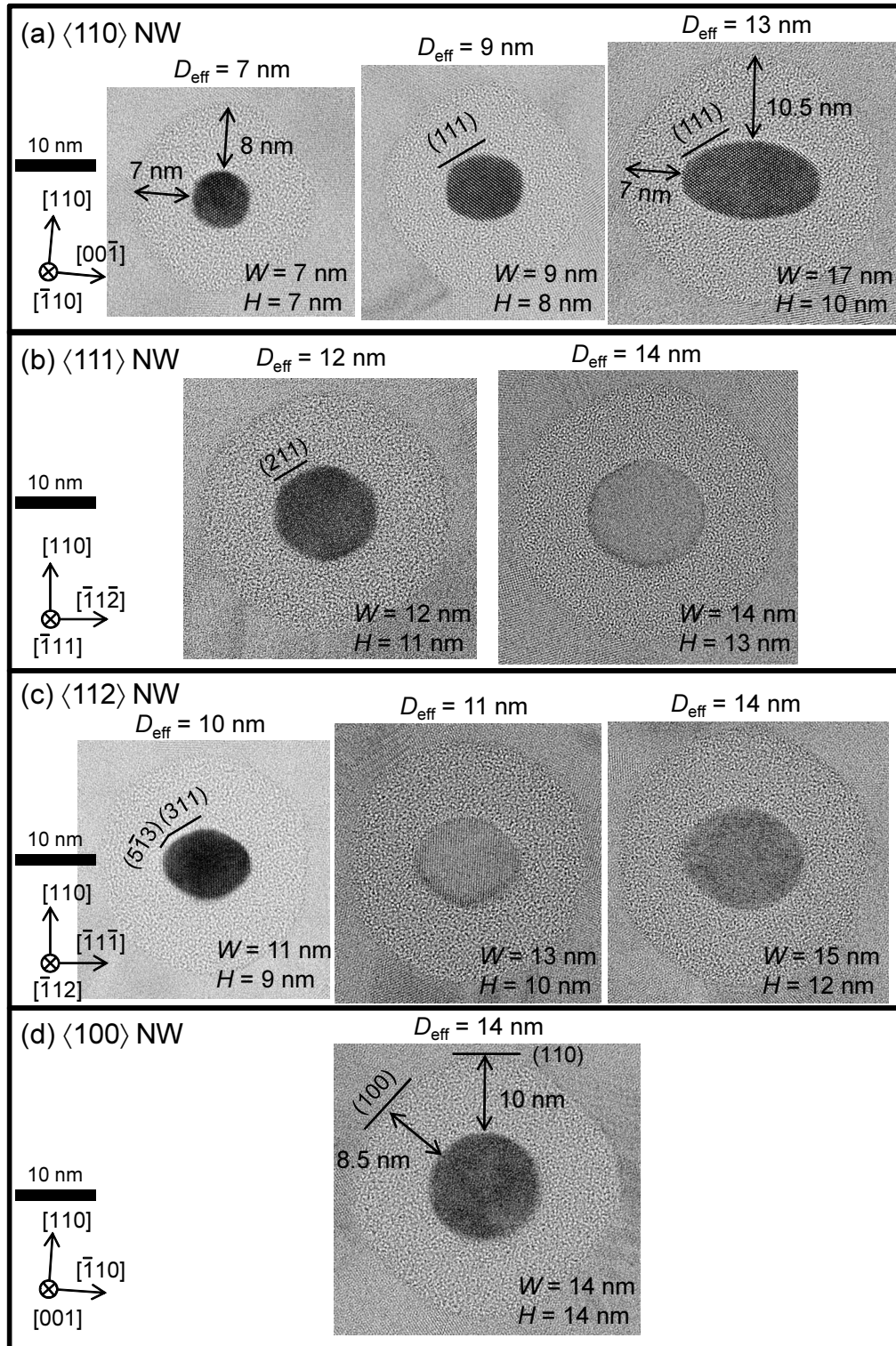


Figure 7.19: Cross-sectional HRTEM images of Si NW channels in multi-NW MOSFETs for hole mobility measurement. NWs with different orientations of (a) $\langle 110 \rangle$, (b) $\langle 111 \rangle$, (c) $\langle 112 \rangle$, and (d) $\langle 100 \rangle$ are shown. W and H written in each image are approximate width and height of the Si NW core.

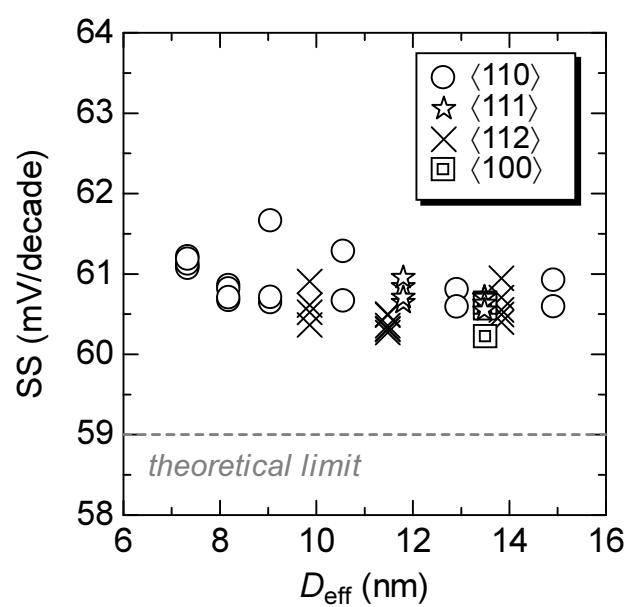


Figure 7.20: Subthreshold slope of multi-NW PMOSFETs as a function of D_{eff} measured at 297 K. The theoretical limit of SS is shown by a dashed gray line.

capacitance $C_G(V_G)$ as

$$\mu_{\text{eff}}(V_G) = \frac{L_{\text{ch}}^2}{Q_{\text{inv}}(V_G)R_{\text{ch}}}, \quad (7.21)$$

$$Q_{\text{inv}}(V_G) = \int^{V_G} C_G(V)dV, \quad (7.22)$$

where Q_{inv} is the total inversion carriers in the channel region. Si NW MOSFETs with series UTB MOSFETs in source and drain, however, suffer from large parasitic resistance and capacitance, and thus the direct application of the split C - V method significantly underestimates the mobility [53]. Figures 7.21(a) and (b) show top-view and cross-sectional-view images of a multi-NW MOSFET (MOSFET1) with the NW length of L_{NW1} and poly-Si gate length of L_{m1} . The poly-Si gate is omitted in Fig. 7.21(a) but is drawn in Fig. 7.21(b). The device has contact resistance $R_{\text{C}}^{(\text{s/d})}$ and extension resistance $R_{\text{ext}}^{(\text{s/d})}(V_G)$ in both source (s) and drain (d). In addition, the device has resistance of series ultra-thin-body (UTB) SOI MOSFETs $R_{\text{SOI}}^{(\text{s/d})}(V_G)$ since the poly-Si gate has overlaps on SOI thin body areas with the lengths of $L_{\text{ov}}^{(\text{s/d})}$. Thus, the total series resistance in source and drain regions becomes

$$R_{\text{S}}^{(\text{s/d})}(V_G) = R_{\text{C}}^{(\text{s/d})} + R_{\text{ext}}^{(\text{s/d})}(V_G) + R_{\text{SOI}}^{(\text{s/d})}(V_G). \quad (7.23)$$

The parasitic capacitance $C_{\text{par}}^{(\text{s/d})}(V_G)$ exists in the UTB SOI MOSFET region and the extension region where the gate overlaps. Therefore, the apparent channel resistance and gate-to-channel capacitance of the NW MOSFET [$R_{\text{ch1}}(V_G)$ and $C_{\text{G1}}(V_G)$, respectively] are the sum of these parasitic components and the true NW channel resistance $R_{\text{NW1}}(V_G)$ and capacitance $C_{\text{GNW1}}(V_G)$.

$$R_{\text{ch1}}(V_G) \equiv \frac{V_{\text{D}}}{I_{\text{D1}}(V_G)} = R_{\text{NW1}}(V_G) + R_{\text{S}}^{(\text{s})} + R_{\text{S}}^{(\text{d})}, \quad (7.24)$$

$$C_{\text{G1}}(V_G) = C_{\text{GNW1}}(V_G) + C_{\text{par}}^{(\text{s})}(V_G) + C_{\text{par}}^{(\text{d})}(V_G). \quad (7.25)$$

To remove these parasitic components, advanced split C - V method (double- L_{m} method) [54] is adopted for NW MOSFETs [53, 55]. This method uses another NW MOSFET (MOSFET2) whose structure is the same as MOSFET1 except for NW length ($L_{\text{NW2}} < L_{\text{NW1}}$) and poly gate length [$L_{\text{m2}} = L_{\text{m1}} - (L_{\text{NW1}} - L_{\text{NW2}})$] with keeping $L_{\text{ov}}^{(\text{s/d})}$ and $L_{\text{ext}}^{(\text{s/d})}$. In MOSFET2, the NW channel resistance and capacitance change in proportion to the NW length, whereas the parasitic components are the same as those in MOSFET1. Therefore, the parasitic resistance and capacitance can be subtracted and the intrinsic channel resistance $R_{\text{chNW}}(V_G)$ and gate capacitance $C_{\text{GNW}}(V_G)$ of NWs with the length ΔL

$$\Delta L \equiv L_{\text{m1}} - L_{\text{m2}} = L_{\text{NW1}} - L_{\text{NW2}} \quad (7.26)$$

are obtained as

$$R_{\text{chNW}}(V_G) = R_{\text{ch1}}(V_G) - R_{\text{ch2}}(V_G) = \frac{V_{\text{D}}}{I_{\text{D1}}(V_G)} - \frac{V_{\text{D}}}{I_{\text{D2}}(V_G)}, \quad (7.27)$$

$$C_{\text{GNW}}(V_G) = C_{\text{G1}}(V_G) - C_{\text{G2}}(V_G), \quad (7.28)$$

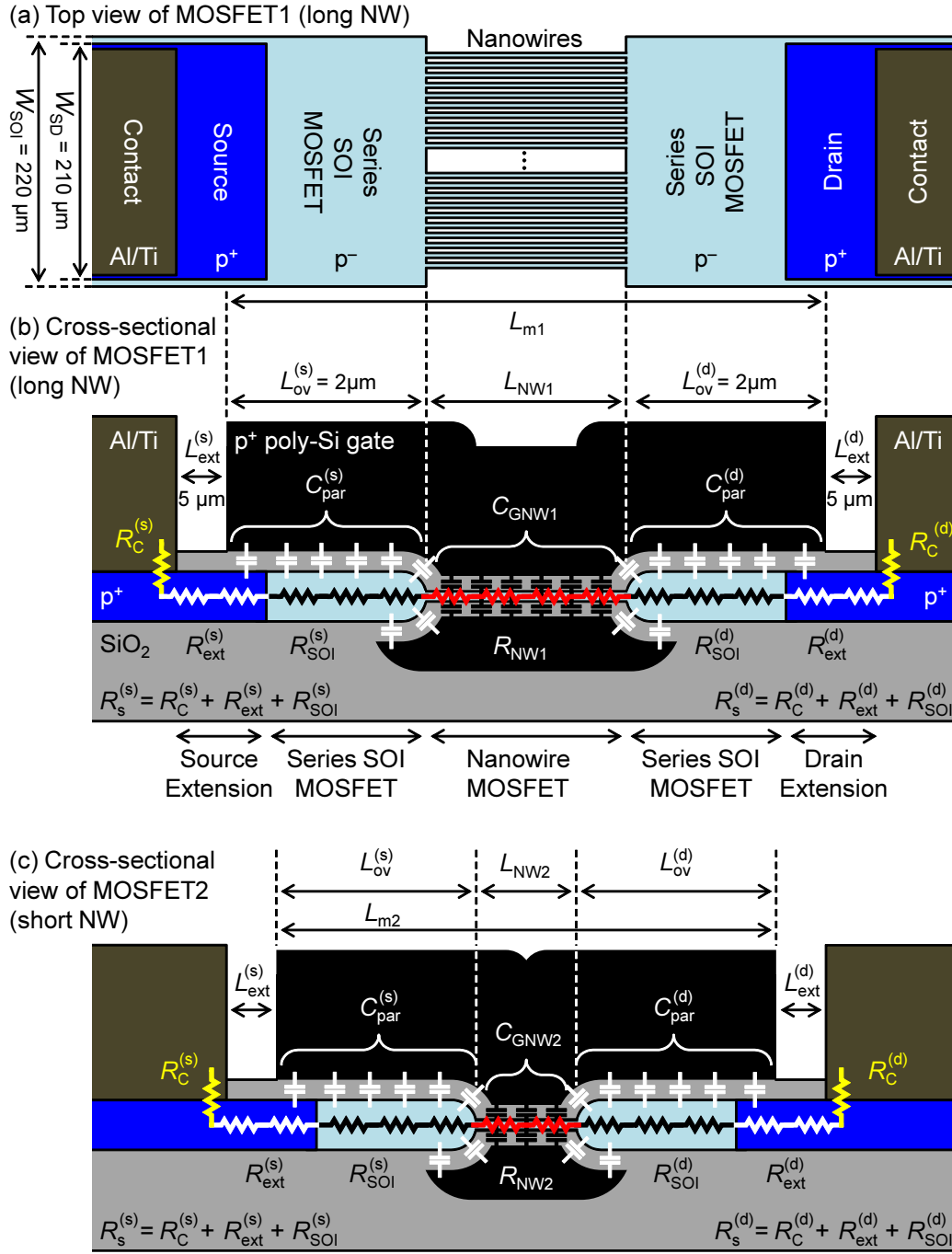


Figure 7.21: Explanation of parasitic resistance and capacitance components which exist in multi-NW MOSFETs. (a) A top view of a multi-NW PMOSFET with the NW length of L_{NW1} . (b) A cross-sectional view of the same multi-NW PMOSFET as (a). The gate electrode is not shown in (a). (c) The same MOSFET as (b) except for the NW lengths (shorter NWs, length = $L_{NW2} < L_{NW1}$) and poly-Si gate lengths. The parasitic resistances and capacitances of MOSFETs (b) and (c) are the same, and the NW channel resistance and gate capacitance are linearly modulated by the NW lengths. Therefore, the intrinsic channel resistance and capacitance can be extracted by using two MOSFETs with different NW lengths (double- L_m method).

when R_{ch1} and R_{ch2} are measured at the same V_D . Therefore, μ_{eff} is obtained by using Eqs. (7.21) and (7.22) as

$$\begin{aligned}
 \mu_{\text{eff}}(V_G) &= \frac{(\Delta L)^2}{Q_{\text{inv}}(V_G)R_{\text{ch}}(V_G)} \\
 &= \frac{(L_{\text{NW1}} - L_{\text{NW2}})^2}{\int^{V_G} [C_{\text{G1}}(V) - C_{\text{G2}}(V)] dV \cdot \left[\frac{V_D}{I_{\text{D1}}(V_G)} - \frac{V_D}{I_{\text{D2}}(V_G)} \right]} \\
 &= \frac{(L_{\text{NW1}} - L_{\text{NW2}})^2}{\int^{V_G} (C_{\text{G1}} - C_{\text{G2}}) dV} \frac{1}{V_D} (I_{\text{D1}}^{-1} - I_{\text{D2}}^{-1})^{-1}. \tag{7.29}
 \end{aligned}$$

In this study, NWs with $L_{\text{NW}} = 1, 1.25$, and $2 \mu\text{m}$ were fabricated with a constant $L_{\text{ov}} = 2 \mu\text{m}$. Hole mobility was extracted using the pairs of $(1 \mu\text{m}, 2 \mu\text{m})$ and $(1.25 \mu\text{m}, 2 \mu\text{m})$ NWs. The width of source/drain (W_{SD}) and the SOI width (W_{SOI}) are 210 and $220 \mu\text{m}$, respectively, and the distance between the contact metal and poly gate ($L_{\text{ext}}^{(\text{s/d})}$) is $5 \mu\text{m}$. t_{ox} of SOI MOSFET parts are 10.4 nm . The gate to channel capacitance measurements were performed with 400 kHz and 30 mVrms ac . I_D was measured with $V_D = -10 \text{ mV}$.

An example of the double L_m analyses for I_D and C_G is shown in Fig. 7.22, for a $\langle 112 \rangle$ NW with $D_{\text{eff}} = 10 \text{ nm}$, $t_{\text{ox}} \sim 8.5 \text{ nm}$, and $L_{\text{NW}} = 1$ and $2 \mu\text{m}$. I_D suffered from series resistance of about 200Ω and the parasitic capacitance of about 3.2 pF . This parasitic capacitance is almost comparable to the expected parasitic SOI MOSFET's capacitance (3.1 pF). After subtracting the parasitic capacitance by using two NW MOSFETs, C_{GNW} of 750 NWs in strong inversion was obtained to be $161 \text{ fF}/\mu\text{m}$, which well agrees with the oxide capacitance $163 \text{ fF}/\mu\text{m}$ calculated using the co-axial oxide approximation in Eq. (7.19). However, due to very small C_{GNW} at near-threshold voltage, the accuracy of the measurement can be affected by a slight variability of the capacitance onset voltage, and thus the mobility with low inversion carrier density may not be very accurate. Therefore, this study focused on the mobility at a high carrier-density region.

To assess the accuracy of the capacitance measurement, the capacitance obtained by double L_m is compared with calculated C_{ox} within the co-axial approximation in Fig. 7.23. The experimentally obtained gate capacitance almost agrees with the calculated C_{ox} for $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ NWs when the shape of NWs is almost axisymmetric. The errors in the gate capacitance are about 10% . Therefore, the mobility values extracted in the next section may contain the error to the same extent. The gate capacitance of the $\langle 100 \rangle$ NW MOSFET is unexpectedly smaller than the calculated C_{ox} . The reason of this small capacitance is unclear, but some portions of 750 NWs may be broken at both ends during the fabrication process.

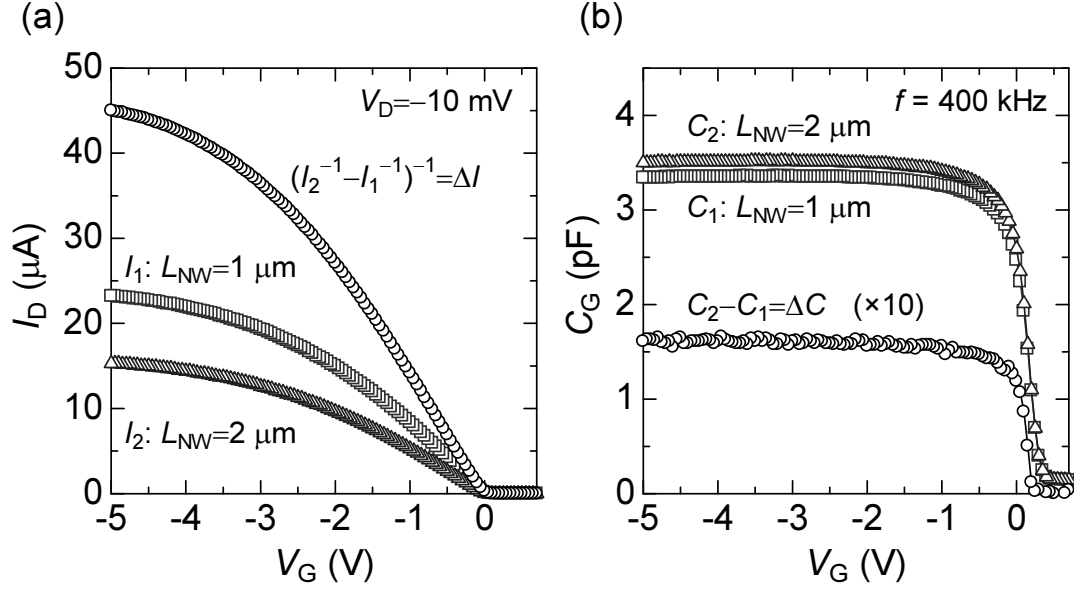


Figure 7.22: Example of Double- L_m analysis of (a) I_D and (b) C_G in NW MOSFETs ($\langle 112 \rangle$ NW with $D_{\text{eff}} = 10$ nm, $t_{\text{ox}} \sim 8.5$ nm, and $L_{NW} = 1$ and 2 μm).

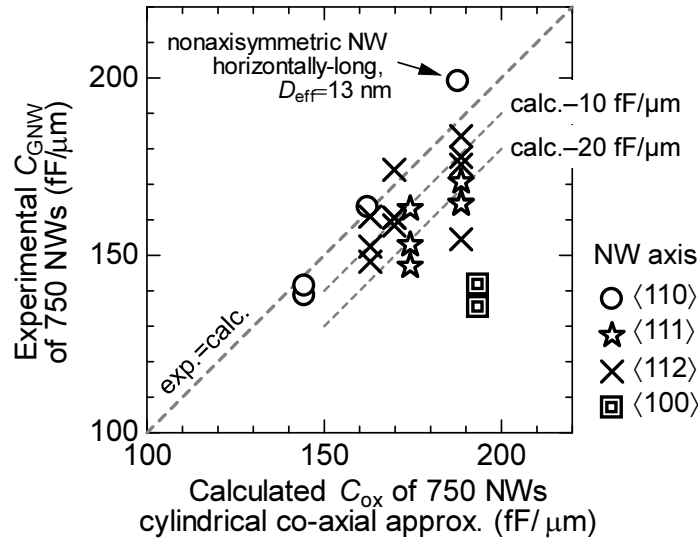


Figure 7.23: Comparison of the gate to channel capacitance of Si NWs obtained by double L_m analysis (experimental) with calculated C_{ox} within the co-axial approximation. The experimentally obtained gate capacitance almost agrees with the calculated C_{ox} for $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ NWs when the shape of NWs is almost axisymmetric. The errors in the capacitance are about 10%. The $\langle 110 \rangle$ NW with the largest capacitance in this plot has a horizontally-long structure [$D_{\text{eff}} = 13$ nm in Fig. 7.19(a)] and thus this calculation does not give a precise capacitance.

7.4.3 Mobility Characterization

The effective hole mobilities of fabricated $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ NW MOSFETs are shown in Fig. 7.24 as a function of D_{eff} of NWs. The effective mobility in this figure is the value at the surface carrier density $N_S = 1 \times 10^{13} \text{ cm}^{-2}$, which is a typical carrier density in advanced LSIs. Here, N_S is defined by the carrier density per unit length divided by the perimeter of the NW. In the same figure, the effective mobilities of UTB MOSFETs fabricated on the same (110)SOI sample are shown (denoted as “UTB”, thick black lines, SOI thickness = 13 nm). The effective mobilities of bulk (100), (110), and (111) MOSFETs reported by Irie *et al.* [56] are also shown as references (denoted as “Bulk”, thick gray dashed lines). In addition, the mobilities in NW PMOSFETs in previous reports [16–21, 53, 55, 57–61] are shown.

The hole mobility of the $\langle 110 \rangle$ NWs with $D_{\text{eff}} = 15 \text{ nm}$ is about $110 \text{ cm}^2/\text{V}\cdot\text{s}$ and it monotonically decreases as D_{eff} decreases. The mobility of the smallest $\langle 110 \rangle$ NW ($D_{\text{eff}} = 7 \text{ nm}$) is about $80 \text{ cm}^2/\text{V}\cdot\text{s}$. The hole mobility of the $\langle 112 \rangle$ NWs looks slightly smaller than that of $\langle 110 \rangle$ NWs, but they are almost comparable. Also in $\langle 112 \rangle$ NWs, the mobility degrades in smaller NWs. The hole mobility of the $\langle 111 \rangle$ NWs are also comparable to that of $\langle 110 \rangle$ and $\langle 112 \rangle$ NWs, but it seems slightly high. These mobilities in NWs are smaller than the hole mobility of the bulk (110) inversion layer with $\langle 110 \rangle$ - and $\langle 100 \rangle$ -oriented channels. However, they are almost comparable to or higher than the bulk (100) channel mobility by Irie *et al.* [56] and hole universal mobility on (100) ($80 \text{ cm}^2/\text{V}\cdot\text{s}$) [62]. The mobility of NWs with these three orientations will be discussed in Sec. 7.4.4.

The mobility of the $\langle 100 \rangle$ NW MOSFETs is about $50 \text{ cm}^2/\text{V}\cdot\text{s}$, which is much smaller than the data of other orientations obtained in this study. The data of $\langle 100 \rangle$ NWs may not be very accurate because the gate capacitance was much smaller than the expected capacitance from the NW structure as shown in Fig. 7.23, and the series resistance component extracted by the double L_m analysis was unexpectedly small ($< 50 \Omega$) when compared to the other devices. This may indicate that some portions of 750 NWs broke by hydrogen annealing and the number of survived NWs may be different between short- L and long- L NWs. Therefore, this data might contain a large error. However, this mobility value is within the range of the mobility in $\langle 100 \rangle$ NW MOSFETs in previous reports: $\mu_{\text{eff}} \sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$ [rectangular NW on (100)SOI, $W = 21 \text{ nm}$, $H = 19 \text{ nm}$] [53], $75 \text{ cm}^2/\text{V}\cdot\text{s}$ [square NW on (100)SOI, $W = H = 15 \text{ nm}$] [61], $70 \text{ cm}^2/\text{V}\cdot\text{s}$ [rectangular NW on (100)SOI NW, $W = 10 \text{ nm}$, $H = 22 \text{ nm}$] [17], and $140 \text{ cm}^2/\text{V}\cdot\text{s}$ [square NW on (110)SOI, $W = H = 18 \text{ nm}$] [58]. Since the diameter of $\langle 100 \rangle$ NWs fabricated in this study is large (14 nm), the conduction channel should be formed on the surface (SiO_2/Si interface). In addition, the cross-sectional shape of NWs is circular [Fig. 7.19(d)]. In $\langle 100 \rangle$ -oriented planar MOSFETs, it is known that the hole mobility is highest on the (110) face and the mobility decreases as the substrate face tilts from (110) to (100) [63]. The bulk MOSFET’s hole mobility is lowest on the (100) face. In circular NWs, the hole mobility can be affected by low-mobility $\{100\}$ faces. In addition, t_{ox}

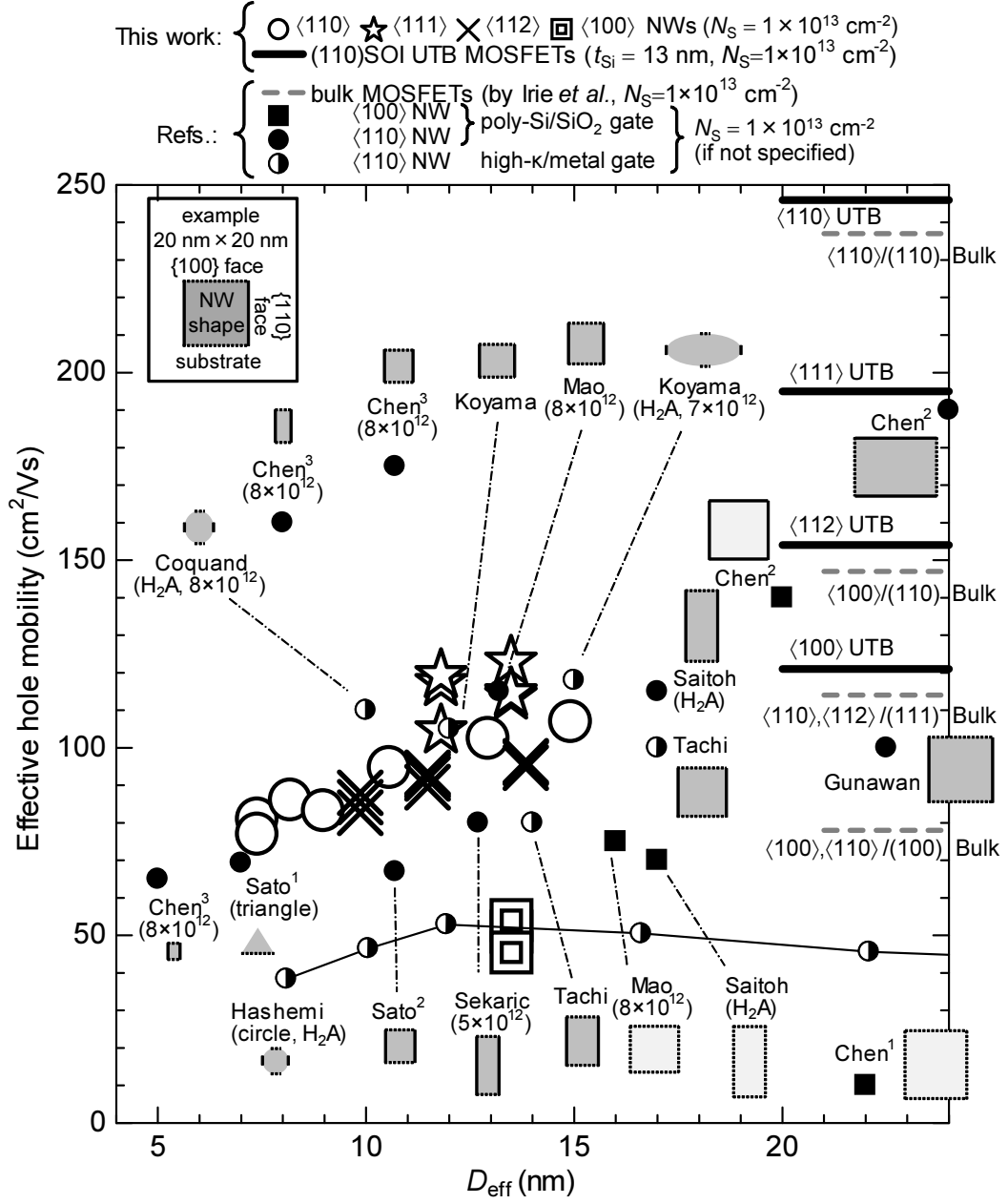


Figure 7.24: D_{eff} dependence of effective hole mobility (μ_{eff}) of fabricated <110>, <111>, <112>, and <100> multi-NW MOSFETs at $N_S = 1 \times 10^{13} \text{ cm}^{-2}$ measured by double- L_m method. μ_{eff} of fabricated (110) UTB MOSFETs with channel directions of <110>, <111>, <112>, and <100> are also shown (SOI thickness = 13 nm). As references, the reported μ_{eff} of bulk <110>/(<110>), <100>/(<110>), <111>, and <100> PMOSFETs [56] are shown. For comparison, μ_{eff} of <110> and <100> NW PMOSFETs in published data (labeled as Chen¹ [53], Chen² [58], Chen³ [16], Coquand [60], Gunawan [55], Hashemi [19], Koyama [21], Mao [61], Saitoh [17], Sato¹ [20], Sato² [59], Sekaric [57], and Tachi [18]) are plotted. For these published data, rough sketches of the cross-sectional shapes of NWs are shown for each data. N_S of these data is $1 \times 10^{13} \text{ cm}^{-2}$ if not specified as $x \times 10^{12}$ (unit: cm^{-2}). NWs in published data treated by hydrogen annealing are denoted as H₂A.

anisotropy was observed in fabricated $\langle 100 \rangle$ NWs; t_{ox} is thicker on $\{110\}$ ($t_{\text{ox}(110)} \sim 10$ nm) and thinner on $\{100\}$ ($t_{\text{ox}(100)} \sim 8.5$ nm), which is caused by faster oxidation rate on (110) than on (100) . This thinner t_{ox} on $\{100\}$ may cause preferential hole accumulation on low-mobility $\{100\}$ faces. Although the obtained mobility suffers from an error, the author guesses that the relatively low mobility in $\langle 100 \rangle$ NWs is affected by the surface orientation effect.

7.4.4 Discussion

Hole Mobility in $\langle 110 \rangle$ Nanowire MOSFETs

In Fig. 7.24, hole mobilities of $\langle 110 \rangle$ Si NW MOSFETs fabricated in this study (big open circle) are compared with the published data (fully filled small circles: $\text{SiO}_2/\text{poly-Si}$ gate, half filled small circles: high- κ /metal gate). To plot the data of NWs with various cross-sectional shapes in the same figure, the sizes of NWs are converted to D_{eff} . The shapes of NWs in literatures are roughly illustrated by gray figures in the plot. These data include mobilities of Si NWs with various cross-sectional structures, substrate faces, gate geometries, and gate stacks. Nonetheless, the mobility values and the trend of the mobility degradation in narrower NWs in this study show agreement with the previous reports. This agreement itself cannot be understood easily because different kinds of factors are strongly mixed. However, it can be said that the Si NW MOSFETs fabricated in this study show good device operations.

One thing to be discussed is the large degradation of the mobility in $\langle 110 \rangle$ NW MOSFETs from the mobility of $\langle 110 \rangle/(110)$ UTB MOSFET by the factor of > 2 even in the largest NWs. The hole mobility of the $\langle 110 \rangle/(110)$ UTB MOSFET is $246 \text{ cm}^2/\text{V}\cdot\text{s}$, which almost equals to reported $\langle 110 \rangle/(110)$ channel mobility of bulk MOSFET ($240 \text{ cm}^2/\text{V}\cdot\text{s}$); meanwhile, the mobility of the horizontally-wide $\langle 110 \rangle/(110)$ NWs ($D_{\text{eff}} = 13$ and 15 nm) in this study is only 100 – $110 \text{ cm}^2/\text{V}\cdot\text{s}$. In general, the hole mobility in rectangular $\langle 110 \rangle$ NW MOSFETs is explained by the average of the mobilities of bulk MOSFETs on top (and bottom) and side faces even in 10 -nm-wide NW MOSFETs [16, 17, 22]. Since the bulk inversion layer on the (110) face exhibit higher hole mobility ($\mu_{\text{eff}}=240 \text{ cm}^2/\text{V}\cdot\text{s}$) than that on (100) ($\mu_{\text{eff}}=80 \text{ cm}^2/\text{V}\cdot\text{s}$) with a $\langle 110 \rangle$ -oriented channel, rectangular $\langle 110 \rangle$ NWs with wider $\{110\}$ ($\{100\}$) faces show higher (lower) mobility, and the mobility value can be approximated by the average of those bulk inversion layer mobilities. The reason for the low mobility in horizontally-wide $\langle 110 \rangle$ NWs fabricated in this study can be qualitatively discussed by the structural change induced by hydrogen annealing. In wide $\langle 110 \rangle$ NWs [see the largest NW in Fig. 7.19(a) ($D_{\text{eff}} = 13$ nm)], the top and bottom $\{110\}$ faces are rounded and the wide $\{111\}$ facets are formed at corners. In addition, narrow $\{100\}$ facets are seen on the sidewalls. In bulk MOSFETs with a $\langle 110 \rangle$ -oriented channel, it is known that (111) and (100) mobilities are low (115 and $80 \text{ cm}^2/\text{V}\cdot\text{s}$, respectively) compared to (110) mobility ($240 \text{ cm}^2/\text{V}\cdot\text{s}$). Therefore, the contribution of $\{111\}$ and $\{100\}$ facets on $\langle 110 \rangle$ NWs can

cause mobility degradation. Moreover, t_{ox} is anisotropic on different facets of $\langle 110 \rangle$ NWs; t_{ox} is thicker on top and bottom $\{110\}$ facets and thinner on $\{111\}$ facets and side $\{100\}$ facets. This thick t_{ox} on $\{110\}$ may prevent holes from accumulating on high-mobility $\{110\}$ facets. The author attempted to estimate the mobility in the fabricated $\langle 110 \rangle$ NWs by averaging the bulk inversion layer mobilities on (100), (110), and (111), taking the facet widths and t_{ox} anisotropy into account. The cross-sectional shape of $\langle 110 \rangle$ NWs was approximated by an octagon surrounded by $\{100\}$, $\{110\}$, and $\{111\}$ facets with total facet widths of $W_{(100)}$, $W_{(110)}$, and $W_{(111)}$, respectively, as shown in Fig. 7.25(a). In addition, average values of t_{ox} on these facets ($t_{\text{ox}(100)}$, $t_{\text{ox}(110)}$, and $t_{\text{ox}(111)}$) were roughly estimated from TEM images. Then, the averaged mobility μ_{avg} was calculated by

$$\mu_{\text{avg}} = \frac{\mu_{(100)} \frac{W_{(100)}}{t_{\text{ox}(100)}} + \mu_{(110)} \frac{W_{(110)}}{t_{\text{ox}(110)}} + \mu_{(111)} \frac{W_{(111)}}{t_{\text{ox}(111)}}}{\frac{W_{(100)}}{t_{\text{ox}(100)}} + \frac{W_{(110)}}{t_{\text{ox}(110)}} + \frac{W_{(111)}}{t_{\text{ox}(111)}}}, \quad (7.30)$$

where $\mu_{(lmn)}$ is the reference hole mobility of $\langle 110 \rangle / (lmn)$ channels. As $\mu_{(lmn)}$, the mobilities reported by Irie *et al.* [56] were used because the planar channel mobilities under the process conditions in this study are unavailable. The calculated μ_{avg} and the experimental μ_{eff} are compared in Fig. 7.25(b). μ_{avg} calculated assuming conformal t_{ox} is also shown. The calculated μ_{avg} in large D_{eff} NWs is decreased from the mobility of bulk (110) MOSFETs by about $100 \text{ cm}^2/\text{V}\cdot\text{s}$ owing to the contribution of $\{111\}$ and $\{100\}$ facets. The additional reduction of the mobility by t_{ox} anisotropy was about $7 \text{ cm}^2/\text{V}\cdot\text{s}$ in this averaging model. Thus, the facet-dependent anisotropy is the main cause of the mobility degradation, and the t_{ox} anisotropy also contributes to the degradation a little. In addition, a slight decrease in μ_{avg} was observed in NWs with smaller D_{eff} due to the narrowing $\{110\}$ facet widths. This result suggests that the mobility degradation in smaller NWs observed in experiments may be partially caused by the facet-dependent mobility. However, the quantitative agreement between the calculation and experiments is not very good in the whole D_{eff} region. There are several possible factors which can cause errors in mobility estimation from this simple model. The surface channel mobilities (not only in NWs, but also in planar MOSFETs by the same process, which were not actually fabricated) might be degraded from those in bulk MOSFETs in the literature and bulk universal mobility [62, 64]. In addition, the accumulation of carriers on different facets may not be properly captured by Eq. (7.30) since the surface potential can be facet-dependent and electric-field crowding at large-curvature corners (on $\{100\}$ side surfaces in large- D_{eff} NWs) can cause preferable charge accumulation on low-mobility side $\{100\}$ facets in large- D_{eff} NWs. Therefore, to clarify the cause of low mobility in the fabricated $\langle 110 \rangle$ NW MOSFETs, and thus further study is necessary. Detailed calculation of the charge distribution and band structure at high gate bias will be a clue to understand the charge distribution and dominant surface channels. In addition, the intensive study on the carrier scattering mechanism is important to assess the effect of Coulomb scattering and surface-roughness scattering, which can be strongly dependent on the fabrication process. Moreover, for small- D_{eff} NWs, careful discussion on applicability of

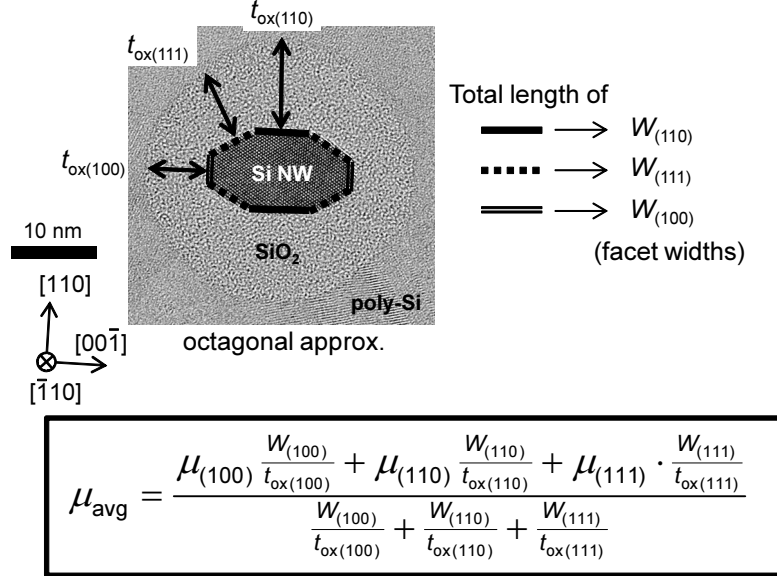
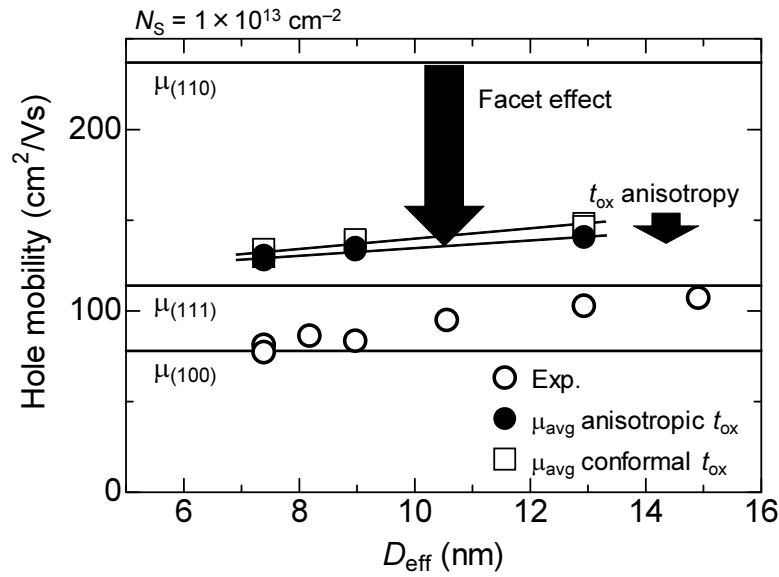
(a) Octagonal approx. of $\langle 110 \rangle$ NWs and averaged mobility μ_{avg} (b) Comparison of exp. μ and calc. μ_{avg} 

Figure 7.25: (a) Calculation method of averaged mobility μ_{avg} of $\langle 110 \rangle$ Si NW MOSFETs taking effects of $\{100\}$, $\{110\}$, and $\{111\}$ facets and anisotropy in t_{ox} into account. The cross-sectional shape of $\langle 110 \rangle$ NWs is approximated by an octagon surrounded by these three facets. (b) Comparison of the hole mobility in $\langle 110 \rangle$ Si NW MOSFETs obtained by experiments and μ_{avg} with anisotropic t_{ox} and conformal t_{ox} . $\mu_{(100)}$, $\mu_{(110)}$, and $\mu_{(111)}$ are reference mobilities of bulk (100), (110), (111) MOSFETs in the $\langle 110 \rangle$ channel direction [56] used in μ_{avg} calculation. $N_S = 1 \times 10^{13} \text{ cm}^{-2}$.

this surface mobility average model is needed. As the cross-sectional size of NWs decreases, quantum confinement effect by the geometry gives stronger effect than the confinement by the electrostatic potential at NW surface (SiO_2/Si interface) formed by the gate electric field, which leads to the transition from surface inversion (charges accumulate on the surface) to volume inversion (charges accumulate at the center of NW rather than the surface). When the volume inversion occurs, the surface channel average model will fail. The volume inversion is reported to appear when NW size decreases down to about 5 nm [15, 65], and another study predicted the onset of volume inversion of holes in $\langle 110 \rangle$ NWs exists at a width of 6–8 nm [66]. Therefore, the estimation of the carrier distribution inside NWs is important even for smaller- D_{eff} NWs.

Orientation Dependence of Hole Mobility

The mobility values in $\langle 111 \rangle$ and $\langle 112 \rangle$ NWs are almost comparable to those in $\langle 110 \rangle$ NWs. Since the diameters of these NWs are large (≥ 10 nm), surface-channel conduction is expected. It is difficult to explain the mobility in $\langle 112 \rangle$ NWs because of the complicated faceting [$\{311\}$ and $\{531\}$, Fig. 7.19(c)]. However, it is a very important finding that $\langle 112 \rangle$ NWs with a diameter down to 10 nm have a potential to exhibit the hole mobilities as high as that in $\langle 110 \rangle$ NWs. Here, the author gives a brief discussion on the mobility of $\langle 111 \rangle$ NWs. The fabricated $\langle 111 \rangle$ NWs have $\{112\}$ facets [Fig. 7.19(b)], and thus the hole mobility in the $\langle 111 \rangle$ NWs can be predicted from the hole mobility of bulk $\langle 111 \rangle / (112)$ MOSFETs. Satô *et al.* systematically studied the field-effect hole mobility μ_{FE} in bulk Si MOSFETs on high-index Si surfaces [63]. According to their report, $\mu_{\text{FE}} = 170 \text{ cm}^2/\text{V}\cdot\text{s}$ in bulk $\langle 111 \rangle / (112)$ MOSFETs. In their report, the mobility in $\langle 110 \rangle$ on (100), (111), and (110), which are channels formed on $\langle 110 \rangle$ NWs fabricated in this study, are also available: 95, 130, and $220 \text{ cm}^2/\text{V}\cdot\text{s}$, respectively. When μ_{avg} of $\langle 110 \rangle$ NWs ($D_{\text{eff}} = 13$ nm) is calculated by using these mobilities as references, it becomes about $150 \text{ cm}^2/\text{V}\cdot\text{s}$, which is very close to μ_{FE} of bulk $\langle 111 \rangle / (112)$ MOSFETs in their reports ($\mu_{\text{FE}} = 170 \text{ cm}^2/\text{V}\cdot\text{s}$). Therefore, it is not a strange result that $\langle 111 \rangle$ NWs and $\langle 110 \rangle$ NWs have similar mobilities.

The obtained orientation dependence of the mobility among $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ NWs was $\mu_{\langle 112 \rangle} < \mu_{\langle 110 \rangle} < \mu_{\langle 111 \rangle}$. From the viewpoint of the effective mass calculated in Chapter 2 for the square NWs (the maximum NW size in calculation: 6–7 nm), $m_{\text{avg},[111]}^* < m_{\text{avg},[110]}^* < m_{\text{avg},[112]}^*$ (Fig. 2.20), and this agrees with the trend of the orientation dependence of the experimental mobility, although this calculation is for square NWs and low V_G . When the channel is formed on the surface of NWs under strong gate bias, the surface channels in $\langle 111 \rangle$ NWs can be virtually regarded as six parallel horizontally-long (width ~ 5 nm) and thin $\langle 111 \rangle / \{112\}$ NWs on the NW surface. In Chapter 2, the author showed that horizontally-long $\langle 111 \rangle / \{112\}$ NWs (Fig. 2.15) have one of the smallest effective mass among rectangular-shaped NWs in any other orientations of $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 112 \rangle$ (Fig. 2.5, Fig. 2.10, and Fig. 2.17, respectively). Therefore, the high mobility in $\langle 111 \rangle$ NWs compared to the other orientations is what is expected from the theoretical study in Chapter 2.

Higher hole mobility in $\langle 111 \rangle$ NWs compared to $\langle 110 \rangle$ and $\langle 100 \rangle$ NWs is also predicted in more detailed mobility calculations [23, 24]. However, the author cannot affirm that the orientation dependence obtained in this study is conclusive enough at this time from two reasons. First of all, the difference of mobilities among $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 112 \rangle$ NWs is only about 10–20%. Since the measured gate capacitance may contain errors of about 10%, the mobility may include the error to the same extent. Secondly, the measured gate capacitances in $\langle 111 \rangle$ NWs were lower by 20 fF/ μm (about 10 %) than the oxide capacitance expected from the simple co-axial approximation in Eq. (7.19) as shown in Fig. 7.23, whereas the measured capacitances of $\langle 110 \rangle$ NWs almost equal to the calculation when the cross-sectional shapes of $\langle 110 \rangle$ NWs are almost axisymmetric [$D_{\text{eff}} \leq 9$ nm, see Fig. 7.19(a)]. When the capacitance is underestimated by 10%, the mobility is overestimated by 10%, which can result in apparently high mobility in $\langle 111 \rangle$ NWs observed in experiments. Although the quantum effect can reduce the capacitance due to the finite depth of the inversion layer from the surface [67], the inversion layer thickness of about 4 nm is necessary to explain the reduction of the capacitance by 20 fF/ μm , which may be too thick unless the volume inversion occurs. This amount of the capacitance decrease possibly occurs if the ΔL_m has an error of only 25–30 nm because of the large parasitic capacitance in series UTB MOSFETs. The orientation-dependent difference in the gate length can occur in a systematic way if the reticle of photolithography has an error. Of course, the calculation method of the capacitance is too simple to examine the precise capacitance of the actual NW structures with facets and t_{ox} anisotropy, and thus the Schrödinger and Poisson equations should be solved rigorously to discuss the amount of the error in the measured capacitance. Nonetheless, the improvement of the accuracy of mobility extraction is crucial to study carrier transport in very thin Si NWs. Therefore, it is very important to redesign the device to become more robust to the error in the gate length by increasing the density and/or length of NWs. It can be also effective to utilize the structure without the gate overlap to SOI parts [55].

Mobility Degradation in Thinner Nanowires

As stated above, the mobility degradation in thinner NWs might be affected by the shape effect in part. However, the degradation can be also caused by the increase of the phonon scattering and/or surface roughness scattering. It is recently observed in experiments that room-temperature phonon-scattering-limited mobility in strong inversion is almost independent of NW width within the range of $W = 11\text{--}35$ nm in trigate rectangular $\langle 110 \rangle / (100)$ NW MOSFETs ($H = 12.5$ nm) [68]. If this observation holds true in the NWs fabricated in this study, surface-roughness scattering may degrade the mobility in smaller NWs. However, for the NWs with $D_{\text{eff}} \leq 10$ nm in this study, the size of NWs is smaller than that in Ref. 68, and thus the situation can be different. To analyze the degradation mechanism of mobility in narrower NWs and the dominant source of carrier scattering, it is very important to measure mobilities at low temperatures because the surface-roughness-scattering-limited

mobility is almost temperature independent while the phonon-scattering-limited mobility significantly increases at lower temperatures because of the reduction in the available number of excited phonons. This measurement of the temperature dependence is one of the future tasks. Theoretical reports predicted that the phonon-scattering-limited hole mobility in $\langle 110 \rangle$ and $\langle 111 \rangle$ Si NWs starts to increase at the diameter of 10 nm at a low carrier concentration [23, 24] due to the modulation of the band structure by quantum confinement effect, and the mobility increase in smaller diameters is calculated to be significant even at a high carrier density when the diameter is scaled to 5–2 nm [24]. Therefore, the fabrication and the mobility evaluation of $\langle 110 \rangle$ and $\langle 111 \rangle$ NWs with such smaller diameters are important. Moreover, the comparative discussion of the mobility from the viewpoint of NW orientations and the difference of the size effect on mobilities of electrons and holes is also important.

7.5 Summary

Gate-all-around Si NW MOSFETs were fabricated by applying surface-smoothing hydrogen annealing process and the transport characteristics in smooth Si NWs were investigated. Using a special structure with p^+ and n^+ source/drain regions in a MOSFET which shares a single $\langle 110 \rangle$ NW channel with the diameter of 5.1–13.5 nm, transport properties of holes (PMOS operation) and electrons (NMOS operation) in an identical single NW were compared at low temperatures down to 8 K. At low temperatures, the oscillations of the drain current and the transconductance were observed in both NMOS and PMOS, and the different periods of oscillation in subthreshold (≤ 0.1 V step) and above threshold (~ 0.3 V in PMOS and ~ 1 V in NMOS) were observed, which indicates different origin of the oscillations in these two regions. The oscillation in subthreshold is attributed to Coulomb blockade. Although the NW channel is identical in NMOS and PMOS, NMOS showed stronger Coulomb blockade, which is probably caused by trapped electrons at SiO_2/Si interface. Above threshold, the oscillation originates from the modulation of the carrier scattering rate by one-dimensional density of states in NWs. The developed simple model combined with the density of states calculated by the tight-binding model was able to explain the spacing of oscillation for both electrons and holes. These observations are helpful to understand the real band structures in fabricated Si NWs, which is very important to optimize the structure of NWs for the realization of high-performance NW MOSFETs.

The hole mobility of Si NW MOSFETs was also extracted at room temperature using NW PMOSFETs with 750 parallel NWs, removing parasitic resistance and capacitance by measuring two MOSFETs with different channel lengths. Almost similar mobilities were obtained for $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ NWs with $D_{\text{eff}} = 12\text{--}14$ nm; at $N_{\text{S}} = 1 \times 10^{13} \text{ cm}^{-2}$, hole mobilities of NWs in these orientations were about 90–120 $\text{cm}^2/\text{V}\cdot\text{s}$ when $D_{\text{eff}} \sim 12$ nm. The mobility degradation was observed in smaller $\langle 110 \rangle$ and $\langle 112 \rangle$ NWs, but the mobility was

as high as $80 \text{ cm}^2/\text{V}\cdot\text{s}$ even in 7-nm $\langle 110 \rangle$ NWs and 10-nm $\langle 112 \rangle$ NWs. These mobilities are still almost the same as or higher than the reported hole mobility in bulk Si(100) PMOSFET ($80 \text{ cm}^2/\text{V}\cdot\text{s}$). This fact offers promising prospects of Si NW MOSFETs in ultrascaled technologies.

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Chapter 8

Conclusions

8.1 Conclusions

Quantum confinement effect (QCE), surface-smoothing process, and carrier transport of Si nanowires (NWs) were investigated to utilize Si NWs for advanced Si MOSFETs. First of all, an intensive theoretical study of QCE on holes was performed and anisotropy of the valence band (VB) structures was clarified. Secondly, a fabrication process of Si NWs with smooth surfaces was established, by a top-down process combining with surface-smoothing hydrogen annealing process. Finally, QCE in NWs was experimentally confirmed from the transport characteristics of Si NW MOSFETs with smooth NW surfaces as a transconductance oscillation, which was expected from quantum-mechanical theoretical calculations. Moreover, the hole mobility in Si NW MOSFETs with various NW orientations was experimentally studied.

In Chapter 2, VB structures of [001]-, [110]-, [111]-, and [112]-oriented Si NWs with square and rectangular cross-sections were calculated by an $sp^3d^5s^*$ tight-binding method, and the hole effective mass m^* averaged by the Fermi distribution, m_{avg}^* , was evaluated at room temperature. In square NWs, m_{avg}^* decreases as the width of NWs (W_{NW}) decreases because subbands with heavy m^* are separated off from top light- m^* subbands by QCE. At $W_{\text{NW}} = 2$ nm, $m_{\text{avg}}^* = 0.13, 0.17, 0.26$, and $1.07m_0$ in the square [111], [110], [112], and [001] NWs, respectively. m_{avg}^* in [111] and [110] NWs is very close to m^* of the light hole of bulk Si. In the thicker square NWs with $W_{\text{NW}} \sim 6$ nm, $m_{\text{avg}}^* = 0.25, 0.47, 0.53$, and $1.15m_0$ in [111], [110], [112], and [001] NWs, respectively. In rectangular NWs, it was found that [110] NWs exhibit very strong confinement-direction dependence of VB structure and m_{avg}^* . Small m_{avg}^* is obtained when W_{NW} along $[1\bar{1}0]$ is kept small, but m_{avg}^* significantly and rapidly increases when W_{NW} along $[1\bar{1}0]$ increases. Unlike [110] NWs, the VB of rectangular [111] NWs does not show confinement-direction dependence and small m_{avg}^* retains in any aspect ratios. Therefore, [111] Si NWs with any aspect ratios and [110] NWs with thin $[1\bar{1}0]$ width and wider [001] width are promising for p-channel NW FETs. In addition, it was proposed that these anisotropic properties of QCE on holes are explainable by the character

of p orbitals which form each subband from the viewpoint of the strength of inter-orbital interactions.

In Chapter 3, a fabrication process of Si NWs was established. Nearly rectangular cross-sectional Si NWs were successfully fabricated in $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ orientations on (110) silicon-on-insulator (SOI) substrates. The minimum H_{NW} (height of NW) was 9 nm and various W_{NW} of ~ 6 –30 nm were obtained, using electron-beam lithography (EBL), inductively-coupled-plasma reactive ion etching (ICP-RIE), and sacrificial thermal oxidation. Even though the minimum size of NWs was 6 nm $\times$ 9 nm, the NW size can be further reduced by thermal oxidation for the gate oxide growth in MOSFET fabrication. The fabricated NWs had small width fluctuations smaller than 2–3 nm thanks to the utilization of hydrogen silsesquioxane (HSQ) resist, overlap exposure in EBL, and well-optimized Cl_2 -based ICP-RIE process.

In Chapter 4, the etching kinetics of hydrogen chloride (HCl) gas etching of Si as a surface-smoothing process was investigated. HCl gas etching at atmospheric pressure and the temperature of 1050°C with low HCl concentration below 0.3% in H_2 exhibited low-rate etching < 10 nm/min, and it can smoothen surfaces of bare Si(100) and (110) by etching the surface by 15–20 nm in thickness. However, a strong dependence of the etching rate on the surface exposure density was observed on the Si surface partially masked by SiO_2 (etching loading effect). The etching rate significantly increased ($\times 30$) in Si- SiO_2 stripe mask patterns with the opening/mask widths of 10 μm /500 μm compared to those of 10 μm /10 μm , which may result in the loss of etching controllability on patterned wafers such as Si NW structures. From dependences of the etching rate on the temperature, HCl concentration, and crystal face, and from thermochemical analyses, the out-diffusion of the etching by-product SiCl_2 in the stagnant layer is identified to be the etching-rate limiting process. The experimentally-observed loading effect was confirmed to be reproducible by a model taking into account of the diffusion of SiCl_2 in the gas phase.

In Chapter 5, hydrogen annealing (thermal treatment in a hydrogen flow) was investigated to obtain smooth Si surfaces at relatively low temperatures ($\leq 850^\circ\text{C}$). It was found that low-temperature hydrogen annealing is susceptible to the surface oxygen contamination, and the surface smoothing can be inhibited by slight surface oxidation caused by the rinse process in ultra-pure water (UPW) after hydrogen termination by hydrofluoric acid (HF) based wet etching. To avoid this oxidation by UPW exposure, which is probably caused by OH^- ions in UPW, hydrochloric acid (HCl) rinse was proposed, and its effectiveness was verified not only by the surface morphology after hydrogen annealing but also by surface chemical analyses with X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The possible surface oxidation by oxygen and moisture impurities in hydrogen ambient was suppressed by adopting a high-rate H_2 flow (> 10 slm) and medium H_2 pressure (75–200 Torr). By taking them together, simultaneous atomic-level surface flattening of (100), (110), and (111) bulk Si was established by short-time (2 min) hydrogen annealing at a low temperature of 810°C and a medium hydrogen pressures of 75

and 150 Torr. Step-terrace structures with the step height of one monolayer on Si(100) and (110) and one bilayer on (111) were obtained by hydrogen annealing at the same time. This feature is crucially important when hydrogen annealing is applied to Si NWs because NWs are three-dimensional structures and they have various facets.

In Chapter 6, hydrogen annealing at 810°C and 75 Torr for 2 min was applied to suspended Si NWs (released from the buried oxide layer) in various orientations of $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$, which were fabricated in Chapter 3. It was confirmed by top-view scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (TEM) that hydrogen annealing can smoothen the width fluctuation and surface roughness of Si NWs with all of the above orientations. The minimum NW diameter (before annealing) that can successfully be annealed and smoothed was about 10, 18, 21, and 23 nm for $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ Si NWs, respectively, and smaller NWs broke by excess surface diffusion of Si atoms. These minimum diameters are smaller than those in previous reports at comparable annealing temperatures for comparable annealing time but at lower hydrogen pressures. The alleviated wire instability in this study is attributed to reduced surface diffusion coefficient at a higher hydrogen pressure. At further high pressure of 150 Torr, wire breaking was more minimized and the minimum diameter was reduced to <8, 14, 16, and 17 nm for $\langle 110 \rangle$, $\langle 112 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$, respectively. However, NWs with very small diameters (except $\langle 110 \rangle$ NWs) were not smoothened enough probably owing to shorter diffusion length compared to 75-Torr annealing. Therefore, 75-Torr annealing gives good results at in the case of the annealing at 810°C for 2 min and there may exist a limitation of maximum pressure of hydrogen that can be utilized for smoothing of very thin Si NWs.

In Chapter 7, gate-all-around Si NW MOSFETs were fabricated by applying surface-smoothing hydrogen annealing process and the transport characteristics in smooth Si NWs were investigated. The hole mobility at room temperature was studied using PMOSFETs with 750 parallel NWs, removing parasitic resistance and capacitance by measuring two MOSFETs with different channel lengths. Almost similar mobilities were obtained for $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ NWs with the diameter of 12–14 nm; hole mobilities of 12-nm NWs with these orientations were about 90–120 cm²/V·s at the surface carrier density $N_S = 1 \times 10^{13}$ cm⁻². In smaller $\langle 110 \rangle$ and $\langle 112 \rangle$ NWs, the mobility degradation was observed, but the mobility was about 80 cm²/V·s in 7-nm $\langle 110 \rangle$ NWs and 10-nm $\langle 112 \rangle$ NWs. These mobilities are still comparable to or higher than the universal hole mobility of Si(100) planer MOSFETs at $N_S = 1 \times 10^{13}$ cm⁻², and this fact offers promising prospects of Si NW MOSFETs in ultrascaled technologies. Using a special structure with p⁺ and n⁺ source/drain regions in a MOSFET with a single $\langle 110 \rangle$ NW with the diameter of 5.1–13.5 nm, the transport properties of both electrons and holes in the identical NW were studied at low temperatures down to 8 K. At low temperatures, the oscillations of the drain current I_D and the transconductance g_m with respect to the gate voltage V_G were observed in both NMOS and PMOS operations. In the subthreshold region, weak oscillations with a short period (≤ 0.1 V) were observed probably due to Coulomb blockade. On the other hand, oscillations

with longer periods were observed above threshold. The oscillation period was longer in NMOS (~ 1 V) than in PMOS (~ 0.3 V). These above-threshold oscillations were modeled by the oscillations in the mobility owing to the oscillatory one-dimensional density of states (DOS) and subband structures. In the model, the scattering rate was assumed to be proportional to DOS, and the subband structures and DOS in Si NWs were calculated by the $sp^3d^5s^*$ tight-binding method for the actual cross-sectional structures reproduced from TEM images of the corresponding NWs for which the electrical characterization was performed. The good agreement of the g_m oscillation behavior was obtained between experiments and the proposed theoretical model, and the different oscillation periods in NMOS and PMOS were explainable by the larger energy splitting in the conduction band than in the valence band. This result suggests that subband structures in Si NWs are observable through g_m and that they are well predicted by theoretical band structure calculation.

8.2 Future Work

This study clarified several issues in the surface smoothing process and carrier transport in Si NWs. There, however, remain several issues to be solved.

- **Detailed mechanisms of orientation-dependent wire instability**

This study found the orientation-dependent wire instability in hydrogen annealing and its mechanism is qualitatively explained from the positions of low-energy $\{111\}$ facets. This discussion, however, is still a rough speculation and based on a stationary situation. The wire instability arises from a dynamic motion of surface Si atoms, and this dynamics is probably influenced by the anisotropy in the surface diffusion coefficient and surface stiffness. Although there exist several reports on the surface stiffness of Si [1], they are investigated in vacuum and at different temperatures from hydrogen annealing for Si NWs. Because the understanding of the wire instability is crucial for modeling and further optimization of surface smoothing by hydrogen annealing, the understanding of these fundamental parameters will make a great help.

- **Development of surface-smoothing process not relying on the surface diffusion and/or NW-slimming process without roughening the surface**

To smoothen Si NWs with extremely-small diameters (widths) less than 10 nm, hydrogen annealing cannot be directly applied owing to the wire breaking. In particular, $\langle 111 \rangle$ NWs, which are expected to exhibit the highest hole transport properties as discussed in Chapter 2, are easy to break up. Because this instability is caused by the surface diffusion, a smoothing method which does not rely on the surface diffusion is necessary. Otherwise, an initially-thicker Si NW than the breaking threshold is first smoothed by hydrogen annealing, and then the size of NWs must be slimmed. This slimming technique must not develop surface roughness. For this purpose, hydrogen chloride gas etching may be a possible candidate. In addition, active oxidation [2] can

be effective to reduce the size of hydrogen-annealed Si NWs, although the applicability to NWs with various orientations has not been clarified yet.

- **More Detailed Theoretical Analysis of Mobility Oscillation**

In this thesis, oscillations in g_m were observed in Si NW MOSFETs at low temperatures. The author interpreted this phenomenon as mobility oscillations which arise from the modulation of the carrier scattering rate by oscillatory one-dimensional DOS. Although the author obtained good agreement of oscillations between the experiment and calculation using a simple model, there are some discrepancies. For example, the agreement of the peak positions in the experiment and calculation becomes slightly poor at high $|V_G|$, and there existed several peaks in the experiment that were not obtained in the calculation. These discrepancy may come from the change of band structures by the nonuniform potential in the NW cross-section induced by the gate voltage, which is neglected in this thesis. To taking this effect into account, band structures should be calculated being coupled with the Poisson equation self-consistently. By the self-consistent calculation, the effect of the gate capacitance oscillation can also be evaluated properly, and thus the comparison of the strength of oscillation originating from the mobility and the gate capacitance can be performed. In addition to this, the accuracy of the scattering rate and the mobility calculation is still not enough in this study because very simple approximation (scattering rate $\propto$ DOS) is used. More rigorous calculation will make it possible to predict the precise amplitude of the oscillation. This is crucial to estimate the detailed information of the subband structure such as effective mass from the experimentally observed oscillations. It is also important to study the quantum effect in NWs with smaller sizes (diameter ≤ 6 nm) and various orientations by comparing the theoretical and experimental results. By changing sizes and orientations, band structure is significantly modulated and thus the validity of the model of subband-induced mobility modulation can be investigated more deeply.

- **Study of Carrier Mobility in Smaller NWs**

In this study, the hole mobilities in Si NWs with diameters within the range of 7–15 nm, 10–14 nm, and 12–14 nm for $\langle 110 \rangle$, $\langle 112 \rangle$, and $\langle 111 \rangle$ NWs, respectively, were studied. In these NWs, the mobilities gradually decrease as the diameter decreases. A significant increase of the hole mobility is predicted in NWs with a diameter below 7 nm for $\langle 110 \rangle$ and $\langle 111 \rangle$ [3, 4], but the report on the mobility in these extremely-small NWs is still limited [5–7] for both electrons and holes, and intensive study of the carrier scattering mechanism in extremely small NWs is necessary. For this purpose, the precise measurement of the extremely small gate capacitance and the device design which is robust to the variability of the gate length and other device parameters are important. To analyze the carrier mobility improvement/degradation induced by the effect of the band structure, the subband spectroscopy by g_m oscillation obtained in

Chapter 7 might be a clue, although improvement of the accuracy of the oscillation model is still necessary. In addition, the study on the effect of surface smoothing process on the carrier mobility is also important especially for smaller NWs because the mobility is significantly influenced by the surface roughness in extremely small NWs [3, 8, 9]. The author fabricated and evaluated Si NW MOSFETs with the surface smoothened by hydrogen annealing, but the comparative study of the carrier mobilities in NWs with and without hydrogen annealing was not conducted. Several studies have reported the effect of hydrogen annealing [10–14], but consensus has not been obtained yet. Thus, systematic study on this subject is necessary.

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Appendix A

Band Structure Calculation of Si Nanowires by Tight-Binding Model

A.1 Nearest-Neighbor Tight-Binding Model with Two-Center Approximation

To calculate a wavefunction of electrons in a crystal exactly, the Schrödinger equation must be solved in the electrostatic potential formed by many numbers of atomic nuclei and electrons in the crystal. However, the calculation of a many-body wavefunction is practically very difficult if the contributions from all electrons and atoms are taken into account. Therefore, to simplify the problem while keeping a good description of the electronic structure, some approximations are introduced for the calculation of bandstructures.

A nearest-neighbor tight-binding model with a two-center approximation is one of the empirical approximation methods to calculate electronic structures. Here, main concepts of the approximation are described. First of all, the atomic nuclei exist at their equilibrium position and do not move (Born approximation). This approximation is justified from the fact that the mass of atomic nuclei is much heavier than that of electrons and the movement of atoms is so slow that the motion of atoms does not affect the electronic structure. (The effect of lattice vibration can be calculated as a perturbation if necessary.) Secondly, the effect of many electrons is treated by a mean field approximation, which replaces many-electron potentials with effective mean field and regards the problem as a single-electron problem. In the third place, the electronic wavefunction is approximated by a linear combination of atomic orbitals of valence electrons (and some excited states) bound to each atom in the crystal (tight-binding approximation), and inner-shell electrons are neglected since they are strongly bound to atomic nuclei and do not affect interactions between atoms. For calculation of the band structure of Si, s and p orbitals have to be considered and in some models d and excited s orbitals (s^*) are taken into account to improve the reproducibility of effective masses [1–3]. Furthermore, the effect of atoms in a

neighborhood of a given atom is taken into account to calculate the interactions involved in the atom and thus the influence of atoms far from the given atom is neglected. In the nearest-neighbor model in this study, only the nearest-neighbor atoms are entered into consideration. Finally, in the calculation of an interaction between two given atoms, the potential by the other atomic nuclei is neglected (two-center approximation) since the calculation of three-center integrals are very complicated. In the following part, the general description of Hamiltonian of a tight-binding model is given, which is originally given by Slater and Koster [4] and not limited to nanowire (NW) structures. The special treatment is necessary for NWs to eliminate surface states originating from dangling bonds. This treatment is discussed in Section A.3.

Assign a number α serially to each atom in a crystal structure to be calculated. Define $\mathcal{C}$ as a set of atoms contained in the unit cell, $\mathcal{A}_\alpha$ as a set of atoms which are identified with the atom α by space-translational operation, $\mathcal{N}_\alpha$ as a set of nearest-neighbor atoms of the atom α , N as the number of unit cells, and $\mathbf{R}_\alpha$ as the position of the atom α . In addition, let $V_\alpha(\mathbf{r} - \mathbf{R}_\alpha)$ be the electrostatic potential formed by atomic nucleus of the atom α and $\phi_{\alpha m}(\mathbf{r} - \mathbf{R}_\alpha)$ be a wavefunction of an orbital m of the atom α . Then the single-electron Hamiltonian H can be written as

$$H = -\frac{\hbar^2}{2m_0}\nabla^2 + \sum_{\alpha \in \mathcal{C}} \sum_{i \in \mathcal{A}_\alpha} V_i(\mathbf{r} - \mathbf{R}_i), \quad (\text{A.1})$$

where m_0 is the electron mass and $\hbar$ the reduced Planck constant. Since an electronic wavefunction in a periodic system should satisfy Bloch's theorem, the tight-binding wavefunction is composed of a linear combination of Bloch sums of each atomic orbital as

$$\Phi_{\alpha m}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{i \in \mathcal{A}_\alpha} e^{i\mathbf{k} \cdot \mathbf{R}_i} \phi_{\alpha m}(\mathbf{r} - \mathbf{R}_i) \quad (\text{Bloch sum}) \quad (\text{A.2})$$

$$\Psi(\mathbf{k}) = \sum_{\alpha \in \mathcal{C}} \sum_{m \in \mathcal{B}} c_{\alpha m}(\mathbf{k}) \Phi_{\alpha m}(\mathbf{k}) \quad (\text{tight-binding wavefunction}) \quad (\text{A.3})$$

The coefficient $c_{\alpha m}(\mathbf{k})$ and the corresponding energy level can be obtained by solving the Hamiltonian using the variational technique (Rayleigh-Ritz method) with the set of Bloch sums as the basis. Therefore, the matrix elements of the Hamiltonian about Bloch sums of orbital m and n , $H_{\alpha m, \beta n}$, have to be calculated.

$$H_{\alpha m, \beta n}(\mathbf{k}) \quad (\text{A.4})$$

$$= \int \Phi_{\alpha m}^*(\mathbf{k}) H \Phi_{\beta n}(\mathbf{k}) d\tau \quad (\text{A.5})$$

$$= \frac{1}{N} \sum_{i \in \mathcal{A}_\alpha} \sum_{j \in \mathcal{A}_\beta} e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)} \int \phi_{\alpha m}^*(\mathbf{r} - \mathbf{R}_i) H \phi_{\beta n}(\mathbf{r} - \mathbf{R}_j) d\tau \quad (\text{A.6})$$

$$= \sum_{j \in \mathcal{A}_\beta \cap \mathcal{N}_\alpha} e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_\alpha)} \int \phi_{\alpha m}^*(\mathbf{r} - \mathbf{R}_\alpha) \left[H_\alpha + \sum_{l \neq \alpha} V_l(\mathbf{r} - \mathbf{R}_l) \right] \phi_{\beta n}(\mathbf{r} - \mathbf{R}_j) d\tau \quad (\text{A.7})$$

$$\equiv \sum_{j \in \mathcal{A}_\beta \cap \mathcal{N}_\alpha} \tilde{H}_{\alpha m, j n}(\mathbf{k}), \quad (\text{A.8})$$

where

$$H_\alpha \equiv -\frac{\hbar^2}{2m_0}\nabla^2 + V_\alpha(\mathbf{r} - \mathbf{R}_\alpha) \quad (\text{A.9})$$

is the single-electron Hamiltonian about a discrete atom α and satisfies

$$H_\alpha \phi_{\alpha m} = E_{\alpha m} \phi_{\alpha m} \quad (\text{A.10})$$

when the energy level of the bound-state atomic orbital m of the discrete atom α is denoted as $E_{\alpha m}$. Note that $\int d\tau$ denotes both of the spatial integration and the summation of the spin coordinate. In $\tilde{H}_{\alpha m, jn}(\mathbf{k})$ in Eq. (A.8), the integral about the term $\sum_{l \neq \alpha} V_l(\mathbf{r} - \mathbf{R}_l)$ is called three-center integrals and it is cumbersome and impractical to calculate this integral with taking all atomic nuclei into account. Therefore, as an approximation, only the potential by the scanned atom j is taken into account (two-center approximation). Note that the case of $j = \alpha$ should be ruled out. In this approximation,

$$\tilde{H}_{\alpha m, jn}(\mathbf{k}) = \begin{cases} E_{\alpha m} \delta_{mn} & (j = \alpha) \\ e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_\alpha)} V_{\alpha m, jn} & (j \neq \alpha) \end{cases} \quad (\text{A.11})$$

$$= E_{\alpha m} \delta_{\alpha m, jn} + (1 - \delta_{\alpha j}) e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_\alpha)} V_{\alpha m, jn} \quad (\text{A.12})$$

$$V_{\alpha m, jn} = \int \phi_{\alpha m}^*(\mathbf{r} - \mathbf{R}_\alpha) V_j(\mathbf{r} - \mathbf{R}_j) \phi_{jn}(\mathbf{r} - \mathbf{R}_j) d\tau. \quad (\text{A.13})$$

Here, $V_{\alpha m, jn}$ is called a two-center integral. This integral is able to be decomposed to the components of inter-atomic $\sigma, \pi, \delta \dots$ bonds, and the tight-binding model within a two-center approximation is parameterized by the strength of this inter-atomic interaction and the energy of atomic orbitals [4]. The parameter set of two-center integrals for Si used in this study was taken from Ref. 3.

From the above calculation, the matrix elements of the Hamiltonian were obtained. By applying Rayleigh-Ritz theorem, the energy levels at a wavevector $\mathbf{k}$ are given by the eigenvalues of the Hamiltonian matrix $[H_{\alpha m, \beta n}(\mathbf{k})]$, and the coefficient vector $c_{\alpha n}(\mathbf{k})$ is obtained as the eigenvector. Therefore, the band structure in a whole Brillouin zone can be calculated by constructing the Hamiltonian matrix for each $\mathbf{k}$ and solving the eigenproblem. In this study, ARPACK (Arnoldi Package) [5] was used for an eigenproblem solver combined with PARDISO [6] sparse linear solver to obtain eigenvalues around the band-edge.

A.2 Spin-Orbit Coupling in Tight-Binding Model

Since the valence band of a semiconductor which is formed by covalent bonds of sp^3 hybridized orbitals is almost composed of p orbitals, it is strongly influenced by spin-orbit (SO) coupling. The valence band of bulk Si, for example, has four-fold (or two doubly degenerated) heavy hole (HH) states and doubly degenerated light hole (LH) states if SO coupling is neglected. Actually, by taking the SO coupling into account, the valence band

is formed by HH, LH, and split-off hole (SOH) states (all of them are doubly degenerated). In nanostructures such as NWs, HH, LH, and SOH states mix with each other and they become indistinctive. Even in this case, however, the SO coupling has to be considered for accurate band calculation. Therefore, the method to consider the SO coupling in the tight-binding method with the two-center approximation described in Section A.1 is given in this section based on the formulation given by Chadi [7].

The s orbital states are not influenced by the SO coupling, In addition, the SO coupling in d orbitals hardly affects the valence band. Therefore, the SO coupling only in p orbital states is considered. Then, the Hamiltonian of SO coupling is given by

$$H^{(\text{SO})} = \frac{\hbar}{4m_0^2c^2} \left\{ \nabla \left[\sum_j^{\text{all atoms}} V_j(\mathbf{r}_j) \right] \times \mathbf{p} \right\} \cdot \boldsymbol{\sigma}, \quad (\text{A.14})$$

where c is the speed of light, $\mathbf{p}$ and $\boldsymbol{\sigma}$ are the momentum operator and Pauli spin matrices, respectively, and $\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$. Assume that the SO coupling does not arise between orbitals of different atoms but gives effects on orbitals of an identical atom, the Hamiltonian can be decomposed into parts for each atom. Define the Hamiltonian of the SO coupling in the atom j as $H_j^{(\text{SO})}$. Since the potential by atomic nucleus is a central field centered on the atom, the gradient of the potential can be rewritten as

$$\nabla V_j(\mathbf{r}_j) = \frac{1}{r_j} \frac{dV_j}{dr_j} \mathbf{r}_j. \quad (\text{A.15})$$

Thus, using the angular orbital momentum operator (centered on the atom position $\mathbf{R}_j$) $\mathbf{L}_j = \mathbf{r}_j \times \mathbf{p}$ and spin operator $\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$, the SO Hamiltonian becomes

$$H_j^{(\text{SO})} = \frac{1}{2m_0^2c^2} \left(\frac{1}{r_j} \frac{dV_j}{dr_j} \right) \mathbf{L}_j \cdot \mathbf{S} \equiv f_j(r_j) \mathbf{L}_j \cdot \mathbf{S}. \quad (\text{A.16})$$

Here, $\mathbf{L}_j \cdot \mathbf{S}$ is able to be diagonalized by the basis functions of the resultant angular momentum $\mathbf{J}$ of L - S coupling $\mathbf{J} = \mathbf{L}_j + \mathbf{S}$. Since now p orbitals are considered, $L_j = 1$ and $S = 1/2$, that is, $J = 3/2$ or $J = 1/2$. Write the eigenstate of the angular momentum J with the magnetic quantum number m_J as $|J, m_J\rangle$, then the basis set

$$\left\{ \left| \frac{3}{2}, \frac{3}{2} \right\rangle, \left| \frac{3}{2}, \frac{1}{2} \right\rangle, \left| \frac{3}{2}, -\frac{1}{2} \right\rangle, \left| \frac{3}{2}, -\frac{3}{2} \right\rangle, \left| \frac{1}{2}, \frac{1}{2} \right\rangle, \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right\} \quad (\text{A.17})$$

diagonalizes the matrix element of $H_j^{(\text{SO})}$ as

$$\left[H_j^{(\text{SO})} \right]_J = \begin{bmatrix} \lambda_j & & & & & \\ & \lambda_j & & & & \\ & & \lambda_j & & & \\ & & & \lambda_j & & \\ & & & & -2\lambda_j & \\ & & & & & -2\lambda_j \end{bmatrix}, \quad (\text{A.18})$$

where $2\lambda_j \equiv \langle J, m_J | f_j(r_j) | J, m_J \rangle$. By applying a unitary transform from the basis set of Eq. (A.17) to the p -orbital subset

$$\{|p_x \uparrow\rangle, |p_y \uparrow\rangle, |p_z \uparrow\rangle, |p_x \downarrow\rangle, |p_y \downarrow\rangle, |p_z \downarrow\rangle\} \quad (\text{A.19})$$

of the basis $\mathcal{B}$, the matrix elements of $H_j^{(\text{SO})}$ expanded by the basis Eq. (A.19) are obtained as

$$\left[H_j^{(\text{SO})} \right] = \begin{bmatrix} 0 & -i\lambda_j & & & & \lambda_j \\ i\lambda_j & 0 & & & & -i\lambda_j \\ & & 0 & -\lambda_j & i\lambda_j & \\ & & -\lambda_j & 0 & i\lambda_j & \\ & & -i\lambda_j & -i\lambda_j & 0 & \\ \lambda_j & i\lambda_j & & & & \end{bmatrix}. \quad (\text{A.20})$$

The matrix elements which correspond to the other orbitals (s , d , s^*) are zero. By solving the eigenproblem of the Hamiltonian $[H_{\alpha m, \beta n}(\mathbf{k})] + [H^{(\text{SO})}]$, the SO coupling can be taken into account in the band structure.

A.3 Termination of Dangling Bonds on Nanowire Surface

In calculation of Si NWs, surface dangling bonds have to be passivated to remove unphysical surface states. Hydrogen termination is one of the most simple and common treatment for calculation of Si nanostructures. However, explicit hydrogen termination increases the number of atoms in the crystal structure and this results in the increase of the computation time. Furthermore, the determination of appropriate Si–H bonding parameters is also a difficult problem. To avoid these difficulties, an energy-termination method in which an electron prohibited from occupying a surface sp^3 -hybridized dangling bond by giving a certain energy to the bond and forming a potential barrier to the orbital [8] is used in tight-binding approximations. Since the bond angle of sp^3 -hybridized orbitals is not altered, this method is expected to have a similar effect to the explicit hydrogen termination. In this study, the energy-termination method was adopted for the calculation of NWs. In this method, the contribution of s^* and d orbitals to dangling bonds is neglected because of their small effects.

The diamond lattice (the crystal structure of Si) has two atomic sites, cation sites $\mathbf{r}_c = (-a_0/8 + (u + v)a_0/2, -a_0/8 + (w + u)a_0/2, -a_0/8 + (v + w)a_0/2)$ and anion sites $\mathbf{r}_a = (a_0/8 + (u + v)a_0/2, a_0/8 + (w + u)a_0/2, a_0/8 + (v + w)a_0/2)$ (a_0 : lattice constant, u, v, w : integers). The sp^3 hybridized orbitals at each site $[\phi_c^{sp^3}(\mathbf{r}_c)]$ and $\phi_a^{sp^3}(\mathbf{r}_a)$ for the

cation and anion sites, respectively] are

$$\begin{cases} 2\phi_{c[111]}^{sp^3}(\mathbf{r}_c) = \phi_{cs}(\mathbf{r}_c) + \phi_{cx}(\mathbf{r}_c) + \phi_{cy}(\mathbf{r}_c) + \phi_{cz}(\mathbf{r}_c), & (\text{A.21a}) \\ 2\phi_{c[\bar{1}\bar{1}\bar{1}]}^{sp^3}(\mathbf{r}_c) = \phi_{cs}(\mathbf{r}_c) - \phi_{cx}(\mathbf{r}_c) - \phi_{cy}(\mathbf{r}_c) + \phi_{cz}(\mathbf{r}_c), & (\text{A.21b}) \\ 2\phi_{c[\bar{1}\bar{1}1]}^{sp^3}(\mathbf{r}_c) = \phi_{cs}(\mathbf{r}_c) - \phi_{cx}(\mathbf{r}_c) + \phi_{cy}(\mathbf{r}_c) - \phi_{cz}(\mathbf{r}_c), & (\text{A.21c}) \\ 2\phi_{c[1\bar{1}\bar{1}]}^{sp^3}(\mathbf{r}_c) = \phi_{cs}(\mathbf{r}_c) + \phi_{cx}(\mathbf{r}_c) - \phi_{cy}(\mathbf{r}_c) - \phi_{cz}(\mathbf{r}_c), & (\text{A.21d}) \end{cases}$$

and

$$\begin{cases} 2\phi_{a[\bar{1}\bar{1}\bar{1}]}^{sp^3}(\mathbf{r}_a) = \phi_{as}(\mathbf{r}_a) - \phi_{ax}(\mathbf{r}_a) - \phi_{ay}(\mathbf{r}_a) - \phi_{az}(\mathbf{r}_a), & (\text{A.22a}) \\ 2\phi_{a[111]}^{sp^3}(\mathbf{r}_a) = \phi_{as}(\mathbf{r}_a) + \phi_{ax}(\mathbf{r}_a) + \phi_{ay}(\mathbf{r}_a) - \phi_{az}(\mathbf{r}_a), & (\text{A.22b}) \\ 2\phi_{a[\bar{1}\bar{1}1]}^{sp^3}(\mathbf{r}_a) = \phi_{as}(\mathbf{r}_a) + \phi_{ax}(\mathbf{r}_a) - \phi_{ay}(\mathbf{r}_a) + \phi_{az}(\mathbf{r}_a), & (\text{A.22c}) \\ 2\phi_{a[1\bar{1}\bar{1}]}^{sp^3}(\mathbf{r}_a) = \phi_{as}(\mathbf{r}_a) - \phi_{ax}(\mathbf{r}_a) + \phi_{ay}(\mathbf{r}_a) + \phi_{az}(\mathbf{r}_a). & (\text{A.22d}) \end{cases}$$

Thus, the unitary matrix $U_c^{sp^3}$ that transforms from the basis set of non-hybridized orbitals $\{\phi_{cs}, \phi_{cx}, \phi_{cy}, \phi_{cz}\}$ to hybridized ones $\{\phi_{c[111]}^{sp^3}, \phi_{c[\bar{1}\bar{1}\bar{1}]}^{sp^3}, \phi_{c[\bar{1}\bar{1}1]}^{sp^3}, \phi_{c[1\bar{1}\bar{1}]}^{sp^3}\}$ is given by

$$U_c^{sp^3} = \frac{1}{2} \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \end{bmatrix} \quad (\text{A.23})$$

for a cation site. The unitary matrix at an anion site can be defined in the similar way. Define $\theta_{c[111]}^{sp^3}$, $\theta_{c[\bar{1}\bar{1}\bar{1}]}^{sp^3}$, $\theta_{c[\bar{1}\bar{1}1]}^{sp^3}$ and $\theta_{c[1\bar{1}\bar{1}]}^{sp^3}$ as parameters which describe whether the sp^3 -hybridized bonds elongated to $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}\bar{1}1]$, and $[1\bar{1}\bar{1}]$ are a dangling bond ($\theta = 1$) or not ($\theta = 0$), respectively. The passivation of a sp^3 dangling bond is realized by giving the energy ϵ_{sp^3} to the bond. In the tight-binding Hamiltonian, the on-site elements of $\{s, p_x, p_y, p_z\}$ of the atom c are given by

$$[H]_{c,xyz}^{(\text{on-site})} = \begin{bmatrix} E_{cs} & & & \\ & E_{cp} & & \\ & & E_{cp} & \\ & & & E_{cp} \end{bmatrix}. \quad (\text{A.24})$$

This matrix is transformed into the representation on the sp^3 -hybridized basis by the following unitary transformation

$$[H]_{c,sp^3}^{(\text{on-site})} = U_c^{sp^3\dagger} [H]_{c,xyz}^{(\text{on-site})} U_c^{sp^3}. \quad (\text{A.25})$$

In this representation, the passivation energy is given to the dangling bonds.

$$[H]_{c,sp^3}^{(\text{on-site, passivated})} = U_c^{sp^3\dagger} [H]_{c,xyz}^{(\text{on-site})} U_c^{sp^3} + \epsilon_{sp^3} \begin{bmatrix} \theta_{c[111]}^{sp^3} & & & \\ & \theta_{c[\bar{1}\bar{1}\bar{1}]}^{sp^3} & & \\ & & \theta_{c[\bar{1}\bar{1}1]}^{sp^3} & \\ & & & \theta_{c[1\bar{1}\bar{1}]}^{sp^3} \end{bmatrix}. \quad (\text{A.26})$$

Again, the representation of the matrix is moved back to the basis $\{s, p_x, p_y, p_z\}$ and then the passivated on-site Hamiltonian matrix elements are obtained.

$$\begin{aligned}
[H]_{c,xyz}^{(\text{on-site, passivated})} &= U_c^{sp^3} [H]_{c,sp^3}^{(\text{on-site, passivated})} U_c^{sp^3\dagger} \\
&= U_c^{sp^3} U_c^{sp^3\dagger} [H]_{c,xyz}^{(\text{on-site})} U_c^{sp^3} U_c^{sp^3\dagger} + \epsilon_{sp^3} U_c^{sp^3} \begin{bmatrix} \theta_{c[111]}^{sp^3} & & & \\ & \theta_{c[\bar{1}\bar{1}1]}^{sp^3} & & \\ & & \theta_{c[\bar{1}1\bar{1}]}^{sp^3} & \\ & & & \theta_{c[1\bar{1}\bar{1}]}^{sp^3} \end{bmatrix} U_c^{sp^3\dagger} \\
&= [H]_{c,xyz}^{(\text{on-site})} + \epsilon_{sp^3} U_c^{sp^3} \begin{bmatrix} \theta_{c[111]}^{sp^3} & & & \\ & \theta_{c[\bar{1}\bar{1}1]}^{sp^3} & & \\ & & \theta_{c[\bar{1}1\bar{1}]}^{sp^3} & \\ & & & \theta_{c[1\bar{1}\bar{1}]}^{sp^3} \end{bmatrix} U_c^{sp^3\dagger} \quad (\text{A.27})
\end{aligned}$$

The dangling bonds at anion sites are passivated in the same way. By applying above operations to all of surface atoms which have dangling bonds, the completely passivated Hamiltonian matrix is obtained. In this study, $\epsilon_{sp^3} = 30$ eV was used.

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Appendix B

Fabrication Process of Si Nanowire MOSFETs

This appendix describes the detailed fabrication process of Si nanowire (NW) MOSFETs. The basic and important ideas of fabrication process are given in Chapter 7 (see Sec. 7.2.3). In this study, two types of devices, referred as “dual MOSFETs” [Fig. 7.1(a)] and “multi-NW MOSFETs” [Fig. 7.1(b)], were fabricated on (110) silicon-on-insulator (SOI) with different Si thicknesses. The dual MOSFETs (fabricated on 42-nm-thick SOI) have both n^+ and p^+ regions in source and drain with a single Si NW channel. These devices were used for the measurement of transconductance oscillations at low temperatures (Sec. 7.3). The multi-NW MOSFETs (fabricated on 33-nm-thick SOI) have parallel 750 Si NWs in a channel. These devices were used for hole mobility measurement. The time of the thermal oxidation and reactive ion etching and the ion implantation dose were adjusted for each device. Here lists the fabrication sequence of these devices. If not otherwise specified, the processes are common in both types of the devices. The starting Si/buried oxide (BOX) thicknesses of (110)SOI wafers are 100 nm/200 nm, and the detailed specifications are given in Table 3.1.

1. Cutout of 20 mm square chips from SOI wafers

- (1) photoresist spincoat (surface protection)
- (2) wafer dicing
- (3) resist removal (acetone/SPM/DHF)

2. SOI thinning oxidation

- (1) cleaning (SPM/DHF/SPM/DHF/SC-1/DHF/SC-2/DHF)
- (2) thermal oxidation (100% O_2 , 1150°C, 27.5 min)
- (3) spectroscopic ellipsometry (SiO_2 /Si thicknesses)
 - 117–118 nm/41–42 nm

3. Additional SOI thinning oxidation (for Multi-NW MOSFETs only)

- (1) cleaning (SC-1)
- (2) SiO₂ etching (BHF 3 min, 105-nm-deep etching of 117–118-nm-thick SiO₂)
- (3) cleaning (SC-1/SC-2)
- (4) SiO₂ complete etching (DHF)
- (5) thermal oxidation (100% O₂, 1000°C, 3 min)
- (6) spectroscopic ellipsometry (SiO₂/Si thicknesses)
 - 15 nm/33–34 nm

4. Alignment mark formation

- (1) SiO₂ etching and cleaning (SC-1/BHF/SPM)
- (2) alignment mark photolithography (AZ5218E 2.2 μm)
- (3) RIE [CF₄, 16 sccm, 1.0 Pa, 16 W (0.40 W/cm²), 42 min, 0.55 μm]
- (4) resist removal (SPM)

5. Device isolation

- (1) isolation photolithography (AZ5218E 2.2 μm)
- (2) surface oxide etching (BHF 30 sec)
- (3) ICP-RIE Si/SiO₂ selective etching (ICP 100 W, Bias 7.0 W, Cl₂ 5.0 sccm, 0.10 Pa, ~ 25 nm/min)
 - Dual MOSFETs: 3 min 15 sec
 - Multi-NW MOSFETs: 2 min 40 sec
- (4) resist removal and cleaning (hot H₂SO₄/SPM)

6. Nanowire definition (hybrid lithography technique)

- (1) cleaning (SPM/SC-1/SC-2)
- (2) SiO₂ hard mask growth by thermal oxidation (100% O₂, 1000°C, 1 min)
- (3) spectroscopic ellipsometry (SiO₂/Si thicknesses)
 - Dual MOSFETs: 8.7–8.8 nm/37–38 nm
 - Multi-NW MOSFETs: 8.7–8.8 nm/26–27 nm
- (4) active area definition EB lithography (ZEP520A 110 nm, 100 kV, 100 pA, 180 $\mu\text{C}/\text{cm}^2$)
- (5) active area opening SiO₂ etching (BHF 30 sec)

- (6) resist removal (N-methylpyrrolidone/SC-1)
 - (7) nanowire EB lithography (Espacer 300HX-02 40 nm/HSQ 50 nm, 100 kV, 100 pA, 1800 $\mu\text{C}/\text{cm}^2$, development 50 sec)
 - (8) ICP-RIE Si etching (ICP 100 W, Cl_2 5.0 sccm, 0.10 Pa)
 - step 1. Bias 7 W, 30 sec (surface chemical oxide etching)
 - step 2. Bias 4.5 W (main etching: ~ 22 nm/min)
 - Dual MOSFETs: 3 min 15 sec
 - Multi-NW MOSFETs: 2 min 30 sec
 - (9) resist removal and cleaning (hot H_2SO_4 /SPM/SC-1)
7. Nanowire sacrificial oxidation
- (1) cleaning (SPM/SC-1/SC-2)
 - (2) thermal oxidation (10% O_2/N_2 , 1000°C, 30 min)
[SiO_2 thickness on bulk Si: (100) 10.8 nm, (110) 14.9 nm, (111) 12.8 nm]
 - (3) spectroscopic ellipsometry (SiO_2/Si thicknesses)
 - Dual MOSFETs: 14 nm/27 nm
 - Multi-NW MOSFETs: 15 nm/17 nm
8. Cleaning and NW release before hydrogen annealing
- (1) cleaning (SPM/SC-1/SC-2)
 - (2) sacrificial oxide and buried oxide etching (47% HF : 35% HCl = 1 : 100 12 min, 110 nm)
 - (3) HCl rinse (35% HCl, ~ 10 sec)
9. Surface-smoothing hydrogen annealing (H_2 11 slm, 810°C, 75 Torr, 2 min)
10. Gate oxidation
- thermal oxidation (2.5% O_2/N_2 , 1100°C)
 - Dual MOSFETs (thick gate oxide): 35 min
[SiO_2 thickness on bulk Si: (100) 14.3 nm, (110) 16.2 nm, (111) 13.5 nm]
 - Multi-NW MOSFETs (thin gate oxide) : 10 min
[SiO_2 thickness on bulk Si: (100) 8.6 nm, (110) 10.4 nm, (111) 8.2 nm]
11. Poly-Si deposition/doping
- (1) 210-nm-thick (on an average) undoped poly-Si deposition (LPCVD, 20% SiH_4/N_2 50 sccm, 580°C, 40 Pa, 31 min)

- (2) cleaning (SC-1)
- (3) $^{49}\text{BF}_2^+$ ion implantation (15 keV, $4.0 \times 10^{15} \text{ cm}^{-2}$, tilt angle 7°)

12. Poly-Si gate pattern formation

- (1) cleaning (SPM)
- (2) gate pattern photolithography (AZ5218E $2.2 \mu\text{m}$)
- (3) surface oxide etching (BHF 15 sec)
- (4) ICP-RIE poly-Si gate etching (ICP 100 W, Cl_2 5.0 sccm, 0.10 Pa)
 - step 1. Bias 30 W, 2 min (main etching 1: $\sim 47 \text{ nm/min}$)
 - step 2. Bias 7 W, 2.5 min (main etching 2: $\sim 25 \text{ nm/min}$)
 - step 3. Bias 4.5 W, 7 min (landing and overetching: $\sim 22 \text{ nm/min}$)
- (5) resist removal and cleaning (MIBK/SPM)
- (6) spectroscopic ellipsometry (SiO_2/Si thicknesses) (corresponding to the source/drain thickness)
 - Dual MOSFETs: 12–13 nm/20 nm
 - Multi-NW MOSFETs: 7–8 nm/13 nm

13. Source/drain implantation

- (1) source/drain p^+ photolithography (AZ5218E $2.2 \mu\text{m}$)
- (2) $^{49}\text{BF}_2^+$ ion implantation (15 keV, tilt angle 0°)
 - implantation dose/average B concentration in Si
 - Dual MOSFETs: $3.0 \times 10^{14} \text{ cm}^{-2}/8.8 \times 10^{19} \text{ cm}^{-3}$
 - Multi-NW MOSFETs: $2.5 \times 10^{14} \text{ cm}^{-2}/9.7 \times 10^{19} \text{ cm}^{-3}$
- (3) resist removal (acetone/SPM)
- (4) source/drain n^+ photolithography (AZ5218E $2.2 \mu\text{m}$)
- (5) As^+ ion implantation (15 keV, tilt angle 0°)
 - implantation dose/average As concentration in Si
 - Dual MOSFETs: $2.5 \times 10^{14} \text{ cm}^{-2}/9.6 \times 10^{19} \text{ cm}^{-3}$
 - Multi-NW MOSFETs: $2.0 \times 10^{14} \text{ cm}^{-2}/1.1 \times 10^{20} \text{ cm}^{-3}$
- (6) resist removal (acetone/SPM)

14. Dopant diffusion/activation and forming gas annealing

- (1) cleaning (SC-2)

- (2) 90-nm-thick capping SiO₂ deposition
(PECVD, 400°C, TEOS/O₂=0.3 sccm/300 sccm, 100 W, 28 Pa, 38 min)
- (3) dopant diffusion/activation annealing (RTA, N₂ 0.5 slm, 1050°C, 25 sec)
- (4) forming gas annealing (RTA, 10% H₂/N₂ 600 sccm, 450°C, 30 min)

15. Metalization

- (1) contact hole photolithography (AZ5218E 2.2 μm)
- (2) contact hole etching (BHF 3.5 min)
- (3) resist removal (acetone/SPM)
- (4) metal pattern photolithography (AZ5218E 2.2 μm)
- (5) surface oxide etching (BHF 15 sec)
- (6) metal deposition [vacuum deposition, Al(300 nm)/Ti(13 nm)(/Si)]
- (7) lift-off (N-methylpyrrolidone)
- (8) contact annealing (RTA, 10% H₂/N₂ 600 sccm, 350°C, 10 min)

List of Publications

A. Full Length Papers

1. N. Morioka, H. Yoshioka, J. Suda, and T. Kimoto,
“Quantum-confinement effect on holes in silicon nanowires: Relationship between wave function and band structure,”
Journal of Applied Physics **109**, 064318 (2011).
2. N. Morioka, J. Suda, and T. Kimoto,
“Etching-limiting process and origin of loading effects in silicon etching with hydrogen chloride gas,”
Japanese Journal of Applied Physics **53**, 016502 (2014).
3. N. Morioka, J. Suda, and T. Kimoto,
“Effects of pressure and anisotropic surface self-diffusion on wire stability in surface-smoothing hydrogen annealing of silicon nanowires,”
submitted to *Journal of Applied Physics*.
4. N. Morioka, J. Suda, and T. Kimoto,
“Inhibition of surface oxidation of hydrogen-terminated Si surface in rinse process after hydrofluoric acid treatment using low-pH hydrochloric acid rinse,”
in preparation.
5. N. Morioka, J. Suda, and T. Kimoto,
“Comparative study of subband effect on electron and hole transport characteristics in identical single silicon nanowire,”
in preparation.

B. International Conferences

1. N. Morioka, H. Yoshioka, J. Suda, and T. Kimoto,
“Tight-Binding Study of Size and Geometric Effects on Hole Effective Mass of Silicon Nanowires,”
2010 Silicon Nanoelectronics Workshop, Honolulu, USA, June 2010, P1-18.

2. N. Morioka, J. Suda, and T. Kimoto,
 “Rate Determining Process and Loading Effects in Si Etching with HCl Gas,”
2012 International Conference on Solid-State Devices and Materials, Kyoto, Japan, September 2012, PS-1-14.
3. N. Morioka, J. Suda, and T. Kimoto,
 “Anisotropy in Surface Self-Diffusion on Si Nanowires and Its Impact on Wire Instability in Hydrogen Annealing,”
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