

**A study of defect generation phenomena in single
crystalline silicon substrate during plasma processing and
the characterization techniques**

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Preface

The present research has been carried out during 5 years from 2007 to 2012 at Department of Aeronautics and Astronautics, Kyoto University.

This thesis focuses on a technological problem—"plasma process-induced damage"—in the present-day Si-based semiconductor manufacturing, which is caused by undesired physical interactions between plasma and Si substrate surface. With the aggressive scaling of semiconductor devices, defect creation in single crystalline Si substrate by energetic ion bombardment has been recognized as one of the critical issues which degrade the performance of advanced metal–oxide–semiconductor devices. To solve this issue, quantitative evaluation and understanding of the damage is required. In this thesis, a methodology quantifying the damage creation mechanisms and the damage structures was studied.

In Chapter I, a brief historical review of metal–oxide–semiconductor field-effect transistors is given, and then, explanation of conventional plasma etching and plasma process-induced damage mechanisms is provided. In Chapter II, plasma reactors, sample treatments, and evaluation techniques are given. In Chapter III, effects of superposed bias frequency—recently regarded as one of promising techniques to improve plasma etch performance—on the damage are examined. In Chapter IV, the damaged structures are investigated from a viewpoint of plasma parameters and the detection limit of analysis techniques. In Chapters V and VI, effects of gas chemistries such as O₂- and H₂-containing processes on the damage creation are provided, including discussions on possible damaged layer removal by wet-stripping processes widely employed in mass production lines. The conclusion remarks are given in Chapter VII, with a summary of this research and remaining issues to be solved in the future.

In the course of finishing this thesis, I have been encouraged by many people. Firstly, I would like to appreciate Prof. Kouichi Ono for giving me the opportunity to perform this

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Symbols

A^*	modified Richardson constant
a_{Si}	lattice constant of Si
C	amplitude of spectrum
C_{dam}	material-dependent constant
C_{inv}	measured differential capacitance in inversion [F/cm^2]
C_{ox}	differential SiO_2 capacitance [F/cm^2]
C_{m}	measured differential capacitance [F/cm^2]
C_{SL}	differential capacitance of a surface layer [F/cm^2]
$d_{\text{CCP}}, d_{\text{ICP}}$	thickness of a damaged layer by CCP, or ICP, respectively [nm]
d_{dam}	thickness of a damaged layer [nm]
d_{IL}	thickness of an interfacial layer [nm]
d_{ox}	thickness of a gate oxide layer [nm]
d_{R}	Si recess depth [nm]
d_{SiO_2}	thickness of SiO_2 layer [nm]
d_{SL}	thickness of a surface layer [nm]
e, q	elementary charge ($= 1.602 \times 10^{-19} \text{ C}$)
E	photon energy [eV] or energy in band diagram [eV]
E_{C}	energy of the conduction band edge in silicon substrate [eV]
E_{F}	Fermi level of silicon substrate [eV]
E_{F}^{Hg}	Fermi level of mercury (Hg) electrode [eV]
$E_{\text{F}}^{\text{n-Si}}$	Fermi level of n-type Si substrate [eV]
E_{g}	transition energy [eV]
E_{ion}	energy of incident ion [eV]
E_{trap}	energy level of carrier trapping [eV]
E_{V}	energy of the valence band edge in silicon substrate [eV]
$\bar{E}_{\text{ion}}$	the average energy of incident ions [eV]
$f_{\text{c-Si}}$	volume fraction of crystalline silicon
f_{SiO_2}	volume fraction of SiO_2
$f_1, f_2, f_{\text{bias}}$	frequency of power supply [Hz]
h	Planck's constant ($= 6.626 \times 10^{-34} \text{ J/s}$)
i	imaginary unit
$I_{\text{ds}}, I_{\text{on}}$	drain current or on-state current [$\text{A}/\mu\text{m}$]
I_{off}	leakage current or off-state current [$\text{A}/\mu\text{m}$]
I_{p}	laser power [mW]
J_{DT}	direct tunneling current [A]
J_{FN}	Fowler–Nordheim tunneling current [A]

J_0	dark current density [A/m^2]
J_{pc}	photoinduced current density [A/m^2]
$\mathbf{k}$	wave vector
k, k_{B}	Boltzmann constant ($= 1.3807 \times 10^{-23} \text{ J/K} = 1/11605 \text{ eV/K}$)
L_{d}	diffusion length of the minority carriers [nm]
L_{g}	gate length [nm]
m	mass of atom
M_1	mass of projectile atom
M_2	mass of target atom
n	dimensionality of interband critical point
n_{cr}	critical defect density detectable
n_{dam}^0	initial defect density [cm^{-3}]
n_{dam}	density of defects [cm^{-3}]
n_0	atomic density of the target [cm^{-3}] (<i>e.g.</i> , $5 \times 10^{22} \text{ cm}^{-3}$ for silicon)
n_0^{CCP}	initial defect density by CCP-reactor [cm^{-3}]
n_0^{ICP}	initial defect density by ICP-reactor [cm^{-3}]
n_{e}	electron density in plasma [cm^{-3}]
n_{ion}	ion concentration in a target material [cm^{-3}]
n_{p}	plasma density [cm^{-3}]
N_{D}	impurity doping concentration [cm^{-3}]
N_{dam}	areal density of defects [cm^{-2}]
N_{ion}	amount of ions injected into a target from plasma [cm^{-2}]
p	vertical component of polarized light or impact parameter in two-body collision
R	reflectance
R_{Cont}	reflectance at the surface of "control" Si substrate
R_{dam}	reflectance at the surface of "damaged" Si substrate
R_{ion}	total distance that an ion travels in a target material [nm]
R_{p}	projection range [nm]
$R_{\text{p}}^{\text{CCP}}$	projection range of ions in CCP-damaged sample [nm]
$R_{\text{p}}^{\text{ICP}}$	projection range of ions in ICP-damaged sample [nm]
s	horizontal component of polarized light
S_{d}	nuclear stopping power
t_{proc}	process duration [s]
T	energy transferred to the target atom
T_{SiO_2}	thickness of thermal SiO_2 layer [nm]
T_{sub}	Si substrate temperature during an electrical measurement [K]

T_e	electron temperature in plasma in units of volts [V]
u_B	Bohm velocity [m/s]
V_b	bias voltage [V]
V_{ds}	drain voltage [V]
V_{dc}	self-dc bias voltage in plasma processing [V]
V_g	gate voltage [V]
V_m^{dam}	surface voltage of a sample after plasma exposure [V]
V_m^{ref}	surface voltage of a sample before plasma exposure [V]
V_p	plasma potential [V]
V_{pp}	peak-to-peak voltage [V]
V_s^{dam}	substrate voltage of damaged Si substrate [V]
V_s^{ref}	substrate voltage of reference Si substrate [V]
V_s	surface voltage [V]
V_{sub}	substrate voltage [V]
V_{th}	threshold voltage [V]
w	depletion width [nm]
α	power-law component
α_{ab}	absorption coefficient
ϵ_0	permittivity of vacuum ($= 8.85 \times 10^{-12}$ F/m)
ϵ_{Si}	relative permittivity of silicon ($= 11.7$)
ϵ_{ox}	dielectric constant of gate oxide (SiO ₂) ($= 3.9$)
ΔC_{max}	maximum differential capacitance [F]
ΔE_g	transition energy shift [eV]
ΔR	reflectance change
ΔV_b	bias voltage shift [V]
ΔV_m^{dam}	surface voltage change under photo-modulation [V]
ΔV_m^{ref}	surface voltage change under photo-modulation [V]
ΔV_s	surface voltage change [V]
ΔV_{th}	threshold voltage shift [V]
γ	quantum efficiency or material-dependent constant
γ_{proc}	process-dependent correction factor
Γ	broadening parameter [eV]
Γ^{CCP}	ion flux from CCP-plasma [$\text{cm}^{-2}\text{s}^{-1}$]
Γ^{ICP}	ion flux from ICP-plasma [$\text{cm}^{-2}\text{s}^{-1}$]
Γ_{ion}	ion flux from plasma [$\text{cm}^{-2}\text{s}^{-1}$]
η	ideal factor / ideality factor
θ	phase factor
κ	extinction coefficient

$\langle K \rangle$	pseudo-extinction coefficient
$\mu_{\parallel}$	interband reduced mass
ν	frequency of light [Hz]
ρ	area factor
ρ_{IL}	volume densities of the carrier trap sites in IL
ρ_{SL}	volume densities of the carrier trap sites in SL
σ_{p}	straggling
σ_{SE}	unbiased estimator in spectroscopic ellipsometry

Abbreviations

BHF	buffered hydrofluoric acid
CCP	capacitively-coupled plasma
CPU	central processing unit
CV, $C-V$	capacitance–voltage characteristics or capacitance–voltage measurement
DC	direct current
DHF	diluted hydrofluoric acid
DL	damaged layer
DRAM	dynamic random access memory
ECR	electron cyclotron resonance
EMA	effective medium approximation
EOT	electrical oxide thickness
FD	fully-depleted
HF	hydrofluoric acid
HRBS	high-resolution Rutherford backscattering spectroscopy
IR	infrared ray
GP-IB	general purpose interface bus
HP	high performance
ICP	inductively-coupled plasma
IEDF	ion energy distribution function
IL	interfacial layer
ILD	inter-layer dielectric
IR	infrared radiation
IV, $I-V$	current–voltage characteristics or current–voltage measurement
LCR	inductance-capacitance-resistance
LOP	low operation power
LSP	low standby power
MD	molecular dynamics
MFC	mass flow controller
MG	metal-gate
MOS, MOSFET	metal–oxide–semiconductor (field-effect transistor)
MPU	micro-processing unit
OP	original plane
PID	plasma process-induced damage
PMD	pre-metal dielectric
PPD	plasma-induced physical damage
PR, PRS	photorefectance spectroscopy

QMS	quadrupole mass spectrometers
RBS	Rutherford backscattering spectroscopy
rf, RF	radio frequency
RIE	reactive ion etching
RP	rotary vacuum pump
RTA	rapid thermal annealing
SE	spectroscopic ellipsometry
SIMS	secondary ion mass spectroscopy
SL	surface layer
SMA	sub-miniature type A
STI	shallow trench isolation
sub, Sub	substrate
TCAD	Technology-Computer Aided Design
TDS	thermal desorption spectrometer
TEG	test elementary group
TEM	transmitted electron microscope
TMP	turbo-molecular pump
ULSI	ultra-large scale integration

Chapter I

General introduction

1.1 Metal–oxide–semiconductor field-effect transistors

In the present-day consumer electronics, metal–oxide–semiconductor field-effect transistors (MOSFETs) are the core of silicon-based ultra-large scale integration (ULSI) circuits.^{1,2)} The structure of MOSFET was first invented around the mid-20th Century³⁾ and opened the way to various electronic components such as micro-processing units (MPUs) and central processing unit (CPU). To meet an increasing demand for higher operation speed and larger integration in a single chip, the feature sizes of MOSFETs have been shrunk aggressively—the rule of this shrinkage is called "Moore's law"⁴⁾—as discussed extensively in microelectronic industries. Figure 1.1 shows the typical feature sizes in devices against the year of mass production. As seen, the size has exponentially decreased, and the characteristic gate length L_g —the principal parameter determining the performance—of current MOSFETs in mass productions is around 20–30 nm.⁵⁾ Figure 1.2 shows the operation scheme with gate bias application under drain bias. By changing the gate voltage (V_g) under a constant drain voltage (V_{ds}), the current (I_{ds}) passing through the region underneath a gate dielectric layer—called "channel"—varies exponentially, thus, the MOSFET accordingly functions as "on-state" or "off-state".⁶⁾ In this scheme, threshold voltage (V_{th}) is defined rigidly and used as a measure of the operation voltage. In terms of

ULSI circuit performance, I_{ds} primarily corresponds to the operation speed or the clock frequency, while V_{th} or the off-state current, to the power consumption. Various types of MOSFETs are now designed for specific purposes of electronic devices,^{2,5)} *i.e.*, low standby power (LSP), low operation power (LOP), and high performance (HP) operations, and built in ULSI circuits such as dynamic random access memory (DRAM) and MPU. New structured MOSFETs such as fully-depleted (FD) and metal-gate (MG) devices have been recently proposed.⁵⁾ Figure 1.3 illustrates one of significant material and structure transitions occurring in the recent MG technology.⁷⁾ This geometrical structure change has imposed a new precisely-controlled manufacturing technology in the mass production. Recently, the structure itself has become three dimensional^{8,9)} where an atomic-scale control in the manufacturing is required. According to "the international technology roadmap for semiconductors (ITRS)" by the Semiconductor Industry Association (SIA), the shrinkage of feature size will be expected to be kept, further accelerated, in harmony with the three-dimensional topological changing and chip-packaging. Therefore, development of process technologies enabling atomic-scale controls and understanding of physics behind the fabrication are indispensable to realize future scaled MOSFETs and novel electronic devices.

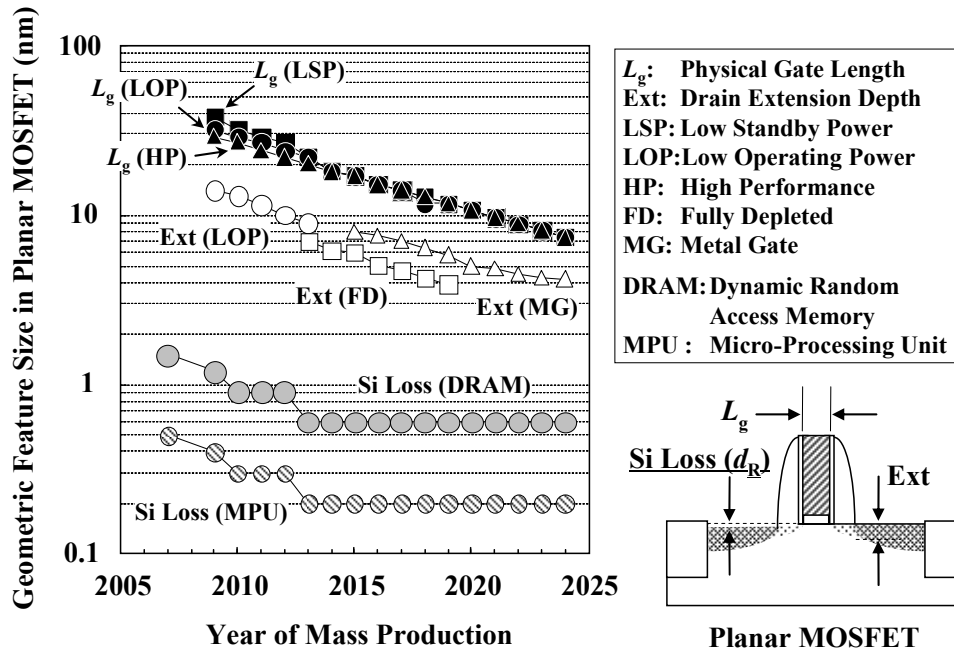


Figure 1.1: Scaling trend of feature sizes in a metal-oxide-semiconductor field-effect transistor (MOSFET) in an ultra-large-scale integration (ULSI) circuit.

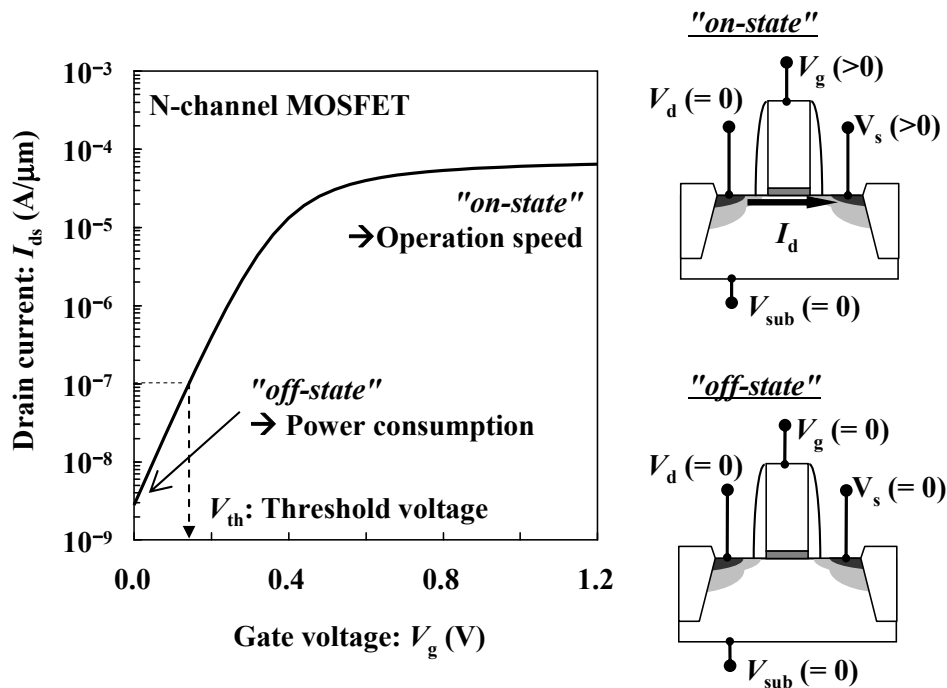


Figure 1.2: MOSFET operation scheme—"on-state" and "off-state" by gate voltage application under drain bias.

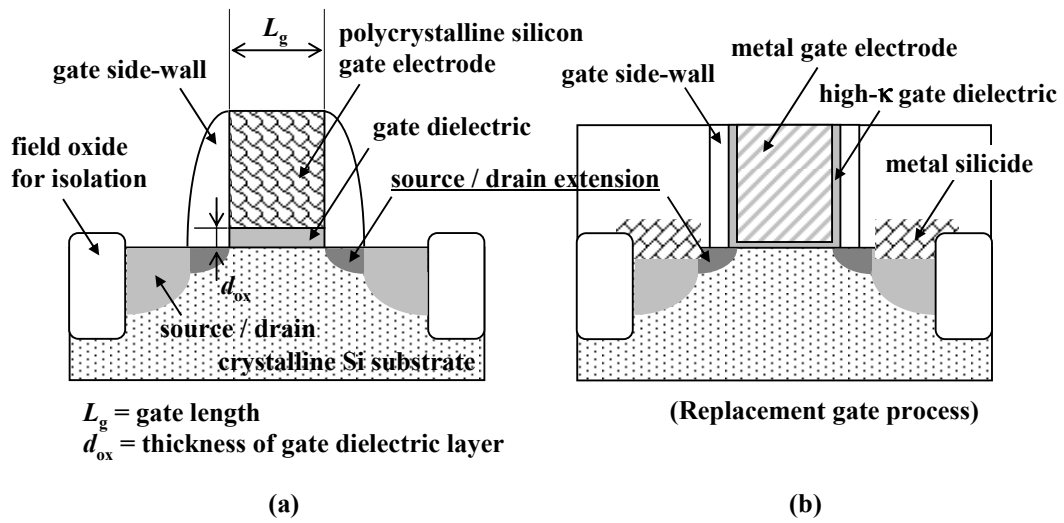


Figure 1.3: Transitions from (a) conventional to (b) replacement gate structures of MOSFETs. New materials such as metal gate electrode (MG) and high- κ gate dielectric layer (high- κ) are implemented in (b). (a) Conventional gate first process. (b) Replacement gate process with MG and high- κ .

1.2 Plasma etching and plasma process-induced damage

Plasma processing is now indispensable in various fields of industries such as microelectronics,¹⁰⁾ mechanical engineering,¹¹⁾ chemical and medical treatment,¹²⁾ and etc. In accordance with the scaling law of microelectronics, a decrease in the dimension of MOSFETs is required as shown in Fig. 1.1. Among manufacturing processes of MOSFETs in ULSI circuits, plasma etching is widely used for removal of materials from the surfaces. Figure 1.4 shows an example of a basic processing module—cleaning of a surface → deposition of a material → patterning by lithography → the pattern transfer by plasma etching—in the manufacturing steps of MOSFETs. The mask pattern should be faithfully transferred into the film in the process by plasma etching. To meet the requirements such as fabricating finer patterns with anisotropic features, at present, the control of the pattern transfer by plasma etching needs to be within the variation of a few nanometers.⁵⁾ In such regimes, the feature size of the region where plasma-etch reactions are occurring becomes no more negligible with respect to the scale of MOSFET. Thus, precise control of the surface reaction between plasma and device to be etched is strongly required.

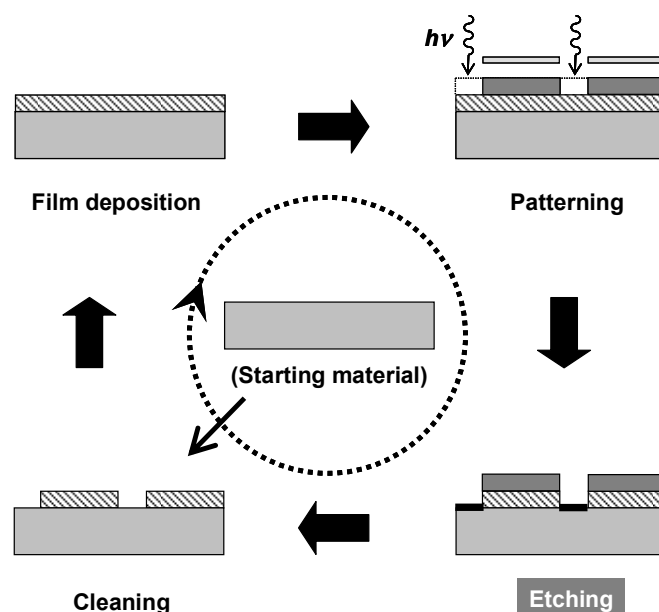


Figure 1.4: Typical device processing units in MOSFET fabrication.

Historically, the operating pressure has been decreased and the plasma density increased in advanced plasma etching.¹³⁾ The plasma etching systems with magnetically enhanced discharges, electron cyclotron resonance discharges, and inductive discharges are widely used for these purposes. In the case of an ICP (Inductively Coupled Plasma) system, the electron density (n_e) is of the order of 10^{11} cm^{-3} . In plasma etch process, radicals (atoms or molecules in an excited state) react with surface material with a help of the energy of incident ions accelerated in the "sheath" between plasma and device surface. This reaction mechanism is commonly referred to as "reactive ion etching (RIE)".^{13,14)} In some plasma etch processes, the energy of an ion becomes larger than 1 keV to obtain high etch rate. In such schemes, an unexpected reaction may occur. This unexpected ("unwanted") reaction mechanism is usually called as "plasma process-induced damage",^{13,15-17)} which has been bringing out many key problems in the development of scaled MOSFETs.

Plasma process-induced damage (PID) is regarded as one of the serious issues causing degradation of MOSFET performance and reliability. Figure 1.5 illustrates an example of PID in a typical plasma etch process. A Si wafer is placed on a wafer stage in a plasma chamber. Reactive plasma is generated by power supply. This figure corresponds to an ICP system, where powers with frequencies of f_1 and f_2 are supplied to a plasma source (f_1) and a wafer stage (f_2), respectively. During etching, MOSFET is exposed to the plasma and energetic ions from the plasma impact on the surface. This energetic ion bombardment results in creation of defects¹⁸⁻²⁰⁾ (ex. displaced Si atom, interstitial) in the Si surface region of MOSFET. This mechanism is one of examples of PID. Figure 1.5 also illustrates another PID mechanism indicated as "stress current". In the plasma etching, the gate oxide layer in MOSFETs (See Fig. 1.3) is subjected to an electrical stress induced by conduction current from the plasma.^{17,21)} This plasma-induced electric field could be larger than that under the device operation voltage, leading to generation of defects in the gate oxide, hence accelerating

the wear-out of the gate oxide, *i.e.*, shorten the lifetime of the gate oxide.

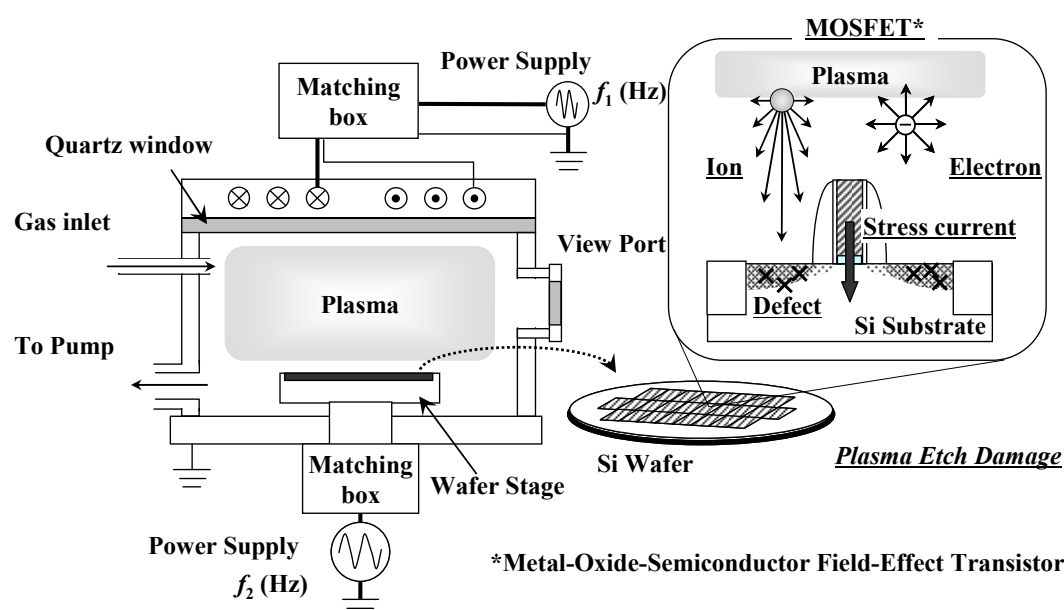


Figure 1.5: Typical plasma equipment and schematic view of plasma process-induced damage.

Figure 1.6 summarizes the PID mechanisms. PID consists of three major mechanisms, namely, charging damage, radiation damage, and physical damage.¹⁶⁾ Charging damage [(A) in Fig. 1.6]^{17,22-26)} is induced by conduction current from plasma flowing into MOSFETs, resulting in the degradation of performance by electrical stress as mentioned above. Radiation damage [(C) in Fig. 1.6]²⁷⁻²⁹⁾ corresponds to bond-breaking in materials exposed to plasma due to high-energy photon interactions. Physical damage [(B) in Fig. 1.6] is induced by high-energy ion bombardment on Si substrates or other material surfaces. The physical damage creates "defects" such as Si-Si broken or strained bonds, displaced Si atoms, vacancies, and interstitial atoms in crystalline Si substrates.

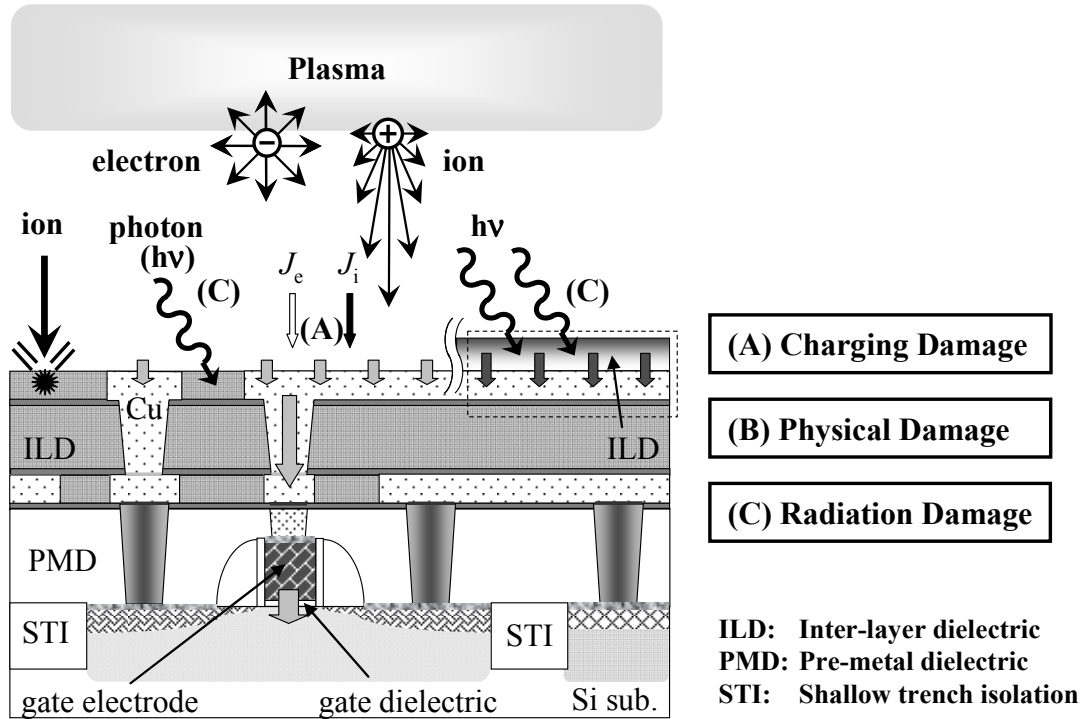


Figure 1.6: Three plasma process-induced damage mechanisms. (A) Charging damage induced by conduction current from plasma, (B) Physical damage induced by bombardment of ions accelerated in the sheath, and (C) Radiation damage induced by high energy photons from plasma.

During more than the last three decades, PID has been studied extensively to understand the mechanisms and to solve practical problems with various approaches. In order to obtain the statistical data in mass production and to clarify the source of PID, a use of specifically designed devices called "test elementary group (TEG)"⁵⁾ has been one of major approaches. In addition to the use of TEG, physical and electrical analyses have been conducted using a bare Si wafer to gain fundamental understanding of PID.

Among three mechanisms above, the plasma-induced physical damage (PPD) on Si substrate surface [(B) in Fig. 1.6] has been, in particular, intensively focused on, because the mechanism of PPD, *i.e.*, the amount of the damage, is naturally governed by basic plasma

parameters.^{16,18)} Therefore, in near future, as shown in Fig. 1.1, the critical dimension of device feature size is believed to conflict with the thickness of plasma-damaged-layer governed by plasma parameters. *This PPD mechanism is the main subject of this thesis.*

Figure 1.7 shows one of crucial PPD issues recently discussed—"Si recess".³⁰⁻³⁴⁾ Si recess formed on the source/drain extension region in a planar MOSFET is ascribed to one of PPD mechanisms. As noted in detail in Chapter III, Si recess is a resultant structure determined from the profile of created defects in a Si substrate. Si recess is considered to induce the performance degradation such as threshold voltage shift (ΔV_{th}),³³⁾ while the residual defects remaining after a wet-etch process following the plasma etching degrades drain saturation current (I_{ds})³⁵⁾ that corresponds to device operation speed. This damage creation mechanism was modeled by a modified range theory³⁶⁾ as also mentioned later in this thesis. As presented in Chapter III, the thickness of the damaged layer and Si recess depth show a power-law dependence on the average ion energy, and was a weak function of substrate bias frequency such as f_2 in Fig. 1.5 due to stochastic effect called "straggling".^{10,37-39)}

Figure 1.8 illustrates in more detail damaged structure formation where "defects" are created. Created defects significantly impact MOSFET performance because of their electronic characteristics.⁴⁰⁾ Therefore, quantitative identification of those defects is requisite to design the performance degradation by PPD. In Chapter II, quantitative evaluation methods employing optical and electrical measurements are provided. The optical method utilizes photoreflectance spectroscopy^{41,42)} to measure the surface potential change by PPD.^{43,44)} The electrical method is based on capacitance–voltage (C – V) measurement, which focuses on differential inversion capacitance of the damaged layer. These evaluation techniques are applied throughout this thesis to clarify physics behind the PPD mechanisms.

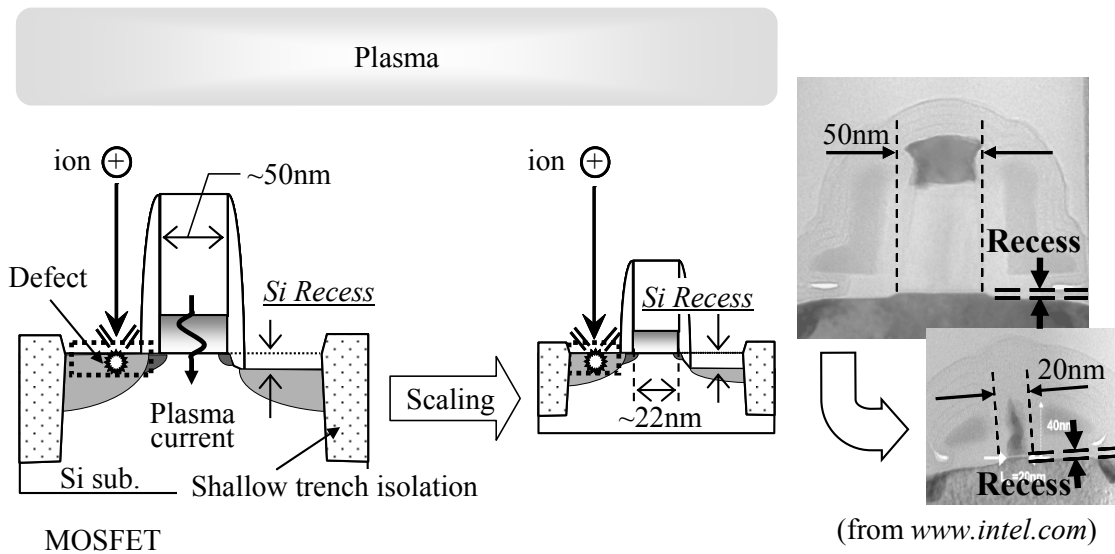


Figure 1.7: Si loss (Si Recess formation) due to PPD and the comparison with device feature sizes.

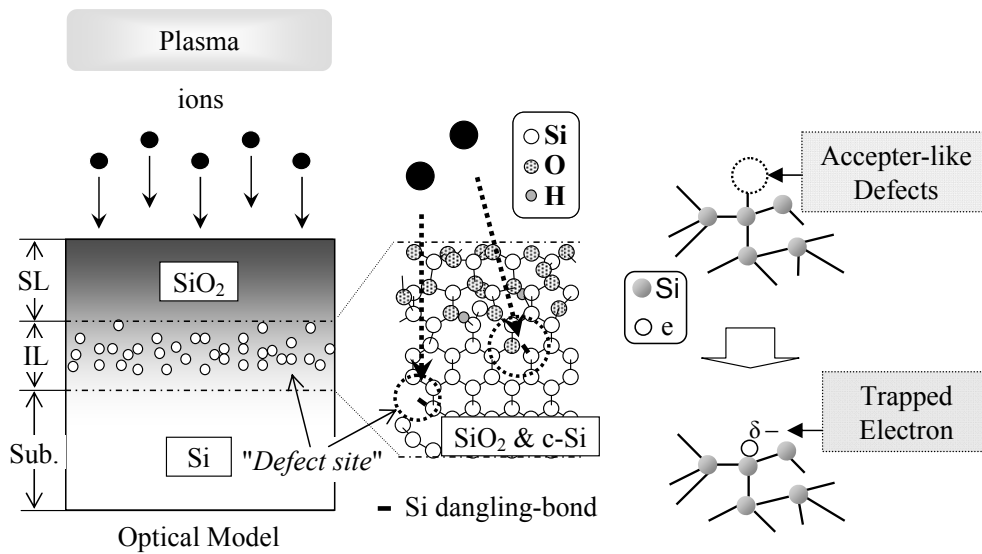


Figure 1.8: Illustrations of defect creation within a Si substrate exposed to plasma (left) and the role of defects (right).

Tremendous efforts have been devoted to understanding the nature of defects in a single crystalline silicon substrate. Figure 1.9 illustrates the unit structure of crystalline silicon [(a)] and typical defect structures [(b)]. As predicted by classical molecular dynamics (MD) simulations⁴⁵⁻⁴⁷⁾ and quantum mechanical calculations using clustered Si atoms,⁴⁸⁻⁵⁴⁾ these structures are stable in terms of their formation energy. In addition to these defect structures,

vacancies and interstitials are also categorized in "defects". Since comprehensive discussions on these defect structures may be beyond the scope of this thesis, I focus on the defects detectable by the techniques proposed in Chapter II. It is speculated from MD simulations that defect structures commonly identified are displaced Si atoms, interstitials [ex. (A) Tetrahedral or (C) Dumbbell in Fig. 1.9(b)], and vacancies.

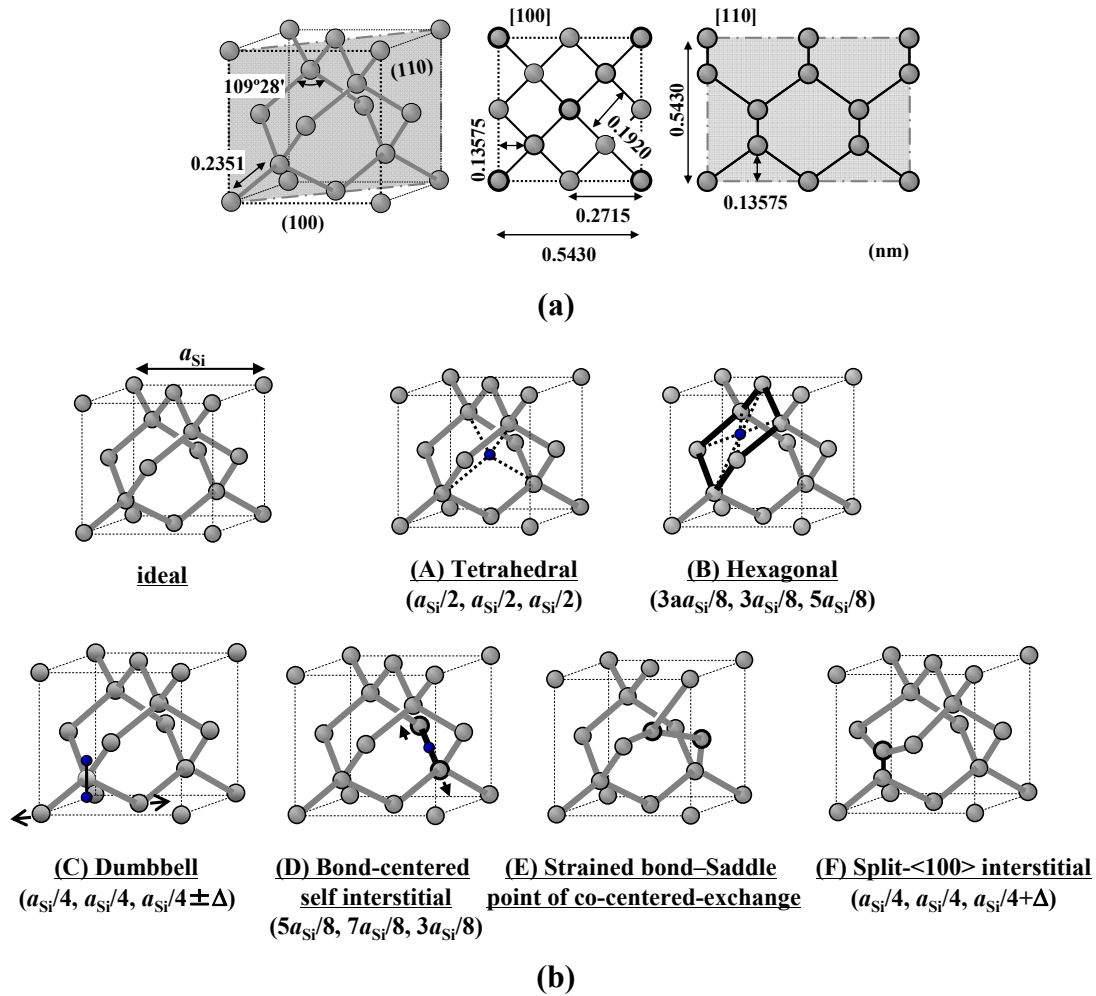


Figure 1.9: (a) The unit structure of crystalline Si. Two directions of planes are shown. (b) The unit structure of crystalline Si and the typical defect structures predicted by various simulations. (a_{Si} = lattice constant)

Historically, to realize future high-performance MOSFETs, various process optimization methodologies have been proposed from the viewpoints of plasma parameters such as

temperature and plasma density using new plasma sources—surface wave plasma¹³⁾ and neutral beam etching.⁵⁵⁾ In Chapters V and VI, by employing the quantitative defect analysis techniques, the effects of gas chemistries on PPD formation are investigated. Defect generation processes are compared between pure Ar and Ar/O₂ gas chemistries in Chapter V. The addition of O₂ in Ar plasma was found to dramatically suppress defect generation. In Chapter VI, H₂-containing plasmas which are now widely employed and a key etching step in the manufacturing are focused on. The damaged structures by H₂ and HBr/O₂ plasmas are studied in terms of damaged layer thickness and defect density.

With regard to fabrication steps in mass production, one can expect that the subsequent wet etch process after plasma exposure may remove the damaged layer as well as contaminants on the plasma-exposed surface. Note that as seen in Fig. 1.7, such wet etching, as a consequence, forms Si recess. Even if the wet-stripping step is employed, there are residual (latent) defects underneath the wet-etched surface. Since the residual defects degrade MOSFET performance as mentioned above, it is extremely important to quantify the residual defects or to clarify the profile of defects formed by PPD. Due to the lack of defect quantification techniques, there have been few discussions on the profile of created defects in as-exposed structure and that of residual defects after a wet-etch. In Chapter IV, profiling of defects by a wet-stripping technique is demonstrated. Two types of custom-built plasma sources—ICP and CCP—are employed for the PPD comparison. By taking into account the obtained results in Chapter V, it is confirmed that not only the energy of incident ions but also the ion flux from plasma strongly affect evaluated data, which is ascribed to the defect profile in "as-damaged" structures and the detection limits of analytical techniques. Chapter V addresses an importance of detailed consideration of the plasma parameter effects on PPD in designing future high performance MOSFETs.

Finally, Fig. 1.10 shows the structure of this thesis. The primary purposes of this

thesis are to establish quantitative evaluation techniques for the PPD and to examine the PPD mechanisms under various plasma processes including two different reactors—ICP and CCP using the proposed techniques. Firstly, I designed a new plasma reactor with an interchangeable top part, which functions in the ICP and CCP modes. Chapter II presents the systems with a new plasma diagnostics module using a semiconductor parameter analyzer capable of convenient measurements compatible to MOSFET characterizations. Then, the thesis proposes two defect quantification techniques: One is photoreflectance spectroscopy to measure the surface potential change by PPD and the other is an electrical $C-V$ measurement, which focuses on differential inversion capacitance of the damaged layer. Using these methods, Chapter III presents critical evidences, *i.e.*, the damage layer thickness assigned by conventional and present techniques is a weak function of substrate bias frequency, which may be in sharp contrast to previously accepted pictures. Chapter IV derives profiling of created defects using a practical wet-etch technique, and then estimates residual defect densities, which is indispensable to design MOSFETs. By comparing evaluated results by the ICP and the CCP, it was found that, in addition to the average energy of incident ions on the surface, the flux plays crucial roles in determining "measured" PPD data. A model is proposed to explain the conflicting results, where the profiles of defects and the sensitivities of each analysis technique are taken into account. Chapters V and VI discuss the effects of gas chemistries on PPD creation by implementing the quantitative techniques provided in Chapter II and employing the wet-etch technique in Chapter IV. In Chapter V, the defect generation processes are compared between pure Ar and Ar/O₂ gas chemistries. Chapter VI presents data on H₂-containing plasmas which are now widely employed and a key etching step in the manufacturing. The damaged structures by H₂ and HBr/O₂ plasmas are studied in terms of damaged layer thickness and defect density. Profiling of the defects and possible reconstruction of the defects—annealing of the damage—are also discussed in Chapter VI.

Then, Chapter VII provides concluding remarks and future outlook. Throughout the experiments combined new defect quantification techniques, the thesis proposes various methodologies and findings, to contribute advancements of scaled electronic devices with higher performance and reliability in the future.

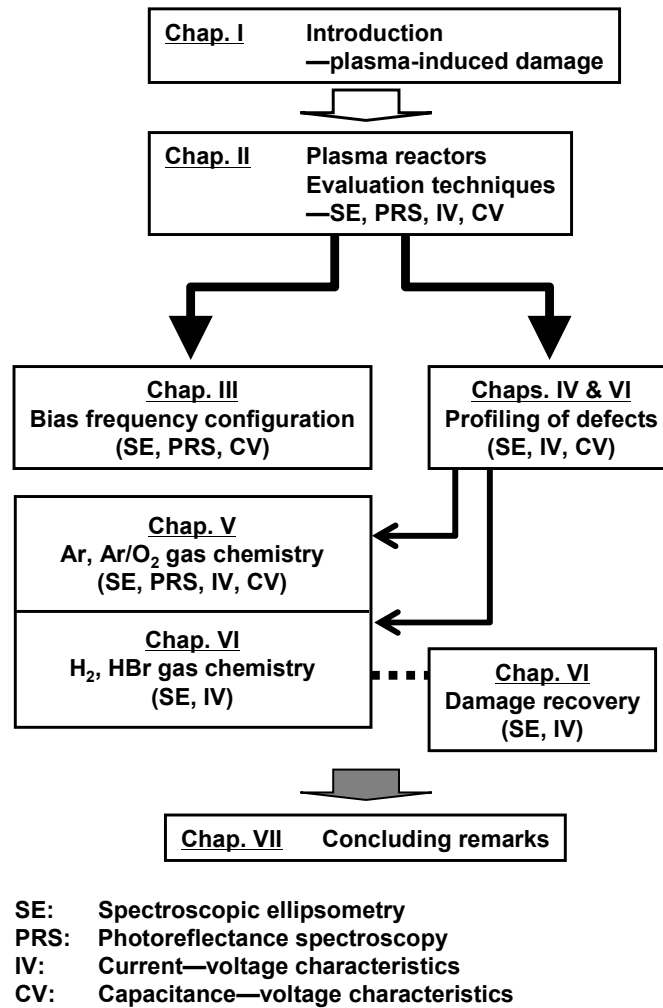


Figure 1.10: Structure of this thesis. The primary purposes of this thesis are to establish quantitative evaluation techniques for the PPD and to examine the PPD mechanisms under various plasma processes by designing custom-built systems. The thesis presents new findings and critical concerns in plasma process technologies regarding the PPD identifications by conventional and present methodologies.

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Chapter II

Plasma equipments, sample treatments, and evaluation techniques

2.1 Plasma reactors—CCP and ICP systems

In this thesis, two plasma reactors were used for PPD creation; one is a capacitively-coupled plasma (CCP) system, and the other is an inductively-coupled plasma (ICP) system. Figures 2.1 and 2.2 show the schematic illustrations of the CCP and the ICP systems equipped with peripheral diagnostics modules, respectively. (Unless otherwise stated, all the plasma treatments were performed by the systems. In Chapters V and VI, plasma systems similar to these platforms were used. Thus, results obtained throughout this thesis are valid for understanding PPD mechanisms.) As shown in Figs. 2.1 and 2.2, the vacuum chamber platform was custom-designed with a vacuum system consisting of a turbo-molecular pump (TURBOVAC361 and Turbo Drive TD20 produced by Oerlikon Leybold Vacuum) and a rotary pump (M2010SD produced by Alcatel, inc.). Pressure during plasma processing was controlled manually by a butterfly valve and monitored by a capacitance gauge M341DG-01 and a crystal ion gauge M346MX-SP with M-601GC panels by Canon-Anelva Corporation. Gas flow was controlled by a mass flow controller M100B produced by MKS with a power supply unit SP-832 by UNICS Co., LTD. Rf power supply

Chapter II

units (400 kHz and 13.56 MHz) were designed by NRF-technologies. The rf power during plasma processing was supplied to a wafer stage through an impedance matching network with an automatic controller adjusting "LOAD" and "TUNE" values. In the ICP system, the 13.56-MHZ rf supplies to a 6-turn coil and to the wafer stage could be adjusted (synchronized) by a phase shifter designed by NRF-technologies. The vacuum chamber platform has an interchangeable top part—a stainless steel plate for CCP mode and the 6-turn coil unit with a matching network for ICP mode.

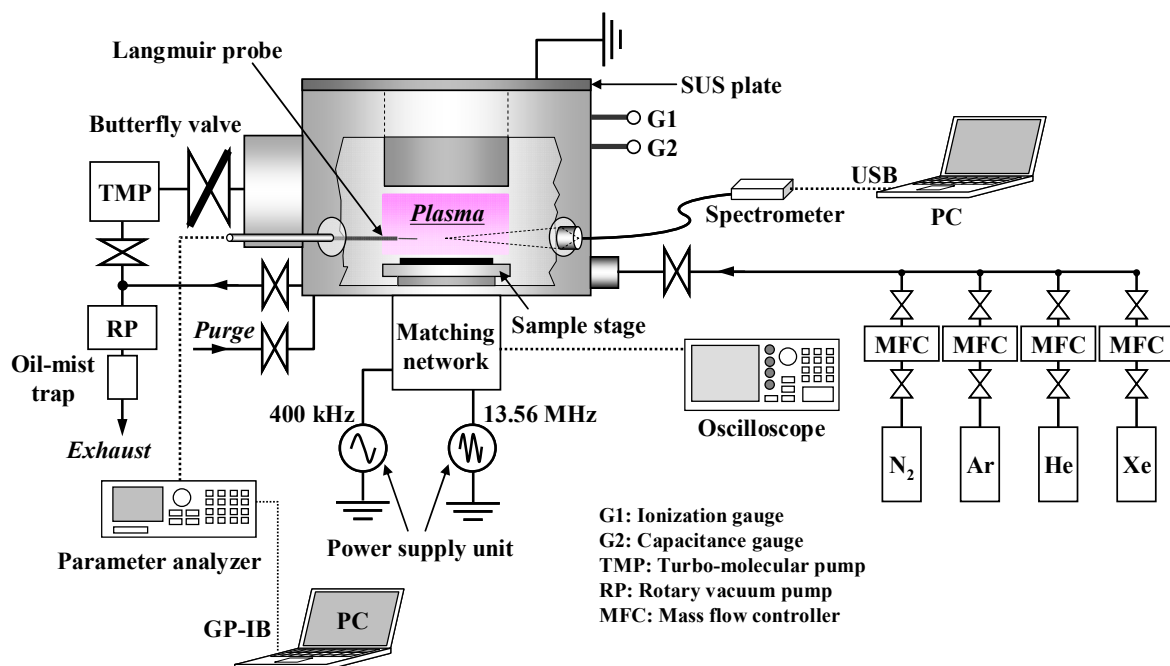


Figure 2.1: Capacitively-coupled plasma system used in this thesis. The platform in this system is the same as that in the ICP system in Fig. 2.2.

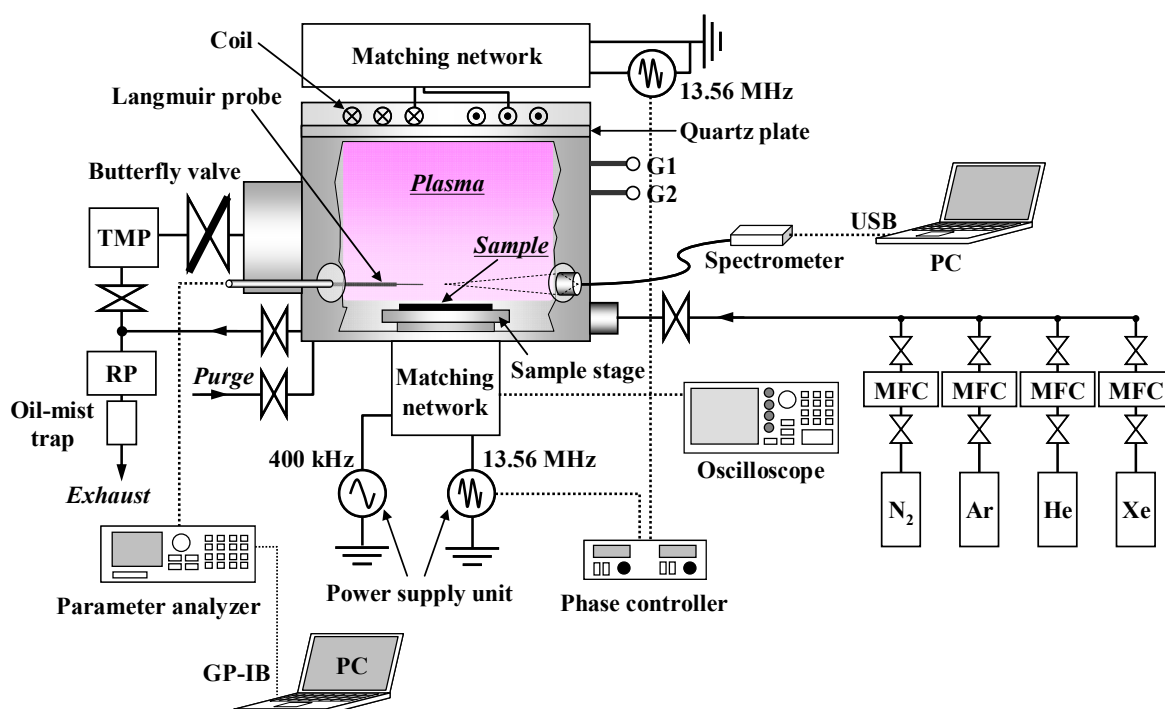


Figure 2.2: Inductively-coupled plasma system used in this thesis. A phase controller was attached in the ICP system.

Figures 2.3 and 2.4 show typical bias voltage waveforms measured by a high-voltage probe and an oscilloscope, for the CCP under various operating pressures and the ICP under various superposed bias frequencies, respectively. As seen in Fig. 2.3, in the present CCP system, the self-dc bias voltage (V_{dc}) strongly depends on the operating pressure. As seen in Fig. 2.4 of the ICP bias waveforms, when the higher frequency bias (13.56 MHz) was superimposed on the lower frequency bias (400 kHz), V_{dc} increases with an increase in the power fraction of 13.56-MHz bias as indicated in Fig. 2.5. Thus, superposed bias configurations can modulate an ion energy distribution function (IEDF)¹⁾ as pointed out in optimizing dual frequency plasma processes. In the present ICP system, the effects of bias configurations on PPD are studied in detail in Chapter III using various characterization techniques as described later in this chapter.

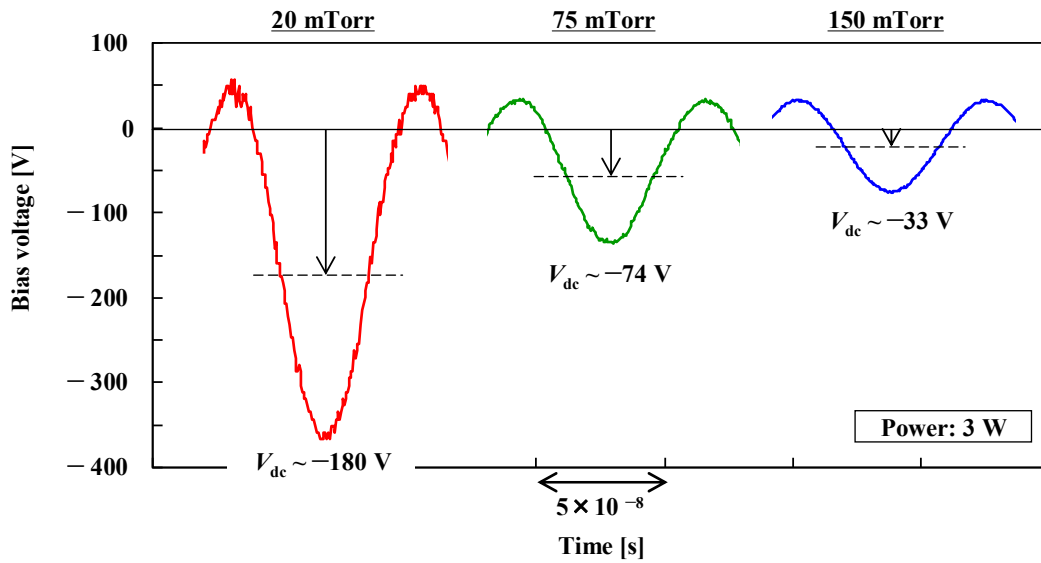


Figure 2.3: Measured bias voltage waveforms in the CCP system under various operation pressures. Ar gas was used.

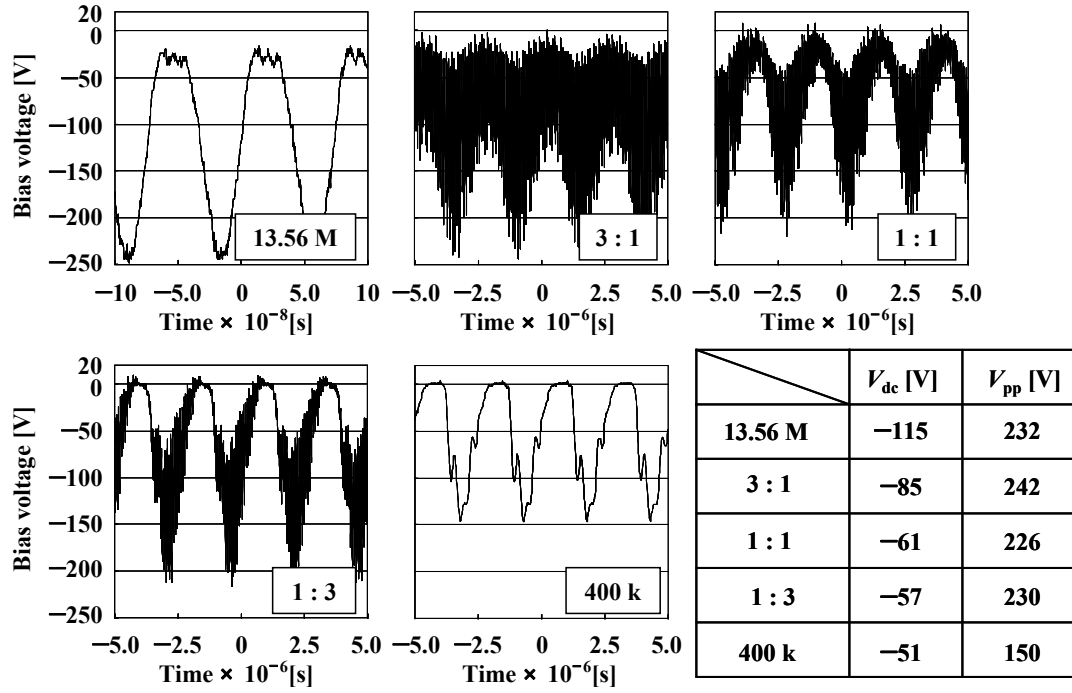


Figure 2.4: Measured bias voltage waveforms in the ICP system under various superposed bias frequencies. Ar gas was used. On the right bottom, estimated V_{dc} and peak-to-peak voltage (V_{pp}) values are shown.

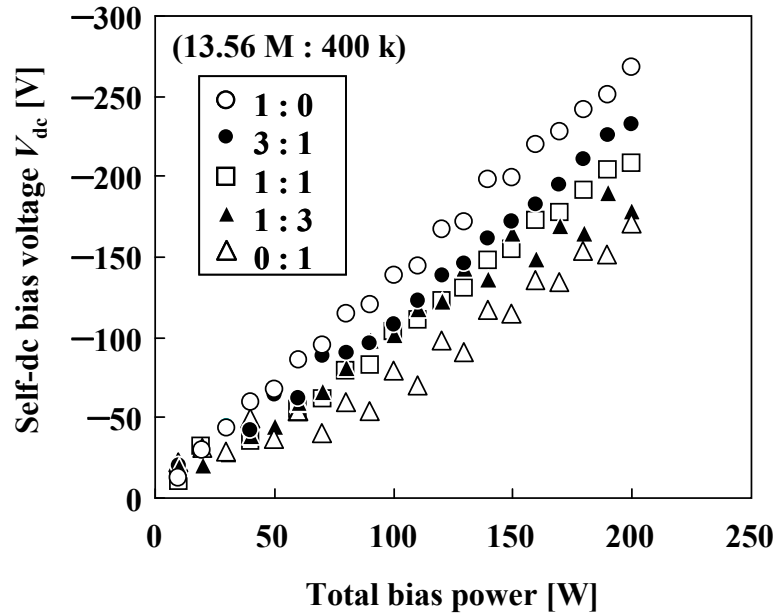


Figure 2.5: Dependence of V_{dc} on the total input power in the ICP system for various bias configurations.

2.2 Plasma diagnostics

Probe diagnostics are usually carried out by inserting a metal probe into a plasma and measuring electron or ion current from plasma. Langmuir probe measurement¹⁾ is one of the most useful techniques. The probe consists of a thin wire (ex. tungsten wire) surrounded by a thin insulator. I designed a Langmuir probe contacted to sub-miniature type A (SMA) connector with a stainless steel (SUS) guard line as shown in Fig. 2.6. The probe current–voltage (I – V) characteristics were obtained using a semiconductor parameter analyzer (Hewlett-Packard (HP)-4145B) automatically controlled by a personal computer with a GP-IB (General Purpose-Interface Bus) interface board. Figure 2.7 shows a typical measured I – V curve obtained by this probe.

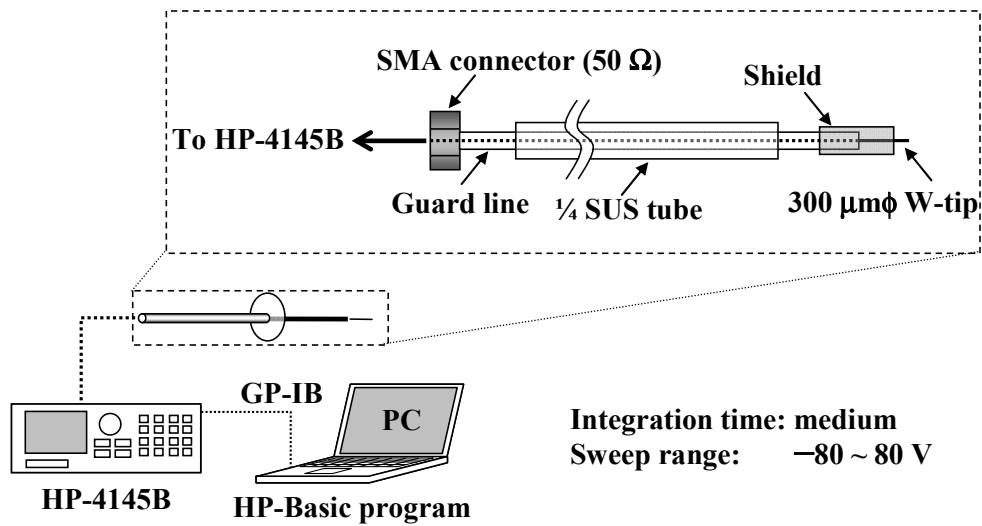


Figure 2.6: Schematic illustration of a Langmuir probe equipped with a semiconductor parameter analyzer.

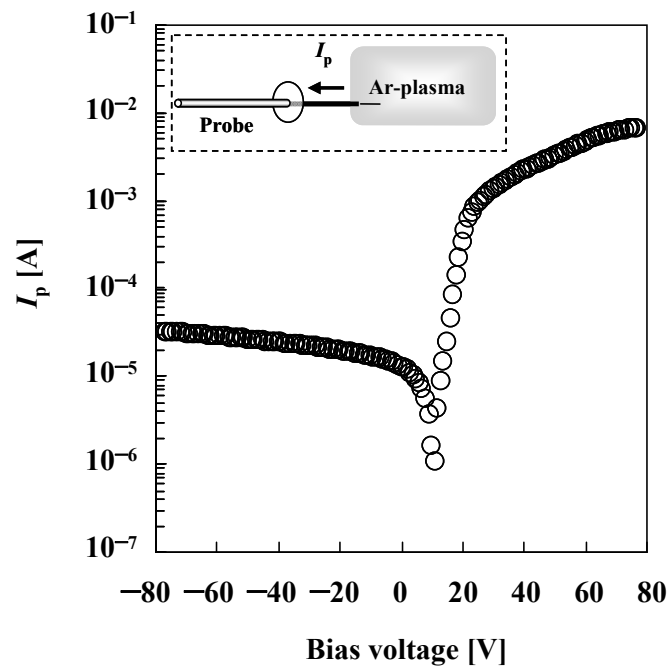


Figure 2.7: Typical measured I - V curve obtained by Langmuir probing in Fig. 2.6.

2.3 Test sample structures and treatments

N-type or p-type (100) Si blanket wafers were used in this study. Unless otherwise noted, the resistivity was $0.02 \, \Omega \, \text{cm}$, giving a dopant concentration of $\sim 10^{18} \, \text{cm}^{-3}$.²⁾ Figure 2.8 shows the flowchart of a surface preparation procedure before plasma exposures using diluted-hydrofluoric-acid (DHF) wet etch and chemical oxide formation by H_2O_2 solution. After pre-cleaning of the surface, then, Si wafers were exposed to the ICP or CCP. Figure 2.9 illustrates a typical test sample indicating the structure of a native oxide layer / an interfacial layer / a Si substrate. This structure is used for a model prediction by spectroscopic ellipsometry (SE),³⁾ where an interfacial layer is inserted to represent the interfacial damaged region after the plasma exposure. As suggested in Fig. 2.10, a plasma damaged structure is composed of a surface oxidized layer, an interfacial region, and a silicon substrate.

Some of the damaged samples were then immersed in $\sim 0.1\%$ DHF to emulate the post-treatment with a wet-etching step in the present-day mass productions. In Chapter VI, the surfaces of plasma exposed samples were covered by a capping SiO_2 layer, which is usually adopted in mass productions. The unexposed sample is denoted as "Ref" in this study. Even if a sample is wet-etched by the DHF solution, a native oxide layer (SiO_2) is again formed by air exposure. In Chapters IV, V, and VI, the wet-stripping process was repeated for various layer-by-layer characterizations as shown in Fig. 2.11. For example, a damaged sample was firstly immersed for 60 s, followed by SE and $C-V$ measurements (as mentioned below in detail) immediately, and then immersed again in the DHF for additional 300 s. Finally SE and $C-V$ measurements were performed again to assign the final thickness and residual defect densities, respectively.

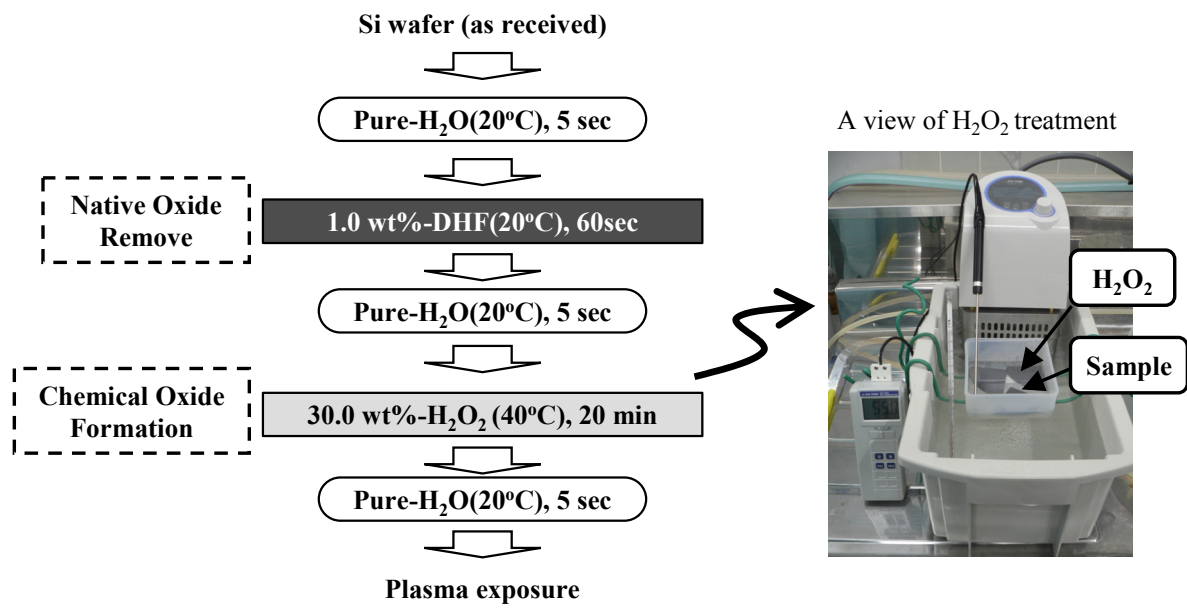


Figure 2.8: Flowchart of a surface preparation procedure before plasma exposures.

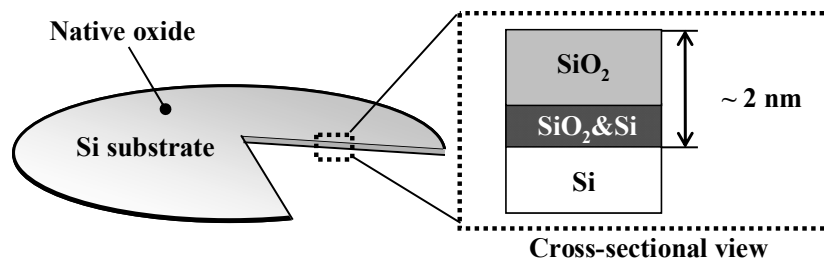


Figure 2.9: Typical test Si wafer with a native oxide layer. An optical model of the structure employed in spectroscopic ellipsometry is shown in the inset.

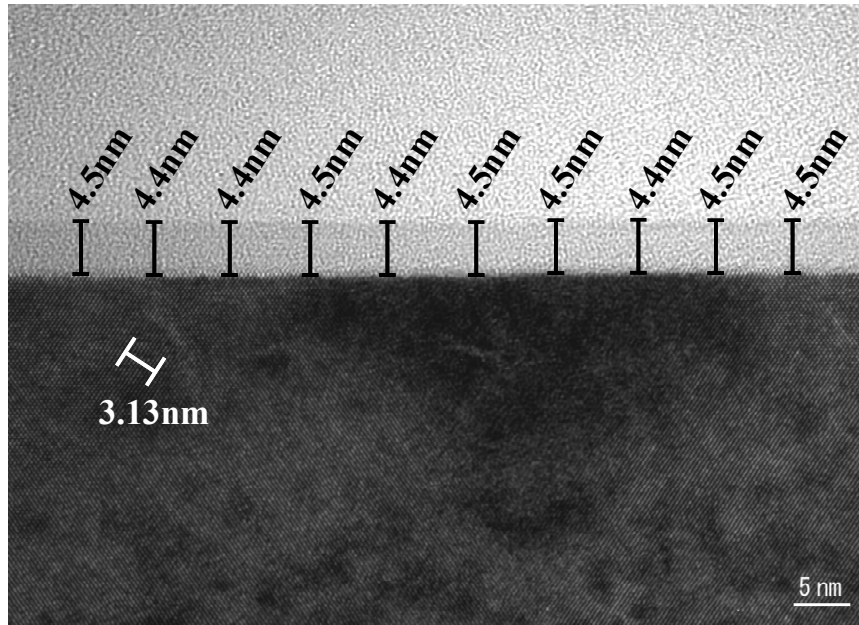


Figure 2.10: Transmission electron microscope image of a plasma exposed Si with surface oxide layer with a thickness of ~ 4.5 nm and a rough interface underneath.

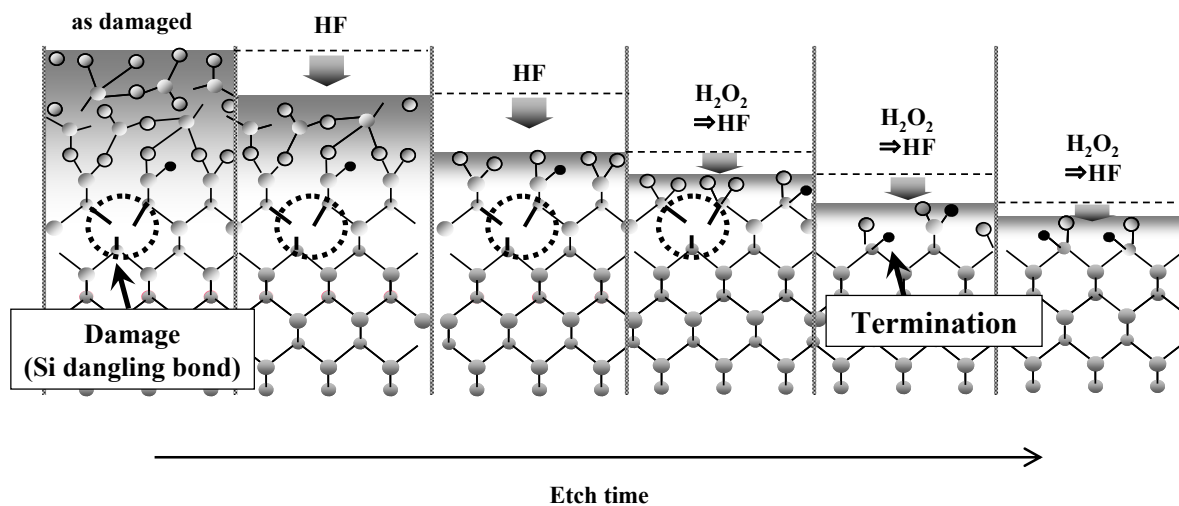


Figure 2.11: Layer-by-layer wet etching procedure using diluted HF solution. In the course of time, the damaged layer is removed and the residual region is subject to oxidation due to an air exposure. Thus, one should focus on the difference of obtained data along the succeeding steps.

2.4 Damage characterization techniques

2.4.1 Examples of physical analyses and the results

In order to evaluate PPD, there have been tremendous works carried out in terms of physical analyses—SE, high-resolution transmission electron microscope (TEM) observation, Rutherford backscattering spectroscopy (RBS), and photoreflectance spectroscopy (PRS). Figure 2.12 shows a TEM image of a plasma damaged sample. Compared to Fig. 2.10, dislocations in the crystalline Si substrate are observable underneath the interface. One can see the rough interface between the surface oxide layer and the Si substrate. Figure 2.13 shows V_{dc} dependence of the damaged structures, with an RBS analysis data for "Power = 300 W" case in the inset. As seen, with an increase in V_{dc} , the interface meanders drastically, implying heavier damage. The RBS data indicates the presence of an interfacial layer, which consists of crystalline silicon and SiO_2 . Therefore, it is concluded that a plasma damaged sample has the interfacial region between surface oxide layer and the substrate.

Figure 2.14 shows oxygen concentration profiles of plasma damaged samples, identified by secondary ion mass spectroscopy (SIMS). Compared to Ref, oxygen atoms distribute in the deeper region of a Si substrate and the peaks of distributions shifts deeper in accordance with V_{dc} . Note that the observed oxygen atoms were coming from a surface native oxide layer through "knock-on" processes. Furthermore, residual Ar species were analyzed by thermal desorption spectrometer (TDS) (TDS1200 by ESCO, Ltd.) as illustrated in Fig. 2.15(a). The results are shown in Fig. 2.15(b) and listed in Table II-1 with detailed sample preparation conditions. One can confirm the presence of Ar species after plasma exposures and the residual density strongly depends on V_{dc} and the flux of ions.

From the discussions in the above, the plasma damaged structure is identified as follows.

- (1) A Si substrate damaged by plasma is composed of three characteristic regions; a surface oxidized layer due to air exposure (denoted as "SL"), a boundary region sometimes with a rough interface (denoted as "IL"), and the substrate sometimes with dislocations.
- (2) The IL consists of primarily SiO_2 and Si.
- (3) Incident species from plasma are present in the Si substrate and the distribution extends to deeper with an increase in V_{dc} . Regarding Ar atoms, one can speculate that they are located at the interstitial sites as displayed in Fig. 1.8(b). Moreover, the knock-on oxygen is also present deeper in the Si substrate in accordance with V_{dc} . (The presence of oxygen in the region of a plasma exposed surface has been focused on recently, because this region is believed to result in "Si recess" as the final structure.⁴⁾)

Figure 2.16 summarizes these findings. Not only a surface damaged layer but also an IL and the interfacial region underneath the IL should be investigated in detail for PPD analysis because they may contain local defects which induce MOSFET performance degradation.^{5,6)} This thesis provides quantitative evaluation methods to characterize these defects underneath the surface region.

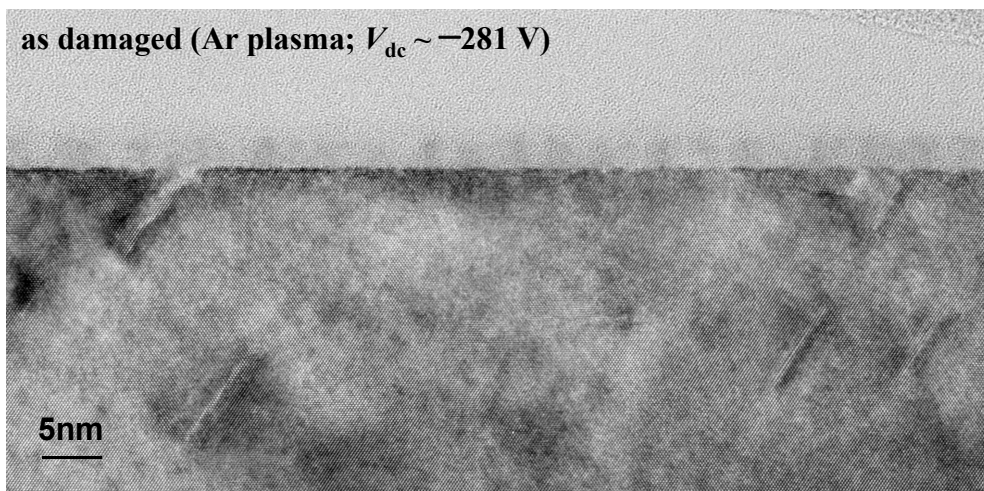


Figure 2.12: Transmission electron microscope (TEM) image of a plasma exposed Si with a rough interface and dislocations.

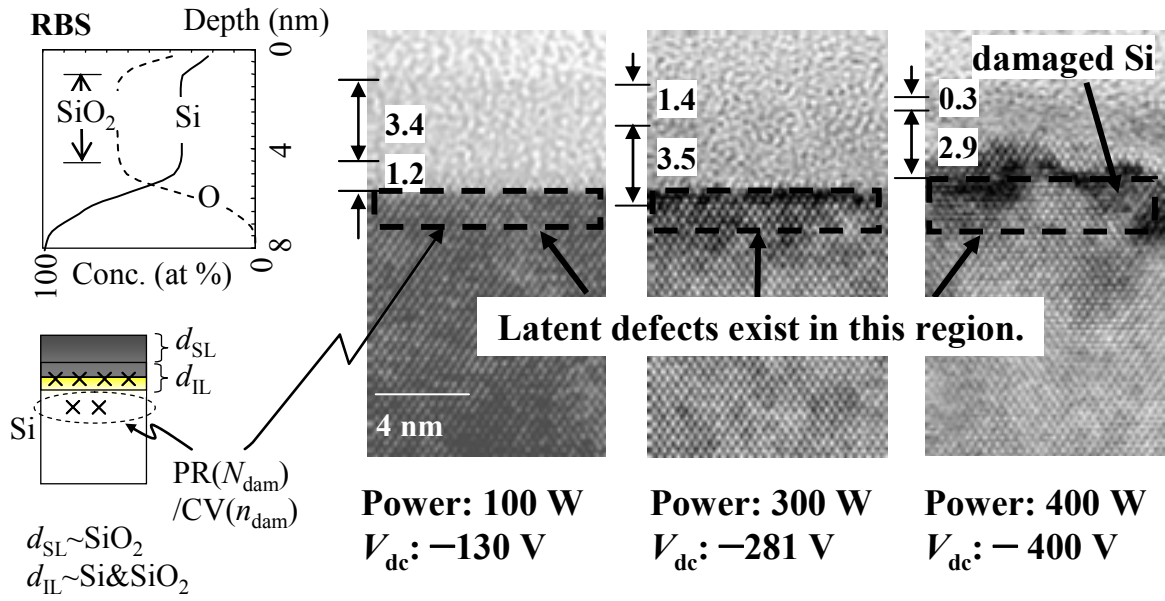


Figure 2.13: TEM images of the samples damage by various conditions (on the right). RBS analysis result for the case of $V_{dc} = -281 \text{ V}$ (on the left). Intermixing of SiO₂ and Si is confirmed near the interfacial region.

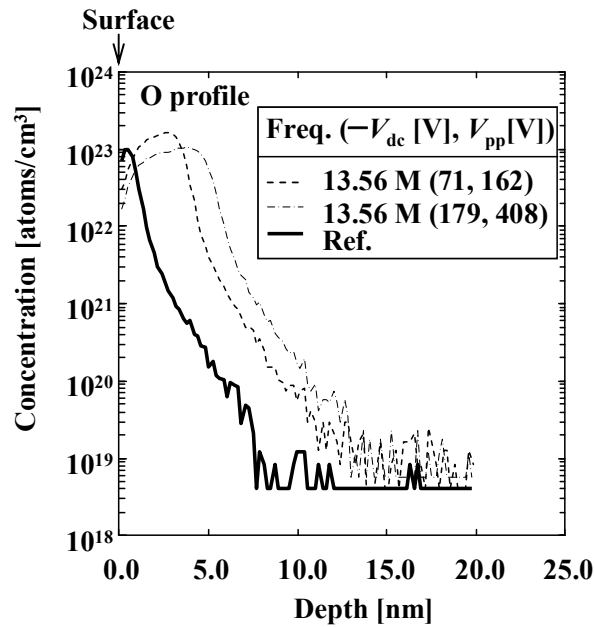


Figure 2.14: Oxygen concentration profile determined by secondary ion mass spectrometry (SIMS). Samples were exposed to plasmas with different V_{dc} .

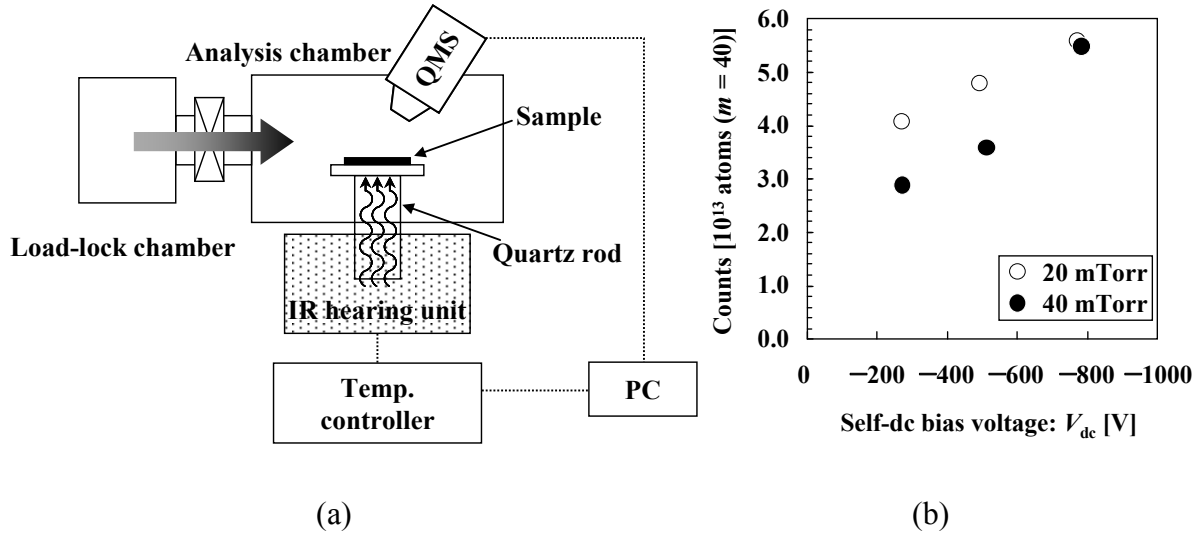


Figure 2.15: (a) Schematic illustration of a thermal desorption spectrometer (TDS) system designed by ESCO, Ltd. (b) Residual Ar counts in the damaged samples as a function of V_{dc} for different gas pressures. As seen, the presence of Ar atoms is confirmed.

Table II-1: Residual Ar counts by TDS.

Sample ID	Counts	p [mTorr]	P [W]	V_{dc} [V]	Flux [$\text{cm}^{-2}\text{s}^{-1}$]	d_{SL} [nm]	d_{IL} [nm]
1	4.1×10^{13}	4.1	10	-270	1.1×10^{13}	2.4	1.8
2	4.8×10^{13}	4.8	28	-490	1.1×10^{13}	3.3	2.6
3	5.6×10^{13}	5.6	62	-770	1.1×10^{13}	4.6	3.0
4	2.9×10^{13}	2.9	10	-270	1.8×10^{13}	2.2	1.8
5	3.6×10^{13}	3.6	35	-510	2.8×10^{13}	3.9	2.3
6	5.5×10^{13}	5.5	75	-780	3.5×10^{13}	5.2	3.3
7 (Ref.)	—	—	—	—	—	0.3	0.3

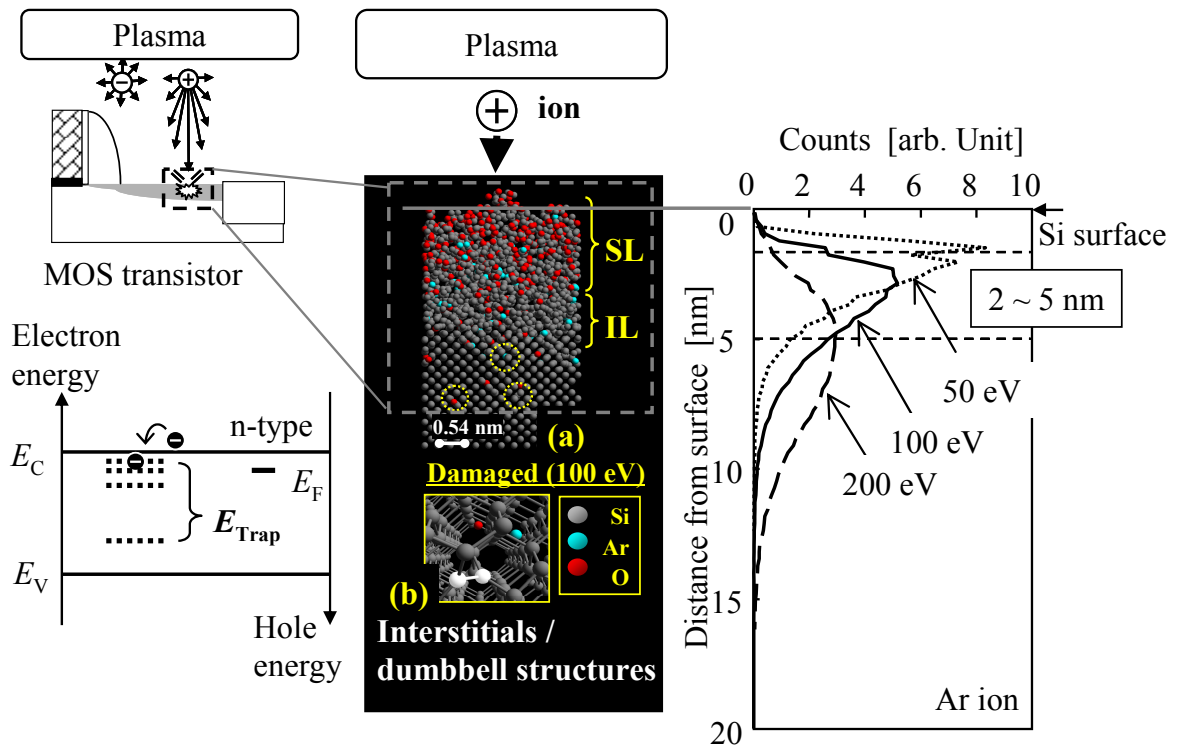


Figure 2.16: Summary of a structure of a plasma damaged Si substrate. PPD creates various defects such as interstitials which may play roles as carrier trapping sites (left and middle). The distribution of defects strongly depends on the energy of incident ions (right). Notice that oxygen diffuses deeper into the Si substrate through knock-on processes even if no O-containing gas chemistry was employed.

2.4.2 Spectroscopic ellipsometry

To identify damaged structures as illustrated in Fig. 2.16, in particular, the thickness, spectroscopic ellipsometry (SE) was employed in this thesis. SE is an optical, non-destructive method that can investigate wafer surface structures,^{3,7)} and is widely used as in-line monitors.⁸⁾ Figure 2.17 illustrates the basic set-up of an SE system used in this study. The platform was the spectroscopic ellipsometer MLM produced by SOPRA (presently, Semilab Co. Ltd.). SE measures the changes in amplitude and phase between the p and s components of polarized light reflected from the sample. In this study, measurements were carried out in the photon energy ranging from 1.60 to 5.50 eV at 0.05 eV intervals. All the SE spectra were taken at an angle of incidence of 75°. For the SE analysis of substrate damage, an optimized optical model derived in the previous section—air/SiO₂/SiO₂:c-Si/Si substrate—was used, as indicated in the right-bottom inset of Fig. 2.17. The surface layer (SL) is assumed to be thin SiO₂. The thickness (d_{SL}) is determined. As discussed above, the interfacial layer (IL) between SL and Si substrate is introduced as a composite of SiO₂ and crystalline silicon with the Bruggeman effective medium approximation (EMA)^{3,9)} with the thickness (d_{IL}) and volume fraction ($f_{\text{c-Si}}$) being used as the fitting parameters. In these analyses, the optical constant of crystalline Si is used instead of that of amorphous silicon, since more parameters are to be fitted in the analysis with amorphous Si, compared to the crystalline case. With this model, three parameters (d_{SL} , d_{IL} , and $f_{\text{c-Si}}$) are determined. Figure 2.18 shows examples of obtained SL and IL thicknesses in the samples damaged by the ICP using the four-layer (air/SL/IL/Si substrate) optical model. Those of Ref are also shown. As seen, both SL and IL increase by plasma exposures.

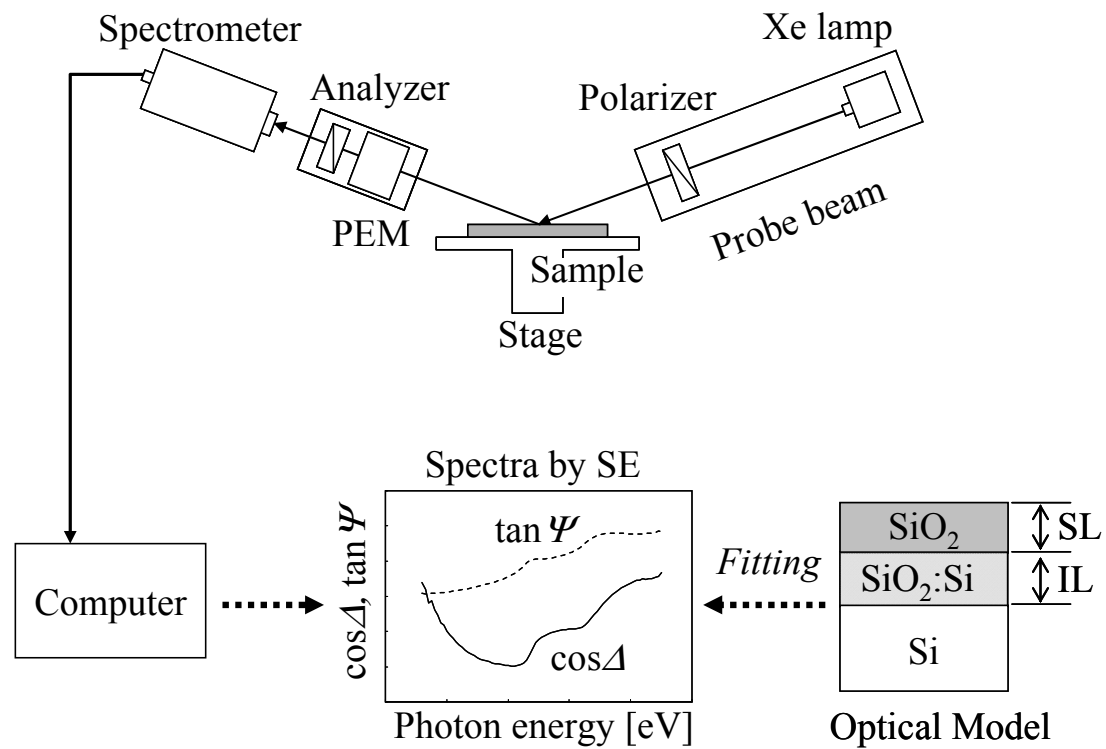


Figure 2.17: Illustrations of spectroscopic ellipsometry, typical measured spectrum, and an optical model employed for damaged structure analyses.

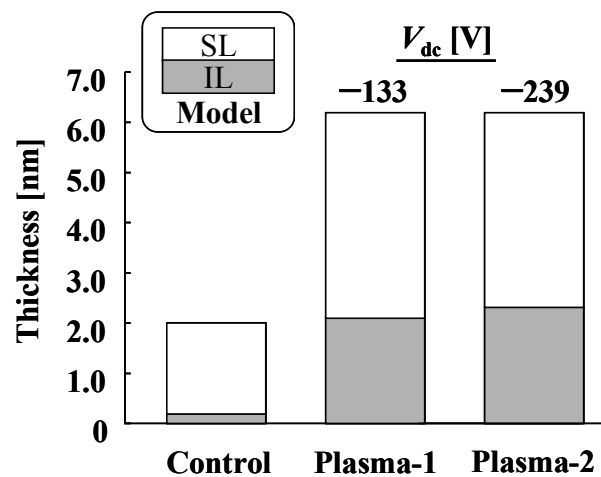


Figure 2.18: Example of obtained thicknesses by the SE analysis for various samples.

2.4.3 Photorefectance spectroscopy

To quantify the density of defects in a damaged structure, photorefectance spectroscopy (PRS)^{3,10,11)} was employed in this thesis. Photorefectance is one of modulation spectroscopy in which a semiconductor is periodically perturbed and the resulting change in dielectric constant is detected by reflectance (R). In this technique, the analysis of a reflective spectrum is based on the mechanism that the change in R corresponds to that in the permittivity of silicon substrate surface by photo-modulation. In this mechanism, photo-generated minority carriers migrate to the interface and recombine with charge accumulated in the vicinity of surface layer. Figure 2.19 shows a schematic diagram of the present PR analysis setup. The system was based on the UVISEL platform produced by JOBIN YVON. The reflected beam was detected by a photomultiplier Hamamatsu R928S through optical fibers and a monochromator HR460 with a focal length of 250 mm and gratings of 1200 gr/mm. The modulation beam part and signal processing unit were attached to obtain the change in R .

In the present PR system in Fig. 2.19, the surface field was modulated by the light from Ar^+ ion laser (514.5 nm) chopped with a frequency of 500 Hz. A Xe discharge lamp was used as a probe light source. The p polarized probe beam through a polarizer was irradiated in this system. Since the spectral line-shape was found to be clearly observable for an angle of incidence near the pseudo Brewster angle, all the PR spectra were taken at the angle in the range from 75° to 80°. The measurement was performed over the 2.9–3.9 eV range at 0.01 eV intervals.

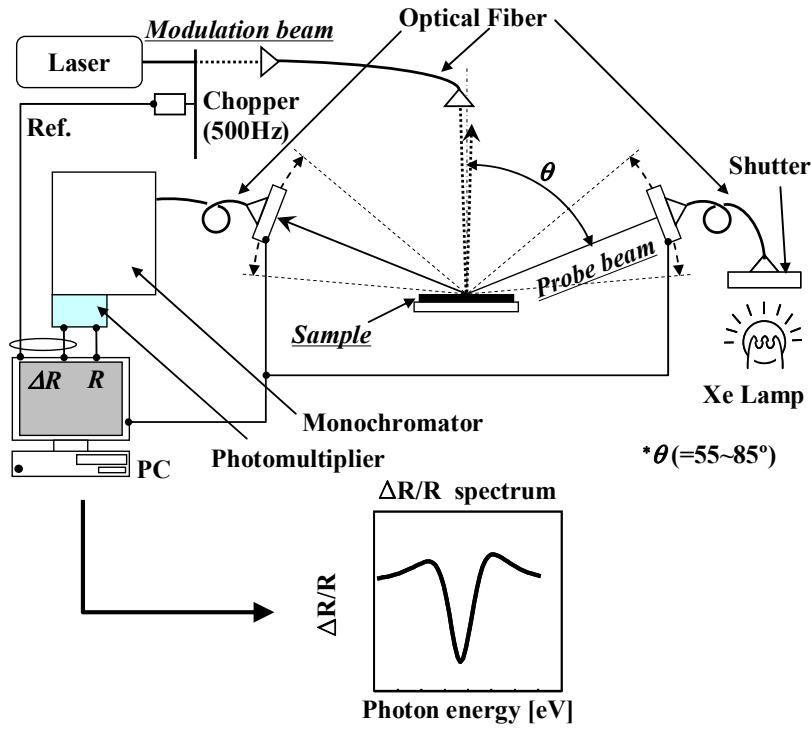


Figure 2.19: Illustrations of a photoreflectance spectroscopy set-up and a typical obtained spectrum.

On the basis of the third derivative theory in the low field limit,¹²⁾ the spectral line shape of the reflectance change $\Delta R/R$ is expressed by

$$\frac{\Delta R}{R} = \Re \left[C e^{i\theta} (E - E_g + i\Gamma)^{-n} \right], \quad (2.1)$$

where C , θ , and E are amplitude, phase factor and photon energy in eV, respectively, and the exponent n depends on the dimensionality of the critical points corresponding to the structures of conduction and valence bands.¹³⁾ E_g and Γ are the transition energy at the critical point and the broadening parameter, respectively. Figure 2.20 shows a typical PR spectrum (on the left) and the energy band diagram of Si (on the right). The feature of PR line shape near

3.4 eV observed for Si should be analyzed carefully as the interband transitions associated with the L-point ($n=3$) and the Γ -point ($n=5/2$) as indicated in Fig. 2.20. There have been many reports discussing on the origin of the line shape at around 3.4 eV.¹⁴⁻¹⁷⁾ Since the differences are focused on as a measure for changes in surface structures, I fitted the experimentally observed spectra based on the Γ -point transition with E_g , Γ and C being determined. The change in the structure is analyzed, in particular, by those in E_g and C . Note that, since the penetration depth of the probe beam is approximately 10 nm¹³⁾ in a single crystalline Si substrate from the surface at the energy around 3.4 eV, the obtained results are reflecting the structure change in the vicinity of the surface.

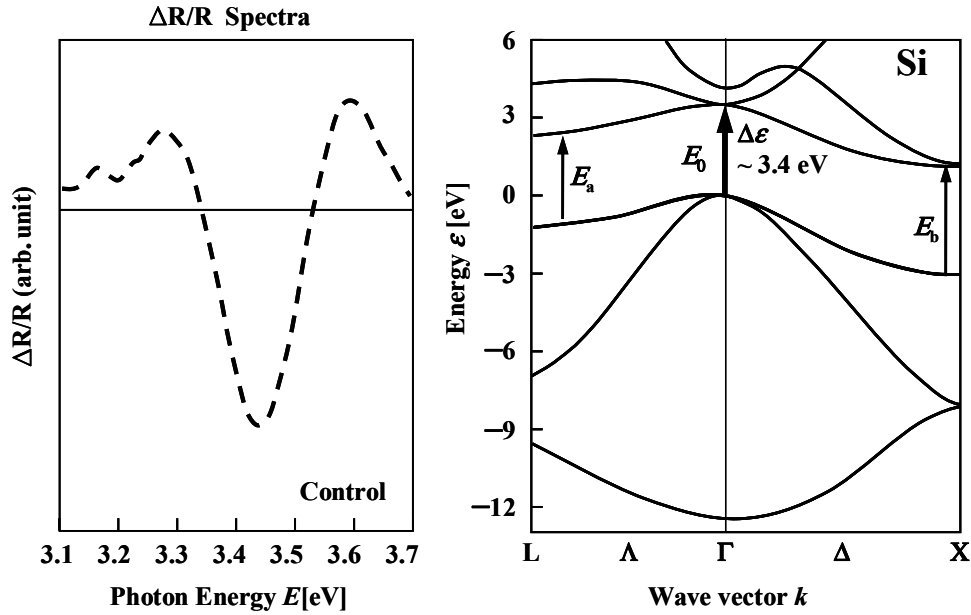


Figure 2.20: Typical obtained PR spectrum (left) and the energy band diagram of Si (right). The characteristic PR peak at 3.4 eV is associated with the transitions at L- and/or Γ -points.

Figure 2.21 shows typical PR spectra obtained. The obtained spectra were fitted using Eq. (2.1) as indicated by the solid lines. In these cases, the decreases in the peak intensity as well as the shifts are observable by plasma exposure. In this study, the peak intensity change

is focused on as follows.

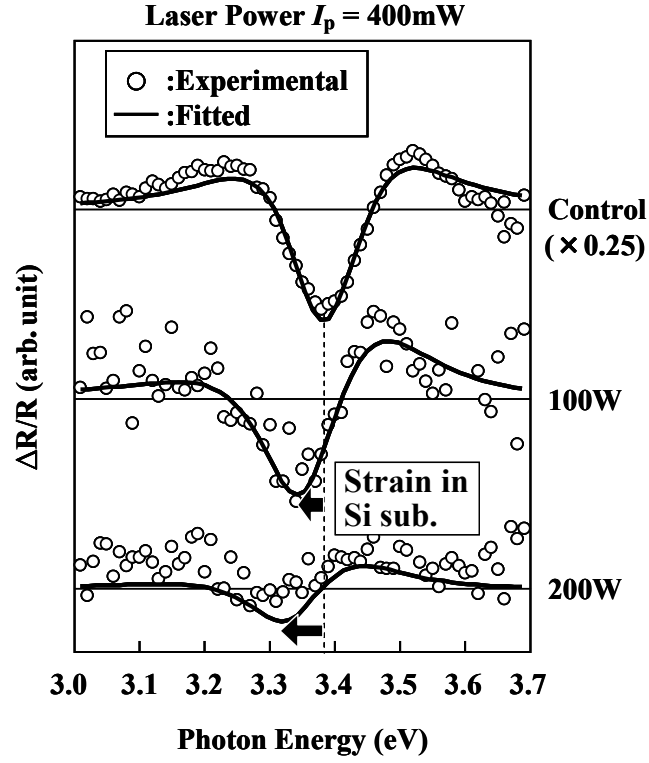


Figure 2.21: Obtained PR spectra for various samples. The solid lines were determined from the least-square fits using Eq. (2.1).

The PR amplitude $\Delta R/R$ (C) scales linearly with the surface voltage change ΔV_s induced by photomodulation, which is written by²⁶⁾

$$\left| \frac{\Delta R}{R} \right| \propto \Delta V_s. \quad (2.2)$$

On the otherhand, ΔV_s obeys the following relation²⁶⁾

$$\Delta V_s = \frac{\eta k_B T_{\text{sub}}}{q} \ln \left[\frac{J_{\text{pc}}}{\rho J_0} + 1 \right], \quad (2.3)$$

Chapter II

where J_{pc} , J_0 , ρ , q , η , k_B , and T_{sub} are photoinduced current density to the Si substrate surface, the corresponding dark current density, an area factor, elementary charge, the ideal factor or ideality factor,¹⁹⁾ Boltzmann constant, and substrate temperature, respectively. The photocurrent J_{pc} can be scaled linearly with laser power I_p as²⁶⁾

$$J_{pc} = \frac{qI_p\gamma(I_p - R)}{h\nu} \left[1 - e^{-\alpha w} + \frac{\alpha L_d}{1 + \alpha L_d} e^{-\alpha w} \right], \quad (2.4)$$

where α , w , L_d , γ , R , h , and ν are the absorption coefficient, depletion width, the diffusion length of the minority carriers, quantum efficiency, reflectance of the probe beam, Planck's constant, and the frequency of the light, respectively. The dark current J_0 in Eq. (2.3) to the surface represents thermal carrier generation and contains V_s as²⁶⁾

$$J_0 = A^* T_{sub}^2 \exp\left(-\frac{qV_s}{k_B T_{sub}}\right), \quad (2.5)$$

where A^* and V_s are modified Richardson constant¹⁹⁾ and surface voltage. In order to quantify the plasma-induced defect density, I focus on the characteristic mechanism that $\Delta R/R$ (C) is related to Si surface potential from the Eqs. (2.3)–(2.5),¹⁸⁾ as expressed by

$$C = A_1 \ln \left[A_2 I_p \exp\left(\frac{qV_s}{k_B T_{sub}}\right) + 1 \right] = A_1 \ln(P_2 I_p + 1). \quad (2.6)$$

A_1 and A_2 are material and structural dependent parameters described by the following equations.

$$A_1 = \frac{c_1}{\mu_{||}} \frac{\eta k T}{q}, \quad (2.7a)$$

$$A_2 = c_2 \frac{q\gamma(1-R)}{A^*T^2h\nu}, \quad (2.7b)$$

where $\mu_{\parallel}$ is the interband reduced mass evaluated in the field direction¹⁹⁾. c_1 and c_2 are constants. In this thesis, parameters A_1 and A_2 are assumed to be constant.

Here I modify and apply this model to evaluate the plasma-induced defect site per unit area (N_{dam}).²⁰⁾ The basic concepts are shown in Figs. 2.22 and 2.23. In this model, the effect of the carriers trapped into plasma-induced defect sites are taken into consideration. Due to the presence of defects, the surface potential change becomes suppressed because photo-generated carriers are trapped and/or the trapped charges change (decrease) the electrostatic potential at the surface. Thus, as indicated in Fig. 2.22, $\Delta V_{\text{m}}^{\text{dam}}$ becomes smaller than $\Delta V_{\text{m}}^{\text{ref}}$, resulting in a decrease in $\Delta R/R$ (C). Thus, from $\Delta V_{\text{m}}^{\text{dam}}$ and $\Delta V_{\text{m}}^{\text{ref}}$, the surface potential change by PPD can be estimated. As shown in Fig. 2.23, by assuming that the trapped carriers induce the change in V_s ($\Delta V_s = |V_s^{\text{dam}} - V_s^{\text{ref}}|$), N_{dam} in an as-damaged sample can be calculated from V_s by solving Poisson equation. In the case of a simplified defect distribution model, one can obtain the expression as

$$N_{\text{dam}} = \frac{2\varepsilon_0\varepsilon_{\text{Si}}\Delta V_s}{ed_{\text{dam}}}, \quad (2.8)$$

where ε_0 and ε_{Si} are the permittivity of vacuum and relative permittivity of silicon, respectively. ΔV_s is the difference of Si surface potential between the control (Ref) and the damaged samples. d_{dam} is the thickness of damaged layer. Note that ΔV_s can be determined from the ratio of P_2 in Eq. (2.6) in Ref to that in plasma exposed samples by using the least square fit of C versus I_p . Thus, N_{dam} determined from this model is used as a measure of damage. Also this technique was preliminary applied to n_{dam} analysis in the study of a

different PRS system by Matsuda.²¹⁾

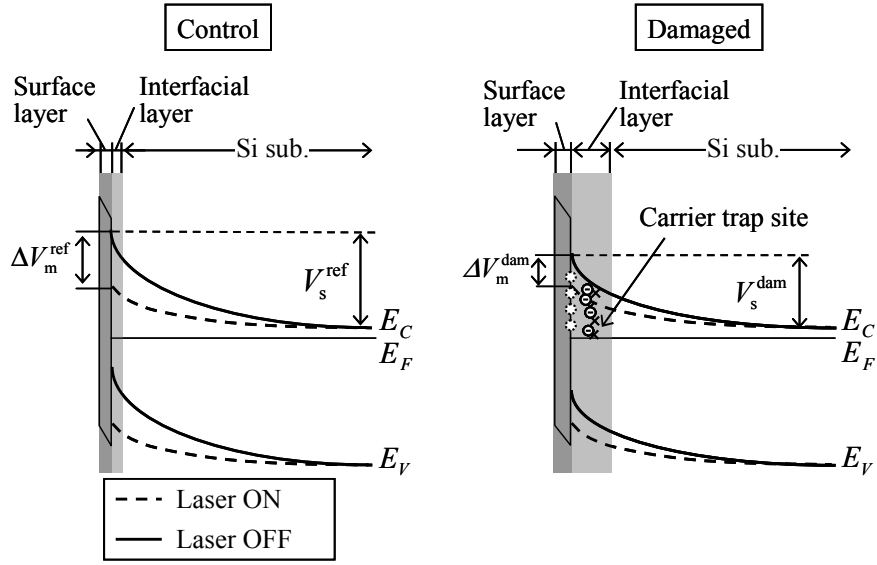


Figure 2.22: A model for potential modulation change in a PR measurement due to the presence of defects created by PPD.

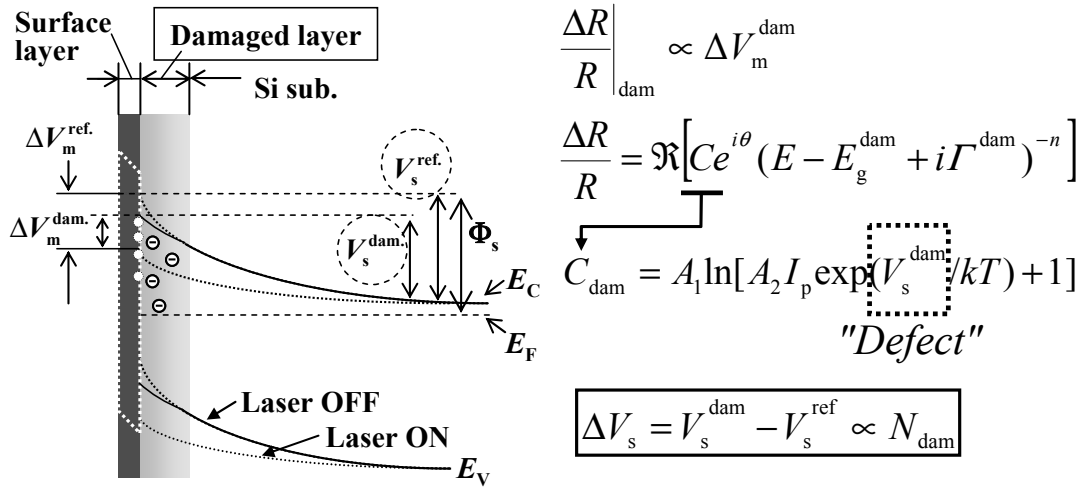


Figure 2.23: A model for N_{dam} calculation from the surface potential change through the parameter C on the basis of photo-generated carrier diffusion and trapping in the PRS measurement.

2.4.4 Electrical tests by mercury-probing system— $1/C^2$ -method

Figure 2.24 illustrates the schematic view of an electrical measurement set-up employed in this study. All the following electrical stress tests are performed with a mercury (Hg) probe platform in a shield box (SSM 495 CV SYSTEM by Solid State Measurement, Inc., presently Semilab Co. Ltd.). The system was equipped with semiconductor parameter analyzers (Hewlett-Packard (HP)-4156A or HP-4145B) for I - V measurement and with Agilent 4284 Precision LCR meter for C - V measurement, which are indicated as the measurement apparatus in this figure. Unless otherwise stated, a pseudo-MOS structure (Hg/SiO₂/Si) was assumed to be a primal structure for analyses throughout this thesis. In the C - V measurement, a 100-kHz frequency of voltage modulation was superimposed on DC bias as shown in the bottom inset of Fig. 2.24. The amplitude was 10 mV. The integration time in the measurement was set for the medium sweep mode. (= 20 ms) The area of Hg metal contact was $2.1 \times 10^{-2} \text{ cm}^2$. All the measurements were performed at the room temperature. Figure 2.25 shows typical I - V curves for various samples. After plasma exposures, the leakage current decreased, which is attributed to the presence of a surface oxide layer.

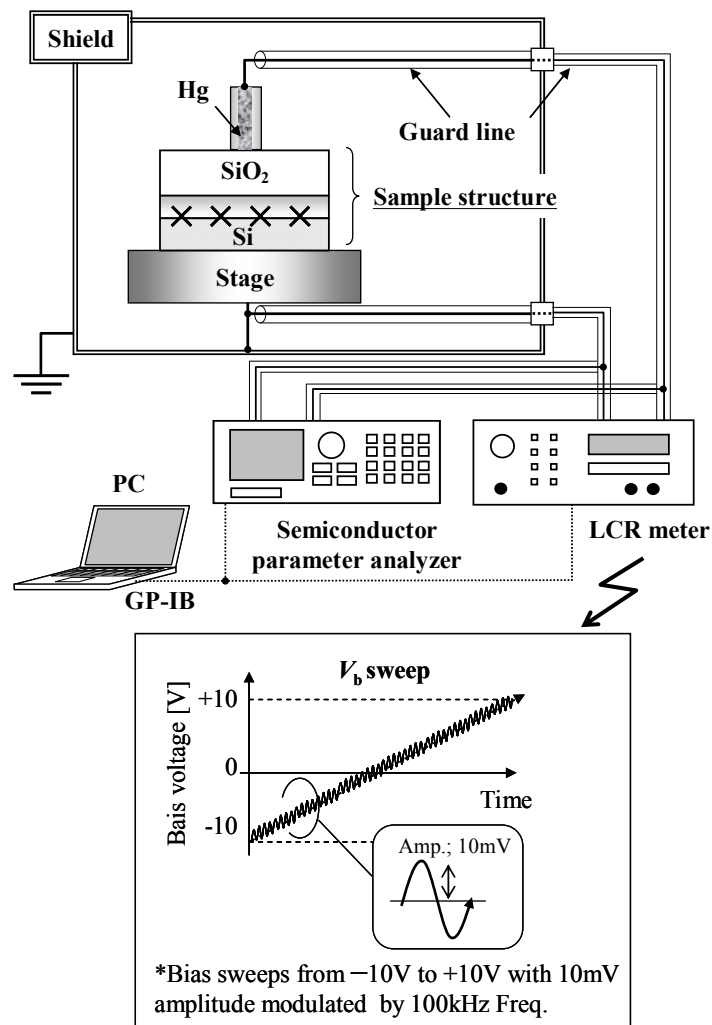


Figure 2.24: Schematic view of an electrical measurement set-up employed in this study.

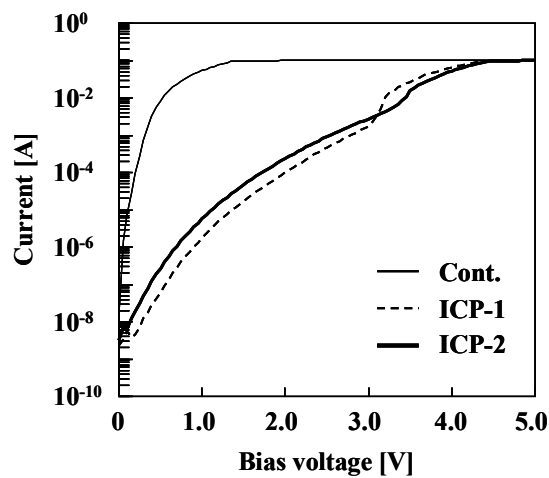


Figure 2.25: Typical $I-V$ curves for various samples. The decrease in leakage current is attributed to the presence of a surface oxide layer by PPD and air exposure.

From C – V measurements, one can obtain various electrical parameters. An electrical oxide thickness (EOT)⁸⁾ is estimated from the maximum capacitance in accumulation.¹⁹⁾ In accumulation, the measured differential capacitance corresponds to EOT of SiO₂ layer (~SL, C_{SL}). The capacitance in inversion defines impurity doping concentration in a substrate. In this thesis, the inversion capacitance is primarily focused on. In inversion, the measured capacitance corresponds to a sum of C_{SL} and the inversion layer capacitance in serial. In this configuration, the slope of $1/C^2$ – V is a function of the density of doping (N_D) of the bulk substrate.^{19,22)} When a wafer with a low resistivity is used, one can measure the differential capacitance in the inversion layer close to the surface (approximately 5 nm thick). If a Si substrate is exposed to a plasma, defects with various structures are formed in the SL and IL. As shown in Fig. 2.16, there exist the surface amorphousized subject to be oxidized and interlayer regions, corresponding to SL and IL. In the C – V measurement, SL is identified by the accumulation capacitance. The density of local defect sites underneath IL may be assigned from the inversion capacitance, although one can not distinguish how much portion of IL belongs to the accumulation capacitance. Since the local defects are stable structures²³⁻²⁵⁾ that act as traps for carriers^{5,6)} as pointed out previously, the change in capacitance corresponds the change in "effective" doping concentration. By introducing the density of defects n_{dam} , one can describe the differential capacitance in inversion as,

$$\frac{d}{dV_b} \left(\frac{1}{C_m^2} \right) = - \frac{2}{q\epsilon_0\epsilon_{Si}(N_D + n_{dam})} \quad (2.9)$$

where C_m is a measured capacitance and V_b is applied bias voltage. Figure 2.26 illustrates the energy band diagram of Hg/IL/Si substrate system (on the left) and the change in measured $1/C^2$ – V characteristics for a damaged structure (on the right). As shown in the top

inset, the capacitance measured depends on V_b . At the ideal thermal equilibrium (A), the differential capacitance becomes ~ 0 . If carrier trapping sites originating from defects exist in the region, the capacitance changes in accordance with the number of density n_{dam} and V_b as indicated by Eq. (2.9). Thus, one can observe the change in the slope of $1/C^2-V$ depending on V_b in the intermediate bias configuration (B). The V_b dependence of the slope is attributed to the depth and energy profiles of the defects created by PPD. Damage causes the slope to decrease in the V_b range from -1.0 to 1.0 V, indicating the presence of defect sites ($N_D + n_{\text{dam}} > N_D$). In strong inversion or under larger V_b (C), few defects contribute to a measured capacitance because the intersection between the Fermi level of Si substrate and the trap level extends deeper in the substrate. Therefore, n_{dam} assigned by the $1/C^2-V$ technique corresponds to those local defect structures underneath the IL region.

The distortion of $1/C^2-V$ curve predicted by the proposed model can be verified by a theoretical calculation. Figure 2.27 shows the calculated dependence of $1/C^2-V$ curve on the thickness of SL d_{SiO_2} (left) and the density of defects n_{dam} (right). As seen, both d_{SiO_2} and n_{dam} induce the formation of plateau in the intermediate bias regions, which is similar to the distortion of $1/C^2-V$ curve observed in Fig. 2.26. Since d_{SiO_2} can be estimated from SE analysis, one can predict n_{dam} by measuring a $1/C^2-V$ curve. This methodology is the main theme in this thesis. I applied this methodology to various PPD characterizations to clarify the physics behind PPD mechanisms.

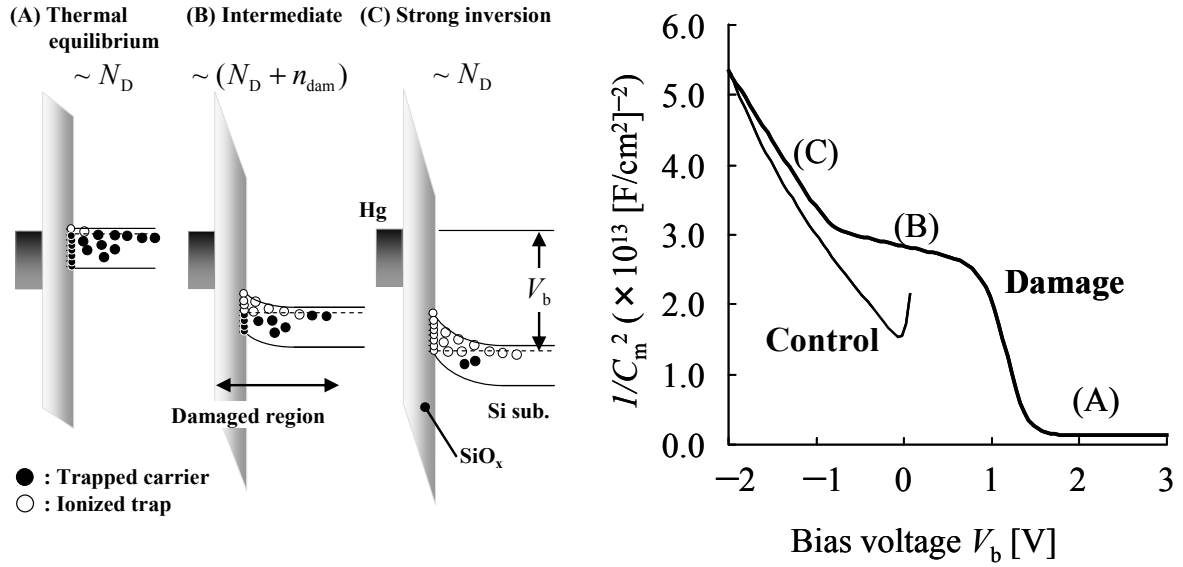


Figure 2.26: Energy band diagrams of a Hg/SiO₂/Si structure (A) in thermal equilibrium, (C) in inversion, and (B) in intermediate configuration (on the left), accompanied with typical $1/C^2$ - V curves of Ref and a damaged sample on the right.

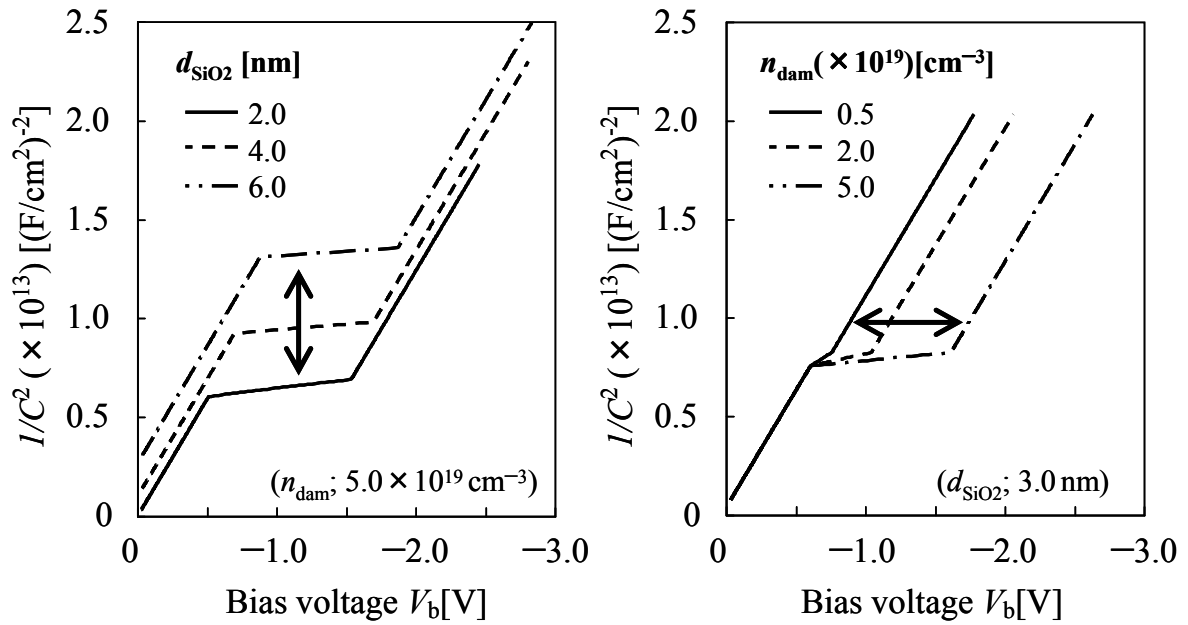


Figure 2.27: Simulated $1/C^2$ - V curves of damaged samples with various surface oxide thicknesses and defect densities.

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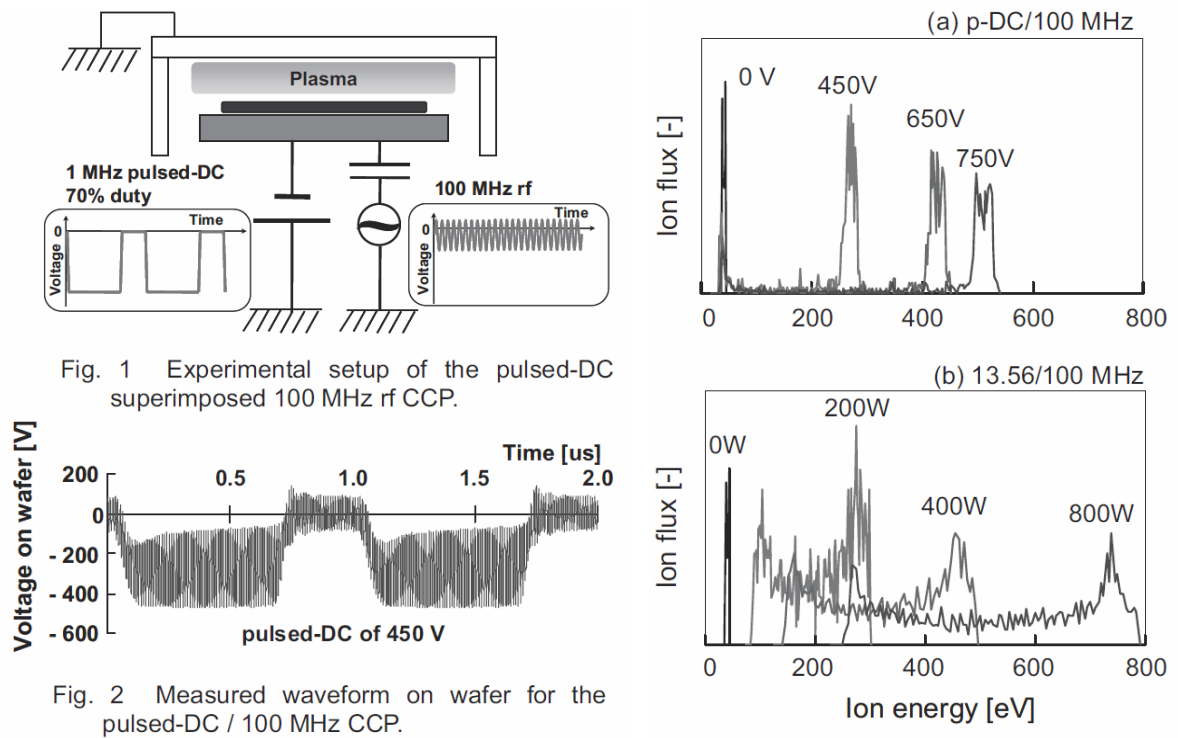
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Chapter III

Bias frequency effects on defect generation

3.1 Introduction

In accordance with shrinkage of feature sizes in a MOSFET, controlling of incident ion energy becomes important in designing plasma etch processes. Optimization of an ion energy distribution function (IEDF)¹⁾ has been a primal issue²⁻⁵⁾ for realizing well-defined and controlled high performance etch processes. Hayashi *et al.*⁵⁾ presented the effects of superposed bias configurations on etch performances. Figure 3.1 shows schematic illustrations of a superimposed dual-frequency system together with obtained IEDFs. Feature profiles and etch rates realized by the systems were discussed in the literatures and improvements of etch performances were presented.²⁻⁵⁾ However, there have been few reports on the effects of dual-frequency configurations on PPD, where an IEDF—energy of incident ions—is considered to play key roles in defect generation mechanisms. In this chapter, the effects of superposed biases on defect generation process are investigated in detail using the ICP system and the quantitative evaluation techniques described in Chapter II. The structure of surface (SL) and interfacial (IL) damaged layers is analyzed by spectroscopic ellipsometry (SE) and photoreflectance spectroscopy (PRS). A capacitance–voltage (C – V) measurement was carried out to clarify electrical characteristic changes in the damaged sample.



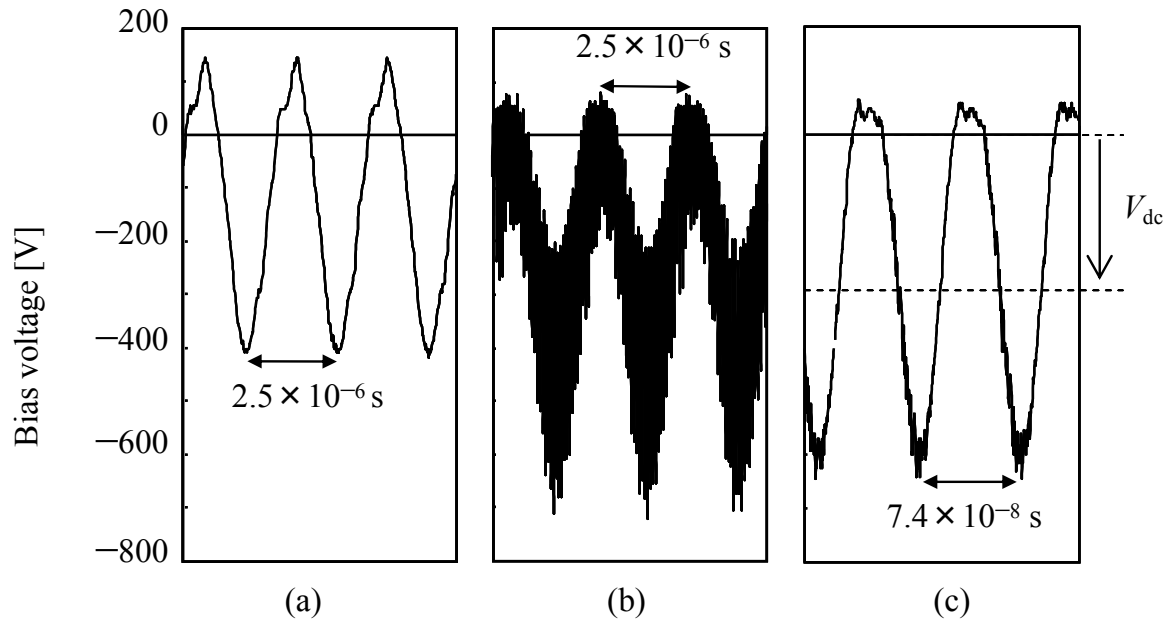
H. Hayashi et al., DPS2009

Figure 3.1: Schematic illustrations of a plasma reactor equipped with a superimposed bias-frequency application system (left top), bias waveforms (left bottom), and various ion energy distribution functions (IEDF) under these dual frequency configurations (on the right). The figure was taken from Ref. 5).

3.2 Experimental

3.2.1 Plasma system and sample treatments

N-type (100) Si substrates ($0.02 \, \Omega \, \text{cm}$) with native oxide layer ($\sim 1 \, \text{nm}$) were mounted on a stage and exposed to an inductively coupled plasma (ICP) reactor shown in Fig. 2.2. No processed sample was to be the control (Ref). Ar gas chemistry was employed for eliminating chemical reactions with Si. Operating pressure was 20 mTorr and background pressure was less than 3.0×10^{-5} Torr. The substrate temperature was measured to be $\sim 500 \, \text{K}$. The Langmuir probe and bias voltage measurements were carried out for plasma diagnostics. As illustrated in Fig. 3.2, rf-bias with a power of 200 W in total was applied with a frequency of 13.56 MHz or that of 400 kHz, and their superposed biases through a filter box. An applied source power in the ICP was 300 W with a frequency of 13.56 MHz. Self-dc bias voltage (V_{dc}) and peak-to-peak voltage (V_{pp}) were monitored by an oscilloscope. From the results by plasma monitoring, it was found that V_{dc} corresponding to the mean impacting ion energy varied with the superposed bias configuration even if the total bias power was the same, as shown in Fig. 3.2. Table III-1 provides these process parameters and the evaluated results of PPD mentioned later. Figures 3.2(a), 3.2(b), and 3.2(c) show the respective waveforms of single- and superposed frequencies realized by the ICP reactor. I analyze the plasma damage on silicon substrate surfaces exposed to plasmas with these bias configurations.



400kHz=200W 400k/13.56MHz=100/100W 13.56MHz=200W

Figure 3.2: Bias waveforms of single and superposed bias frequencies monitored by an oscilloscope in the ICP reactor; (a) 400 kHz, (b) 400 kHz/13.56 MHz, and (c) 13.56 MHz. Total input power was set at 200 W for all cases.

3.2.2 Characterization methods

Two optical analyses, SE and PRS, were employed to identify the damaged layer thickness and the defect density. In the analysis of SE spectra, we adopt a four-layer (air/SL/IL/Si substrate) model.^{6,7)} In the PRS analysis, the surface potential (V_s) is extracted from the spectral line shape ($\Delta R/R$) by Eqs. (2.1) and (2.6).^{8,9)} Then, the areal density of plasma-induced carrier trap site (N_{dam}) is calculated using Eq. (2.8).

The C - V measurement was performed to identify the structure of damage layers from the electrical viewpoint. With regard to defect sites created by PPD, the electrical measurements have been widely performed.¹⁰⁻¹⁵⁾ Among them, a C - V technique has been preliminary proposed¹⁶⁾ as a candidate to assign the defect density in damaged structures. Historically, there have been many studies conducted so far using C - V techniques in ion-implantation or other processes¹⁷⁻¹⁹⁾ for the purpose of quantifying dopant density. Dependence of measured capacitance (C) on bias voltage shift (ΔV_b) and the distortion of C - V curve were investigated. Density of defects (n_{dam}) created in a Si substrate was estimated using the $1/C^2$ - V technique presented in Chapter II.

3.3 Results and discussion

3.3.1 Damaged layer thickness and defect density

Table III-1 summarizes the results obtained from optical analyses for various bias-frequency configurations. In Table III-1, f_{SiO_2} is the volume fraction of SiO_2 in the IL. Figure 3.3 shows examples of $(\tan\Psi, \cos\Delta)$ spectra obtained by SE. Figure 3.4 shows the thicknesses of SL and IL (d_{SL} and d_{IL}) determined from the SE for various bias configurations as a function of measured V_{dc} . The V_{dc} corresponds to the average impacting ion energy. As described previously, V_{dc} varies with a superposed bias configuration even if the total power is the same (100 W and 200 W in total). As seen in Fig. 3.4, the d_{IL} increases monotonically with V_{dc} , almost irrespective to the bias configurations, indicating creation of more severe damage. On the other, the d_{SL} increases with V_{dc} and then tends to decrease in the higher V_{dc} region. This observed trend may be attributed to sputtering of the surface layer by Ar ion with higher energy.²⁰⁾

Table III-1: Examples of sample preparation conditions and extracted parameters by SE and PRS analyses. (d_{SL} : SL thickness, d_{IL} :IL thickness, f_{SiO_2} : fraction of SiO_2 in the IL)

Process	Bias[W] (400k/13.56M)	d_{SL} [nm]	d_{IL} [nm]/ f_{SiO_2}	E_g [eV]	ΔV_s [mV]	V_{dc} [V]
ICP-A	100/0	4.1	0.6/0.75	3.40	−1.8	−52
ICP-B	75/25	3.5	0.7/0.73	3.39	−11.0	−62
ICP-C	50/50	3.5	0.7/0.74	3.38	−11.7	−74
ICP-D	25/75	3.4	0.8/0.68	3.38	−16.6	−87
ICP-E	0/100	3.1	1.0/0.78	3.38	−30.6	−115
ICP-F	200/0	4.5	0.7/0.78	3.40	−16.5	−82
ICP-G	150/50	3.4	1.1/0.72	3.39	−33.3	−93
ICP-H	100/100	3.2	1.4/0.77	3.39	−80.1	−103
ICP-I	50/150	2.2	1.6/0.72	3.37	−114.0	−175
ICP-J	0/200	1.7	1.6/0.58	3.38	−18.5	−211
Control	-	0.9	0.2/0.59	3.40	-	-

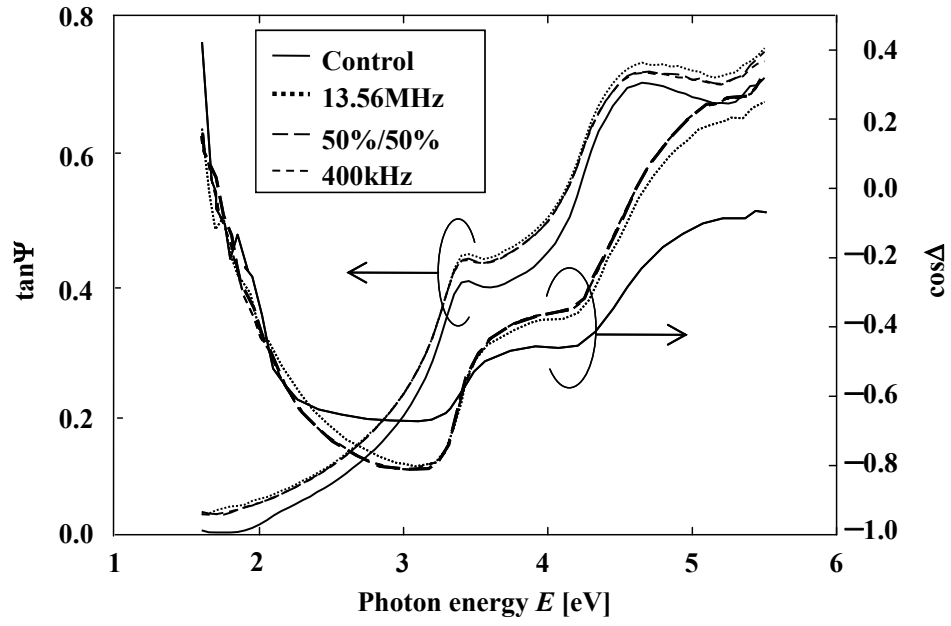


Figure 3.3: Typical SE spectra ($\tan\Psi$, $\cos\Delta$) as a function of photon energy. d_{SL} , d_{IL} , and f_{SiO_2} are determined from the spectra for various plasma process conditions.

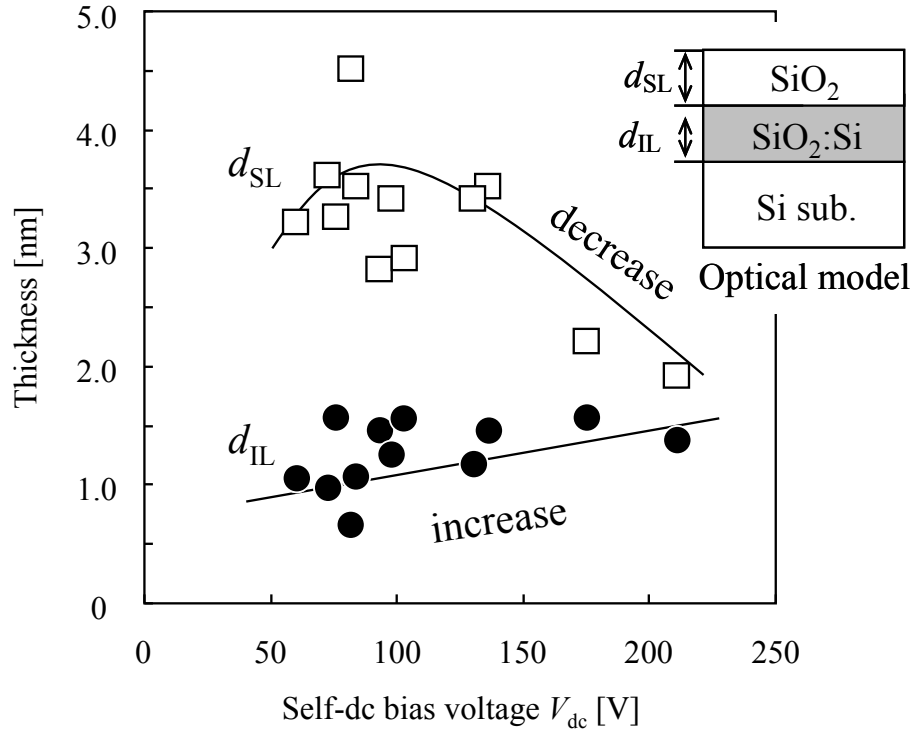
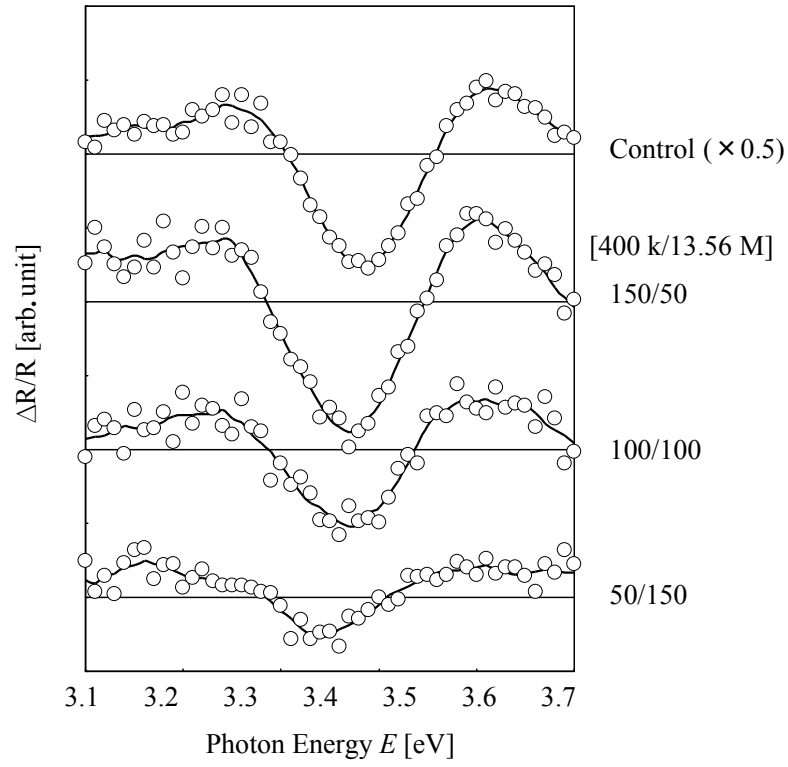


Figure 3.4: Calculated d_{SL} and d_{IL} from SE as a function of V_{dc} for various plasma process conditions.

Figure 3.5 shows examples of $\Delta R/R$ spectra. By fitting the obtained spectra with Eq. (2.1), one can obtain the shift of $E_g^{21,22}$ which may originate from a mechanical strain change developing in the IL, as listed in Table III-1. On the basis of the hydrostatic strain model,^{23,24)} the change in strain developing in the IL can be estimated, as approximately 0.004 ($\Delta E_g = 0.02$ eV) between the control (Ref) and damaged samples. Figure 3.6 shows the relationship between C and I_p for the samples fitted with Eq. (2.1). From this relationship, the surface potential change (ΔV_s) in damage samples were extracted by using Eq. (2.6) as listed in Table III-1. Once ΔV_s is determined, one can estimate N_{dam} . Figure 3.7 shows N_{dam} calculated from Eq. (2.8) as a function of $(V_p - V_{\text{dc}})$ for various bias configurations, including no-bias conditions—only the source plasma was generated and no bias power was applied to the wafer stage. As seen in Fig. 3.7, N_{dam} increases monotonically with $(V_p - V_{\text{dc}})$, almost irrespective to bias configurations. This result may be in sharp contrast to previous PPD pictures, *i.e.*, ions impacting on a surface under a low bias frequency (that has the higher energy component) become key to defect generation—more severe damage in a low bias frequency. The areal defect density of $\sim 10^{13} \text{ cm}^{-2}$ is estimated in this case in the exposed surface region (near the IL and Si substrate interface). Wada *et al.*²⁵⁾ determined plasma-induced defect site density as $\sim 10^{18} \text{ cm}^{-3}$. Both experimental observations discuss the distribution of defect sites located within 10 nm from the surface because the probe beam penetration depth is approximately 10 nm. Thus, by comparing the above values ($\sim 10^{13} \text{ cm}^{-2}$ and $\sim 10^{18} \text{ cm}^{-3}$), it can be speculated that plasma-induced carrier trap sites are locally distributed near the IL region.

It is confirmed from Fig. 3.7 that no apparent trend is observed with respect to the bias configurations, in other words, N_{dam} is dependent primarily on V_{dc} . This observation is consistent with the results provided by Fig. 3.4.



Ar : 20 sccm , 20 mTorr ICP source power : 300 W

Figure 3.5: Measured PR spectra for various bias configurations.

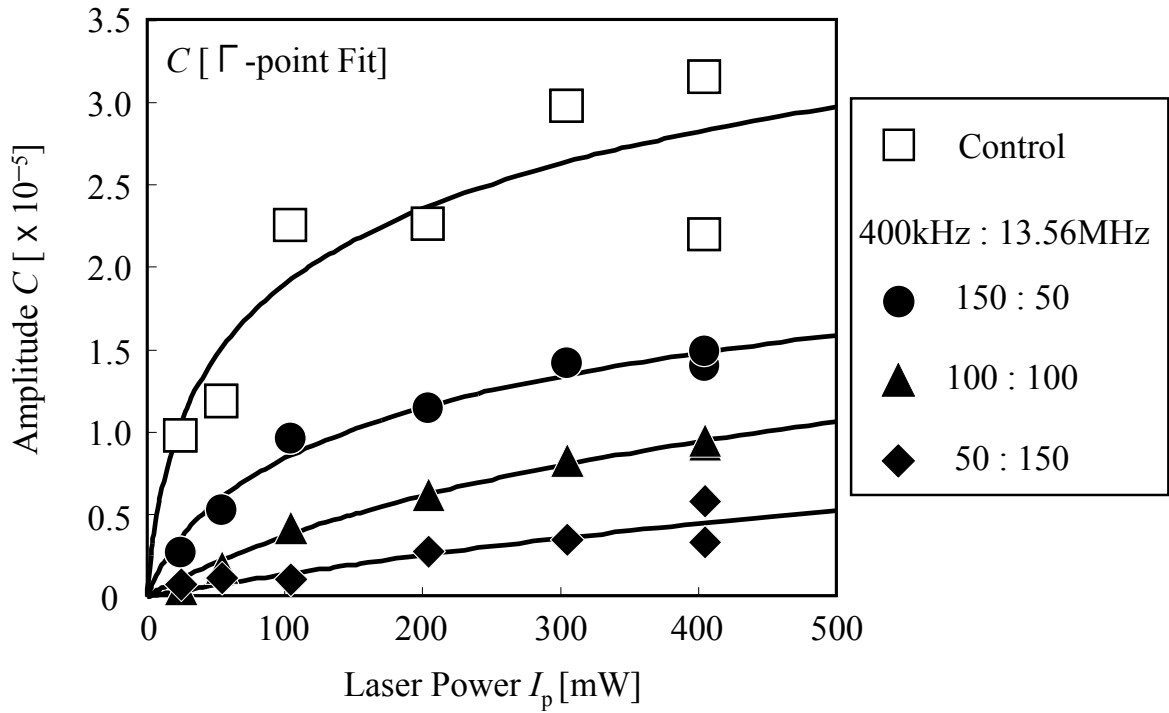


Figure 3.6: Calculated amplitudes of PR spectra C as a function of the modulation laser power for various plasma process conditions.

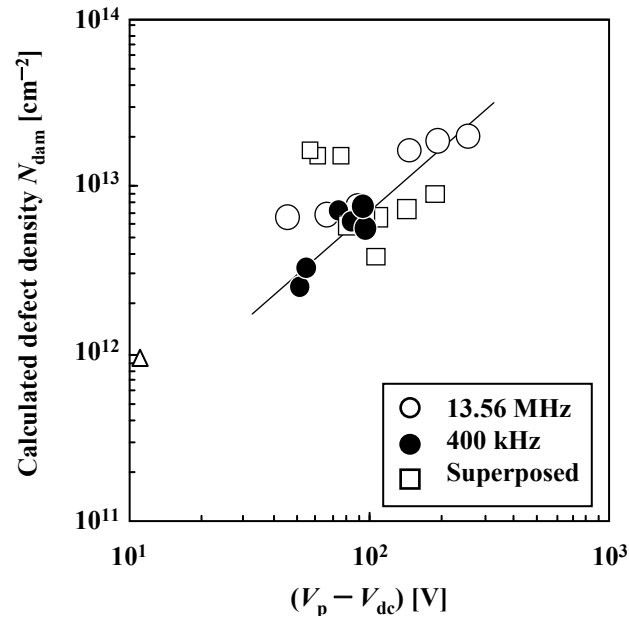


Figure 3.7: Estimated areal defect density as a function of $(V_p - V_{dc})$ for various bias configurations. The solid line is a guideline for the reader's eye. (Ar plasma).

Figure 3.8 shows C - V characteristics for the control (Ref) and plasma-exposed samples obtained by a mercury probe system (Fig. 2.24). Distortion of C - V curve is observable for the plasma-exposed samples. Two mechanisms are speculated for the distortion; (1) the shift of curve toward the positive bias implies the generation of negative charge trapping near the interfacial layer in the measurement, and (2) the decrease in capacitance in the region of positive bias voltage corresponds to the increase in surface layer thickness. This is consistent with the results (d_{SL}) by SE analysis. Figures 3.9(a) and 3.9(b) show the bias voltage shift (ΔV_b) as a function of the decrease in maximum differential capacitance (ΔC_{max}) and of V_{dc} , respectively. Since ΔV_s is in proportion to the trapped charge density, ΔV_s is considered to be dependent on the plasma-induced defect density N_{dam} . On the other hand, since ΔC_{max} is in proportion to the inverse of surface layer thickness, ΔC_{max} depends on d_{SL} . Therefore, Fig. 3.9(a) implies the relationship between N_{dam} and d_{SL} . Fig. 3.9(b) indicates that ΔV_b ($\sim N_{dam}$) approximately depends on V_{dc} (except the high V_{dc} region) for various

superposed configurations, which is consistent with the result in Fig. 3.7. Thus, it is confirmed that C - V measurement can identify plasma-damaged structures with defects created by PPD.

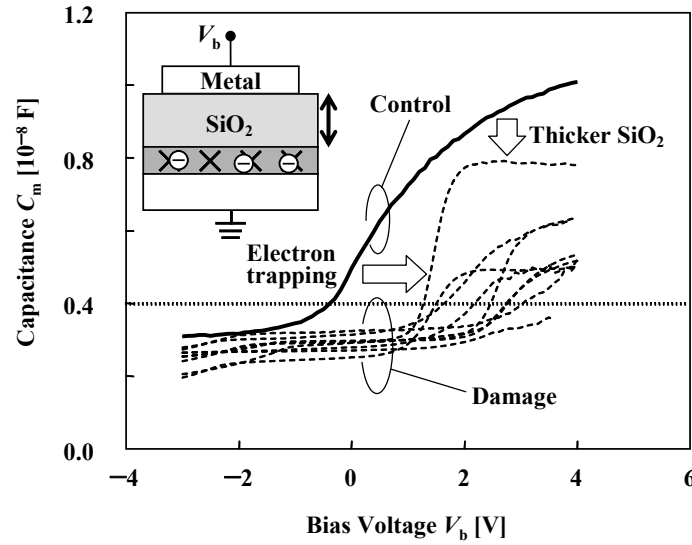


Figure 3.8: Measured capacitance as a function of bias voltage for various samples treated under different bias configurations.

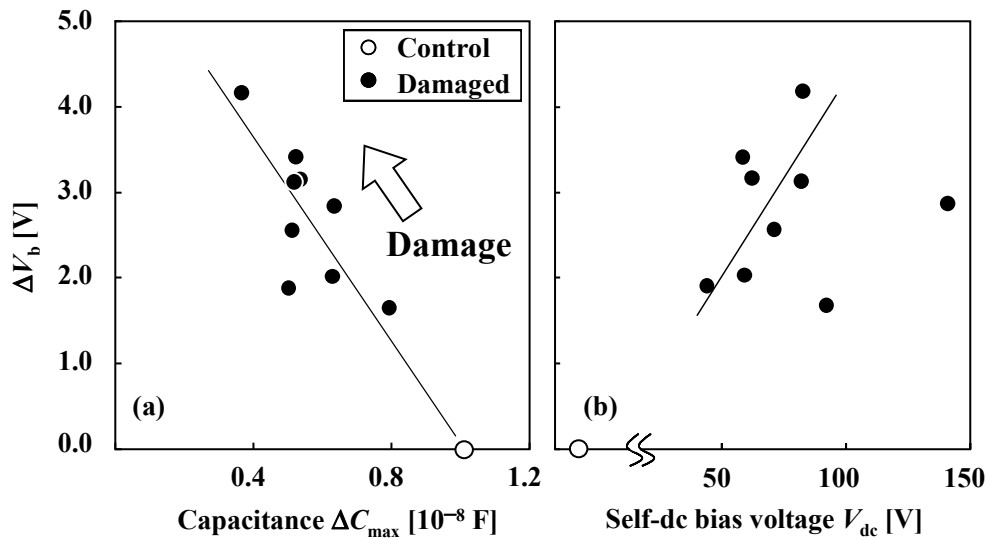


Figure 3.9: (a) Extracted bias voltage shift ΔV_b as a function of capacitance and (b) V_{dc} for various samples treated under plasma process conditions.

Figures 3.10(a) and 3.10(b) show, respectively, the energy band diagram of a pseudo-MOS (Metal–Oxide–Semiconductor) structure on an n-type Si wafer under inversion bias and $1/C^2-V$ plots for various samples. As seen, the $1/C^2-V$ curve of the control (Ref) exhibits a linear relationship between $1/C^2$ and V_b in the region from -2.0 to ~ 1.0 V, giving a constant carrier concentration ($N_D \sim 2.0 \times 10^{18} \text{ cm}^{-3}$) along the depth of Si substrate. In the case of the damaged samples, on the other, the slope of $1/C^2-V$ curves becomes gentle in the corresponding region for all bias configuration cases. Notice that this characteristic region is the intermediate range (B) as indicated in Fig. 2.26. Based on Eq. (2.9), this finding implies the presence of defects (carrier trap sites) affecting a differential capacitance in the Si substrates as illustrated in Fig. 3.10(a). Created defects are easily ionized or charged like impurity dopants under bias modulation in the $C-V$ measurement. Thus, the effective impurity concentration apparently increases, resulting in the decrease in the slope of $1/C^2-V$ plot as suggested in Fig. 2.26. By assuming that no plasma-induced defect is present in a non-processed Si substrate, one can estimate the defect density n_{dam} from the difference in the effective impurity concentration as suggested by Eq. (2.9). Note that, in this estimation, the profile of n_{dam} in the substrate from the surface region and the energy level are not considered. Figure 3.11 shows calculated n_{dam} as a function of $(V_p - V_{\text{dc}})$ for various bias configurations. Two features are found; (1) n_{dam} increases with an increase in $(V_p - V_{\text{dc}})$, almost irrespective of single- and superposed-bias frequencies, and (2) the estimated defect density ranges $\sim 10^{18} - 10^{19} \text{ cm}^{-3}$. The observed independence of n_{dam} on bias configurations is consistent with the results in Figs. 3.4 and 3.7. Therefore, it is concluded experimentally that the defect generation mechanism is governed dominantly by the resultant average ion energy, rather than by the bias configuration. In designing a bias configuration for realizing low PPD process, one had better focusing on V_{dc} . Note that this conclusion has been derived from the present evaluation methods. Due to the detection limits in analyses, one solely measures a part of

defects present in the damaged structure. In Chapter IV, this issue is discussed in detail.

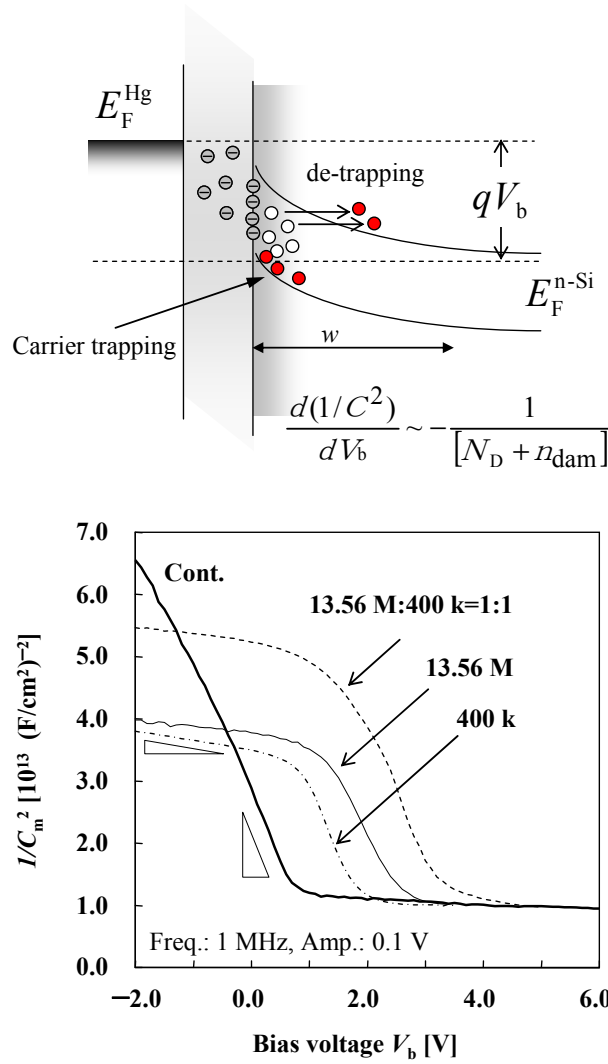


Figure 3.10: (a) Energy band diagram of a damaged Si structure with defects created by PPD in inversion and (b) measured C - V curves of the damaged samples. An n-type Si substrate is assumed.

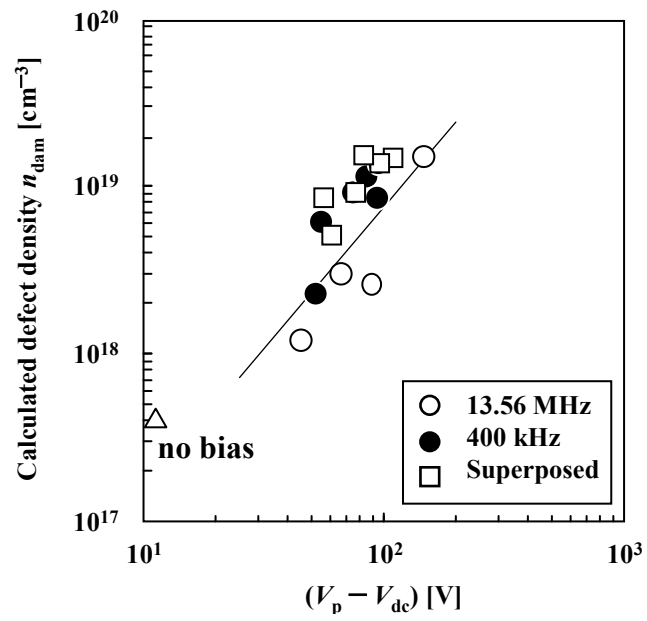


Figure 3.11: Calculated defect density as a function of $(V_p - V_{\text{dc}})$ for various bias configurations. The solid line is a guideline for the reader's eye. (Ar plasma).

3.3.2 PPD-range theory for bias frequency effects

In the previous subsections, it was found that N_{dama} and n_{dam} assigned by the PRS method and the C - V technique were primarily dependent on the average energy of incident ions defined by the IEDF. In this subsection, the effects of IEDF on defect generation are investigated on the basis of the so-called range theory.^{26,27)} During plasma processing, owing to an rf oscillating bias, the energy of incident ions obeys IEDF as shown in Fig. 3.12(a). As the bias frequency increases, the spectrum width of IEDF becomes narrower. By introducing the IEDF into the range theory, one can obtain the profile of incident ions. For details of the range theory, see Appendix A.1.

Figures 3.12(b) shows the predicted concentration profiles of injected Ar under various bias frequencies. Figure 3.12(b) corresponds to the distribution of injected ions. By implementing a defect generation rate dependent on the energy of each ion, the defect-site profile can be estimated by the PPD model²⁸⁾ as shown in Fig. 3.12(c). In this case, V_{dc} and $|V_{\text{pp}}|/2$ were set to -150 and 150 V, respectively. Since the spectrum of IEDF becomes narrower as the bias frequency increases, the depth profile of $n_{\text{ion}}(x)$ for 100 MHz becomes shallower as seen. However, the difference in depth profiles among the frequency ranges is less than 1 nm. This small difference is attributed to the power-law dependence of the nuclear stopping power $S_{\text{d}}(E_{\text{ion}})$ as well as the effect of range straggling—stochastic effects.

From the intersection between the defect density $n_{\text{dam}}(x, \omega)$ and the critical density (n_{cr}), one can estimate the damaged-layer thickness. As shown as a broken line in Fig. 3.12(c), if n_{cr} is assumed to be 10^{-4} , the damaged-layer thickness is estimated to be, approximately 5 nm, and the difference between the frequencies is less than 1 nm. This result implies that the damaged-layer thickness is a weak function of bias frequency, and the average self-dc bias voltage (V_{dc}) can be used as a simple and practical measure of the damage.

Figure 3.13 shows the damaged-layer thickness determined from $(d_{\text{SL}} + d_{\text{IL}})$ as a

function of average ion energy $\bar{E}_{\text{ion}}$ extracted from $q(V_p - V_{\text{dc}})$ (Table III-2). In this estimation, the effect of native oxide layer formation⁷⁾ after plasma exposure is taken into account as shown in the lower figure. The thickness increase due to the oxidation of Si was estimated as 0.67 nm (40 %⁸⁾ of native oxide thickness on Ref. determined by spectroscopic ellipsometry). Although it is difficult to assign whether the defects were created by Ar or O, Fig. 3.13 shows the damaged-layer thickness as a result of Ar plasma exposure. Figure 3.13 also shows the calculated results from Fig. 3.12(c) for the case of $n_{\text{cr}} = 10^{-4}$: In the present ICP system, the ion flux was approximately $5.0 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ and the process time was 30 s. From Fig. 3.12(b), most of the injected Ar is located within a layer 3 nm thick. Thus, the peak volume density is approximately $5.0 \times 10^{24} \text{ cm}^{-3}$, which is an effective value when the sputtered and reflected Ar ions are neglected. The detection limit for commonly used techniques such as secondary ion mass spectroscopy (SIMS) is assumed to be $5.0 \times 10^{20} \text{ cm}^{-3}$ (1 % of the Si atomic density). As seen in Fig. 3.13, the power-law dependence of damaged-layer thickness is clearly observed and the agreement between the model prediction and the experimental data is excellent, especially when no parameter optimization was undertaken. (The parameters only from the Moliere-based stopping power were used in this estimation.) The power-law constants determined by the least-square fits are $400 \text{ kHz} = 0.35 / 0.33$ and $13.56 \text{ MHz} = 0.32/0.29$ (experimental / calculation), respectively. The power-law dependent features are in agreement with each other.

Finally, to verify these findings, structural analysis by SIMS was performed. Since Ar is difficult to assign by SIMS, we traced (knock-on) O as a measure in this case. The plasma-exposed samples treated with different bias frequencies were analyzed. Figure 3.14 indicates the oxygen profile in the Si substrate. By plasma exposure, O atoms penetrate deeper into the Si substrate. As the V_{dc} ($\sim \bar{E}_{\text{ion}}$) increases, the depth of O distribution

becomes greater as seen for the 13.56 MHz case. In addition, samples with similar V_{dc} (400 kHz = -72 V, 13.56 MHz = -71 V) were compared. When comparing the O-profile of 400 kHz with that of 13.56 MHz, both of the profiles are almost "identical", regardless of the bias frequency (IEDF). This observation is consistent with the model discussed in the above. Therefore, it is concluded that under a certain plasma conditions, the damaged-layer thickness is a weak function of the bias frequency; in other words, the average self-dc bias voltage V_{dc} ($\sim \bar{E}_{ion}$) can be used as a simple and practical measure of the damage. The damaged-layer thickness has a simple power-law dependence on ion energy.

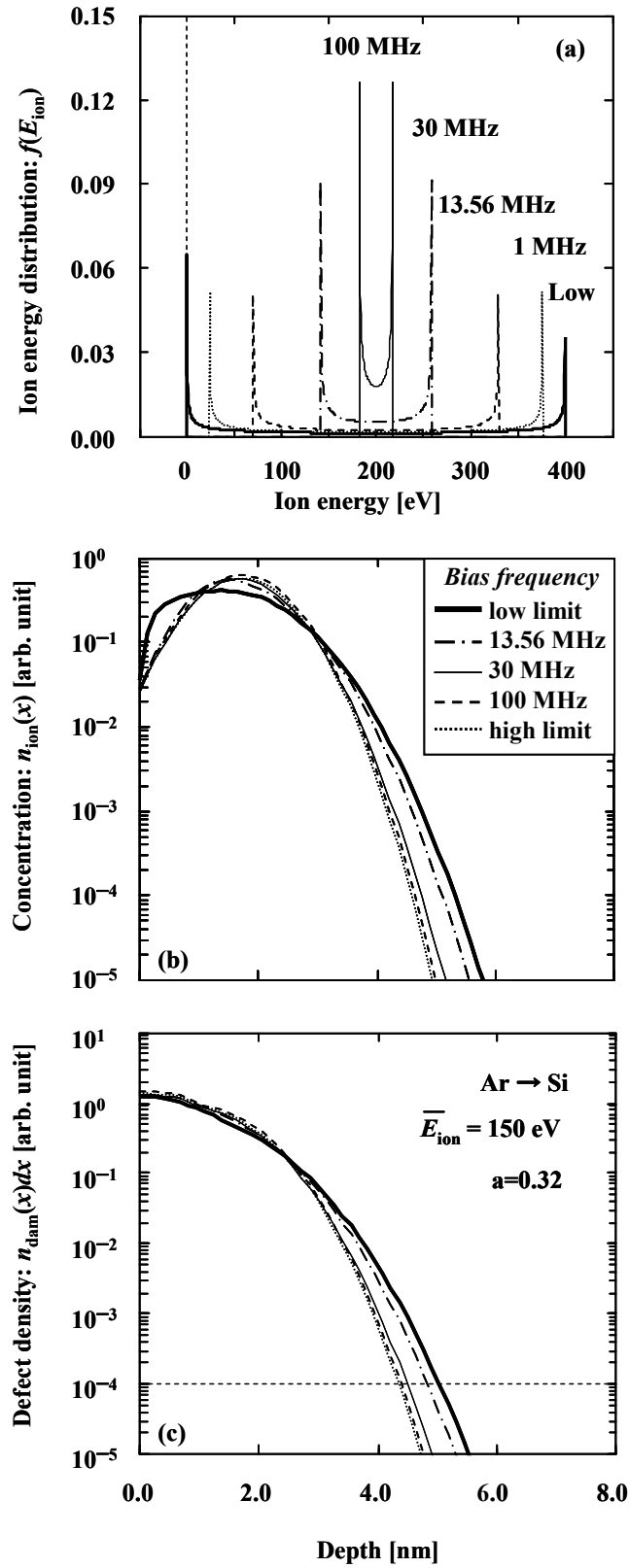


Figure 3.12: (a) Examples of IEDFs in various bias frequencies. (b) Profiles of incident Ar ions in Si substrates under various bias frequencies. The average energy was assumed to be 150 eV. (c) Profiles of defect density created under various bias frequencies.

Table III-2: Sample preparation conditions and extracted parameters by SE and PRS analyses. (d_{SL} : SL thickness, d_{IL} : IL thickness, f_{SiO_2} : fraction of SiO_2 in the IL)

400 kHz			13.56 MHz	
Bias power [W]	$V_p - V_{\text{dc}}$ [V]	$d_{\text{SL}} + d_{\text{IL}}$ [nm]	$V_p - V_{\text{dc}}$ [V]	$d_{\text{SL}} + d_{\text{IL}}$ [nm]
25	51	3.6	45	4.1
50	54	4.4	66	4.6
75	73	4.6	82	4.9
100	83	4.8	144	5.2
150	94	5.0	190	5.8

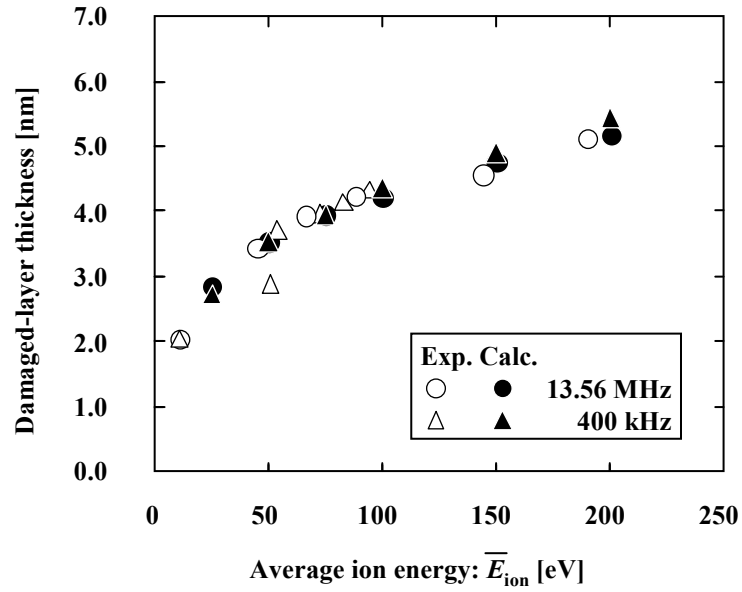


Figure 3.13: Estimated damaged-layer thicknesses (Calc.) as a function of incident ion energy for bias frequencies of 13.56 MHz and 400 kHz. (Ar plasma case) Experimentally obtained thicknesses by SE (Exp.) are compared by adjusting $q(V_p - V_{\text{dc}})$ to the average ion energy. For estimation of the damaged-layer thickness, see the text.

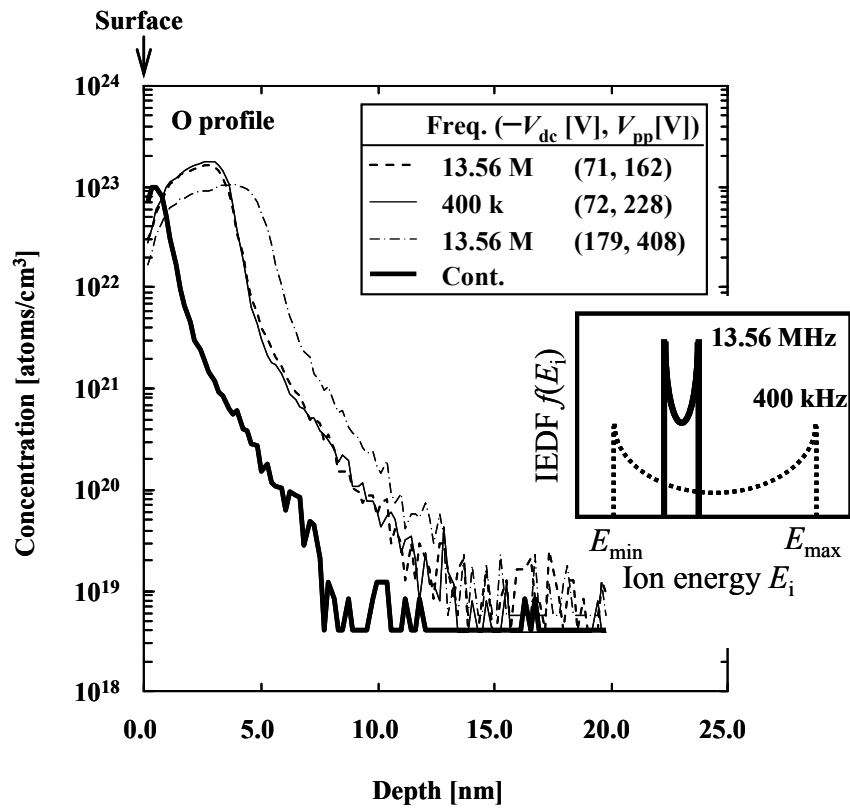


Figure 3.14: Oxygen concentration profile determined by secondary ion mass spectrometry (SIMS). Samples exposed to plasmas with different bias frequencies of 400 kHz and 13.56 MHz are compared. The profile in the 13.56-MHz case (dotted curve) is identical to that of the 400-kHz case (thin solid curve) when $|V_{dc}|$ values are similar.

3.4 Conclusion

The plasma-induced defect generation mechanism in a Si substrate was quantitatively studied for various bias-frequency configurations using the SE, PRS, and $C-V$ techniques. The growth of surface and interfacial layers was assigned by both SE and $C-V$ measurement. The density of local defect structure was identified by PRS and $C-V$ measurement—the defect sites ($\sim$ charge trap site) which degrade device performances were identified as an areal density of $\sim 10^{12} \text{ cm}^{-2}$ and a volume density of $\sim 10^{19} \text{ cm}^{-3}$. The defect generation was found to depend primarily on V_{dc} . Regarding bias frequency effects (IEDF effects), the damaged-layer formation was modeled on the basis of a modified PPD range theory. The damaged-layer thickness exhibits a simple power-law dependence on V_{dc} and is a weak function of the bias frequency. The feature was verified experimentally. The findings also suggest that the damaged-layer thickness to be measured depends also on the sensitivity of analytical technique. In other words, in some cases, conflicting results may be incurred regarding the bias frequency effects. The obtained results propose a key guideline for the future plasma equipment and process designs.

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Chapter IV

Profiling of defect density by wet-stripping

4.1 Introduction

Plasma processing plays an important role in manufacturing present-day microelectronics. As mentioned in Chapter I, plasma-induced damage (PID) consists of three major mechanisms.¹⁾ The first mechanism is damage induced by conduction current from plasma flowing into MOSFETs, resulting in degradation of the performance and increase in the parameter variability owing to plasma-induced electrical stress.²⁻⁵⁾ The second mechanism is damage induced by incident photons on material surface.⁶⁻⁸⁾ The third mechanism is damage induced by high-energy ion bombardment on Si substrates or other materials,⁹⁻¹⁵⁾ which is the main topic of this thesis. In this chapter, this mechanism is focused on, which is denoted as "plasma-induced physical damage (PPD)" for simplicity. PPD usually creates "defects"^{11,15-17)} such as Si-Si broken or strained bonds, displaced Si atoms, vacancies, and interstitial atoms in crystalline Si substrates. The PPD on Si substrate surfaces has been extensively studied recently, because the mechanism of PPD is naturally governed by basic plasma parameters such as sheath structure, plasma density, and so on. For example, a Si recess^{12,13,18)} formed on the source/drain extension region in a MOSFET is considered to have a negative impact on device performance such as threshold voltage shift.¹⁸⁾ Moreover, the latent defects remaining after a wet-etch step following plasma etching

degrades drain saturation current (I_{on}), which means device operation slow down.^{17,19)} This damage creation mechanism was clarified using the modified range theory.²⁰⁾ Eriguchi *et al.* recently modeled²⁰⁾ the dependence of the surface damaged-layer thickness on the incident average ion energy $\bar{E}_{ion}$ and rf-bias frequency applied to a wafer stage. As presented in Chapter II, the thickness of the damaged layer showed a power-law dependence on the average ion energy $\bar{E}_{ion}$, which may be owing to a stochastic effect called "straggling" in the vertical direction, that is, along the axis of incidence.²⁰⁻²²⁾ Since the thickness of the damaged layer may be equivalent to the Si recess depth (d_R), d_R is considered to be governed significantly by $\bar{E}_{ion}$. Thus, controlling the $\bar{E}_{ion}$ is the principal approach for suppressing the PPD.

Spectroscopic ellipsometry (SE) is widely used as in-line monitoring for PPD measurement. In the analysis, the sensitivity relies on the observed changes in dielectric constants and other optical parameters such as an extinction coefficient. Using SE, several reports discussed depth profiles of dielectric constant change.²³⁻²⁸⁾ For example, H-plasma damaged samples were found to have relatively thick IL ~ 10 nm,^{15,29)} which was difficult to remove by wet-etching¹⁵⁾ as discussed in Chapter VI. These findings related to SL and IL are of great importance to device designs under process constraints, because the final topological structure of MOSFETs with a Si recess defines the performance. Regarding defect sites created by PPD, electrical measurements have been widely performed³⁰⁻³⁵⁾ as also performed in Chapter III. Among them, a $C-V$ technique has been primarily proposed³⁶⁾ to probe the density (n_{dam}) in damaged structures. Chapter III, by using the $C-V$ technique to PPD,^{36,37)} led to the conclusion that, under typical plasma etching processes, n_{dam} ranges from 10^{18} to 10^{19} cm⁻³.

In addition to n_{dam} of as-damaged samples, addressing the residual n_{dam} after a wet-etching step is indispensable to design the drain current of a MOSFET, because n_{dam}

directly affects the resistance change in the source/drain extension region. However there have been only few discussions regarding the residual n_{dam} after a wet-etching. A methodology to evaluate quantitatively the n_{dam} profile is requisite to design a device of the final structure in ultimately scaled regime as well as to understand the damage creation for the low ion energy case such as atomic layer etching (ALEt) process. In this chapter, I demonstrate a comprehensive evaluation of the PPD profile using SE and a customized $1/C^2-V$ method capable to quantify n_{dam} in the nano-scale regime. Surface structures of plasma-exposed Si substrates are investigated in detail by focusing on the profiles of n_{dam} by using wet-etching. By comparing the obtained data for inductively coupled plasma (ICP) or capacitively coupled plasma (CCP) exposures, I discuss the impacts of the ion flux on the damage characterization. Key issues in the nano-scale damage characterization are presented.

4.2 Experimental

4.2.1 Plasma reactors and sample treatments

4-inch n-type (100) Si wafers with $0.02 \Omega \text{ cm}$ were exposed to Ar-based ICP and CCP (in Figs. 2.1 and 2.2) discharges for 30 s. The unexposed sample is denoted as "Cont." in this chapter. The processing time of 30 s was chosen as a saturation value in terms of the damaged-layer formation process according to the previous results.^{38,39)} Table IV-1 provides process conditions employed in this study. RF biasing at 13.56 MHz was applied to the wafer stage 120 mm in diameter with powers ranging from 50 to 200 W in the ICP or with a power of 10 W in the CCP, respectively. The ICP source power was 100 W. Plasma diagnostics using a Langmuir probe and an oscilloscope determined the plasma density and the average self-dc bias ($V_{\text{dc}} < 0$) and plasma parameters. Ion fluxes (Γ_{ion}) to the Si substrate were estimated from saturation ion current monitored by an oscilloscope as listed in Table IV-1. The average ion energy $\bar{E}_{\text{ion}}$ is defined as $q(V_p - V_{\text{dc}})$ from the estimated plasma potential.

In order to study the effects of wet clean, damaged samples were immersed in $\approx 0.1\%$ diluted hydrofluoric acid (DHF) for 60 s, followed by SE and $C-V$ measurements immediately, and then immersed again in DHF for additional 300 s. Finally, SE and $C-V$ measurements were performed to assign the final thickness and residual defect densities for all samples, respectively.

Table IV–1: Process conditions employed and plasma parameters determined from Langmuir probe measurements.
(Ar gas, 2.7 Pa, 30 s, ICP source power: 100 W)

Source	Bias power [W]	V_{dc} [V]	Electron density [cm^{-3}]	Ion flux [$\text{cm}^{-2}\text{s}^{-1}$]
ICP	25	–34	1.0×10^{11}	3.1×10^{14}
	50	–70		
	75	–90		
	100	–130		
	200	–240		
CCP	10	–260	4.0×10^9	1.2×10^{13}

4.2.2 Optical and electrical characterizations

To clarify the structure of damaged layers and the thickness, spectroscopic ellipsometry (SE) was used as performed previously. Detail of SE was mentioned in Chapter II. The measurements were carried out in the photon energy range of 1.60–5.50 eV at 0.05 eV intervals. As also discussed previously, the damaged layer consists of two regions, *i.e.*, the surface and interfacial layers (abbreviated SL and IL, respectively).

Figure 2.16 in Chapter II shows one of typical damaged structures including local defects, predicted by MD simulation. The MD code used here was originally developed by Ohta and Hamaguchi.⁴⁰⁾ Further details of the MD procedure are described elsewhere.^{40–42)} This simulation was performed for Ar-atom impacts using an SiO_2/Si substrate as a starting structure. The potential model presented by Wilson *et al.*⁴³⁾ for Si–noble gas (Ne, Ar, Kr, Xe) systems was implemented. One thousand ions impinged into this structure. As indicated in Chapter II [Fig. 2.16(a)], the SL is primarily composed of SiO_2 , as a result of oxidation of heavily damaged regions by exposure to air and the presence of knock-on oxygen from the native oxide layer. The IL is a partially oxidized or disordered Si layer, *i.e.*, a

mixed layer consisting of crystalline Si and SiO₂ phases. Thus, in SE analysis, an optical model assuming four layers (air/SL/IL/Si substrate) was applied as performed previously. To obtain the surface (SL: d_{SL}) and interfacial [IL (SiO₂ + crystalline-Si): d_{IL}] layer thicknesses and the composition (f_{Si} : component of crystalline-Si), the spectrum was fitted with the optical model by regression analysis to minimize the unbiased estimator. The thickness of the damaged layers defined as $d_{\text{SL}} + d_{\text{IL}}$ is the principal outcome of the SE measurement. Note that localized structures as indicated in Chapter II [Fig. 2.16(b)] can not be detected by SE. These defect structures can be identified by the C – V method.

In this chapter, an electrical characterization was conducted using the system illustrated in Fig. 2.24 of Chapter II. It is a mercury (Hg) probe platform, employing a pseudo-MOS structure (Hg/SiO₂/Si). An LCR-meter (HP-4284) was used to measure C – V characteristics of damaged structures (Hg/SiO₂/Si). The frequency of voltage modulation superimposed on the DC bias was 100 kHz. The electrical oxide thickness (EOT)⁴⁴⁾ was estimated from the maximum capacitance in accumulation.⁴⁵⁾ I measured the capacitance in inversion for determining the defect density (n_{dam}) of damaged samples as provided in Chapter III. When a Si substrate is exposed to plasma, defects with various structures are formed in the SL and IL. As shown in Chapter II [Fig. 2.16(b)], after thorough inspection of the local defect structures in the MD simulation snapshots, typical structures commonly observed were interstitial atoms⁴⁶⁻⁴⁸⁾⁾ and a dumbbell type.^{37,49,50)} Note that the surface amorphized⁵¹⁾ and interlayer regions in Chapter II [Fig. 2.16(a)] do correspond respectively to the SL and IL measured by SE. In the C – V measurement, the SL is identified by the accumulation capacitance, and local defect sites underneath IL may be assigned from the inversion capacitance, although one can not distinguish how much portion of IL belongs to the accumulation capacitance. Since the local defects observable in MD simulation are stable structures that act as traps for carriers as pointed out in various literatures,⁴⁷⁻⁵⁰⁾ the change in

the inversion capacitance corresponds the change in "effective" doping concentration. From Eq. (2.9), one can estimate the density of defects n_{dam} . As shown in Fig. 2.26 of Chapter II, the change in $1/C^2-V$ characteristics for a damaged structure can be determined. One can see the change in the slope of $1/C^2-V$ depending on V_b . The V_b dependence of the slope is attributed to the depth and energy profiles of the defects created by PPD. Damage causes the slope to decrease in the V_b range from -1.0 to 1.0 V, indicating the presence of defect sites ($N_D + n_{\text{dam}} > N_D$). For typical plasma conditions, I estimate n_{dam} to be in the range $\sim 10^{18} - 10^{19} \text{ cm}^{-3}$, consistent to other evaluation techniques.^{11,16)} This is consistent with defect density found by MD simulation. Therefore, n_{dam} measured by the $1/C^2-V$ technique corresponds to those local defect structures beneath the IL region. In this study, I evaluate PPD and these (residual) defects after wet-etching, primarily using this $1/C^2-V$ technique.

4.3 Results and discussion

Figure 4.1(a) shows $C-V$ curves of typical as-damaged samples including the "Cont". For the damaged sample, the value of the capacitances in the accumulation region ($V_b > 0$) is significantly increased. EOT is thus determined, and the results are compared with ($d_{\text{SL}} + d_{\text{IL}}$) and d_{SL} only in Fig. 4.1(b). Two key features are confirmed: (1) d_{SL} is smaller than the EOT for all damaged samples. (2) ($d_{\text{SL}} + d_{\text{IL}}$) is approximately equivalent to the EOT. This suggests that, in the $C-V$ measurements, ($d_{\text{SL}} + d_{\text{IL}}$) is identified as a surface oxide layer having the capacitance C_{ox} usually extracted from MOS structures.⁴⁵⁾ Therefore, as discussed in the following, the "effective" doping concentration derived from $1/C^2-V$ measurement is related to $N_D + n_{\text{dam}}$ beneath the IL by SE. This methodology enables us to quantify n_{dam} in the Si substrate created by PPD.

To discuss the difference in the detection depth by the optical measurements (SE and PRS) and that by the electrical measurement ($C-V$), two typical cases are simulated for

shallower (< 10 nm) and deeper (> 10 nm) damaged layers in Figs. 4.2(a) and 4.2(b), respectively. In the case of Fig. 4.2(a), damaged layer can be evaluated by the optical and electrical methods. However, in the case of Figs. 4.2(b), the optical measurement such as PRS can not detect defects present deeper than 10 nm from the surface, because the absorption depth of a probe beam is less than 10 nm at around 3.4 eV which is the main peak of PR spectrum.

Figure 4.3 shows an example for the thickness determined by SE for various samples exposed to plasmas before and after DHF wet-etching. One can see decrease in $(d_{SL} + d_{IL})$ after the wet-etching. Figures 4.4 compare the dependence of d_{SL} and d_{IL} on the average ion energy $\bar{E}_{ion}$ in the case of various ICP exposures. As seen in Fig. 4.4(a), with an increase in $\bar{E}_{ion}$, d_{IL} monotonically increases, whereas d_{SL} exhibits no clear dependence on $\bar{E}_{ion}$. This is owing to the fact that a surface damaged layer is reconstructed by air exposure (oxidation) or surface sputtering. Thus, while d_{SL} is independent of it, d_{IL} should be used as a measure of PPD. Moreover, DHF wet-etch changes d_{SL} and d_{IL} in the course of time as shown Figs. 4.4(b) and 4.4(c). d_{IL} is significantly decreased by the 300-s-DHF wet-etch in the lowest $\bar{E}_{ion}$ case, implying the removal of the damaged layer.

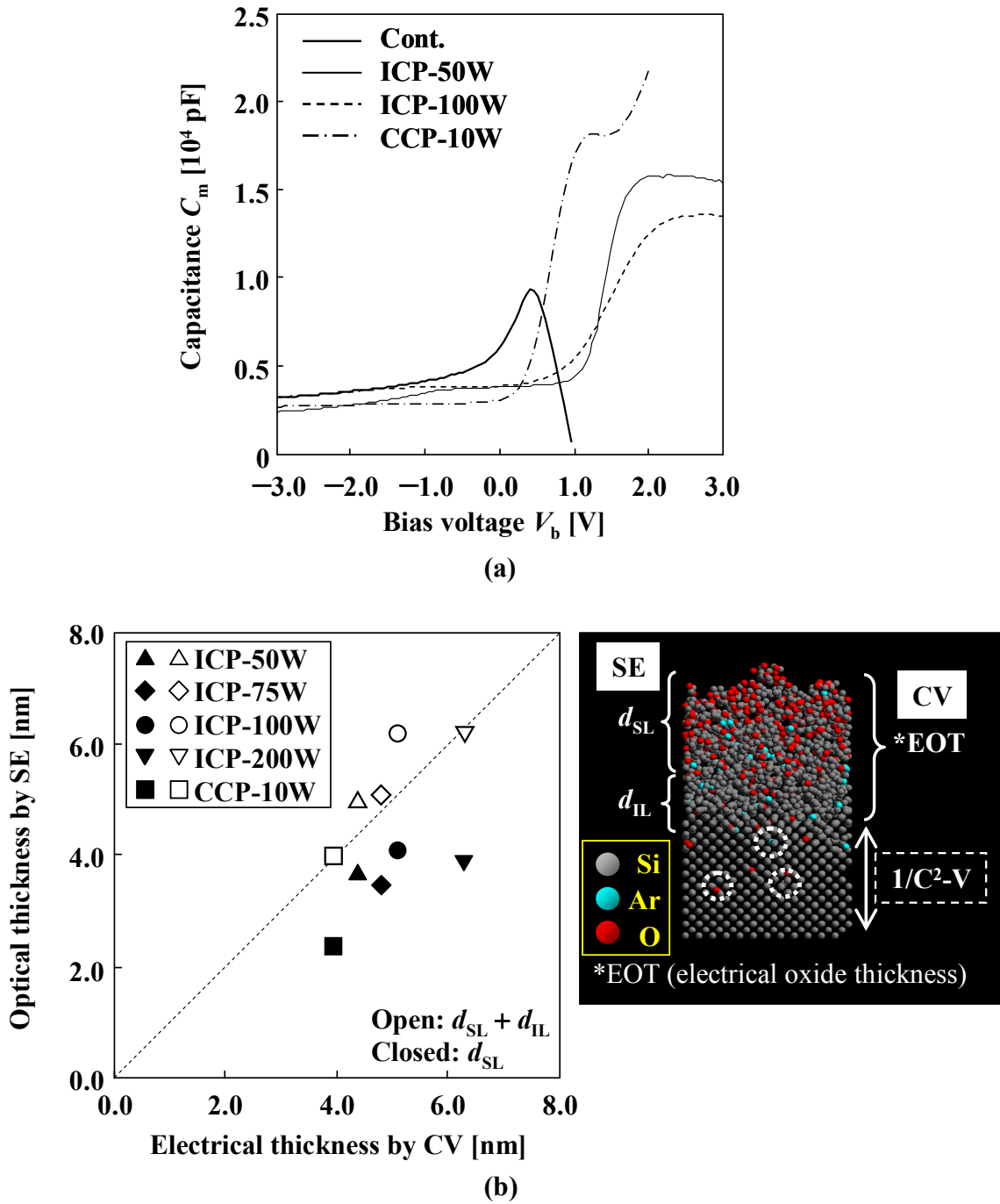


Figure 4.1: (a) Typical C - V curves for various samples. From the maximum capacitance, the electrical thickness is determined. (b) The relationship between the (optical) thickness and the electrical thickness determined from C - V data.

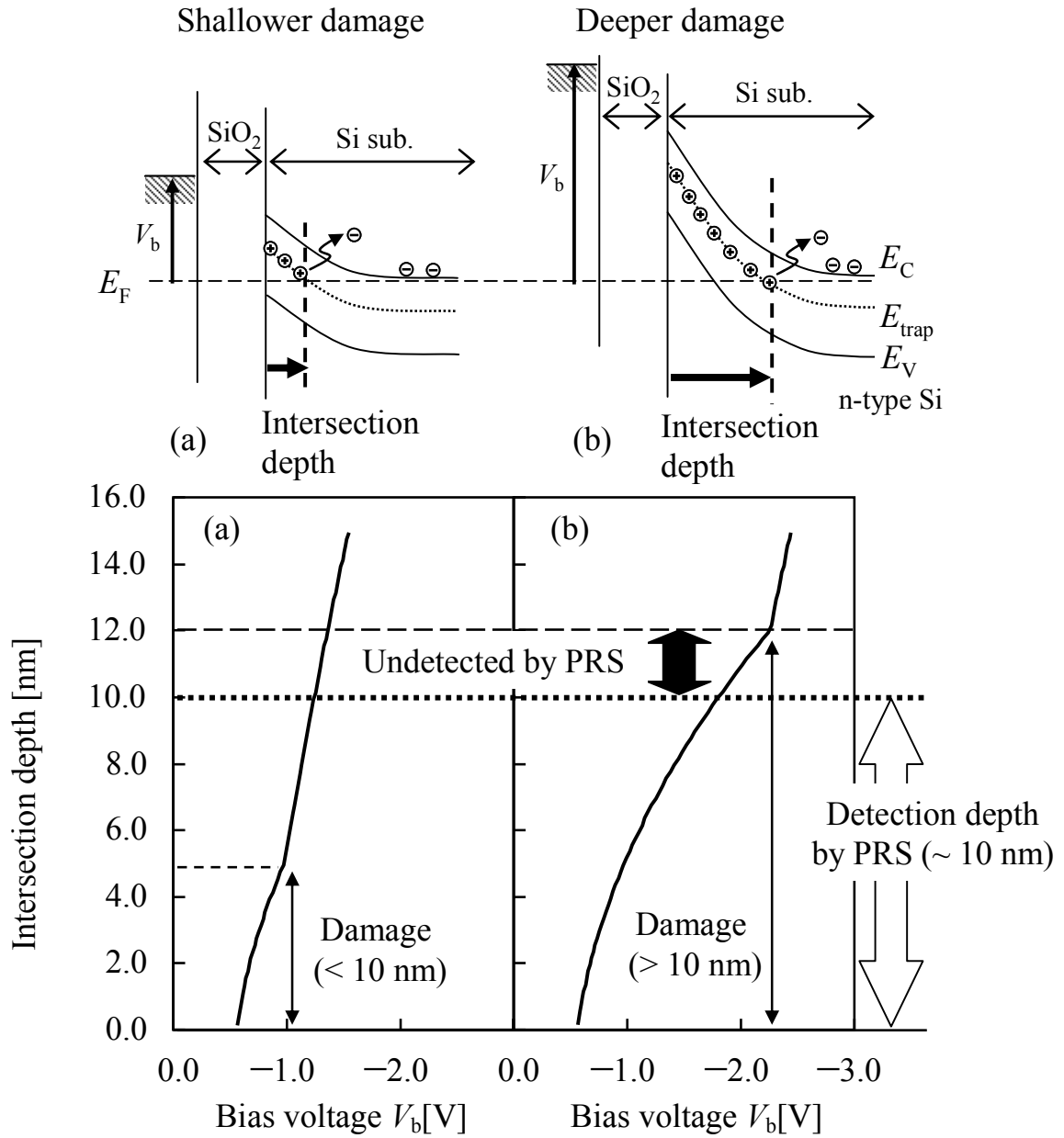


Figure 4.2: Difference between the detection depth by the optical measurements (SE and PRS) and electrical measurement ($C-V$). Two typical cases are simulated for shallower (< 10 nm) and deeper (> 10 nm) damaged layers.

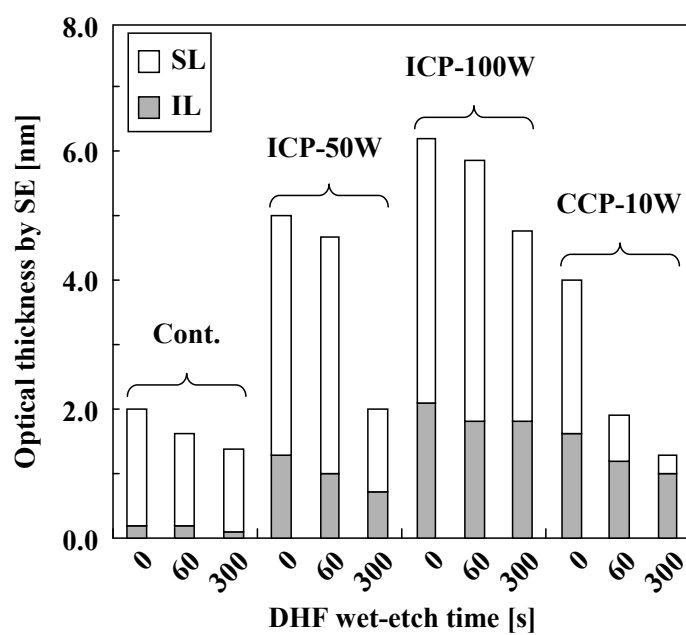


Figure 4.3: Example for the trend in optical thicknesses, d_{SL} and d_{IL} by DHF wet-etching for various damaged structures. The thicknesses of "Cont." are also shown.

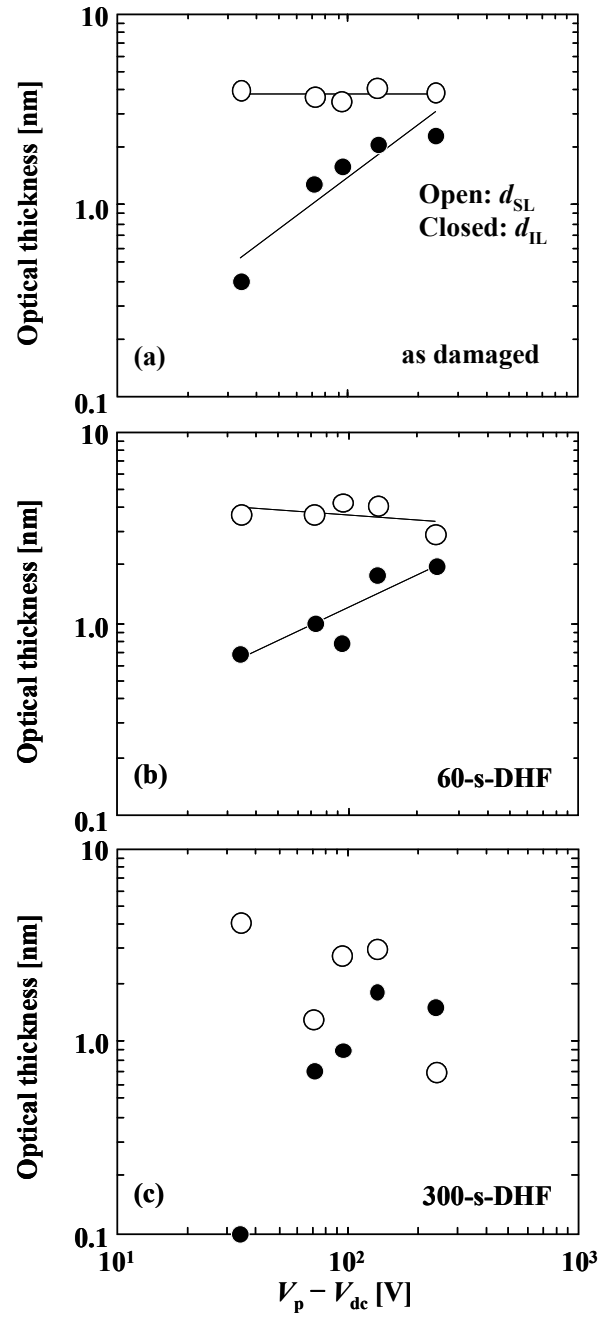


Figure 4.4: Dependence of d_{SL} and d_{IL} on the average incident ion energy in various DHF steps. (a) Before DHF treatment. (b) After 60-s-DHF. (c) After 300-s-DHF.

As discussed above, d_{IL} rather than d_{SL} should be used as a measure of PPD in SE analysis. However, no quantification of defect density can be realized only by SE. Figures 4.5 displays various $1/C^2-V$ curves obtained before and after DHF treatments. One can see a

"plateau"—gentler slope region—in damaged samples clearly (See also in Chapter II Fig. 2.26). Even after the DHF treatments, the plateau remains in most cases, implying the presence of defects. Figure 2.26 in Chapter II illustrates the mechanism explaining the presence of the plateau in the $1/C^2-V$. When V_b is swept in inversion, a depletion layer is formed and extends toward deeper region of the Si substrate in accordance with V_b . The intersection between the Fermi level and the defects determines the depth of defects that contribute the differential capacitance measured (C_m) at the V_b . In the extent configuration such as strong inversion as shown in (C), only the dopants (N_D) can contribute to C_m because no more defects may be present in the deep substrate region. Therefore $1/C_m$ becomes close to $(1/C_{ox} + 1/C_{inv})$ where C_{inv} is defined by N_D . This configuration corresponds to the $1/C^2-V$ curves in the inversion region. In other words, the slope becomes close to that of Cont. in the strong inversion. In the intermediate V_b range as shown in (B), both dopants and defects contribute to $1/C_m$, *i.e.*, the slope becomes gentler than that of Cont. as Eq. (2.9) suggested. Moreover, the range of V_b in the plateau becomes narrower as DHF time increases, indicating a decrease in n_{dam} close to the IL by the wet-etch, *i.e.*, removal of the damaged layer and oxidation of a part of the remaining damaged layer. Figure 4.6 shows typical trends in n_{dam} for damaged samples with DHF treatments and Figure 4.7, n_{dam} as a function of $\bar{E}_{ion}$ for ICP damaged samples before and after DHF treatments. The n_{dam} is estimated from the slope of the plateau. From Figs. 4.7(a) and 4.7(b), the $\bar{E}_{ion}$ dependence of n_{dam} is expressed as

$$n_{dam} = C_{dam} \cdot (\bar{E}_{ion})^\gamma \quad (4.1)$$

where C_{dam} and γ are material-specific constants. In these cases, γ is determined as 1.3 and 1.2 for the cases of Fig. 4.7(a) and 4.7(b), respectively.

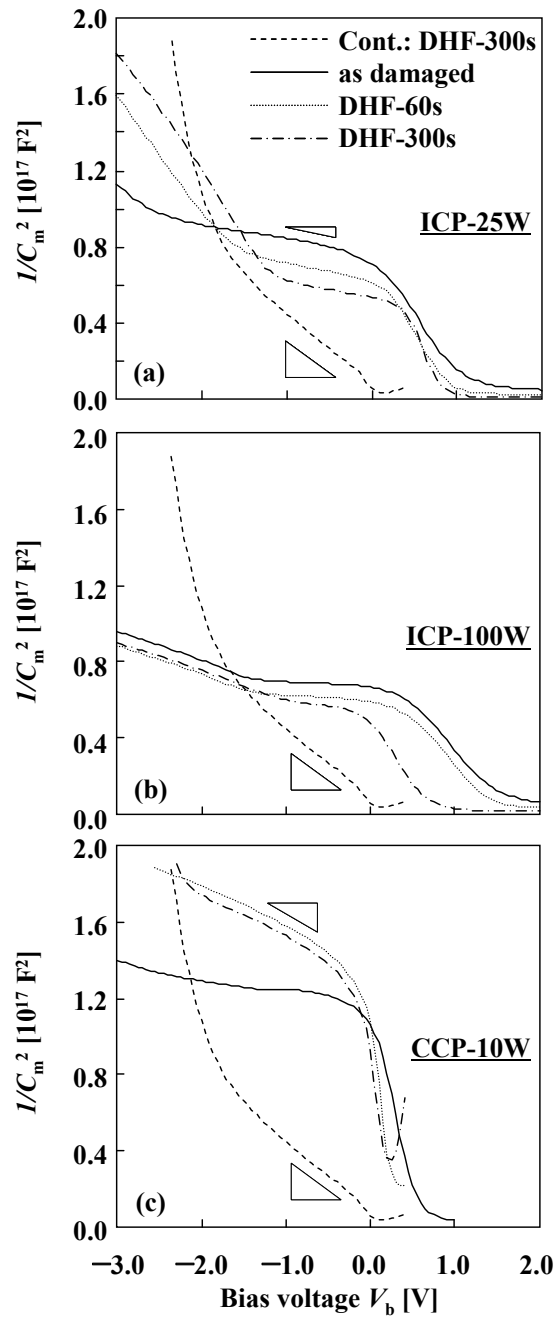


Figure 4.5: Typical $1/C^2$ - V curves of plasma-damaged structures in various DHF steps. The $1/C^2$ - V curves of "Cont." are also shown. (a) 25-W-ICP exposure, (b) 100-W-ICP exposure, and (c) 10-W-CCP exposure.

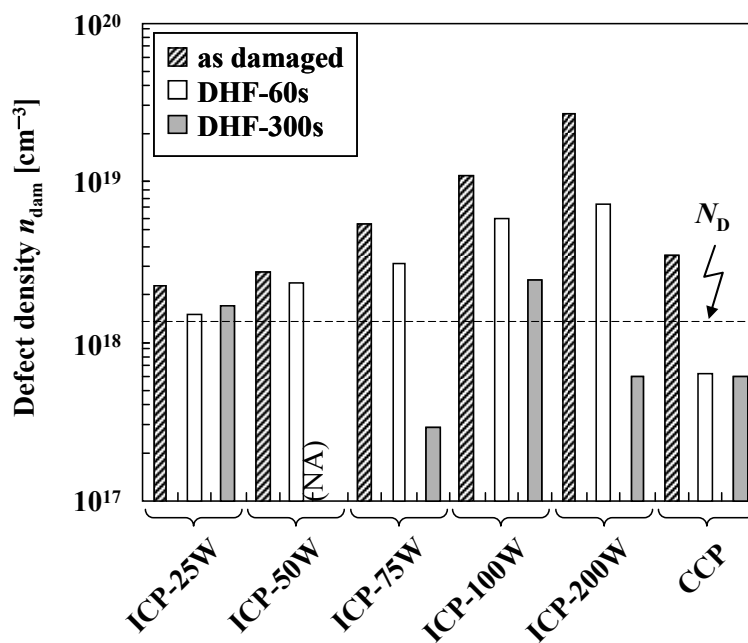


Figure 4.6: Example for the trend in defect densities for damaged structures in various DHF steps.

From the presence of plateaus in the $1/C^2-V$ curves in Figs. 4.5, even after 300-s-DHF wet-etch, it is confirmed that the residual defects are still present in the Si substrate. However, no clear $\bar{E}_{\text{ion}}$ dependence of n_{dam} is seen for Fig. 4.7(c). This feature may be attributed to the fact that residual defects are small in number (close to the dopant concentration), *i.e.*, below the detection limit. These results imply that most of the damaged region has been oxidized and is stripped off by 300-s-DHF wet-etch. (See the similar trend of d_{IL} in Figure. 4.4.) Based on the $1/C^2-V$ methodology, one can quantify the evolution of n_{dam} with various processing steps such as wet-etch stripping. Furthermore, the $1/C^2-V$ methodology is applicable for investigating the effects of Si recess depth (d_{R}) on residual damage as described below,

$$N_{\text{dam}} = \int_{d_{\text{R}}}^{\infty} n_{\text{dam}}^0(x) dx \quad (4.2)$$

where n_{dam}^0 is the initial defect density. Note that the n_{dam} estimated by the $1/C^2-V$ measurement is the volume density of residual defects in the damaged layer. The areal density N_{dam} in Eq. (4.2) is obtained by integration of the n_{dam}^0 . Based on the PPD-range theory noted in Appendix A.1, the dependence of d_R on E_{ion} shows a power-law relationship almost regardless of a wet-etched depth.⁵²⁾

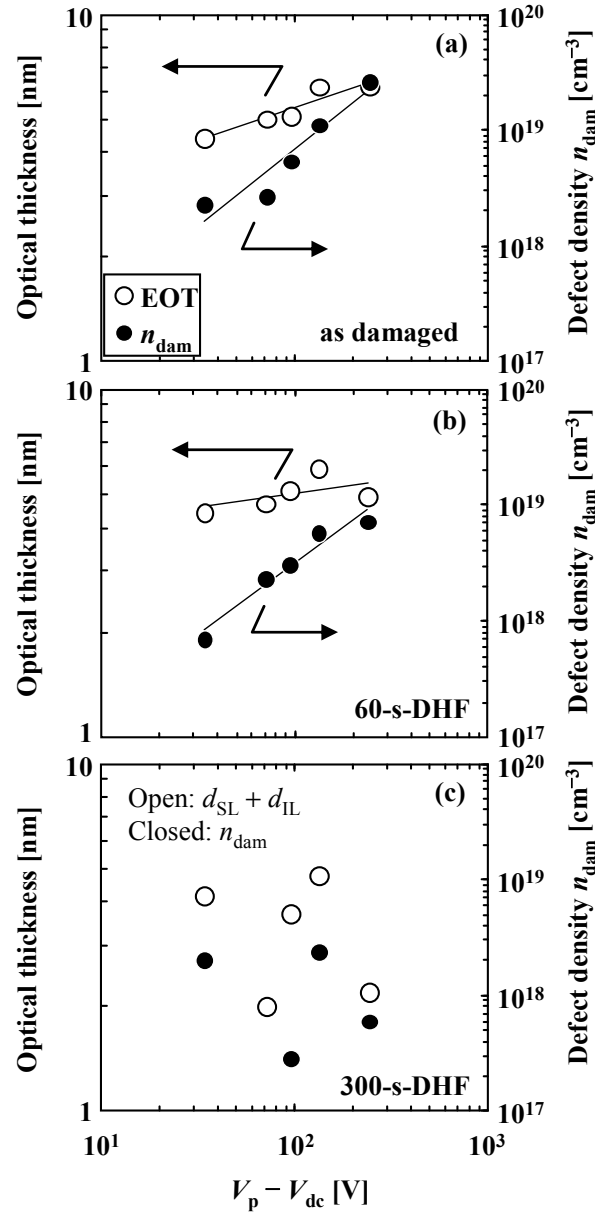


Figure 4.7: Dependences of $(d_{\text{SL}} + d_{\text{IL}})$ (on the left axis) and n_{dam} (on the right axis) on the average incident ion energy in various DHF steps. (a) Before DHF treatment, (b) After 60-s-DHF, and (c) After 300-s-DHF.

Based on the PPD range theory, the defects distributed in the Si substrate have a profile defined primarily by the energy and the flux of incident ions. As seen in Fig. 4.6 and Figs. 4.7(a), a larger $\bar{E}_{\text{ion}}$ result in thicker d_{IL} ($d_{\text{SL}} + d_{\text{IL}}$) and larger n_{dam} . Compared to ICP, CCP has larger $\bar{E}_{\text{ion}}$ as deduced from Table IV-1. However, d_{IL} by SE and n_{dam} by $1/C^2-V$ technique for the CCP case are smaller than those for ICP even after 60-s-DHF wet etch. The mechanism explaining this counter-intuitive result is illustrated in Figs. 4.8. Figures 4.8 show comparisons of the profiles of n_{dam} deduced from the energy (ICP: -130 V and CCP: -260 V) and the flux of incident ions by the PPD range theory. Compared to the ICP sample (Table IV-1), the CCP sample has a wider n_{dam} distribution due to the higher $\bar{E}_{\text{ion}}$ and straggling but lower in the n_{dam} due to the lower ion flux. Note that the SE and $1/C^2-V$ techniques have detection limits as indicated in Figs. 4.8. The intersections with each detection limit define the measured values such as d_{SL} , d_{IL} , and, the areas as highlighted. Due to the lower defect density, d_{CCP} ($=d_{\text{SL}} + d_{\text{IL}}$) for CCP becomes thinner than d_{ICP} by SE with the detection limit as indicated in Fig. 4.8. Moreover, n_0^{CCP} assigned by the $1/C^2-V$ is smaller than n_0^{ICP} . A lower ion flux results in a lower n_{dam} in the deep substrate region—below the detection limit. Therefore, when comparing the PPD, one should pay careful attention to the fact that not only incident energy, but also the ion flux strongly affects the measured defect density. Figure 4.9 schematically illustrates how the defects distribute and the PPD values are measured. The present V_{b} -sweeping range in the $C-V$ test corresponds to the depth of 3–5 nm in the substrate, deduced from the wafer resistivity—lower resistive wafer is indispensable to address PPD distributed in a few nanometers. The changes of n_{dam} occur in the surface region within a few nanometers. It is concluded that the $1/C^2-V$ technique is a powerful tool for PPD quantification, but one should

Chapter IV

pay careful attention to the profiles of defects in the nano-scale regime as well as the detection limits of analysis techniques employed.

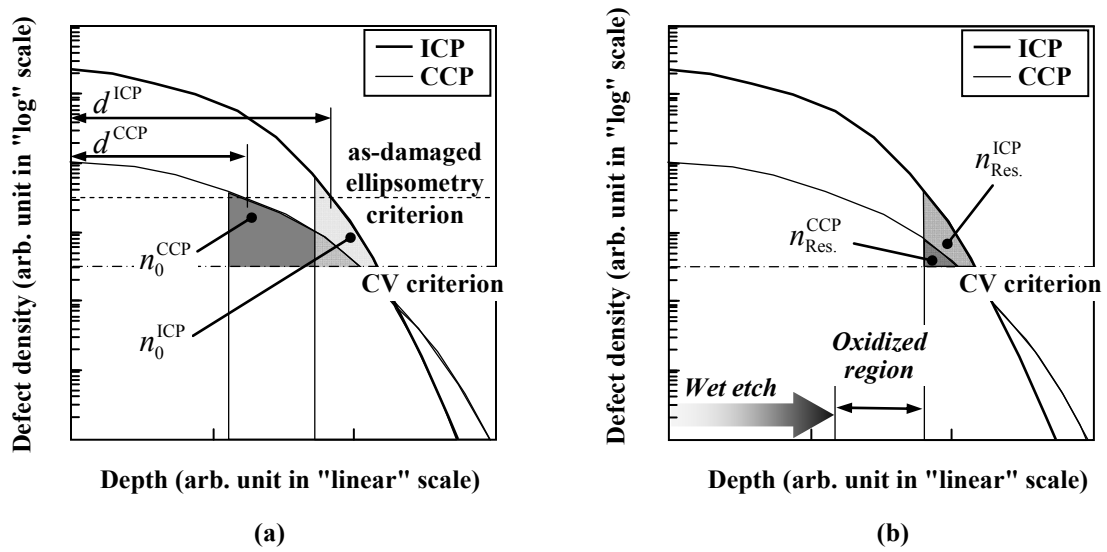
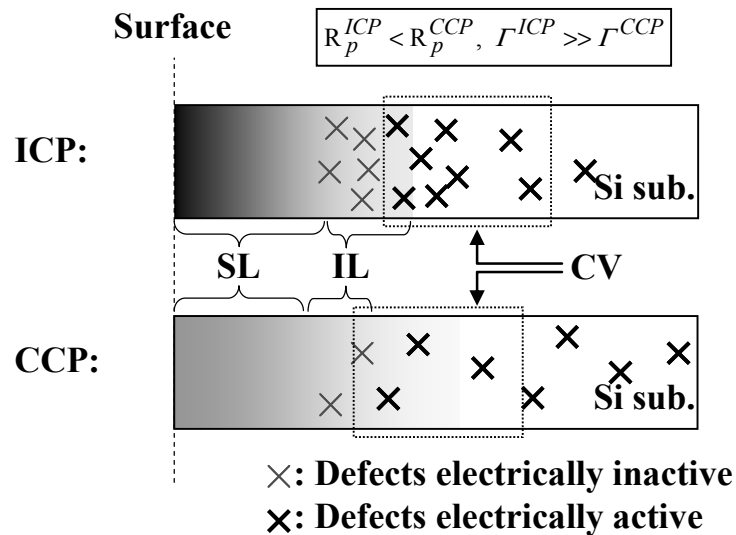


Figure 4.8: Schematic illustrations for the profiles of n_{dam} in the present ICP- and CCP-damaged samples; (a) as-damaged and (b) wet-etched structures. Highlighted areas correspond to the n_{dam} identified by the $1/C^2-V$ technique. The labels "as-damaged ellipsometry criterion" and "CV criterion" mean the detection limits by SE and $C-V$ method, respectively.



*Ion Flux ratio ($\Gamma^{\text{ICP}} / \Gamma^{\text{CCP}}$): ~ 30

Figure 4.9: Schematic illustrations for the distributions of defects in the present ICP- and CCP-damaged samples. Owing to the higher incident ion energy in the CCP, the defects are distributed deeply in the Si substrate. However, the lower ion flux results in smaller n_{dam} , in particular, in the deeper Si substrate region.

Finally, the effect of residual defects on MOSFET performance is investigated. The defects are considered to create additional energy levels in the band gap ("band-gap states"),⁵³⁻⁵⁵⁾ which plays the role of a carrier trap site. Thus, the defects induce drain current decrease¹⁷⁾ due to the latent defects. With the present methodology, the residual density degrading the device performance was already identified. The "residual" density after DHF wet-etch widely employed in mass productions is determined around $5 \times 10^{18} \text{ cm}^{-3}$ for the present PPD. Technology-Computer Aided Design (TCAD) simulations⁴⁴⁾ were performed to estimate the decrease in the drain current as shown in Fig. 4.10. Details of the simulation scheme were mentioned elsewhere.¹⁷⁾ Based on the present result, a residual defect density of $\sim 5 \times 10^{18} \text{ cm}^{-3}$ leads to the decrease in drain current by $\sim 3\%$. This amount is significant for LSI circuit designers. Thus, both a precise and quantitative identification of n_{dam} and an optimization of damaged layer removal process are necessary for future low damage process designs.

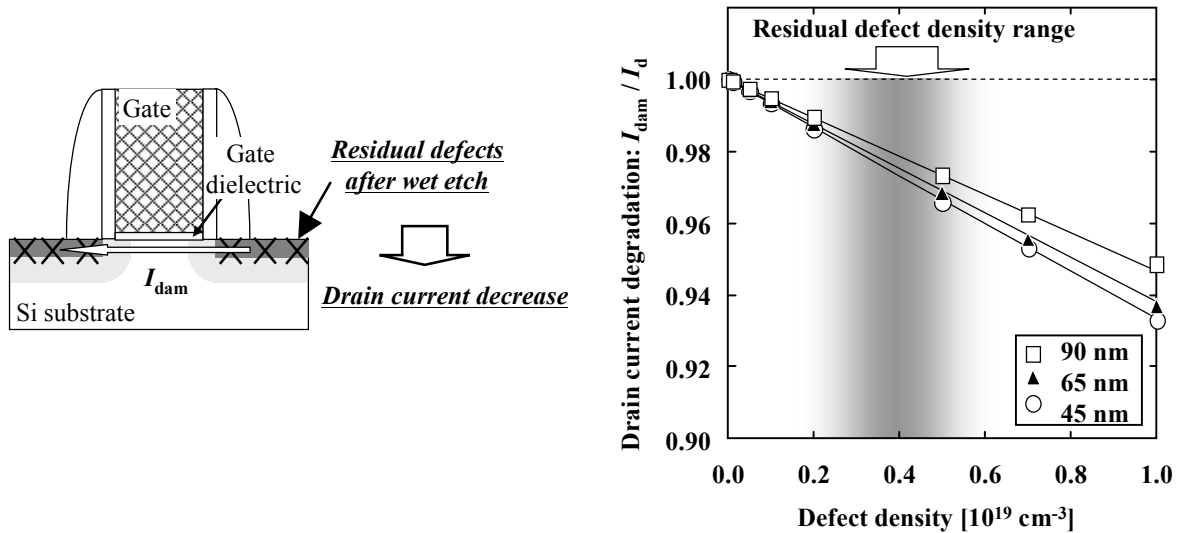


Figure 4.10: Drain current degradation as a function of the residual defect density predicted by TCAD simulations. The simulations were performed with the assumption that the residual defects after a wet-etch step increased channel resistance, leading to the decrease in drain current as shown in the left panel. The range of residual defect density by typical PPD is highlighted on the basis of the present results.

4.4 Conclusion

A quantitative nano-scale characterization of PPD was demonstrated for ICP and CCP sources using a $C-V$ technique combined with SE. A DHF wet-etch step was carried out to address the residual defect density in damaged samples, which is key to MOSFET performance design. The optical thickness by SE was compared with the electrical oxide thicknesses by the $C-V$ technique. The defect density (n_{dam}) assigned by the $C-V$ technique under various process treatments suggests that one should pay careful attentions to the nature of PPD such as the profiles of defects as well as the sensitivity of each analysis techniques in the nano-scale regime. The present methodology should be implemented for designing low-damage process such as ALEt and addressing the residual defect impacts on the performance of ultimately-scaled devices.

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Chapter V

Effects of O₂ addition in Ar plasma

5.1 Introduction

In semiconductor industries, there is an increasing demand for higher performance LSI circuits. To meet this demand, plasmas with higher density and lower pressure have been developed to fabricate finer and precisely controlled patterns. However, as mentioned previously, these plasmas create "defect" on device surface due to high-energy ion bombardment known as plasma-induced physical damage.¹⁻⁵⁾ Plasma-induced Si substrate damage has become one of the critical issues in advanced MOSFETs,⁶⁻⁸⁾ since the damaged layer thickness is considered to be determined by plasma parameters,³⁾ *i.e.*, this thickness will be in conflict with the device design margin. For understanding the mechanisms and controlling the damage, the plasma-induced defects in Si surface should be quantitatively estimated. There have been several methodologies proposed on the basis of photorefectance spectroscopy (PRS)⁹⁻¹²⁾ and capacitance–voltage ($C-V$) measurement,¹³⁻¹⁷⁾ which can quantify the defect in Si substrates. Based on the methodologies above, the fundamental relationship between the defect density (carrier trapping sites) and the plasma parameter by using Ar plasma was clarified.^{15,16,18,19)} In order to implement the low-damage plasma processing, the damage should be quantitatively compared under various plasma gas chemistries and sources. One of commonly-used gases is O₂.²⁰⁻²⁴⁾ The roles oxygen plays

in plasma processing have been extensively studied from the viewpoint of elemental reaction processes proceeding in the bulk plasma and on the material surface. However, few works have been reported on the effect of O₂ addition on the plasma-generated Si substrate damage.^{1,23)} Moreover, one needs to clarify the electrical characteristics of generated defects in order to estimate the impact of the damage on device performances. In this chapter, the effects of O₂ addition to Ar plasmas on the damage mechanism are investigated. I employ spectroscopic ellipsometry (SE) to assign the damaged layer and then estimate the defect density using the capacitance–voltage (C – V) technique outlined previously. Bias voltage shift and the bias dependence of inversion layer capacitance change in the C – V characteristics are focused on to quantify the damage. Current–voltage (I – V) characteristics are measured to define tunneling current components. In addition, by using a wet-etching technique with buffered hydrofluoric acid (BHF), I investigate the structural change (time-dependent residual thickness) in plasma-damage layers.

5.2 Experimental

5.2.1 Plasma exposure and sample treatments

N-type (100) Si substrates ($0.02 \text{ } \Omega\text{cm}$) with native oxide layer ($\sim 1 \text{ nm}$) were used. They were mounted on a stage and exposed to an inductively coupled plasma (ICP) of a similar platform to the system shown in Fig. 2.2. No processed sample was to be the control. Table V-1 shows process conditions employed in this study. The effect of O_2 addition to Ar was studied by varying O_2 flow rate. The flow rate was kept to be 20 sccm in total. All the samples were exposed to Ar or Ar/ O_2 plasmas for 30 s. A 13.56 MHz bias with a power of 300 W was applied to the ICP source. The substrate temperature was $\sim 500 \text{ K}$. The plasma potential (V_p) was measured by a Langmuir probe inserted 10 mm above the center of the wafer stage. The dc self bias voltage (V_{dc}) was measured by an oscilloscope. I - V and C - V measurements were conducted for the samples exposed to plasmas. Wet-etching for the damaged layers was carried out using buffered HF solution (0.1% BHF). The samples were immersed into the BHF solution for several tens of seconds at each step. After the etching process was finished, PRS²⁵⁻²⁷⁾ was also performed to monitor the Si surface potential change.

Table V-1: Process conditions employed in this study.

Gas	Pressure [mTorr]	Flow ratio [sccm]	Power [W]	Duration [s]
Ar	20	20	0 ~ 200	30
Ar	20	20	100	30
Ar	100	20	100	30
Ar/ O_2	20	15/5 (Ar/ O_2)	100	30
Ar/ O_2	100	15/5 (Ar/ O_2)	100	30
Ar/ O_2	20	10/10 (Ar/ O_2)	100	30
Ar/ O_2	100	10/10 (Ar/ O_2)	100	30

5.2.2 Characterization methods

The thickness and the refractive index of damaged layer were measured by SE before and after plasma exposure. The measurement was performed over the 1.6–5.5 eV range at 0.05 eV intervals. All the SE spectra were taken at an angle of incidence of 75°. For the quantitative analysis of the substrate damage, an optimized optical model (air/SiO₂/SiO₂&Si/Si Sub.) was introduced,¹⁹⁾ where surface layer (SL) consists of SiO₂, and interface layer (IL) consists of SiO₂ and Si, respectively. The interface layer between SiO₂ and Si substrate was introduced as a composite of SiO₂ and c-Si with the Bruggeman effective medium approximation (EMA)^{28,29)} with the thickness and volume fraction of c-Si (f_{Si}) being used as the fitting parameters. Plasma-induced defect sites are considered to be distributed mainly in IL.

The damaged structures were analyzed by the $C-V$ measurement proposed previously¹³⁻¹⁷⁾ to estimate the defect density and to clarify its electrical characteristics. The samples were assumed to be pseudo-MOS (metal/damaged layer/Si substrate) structures: As will be discussed later, the damaged layer was assigned to include SiO₂ layer, thus, this structure is denoted as pseudo-MOS. The frequency of modulation bias was 100 kHz. The amplitude was 100 mV. The modulation bias was superimposed on the DC voltage sweeping from 0 V to the respective saturation voltage in capacitance. The area of metal contact was $2.1 \times 10^{-2} \text{ cm}^2$. All the measurements were performed at the room temperature.

When a damaged layer was formed on a Si substrate and the charge trap site (defect) was created in the damaged layer, the capacitance is changed due to the change of the thickness. Shift of $C-V$ curves is also expected by the trapped charges in the damaged layer. The shift can be detected by the bias voltage shift to accumulate the respective charges (to reach the respective capacitance). Thus, the difference between the bias voltage for the control and that for the damaged sample in $C-V$ curve, ΔV_b , can be described by the

following equation,³⁰⁾

$$\Delta V_b = \frac{1}{C_{\text{dam}}} \left(\int_0^{d_{\text{SL}}} x \rho_{\text{SL}}(x) dx + \int_{d_{\text{SL}}}^{d_{\text{SL+IL}}} x' \rho_{\text{IL}}(x') dx' \right), \quad (5.1)$$

where d_{SL} , d_{IL} and $d_{\text{SL+IL}}$ are the thickness of SL, IL and SL+IL, respectively. These thicknesses can be determined by SE. C_{dam} is the effective capacitance of damaged layer. ρ_{SL} and ρ_{IL} are the volume densities of the carrier trap (defect) sites distributing within SL and IL, respectively. Note that the direction of the shift ("±" sign of ΔV_b) corresponds to the polarity of charges trapped into the defect sites.

5.3 Results and discussion

Figure 5.1 shows the ion flux (Γ_{ion}) as a function of O_2 flow rate. The Γ_{ion} was estimated from the Langmuir probe measurement by assuming the Bohm sheath criterion²²⁾ with the electron temperature (T_e) and density (n_e) being used. Note that the plasma sources used in this study (Ar gas mixture) assumed to be electropositive plasmas. Thus, the quasi-neutrality condition ($n_{\text{ion}} \sim n_e$) can be introduced. As seen, the incident ion flux on Si surface decreases with the increase in O_2 flow rate. The decrease in the Ar ion density, *i.e.*, the decrease in n_e , is due to the loss of electrons by dissociative attachment of O^{2+} or other interactions with oxygen related species.²²⁻²⁴⁾

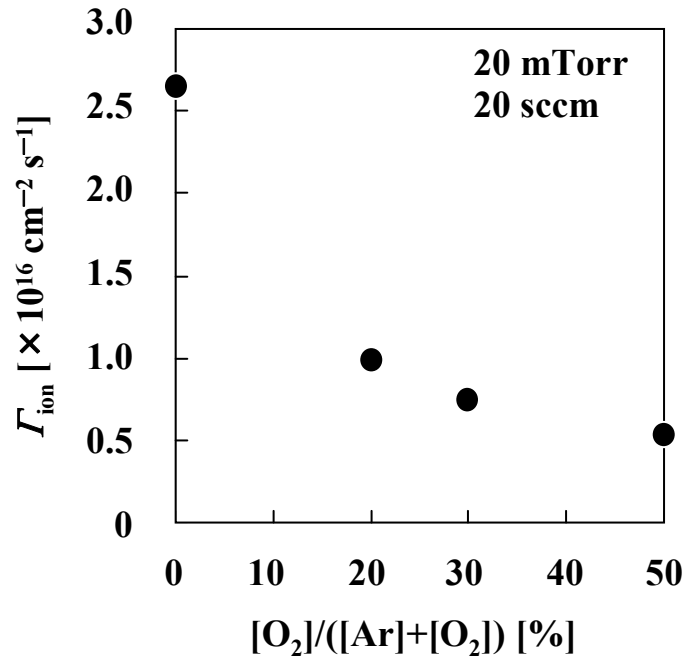


Figure 5.1: Ion flux as a function of O_2 flow rate determined by plasma diagnostics. The Bohm sheath criterion was assumed in this estimation.

Figures 5.2(a) and 5.2(b) show $(\tan\Psi, \cos\Delta)$ spectra of Ar and Ar/O₂ samples obtained by SE. Figure 5.3 shows d_{SL} , d_{IL} , and $d_{\text{SL+IL}}$ calculated from the $(\tan\Psi, \cos\Delta)$ spectra in Figs. 5.2(a) and 5.2(b) as a function of $(V_p - V_{\text{dc}})^{1/2}$. In this chapter, the value $(V_p - V_{\text{dc}})^{1/2}$ is used as a measure of the damage. This is based on the assumption that the damaged layer is formed by an ion impact on Si and the subsequent recoiling process which is deduced to be similar mechanisms such as the sputtering yield of Si by an Ar ion impact.^{31,32)} This mechanism obeys dominantly the momentum-transfer-based dependence³³⁻³⁵⁾ or other nuclear stopping mechanisms.³⁶⁻⁴⁰⁾ The average incident ion energy $\overline{E}_{\text{ion}}$ is thought to be approximately in proportion to the potential drop between plasma and sample-stage; $(V_p - V_{\text{dc}})$. As shown in Fig. 5.3, $(V_p - V_{\text{dc}})^{1/2}$ increases with the increase in O₂ flow rate.²²⁾ Moreover, $d_{\text{SL+IL}}$ is found to increase in proportion to $(V_p - V_{\text{dc}})^{1/2}$. In the Ar plasma, the increase in d_{IL} up to 2 nm is observed with the increase in $(V_p - V_{\text{dc}})^{1/2}$, indicating more severe damage in this range. On the other, the d_{SL} increases with the increase in $(V_p - V_{\text{dc}})^{1/2}$ (~ 4 nm), then, tends to decrease in higher region. The characteristic behavior in the higher region may be attributed to the sputtering of atoms on the SL surface by Ar ion.⁴¹⁾ In the Ar/O₂ treatment, d_{SL} became thicker (~ 5 nm) and d_{IL} remained thinner (~ 1 nm) than that in the Ar treatment for the higher $(V_p - V_{\text{dc}})^{1/2}$. This turnover behavior implies oxidation of the damaged layer by O₂ addition and the resultant SL-thickness increase.

Figure 5.4 schematically illustrates characteristic developments of damaged layers for Ar and Ar/O₂ plasma treatments in the higher energy region [$(V_p - V_{\text{dc}})^{1/2} \sim 15$ in Fig. 5.3]. The difference between these processes is assigned as the residual IL thickness. The damaged layer (DL) depicted as (a) in Fig. 5.4 includes Si dangling bonds, the disordered crystalline Si structure formed by Ar ion bombardment, as well as O atoms diffusing from the native oxide layer. This damaged layer is subject to be partly oxidized by the subsequent air exposure [(c) in Fig. 5.4]. On the other hand, for the Ar/O₂ treatment indicated as (b) in Fig.

5.4, the damaged layer (*DL*) is oxidized by incoming oxygen ions from plasma accelerated in the sheath. As pointed out by Y. C. Liu *et al.*,⁴²⁾ Si atoms on the substrate react with the reactive O ions to form a SiO_x network, and this SiO_x film condenses by the bombardment energies of Ar and O ions. The Si dangling bond and disordered crystalline Si formed were terminated by Si-O bonds. These mechanisms are thought to be the primary process in O₂ addition.

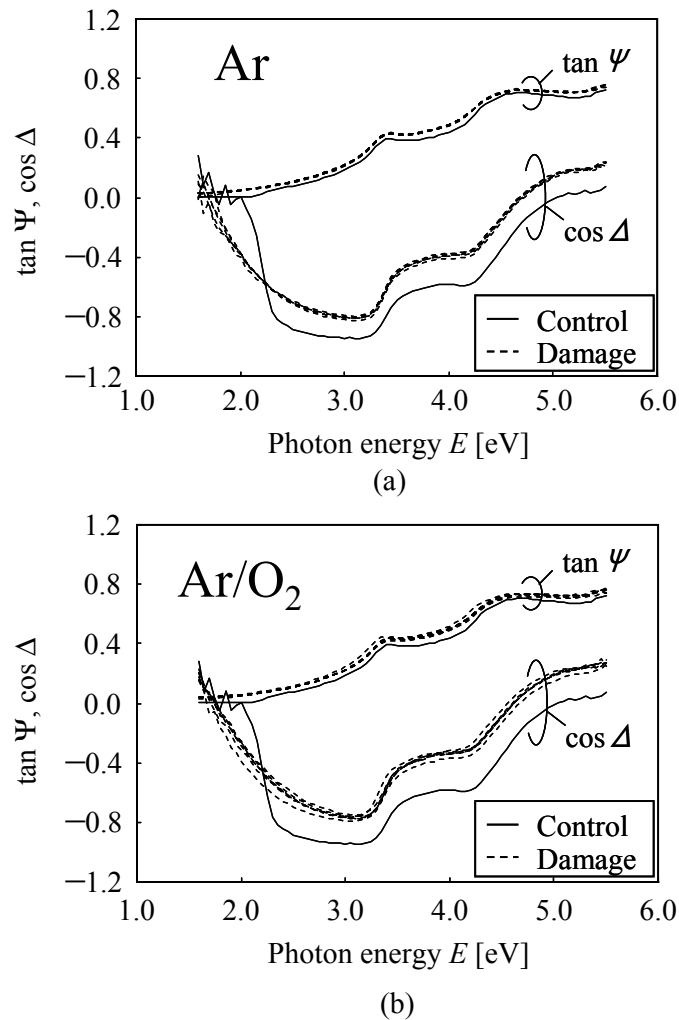


Figure 5.2: Obtained ($\tan \Psi$, $\cos \Delta$) spectra by SE analysis. (a) Exposed to Ar plasma with the superposed bias (400 kHz / 13.56 MHz) of 100 W in total. (b) Exposed to Ar/O₂ plasma with the bias (13.56 MHz) of 100 W.

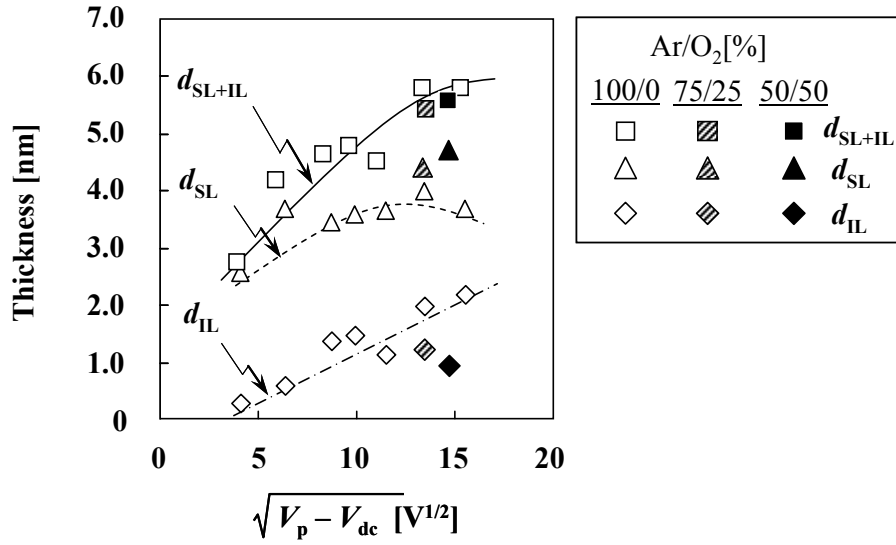


Figure 5.3: Surface and interface layer thicknesses as a function of $(V_p - V_{dc})^{1/2}$ for various bias configurations. Samples were exposed to Ar and Ar/O₂ plasmas with the bias ranging from 0 to 200 W, respectively. The bias frequency was 13.56 MHz. The solid and broken lines are guidelines for the reader's eye.

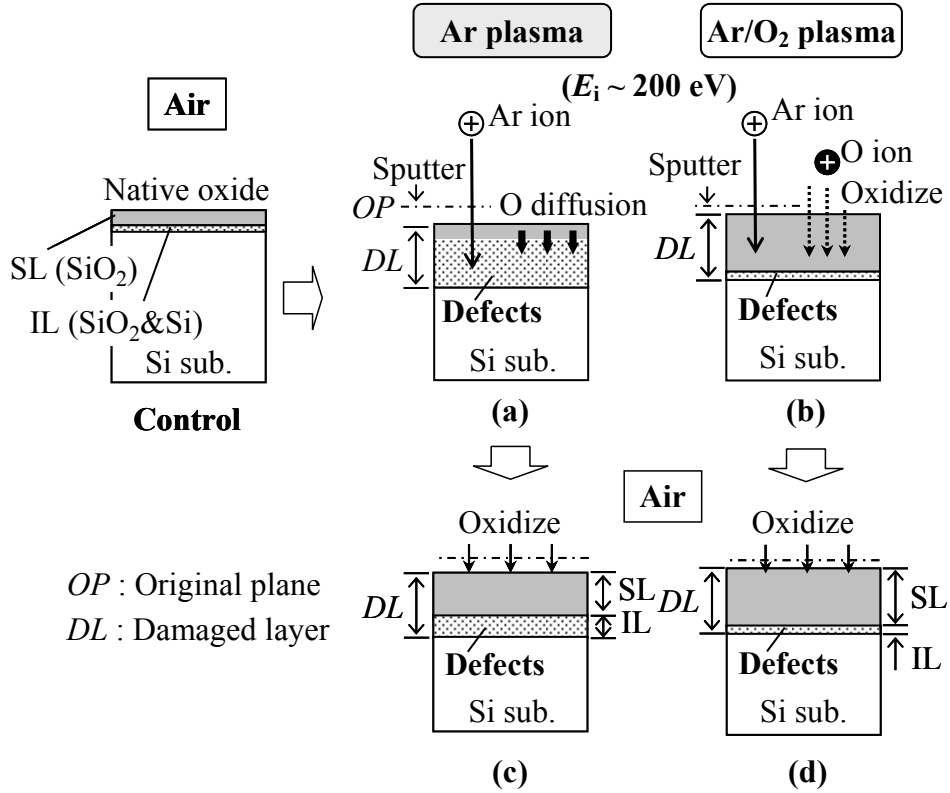


Figure 5.4: Schematic diagrams for developments of damaged layers in the higher ion energy regions for Ar and Ar/O₂ plasma exposures.

Figure 5.5 shows the I - V characteristics for the control and the plasma-exposed samples. As seen in Fig. 5.5, the tunneling current through SL of Ar/O₂-exposed sample exhibits lower than that of Ar-exposed sample. This result indicates that the increase of an insulating layer (presumably SL) thickness in the Ar/O₂-exposed sample, corresponding to the SL-thickness increase observed by SE was confirmed. Figure 5.6(a) shows C - V characteristics for the control and the plasma-exposed samples. One can see the abrupt decrease in the capacitance of the control in the accumulation region (positive bias voltage) (> 0.7 V). This is attributed to larger leakage current through the thin native oxide layer since a parallel equivalent circuit is assumed in the C - V measurement.⁴³⁾ For the plasma-exposed samples, the distortion of C - V curve is clearly seen, compared with the curve for the control. Moreover, the shift of C - V curve is also observable. Two mechanisms are speculated from this observation; (1) the saturation of capacitance (the absence of the decrease in capacitance) for damaged sample corresponds to the presence of thicker SL than the control. This is consistent with the results by SE analysis. (2) The shift of V_b (ΔV_b) toward the positive direction implies the generation of negative charge trap sites by PPD as depicted in Fig. 5.6(b). As suggested by Eq. (5.1), ΔV_b depends on the number of trapped charges in the damaged layer. One can see that ΔV_b by the Ar/O₂ treatment is smaller than that by the Ar treatment, even though the surface layer by Ar/O₂ treatment is thicker than that by Ar treatment (Fig. 5.3). From these results, it is considered that the number of trapped sites in the damaged layer (SL + IL) by Ar/O₂ treatment is smaller than that by Ar treatment.

Figure 5.7 shows the amplitude ratio of $\Delta R/R$ spectra $(\Delta R/R_{\text{dam}})/(\Delta R/R_{\text{Cont}})$ as a function of $(V_p - V_{\text{dc}})^{1/2}$. The $\Delta R/R_{\text{dam}}$ is the spectrum of the plasma-exposed sample and the $\Delta R/R_{\text{Cont}}$, that of the control. Here, $(\Delta R/R_{\text{dam}})/(\Delta R/R_{\text{Cont}})$ is defined as an index for the damage on a Si substrate since the amplitude of $\Delta R/R$ spectrum is sensitive to the surface potential change on a substrate surface—an decrease in $(\Delta R/R_{\text{dam}})/(\Delta R/R_{\text{Cont}})$ means an increase in PPD. As seen

in Fig. 5.7, Ar/O₂-plasma-exposed samples exhibit relatively smaller PPD than Ar-plasma-exposed samples even in the higher $(V_p - V_{dc})^{1/2}$ range ($\sim 10 \text{ V}^{1/2}$). These results are in consistency with the ΔV_b assigned by the $C-V$ method in Fig. 5.6.

Figure 5.8 shows the development of residual damage layers in Ar- and Ar/O₂-plasma-exposed samples after succeeding wet-etching steps, including the control. As shown in Fig.5.8, the Ar-plasma-exposed sample shows thick residual layer ($\sim 2.5 \text{ nm}$) after 200 s wet-etching. On the other, Ar/O₂-plasma-exposed sample shows thin residual layer ($\sim 1 \text{ nm}$) approximately equal to control. The thick IL is seemed difficult to remove by conventional wet-etch processes. Figure 5.9(a) shows d_{SL} and d_{IL} of the control and the damaged samples by Ar and Ar/O₂ plasmas. After the plasma exposure ("0 s" = before the wet-etching), thicker layers (SL and IL) were identified, compared with those of the control sample. Formation of thicker SL is owing to natural oxidation of a part of the IL on the plasma-exposed surface. Furthermore, O₂ addition to Ar enhances the oxidation of IL. Even after the HF-etching (200 s), the thicker IL (presumed to be disordered crystalline Si) is still observable for both samples (Ar, Ar/O₂), whereas SL (the presence of rich SiO₂) is mostly stripped off. These findings indicate that IL is difficult to be removed by HF-etching even over several minutes. Figure 5.9(b) shows the PRS spectra of damaged samples after HF-etching in comparison with that of the control sample. The peak near 3.4 eV corresponds to the optical transition energy of Si at Γ - or L -point in $E-k$ space (see Fig. 2.20).^{27,44)} Lowering of the peak height indicates the surface potential change at the Si surface.^{26,27)} Thus, this result implies the presence of carrier-trap sites (vacancies, interstitials, displaced Si atoms, Si dangling bonds) within the residual IL, which is consistent with the result by SE in Fig. 5.9(a).

Figure 5.10 shows the dependence of ΔV_b (estimated by the difference in V_b at $6.0 \times 10^{-9} \text{ F}$ in Fig. 5.6) on Δd_{SL} (= difference of the thickness between the control and the damaged

samples in Fig. 5.3). In Fig. 5.10, the linear dependence of ΔV_b on Δd_{SL} is observable by Ar treatment. This relationship suggests that, ρ_{IL} in Eq. (5.1) is larger than ρ_{SL} . Therefore, the present observation implies that plasma-induced defect plays a role as a charge (electron) trapping site which locates within the IL.

In order to clarify quantitatively the decrease in the defect density by O_2 addition, the $1/C^2$ - V method was conducted. According to Eq. (2.9), one can estimate the volume density of impurity doping and that of plasma-induced defect sites in the substrate region. Figure 5.11 shows the estimated areal density of carrier trapping sites ($N_{dam} = n_{dam} \times d_{IL}$) within IL as a function of $(V_p - V_{dc})^{1/2}$. As seen, by adding O_2 to Ar plasma, N_{dam} decreases from $\sim 10^{12}$ to $\sim 10^{10} \text{ cm}^{-2}$ in the higher $(V_p - V_{dc})^{1/2}$ regions. Note that the reduction of N_{dam} ($< 1/10$) is larger than that of F_{ion} ($\sim 1/5$). By taking into consideration the results in Fig. 5.3 and Fig. 5.11, a slight increase in SL thickness drastically decreases in N_{dam} in the Ar/ O_2 treatment. In addition to the oxidation of damaged layer, the presence of thicker SL by O_2 addition suppresses PPD creation. The observed decrease in N_{dam} is considered similar to masking techniques widely used in ion implantation.^{33,34,45)}

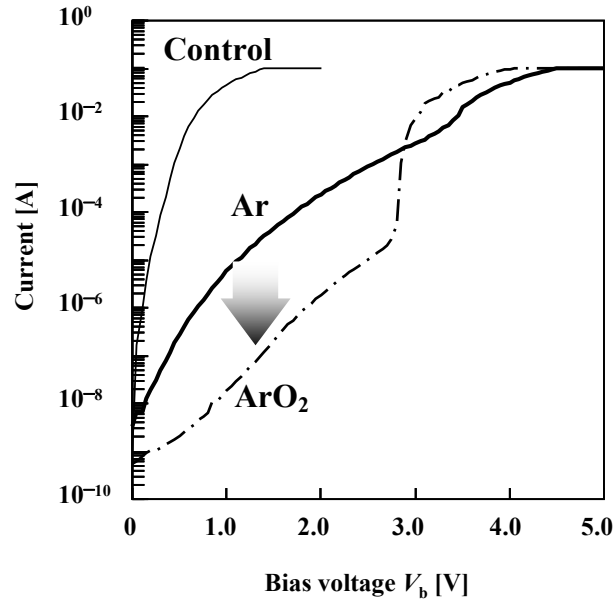


Figure 5.5: Current–voltage characteristics of pseudo-MOS structures. Suppression of leakage current is observable by adding O₂ to Ar plasma.

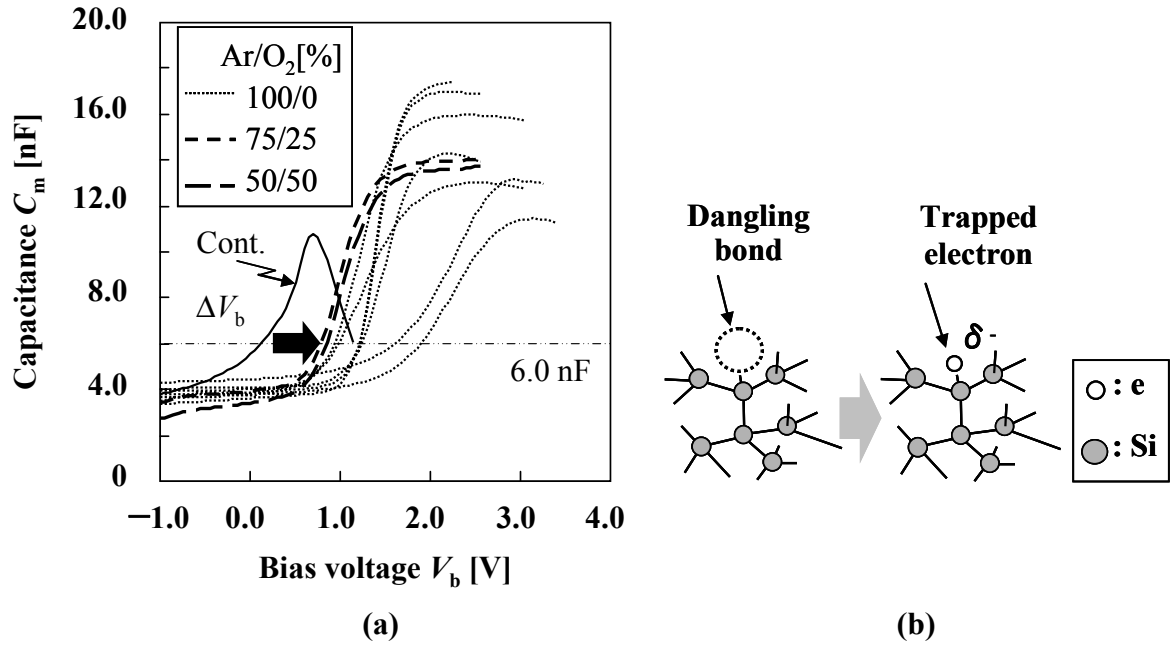


Figure 5.6: (a) Capacitance–voltage characteristics for various plasma conditions. The bias voltage shift (ΔV_b) toward the positive bias direction from the control is observed for all damaged samples. This shift is thought to be an electron trapping by Si dangling bonds (plasma damage) as depicted in (b).

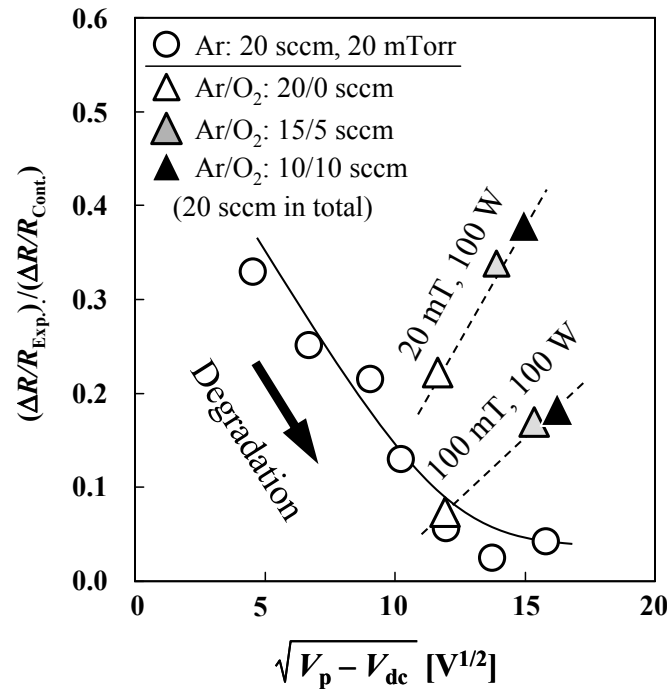


Figure 5.7: Ratio of PR spectra amplitude C (Plasma-damaged / Control) as a function of $(V_p - V_{dc})^{1/2}$. The solid curves and dashed lines are the guidance for the reader's eye.

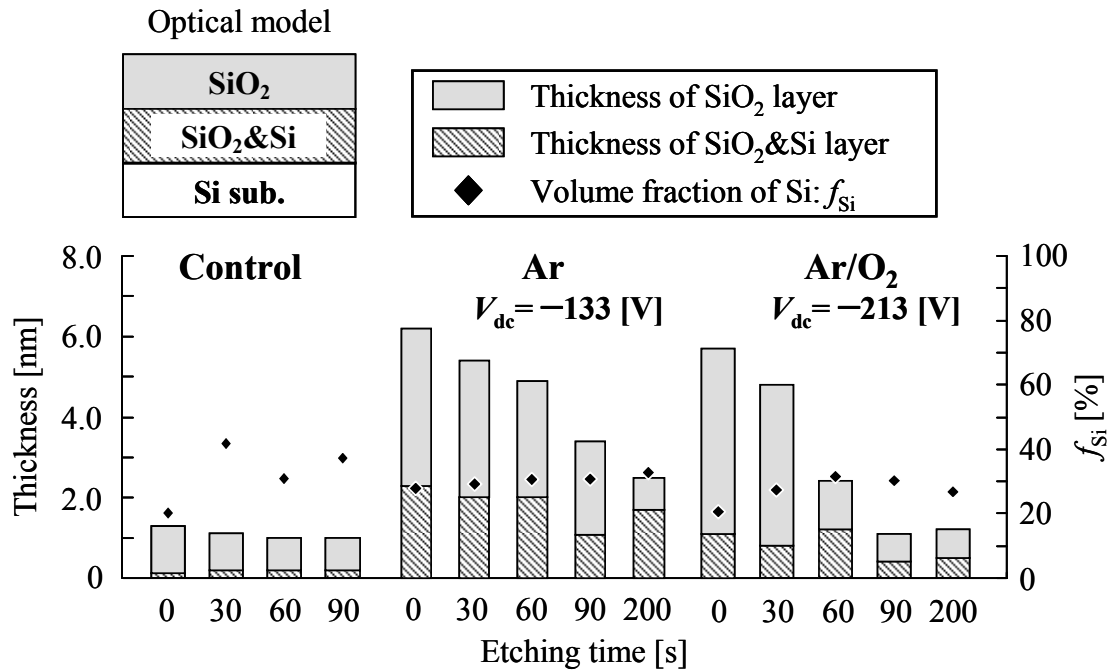


Figure 5.8: Optical thicknesses of remaining damaged layer after wet-etching. 0.1% BHF was used in this study. Ar: 20 sccm and 20 mTorr. Ar/O₂: 10/10 sccm and 20 mTorr. Bias frequency = 13.56 MHz. The exposure time = 30 s.

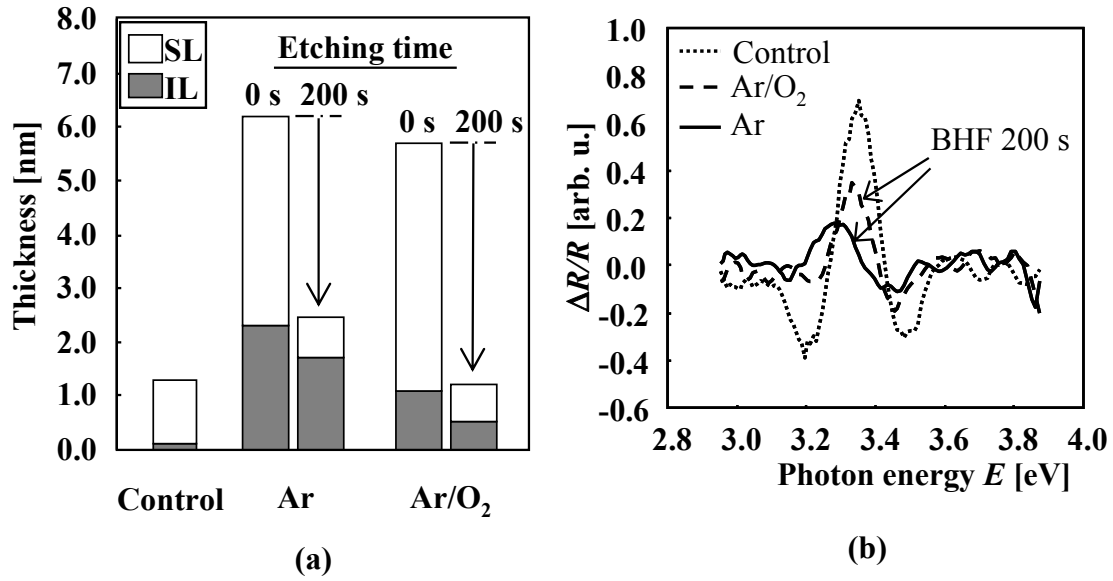


Figure 5.9: (a) Damaged layer thickness by SE before and after 200-s wet-etching. (b) $\Delta R/R$ spectra of Ar and Ar/O₂ plasma damaged structures after 200-s wet-etching, including that of Control.

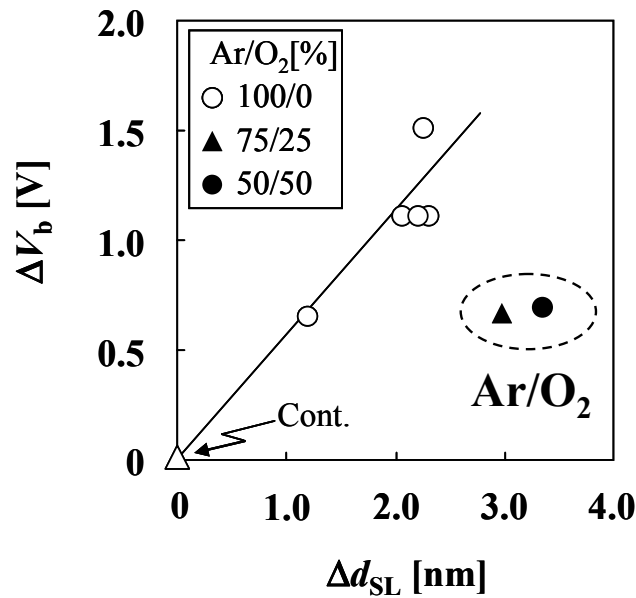


Figure 5.10: Relationship between ΔV_b (estimated by the difference in V_b at the capacitance of 6.0×10^{-9} F in Fig. 5.6) and Δd_{SL} . The solid line is a guideline for the reader's eye.

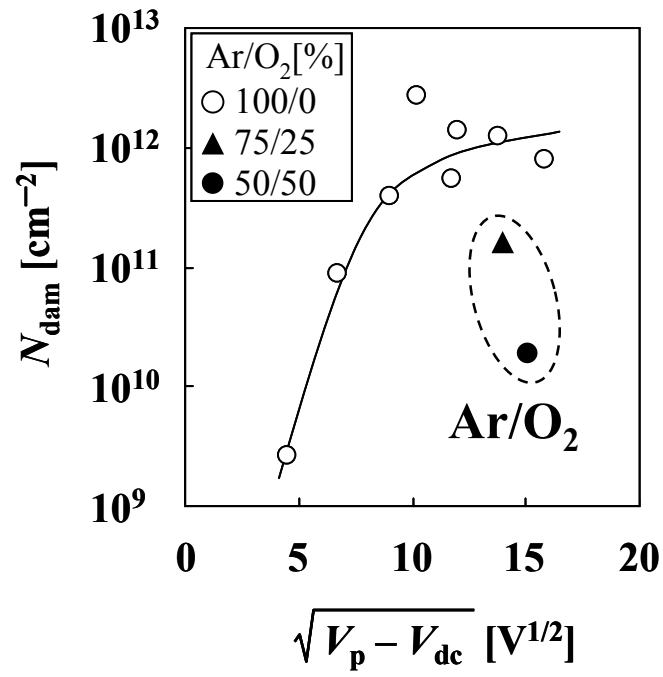


Figure 5.11: N_{dam} (cm^{-2}) as a function of $(V_p - V_{\text{dc}})^{1/2}$ estimated from C - V measurements. The solid line is a guideline for the reader's eye.

5.4 Conclusion

Effect of O₂ addition to Ar plasma was studied quantitatively in terms of the damaged layer thickness and defect density. O₂ addition induces O-termination of Si dangling bonds in the damaged layer, thus, increases the thickness of SL. This surface layer increase brings masking effects, resulting in the reduction of defect creation. The distortion of C – V curve was observed by the plasma exposure and dependent on the plasma conditions. From the SL thickness dependence of the shift and its direction, the defects mainly located within the IL and the negative charges (electrons) were trapped. It was confirmed that the IL formed by plasma damage was difficult to be removed completely by conventional wet-etching techniques. The remaining IL includes defects (carrier-trap sites), which can be identified by optical and electrical methods. Since the residual (latent) defects after wet etching degrade MOSFET performance drastically, one should quantitatively evaluate the density for understanding the mechanism of damage creation and designing future low-damage plasma processes.

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Chapter VI

Damage formation in Hydrogen containing plasma

6.1 Introduction

With aggressive scaling of metal–oxide–semiconductor field-effect transistors (MOSFETs), plasma process-induced damage has become a key issue.¹⁾ Physical damage induced by high-energy ion bombardment forms the damaged-Si layer during shallow trench isolation, gate, and offset-spacer etch processes,²⁾ which includes Si vacancy, displaced Si atoms, and interstitials. This Si damage is considered to result in Si loss by a subsequent wet-etch process—often referred to as "Si recess"³⁻⁵⁾—and latent defect site underneath the damaged surface.⁶⁾ The former leads to threshold voltage (V_{th}) shift⁷⁾ and the latter, to drain current degradation⁶⁾, *e.g.*, in 45-nm-technology MOSFETs, 0.1 V of shift in V_{th} for 6 nm recess depth, and 10% of degradation in drain current with a defect density of 10^{19} cm^{-3} . Regarding Si recess, Ohchi *et al.* have reported⁵⁾ that the layer damaged by H₂-containing plasma was thicker than that damaged by plasma without H₂, which might result in deeper Si recess depth. As pointed out in previous chapters, the depth is governed by plasma parameters difficult to be scaled. It is predicted that the damage-layer thickness will conflict with the device design margin in the near future.⁸⁾ This prediction suggests that

H₂-containing plasma processes induce more serious device degradation because of thicker damage layers. To realize a low-damage plasma process, the damage layer and its formation mechanisms should be clarified. However, the analysis previously performed⁵⁾ is insufficient for the detailed understanding of H₂-containing plasma damage, because the evaluation should be carried out from various aspects such as detailed microstructure and electrical characteristics. For example, Neitzert and coworkers have reported^{9,10)} change in the structure of a Si surface exposed to H₂ plasma on the basis of an in-situ time-resolved microwave conductivity measurement and spectroscopic ellipsometry (SE). Although the time-dependent over-layer formation during plasma exposure was studied in detail, few practical models of the H₂-plasma damage layer for process monitoring have been proposed.

Regarding recovery of PPD, as demonstrated in Chapters IV and V, wet-etch removal process is one of major approaches in mass production. In addition to the wet-etch stripping of PPD region, high temperature annealing is also a primal step to recover—reconstruct—the damage structure. However, both approaches are facing at process constraints imposed on the present-day MOSFETs, because the removal results in Si recess that increase a power consumption¹¹⁾ and the annealing increases a thermal budget^{12,13)} leading to uncontrollable impurity diffusion in the channel of MOSFETs. To design precisely device performance in the final structure, understanding the effects of wet-etch stripping and annealing is extremely important. As conducted in Chapters IV and V, there are significant numbers of residual defects remaining in damaged structures after wet-etch steps in the case of Ar-based gas chemistries. However, there have been few detailed studies in the case of H₂-containing plasma processes which are now widely employed in mass production lines. This chapter focuses on (1) removability of H₂-damaged structure by a wet-etch stripping and (2) availability of recovering the damaged structure by a conventional thermal annealing process. The damaged structures were evaluated using the optical and electrical techniques provided in

this thesis. Spectroscopic ellipsometry (SE) was employed to measure the optical constants such as refractive index and extinction coefficient. The electrical technique measures current–voltage (I – V) characteristics focusing on tunneling current. By using a layer-by-layer wet-etching technique with buffered hydrofluoric acid (BHF) solution, the structural changes (time-dependent residual thickness) for various plasma-damage layers were investigated. Finally, I proposed an optical model for the H₂-plasma damage layer intended for in-line monitoring.

6.2 Experimental

6.2.1 Plasma exposure and sample treatments

P-type (100) Si substrates with 2-nm-thick SiO₂ layer were exposed to a dual-frequency (60/13.56 MHz) capacitively coupled plasma (CCP)⁵⁾ for 600 s. Pressures in the chamber were 60 mTorr (HBr/O₂) and 30 mTorr (H₂, H₂/Ar, Ar, Ar/O₂, and O₂). The gases and their flow rates were; H₂ = 500 sccm, H₂/Ar = 250/250 sccm, Ar = 500 sccm, O₂/Ar = 250/250 sccm, and O₂ = 500 sccm, and HBr/O₂ = 80/4 sccm. The peak-to-peak voltage of rf-biased stage (V_{pp}) was kept at approximately 500 V by optimizing the RF source power. The measured V_{dc} was approximately 260 V for all process conditions. Figure 6.1 shows the flowchart of experimental procedures. After the 1st structure characterizations following the plasma exposure, the samples were cleaned by dilute-HF solution (DHF) for 2 min before rapid thermal annealing (RTA; 1035 °C, 10 s, N₂). Figure 6.2 shows schematic illustration of the RTA system used in this study. After the RTA, the layer thicknesses of samples were assigned by SE and the electrical characteristics were evaluated by I - V measurement. To remove the SL and IL, processed samples were then immersed into dilute hydrofluoric acid solution (DHF; 0.1 wt% HF-solution) for 60 and 300 s, followed by rinsing in high-purity water at room temperature. In this study, the wet-etch rate of thermally-grown SiO₂ layer by DHF was approximately 0.2 nm / min at room temperature. After the HF treatments, the samples were again analyzed by SE and I - V techniques.

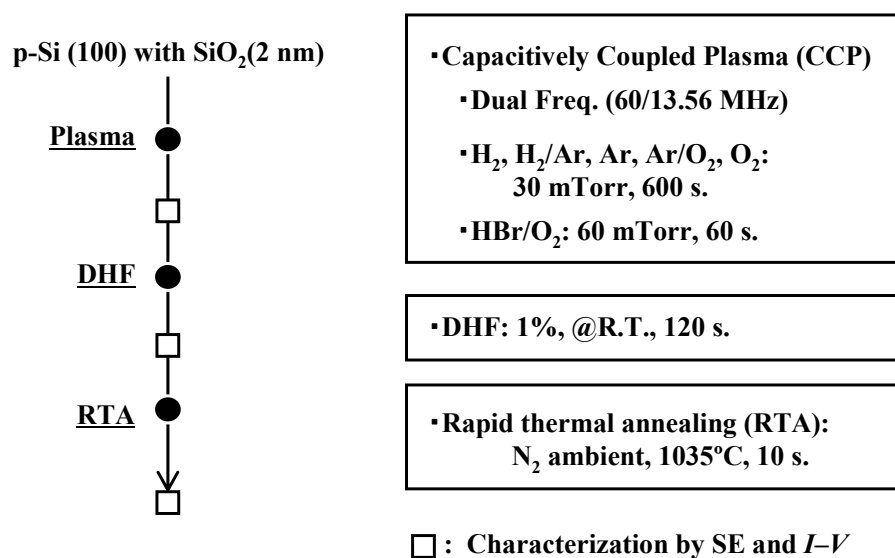


Figure 6.1: Flowchart of the present experimental procedures. A sample without plasma exposure was also processed for DHF and RTA for SE and *I-V* analyses.

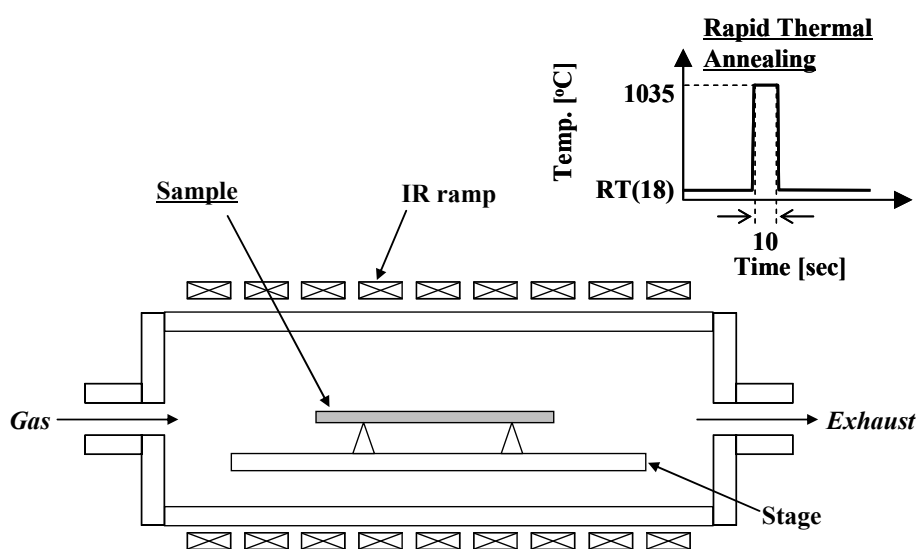


Figure 6.2: Schematic illustration of an RTA system used in this study. High ramping and descending rate of the temperature is realized as indicated on the right-top panel.

6.2.2 Characterization methods

SE was performed to study the optical structure, the layer thickness, and the optical constant of plasma-exposed samples. The measurement was performed over the 1.6 – 5.5 eV range at 0.05 eV intervals. All the SE spectra were taken at an angle of incidence of 75°. From the obtained spectra, the optical constants, such as the pseudo-extinction coefficient $\langle\kappa\rangle$, were determined.¹⁴⁻¹⁶⁾ Two different optical models¹⁷⁾ were compared to clarify the characteristics of damage layers. One was a conventional four-layer model (air/SL/IL/Si sub.). The other was a three-layer model (air/IL/Si sub.). The dielectric function of the IL was determined by the Bruggeman effective medium approximation (EMA).^{14,16,18)} More details about the models have been reported elsewhere.¹⁷⁾ I – V measurement was carried out using the mercury (Hg) probe system as shown in Fig. 2.6. The area of metal contact was $2.1 \times 10^{-2} \text{ cm}^2$. All the measurements were performed at room temperature.

6.3 Results and discussion

6.3.1 Optical and electrical characterizations

Figure 6.3 shows $(\tan\Psi, \cos\Delta)$ spectra for the samples obtained by SE. In Fig. 6.3, one can clearly see a larger difference in $\cos\Delta$ between the case of H_2 -containing plasma and the other plasmas without H_2 , particularly in the lower photon energy region (2.0 – 3.5 eV). This difference is considered to originate from the damage-layer structure formed upon H_2 -plasma exposure. Table VI-1 lists the surface and interface layer thicknesses determined from $(\tan\Psi, \cos\Delta)$ spectra shown in Fig. 6.3. From the larger unbiased estimators (σ_{SE}) for H_2 -plasma damage samples, it is concluded that the conventional four-layer model¹⁷⁾ (air/SL/IL/Si sub.) is not appropriate. (As will be discussed in the next subsection, the damage layer was found to include an SiO_2 layer.) Table VI-1 also lists the results of fitting by using three-layer models. The σ_{SE} for H_2 -damage samples is lower than that when using four-layer models. H_2 -damage samples were assigned to have a thicker IL in the case of other plasmas without H_2 .

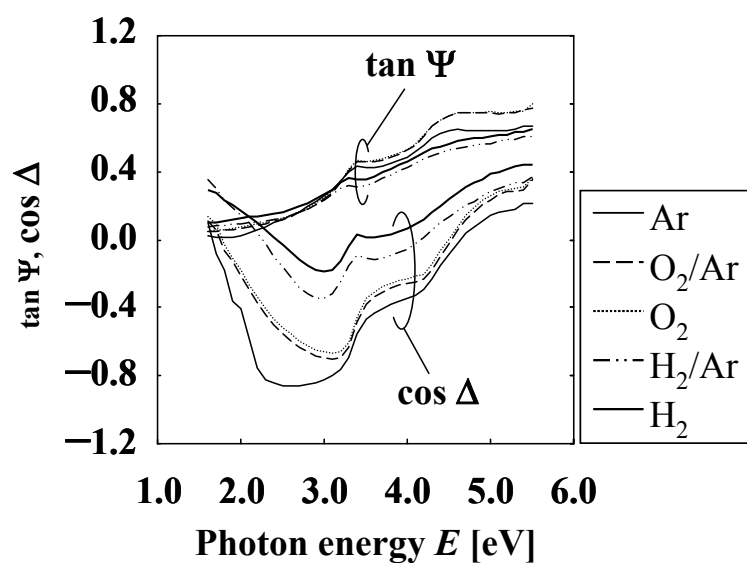


Figure 6.3: Obtained $(\tan\Psi, \cos\Delta)$ spectra by SE analysis for various gas mixtures.

Table VI-1: Optical parameters determined by SE analysis for the samples treated by various gas mixtures.

Gases	Optical Model	$d_{SL}[\text{nm}]$	$d_{IL}[\text{nm}]$	$f[\%]$	σ_{SE}
Four-layer					
Ar	[air/SiO ₂ /SiO ₂ : <i>c</i> -Si/Si sub.]	0.2	3.1	28.0 (<i>c</i> -Si)	0.044
O ₂ /Ar		6.1	0.8	23.1	0.016
O ₂		6.6	0.8	23.9	0.016
H ₂ /Ar		8.7	0.1	40.6	0.148
H ₂		10.3	0.6	41.9	0.139
Three-layer					
H ₂ /Ar	[air/SiO ₂ : <i>c</i> -Si/Si sub.]	-	10.1	53.0 (<i>c</i> -Si)	0.057
H ₂		-	11.3	43.4	0.029
H ₂ /Ar	[air/SiO ₂ : <i>a</i> -Si/Si sub.]	-	49.7	86.1 (<i>a</i> -Si)	0.019
H ₂		-	21.5	72.9	0.037
H ₂ /Ar	[air/ <i>a</i> -Si: <i>c</i> -Si/Si sub.]	-	53.6	<i>N/A</i>	0.075
H ₂		-	53.6	<i>N/A</i>	0.113

Figure 6.4 shows a depth profile of dislocated c-Si in the H₂-damage sample identified by higher resolution Rutherford backscattering spectrometry (RBS). As seen, the dislocation depth becomes nearly 10 nm when H-ions are projected with 270 eV into Si substrate. This depth range seems to be well explained by the range theory,¹⁹⁻²³⁾ and the range is consistent with the thickness of the IL using SiO₂:c-Si in Table VI-1. From these results, the present H₂-damage samples are considered to be well modeled by the three-layer (air/SiO₂:c-Si/Si sub.) model. Thus, one should use the present three-layer model to monitor the H₂-damage when applying a bias voltage to a Si substrate.

Figure 6.5(a) shows the extracted pseudo-extinction coefficient $\langle\kappa\rangle$ for the samples. The peak near 3.4 eV corresponds to the optical transition energy of Si at the Γ - or L-point in the E - k space of Si.²⁴⁾ In particular, in a case of H₂-containing plasma exposure [Fig. 6.5(a)], the decrease in $\langle\kappa\rangle$ is observed in the higher photon energy region (≥ 3.4 eV). Since the peak near 3.4 eV is still observed, the disordering of c-Si,^{25,26)} that is, the H₂-damage layer, is considered to be in a transition state from c-Si to a-Si. (Note that the spectra for a-Si do not exhibit a clear peak at around 3.4 eV and the pseudo-extinction coefficient $\langle\kappa\rangle$ is smaller than 2.0 in most cases.) Thus, the decrease in $\langle\kappa\rangle$ in the high-energy region is associated with carrier trap site generation in the H₂-plasma damage layer.²⁶⁾ In the lower photon energy region (< 3.4 eV), on the other hand, an increase in $\langle\kappa\rangle$ is observed. This increase in the lower energy region corresponds to an enhancement of photon absorption in the damage layer. Two factors are considered for this mechanism. One is an increase in the number of carrier trap sites²⁷⁻³⁰⁾ (Si dangling bonds³¹⁾). The other is an increase in the thickness of the SiO₂ over layer.³²⁾ For the over-layer effect in the latter, we simulated the spectra by introducing an over layer on the Si substrate, as shown in Fig. 6.5(b). As seen, with an increase in the thickness of over layer, the calculated $\langle\kappa\rangle$ increases in the energy region (< 3.4 eV). However, as seen in Fig. 6.5(a), the decrease in $\langle\kappa\rangle$ in the case of H₂-plasma exposure cannot

be reproduced. [This characteristic feature in the spectrum is observable only with H_2 -plasma exposure, but not with Ar-plasma exposure. Note that in the case of Ar-plasma exposure, only the increase in $\langle \kappa \rangle$ in the lower energy region was found, as shown in Fig. 6.5(c), for the samples damaged by an inductively coupled plasma reactor with Ar gas.³³⁾] Therefore, by taking into account the findings that the surface over layer exhibits an increase in $\langle \kappa \rangle$ in the lower energy region, one can conclude that the increase in $\langle \kappa \rangle$ in the lower energy region is attributed primarily to the generation of carrier trap sites. In other words, H_2 -plasma exposure causes the formation of the damage layer with carrier trap sites (disordered c-Si layer³¹⁾), which results in energy gap lowering in the $E-k$ space of Si.^{34,35)}

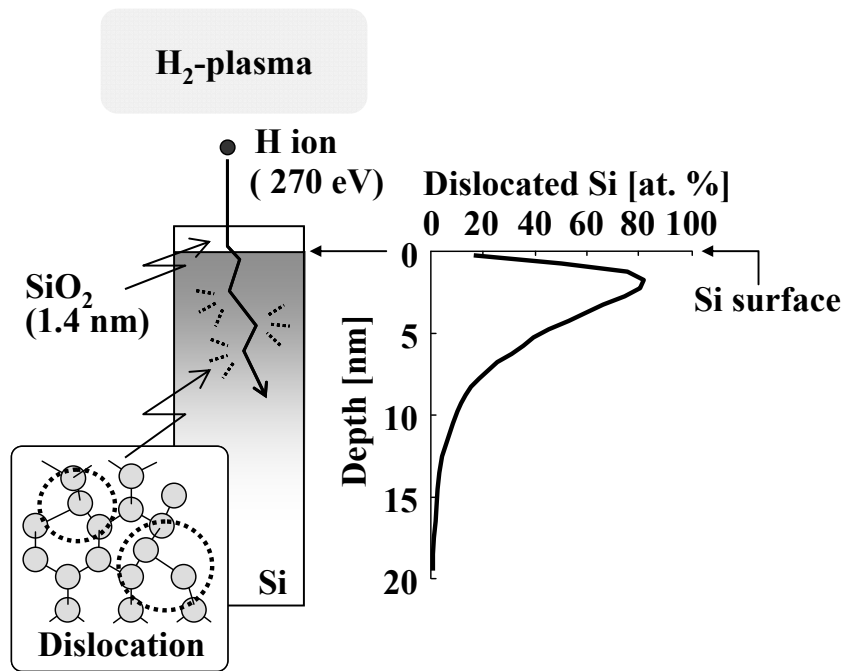


Figure 6.4: Depth profile of c-Si disordered by H_2 -plasma exposure, observed by high-resolution Rutherford backscattering spectrometry (HRBS).

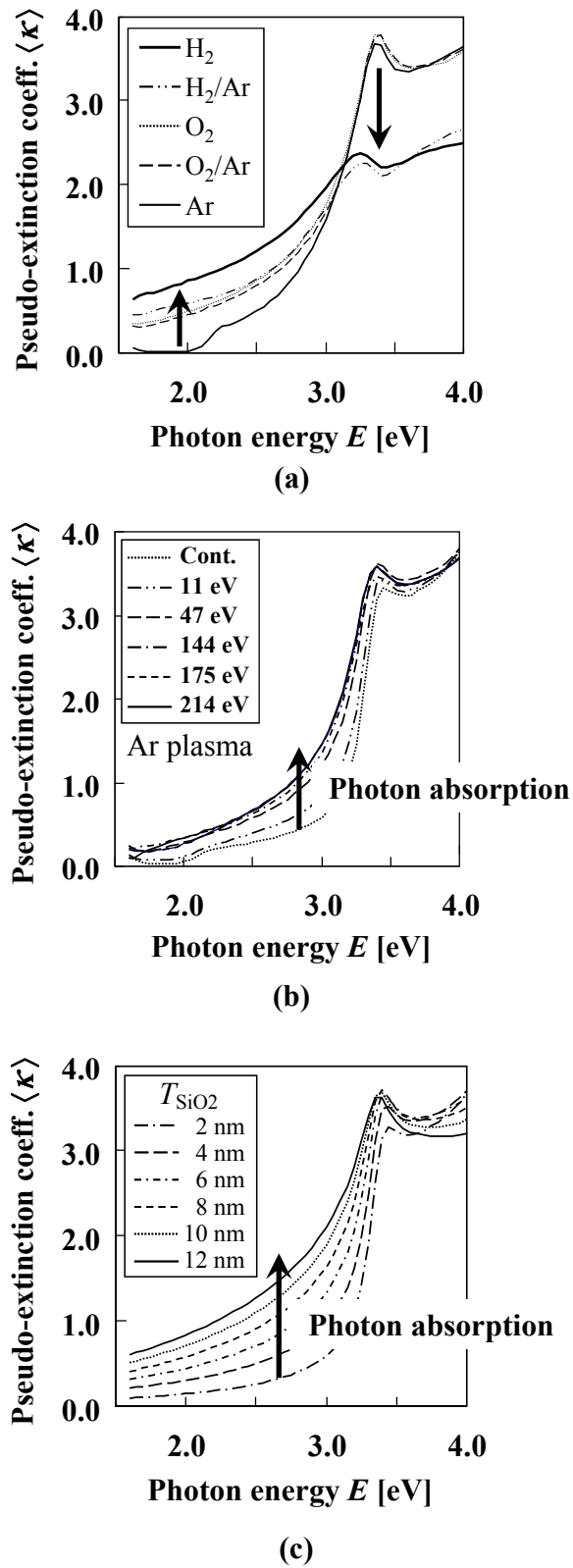


Figure 6.5: Pseudo-extinction coefficient $\langle \kappa \rangle$ of damage layers. (a) Capacitively coupled plasma (CCP); Ar, O₂, H₂ ($V_{dc} \sim 260$ V). (b) Inductively coupled plasma (ICP); Ar ("Cont." indicates unexposed control sample.). (c) Simulated $\langle \kappa \rangle$ for SiO₂-layer thicknesses (d_{SiO_2}) on crystalline Si substrate.

Figure 6.6(a) shows I – V characteristics for the damage samples. As seen, the result for the O_2 -containing plasma shows a lower tunneling current. This is the Fowler–Nordheim conduction mechanism^{12,36)} attributed to the presence of thicker oxide layers on Si.³⁷⁾ On the other hand, for the H_2 -containing plasma, a higher tunneling current is observed. Figure 6.6(b) shows the I – V characteristics for the thermally oxidized layers (MOS structure) with different SiO_2 thicknesses and the H_2 -damage samples. As seen in Fig. 6.6(b), the thermal SiO_2 exhibits much lower tunneling current than that of the H_2 -damage samples. Thus, the observed high tunneling current of the H_2 -damage sample indicates the absence of an SiO_2 layer with any appreciable thickness on the surface. These results imply the presence of only "ultrathin" SiO_2 (native oxide) in H_2 -damage samples, because SiO_2 is formed by air exposure even on an HF treated Si surface.³⁸⁾ Figure 6.7 illustrates energy band diagrams of the H_2 - and the O_2 -damage samples. A positive bias of 4.0 V is applied to the metal (Hg) in this figure. Possible mechanisms behind the observed higher tunneling current in H_2 -containing plasma cases are as follows:

1. With H-ion penetration into c-Si,^{19-23,39,40)} Si dangling bonds are generated down to the depth of 10 nm below the surfaces. Some of these dangling bonds can be terminated by hydrogen (Si–H), resulting in an ultrathin SiO_2 layer upon air exposure on the surface.
2. The conduction band edge of Si becomes lower.⁴¹⁾ The increase in the number of Si dangling bonds induces the increase in the gap-state density,^{29,30)} because they behave electrically as carrier trap sites (depicted in Fig. 6.7 as "Plasma-induced trap site"). The increase in gap-state density leads to energy gap narrowing.
3. Under forward biasing, the ultrathin SiO_2 layer (< 1 nm) formed at the surface increases the conduction current by the direct tunneling mechanism (J_{DT}). It should also be noted that valence-band electrons can easily tunnel through this ultrathin SiO_2 layer

under this bias condition.

On the other hand, the O₂-containing plasma oxidizes the surface during plasma exposure, resulting in the growth of a thick (~ 6 nm) SiO₂ surface layer. Since the Si dangling bonds created in the damage layer are also oxidized by impinging O ions, most of the bonds are terminated as Si–O bonds (electrically inactive in terms of tunneling current), resulting in a thick SiO₂ layer. In this case, the electron conduction mechanism is attributed to Fowler–Nordheim tunneling (J_{FN}). Under these biases (*i.e.*, 4.0 V in the forward direction), J_{FN} is considerably lower than J_{DT} ($J_{\text{FN}} \ll J_{\text{DT}}$).

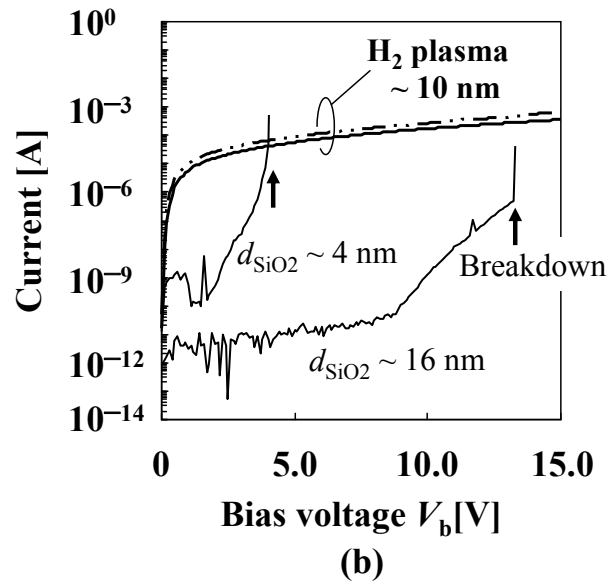
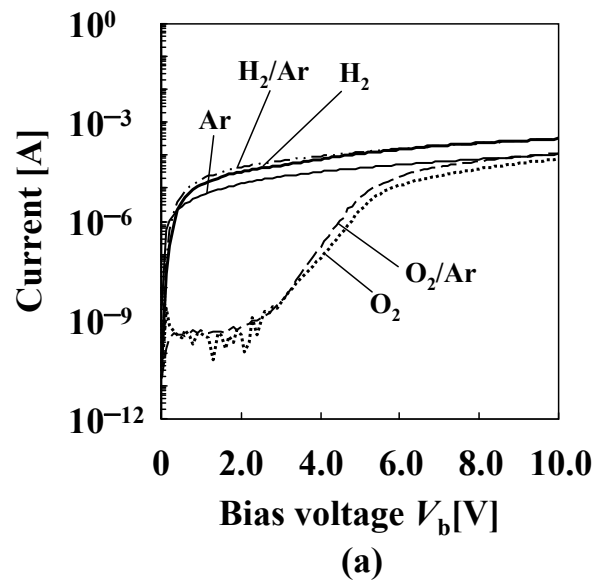
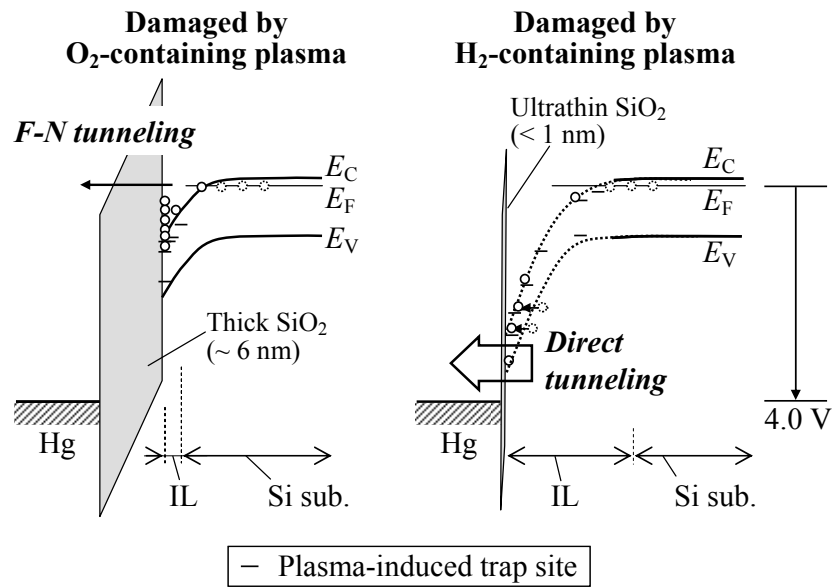


Figure 6.6: (a) Current–voltage (I – V) characteristics of various damage layers. (b) Comparison with the tunneling current of H_2 -damage layer and that of thermally SiO_2 .



$$J_{\text{FN}} \ll J_{\text{DT}}$$

Figure 6.7: Energy band diagrams of H₂-containing-plasma damage and O₂-containing-plasma damage. The characteristic structure of H₂-damage layer of ultrathin SiO₂ and the plasma-induced trap sites in energy gap are depicted. (For n-type Si sub, under positive bias to the gate.)

6.3.2 Wet-etch time dependence

Figure 6.8 shows the results of the wet-etching treatment for Ar-, O₂-, and H₂-damage samples. The vertical axis indicates the damage-layer thickness determined by SE with the four-layer (Ar, O₂) and the present model (H₂). The horizontal axis indicates the total wet-etching time. For all plasma-exposed samples, the thickness of damage layers (SL and/or IL) decreases with etching time. The present etch treatment consists of SiO₂ removal by BHF and subsequent surface oxidation by water and/or air exposure. For Ar damage exposed samples, the thickness of the IL decreased with the etching time. This decrease is due to the mechanisms of oxidization and the removal of oxide by the following wet-etching treatment. For O₂-damage samples, SL was etched with time, which is deduced from the decrease in the thickness. It is worth noting that the IL thickness apparently did not decrease after the removal of the initial SL. It is speculated that the damage layer, which can be oxidized as observed in the Ar-plasma-exposure case, has already been oxidized by the O-ions during O₂-plasma exposure,^{42,43)} as mentioned above. Although most of the Ar- or O₂-damage layer was removed by the present wet etching treatment, the IL, in which plasma-induced defects are contained, is still observed. This means that the damage layer is difficult to remove completely by the conventional wet-etching time (~ 60 s). Thus, this layer is considered to exist as a latent defect site, leading to device performance degradation.⁴⁴⁾ For H₂-damage samples, although the slight decrease in the IL thickness was observed with etching time, the residual thickness was found to be much greater (~ 10 nm) than those of Ar- or O₂-damage samples. This result indicates that H₂-damage is more difficult to remove. This may be attributed to the H-termination of Si bonds created by the plasma. However, H-terminated Si bond can easily desorb hydrogen, and thus, become an electrical defect under a specific condition of annealing in the following manufacturing processes.^{45,46)} Therefore, H₂-plasma damage may induce more serious device performance

degradation. Figures 6.9(a), 6.9(b), and 6.9(c) show the $\langle\kappa\rangle$ determined from $(\tan\Psi, \cos\Delta)$ spectra for the Ar-, O₂-, and H₂-damage samples before ("as-damaged") and after ("HF etched") wet etching. As seen particularly in Figs. 6.9(a) and 6.9(b), a decrease in $\langle\kappa\rangle$ in the lower energy region (< 3.4 eV) is observed. This corresponds to the decrease in photon absorbance owing to the removal of plasma-induced carrier trap sites. However, as shown in Fig. 6.9(c), for H₂-damage samples, although the decrease in $\langle\kappa\rangle$ in the lower energy region (< 3.4 eV) is seen, the $\langle\kappa\rangle$ exhibits only a slight increase near 3.4 eV, *i.e.*, there still exists a discrepancy between the wet-etched and control samples. This result is consistent with the presence of an IL in the wet-etched sample, as identified in Fig. 6.8. Therefore, these findings imply that the damage formation mechanism upon H₂-plasma exposure is quite different from that upon Ar- or O₂-plasma exposure. The details of damage-layer structures are presented in Fig. 6.10. Figure 6.10 also indicates an optical model for possible in-line monitoring usage. As seen, H₂-damage is quite different from O₂-damage from the viewpoint of both optical and electrical properties, as already shown in this study. The noteworthy structural characteristics of H₂-damage are attributed to the presence of an extremely thin SL on the surface and a thick IL (difficult to remove). Furthermore, it is inferred that the energy gap is effectively lowered by the presence of plasma induced trap sites. These results suggest that an optimum optical model should be used to precisely evaluate H₂-damage in mass production lines.

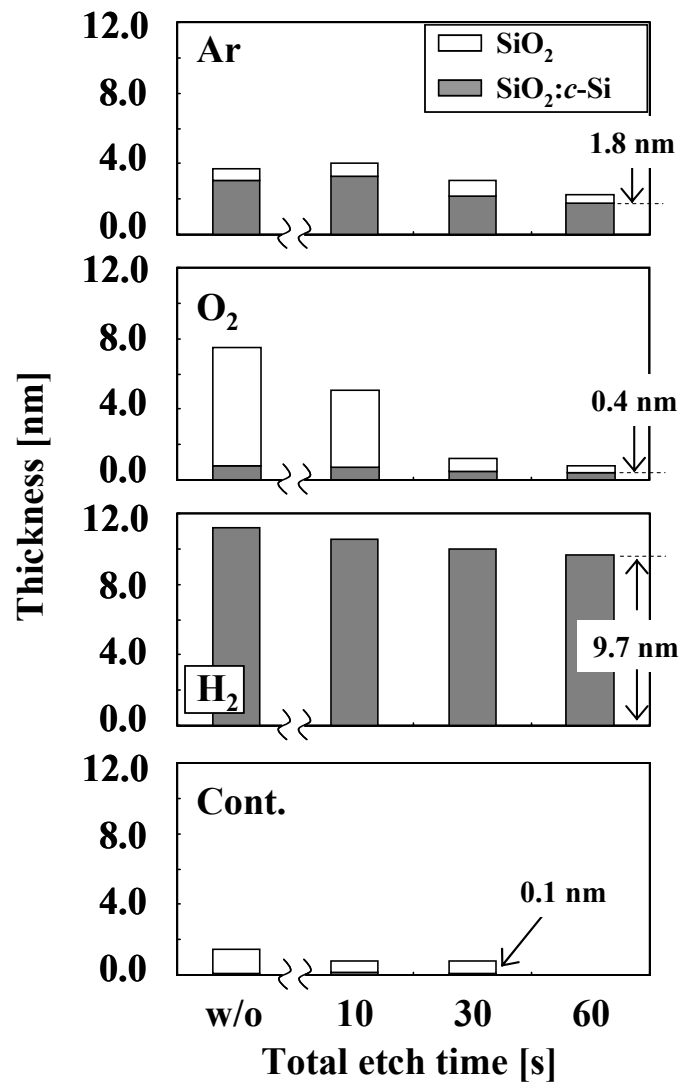
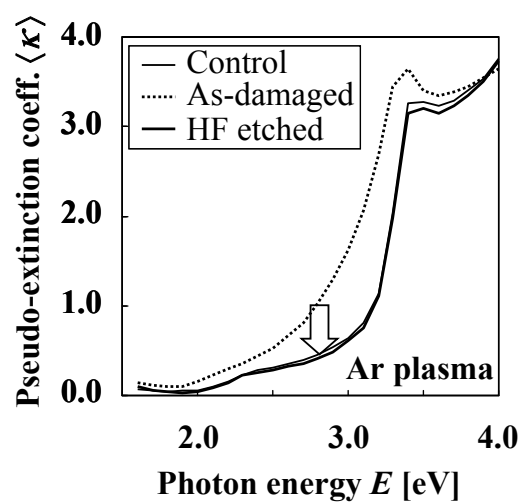
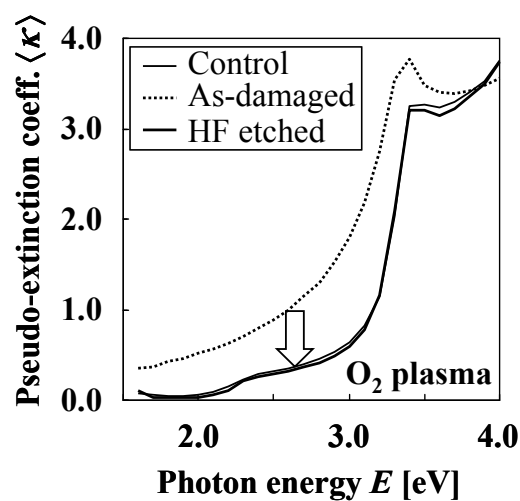


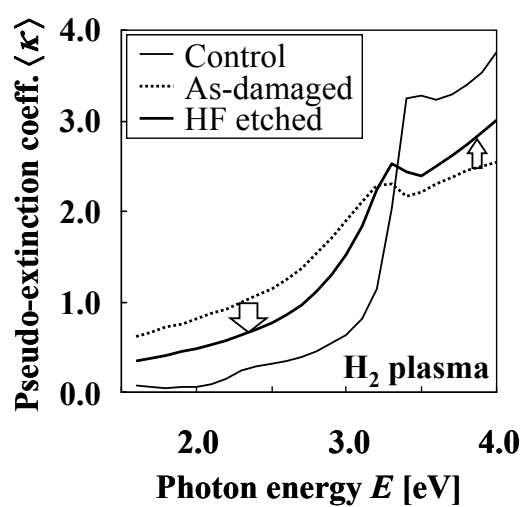
Figure 6.8: Time dependence of the thickness decrease in damage layer upon BHF etching. Four-layer model (air/SiO₂/SiO₂:c-Si/Si sub.) was employed for Ar- and O₂-damage layers (and unexposed layer), and the three-layer model (air/SiO₂:c-Si/Si sub.) for H₂-damage layer.



(a)



(b)



(c)

Figure 6.9: Pseudo-extinction coefficients $\langle \kappa \rangle$ of the damage layer before and after wet-etching treatment. (a) Ar-, (b) O_2 -, and (c) H_2 -plasma exposures.

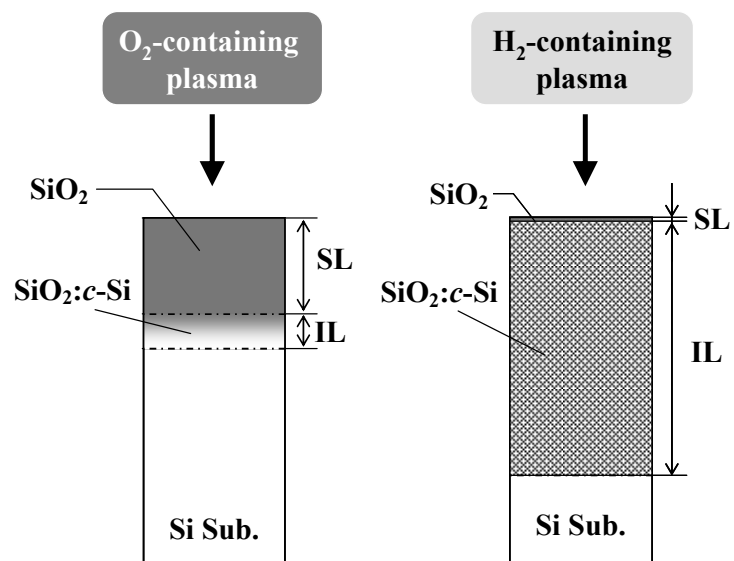


Figure 6.10: Structures damaged by O₂-containing (left) and H₂-containing plasma (right).

6.3.3 Effects of annealing on damage recovery

Finally, how the damaged structure changes by annealing process is investigated. The annealing process was carried out in the RTA system as shown in Fig. 6.2. Figure 6.11 shows changes in the damaged structure (SL, IL) identified by SE before and after the annealing. The samples were treated by DHF before annealing to remove contaminants the damaged surface. Since the IL thickness (d_{IL}) can be a measure of PPD amount, d_{IL} is primarily focused on. In the case of HBr/O₂ case, the as-damaged sample has thick d_{SL} and after the wet-etching (DHF), the decrease in d_{SL} is observable. However, no apparent change in d_{SL} or d_{IL} was found, compared with that in the control sample. Moreover, in the case of H₂ case, the decrease in d_{IL} by the RTA is limited, implying the presence of residual defects in the sample even after the high temperature annealing. Recently, Fukasawa *et al.* reported⁴⁷⁾ that high temperature annealing is requisite to recovery PPD and the annealing process design based on a thermal budget is insufficient. They found that the activation energy for the annealing of PPD located in the thinner region (~ 10 nm) becomes relatively higher than that for the conventional impurity activation usually performed after ion implantation processes. Since defects formed by PPD are localized such as interstitials or dumbbells, it is considered that both the localized defect structure and the profile in damaged region play major role in the recovery mechanism—difficult to reconstruct the structure due to constraint. Therefore, one should pay careful attention to the presence of latent defects created by PPD, even after a wet-stripping step as well as a thermal annealing process, which have been believed to be effective to recover PPD.

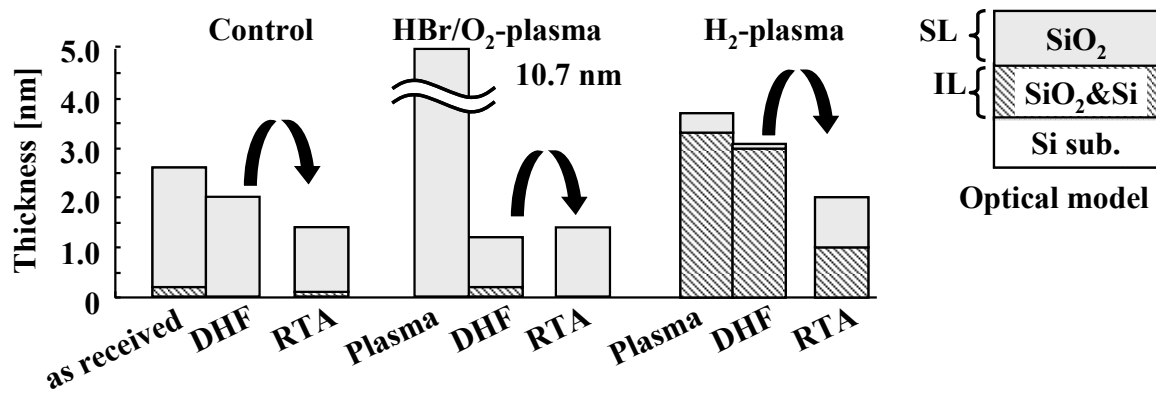


Figure 6.11: Structural changes in d_{SL} and d_{IL} evaluated by SE before and after the annealing (RTA). Effects of wet-etching by DHF are also compared.

6.4 Conclusion

H₂-plasma-induced Si damage was evaluated using SE with the pseudo-extinction coefficient and the electrical measurement. Wet etching was conducted to analyze the damage-layer structure. It was revealed that the damage layer consists of a disordered c-Si layer with a lower energy gap in the $E-k$ space of Si. Through the $I-V$ measurement, the presence of ultrathin SiO₂ layers was confirmed in H₂-plasma-damaged samples, consistent with the SE results, which is in contrast to the structures (with thicker SL) damaged by conventional plasma chemistry. Moreover, the H₂-damage structure was found to be difficult to remove by the wet-etching, or even by conventional annealing processes. Thus, one should pay careful attention to the presence of latent defects in the layer and the resultant device performance degradation. These observations also imply that the thermal annealing process should be carefully conducted to recover PPD in terms of the reliability of device performance.

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Chapter VI

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Chapter VII

Concluding Remarks

This thesis discussed defect generation mechanisms in single crystalline silicon substrates during plasma processing (plasma-induced physical damage: PPD), and proposed defect quantification techniques based on optical reflectance and electrical capacitance measurements. By focusing on "practical manufacturing processes", the effects of substrate bias frequency and wet-stripping on the defect structures have been extensively discussed. The following key features are found:

1. By employing a custom-built inductively couple plasma (ICP) system capable to apply a superposed bias frequency (13.56 MHz and 400 kHz) to a wafer stage, defect generation processes were characterized by spectroscopic ellipsometry (SE), photorefectance spectroscopy (PRS), and capacitance–voltage (C – V) measurement. The thickness of damaged layer by plasma exposure was found to exhibit a simple power-law dependence of the average energy of incident ions and to be a weak function of the bias frequency (f_{bias}). The defect densities estimated by the PRS and the C – V were also weak functions of f_{bias} . These features are attributed to stochastic effects and the detection limit of a monitoring method used. The damaged-layer formation was modeled on the basis of the range theory, *i.e.*, the stopping power in the Si substrate, by considering an ion energy distribution function (IEDF). The model prediction was in

good agreement with experimental data. The obtained results suggest that the damaged-layer thickness depends on sensitivity of the analytical technique, and imply that, in some cases, conflicting results may be incurred for PPD assignments.

2. A quantitative characterization of PPD was demonstrated for the ICP and a capacitively coupled plasma (CCP) sources using the C - V technique. A diluted HF (DHF) wet-etch step was carried out to address the residual defect density in damaged samples, which is key to metal-oxide-semiconductor field-effect transistor (MOSFET) performance design. The optical thicknesses by SE were compared with the electrical thicknesses by the C - V technique. The defect density (n_{dam}) assigned by the C - V technique under various process treatments suggested that one should pay careful attentions to the nature of PPD such as the profiles of defects as well as the sensitivities of analysis techniques. Not only the average energy of incident ions but also the ion flux significantly impact on the PPD evaluation results, while substrate bias frequency is less dominant due to the stochastic effects.
3. The effect of gas mixtures was studied quantitatively in terms of the damaged layer thickness and defect density. Regarding to O_2 addition in Ar plasma, the addition induces the O-termination of Si dangling bonds, thus, increases the thickness of surface SiO_2 layer (SL). This surface layer brings about an effect of masking, resulting in the decrease in the defect generation rate within the residual damaged layer. The distortion of C - V curves was observed by the plasma exposure. From the SL thickness dependence of the shift of C - V curve and its direction, it is speculated that the defects mainly located near the interface layer and the negative charges (electrons) were trapped.
4. H-containing gas chemistries, which have been widely used in the present-day manufacturing, were investigated using various characterization techniques presented

above. Wet-etching for damage removal and annealing for the damaged structure recovery were studied, by taking into account practical process constraint in mass production lines. H-induced Si substrate damage was evaluated using the pseudo-extinction coefficient $\langle\kappa\rangle$ and current–voltage (I – V) characteristics. Wet etching was conducted to analyze the depth profile of damage-layer structure. It was revealed that the damage layer consists of a disordered crystalline Si layer with a lower energy gap in the E – k space of Si—the energy band diagram. Through I – V measurement, the presence of ultrathin SiO_2 layer was confirmed, which is consistent with SE results. These observations are in sharp contrast to the structures damaged by conventional plasma chemistries. The damaged structure results in characteristic features in terms of wet etch removal. Since the H-damage layer was found to be difficult to remove, one should pay careful attention to the presence of residual (latent) damage in the layer and the resultant device performance degradation. In order to monitor the damage layer correctly in the manufacturing processes, the present three-layer [$\text{air}/(\text{SiO}_2 + \text{c-Si})/\text{c-Si}$] optical model should be used in the case of H-damaged Si substrates.

In accordance with aggressive scaling of device feature sizes, plasma-induced damage (PID), in particular, plasma process-induced physical damage (PPD) has been recently focused on again. Owing to the nature of complicated elementary processes in plasma, the PPD mechanisms have been still a source of controversy. By employing defect quantification techniques provided in this thesis, one can overview time-dependent defect generation processes as well as various process condition impacts. However, stochastic effects discussed in Chapter III impose the necessity of dealing with statistics in plasma process designing, which implies that low-damage design is "an optimization problem."¹⁾

Sensitivity of evaluation methods should be advanced to identify latent (residual) defects in ultimately-scaled regions.²⁾

With regard to the C – V technique, for example, the present methodology only assigns the total number of defects present in a damaged structure. To clarify the profile, one should conduct a wet etching step as demonstrated in Chapter IV. Since one measures V -dependence of $1/C^2$, the distortion including a plateau in the $1/C^2$ – V curve gives the depth profile of defects in Si substrate. Thus, it is available to address the defect profile directly from the obtained $1/C^2$ – V curve by optimizing the model where the energy and depth profiles of the carrier trap sites are implemented.

To suppress PPD as much as possible, optimization of gas chemistries is requisite in future ultimately-scaled regimes. As demonstrated in Chapters V and VI, the defect generation mechanisms are strongly dependent also on plasma process conditions in addition to the energy of incident ions and the plasma density, a precise optimization on the basis of the proposed evaluation techniques is versatile.

Finally, the author expects that the methodology and findings provided in this thesis can contribute to advancements of scaled electronic devices with higher performance and reliability in the future.

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Appendix

A.1 PPD range theory

Si substrate damage in a MOSFET was modeled by means of the so-called range theory, as follows.

Traditionally, the range theory^{1,2)} has been widely implemented in ion implantation processes.³⁻⁶⁾ In the range theory for ion implantation processes, the energy of ions usually in the range from keV to MeV, significantly larger than plasma etching is discussed. Moreover, the energy of impinging ions is monochromatic in many cases, while, in conventional plasma etching, rf-bias is applied to a wafer stage.⁷⁾ This bias-frequency configuration leads to a wider energy spectrum of the incident ions in addition to a natural fluctuation due to the collisions in the sheath. Thus, in the PPD range theory, the ion energy distribution function (IEDF) should be taken into account in the range theory to understand the statistical behavior.

The distribution range of injected ions can be determined from the stopping power.²⁾ Energy loss by an ion is considered to arise from two major processes on the basis of the range theory^{2,4,8,9)}: the nuclear stopping and electronic stopping processes, respectively. Nuclear energy loss is treated as an elastic collision of the charged particle with the Coulomb field of a positively charged nucleus, partially screened by the outer valence electrons. The nuclear energy loss depends on the potential of the nucleus and the distance of closest approach, often called the impact parameter. Electronic energy loss of ions to a free electron is attributed to the drag force that a moving ion experiences in a dielectric medium. This energy loss is directly proportional to the particle's velocity and an inelastic

process—the transferred energy sometimes is dissipated through the electron cloud into thermal vibrations of the target, leading to the generation of electron—hole pairs. In the low-energy region, the nuclear stopping is considered to be dominant, whereas in the high-energy region, the electronic stopping is dominant. In typical plasma etching, the energy of ions is much lower than that in ion implantation processes. Thus, a large amount of energy that can possibly create defects is primarily transferred during the nuclear stopping process rather than the electronic stopping process. Therefore, we can focus solely on the nuclear stopping process for investigating the formation of damage during plasma etching. Regarding the nuclear stopping power S_d , a two-body scattering process is usually employed.⁸⁾ The energy loss by scattering depends on the impact parameter p in the incident and target atoms under consideration. The two-body collision process is correlated with a well-known problem in classical mechanics in the center of mass coordinates.^{4,10)} To estimate the energy loss by a series of collisions, the energy transferred to the target atom, T , is usually used.^{11,12)} Once T as a function of p and E_{ion} is determined, one can calculate $(-dE_{\text{ion}}(x)/dx)$ from T as

$$-\frac{dE_{\text{ion}}}{dx} = n_0 S_d(E_{\text{ion}}) = n_0 \int_0^\infty T(E_{\text{ion}}, p) \cdot 2\pi p dp, \quad (\text{A.1})$$

where n_0 is the atomic density of the target (*e.g.*, $5 \times 10^{22} \text{ cm}^{-3}$ for silicon). The energy transfer parameter T has been discussed extensively in the literature.^{8,13-16)} The dependence of S_d on E_{ion} [$S_d(E_{\text{ion}})$] is determined in accordance with the potential assumed in the two-body collision process. Lindhard *et al.* provided²⁾ a comprehensive guideline for the dependence of stopping power on E_{ion} for power-law potentials. Wilson *et al.* calculated¹⁵⁾ the nuclear stopping power for various potentials in the low-ion-energy limit and proposed a universal

expression with a power-law dependence, which has been applied to many materials. The stopping power $S_d(E_{\text{ion}})$ for incident ions from plasmas in the low-ion-energy cases is described as,

$$S_d(E_{\text{ion}}) = A_d \cdot E_{\text{ion}}^{1-\alpha}, \quad (\text{A.2})$$

where α corresponds to the power-law component and A_d is a constant that depends on the identity of the material. The relationship in Eq. (A.2) can also be derived from the calculation by Wilson *et al.*¹⁵⁾

The total distance that an ion travels in coming to rest is called its range R_{ion} , and the projection of this distance along the axis of incidence, the projection range R_p . Note that R_p is a measure of damaged-layer thickness obtained by analysis of the surface structure. For plasma-induced damage (low energy case), Eq. (A.1) is then integrated with Eq. (A.2). By integrating Eq. (A.1), one can determine the total traveling distance of ion R as

$$R = \int_0^R dx = \frac{1}{n_0} \int_0^{E_{\text{ion}}} \frac{dE_{\text{ion}}}{S_d(E_{\text{ion}})} \propto \int_0^{E_{\text{ion}}} \frac{dE_{\text{ion}}}{E_{\text{ion}}^{1-\alpha}} = (E_{\text{ion}})^\alpha. \quad (\text{A.3})$$

The projected range R_p is proportional to R ,^{5,10,11,17,18)} *i.e.*,

$$R \approx \left(1 + K \frac{M_2}{M_1} \right) R_p, \quad (\text{A.4})$$

where M_1 and M_2 are the mass of projectile and target (Si) atoms, respectively. K is a constant. Equations (A.3) and (A.4) indicate that the damaged-layer depth is proportional to

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$$R_p = A_{\text{ppD}} \cdot (\overline{E}_{\text{ion}})^\alpha, \quad (\text{A.5})$$

where A_{ppD} is a material-dependent constant.

Each injected ion has a random path as it moves through the substrate, losing energy by the nuclear stopping process. The relationship obtained is the average behavior. Because ion flux from plasma is usually larger than $10^{15} \text{ cm}^{-2}\text{s}^{-1}$, one should take into account the distribution of injected ions. The profile of injected ions around the depth R_p can be approximated as a Gaussian distribution with a standard deviation called the projected straggle σ_p .^{4,8,10,17)} Thus, the typical distribution of injected ions is described by a normal distribution function. Note that one should also consider the channeling effect. However, the channeling effect becomes observable only for higher-ion-energy cases ($> 500 \text{ eV}$).¹⁹⁾ Thus, one can neglect the channeling effect in this low-ion-energy case. Therefore, concerning the spatial distribution of impinging ions in the Si substrate, stochastic processes by a large number of incident particles lead to a characteristic profile in the substrate, where both R_p and the straggling^{4,8,10,17)}—the variance of R_p , σ_p^2 —are defined. Then, the ion concentration $n_{\text{ion}}(x)$ along the axis of incidence is written as

$$n_{\text{ion}}(x) = \frac{N_{\text{ion}}}{\sqrt{2\pi}\sigma_p} \exp\left[-\frac{(x - R_p)^2}{2\sigma_p^2}\right]. \quad (\text{A.6})$$

N_{ion} is determined from the amount of ions injected into the Si substrate from plasma. N_0 in Eq. (A.6) is expressed as

$$N_0 = \int_0^\infty n_{\text{ion}}(x)dx = \gamma_{\text{proc}} \cdot \Gamma_{\text{ion}} \cdot t_{\text{proc}}, \quad (\text{A.7})$$

where Γ_{ion} is the ion flux from plasma, expressed as $0.61u_B n_p$ on the basis of the Bohm criterion, where u_B and n_p are the Bohm velocity and plasma density, respectively. t_{proc} is the process duration. γ_{proc} is a process-dependent correction factor, which includes sputtering and desorbing processes at the surface ($\gamma=0$ means that all ions are reflected at the surface). $\gamma \sim 1$ is adopted in this case. Once R_p is determined, σ_p is estimated as

$$\sigma_p \approx K' \left(\frac{\sqrt{M_1 M_2}}{M_1 + M_2} \right) R_p, \quad (\text{A.8})$$

where K' is a constant.^{5,10,17,20)} Therefore, the energy dependence of the projected range and of the distribution are described by the equations given. The projected range R_p depends on the power-law component α .

In typical plasma processes, rf-bias is applied to a wafer stage to extract ions with high energy. The ion energy distribution function (IEDF) defined primarily by the bias frequency⁷⁾ is illustrated in Fig. 3.12(a). The PPD range theory includes the IEDF effects with a Monte Carlo method to obtain the final profiles of defect density as indicated in Fig. 3.12(c). The predicted results are in good agreement with experimentally obtained data as discussed in Chapter III in terms of single and superposed biases. The PPD range model can be applied not only to various bias configuration optimization but also to defect generation prediction in three dimensional structures.²¹⁾

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- (B-19) K. Eriguchi, Y. Nakakubo, A. Matsuda, M. Kamei, H. Ohta, H. Nakagawa, S. Hayashi, S. Noda, K. Ishikawa, M. Yoshimaru, and K. Ono
"A New Framework for Performance Prediction of Advanced MOSFETs with Plasma-Induced Recess Structure and Latent Defect Site"
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- (B-20) Y. Nakakubo, Y. Ueda, M. Yoshida, D. Hamada, M. Kamei, K. Eriguchi, and K. Ono
"Scaling of Plasma-Induced Defect Generation Probability in Si: Effects of Bias Voltage at Single- and Superposed-Frequencies"
Proc. 29th International Symposium on Dry Process (DPS), pp.287-288 (2007).

C. Invited talks

- (C-1) 江利口浩二, 中久保義則, 松田朝彦, 鷹尾祥典, 斧 高一
"物理的プラズマダメージによる MOSFET バラツキ増大予測のための包括モデル"
電子情報通信学会技術研究報告 SDM 2011(Sendai, Japan), pp.73-78 (2011).
- (C-2) K. Eriguchi, Y. Nakakubo, A. Matsuda, M. Kamei, H. Ohta, H. Nakagawa, S. Hayashi, S. Noda, K. Ishikawa, M. Yoshimaru and K. Ono
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IEEE EDS Kansai, 第9回 関西コロキウム電子デバイスワークショップ (2009) .

D. Book chapter

- (D-1) Y. Nakakubo, A. Matsuda, M. Kamei, H. Ohta, K. Eriguchi, and K. Ono
"Analysis of Si Substrate Damage Induced by Inductively Coupled Plasma Reactor with Various Superposed Bias Frequencies"
"Emerging Technologies and Circuits", Lecture Notes in Electrical Engineering, Vol. 66, Part 4, pp. 107-120 (A. Amara, T. Ea, M. Belleville (Eds.)), 1st Ed. (Springer, 2010).

E. List of presentations**International conferences**

- (E-1) A. Matsuda, Y. Nakakubo, M. Fukasawa, Y. Takao, K. Eriguchi, T. Tatsumi, and K. Ono
 "Effects of Plasma-Induced Si Damage Structures on Annealing Process Design—Gas Chemistry Impact"
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- (E-2) A. Matsuda, Y. Nakakubo, Y. Takao, K. Eriguchi, and K. Ono
 "Optical Characterization of Plasma-Induced Si Damage by Ar and Cl₂ Inductively Coupled Plasmas"
 Plasma Etch and Strip in Microelectronics (PESM), (2012).
- (E-3) K. Eriguchi, Y. Nakakubo, A. Matsuda, Y. Takao, and K. Ono
 "Unified Model-Prediction Framework for MOSFET Performance Degradation by Plasma-Induced Si Damage and its Application to Process Parameter Optimization"
 Plasma Etch and Strip in Microelectronics (PESM), (2012).
- (E-4) Y. Nakakubo, A. Matsuda, M. Fukasawa, Y. Takao, T. Tatsumi, K. Eriguchi, and K. Ono
 "Detailed Analysis of Si Substrate Damage Induced by HBr/O₂- and H₂-plasma etching and the Recovery Process Designs"
 AVS 59th International Symposium & Exhibition, PS-MoM10 (2012).
- (E-5) A. Matsuda, Y. Nakakubo, Y. Takao, K. Eriguchi, and K. Ono
 "Improvement in the Evaluation Technique for Plasma-Etch Si Damage using Photoreflectance Spectroscopy with Temperature Control"
 AVS 58th International Symposium & Exhibition, PS-ThM9 (2011).
- (E-6) Y. Nakakubo, A. Matsuda, M. Fukasawa, Y. Takao, T. Tatsumi, K. Eriguchi, and K. Ono
 "Effect of Rapid Thermal Annealing on Si Surface Damage by HBr/O₂- and H₂-Plasma"
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- (E-7) Y. Nakakubo, A. Matsuda, Y. Ueda, H. Ohta, K. Eriguchi, and K. Ono
 "Clarification of Surface and Interface Structures exposed to Inductively Coupled Plasma with Various Superposed Bias Frequencies and Its Implication in Plasma Damage Control"
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Domestic conferences

- (E-8) 江利口浩二, 松田朝彦, 中久保義則, 鷹尾祥典, 斧高一
 "古典的分子動力学計算による物理的プラズマダメージ形成機構の検討—Fin 型 MOSFET での欠陥生成機構—"
 電子情報通信学会 シリコン材料・デバイス研究会 (IEICE-SDM), 2013 年 10 月 17 日～18 日, 東北大学.
- (E-9) 亀井政幸, 中久保義則, 鷹尾祥典, 江利口浩二, 斧高一
 "プラズマチャージングダメージが MOSFET の Random Telegraph Noise 特性に及ぼす影

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- (E-10) Y. Nakakubo, A. Matsuda, Y. Ueda, D. Hamada, M. Kamei, K. Eriguchi, K. Ono
"シリコン表面ダメージ層形成過程におけるバイアス周波数重畳効果—Effects of the superposed bias-frequency configurations on the defect generation probability in Si surface region"
Proceedings of the 25th Symposium on Plasma Processing (SPP-25), 2008, pp. 271-272.
- (E-11) 中久保義則, 松田朝彦, 上田義法, 太田裕朗, 江利口浩二, 斧高一
"Ar 系プラズマにおける Si 表面層内誘起欠陥形成過程の O₂ 添加効果"
2008 年秋季 第 69 回応用物理学会学術講演会 (中部大学) 9 月 3 日, 3a-ZC-11.
- (E-12) 松田朝彦, 中久保義則, 鷹尾祥典, 江利口浩二, 斧高一
"温度制御型フォトリフレクタンス分光法を用いたプラズマ誘起 Si 基板ダメージの定量化とそのプロファイル解析"
電子情報通信学会 シリコン材料・デバイス研究会 (IEICE-SDM), 2012 年 10 月 25 日～26 日, 東北大学, 4.
- (E-13) 中久保義則, 松田朝彦, 深沢正永, 鷹尾祥典, 江利口浩二, 辰巳哲也, 斧高一
"H を含むプラズマによる Si 基板ダメージ構造とその回復プロセスについての検討"
2012 年秋季 第 73 回 応用物理学会学術講演会 (愛媛大学) 9 月 12 日, 12a-E1-10.
- (E-14) 中久保義則, 江利口浩二, 松田朝彦, 鷹尾祥典, 斧高一
"電気的手法を用いた物理的 Si 基板ダメージのプラズマプロセス依存性の検討"
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- (E-15) 江利口浩二, 中久保義則, 松田朝彦, 鷹尾祥典, 斧高一
"物理的プラズマダメージによる MOSFET バラツキ増大予測のための包括モデル"
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- (E-16) 中久保義則, 江利口浩二, 松田朝彦, 鷹尾祥典, 斧高一:
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- (E-18) 松田朝彦, 中久保義則, 鷹尾祥典, 江利口浩二, 斧高一
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- (E-19) 深沢正永, 中久保義則, 松田朝彦, 鷹尾祥典, 江利口浩二, 斧高一, 南正樹, 上澤史且, 辰巳哲也
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- (E-20) 江利口浩二, 中久保義則, 松田朝彦, 鷹尾祥典, 斧高一
 "プラズマによる Si 基板ダメージと MOS デバイス特性劣化の相関モデル"
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- (E-21) Y. Nakakubo, A. Matsuda, R. Ogino, M. Kamei, K. Eriguchi, K. Ono
 "Identification of Carrier Trapping Defect Sites in Plasma-Exposed Si Surface by Optical and Electrical Techniques"
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- (E-22) A. Matsuda, R. Ogino, Y. Nakakubo, H. Ohta, K. Eriguchi, K. Ono
 "Detailed Analysis of Plasma-Damaged Layer and Its Significance in Si Surface Structures by Spectroscopic Ellipsometry and Molecular Dynamics Simulations"
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- (E-23) 松田朝彦, 中久保義則, 深沢正永, 鷹尾祥典, 辰巳哲也, 江利口浩二, 斧高一
 "H₂ を含むプラズマによる Si 基板ダメージの光学的・電氣的構造"
 2009 年秋季 第 70 回応用物理学学会学術講演会 (富山大学) 9 月 9 日, 9a-ZG-13.
- (E-24) 中久保義則, 松田朝彦, 荻野力, 上田義法, 江利口浩二, 斧高一
 "O₂ 添加 Ar プラズマによる Si 基板表面層内誘起欠陥の電氣的解析"
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- (E-25) 松田朝彦, 荻野力, 中久保義則, 太田裕朗, 江利口浩二, 斧高一
 "Si 表面のプラズマダメージの精確な解析における界面層の重要性"
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- (E-26) A. Matsuda, Y. Nakakubo, Y. Takao, K. Eriguchi, K. Ono
 "Modeling of Ion-Bombardment Damage on Si Surfaces for In-Line Analysis"
 The 22nd Symposium on Plasma Science for Materials Abstracts of Papers, p. 30 (2009).
- (E-27) Y. Nakakubo, A. Matsuda, Y. Takao, K. Eriguchi, K. Ono
 "Effects of O₂ addition on Si substrate surface damage exposed to Ar plasma"
 The 22nd Symposium on Plasma Science for Materials Abstracts of Papers, p. 29 (2009).
- (E-28) M. Kamei, Y. Nakakubo, K. Eriguchi, K. Ono
 "Bias frequency dependence of pn junction charging damage induced by plasma processing"
 The 22nd Symposium on Plasma Science for Materials Abstracts of Papers, p. 27 (2009).

F. Award

- 2010年11月 31st Dry Process Symposium, 2009 Best Paper Award (共著)
 (応用物理学会)
- 2011 年 8 月 2011 年度 応用物理学会優秀論文賞 (共著) (応用物理学会)

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