

**Heteroepitaxial Growth of High-Quality
AlN on SiC by Molecular-Beam Epitaxy toward
Electronic Device Application**

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Abstract

In this thesis, heteroepitaxial growth of high-quality AlN on SiC is studied using molecular-beam epitaxy (MBE) toward the goal of electronic device applications. The interface structure of AlN/SiC (or SiC surface structure) is investigated in detail to obtain AlN and subsequent GaN films with excellent crystalline quality, and to achieve the AlN/SiC interface with superb electronic properties. Besides the lattice mismatch of 0.9% for the (0001) basal planes, AlN/SiC is a heteropolytypic (2H/4H or 6H) and heterovalent (III-V/IV-IV) system, so that interface control, or tailoring the interface structure, is very important. In heteropolytypic epitaxy of 2H-AlN on 4H- or 6H-SiC(0001) surfaces, the stacking mismatch at the SiC step edges is one of the crucial issues to be solved. In this work, to solve the problems related to the polytype mismatch, control of the SiC surface steps is conducted, which leads to coherent coalescence of the AlN nuclei on different terraces of the SiC surface. In the heterovalent system, charge accumulation or depletion at the interface could be avoided by introducing some measure of atomic mixing in such a way as to compensate III-V and IV-IV bonds. In this work, control of the atomic arrangement at the AlN/SiC interface using pre-irradiation by atomic nitrogen is investigated to achieve the interface with excellent electronic properties toward metal-insulator-semiconductor (MIS) device applications. Also, as another viable approach to solve both the polytype mismatch and the instability problem of polar interface, perfect polytype matching and formation of electronically-stable interface are attempted using nonpolar SiC(11 $\bar{2}$ 0) substrates which has the information of stacking sequence on the surface.

In chapter 2, the MBE growth system used in this work and detailed experimental procedures are described. The current status of as-received SiC substrate is explained, and growth features of AlN on as-received substrates are shown.

In chapter 3, surface control of the on-axis SiC(0001) substrate is studied to obtain AlN epilayers with excellent crystalline quality. Initial two-dimensional (2D) growth is realized owing to the surface control of not only the step-and-terrace structure but also the surface chemistry, i.e., removal of residual oxygen species and realization of a 1/3 monolayer (ML) silicon-adsorbed superstructure. It is shown that AlN films with initial 2D nucleation have markedly reduced densities of both screw-type and edge-type threading dislocations. Evolution of surface features in the initial stages of AlN growth is characterized, and the effectiveness of surface step control in reducing the density of stacking mismatch bound-

aries (SMBs) is experimentally demonstrated, which is due to coherent coalescence of AlN nuclei originating from different SiC terraces. The high-quality AlN film grown on the SiC substrate is applied as a buffer layer for GaN growth, and the great impact of AlN film quality on the properties of subsequent GaN epilayers, especially the density of screw-type dislocations, is revealed.

In chapter 4, AlN growth on off-axis SiC(0001) epilayers is studied toward SiC MIS device applications. Remarkable improvement in the surface morphology of AlN films grown on off-axis SiC substrates is obtained by lowering the growth temperature, probably due to modification of the initial growth kinetics. Control of the atomic arrangement at the AlN/SiC interface, i.e., artificial manipulation of the interface bonding configuration, is investigated to achieve MIS structures with excellent electrical characteristics. The electronic properties of AlN/SiC change dramatically with atomic-nitrogen pre-irradiation. Since interface traps are the product of surface reactions during the initial stages of growth, their density can be controlled by varying the growth procedure. Owing to pre-irradiation, a quite small interface state density is obtained.

In chapter 5, AlN growth on SiC(11 $\bar{2}$ 0) substrates is studied. The nonpolar interface of AlN/SiC(11 $\bar{2}$ 0) would be expected to neutralize/balance the charges at the interface due to the equal numbers of Si-N and C-Al bonds. In the (11 $\bar{2}$ 0) face, polytype replication from the SiC substrate to the AlN epilayer is essential to obtain epilayers with excellent crystalline quality. It is worth noting that if the polytype of the SiC substrate is successfully replicated to the AlN epilayer, problems related to stacking mismatches between the epilayer and the substrate, which is a major concern in AlN growth on SiC(0001) substrates, can be eliminated. In this study, AlN growth on 4H- and 6H-SiC(11 $\bar{2}$ 0) substrates is performed. It is shown that 2H-AlN, which is the thermodynamically stable phase for AlN, is grown on the 6H-SiC(11 $\bar{2}$ 0) substrate, resulting in poor structural quality. On the other hand, 4H-AlN, which is a novel polytype for group-III nitrides, is successfully grown on 4H-SiC(11 $\bar{2}$ 0) due to the atomic-template effect of the substrate. Owing to polytype replication from the substrate to the epilayer, the interface between 4H-AlN and 4H-SiC(11 $\bar{2}$ 0) is not disordered, and the grown film exhibits superior structural quality.

In chapter 6, a summary of the present work is given, together with the remaining issues to be solved and suggestions for future works.

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Chapter 1

Introduction

1.1 Background

Toward the further evolution and development of electronics, there has been increasing emphasis on high-potential semiconductor materials and novel structures. The recent rapid progress in communication systems has been largely indebted to advances in semiconductor engineering. For instance, the foundation of high-speed integrated circuit (IC) technology has been provided by silicon (Si) bipolar devices and gallium arsenide (GaAs) metal-semiconductor field-effect transistors (MESFETs). For the future “ubiquitous” network society, the practical use of high-power and high-speed devices, such as heterojunction field-effect transistors (HFETs) and heterojunction bipolar transistors (HBTs), will be in much demand. However, conventional semiconductors such as group-III arsenides or phosphides are strictly limited by the trade-off relation between the cut-off frequency and breakdown field, i.e., high-speed and high-power performance.

Recently, much attention has been paid to wide bandgap semiconductors for realizing high-power microwave transistors. Gallium nitride (GaN) and its alloys with aluminum nitride (AlN) and indium nitride (InN) are most viable owing to the availability of their heterojunctions, i.e., bandgap engineering. Semiconductor heterostructures enable us to expand the design of device structures and to develop new functional devices. Under the circumstances, nitride technologies have attracted many researchers addressing both fundamental aspects as well as device applications.

On the other side of these exponential advances, energy resources are being more and more exhausted. The energy problem is a matter of great importance to us in the 21st century. From the viewpoint of power electronics, which is an advanced technology for control of electricity using semiconductor power devices, ultra low-loss and high-power devices are needed to handle large amounts of electric power with high efficiency. Most of the present power devices are made of technologically-mature Si owing to the availability of high-quality and large-area wafers and a convenient native oxide (silicon dioxide: SiO₂). Utilizing the highly-developed Si process technologies, the performances of Si power devices

have been improved markedly. And now, this intensive and extensive progress has brought the technologies close to the theoretical limits from the material properties. In this aspect, silicon carbide (SiC) is a most promising semiconductor material for power devices, owing to its superior material properties.

1.2 Group-III Nitrides and SiC

1.2.1 Important Properties and Current Status of Group-III Nitrides

Group-III nitrides (InN, GaN and AlN) are III-V compound semiconductors composed of tetrahedrally bonded cation and anion atoms in a close-packed structure. All three binaries and their alloys crystallize in both wurtzite and zinc-blende structures, where the wurtzite structure is thermodynamically more stable [1]. Here, wurtzite and zinc-blende structures are also referred to as 2H and 3C structures in Ramsdell's notation, respectively. Since these compounds are direct-transition-type semiconductors¹, they have garnered much attention as attractive candidates for use as light emitters or detectors [3]. These materials can cover continuously, by appropriate alloying, from 0.7 eV (the bandgap of wurtzite InN) to 6.2 eV (the bandgap of wurtzite AlN) [Fig. 1.1]. (It should be noticed here that such a smaller bandgap of InN, 0.7 – 0.9 eV (not 1.9 eV), has been reported only very recently from optical experiments using high-quality epitaxial films [4–6].) In the mid-1990s, light-emitting diodes (LEDs) for the blue and green regions of the spectrum and blue lasers emitting at 405 nm were developed and commercialized [7–13].

Besides optical devices, applications in high-power and high-frequency electronic devices have also attracted much attention. This is because group-III nitride materials show relatively high electron saturation drift velocity and high breakdown field (see Table 1.1 [14–16]): for example, GaN shows an electron saturation velocity of 2 to 3 times higher, and a breakdown field one order or more greater than that of Si [17]. Although GaN exhibits a lower electron mobility compared to GaAs, its saturation velocity and breakdown field are far superior to those of GaAs. In addition to these superb properties, nitride-based heterostructures such as AlGaIn/GaN can induce high-density sheet carriers (called two-dimensional electron gas: 2DEG) at the interface [18]. Due to the noncentrosymmetric nature of wurtzite structure, a strong built-in electrostatic field can exist in the [0001] direction because of spontaneous and piezoelectric polarization. These internal fields remarkably enhance the 2DEG density at the AlGaIn/GaN interface, which is one order of magnitude higher than in AlGaAs/GaAs [19], making possible high current handling capability. Consequently, these features make the system most promising for future applications in high-power and high-frequency electronics.

¹Zinc-blende AlN is theoretically expected to have an indirect bandgap [2].

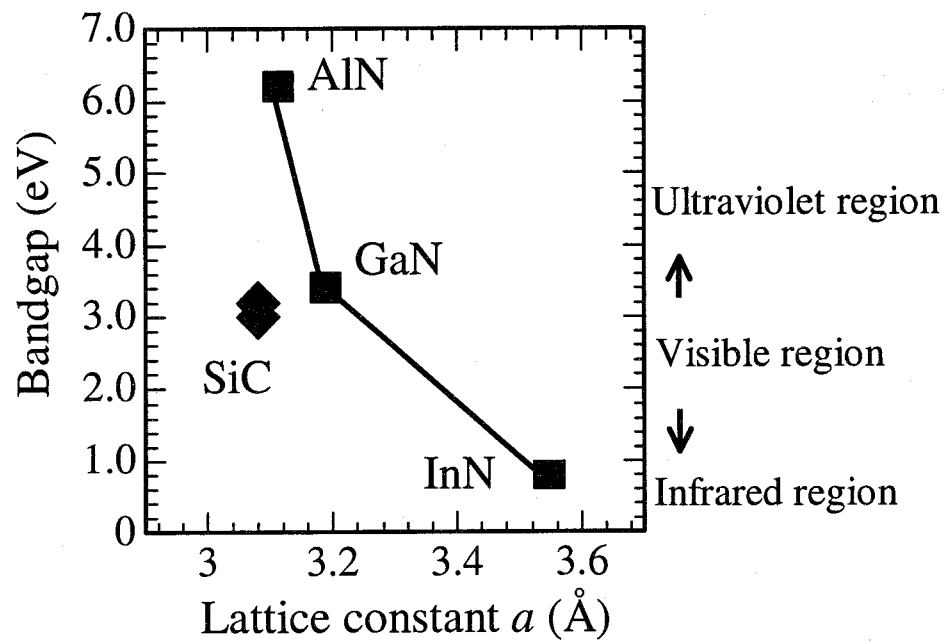


Figure 1.1: Relationship between bandgap and in-plane (a -axis) lattice constant for group-III nitrides and SiC.

Table 1.1: Physical properties of GaN, SiC and most common other semiconductor materials, and their technological characteristics. [14–16]

Properties	GaN	4H-SiC	6H-SiC	Si	GaAs
Crystal Structure	WZ	4H	6H	Dia.	ZB
Lattice Constant	$a=3.18$	$a=3.08$	$a=3.08$		
(Å)	$c=5.19$	$c=10.08$	$c=15.12$	5.43	5.65
Band Structure	D.	I.D.	I.D.	I.D.	D.
Bandgap : E_G (eV)	3.39	3.26	3.02	1.12	1.42
Electron Mobility :					
μ_n (cm ² /Vs)	1000	900	450	1500	8500
Hole Mobility :					
μ_p (cm ² /Vs)	20	100	50	450	400
Breakdown Field :					
E_B (V/cm) $\times 10^6$	3	3	3	0.3	0.4
Thermal Conductivity					
(W/cm°C)	1.3	4.9	4.9	1.5	0.46
Saturation Drift Velocity :					
v_s (cm/s) $\times 10^7$	2.7	2.2	1.9	1	2
Relative Dielectric					
Constant : ϵ_s	10.4	9.7	9.7	11.9	12.8
Conductivity Control	Δ	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$
Thermal Oxide	$\times$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\times$
Conductive Wafer	Δ (SiC)	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$
Insulating Wafer	$\bigcirc$ (Sapphire)	$\bigcirc$	$\bigcirc$	$\times$	$\bigcirc$

ZB : Zinc-blende WZ : Wurtzite Dia. : Diamond

I.D. : Indirect D. : Direct

 $\bigcirc$: Excellent Δ : Fair $\times$: Difficult

One of challenges for nitride technology is heteroepitaxy on foreign substrates with lattice and thermal mismatches, such as sapphire. Although bulk GaN is available now [20, 21], it will take a long time to achieve high-quality and large-area wafers at a reasonable cost. With present growth techniques, heteroepitaxial GaN films usually contain a high density of defects due to those mismatches with the substrates [22]. These defects significantly deteriorate the performance of GaN-based electronic and optical devices [23], and improving the quality of GaN materials has been a subject of extensive research effort.

SiC has been studied as a suitable substrate material for GaN-based high-power devices owing to its excellent thermal conductivity as well as its close lattice constant with AlN ($\Delta a \sim 0.9\%$) [24]. According to Gaska *et al.* [25], the introduction of SiC substrates results in very effective heat removal from the active region.

1.2.2 Important Properties and Current Status of SiC

SiC is a IV-IV compound semiconductor with Si and carbon (C) atoms with the ratio of unity. The Si and C atoms in SiC have tetrahedral bonding configurations, such that each Si and C atom has only Si-C bonds. Due to strong bonding of Si-C, SiC has superior thermal and chemical stabilities. SiC is also famous for its polytypism: in spite of fixed chemical composition of Si and C, the difference in the stacking sequence along the hexagonal $\langle 0001 \rangle$ direction brings various crystal forms (i.e., polytypes). Considering the Si-C pair as a sphere, there are three possible occupation sites denoted by A, B, and C as shown in Fig. 1.2. For example, the B- or C-site bilayer can place on the A-site bilayer. Table 1.2 gives stacking sequences of several popular polytypes. The polytypes in the table are written in Ramsdell's notation. In Ramsdell's notation, polytypes are represented by the number of bilayers in the unit cell and the crystal structure (C for cubic, H for hexagonal, and R for rhombohedral). In the case of SiC, a lot of polytypes (more than 200 kinds) have been found. The most popular and important polytypes for electronic device applications are 3C-, 4H-, and 6H-SiC. The structures of 3C-, 4H-, and 6H-SiC are presented schematically in Fig. 1.3.

The physical properties of SiC are different for each polytype, as shown in Table 1.1, where 4H- and 6H-SiC are considered. Both 4H- and 6H-SiC have wide bandgaps [26], suggesting that SiC devices can operate at high temperatures. The breakdown field of 3 MV/cm is one order of magnitude larger than for Si and GaAs [15]. This parameter is important to reduce the on-resistance in power devices. The high saturation drift velocity enables devices to operate at high frequencies [16, 27, 28]. Heat generated in devices by Joule heating can be easily transferred to a heat sink due to the high thermal conductivity of SiC [29, 30].

There have been many reported SiC power devices. Intensive studies on fundamentals of SiC Schottky diodes [31–33] have led to commercial production of 4H-SiC Schottky diodes. As for switching devices, MISFETs are considered promising owing to their high

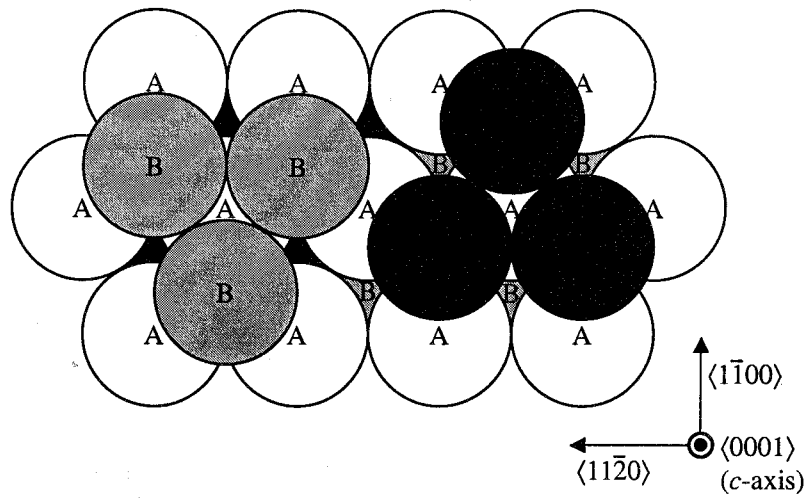


Figure 1.2: Hexagonal close packing of Si-C pairs.

Table 1.2: Stacking orders of several polytypes.

polytype	stacking
3C-SiC	ABC...
4H-SiC	ABCB...
6H-SiC	ABCACB...
15R-SiC	ABCACBCABACABCB...

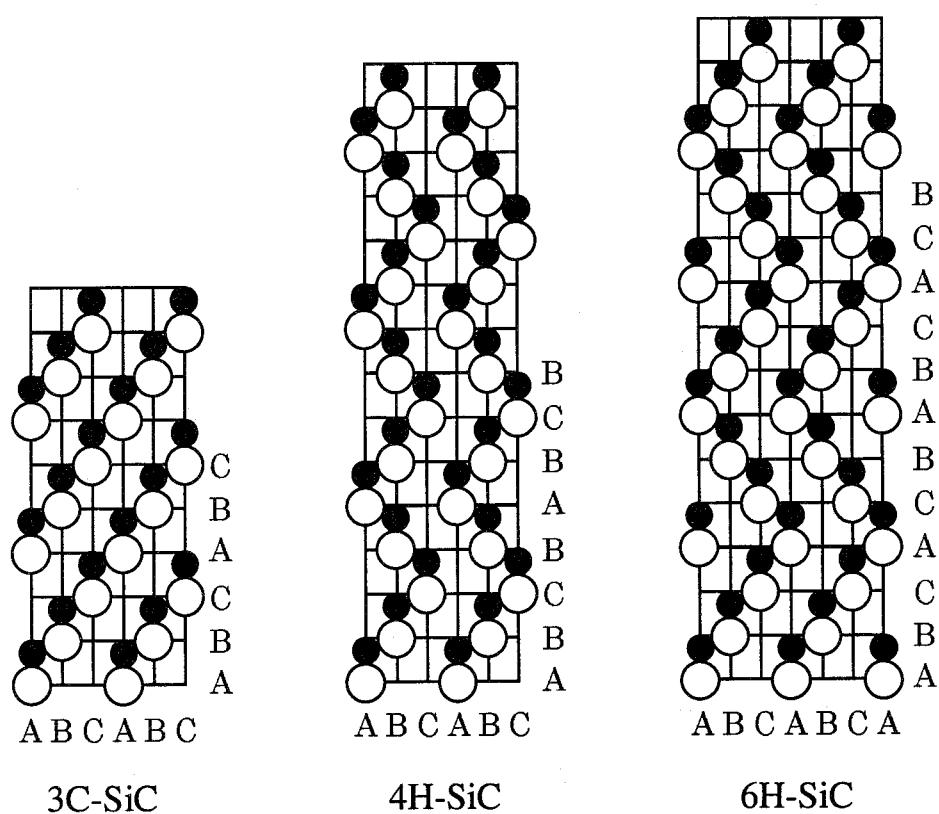


Figure 1.3: Stacking orders along c -axis for 3C-, 4H-, and 6H-SiC. Open and closed circles represent Si and C atoms, respectively.

switching frequency and have been investigated extensively. Since SiC is the only compound semiconductor to yield SiO₂ by thermal oxidation, MOS devices can be fabricated on SiC substrates. SiC power MOSFETs are attractive power switching devices because of the possibility to realize high capacity with low loss and high switching speed. However, a high interface-state density, in particular for 4H-SiC(0001), has been found to cause large inversion channel resistivity [34, 35], limiting the performance of SiC MOSFETs. It turns out that the SiO₂/SiC interface has one to two orders of magnitude higher interface state density than the SiO₂/Si interface. This renders the as-grown thermal oxide rather useless as dielectric for SiC-based MOS devices [36, 37].

Two principle reasons have been suggested for this behavior [38]. (i) Incomplete oxidation of carbon atoms in SiC leads to the formation of carbon clusters which are believed to contribute to interface states on account of their graphitic and therefore semi-metallic nature. (ii) The steep increase in interface states toward the conduction band edge E_C , especially in 4H-SiC, is due to so-called near interface traps (NITs). Their microscopic origin is as yet unclear but it was suggested that they result from oxygen deficiency [37]. These states act as interface traps for electrons and cause the large channel resistivity in MOS devices. Therefore, many efforts have been made to reduce the channel resistivity at the SiO₂/SiC interface.

Fabrication of MOS structures on other crystal faces like (11 $\bar{2}$ 0) [39, 40] and (03 $\bar{3}$ 8) [41] has been attempted to improve SiC MOSFET performance. Use of oxynitride as well as high-temperature oxidation has also been attempted as a means to reduce interface states [36, 37, 42–46].

In this work, an alternative dielectric material, AlN, was studied intensively toward SiC MIS device applications, which can solve the problems mentioned above. AlN is a suitable insulating material due to its high relative dielectric constant ($\epsilon_{\text{AlN}} = 8.5$) compared to SiO₂ ($\epsilon_{\text{SiO}_2} = 3.9$) [47–51].

1.3 AlN/SiC Heterostructure

AlN epitaxially grown on SiC has been proposed as a potential replacement for SiO₂ in SiC MIS devices [52, 53]. In contrast to amorphous SiO₂ formed by thermal oxidation of SiC, the interface between epitaxially-grown AlN and SiC is expected to be superior because of the small lattice mismatch (0.9%) for the (0001) basal planes (SiO₂/SiC $\sim$ 5%). Unsaturated dangling bonds due to lattice mismatch are thought to cause electronically-active traps at the interface [54].

AlN also plays an important role as the buffer layer for the epitaxial growth of high-quality GaN on SiC substrates. In addition to the small lattice mismatch, the thermal expansion coefficients along the basal plane are also quite close between AlN and SiC. This superb matching for the basal planes is expected to facilitate the formation of nearly perfect

junctions. However, GaN epilayers grown on SiC substrates contain a significant number of threading dislocations, which are mainly generated in the AlN buffer layer. In most heteroepitaxial situations, the structure of interface with the substrate is critical for the overall properties of the epilayer. It is thus important to improve the interface structure between AlN and SiC.

In this work, the AlN/SiC hetero-interface is studied intensively to achieve AlN epilayers with excellent crystalline quality as well as a superb interface structure toward high-quality GaN epitaxy on SiC substrates and AlN/SiC MIS device applications.

1.4 Challenges in AlN Growth on SiC

1.4.1 Polytype Mismatch

Lattice mismatch in epilayer/substrate is often cited as a major obstacle in heteroepitaxial growth of group-III nitrides, and is a cause of the observed defects. In the case of the AlN/SiC system, their in-plane lattice parameters are relatively similar (0.9%), which should lead to high-quality epilayers. In the AlN/SiC system, however, other structural defects, namely stacking mismatch boundaries (SMBs), have been identified as defects spreading into the epilayers because of their different polytypes between AlN (2H) and SiC (4H or 6H). If the substrate surface did not contain any steps, then SMBs would not form. However, substrates invariably contain steps. For example, in 6H-SiC the stacking sequence is ABCACB..., so three stacking sequences would be possible for wurtzite 2H-AlN: (i) SiC ...ABC leading to BCBC AlN; (ii) SiC ...BCA leading to CACA AlN; and (iii) SiC ...CBA leading to BABA AlN, and all lead to vertical defects between differently stacked domains in AlN epilayers. Consider a 6H-SiC substrate region terminated as ...ABC and an adjacent region separated by a bilayer step terminated as ...ABCA. With subsequent AlN growth, the stacking sequence BCBC would form over the first region while the stacking sequence CACA would form over the second region and inevitably lead to an SMB (see Fig. 1.4). To avoid SMB generation, the surface step structure of SiC substrate should be manipulated. Control of the surface step structure with one-unit-cell height is a promising means to eliminate these defects. Supposing all terraces of SiC surface are terminated only as ...CBA, they lead to only BABA AlN. The height of one unit cell (4ML for 4H-SiC and 6ML for 6H-SiC) is $2\times$ or $3\times$ AlN 1 unit-cell (2ML), respectively (see Fig. 1.4). Thus, SMBs can be eliminated by surface control of the SiC step structure. In this work, HCl-gas etching, which forms an atomically-smooth and uniform step-and-terrace structure with one-unit-cell-height steps, is shown to be effective to eliminate SMBs, which will be presented in chapter 3.

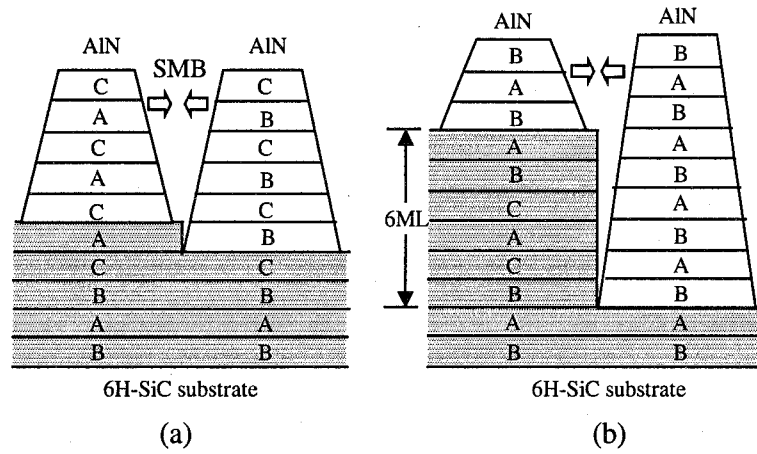


Figure 1.4: Schematic models of 2H-AlN growth on (a) as-received (not step-controlled) 6H-SiC(0001) substrate and (b) step-controlled 6H-SiC(0001) substrate.

1.4.2 Heterovalent Interface

For heterovalent (nonisovalent) heterojunctions such as AlN/SiC (III-V/IV-IV), abrupt polar interfaces would be characterized by the occurrence of either oversaturated or undersaturated bonds [53]. It is well known that ideal, abrupt polar interfaces between heterovalent semiconductors suffer from instability problems, as first pointed out by Harrison *et al* [55]. Indeed, if one calculates the electrostatic potential as a function of position along the growth direction, it is found that charge accumulation or depletion at the ideal interface gives rise to a nonzero average electric field that extends throughout the overlayers. Such an electric field could be supported in thin overlayers, but would cause the system to become unstable once the overlayer exceeds a certain thickness. Harrison *et al.* and Stirman *et al.* suggested that charge accumulation or depletion at the interface could be avoided by introducing some measure of atomic mixing in such a way as to compensate III-V and IV-IV bonds [55, 56].

Ponce and co-workers concluded from the results of cross-sectional HRTEM studies that the most favorable atomic arrangements at the abrupt interface between AlN and silicon-terminated SiC(0001) are the intermixed configurations of Si-N and Al-C bonds, which produce no significant changes in the Si-C or Al-N backbond lengths [57]. The image contrast and interplanar distances corresponding to C-N and Al-Si bonds were not observed in their HRTEM studies.

To apply an AlN film as a gate insulator for MIS devices, electronic properties of the AlN/SiC interface (density of interface traps, channel mobility etc.) should be controlled. Although the AlN/SiC heterostructure is expected to be a promising alternative to SiO₂/SiC MOS structures, the interface characteristics, especially correlations between the interface structure and electronic properties, have not been understood in detail. Molecular-beam epitaxy (MBE), employed in this work, is a very suitable growth method to manipulate the interface structure between AlN and SiC owing to its atomic-scale controllability. In this study, control of the atomic arrangement at the AlN/SiC interface, i.e., artificial manipulation of interface bonding configuration, is investigated to achieve MIS structures with excellent electrical characteristics, which will be described in chapter 4.

1.5 Outline of Thesis

Figure 1.5 shows the contents of this thesis. In this thesis, heteroepitaxial growth of high-quality AlN on SiC is studied using MBE toward electronic device applications. The interface structure of AlN/SiC (or SiC surface structure) is investigated in detail to obtain AlN epilayers with excellent crystalline quality and to achieve superb interface characteristics in MIS structures. The AlN/SiC heterostructure is a heteropolytypic (2H/4H or 6H) and heterovalent (III-V/IV-IV) system, so that interface control, i.e., tailoring the interface structure, is very important. In heteropolytypic-epitaxy of 2H nitrides on 4H- or 6H-SiC(0001) surfaces, the polytype mismatch at the SiC step edges is one of the crucial

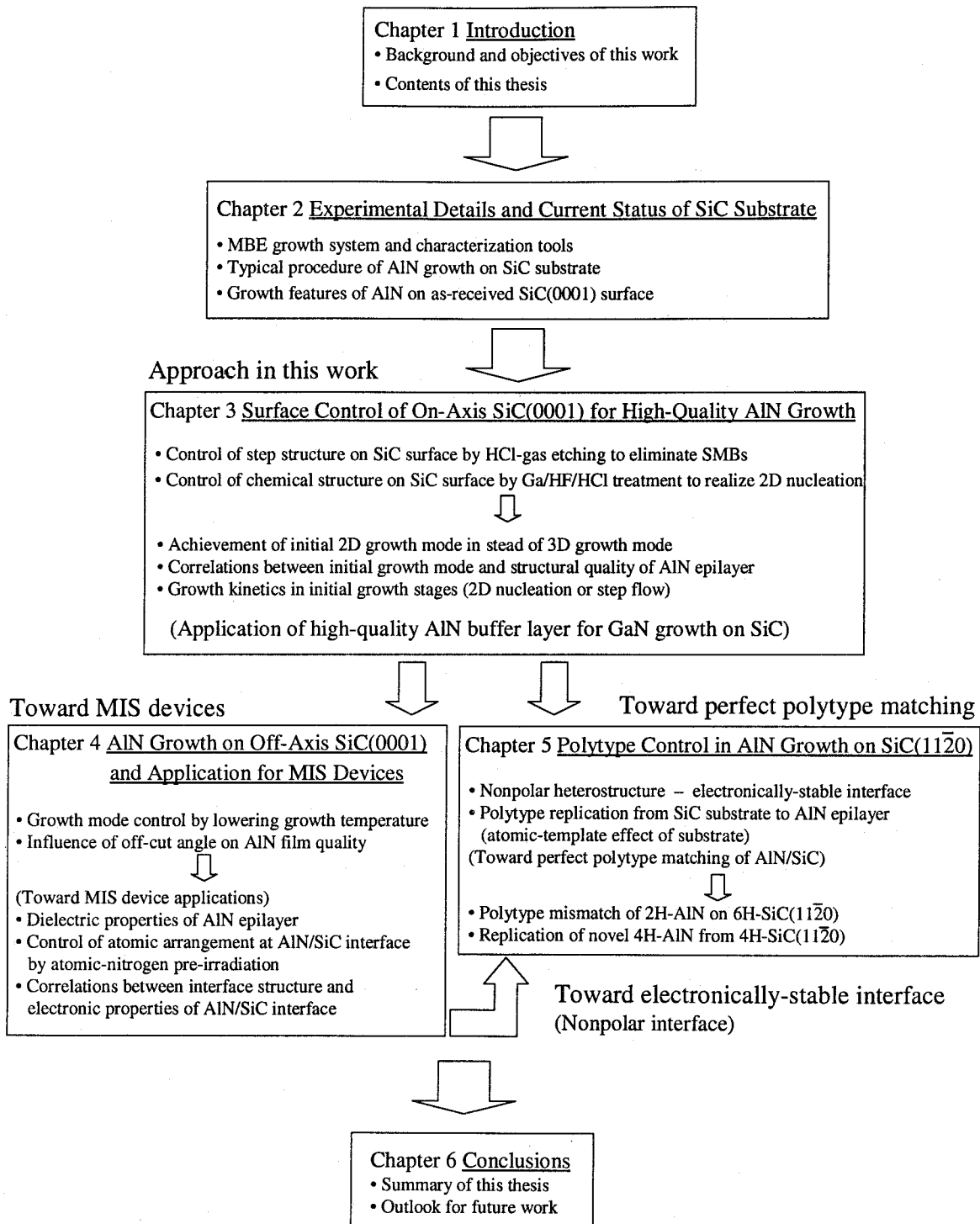


Figure 1.5: Contents of this thesis.

issues to be solved. In this work, to solve the problems related to stacking mismatch, control of the SiC surface steps is conducted, which leads to coherent coalescence of AlN nuclei originating from different SiC terraces. In the heterovalent system, charge accumulation or depletion at the interface could be avoided by introducing some measure of atomic mixing in such a way as to compensate III-V and IV-IV bonds [55, 56]. In this work, control of the atomic arrangement at the AlN/SiC interface, i.e., artificial manipulation of the interface bonding configuration, is investigated to achieve MIS structures with excellent electrical characteristics. Also, as a novel approach, perfect polytype matching and formation of an electronically-stable interface between AlN and SiC are attempted using nonpolar SiC(11 $\bar{2}$ 0) substrates which have the information of stacking sequence on the surface. The outline of each chapter is as follows.

In chapter 2, the MBE growth system and characterization tools used in this work are described first, and then the typical growth procedure is explained. The growth features of AlN on as-received SiC(0001) substrates are presented, and the necessity of eliminating SiC surface imperfections is described.

In chapter 3, SiC surface control involving not only the surface structure but also the surface chemistry is performed to eliminate SMBs and realize initial two-dimensional (2D) layer-by-layer growth. Remarkable improvement in the structural quality of AlN epilayers is exhibited owing to the initial coalescence of 2D nuclei. Microscopic analysis of kinetics in the initial stages of AlN growth is conducted, which experimentally reveals the effectiveness of surface step control in reduction of SMBs. The high-quality AlN film grown on the SiC substrate is applied as a buffer layer for GaN growth, and the great impact of AlN film quality on the properties of subsequent GaN epilayers is revealed.

In chapter 4, AlN growth on off-axis SiC(0001) substrates is studied toward SiC MIS device applications. Dependence of growth kinetics on the off-cut angle of the SiC substrate is discussed, and growth mode control in AlN growth is demonstrated. The band offsets at the AlN/SiC interface and the dielectric properties of AlN epilayers are investigated. Control of the atomic arrangement at the AlN/SiC interface is demonstrated to achieve excellent interface characteristics.

In chapter 5, AlN growth on 4H- and 6H-SiC(11 $\bar{2}$ 0) substrates is studied. The nonpolar interface of AlN/SiC(11 $\bar{2}$ 0) would be expected to neutralize/balance the charges at the AlN/SiC interface due to the equal numbers of Si-N and C-Al bonds. In the (11 $\bar{2}$ 0) face, polytype replication from the SiC substrate to the AlN epilayer is essential to obtain epilayers with excellent crystalline quality. It is worth noting that if the polytype of SiC substrate is successfully replicated to the AlN epilayer, problems related to the stacking mismatch between the epilayer and substrate can be eliminated, which is a major concern in AlN growth on SiC(0001) substrates. Our obtained results demonstrate that the remarkable impact of SiC substrate polytype on the crystalline structure of AlN epilayer.

In chapter 6, conclusions and suggestions for future work are presented.

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Chapter 2

Experimental Details and Current Status of SiC Substrate

2.1 Introduction

Despite the similar crystal parameters such as lattice constant and thermal expansion coefficient, AlN epilayers on SiC surfaces are still highly defective, and the quality must be improved for high-performance devices [1]. Generally, growth kinetics during epitaxy affect the resulting crystalline quality of grown layers. Particularly, the growth mode at the early stages of epitaxial growth, such as the nucleation process or the coalescence of nuclei, strongly impacts the overall quality of the epilayer [2, 3]. So far, detailed understanding of the growth mechanism for AlN on SiC as well as for other group-III nitrides on foreign substrates is far from complete despite of their importance as device materials [4, 5]. In most cases, epitaxial growth of nitrides is accomplished via metalorganic vapor phase epitaxy (MOVPE) techniques [6–9]. However, since there are few tools for the *in situ* analysis of the growth mode and growth mechanism in MOVPE, the number of studies on growth behavior of nitrides using MOVPE has been quite small.

In this work, molecular-beam epitaxy (MBE) was employed for AlN growth on SiC. By using an MBE growth system, *in situ* analysis of crystal growth kinetics and real-time monitoring of transitional surface structure are possible owing to incorporated characterization tools in ultra-high vacuum [5, 6, 10, 11]. As described in chapter 1, the AlN/SiC system is lattice-mismatched ($\sim 0.9\%$ for the basal planes), heterovalent (III-V vs. IV-IV) and, above all, heteropolytypic (2H vs. 4H or 6H). Consequently, heteroepitaxy of AlN with excellent crystalline quality on SiC surfaces is a quite challenging issue, where these problems must be overcome by some means or other.

In this study, aimed at exploring the potential of the AlN/SiC system and expanding the frontiers of heteroepitaxy, the growth kinetics during MBE and the control of the interface structure were investigated.

2.2 Ultra-High Vacuum System

2.2.1 Molecular-Beam Epitaxy System

Overview

The epitaxial growth of AlN described in this work was carried out using an MBE growth system shown schematically in Fig. 2.1 (EV-100S, Eiko). The system consisted of a growth chamber, a sample-transfer chamber and a sample-exchange chamber. The sample-transfer chamber and sample-exchange chamber separated by gate valves were installed to prevent air from coming directly into the growth chamber when loading and taking out a substrate.

The growth chamber was equipped with Knudsen effusion cells for elemental aluminum (Al) and gallium (Ga) evaporation and a radio frequency (rf) plasma cell for producing active nitrogen (N^*). All cells had individual shutter blades made of tantalum (Ta). The growth chamber was also equipped with a reflection high-energy electron diffraction (RHEED) system for *in situ* real-time observation of the surface structure and analysis of the growth mode and growth mechanism. The growth chamber was connected through an ultra-high vacuum tunnel to a chamber for x-ray photoelectron spectroscopy (XPS), which enabled us to do *in situ* XPS measurements.

Pumping System

A schematic diagram of the pumping system is presented in Fig. 2.2. The sample-exchange chamber was exhausted by a turbomolecular pump connected to a rotary pump, and the pressure reached 5×10^{-7} Torr in 30 min. The pressure in the sample-transfer chamber was normally lower than 5×10^{-8} Torr, achieved using an ion pump. The growth chamber was pumped by a turbomolecular pump all the time except during growth, and the pressure was as low as 10^{-9} Torr. During growth, the growth chamber was evacuated by an oil-diffusion pump (EO9K, Edwards), equipped with a liquid nitrogen trap and supported by a rotary pump. The pumping speed utilizing the oil-diffusion pump was about 1350 l/s. The growth chamber was also equipped with a liquid nitrogen cryo-shroud, cooled to liquid nitrogen temperature (77K) during growth for adsorption of residual gases. At optimal conditions, the background pressure inside the chamber was below 1×10^{-10} Torr. During epitaxial growth of AlN, the pressure was 10^{-5} Torr due to the inflow of nitrogen gas. The XPS chamber was exhausted by a turbomolecular pump, and the base pressure was as low as 10^{-9} Torr.

Substrate Heating System

The SiC substrates used in this work were installed into a substrate holder. The substrate holder was made of molybdenum (Mo), and heated up to 1000°C by a Ta heater placed behind it. The substrates were secured to the holder using a retaining (snap) ring. A diffuser plate made of pyrolytic boron nitride (PBN) was used for improved heating uni-

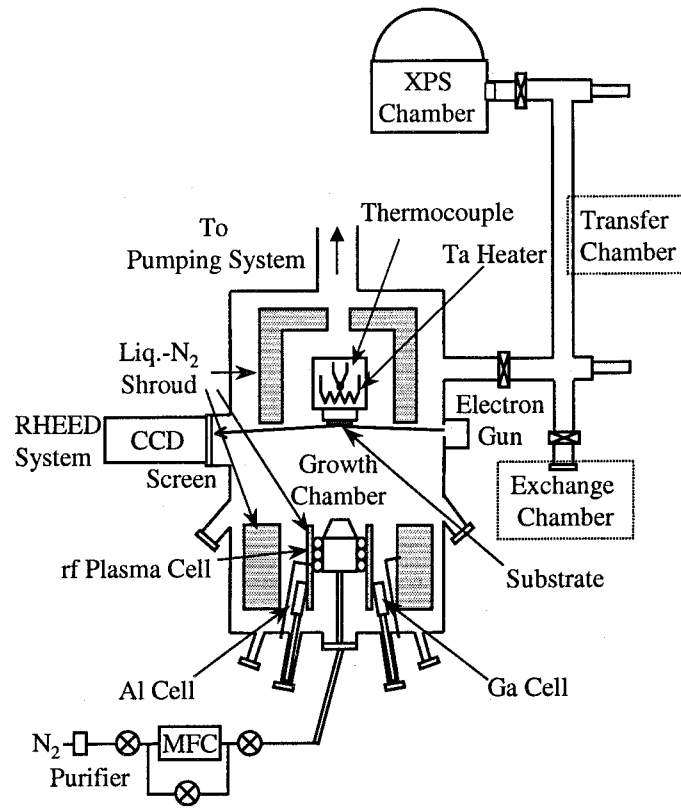


Figure 2.1: Schematic picture of MBE growth system used in this work.

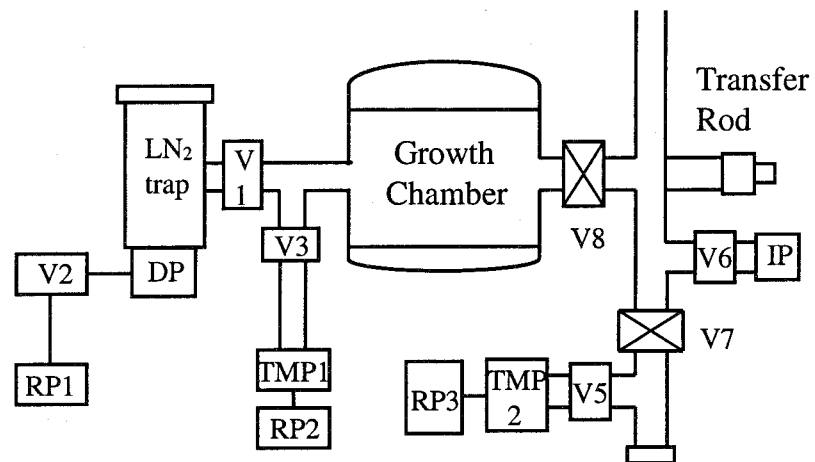


Figure 2.2: Schematic diagram of pumping system.

formity. The substrate temperature (T_{sub}) was measured by a thermocouple located just behind the substrate. Although the actual substrate temperature may be lower than the thermocouple temperature, the measured temperature without any corrections will be given as the substrate temperature in this work.

2.2.2 Effusion Cells and Radio-Frequency Plasma Source

Elemental Al of 6N purity and Ga of 7N purity were evaporated from Knudsen effusion cells (Applied EPI). Al and Ga metals were held in 200g-SUMOTM effusion cell crucibles made of PBN. The SUMO effusion cell was developed to offer increased charge capacity without sacrificing material quality or cell performance. The crucible is comprised of a cylindrical reservoir with a small tapered orifice, thereby combining large capacity with excellent flux uniformity. For the Al effusion cell, the crucible includes a wide lip extending into a thermally isolated cold zone to prevent Al creep which can damage the cell. The Al effusion cell and Ga effusion cell had different heater configurations. For use with Al, a cold-lipped SUMO effusion cell, which was operated with the bottom filament only, was used. This cell is designed to prevent overflow caused by Al wetting of the PBN crucible. The heat shielding and heater filament are carefully positioned to allow efficient heating of the crucible body while maintaining an intentional cold lip. For use with Ga, a hot-lipped SUMO cell with a dual filament configuration was employed since metallic Ga tends to recondense at the crucible orifice. The two independent heater filaments provide a more efficient heating configuration, which allows the cell to operate at a lower power while still ensuring optimal heating of the crucible orifice.

Intensities of the Al and Ga beam fluxes on the substrate surface were measured by a nude ion gauge located at the same position as the sample in order to optimize the operating temperature for each cells. The operating temperature for the Al effusion cell during MBE growth ranged from 1100°C to 1200°C, which corresponded to beam flux of $1 \sim 6 \times 10^{-7}$ Torr. The Ga effusion cell was employed for pretreatment of SiC surface, and the typical operating temperature was 970°C, the beam equivalent pressure of 4.5×10^{-7} Torr.

Epitaxial growth of AlN in this work required precise control of the Al beam flux intensity. The operating temperature for the Al effusion cell was controlled by a temperature control system (Eurothermo model 818), and the temperature was stabilized within $\pm 0.3^\circ\text{C}$.

As for a source to produce active nitrogen, an rf plasma cell was employed. A microwave of 13.56 MHz was applied for nitrogen activation. The plasma unit (EPI UNI-Bulb RF Plasma Source, Applied EPI) was fitted with an optical emission detector that gives a photo-current reading correlated with the active nitrogen flux intensity. Nitrogen gas of high-purity (6N) first passed through a purifier, and then on to the rf plasma cell. The flow rate of nitrogen gas was controlled by a mass flow controller, and ranged from 0.1~0.5 sccm in this work. Applied power was set to 200 W or 400 W. As shown in Fig. 2.3, the emission

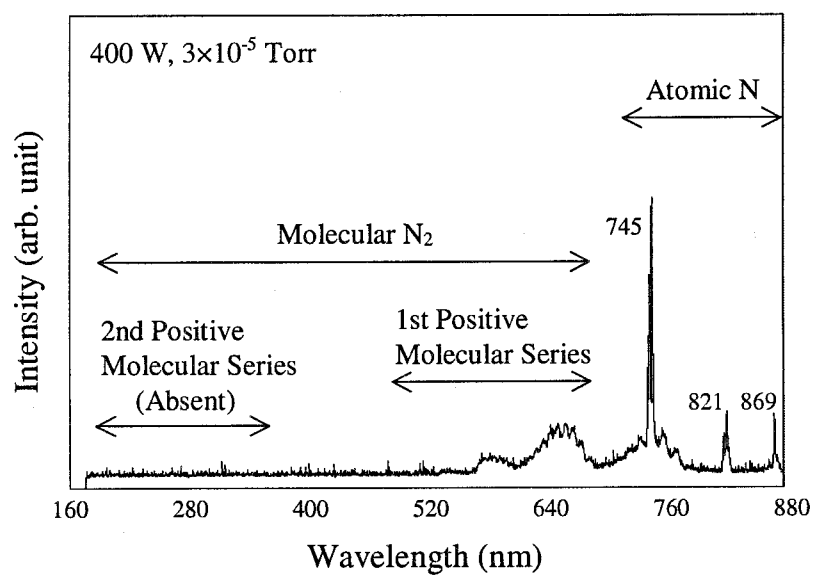


Figure 2.3: Typical emission spectrum of nitrogen plasma activated by rf cell.

spectrum from the rf plasma cell was dominated by an atomic transition peak at 745 nm, and the color during operation was bright orange to eyes.

2.2.3 Instruments for *In Situ* Analysis

Reflection High-Energy Electron Diffraction

An MBE growth system which operates in ultra-high vacuum allows incorporation of several surface monitoring tools [5, 6, 10, 11]. Among the analytical tools available, RHEED has contributed to advances in epitaxial technology and improvements in the quality of epitaxial layers [12]. The electron beam emitted from a sharpened filament is diffracted at the surface atoms of sample, and builds up a diffraction pattern on a fluorescent screen. In this work, an electron beam accelerated by 20 kV was applied for RHEED observation. RHEED monitoring was conducted for *in situ* analyses of the chemical condition on SiC surfaces and the kinetics in AlN growth, and observed patterns were recorded through a high-resolution CCD camera. The monitoring of diffracted intensities was carried out by using a real-time image processing system (kSA400 RHEED system, k-Space).

X-ray Photoelectron Spectroscopy

XPS is a characterization tool to examine not only the chemical composition on a sample surface but also the chemical bonding of surface atoms and the band offset of a heterostructure. In this work, XPS spectra were obtained using the $\text{AlK}_{\alpha 1}$ (1486.6 eV) x-ray source and a hemispherical electron energy analyzer (ESCA-1000 system, Shimadzu) as shown schematically in Fig. 2.4. The analysis area was normally ϕ 0.6 mm and the pass energy used in this study was 0.3 eV. Since $\text{AlK}_{\alpha 1}$ was employed as the x-ray source, the beam linewidth was about 0.85 eV. The XPS chamber was connected through an ultra-high vacuum tunnel to the growth chamber (see Fig. 2.1), therefore the measurements were performed *in situ* after pretreatment of the SiC surface or AlN growth in the growth chamber.

2.3 Experimental Procedures

2.3.1 Preparation of SiC Substrate

In this work, $\text{SiC}(0001)_{\text{Si}}$ on- and off-axis wafers manufactured at CREE Inc. and $\text{SiC}(11\bar{2}0)$ wafers from CREE Inc. and Nippon Steel Corp. were used as substrates. The wafers were diced into $7 \times 8 \text{ mm}^2$ rectangular pieces to install in the sample holder for MBE growth. The substrates were degreased in trichloroethylene and acetone solvents, and rinsed with deionized water. Next, the substrates were dipped in HCl and aqua regia solutions, and then dipped in HF solution to remove native oxides. Finally the substrates were rinsed with deionized water and blown with dry nitrogen. After these wet chemical processes, the substrates were introduced either directly into the sample-exchange chamber, or else

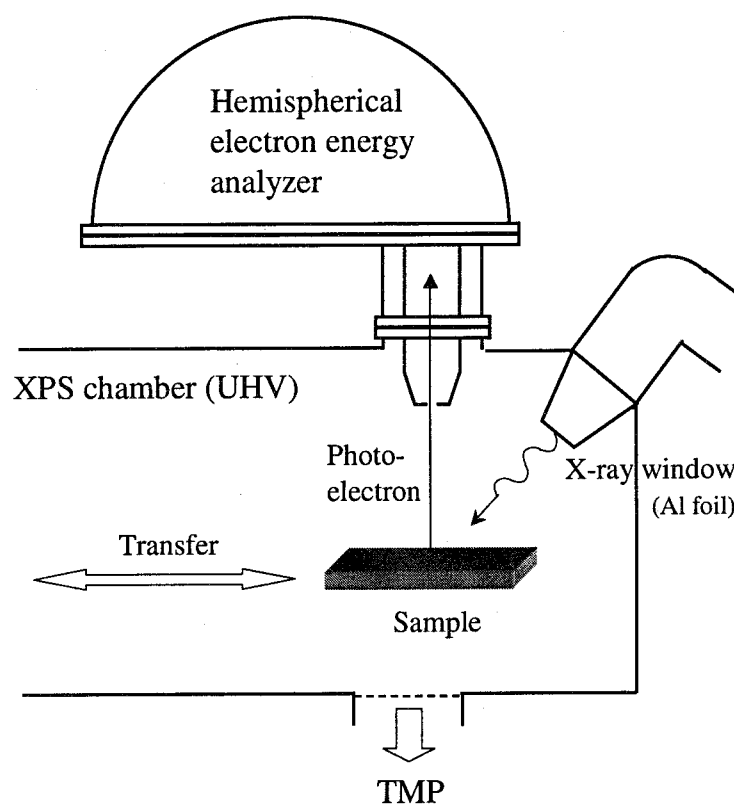


Figure 2.4: Schematic diagram of XPS system.

first into a SiC chemical vapor deposition (CVD) system for high-temperature HCl/H₂-gas etching of the SiC surface, which will be described in chapter 3.

2.3.2 Growth Procedure

After the pressure of the sample-exchange chamber reached 10^{-7} Torr, the substrate was transferred into the growth chamber via the sample-transfer chamber. Figure 2.5 represents a typical procedure for epitaxial growth of AlN. The substrate temperature was raised up to 1000°C at a ramp rate of 20°C/min, and then the substrate was thermally cleaned for 30 min to remove oxides and contamination from the surface. Following the thermal cleaning, active nitrogen was generated by the rf plasma cell with the shutter closed. After a few minutes interval for stabilizing the gas flow, vaporized Al and active nitrogen were introduced simultaneously to the substrate surface. AlN growth was carried out at 1000°C in a pressure of 10^{-5} Torr. After the growth, the shutters of the cells were closed and the substrate temperature was lowered to room temperature at a rate of -20°C/min.

2.3.3 *Ex Situ* Characterization

Surface features, such as the step structure and surface roughness of SiC substrates and AlN epilayers, were characterized using a tapping-mode atomic force microscope (AFM; D-3100, Digital Instruments). Crystalline quality and structural defects in the films were investigated by high-resolution x-ray diffraction (HRXRD) and high-resolution transmission electron microscopy (HRTEM). The XRD measurements were performed with a triple crystalline x-ray diffractometer (SLX-2000, Rigaku). A copper (Cu) K_{α1} line ($\lambda=1.540562$ Å) was selected using a channel cut germanium (Ge) (220) monochromator. The cross-sectional TEM observations were performed on a microscope operating at 300 kV (H-9000NAR, Hitachi). The interface structure of AlN/SiC, especially the intermediate layer at the interface, was investigated by x-ray reflectivity at glancing incidence (GIXRR). Dielectric properties of AlN epilayers were examined by current-voltage (*I-V*) measurements. Electronic properties of the AlN/SiC interface were studied by capacitance-voltage (*C-V*) measurements at a high-frequency of 1 MHz using a precision LCR meter (HP 4284A, HP).

2.4 Current Status of As-Received SiC Substrate

2.4.1 Surface Condition of As-Received SiC Substrate

Figure 2.6 exhibits surface features of the on-axis 6H-SiC(0001) substrate after wet chemical preparation. In this work, SiC substrates without any additional pretreatments are referred to as as-received substrates. Surface polishing scratches of 1~10 nm in depth were evidently observed in the AFM image. In addition, no atomic step structure was clearly observed on

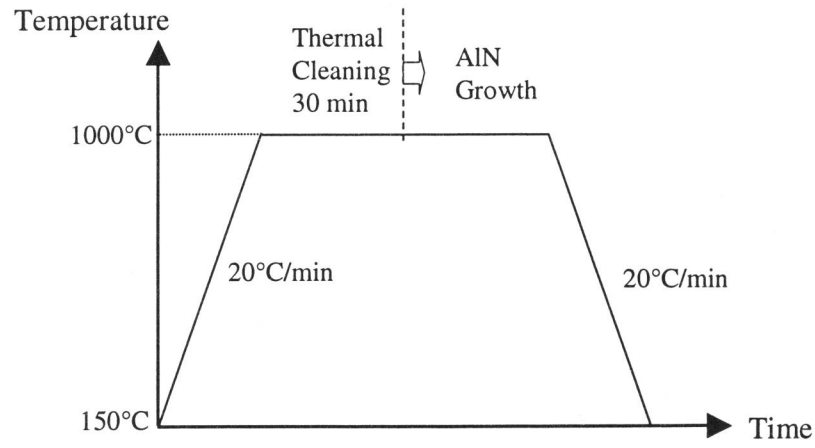
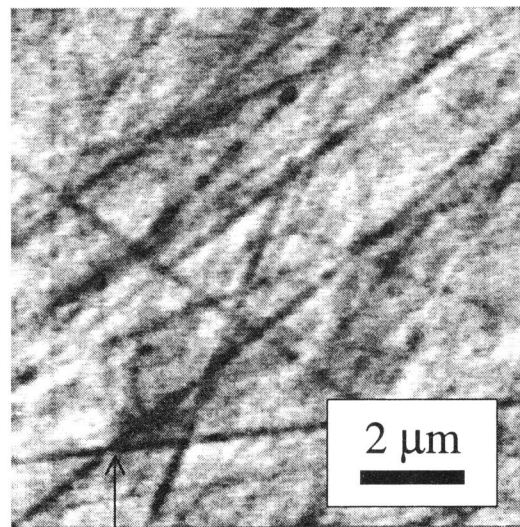


Figure 2.5: Typical procedure for epitaxial growth of AlN used in this work.



polishing scratches
1~10 nm in depth

Figure 2.6: AFM image of as-received 6H-SiC(0001) substrate.

the as-received surface. The value of the root-mean-square (rms) roughness was as large as 1.4 nm in a scan size of $10 \times 10 \mu\text{m}^2$, which is attributed to such surface imperfections.

Thus, SiC surfaces normally show many scratches and nanometer scale roughness fluctuations. Yamada and co-workers pointed out that these features of the substrate introduce planar-type defects in the AlN film, which are generated due to misalignment of the stacking sequence between SiC and AlN [1]. According to Lee *et al.* [8], early work with nitride growth on SiC substrates yielded results which were no better than those using sapphire substrates, despite the superior lattice match of SiC [3]. This is chiefly due to poor surface morphology of as-received SiC substrates. The hardness and high chemical stability of SiC make it difficult to remove surface polishing damage, thus many surface scratches are present even on commercially-available wafers from established vendors [13]. For electronic device applications, removal of surface imperfections from the substrate is very important issue [14]. From the viewpoint of crystal engineering, control of the surface step structure is crucial especially for heteropolytypic epitaxy of AlN on SiC in order to eliminate stacking mismatch boundaries (SMBs) (see Fig. 1.4) [1, 15–18].

2.4.2 Surface Morphology of AlN Epilayers

Figure 2.7 displays an AFM image of a 30-nm-thick AlN film grown on an as-received 6H-SiC(0001) substrate. Stripe-like defects were the dominant features, which originated from polishing scratches on the substrate, resulting in a large surface roughness of 1.3 nm. In the early stages of growth, three-dimensional (3D) AlN nuclei were formed on the as-received substrate. This result was identical to that of Yamada *et al* [1]. AlN nuclei on the as-received SiC surface were crystallographically misaligned and thus induced incoherent boundaries at the coalescence stage, resulting in the delay of the two-dimensional (2D) growth mode transition and additional defect formation in the AlN film. 3D initial nucleation in AlN growth is thought to adversely affect the crystalline quality of subsequent epilayer.

HRXRD investigation of thin AlN films grown on as-received substrates indicated poor structural quality, which is also described in chapter 4. From these results, removal of polishing scratches or surface imperfections of SiC substrates is essential to obtain high-quality AlN films.

2.5 Summary

In this chapter, AlN growth on as-received SiC(0001) substrates was carried out. As-received SiC surfaces had many polishing scratches and nanometer scale roughness fluctuations. The hardness and high chemical stability of SiC make it difficult to remove surface polishing damage using ordinary methods, so many surface scratches are observable even in commercially-available wafers produced by established suppliers. Accordingly, stripe-like defects were the dominant features on the AlN surfaces, which originated from polishing

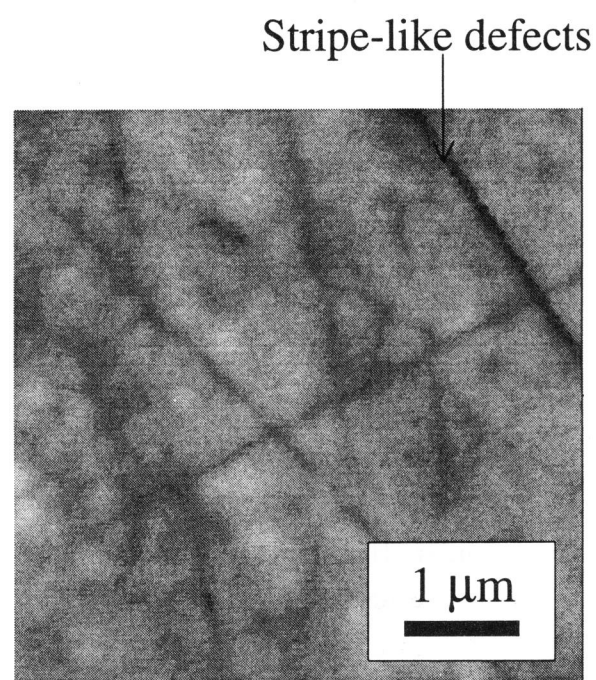


Figure 2.7: AFM image of 30-nm-thick AlN epilayer grown on as-received 6H-SiC(0001) substrate.

scratches on the substrates. These features of the substrate are thought to introduce planar-type defects in the AlN films, related to misalignment of the stacking sequence between SiC and AlN.

In next chapter, surface control of SiC substrates is studied in order to obtain AlN films with excellent crystalline quality. An etching technique of the SiC surface using high-temperature HCl gas is proposed as an effective pretreatment method for MBE growth of high-quality AlN.

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Chapter 3

Surface Control of On-Axis SiC(0001) for High-Quality AlN Growth

3.1 Introduction

As-received SiC substrates typically contain high densities of surface defects and scratches due to mechanical polishing, which can result in the formation of additional defects during AlN growth [1]. In addition, as-received SiC substrates contain a distribution of steps with random terminations so that growth of AlN films on these substrates leads to a high density of mismatch boundaries [2]. Tanaka *et al.* reported on planar defects at step edges in the AlN/6H-SiC(0001) interface using cross-sectional HRTEM [3]. The defects were identified as interface domain boundaries originating from incoherent coalescence of neighboring islands at substrate steps.

In this work, an etching technique using high-temperature HCl gas is suggested as an effective pretreatment method for the SiC surface prior to MBE growth of high-quality AlN. It has been found by AFM that HCl-gas etching removes surface polishing scratches and realizes an atomically-flat terrace structure with one-unit-cell-height steps [4]. Mismatch boundaries should not form when the uppermost layers of adjacent terraces have the same underlying stacking sequence [5]. Therefore, if the step structure of the SiC substrate can be tailored such that all terraces have the same underlying stacking sequence, it should be possible to produce AlN films with reduced defect densities. There have been several reports on the significance of SiC surface treatment for the structural quality of AlN films [1, 6–9]. Yamada and co-workers also used HCl-gas etching as a surface cleaning procedure, and demonstrated its impact on the island coalescence stage in AlN growth by MOVPE [6]. Also, Torres *et al.* reported on the effectiveness of high-temperature H₂ etching (1600°C) of the SiC substrate on reduction of defects in AlN films [1]. Thus, defect formation in AlN epilayers is thought to be mainly due to structural imperfections on the SiC surface.

Although such structural control of SiC surface is found to be effective in enhancement of AlN film quality, growth kinetics during the initial growth stages and the nucleation

mechanism on the atomically-flat step-and-terrace structure has not been studied in detail. According to Yamada *et al.*, three-dimensional (3D) nuclei of AlN were formed on the atomically-flat SiC terraces in the early stages of growth [6]. The 3D initial growth mode probably results in highly-defective epilayers due to incoherent coalescence of nuclei. Hence, a two-dimensional (2D) growth mode from the beginning of growth is favorable to obtain high-quality epilayers with reduced defect densities.

In this chapter, the microscopic nucleation mechanism in the initial stages of growth and the growth kinetics of AlN on the atomically-flat step-and-terrace structure of SiC are investigated. The initial growth mode is revealed to be strongly influenced not only by the surface structure but also the surface chemistry of the SiC substrate. The impact of SiC surface control on the initial nucleation and evolution stages of AlN growth are demonstrated, and remarkable improvements in the crystalline quality of AlN epilayers are presented.

3.2 Step Control on SiC Surface

3.2.1 HCl-Gas Etching

The etching technique of SiC(0001) face by HCl/H₂ gas at a high temperature ($\sim 1300^\circ\text{C}$) has been reported to bunch atomic steps into microsteps with the height of one unit cell as well as to remove polishing scratches [4]. The mechanism of the step bunching by the etching has been suggested to be the minimization of surface free energy. In other words, the step bunching is attributed to the different etching speed between the bilayer step edges with the one dangling bond and two dangling bonds. The bilayer step edges with the two dangling bonds are etched easier and reached the bilayer step edges with the one dangling bond. H₂ carrier gas etches carbon from SiC leaving excess silicon, which is expected to be taken away by the HCl gas.

The substrates used in this chapter were on-axis 4H- and 6H-SiC(0001)_{Si} substrates (off-cut angle $< 0.3^\circ$). After wet chemical preparation (see chapter 2), the substrates were loaded into a horizontal cold-wall chemical vapor deposition (CVD) reactor for the HCl-gas etching. This CVD system is normally employed for SiC growth, and the etching technique is also performed as surface pretreatment for high-quality SiC homoepitaxy [10]. The substrates were etched by HCl (3 sccm) with H₂ carrier gas (1 slm) at 1300°C for 10 min.

Figure 3.1 shows typical AFM images of HCl-treated on-axis 6H-SiC(0001) surfaces slightly misoriented toward $[11\bar{2}0]$. The polishing scratches usually observed on the surfaces of as-received wafers were successfully removed. Microsteps were formed perpendicular to the off-cut direction and were nearly parallel and periodic over the substrate surface. The height of these microsteps was about 1.5 nm, corresponding to the height of the 6H-SiC unit cell (six monolayers, 6ML). The terraces were atomically smooth, and the terrace width was about 300 nm indicating 0.3° tilt. After the etching process, the substrates were transferred

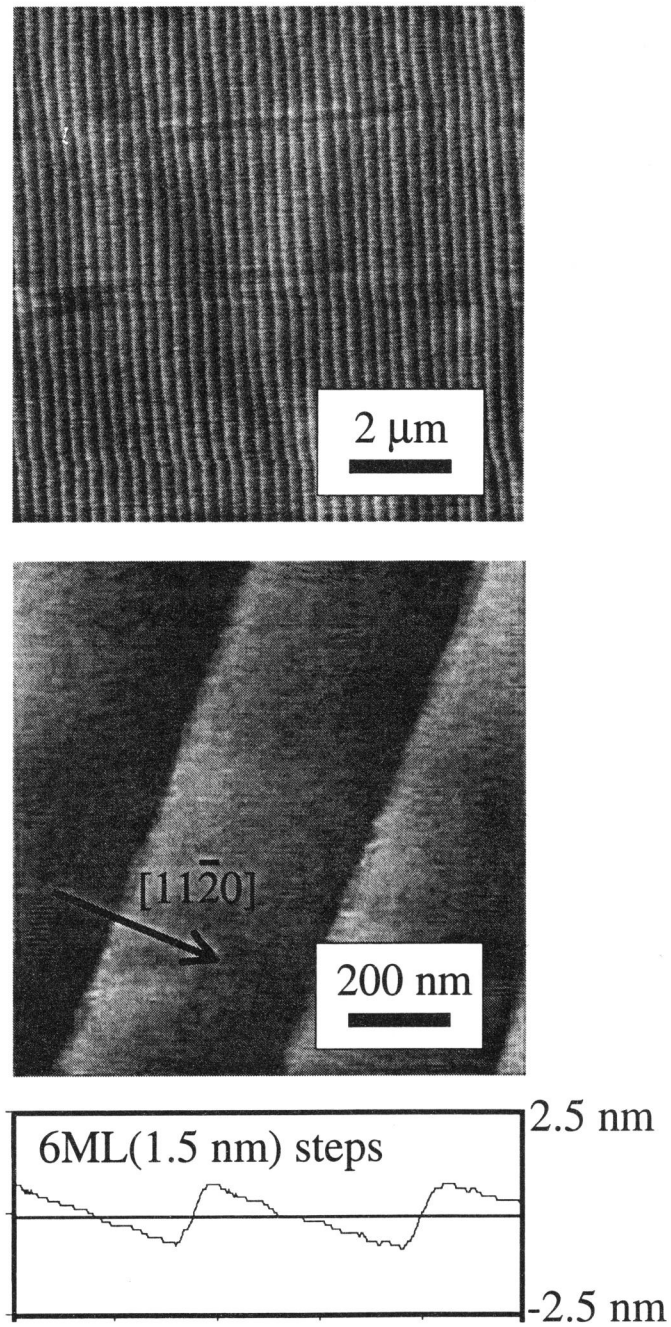


Figure 3.1: Typical AFM images of 6H-SiC(0001) surface treated by HCl-gas etching.

through the air into the MBE growth system for AlN growth.

Surface features of the HCl-gas-etched substrate were further characterized by RHEED. Figures 3.2(a) and (b) display diffraction patterns of the HCl-gas-etched surface along the $[11\bar{2}0]$ azimuth and $[1\bar{1}00]$ azimuth, respectively. Even at room temperature ($\sim 30^\circ\text{C}$), a sharp and intense streak pattern was observed with clear Kikuchi lines, indicative of atomically-flat and highly-ordered surface structure. Surprisingly, an evident 1×3 diffraction pattern originating from $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface reconstruction was confirmed even at such low substrate temperatures. It should be emphasized that the surface reconstruction could be seen without any thermal cleaning at elevated temperatures ($> 1000^\circ\text{C}$). According to the literature [11, 12], *ex situ* chemically-prepared SiC(0001) surfaces normally produce a 1×1 pattern just after introduction into vacuum. Upon heating the substrate at temperatures more than 1000°C , a $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure with $1/3\text{ML}$ silicon adatoms develops. In nitride heteroepitaxy on SiC, the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface reconstruction is commonly thought to be a very clean and epi-ready surface structure.

In situ XPS measurements were performed to examine surface stoichiometry of HCl-gas-etched substrate, and revealed that the silicon-to-carbon ratio on the surface was about 20% larger compared to that of as-received surface [Fig. 3.3]. Therefore, when the author first observed the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface reconstruction from the HCl-gas-etched surface, the reconstruction was interpreted to originate from $1/3\text{ML}$ silicon adsorption. But this interpretation was later found to be incorrect. That is, later experiments revealed that this reconstruction originates from a completely different surface structure. A detailed discussion is presented in this chapter.

3.2.2 Three-Dimensional Initial Nucleation

AlN growth was carried out on HCl-gas-etched substrates at 1000°C . Real-time monitoring was conducted by RHEED during growth. Figure 3.4(a) represents the diffraction pattern of the SiC surface at 1000°C just before growth. The $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure was found to be stable even at high temperatures. RHEED evolution during growth is shown in Figs. 3.4(b)-(d). Just after the start of growth, the pattern became faint, and then a dim spotty pattern was observed. These features suggest that 3D nucleation occurred in the initial growth stage. After a few minutes, a streak 1×1 pattern gradually appeared, and was maintained during the growth. When the growth was stopped, the 1×1 pattern changed to a 1×3 pattern ($(\sqrt{3}\times\sqrt{3})R30^\circ$ structure) under postgrowth atomic-nitrogen (N^*) irradiation (see Fig. 3.4(d)). Further details concerning the surface reconstruction are described below.

The surface evolution of the AlN epilayer was characterized by *ex situ* AFM. Figure 3.5 gives surface morphologies of several AlN epilayers with various thicknesses. Figure 3.5(a) is the surface of the 6H-SiC(0001) substrate before growth, where the step-and-terrace structure is seen. After 1 min growth ($\sim 4.4\text{ nm}$), 3D islands were formed, resulting in

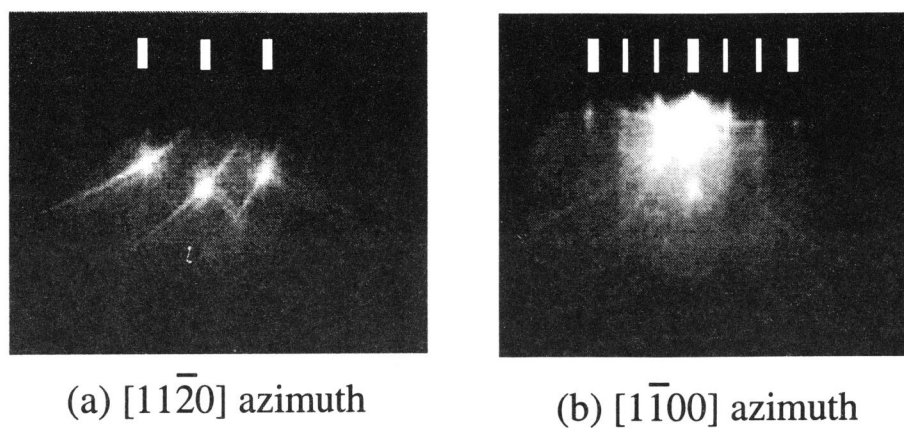


Figure 3.2: RHEED patterns of 6H-SiC(0001) surface treated by HCl-gas etching along (a) $[11\bar{2}0]$ and (b) $[1\bar{1}00]$ azimuth.

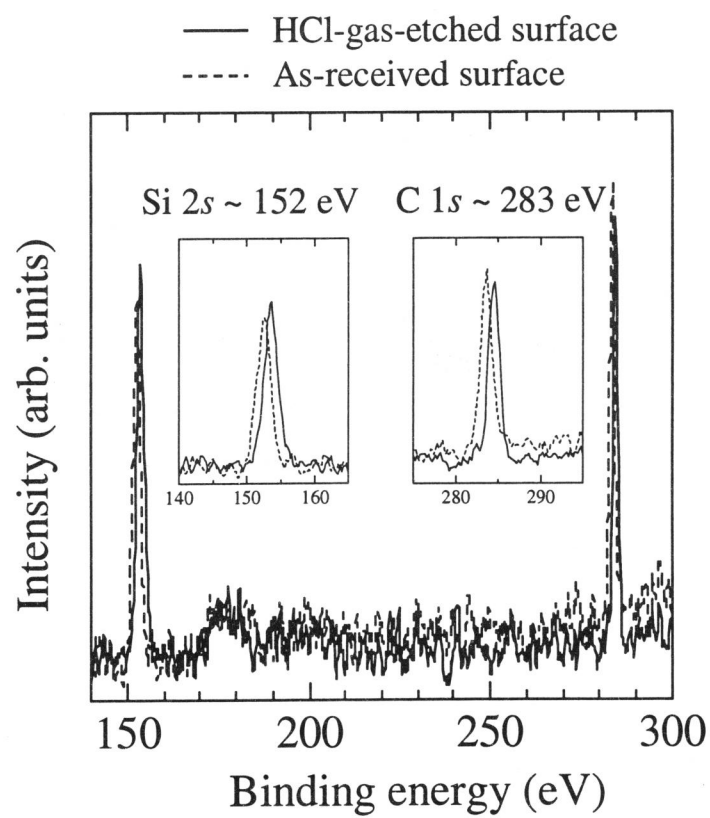


Figure 3.3: XPS spectra of 6H-SiC(0001) surface with and without HCl-gas etching.

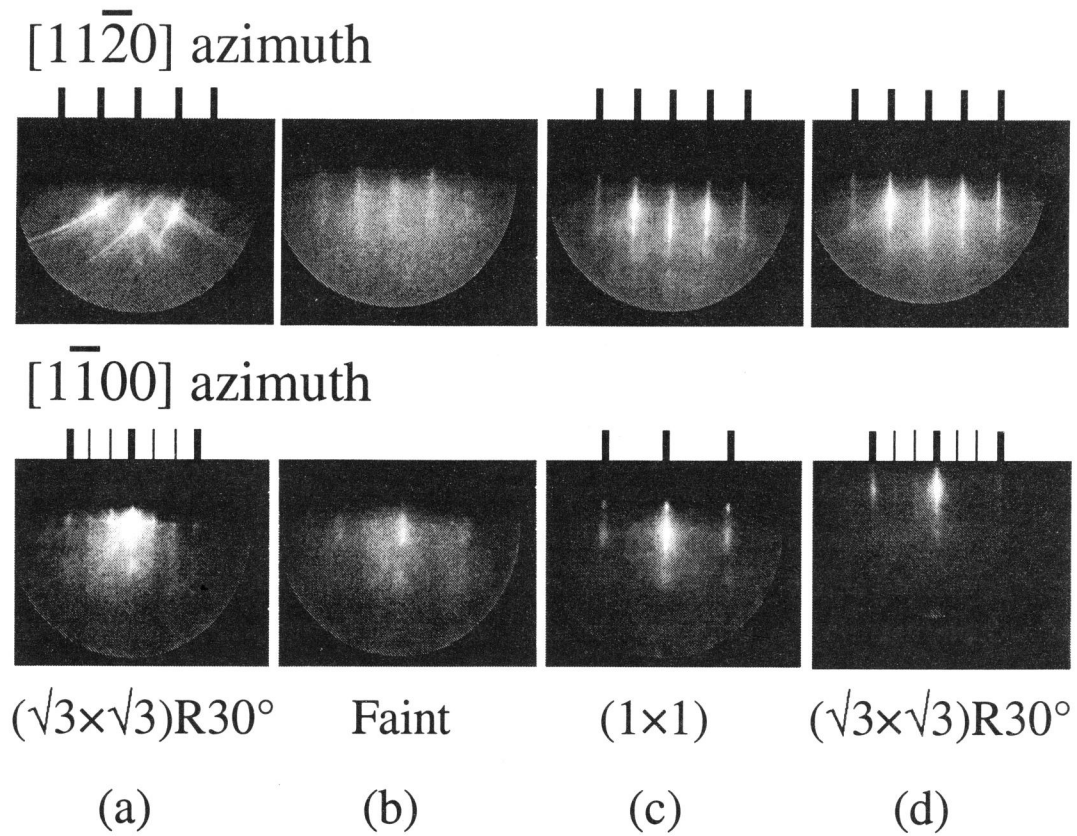


Figure 3.4: RHHED patterns during AlN growth: (a) HCl-gas-etched 6H-SiC surface, (b) AlN surface after 1 min growth, (c) AlN surface after 30 min growth, and (d) AlN surface after growth.

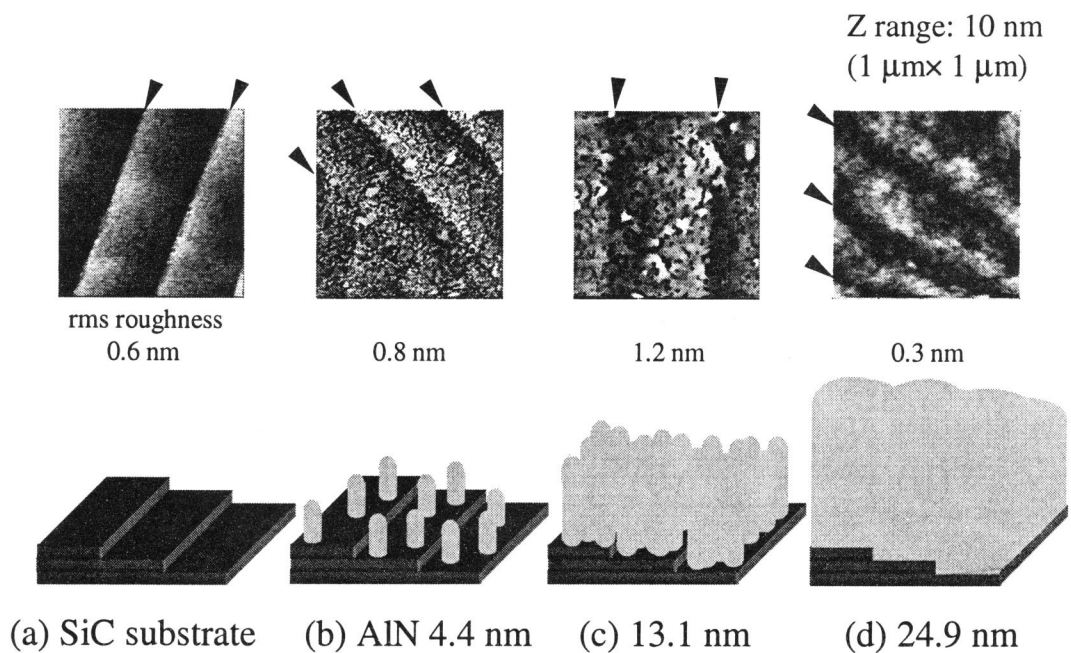


Figure 3.5: AFM images of HCl-gas etched 6H-SiC surface and AlN surfaces. (a) HCl-gas-etched 6H-SiC, (b) AlN 4.4 nm, (c) 13.1 nm, and (d) 24.9 nm.

a considerably rough morphology [Fig. 3.5(b)]. As the growth proceeded, the 3D islands coalesced with each other, and the surface gradually became smooth [Figs. 3.5(c) and (d)]. With increasing AlN thickness, the value of root-mean-square (rms) roughness decreased accordingly, and approached about 0.3 nm in a scan size of $1 \times 1 \mu\text{m}^2$. This surface evolution was entirely consistent with RHEED observations. It should be mentioned that 3D nuclei were formed on the atomically-flat terraces formed by the HCl-gas etching, implying the presence of some kinetic barriers which prevent two-dimensional growth.

3.2.3 Surface Reconstruction after AlN Growth

The $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ surface reconstruction after AlN growth was reported to originate from the Al-polar face of a grown film [13]. In this work, a 2×6 diffraction pattern with/without satellite peaks and 3×6 or 6×6 with satellite peaks at lower temperatures were also observed for cases when atomic nitrogen was not supplied after growth (see Fig. 3.6). In this study, postgrowth irradiation of atomic nitrogen atomic-nitrogen was found to change the diffraction pattern from 2×6 to 1×3 (i.e., $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ surface reconstruction). These findings might suggest that the $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ surface reconstruction reflects a stabilized surface terminated with nitrogen atoms. However, termination by nitrogen atoms is thought to be energetically unfavorable since extra nitrogen atoms are expected to form N_2 (with its strong bond) and thereby desorb from the surface.

There has been a detailed study on surface reconstructions of GaN(0001) and $(000\bar{1})$ reported by Smith and co-workers [14], but there is only limited knowledge at present on the AlN surface structure [15, 16], e.g. a possible model of the surface structure and phase transitions. In a recent report by Lee *et al.*, a detailed investigation on AlN(0001) surfaces was first performed [13]. According to them, the 2×6 diffraction patterns with, and without, satellite peaks originate from a $(2\sqrt{3} \times 2\sqrt{3})\text{R}30^\circ$ and $(5\sqrt{3} \times 5\sqrt{3})\text{R}30^\circ$ surface superstructure for aluminum coverage of 2-3 ML, respectively. They concluded that the $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ surface reconstruction corresponded to a more nitrogen-rich surface than those displaying the 2×6 diffraction pattern, which is consistent with our own observations.

Although concrete structures of those reconstructed surfaces have not been fully understood yet, the streak diffraction patterns with reproducible reconstruction probably indicate atomically smooth and uniform AlN surfaces.

3.2.4 Lattice Relaxation Process in AlN Growth

Owing to the 0.9% lattice mismatch between AlN and SiC for the (0001) basal planes, lattice relaxation, which strongly affects crystalline quality of AlN films, occurs at a certain film thickness termed the critical thickness. Understanding the lattice relaxation process in AlN growth is important to control AlN/SiC heteroepitaxy for high-quality GaN growth on SiC and MIS device applications using the AlN/SiC interface.

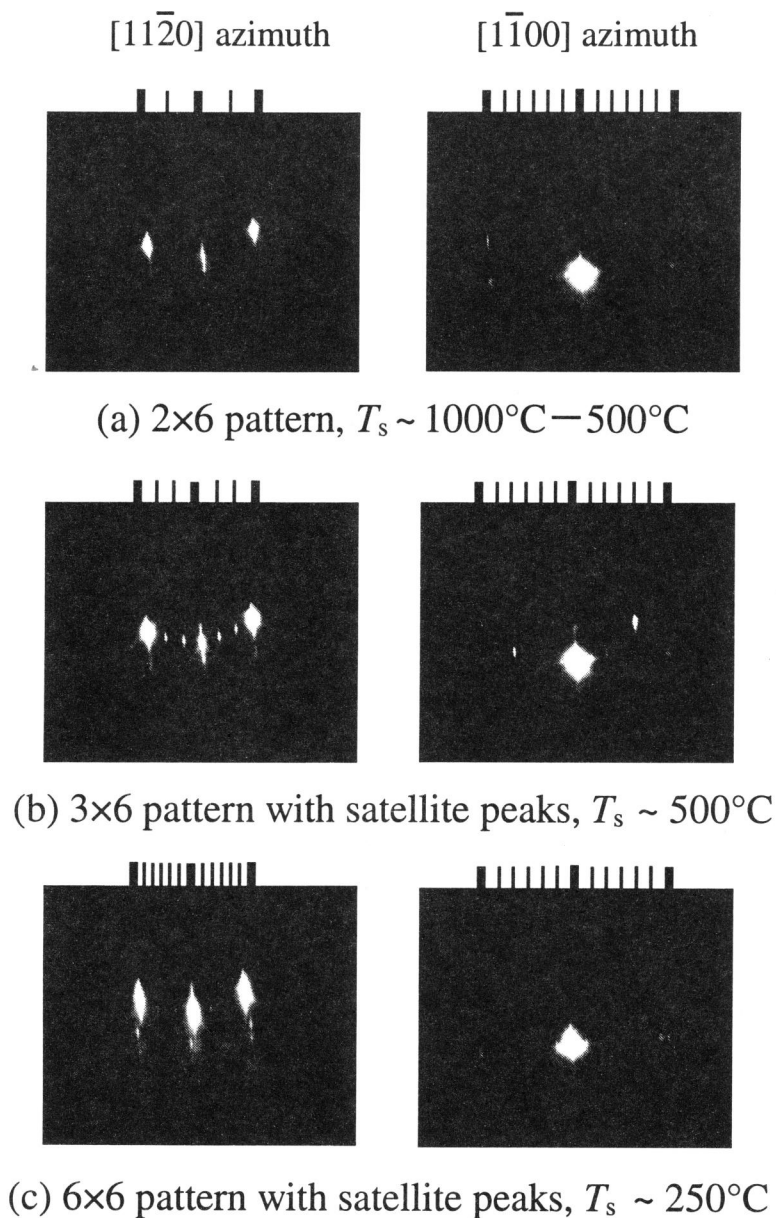


Figure 3.6: Different diffraction patterns observed after AlN growth without postgrowth irradiation by atomic nitrogen: (a) 2 $\times$ 6 pattern, (b) 3 $\times$ 6 pattern with satellite peaks, and (c) 6 $\times$ 6 pattern with satellite peaks.

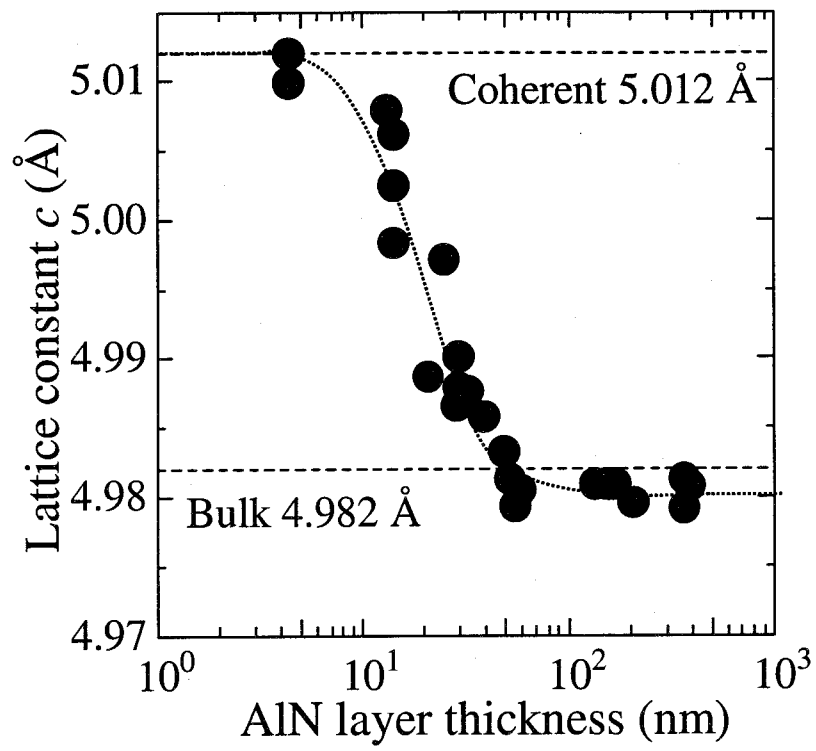


Figure 3.7: Dependence of AlN c -axis lattice constant on film thickness.

In this work, the lattice relaxation process was studied based on HRXRD $2\theta/\omega$ scan measurements. The dependence of c -axis lattice constant on the film thickness is displayed in Fig. 3.7. The film thickness was estimated by using optical interferometry or ellipsometry. The c -axis lattice constants of the AlN films were calculated from the angular difference between the AlN and SiC diffraction peaks assuming that the c -axis lattice constant of the SiC substrate is a known value of bulk (10.08 Å for 4H-SiC, 15.12 Å for 6H-SiC). For a 4.4-nm-thick film, the c -axis lattice constant was approximately 5.012 Å, which is obviously larger than that of bulk AlN (4.982 Å) [17]. This difference is attributed to a biaxial compressive strain induced by the lattice mismatch between AlN and SiC. With increasing film thickness, the c -axis lattice constant gradually decreased accordingly. And beyond the thickness of 50 nm, the value approached 4.980 Å, which is slightly smaller than the bulk value. Using literature values for the elastic constants [18], the a -axis lattice constant of 4.4-nm-thick film was calculated to be 3.081 Å, which is equal to that of SiC. This implies that the 4.4-nm-thick film was grown pseudomorphically on the substrate. For a 13.1-nm-thick film, the c -axis lattice constant was obviously smaller than that of the 4.4-nm-thick film, indicating the occurrence of lattice relaxation. Therefore, the critical thickness of AlN grown on SiC(0001) should be between 4.4 and 13.1 nm. This assumption is in good agreement with the reported critical thickness of 4.6 nm [3, 19].

Supposing that the compressive strain in AlN films beyond the thickness of 50 nm is fully relaxed at the growth temperature, the difference between the measured value (4.980 Å) and that of bulk (4.982 Å) is attributed to the thermal expansion mismatch between AlN and SiC. The measured value was slightly smaller compared to the bulk, indicative of a small tensile strain in the AlN films.

3.2.5 Structural Quality of AlN Epilayers

The structural quality of AlN films was investigated using HRXRD ω scan measurements. Figure 3.8 exhibits the ω scan profiles of AlN(0002) diffraction with various film thicknesses. These curves seemed to consist of two different peaks, a sharp peak and a broad peak. The sharp peak was observed for thin AlN films less than 50 nm. However, for thick AlN epilayers beyond 50 nm, the broad peak gradually became dominant. The sharp peak probably originates from a highly-oriented region, while the broad peak reflects a region of misorientation. Since AlN films seem to be fully relaxed beyond the thickness of 50 nm, these peaks might be closely related to the lattice relaxation. Domagala and co-workers pointed out that the peak broadening of (0002) diffraction is related to the density of misfit dislocations [20].

The structural transition due to lattice relaxation was found to be strongly dependent on the growth conditions, i.e., the effective Al/N ratio. All AlN films described in Fig. 3.8 were grown in stoichiometric or slightly aluminum-rich conditions. In the case of nitrogen-rich conditions, the ω scan curves were dominated only by the sharp peak even at the thickness

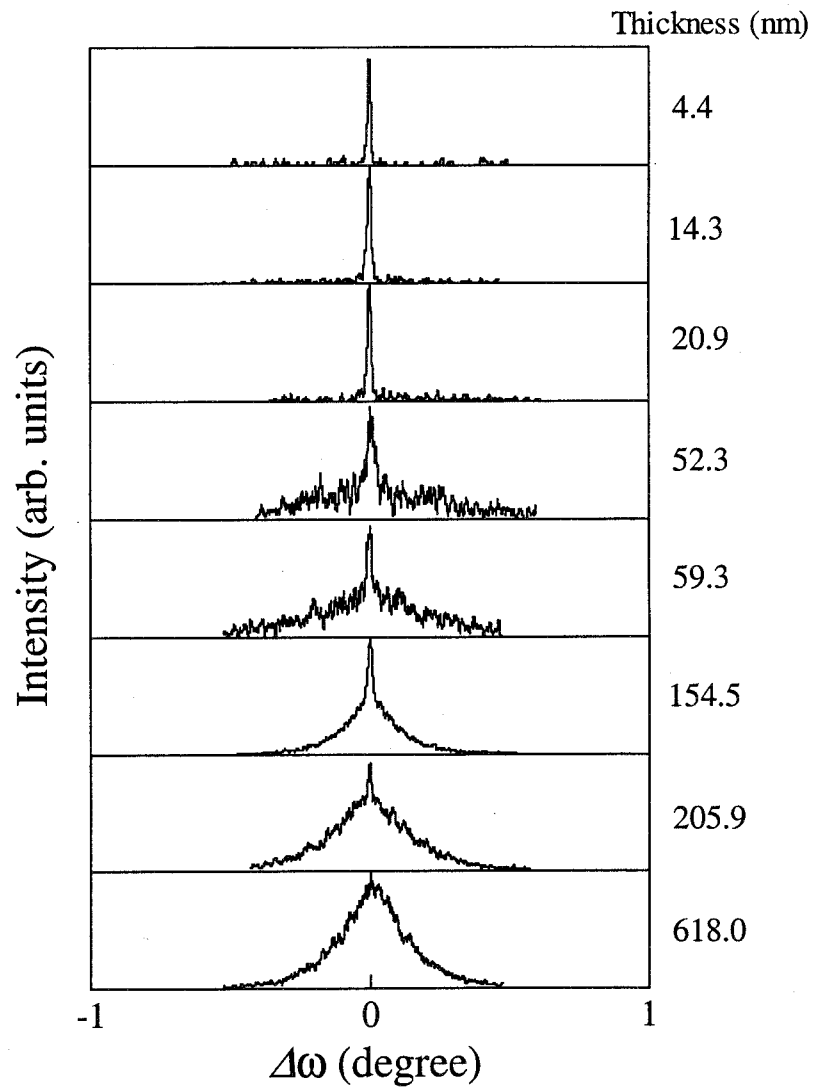


Figure 3.8: HRXRD ω scan profiles of AlN(0002) diffraction with various film thicknesses.

over 300 nm. However, the surface roughness was considerably large (rms roughness > 1 nm) due to 3D columnar growth [21].

A possible model of the structural transition due to the lattice relaxation (or generation of misfit dislocations) in an AlN film is illustrated in Fig. 3.9. In the early stages of growth, 3D islands are formed on atomically-flat terraces of SiC, and these AlN islands are highly-oriented around the *c*-axis, resulting in the sharp peak for thin films. In the case of stoichiometric or slightly aluminum-rich conditions, the growth mode gradually changes from 3D island mode to 2D layer-by-layer mode with increasing film thickness. Since the grown film has a layered structure, misfit dislocations generated by the lattice relaxation deteriorate the film quality, and enlarge the tilt of the *c*-axis (peak broadening) [20]. In contrast, the growth proceeds in a 3D columnar mode under a nitrogen-rich conditions, and all the columns are well aligned around the *c*-axis, resulting in the sharp peak even at the thickness over 300 nm. However, despite the sharper (0002) diffraction peak, it is obvious that the films grown in nitrogen-rich conditions are highly defective (columnar structure) compared to aluminum-rich films.

3.2.6 Intermediate Layer at AlN/SiC Interface

Interface control of AlN/SiC heterostructure is very important not only for MIS device applications using the interface, but also for heteroepitaxy of high-quality AlN and subsequent epilayers. The interface structure formed by MBE is thought to be an abrupt transition from SiC to AlN due to its atomic-scale control of the layer grown. As described above, 3D initial nucleation occurred on atomically-flat terraces of the SiC substrate. It might imply the presence of some kinetic barriers for adsorbed atoms (adatoms) to migrate on the SiC surface. Initial growth features are thought to affect the interface structure, which closely connected with electronic properties at the interface.

Next, the interface structure was characterized by GIXRR. The principle of the GIXRR measurement is described in Ref. [22]. The incident x-ray beam is reflected from both the sample surface and the interface, and the oscillation profile due to interference of those reflected beams is analyzed. The oscillation amplitude is correlated with the interface reflectivity, and the layer thickness can be estimated from the oscillation period. Since the electron densities of AlN and SiC are quite similar (3.23 g/cm³ vs. 3.21 g/cm³) [23], the index of refraction at the AlN/SiC interface is considerably small, which leads to small interference oscillations.

Figure 3.10(a) shows a result of simulation for a 55-nm-thick AlN/4H-SiC heterostructure with an abrupt interface, i.e., no intermediate layer at the interface. It is obvious that the oscillation amplitude is quite small. Figure 3.10(b) shows an experimental result of a 55-nm-thick AlN film grown on the 4H-SiC substrate pretreated by HCl-gas etching. As clearly seen, the oscillation was larger than predicted by the simulation, suggesting the presence of intermediate layer between AlN and 4H-SiC, and the intermediate layer has

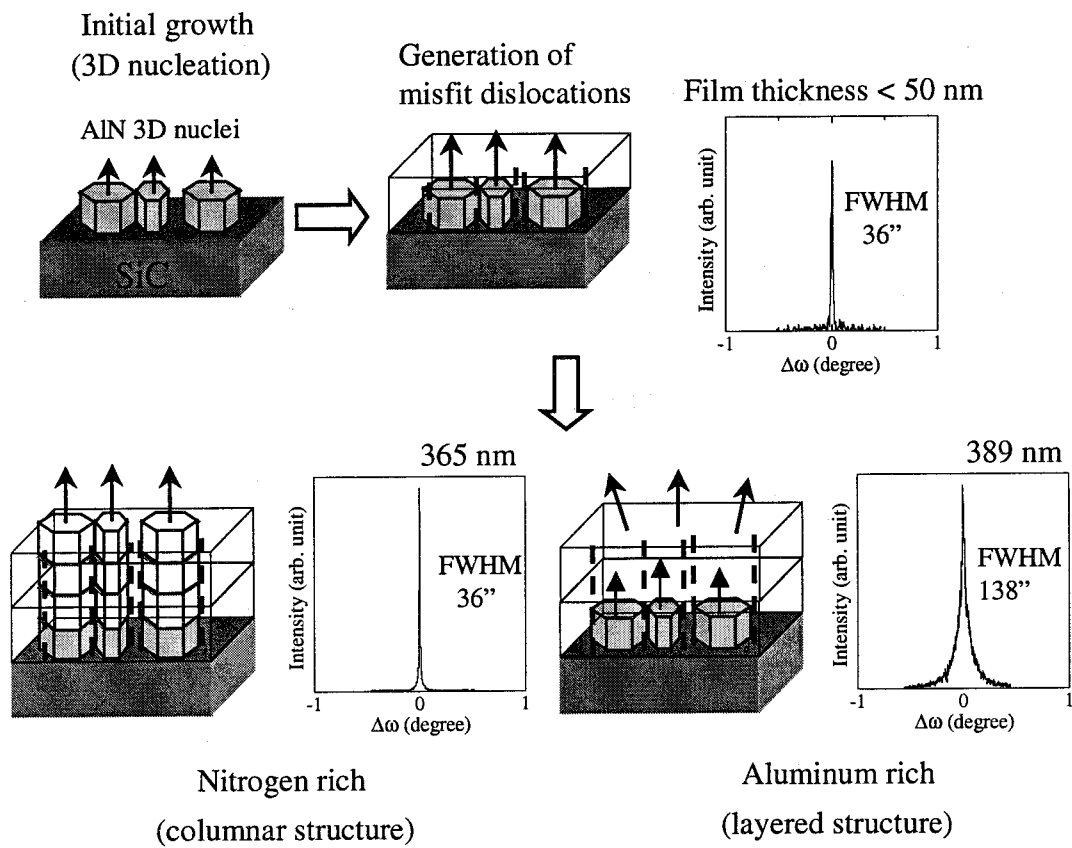


Figure 3.9: Possible model of structural transition due to lattice relaxation (or generation of misfit dislocations) in AlN films.

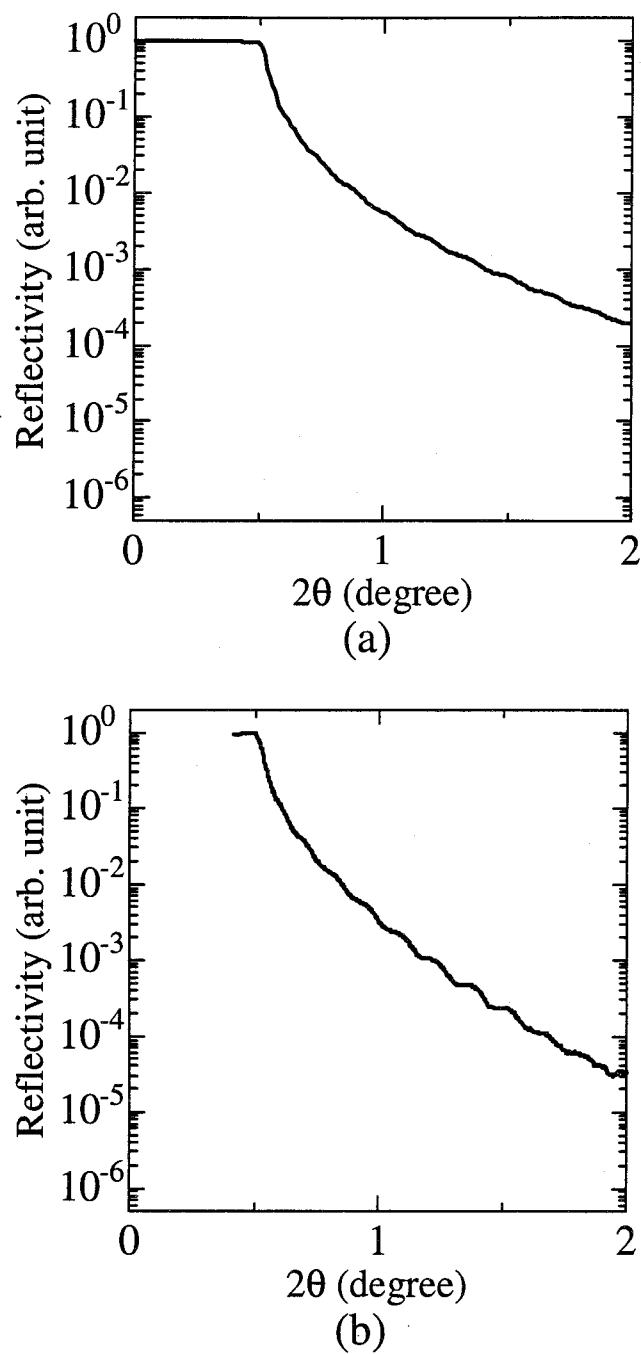


Figure 3.10: GIXRR profiles for 55-nm-thick AlN/4H-SiC heterostructure: (a) simulation and (b) experimental result.

a different index of refraction from that of AlN or SiC. This finding is surprising because almost all the surface contamination of SiC substrate including native oxides should have been removed by wet chemical preparation.

3.2.7 Discussion

In order to obtain a high-quality AlN film, surface control of the SiC substrate is crucial as well as the growth condition (temperature, Al/N ratio). HCl-gas etching was suggested as an effective pretreatment method, which can remove surface scratches and realize an atomically-flat terrace structure with one-unit-cell-height steps. In the initial stages of growth, however, 3D nucleation occurred on atomically-flat terraces. 3D initial nucleation is thought to strongly affect the crystalline quality of subsequent epilayer.

So far in this chapter, two unclear points have arisen concerning the surface of SiC substrates pretreated by HCl-gas etching. One point is the $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction observed before growth. This reconstruction was confirmed even at room temperature, and no thermal cleaning was necessary to achieve this reconstructed surface. Another point is the existence of intermediate layer at the AlN/SiC interface. The surface condition of the SiC substrate after wet chemical preparation and HCl-gas etching should have been atomically flat and clean, an assumption supported by an intense streaky RHEED pattern with clear Kikuchi lines.

In order to elucidate these mysteries, the chemical condition of the SiC surface has to be studied in detail, and surface control prior to growth should be performed to achieve high-quality AlN and subsequent epilayers.

3.3 Control of SiC Surface Chemistry

3.3.1 Highly-Ordered Silicate Adlayer on SiC Surface

To examine the surface chemical composition of the SiC substrate pretreated by HCl-gas etching, *in situ* XPS measurements were carried out. After thermal cleaning at 1000°C for 30 min, the substrate was transferred to the XPS chamber without exposing it to air. In this measurement, not only peaks from silicon and carbon atoms but also an oxygen-related peak, i.e., O 1s, were detected. The O 1s peak intensity was small compared to those of silicon and carbon atoms. The Si 2p spectrum of HCl-treated surface is given in Fig. 3.11(a). The peak located at 102.3 eV, which is shifted from silicon bonded to carbon atoms (100.6 eV) [24]. This chemical shift suggests the formation of silicon oxide on the SiC surface. The chemical shift was also observed in the O 1s spectrum [Fig. 3.11(b)]. The binding energy of the O 1s spectrum was 533.8 eV, representing oxygen combined with two silicon atoms. The O 1s spectrum of the as-received surface without HCl-gas etching is also shown in Fig. 3.11(b). Surprisingly, the surface coverage of oxygen atoms increased after

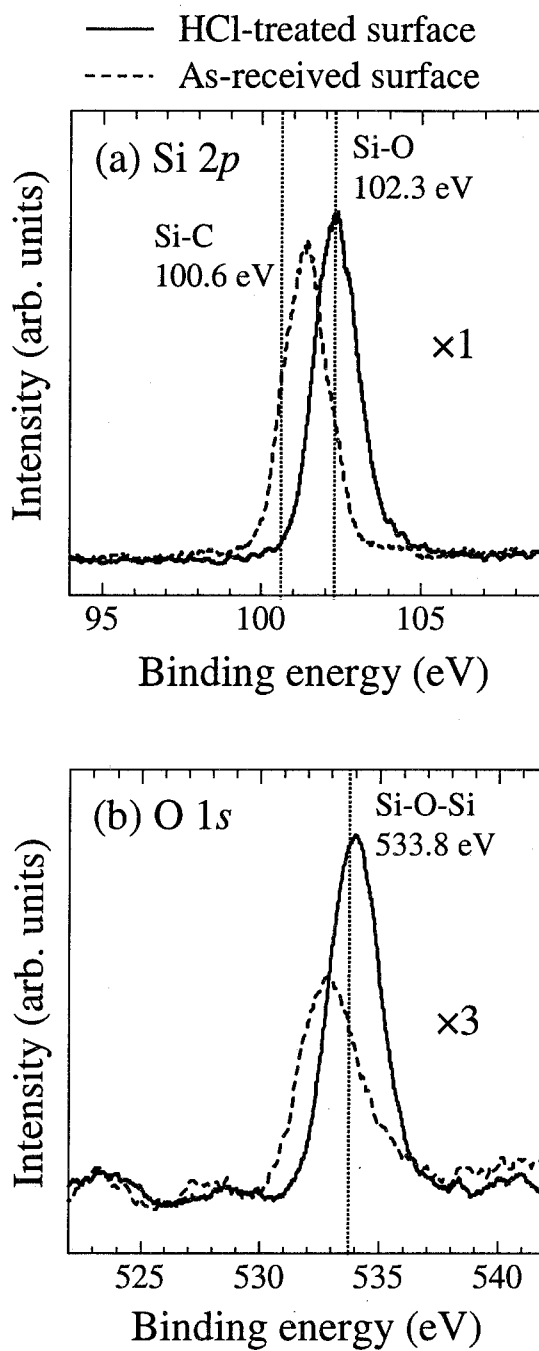


Figure 3.11: XPS spectra of HCl-treated SiC surface: (a) Si 2p and (b) O 1s.

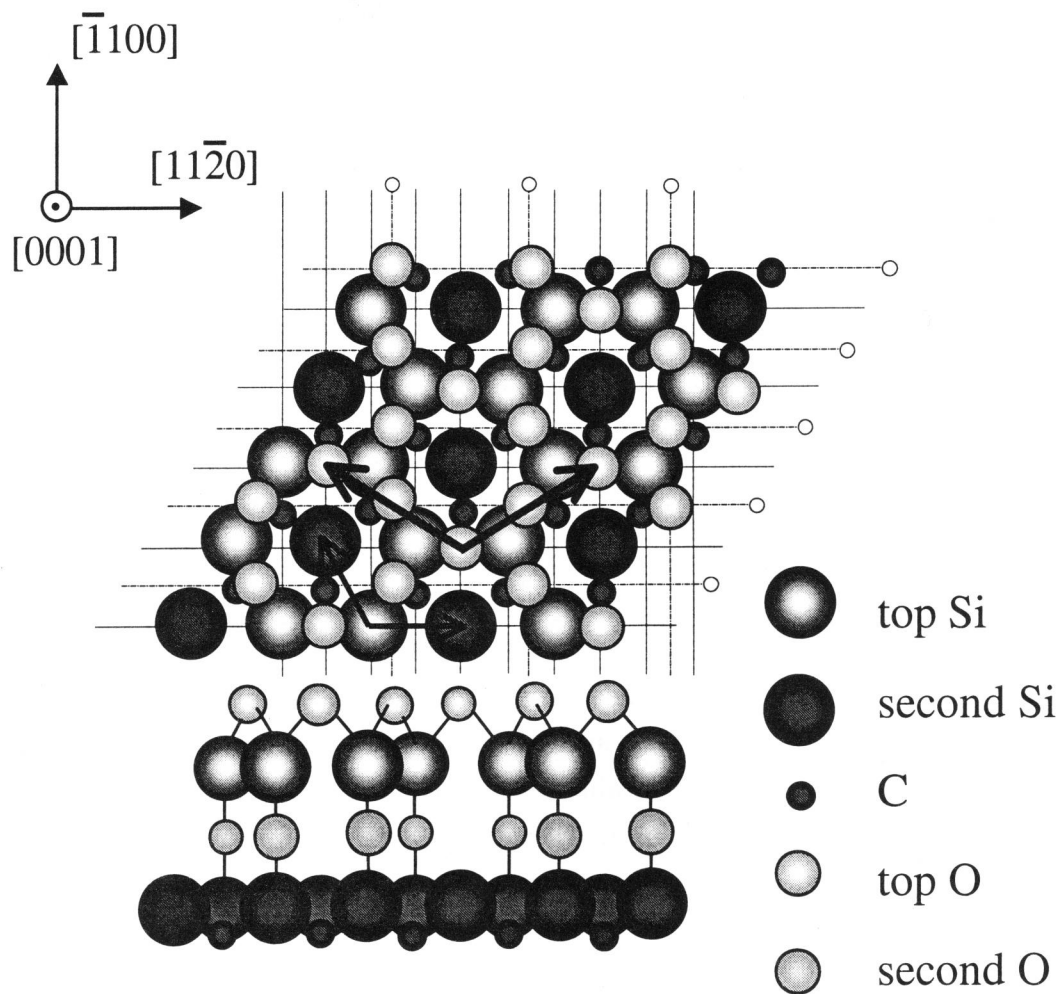


Figure 3.12: Schematic diagram of SiC surface structure with silicate adlayer.

HCl-gas etching.

In recent years, Starke and co-workers reported that H₂-gas etching of SiC surface and subsequent exposure to oxygen in the ambient air produce a highly-ordered ($\sqrt{3} \times \sqrt{3}$)R30° silicate adlayer [25–27]. They carried out the quantitative low-energy electron diffraction (LEED) analysis of the ($\sqrt{3} \times \sqrt{3}$)R30° phase and detected a SiO_x overlayer on the SiC substrate. The schematic diagram of the surface structure with the silicate adlayer has been proposed as shown in Fig. 3.12. The two silicon atoms per unit cell of this adlayer form a honeycomb arrangement. Each oxygen atom connects two of the silicon atoms completing a ring-type structure. The silicate and substrate are not connected via Si-Si bonds but linearly bridged by oxygen, Si-O-Si. This structure maintains a high degree of order even during exposure to the ambient air, and is stable up to 1000°C in ultra-high vacuum conditions due to the saturation of all dangling bonds. In our speculation, the same phenomenon probably occurred in HCl-gas etching. 3D initial nucleation in AlN growth is probably due to this stable silicate adlayer with no dangling bonds.

There are three well-known crystal growth modes, i.e., the 2D mode (Frank-van der Merwe; FM), the 3D mode (Volmer-Weber; VW) and the combination of these modes (Stranski-Krastanov; SK). Among these modes, only in the VW mode, 3D nucleation occurs from the beginning of growth. The reason why such 3D initial growth occurs is attributed to the energetic stability of the system. In the macroscopic point of view, the form of epilayer is subject to classical thermodynamics. The major factors to decide its stability are the surface energy of substrate (σ_s), interface energy of the epilayer/substrate (σ_i), and energy of epilayer (σ_e) including strain energy, surface energy, and internal energy in the epilayer. In the case of $\sigma_s > \sigma_i + \sigma_e$, it is more stable to cover the substrate with the epilayer than to expose the substrate surface, resulting in 2D initial growth, i.e., FM mode (or SK mode). On the contrary, if $\sigma_s < \sigma_i + \sigma_e$, it is energetically favorable to expose the substrate surface, and in this case, 3D nucleation occurs from the beginning of growth, i.e., VW mode.

Usually in heteroepitaxy, epitaxial films are strained due to the lattice mismatch between the epilayer and substrate. In the VW mode, the strain energy can be relaxed elastically by lattice deformation in 3D nuclei. However, since the strain energy depends on the size of 3D nuclei and each part in the nuclei has different degree of strain energy, the lattice deformation causes incoherent coalescence of 3D nuclei, resulting in generation of numerous defects (see Fig. 3.13). Thus 3D initial growth leads to highly-defective films, and therefore 2D growth mode is favorable to obtain high-quality films.

To achieve a 2D growth mode from the beginning of growth, the interface energy (σ_i) should be reduced to improve the wettability between the epilayer and substrate, that is, the energetic stability of the system should be controlled such that $\sigma_s > \sigma_i + \sigma_e$.

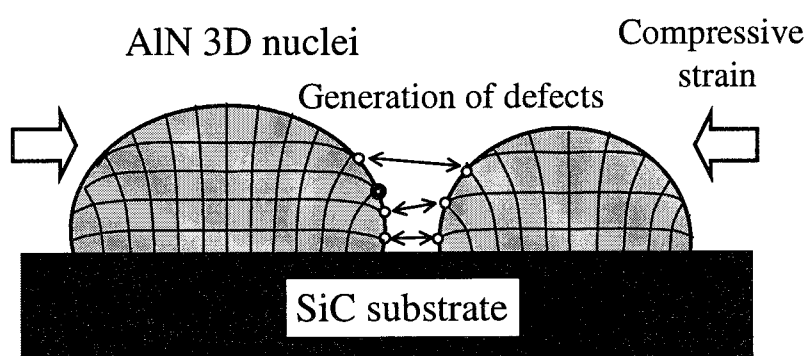


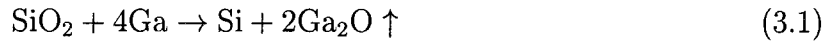
Figure 3.13: Schematic image of incoherent coalescence of 3D nuclei with deformed lattices.

3.3.2 Realization of Oxygen-Free Surface

Although the silicate adlayer was too stable to be decomposed at 1000°C in an ultra-high vacuum, *ex situ* HF treatment could successfully remove it from the HCl-treated surface. HF etching of silicon oxides is a well-known technique, especially in the surface treatment process of silicon [28]. After HCl-gas etching, the substrates were dipped in a 50% HF solution for 5 minutes prior to loading into the MBE system, and those substrates are referred to as HF/HCl-treated substrates in this work.

To examine the surface chemical composition of the HF/HCl-treated substrate, *in situ* XPS measurements were performed again. Figure 3.14(a) displays the Si 2*p* spectrum of HF/HCl-treated surface. The Si 2*p* peak appeared at 100.6 eV, which differs from that of HCl-treated surface (102.3 eV). The binding energy of 100.6 eV corresponds to Si-C bonds, therefore, this chemical shift indicates the successful removal of silicate adlayer from the SiC surface. However, some oxygen atoms still remained on the HF/HCl-treated surface (see Fig. 3.14(b)). This is probably due to oxygen adsorption during transfer into the MBE system through the air. The residual oxygen atoms can be obstacles for the migration of adatoms during growth and also may incorporate as impurities in the epilayer.

To eliminate those residual oxygen atoms, an additional treatment, *in situ* gallium treatment, was introduced. This method has been reported by Kaplan *et al.* as an effective process to remove surface oxygen from SiC surfaces [29]. In this procedure, the following reduction (or deoxidation) process proceeds [30],



In situ silicon treatment is also reported as an effective method, which has similar reduction process [31],



In the MBE growth chamber, gallium metal was deposited on the HF/HCl-treated surface at 500-800°C, and then the substrate temperature was raised to 1000°C to desorb the deposited gallium metal together with residual oxygen atoms. The HF/HCl-treated substrates treated by this process are referred to as Ga/HF/HCl-treated substrates.

In situ XPS measurements were performed for the Ga/HF/HCl-treated surface, and the spectra are presented in Fig. 3.15. As for the Si 2*p* spectrum, there was no difference from the HF/HCl-treated surface [Fig. 3.15(a)]. Some residual oxygen atoms were removed from the SiC surface by one cycle of the gallium treatment, however, oxygen atoms still remained on the surface (see Fig. 3.15(b)). After three cycles of this process, the intensity of O 1*s* peak was reduced below the detection limit, indicating that almost all the residual oxygen atoms were successfully removed from the surface. Thus, the surface oxygen species, silicate adlayer and residual oxygen atoms, were fully removed owing to the additional pretreatments, i.e., Ga/HF/HCl treatment.

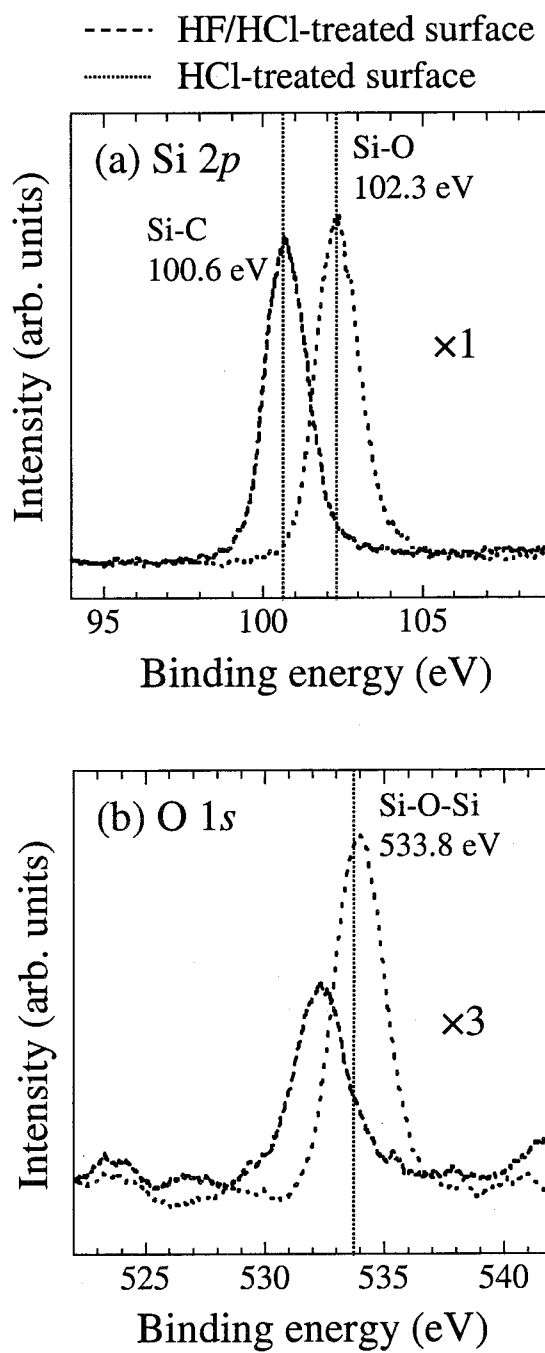


Figure 3.14: XPS spectra of HF/HCl-treated SiC surface: (a) Si 2p and (b) O 1s.

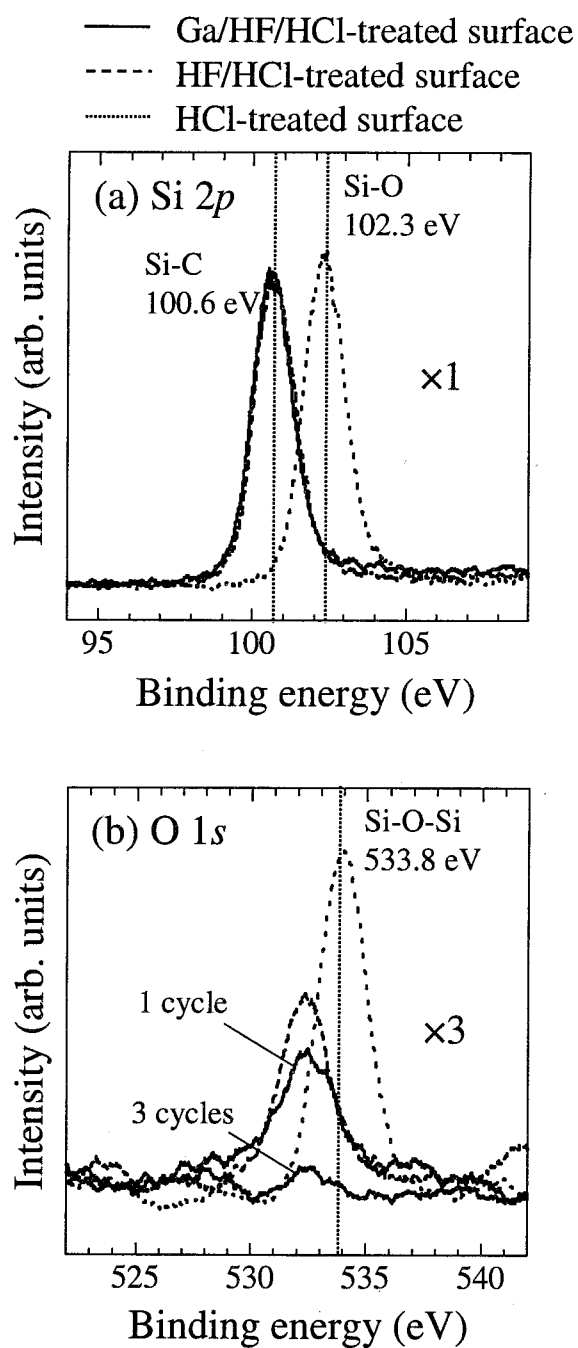


Figure 3.15: XPS spectra of Ga/HF/HCl-treated SiC surface: (a) Si 2p and (b) O 1s.

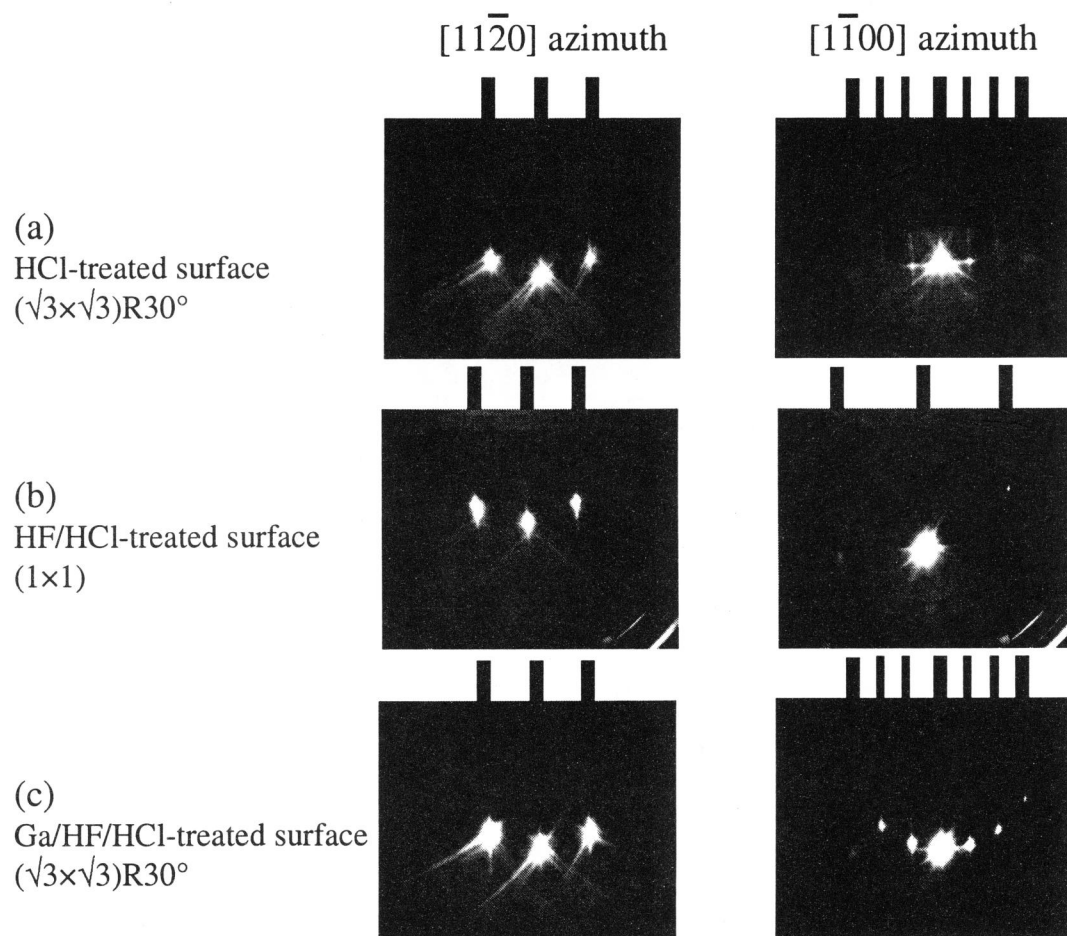


Figure 3.16: RHEED patterns of SiC surfaces with (a) HCl treatment, (b) HF/HCl treatment, and (c) Ga/HF/HCl treatment.

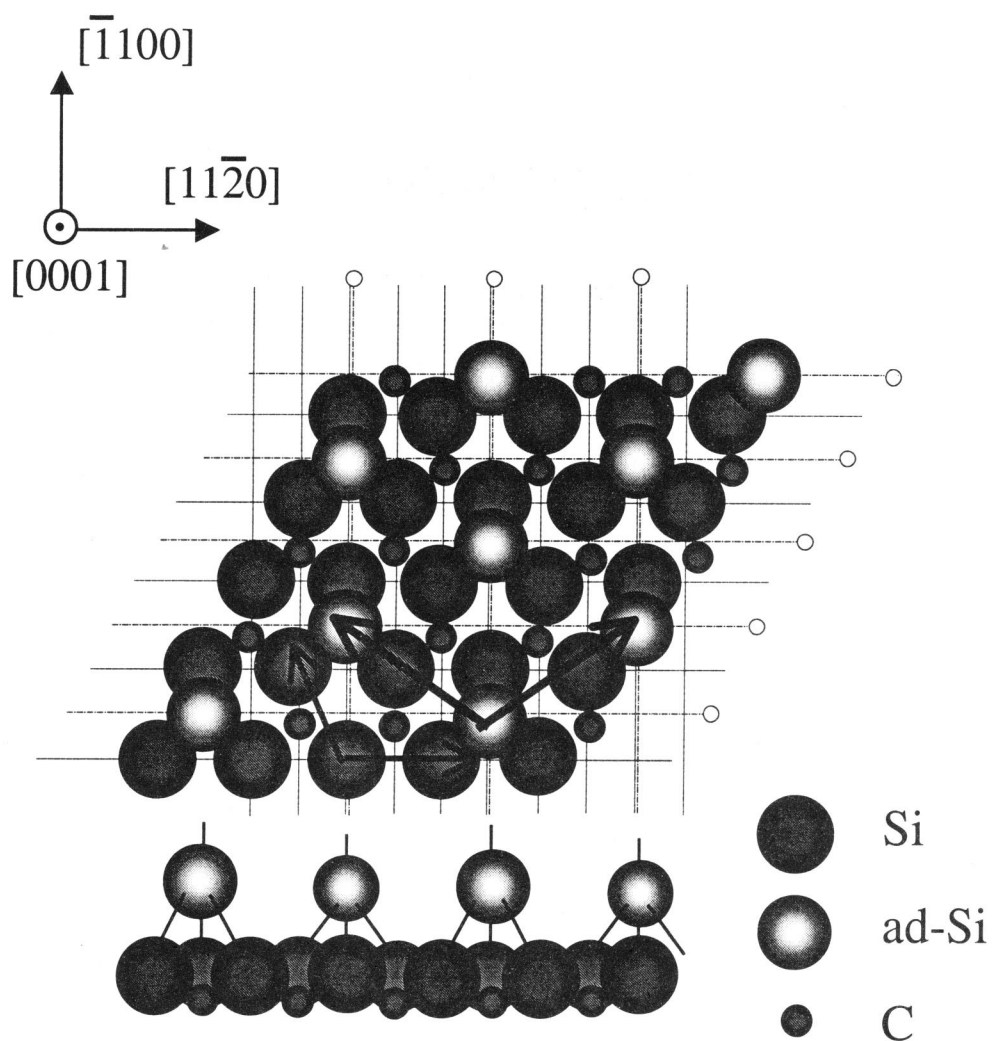


Figure 3.17: Schematic diagram of SiC surface structure with $1/3\text{ML}$ Si adatoms.

Surface structures of each treated substrate were further characterized by RHEED. The RHEED observation was carried out just before AlN growth at 1000°C. The surface structures of HCl-, HF/HCl- and Ga/HF/HCl-treated surfaces were $(\sqrt{3} \times \sqrt{3})R30^\circ$, (1×1) and $(\sqrt{3} \times \sqrt{3})R30^\circ$, respectively. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction of the HCl-treated surface originates from the highly-ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ silicate adlayer as described above [Fig. 3.16(a)]. The silicate adlayer was successfully removed by the HF treatment, and the 1×1 pattern was observed on the HF/HCl-treated surface [Fig. 3.16(b)]. After the gallium treatment was conducted, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction appeared again [Fig. 3.16(c)]. In view of XPS result which showed no residual oxygen atoms on the surface, this reconstruction is thought to originate from a completely different structure from the HCl-treated surface. Since no evident peaks other than silicon or carbon related ones were observed in the XPS measurement, this reconstruction probably comes from an excess silicon adsorbed structure with $1/3$ ML as described previously (see Fig. 3.17).

3.3.3 Two-Dimensional Initial Nucleation

Evolution of the RHEED intensity was monitored to investigate the initial growth mode of AlN on SiC surfaces with three different treatments. The diffraction intensity in the $[11\bar{2}0]$ azimuth was recorded. Figure 3.18 exhibits the intensity profiles for the initial growth stages. On the HCl-treated surface, the diffraction pattern became faint just after the start of growth, indicating 3D island growth [Fig. 3.18(a)]. After 5 min, the pattern changed to a streak one. This evolution is same as described previously. A similar result has been reported in MBE growth of CdSe on GaAs [32]. The initial 3D island growth reflects poor wetting of AlN nuclei on the HCl-treated surface (i.e., silicate adlayer). On the HF/HCl-treated surface, the pattern also became faint at first as shown in Fig. 3.18(b), but immediately an intense streak pattern appeared. This result indicates that surface wettability was improved by the *ex situ* HF treatment which had removed the silicate adlayer from the HCl-treated surface. However, residual oxygen atoms on the HF/HCl-treated surface might still hinder the migration of adatoms, which would lead to 3D initial nucleation. On the Ga/HF/HCl-treated surface, the pattern never disappeared throughout the growth [Fig. 3.18(c)]. It should be emphasized that an evident intensity oscillation was observed just after the start of growth, indicating layer-by-layer growth from the beginning. This is a remarkable result distinguished from other results reported before. The initial layer-by-layer growth was realized owing to surface control of not only the step-and-terrace structure with one-unit-cell-height steps, but also the chemical structure, i.e., removal of residual oxygen and realization of $1/3$ ML silicon-adsorbed superstructure.

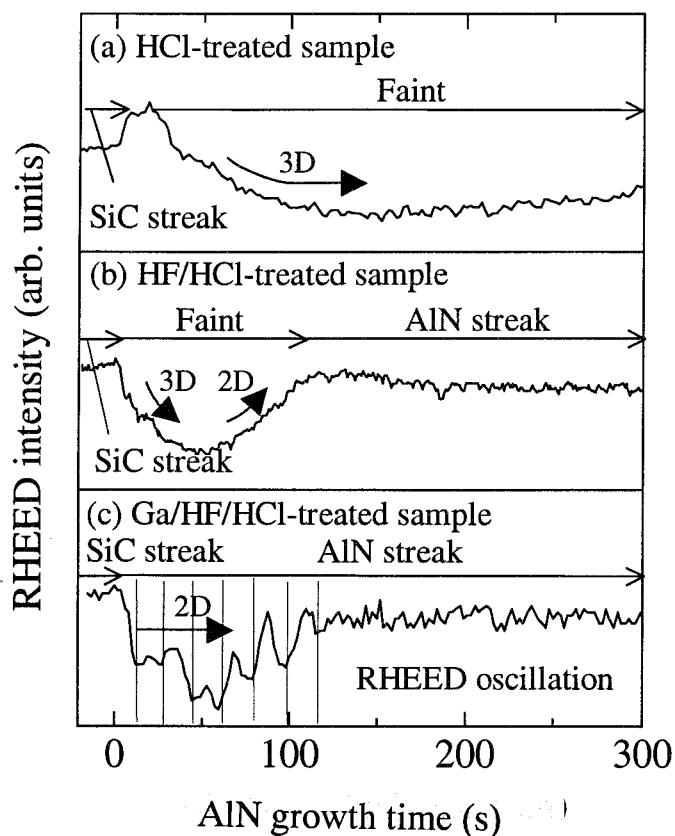


Figure 3.18: RHEED intensity profiles in initial stages of AlN growth on (a) HCl-treated substrate, (b) HF/HCl-treated substrate, and (c) Ga/HF/HCl-treated substrate.

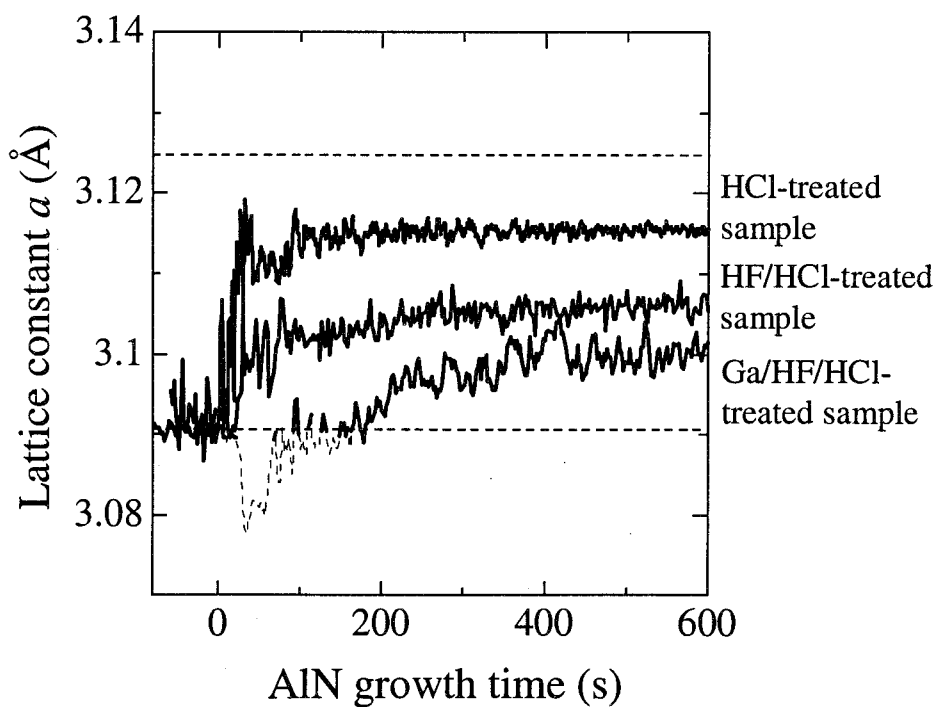


Figure 3.19: Lattice relaxation in initial stages of AlN growth.

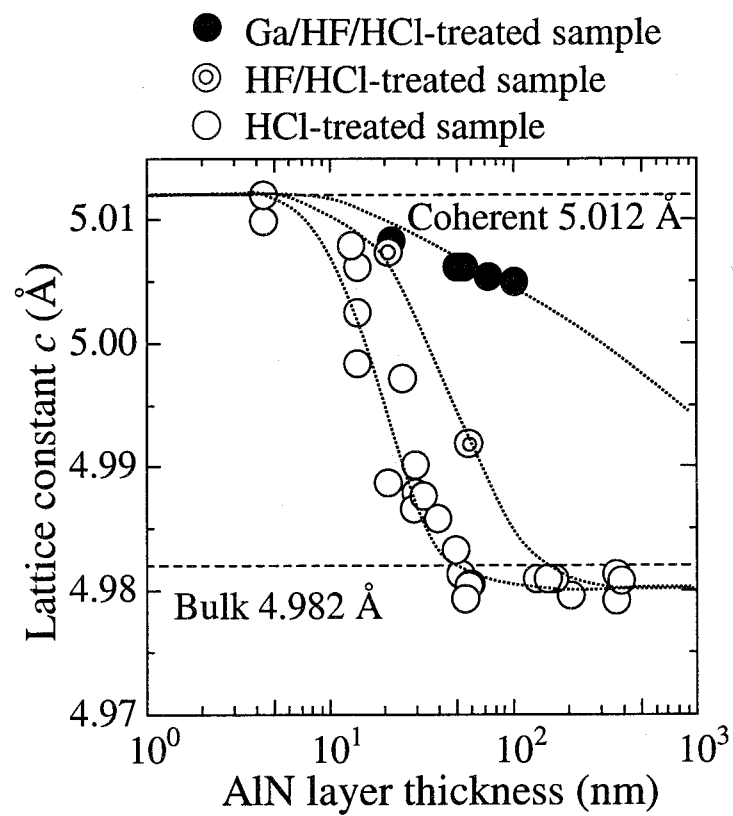


Figure 3.20: Dependence of AlN c -axis lattice constant on film thickness for samples with different substrate treatments.

3.3.4 Improvement in Structural Quality of AlN Epilayers

The a -axis lattice constant of AlN epilayer was examined by using the separation of RHEED streaks. Figure 3.19 shows the lattice relaxation process during the initial stages of AlN growth. The lattice relaxation process was found different for the three samples. The Ga/HF/HCl-treated sample relaxed most slowly, while the HCl-treated sample had most rapid relaxation. For the HCl- and HF/HCl-treated samples, the lattice relaxation began just after the start of growth, probably attributed to initial 3D island growth. In contrast, the Ga/HF/HCl-treated sample, which showed initial 2D growth, was grown pseudomorphically below a certain thickness. This result obviously shows that the initial growth mode strongly influenced the lattice relaxation.

The lattice relaxation process in AlN growth was also studied based on HRXRD $2\theta/\omega$ scan measurements. The dependence of the c -axis lattice constant on the film thickness for samples with three different treatments is displayed in Fig. 3.20. At the critical thickness, lattice relaxation occurred for all samples. The lattice relaxation for the Ga/HF/HCl-treated sample proceeded more slowly compared to other samples. On the contrary, the HCl-treated sample exhibited the most rapid relaxation. Generation of misfit dislocations due to lattice relaxation was remarkably suppressed by initial 2D growth, probably resulting in better structural quality of the AlN film.

The structural quality of AlN films and its correlation with the initial growth mode were examined based on HRXRD ω scan of (0002) and (01 $\bar{1}$ 4) diffraction. Heying *et al.* have mentioned that the (0002) diffraction peak is only broadened by screw and mixed threading dislocations, while the asymmetrical reflection peak such as (01 $\bar{1}$ 4) is broadened by all types of threading dislocations [33, 34].

Figure 3.21 represents ω scan profiles of (0002) diffraction for the HCl-treated sample (initial 3D growth) and Ga/HF/HCl-treated sample (initial 2D growth). Film thickness was 180 nm for both samples. For the HCl-treated sample, the linewidth of diffraction peak was 133 arcsec. On the other hand, it was relatively smaller (75 arcsec) for the Ga/HF/HCl-treated sample, implying a lower density of screw-type dislocations.

A similar trend was observed in profiles of (01 $\bar{1}$ 4) diffraction, but the difference was much larger [Fig. 3.22]. The HCl-treated sample had a quite broad peak (1840 arcsec), indicative of poor structural quality. The linewidth decreased markedly by initial 2D growth, and the Ga/HF/HCl-treated sample had a smaller value of 518 arcsec. The linewidth of the (01 $\bar{1}$ 4) diffraction was considerably larger compared to the (0002) diffraction. Hence, the broadening of the (01 $\bar{1}$ 4) diffraction peak is mainly attributed to the density of edge-type dislocations. These ω scan profiles clearly show that both screw-type and edge-type dislocations were remarkably reduced by initial 2D growth.

Film thickness dependence of (0002) diffraction linewidth is given in Fig. 3.23(a). Thin AlN films less than 50 nm had considerably small linewidths, such as 60 arcsec. It indicates that thin AlN films were highly oriented around the c -axis. For the HCl-treated sample, the

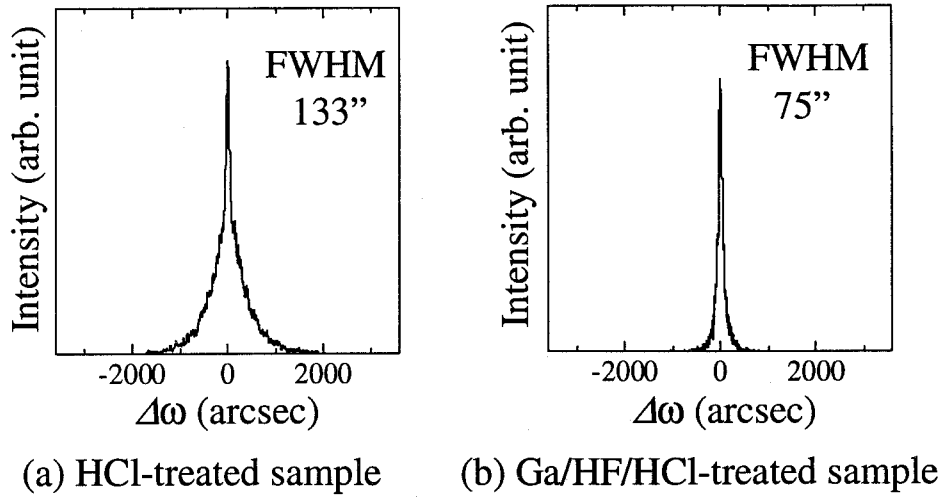


Figure 3.21: HRXRD ω scan profiles of (0002) diffraction for (a) HCl-treated sample (initial 3D growth) and (b) Ga/HF/HCl-treated sample (initial 2D growth).

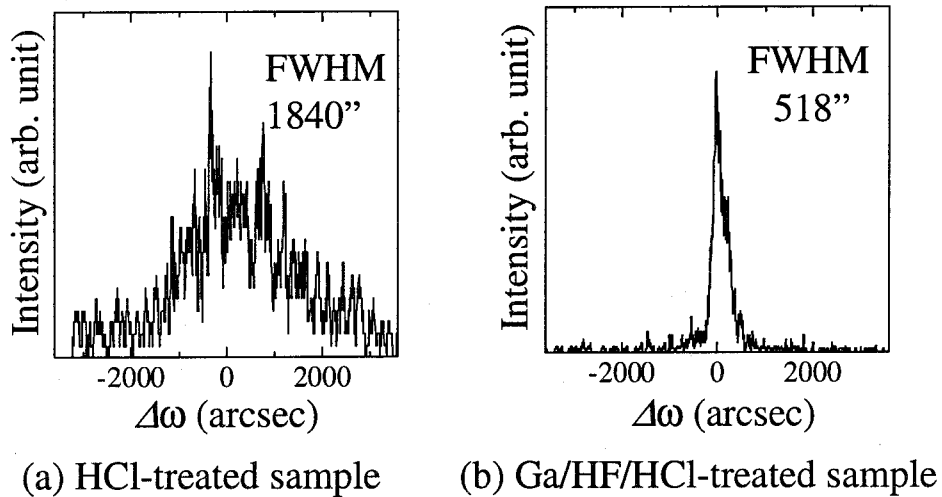


Figure 3.22: HRXRD ω scan profiles of (011̄4) diffraction for (a) HCl-treated sample (initial 3D growth), and (b) Ga/HF/HCl-treated sample (initial 2D growth).

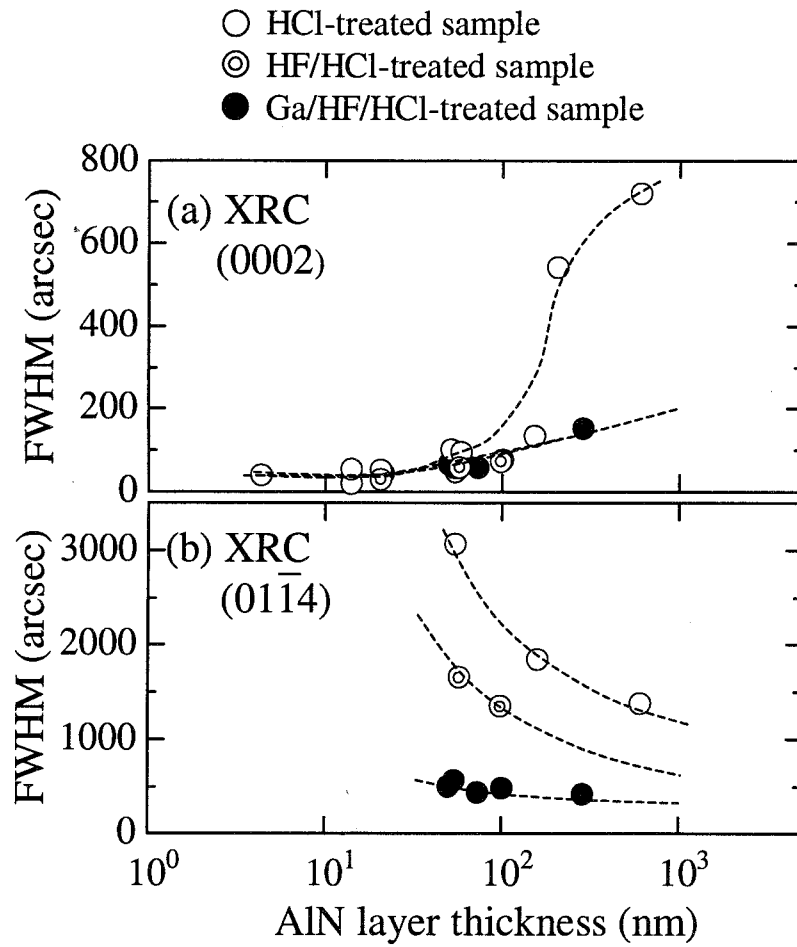


Figure 3.23: Film thickness dependence of ω scan linewidth. Samples are AlN films on HCl-treated substrates, HF/HCl-treated substrates, and Ga/HF/HCl-treated substrates. (a) (0002) diffraction and (b) (01 $\bar{1}$ 4) diffraction.

diffraction peak began to broaden beyond 50 nm. This enlargement of linewidth is probably related to the lattice relaxation, i.e., generation of misfit dislocations. As Heying *et al.* pointed out [33], the (0002) diffraction is only broadened by screw and mixed threading dislocations. Hence, generation of misfit dislocations might cause the increase of screw-type dislocations. For the Ga/HF/HCl-treated sample, the enlargement of linewidth was relatively gradual, which is consistent with the slower lattice relaxation.

The dependence of (01 $\bar{1}$ 4) diffraction linewidth on the film thickness is displayed in Fig. 3.23(b). HCl-treated samples had considerably large linewidths, suggesting large in-plane misorientation. With increasing film thickness, the linewidth gradually decreased. For HF/HCl-treated samples, the linewidth exhibited a similar trend, though they were smaller than those of HCl-treated samples. For Ga/HF/HCl-treated samples, the linewidth was much smaller compared to those of HCl- and HF/HCl-treated samples. The linewidth of Ga/HF/HCl-treated sample was almost independent of the film thickness. These results can be explained by differences in the initial growth mode. The large in-plane misorientation is mainly due to a columnar structure formed by initial 3D island growth. With increasing film thickness, the misorientation decreased due to coalescence of the columns. On the other hand, initial 2D growth dramatically reduced in-plane misorientation through the initial coalescence of 2D nuclei. The linewidth of asymmetrical plane diffraction reflects the density of edge-type dislocations. Therefore, initial 2D growth is essential to suppress the generation of edge-type dislocations in the initial growth stages, and obtain AlN films with excellent crystalline quality.

3.3.5 Surface Features of AlN Epilayers

Figure 3.24 gives an AFM image of a 30-nm-thick AlN film, which showed an initial 2D growth mode. Atomically-flat terraces with 1ML-height steps of AlN (0.25 nm) were observed, and the rms roughness in a scan size of $3 \times 3 \mu\text{m}^2$ was as small as 0.23 nm. In MBE growth of group-III nitrides, typical morphologies are dominated by dislocation mediated surface structures, i.e., the spiral growth hillocks due to the high dislocation densities in the film ($> 10^8 \text{ cm}^{-2}$) [35]. Spiral growth hillocks form around screw-type dislocations under step-flow conditions. In the absence of dislocations, the step-and-terrace structure should be formed with a uniform terrace width inversely proportional to the substrate miscut. As shown in Fig. 3.24, the 30-nm-thick film had uniform step-and-terrace structure, implying that the density of screw-type dislocations was quite low. This is in good agreement with the results of HRXRD (0002) diffraction.

Due to the lattice relaxation, the density of screw-type dislocations increases with increasing film thickness. Accordingly, surface morphologies should change from the uniform step-and-terrace structure to a dislocation mediated structure. The surface morphology of a 290-nm-thick AlN film is displayed in Fig. 3.25. Some spiral growth hillocks could be seen on the surface in a scan size of $3 \times 3 \mu\text{m}^2$, indicating an increased density of screw-type

Z range: 10 nm
(3 μm $\times$ 3 μm)

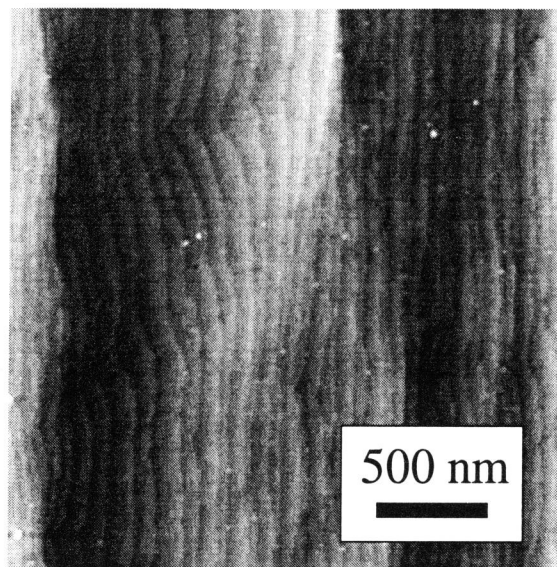


Figure 3.24: AFM image of 30-nm-thick AlN film grown on Ga/HF/HCl-treated substrate (initial 2D growth).

Z range: 10 nm
(3 μm $\times$ 3 μm)

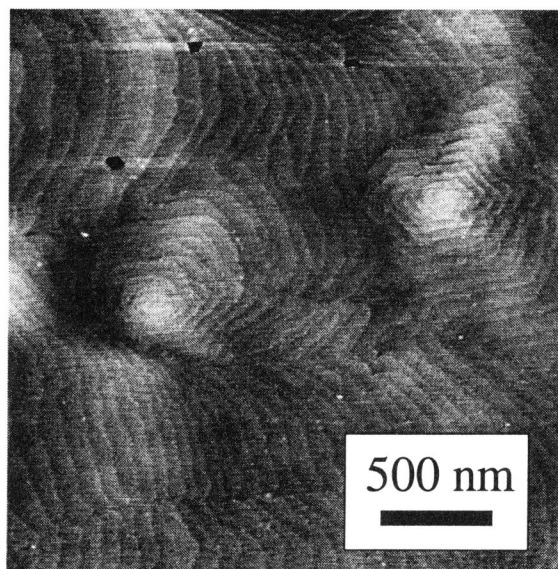


Figure 3.25: AFM image of 290-nm-thick AlN film grown on Ga/HF/HCl-treated substrate (initial 2D growth).

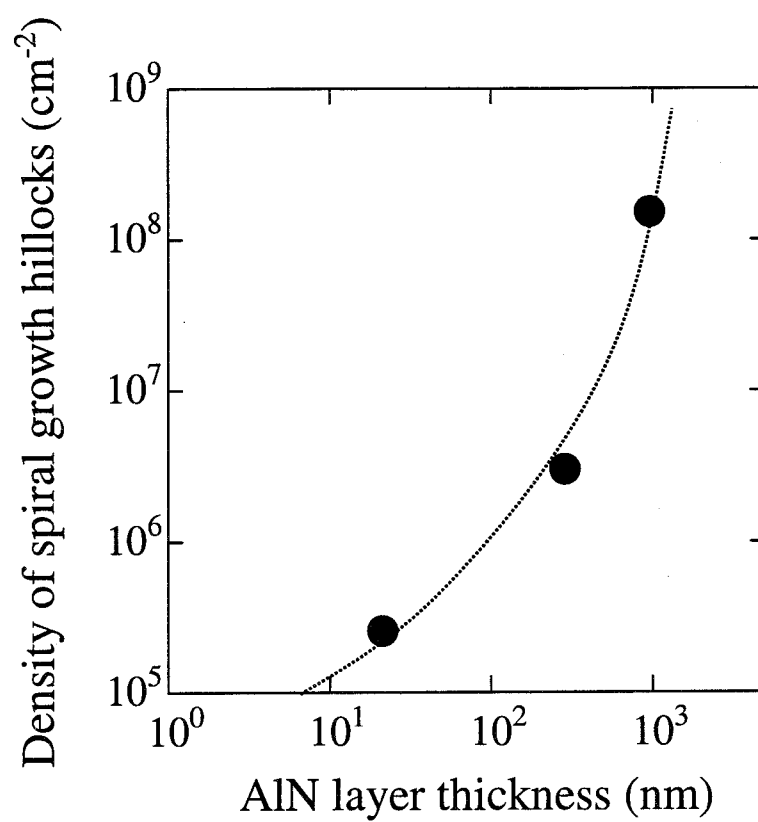


Figure 3.26: Correlation between density of spiral growth hillocks and film thickness.

dislocations, and the surface roughness was a little bit increased (an rms value of 0.33 nm). Spiral growth hillocks cause substantial thickness variations. Figure 3.26 shows correlation between the density of spiral growth hillocks and the film thickness. Although the density of spiral growth hillocks was extremely low for the 30-nm-thick film (10^5 cm^{-2}), the density increased to more than 10^8 cm^{-2} beyond 1 μm thickness.

3.4 Kinetics in Initial Growth Stages

3.4.1 Growth Mode Transition

Growth kinetics in the initial stages of AlN growth are discussed based on the RHEED intensity oscillation and the surface features. As shown in Fig. 3.18(c), the oscillation was not sustained more than seven periods from the beginning of growth. The oscillation reflects the periodic transition of surface roughness, or density of surface steps, and can be observed only in a 2D nucleation growth mode (layer-by-layer growth mode).

In general, two reasons are conceivable for the disappearance of oscillation during growth. One is the transition from 2D nucleation to 3D island growth. This is the SK growth mode, as described above. The reason of transition to 3D island growth is usually to stabilize the internal energy of the epilayer. For AlN growth on SiC, the epilayer suffers from compressive strain due to the lattice mismatch with the substrate. If 3D islands are formed, the strain energy can be relaxed elastically by lattice deformation. In a pseudomorphic condition, more and more strain energy is accumulated as growth proceeds. Therefore, it is possible that the growth mode changes from 2D nucleation to 3D island formation.

In the present case, however, another reason should be considered. That is, the growth mode changed from 2D nucleation to step flow. This view is clearly supported by the AFM image shown in Fig. 3.24, where an atomically-flat step-and-terrace structure was observed. In step-flow growth, the surface roughness, or density of surface steps, hardly changes during growth, resulting in constant RHEED intensity. Hence, the RHEED intensity oscillation gradually disappeared.

Then, why did the growth kinetics change from initial 2D nucleation to step flow? The mechanism of crystal growth can be divided into two parts; nucleation and the advance of steps. The theory of the crystal growth process was first developed by Burton, Cabrera, and Frank in 1951 [36]. The overall process of growth includes the following separate elementary processes:

- adsorption of atoms on the terraces between steps which gives rise to a population of adatoms
- surface diffusion of adatoms toward the steps
- incorporation of adatoms in kinks along the steps which leads to advancement of steps and hence growth of the crystal in a direction normal to its surface

If the adatoms on the surface have a diffusion length (λ_s) greater than the spacing of each steps (terrace width, L), then growth will occur primarily by addition of the adatoms to the step edges. If $\lambda_s < L$, then island nucleation on the terraces will occur in addition to the step-edge growth. Because RHEED oscillation occurs when there is a competition between the island nucleation and the growth from step edges, they will occur only for $\lambda_s < L$ [37]. A 2D nucleus with the radius larger than critical radii can be stable at the terrace region, and gradually becomes larger through incorporation of adatoms and coalescence with other nuclei [38].

In this work, the reason why the growth kinetics changed from initial 2D nucleation to step flow is probably attributed to the reduction of the surface terrace width. Figure 3.27 shows a schematic model of growth kinetics for AlN on a 4H-SiC(0001) surface with one-unit-cell-height steps (4ML $\sim$ 1.0 nm). Due to the step bunching of 4ML, the terraces become wide accordingly ($\sim$ 300 nm). This terrace width (L) is probably longer than the diffusion length of adatoms (λ_s). Consequently, 2D nucleation occurs on the terraces in the initial stages of growth. As growth proceeds, 1ML steps of AlN emerge on the growth surface, and the terrace widths gradually become shorter ($L/4 \sim$ 75 nm). Here, the diffusion length of adatom (λ_s) is probably longer than the terrace width, so that the adatoms are incorporated into the crystal at the step edges, i.e., step-flow growth.

According to Neave *et al.* [39], the surface diffusion length (λ_s) decreases with decreasing the growth temperature, and also decreases with increasing the incident source fluxes (i.e., higher supersaturation). Next, the growth kinetics at lower growth temperatures were investigated, where the diffusion length of adatoms should become smaller.

3.4.2 Two-Dimensional Nucleation or Step Flow

AlN growth at lower growth temperatures, 800°C and 600°C, was carried out to investigate the evolution of growth kinetics. Figure 3.28 presents RHEED intensity profiles in the initial growth stages at different temperatures. RHEED intensity oscillation was sustained for longer time with decreasing the growth temperature. In 1000°C growth and 800°C growth, the oscillation gradually disappeared, indicative of a transition from 2D nucleation to step flow. On the other hand, at 600°C, the oscillation was sustained more than 100 periods (> 25 nm). These results suggest that the 2D nucleation mode was sustained at 600°C growth because the diffusion length of adatoms (λ_s) was shorter than the terrace width (L). Transition from step flow to 2D nucleation at lower temperatures is a well-known phenomenon for homoepitaxy of silicon or gallium arsenide. Xie and co-workers have demonstrated the similar transition of growth kinetics in GaN growth on a thick GaN buffer layer [40]. In this work, however, AlN growth was performed directly on SiC surfaces. It is a surprising result that sustainable oscillation with more than 100 periods could be achieved in such a lattice-mismatched system ($\sim 0.9\%$).

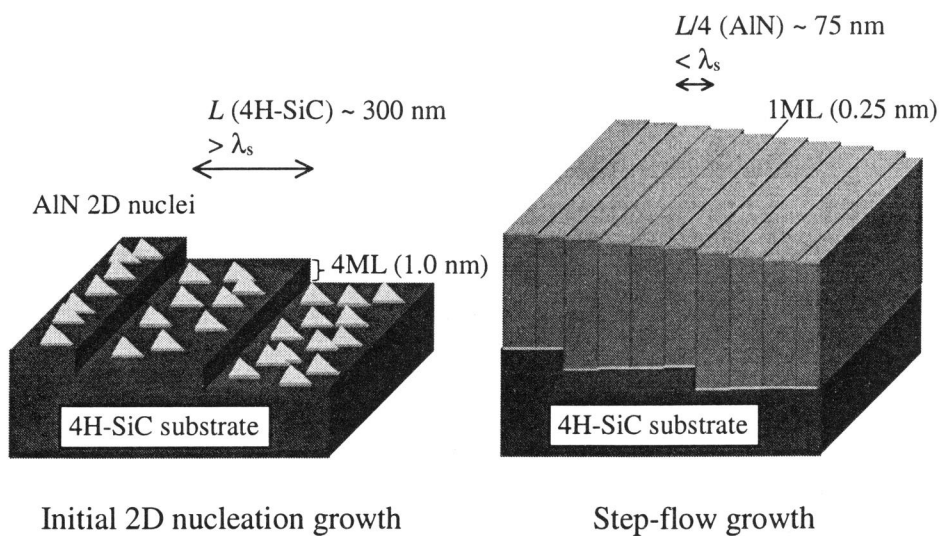


Figure 3.27: Schematic model of growth kinetics of AlN on 4H-SiC(0001) surface with one-unit-cell-height steps.

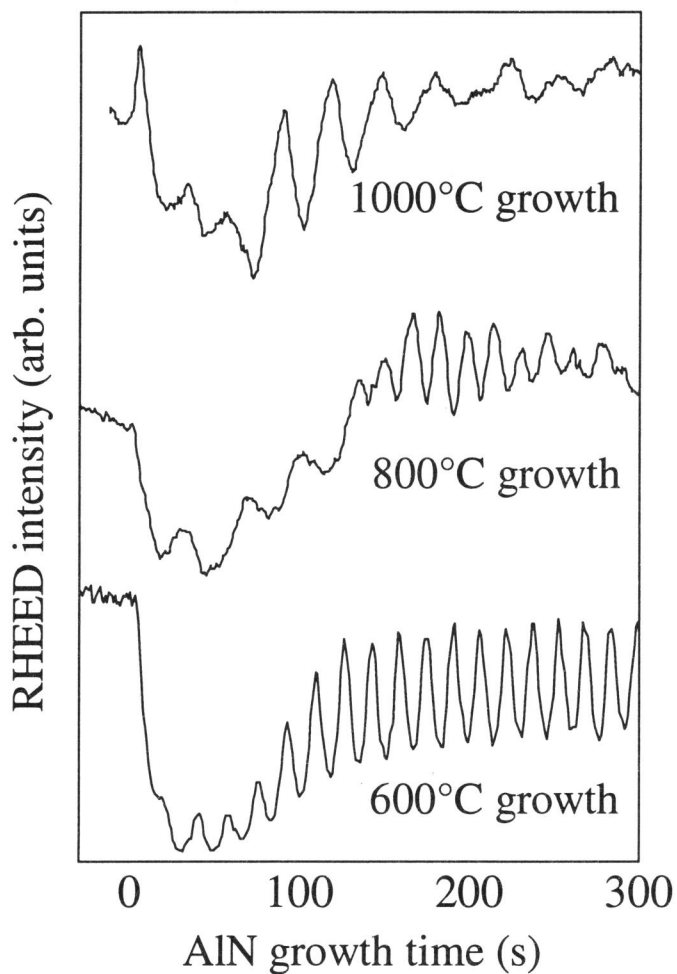


Figure 3.28: RHEED intensity profiles in initial growth stages for different substrate temperatures.

3.4.3 Dissolution Mechanism of Step Bunching

Now, growth kinetics in the initial growth stages will be discussed from more microscopic point of view. Since the SiC surface has a uniform step-and-terrace structure with one-unit-cell-height steps, the transition process from 2D nucleation to step flow, especially how bunched steps are dissolved into monolayer steps, is very interesting. To elucidate the transition process, the evolution of the AlN surface in the initial growth stages was characterized by AFM. 800°C growth was performed, which is suitable to study the transition process from 2D nucleation to step flow due to the gradual transition. RHEED intensity oscillation was monitored during growth, and the growth was stopped after several oscillations.

At 8ML growth (~ 2 nm), many triangular-shaped 2D nuclei were observed on the wide terraces, and 4ML steps still remained [Fig. 3.29(a)]. Triangular-shaped 2D nuclei can be observed not only on *hcp*(0001) surfaces but also *fcc*(111) surfaces such as GaAs(111). To explain the formation mechanism of triangular-shaped 2D nuclei, we refer to the atomic configuration of the *hcp*(0001) bilayer lattice. In view of dangling bonds in the bilayer, there are two types of step edges: type A edges, normal to $[10\bar{1}0]$ or equivalent directions, are characterized by two dangling bonds per edge atom, and type B edges, normal to $[1\bar{1}00]$ or equivalent directions, are characterized by one dangling bond per edge atom (see Fig. 3.30). It is reasonable to assume that type A edges will grow faster than type B edges because of the greater tendency for arriving adatoms to bind to type A edges. The faster growth speed in the direction normal to type A edges will ultimately result in triangularly shaped nuclei whose vertices point toward $[10\bar{1}0]$ and equivalent directions [40].

A most striking feature in Fig. 3.29(a) is that all triangular-shaped nuclei on adjacent terraces pointed toward an identical direction. As shown in Fig. 3.31, an *hcp* film has alternating type A and B edges along the *c*-axis. On the 1ML-upper or lower adjacent terraces, the direction of triangular-shaped nuclei should change $\pm 60^\circ$ or 180° away since the order of type A and B edges is reversed. The result shown in Fig. 3.29(a) suggests that the atomic site of AlN bilayers was identical (like site "B") on the different terraces which have site "A" bilayers, that is illustrated in Fig. 3.32(a). Owing to SiC surface control, the uppermost layers of adjacent terraces had the same underlying stacking sequence. The nucleation site is expected to be controlled by the site of both surface and subsurface atoms via the electrostatic potential; otherwise control of surface steps would be meaningless, and numerous SMBs would be generated even on the same terrace (see Fig. 3.32(b)). Hence, the observed result demonstrates the effectiveness of surface step control in reduction of SMBs owing to coherent coalescence of AlN nuclei originating from different SiC terraces.

At 16ML growth (~ 4 nm), 2D nuclei and the bunched steps gradually coalesced, and the bunched steps began to be dissolved into monolayer steps [Fig. 3.29(b)]. After 32 ML growth (~ 8 nm), almost all the bunched steps were dissolved into monolayer steps, and the density of 2D nuclei went down [Fig. 3.29(c)].

The dissolution mechanism of step bunching during AlN growth is presented in Fig. 3.33.

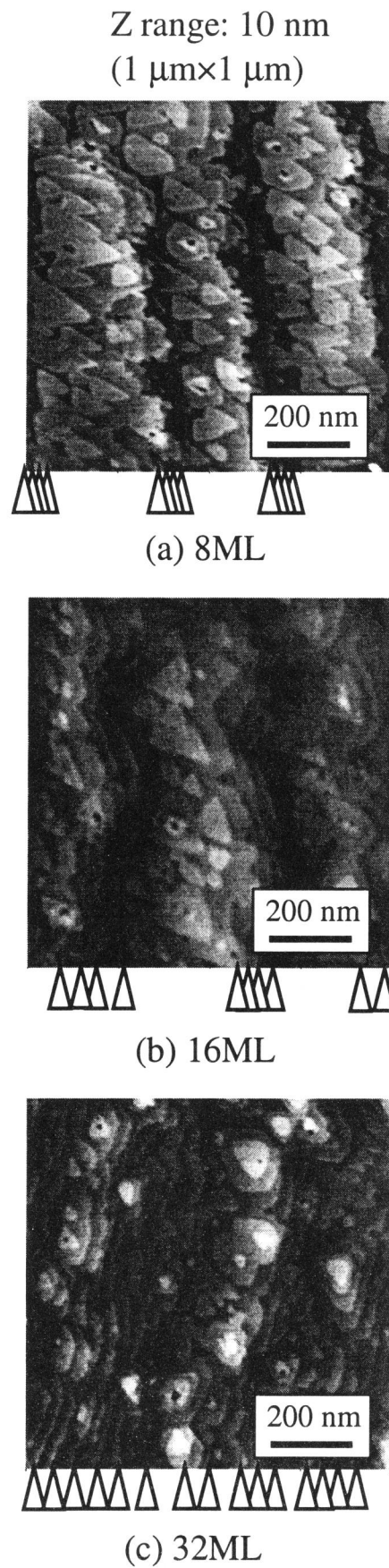


Figure 3.29: Evolution of AlN surface in initial growth stages: (a) 8ML, (b) 16ML, and (c) 32ML.

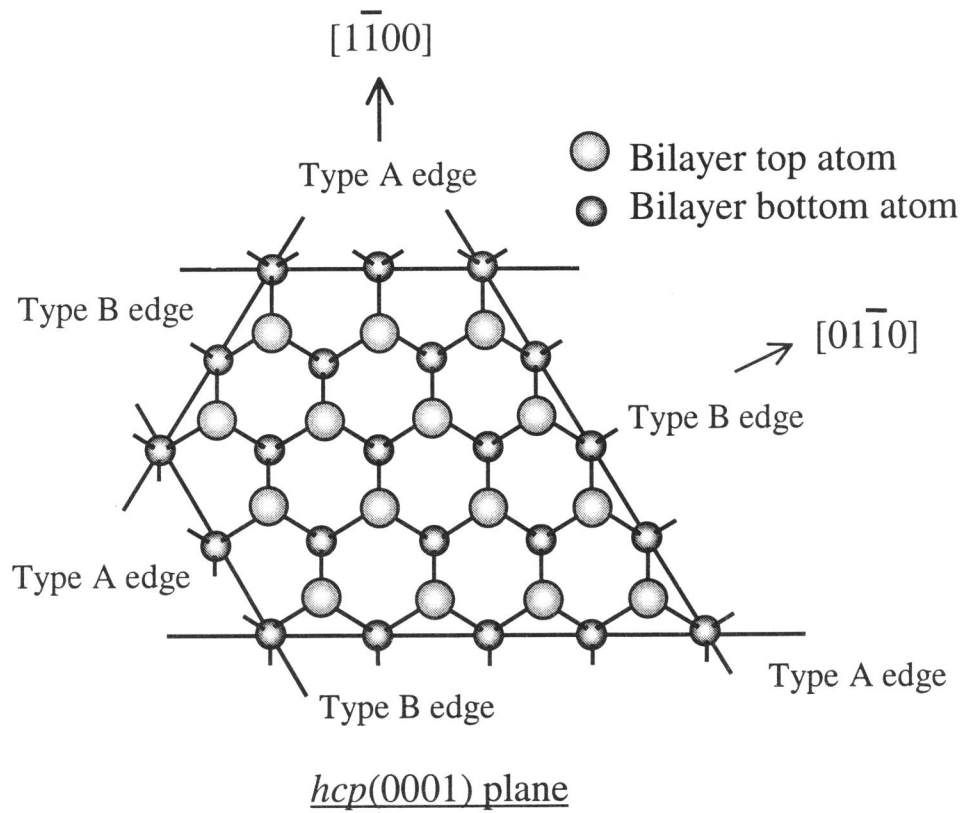


Figure 3.30: Plan-view of atomic configuration of *hcp*(0001) bilayer lattice. (Formation mechanism of triangular-shaped 2D nuclei.)

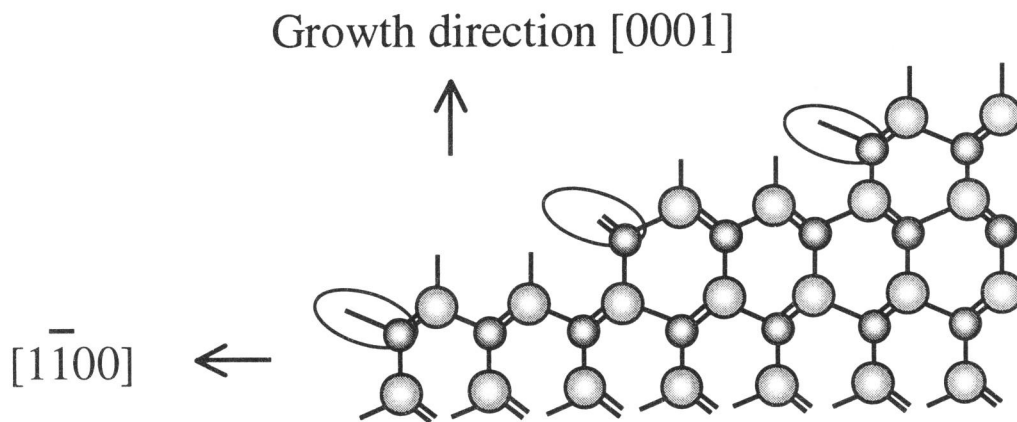


Figure 3.31: Cross-sectional view of atomic configuration of *hcp*(0001) bilayer lattice.

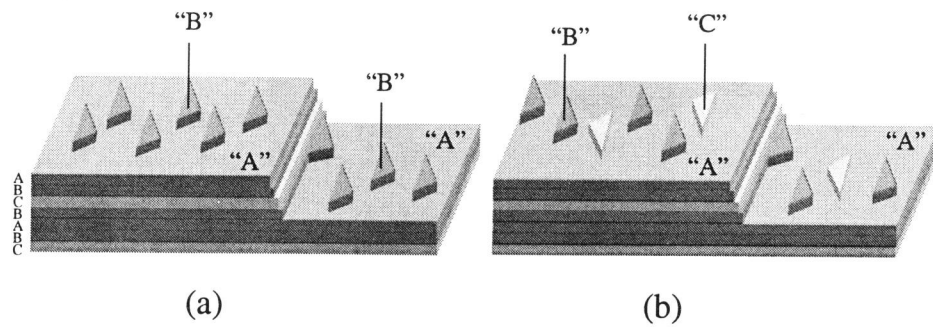


Figure 3.32: Nucleation sites of AlN bilayers on surface-controlled SiC substrate.

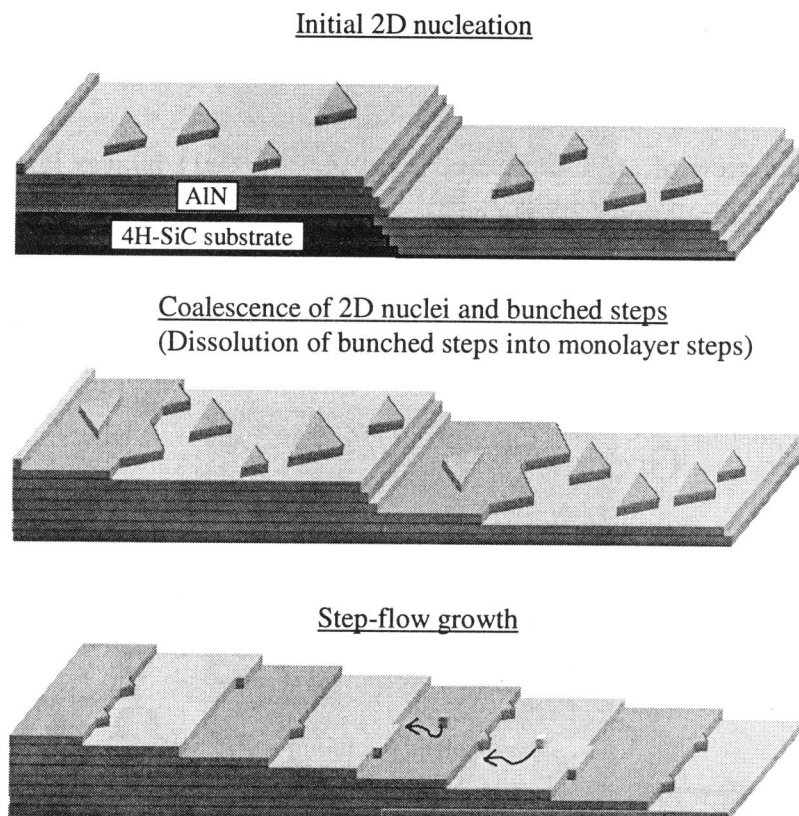


Figure 3.33: Dissolution mechanism of step bunching during AlN growth.

Thus, bunched steps of SiC surface were dissolved, and growth kinetics changed from 2D nucleation to step flow.

3.4.4 Dependence of Structural Quality on Growth Kinetics

As described in Fig. 3.23, the initial growth mode strongly affected the structural quality of grown film. From the HRXRD measurements of both (0002) and (01 $\bar{1}$ 4) diffraction, it was found that the density of both screw-type and edge-type threading dislocations was remarkably reduced owing to initial 2D nucleation. Now, the structural quality of AlN films grown at different temperatures was investigated by using ω scans of (01 $\bar{1}$ 4) diffraction.

Figure 3.34 displays the film thickness dependence of the (01 $\bar{1}$ 4) peak diffraction linewidth for AlN epilayers grown at different temperatures (600°C, 800°C, 1000°C). As clearly seen, the linewidth decreased with decreasing the growth temperature, indicative of improvement in the structural quality of AlN film. To explain this result, two effects are considered. One is the effect of lowering growth temperatures itself. Another is sustaining 2D nucleation, i.e., the 2D nucleation growth mode is better than the step-flow growth mode to obtain superior crystalline quality. Low-temperature growth leads to higher supersaturation and/or shorter migration length, which results in the 2D nucleation growth mode. To clarify these effects, the amount of supplied flux, aluminum and active nitrogen, should be increased to realize a higher supersaturation condition at high growth temperatures, where 2D nucleation will be sustained.

3.5 Impact of AlN Buffer Layer on GaN Film Quality

3.5.1 Significance of AlN Buffer Layer

AlN has been widely used as an initial nucleation layer for GaN growth on SiC substrates because of the intermediate lattice constant and thermal expansion coefficient between those of GaN and SiC [6, 41]. Twigg *et al.* have discussed that maintaining the proper structure of the AlN nucleation layer is crucial for growth of high-quality GaN [42]. Waltereit and co-workers have demonstrated that the growth mode of GaN is determined by its wetting to the underlying layer rather than by the lattice mismatch [43]. Poor wettability of GaN directly on SiC leads to pure 3D nucleation favoring the formation of dislocations at the island edges, and the GaN films are already fully relaxed [44, 45]. In contrast, wetting is much improved for deposition on AlN, resulting in 2D growth of the subsequent GaN epilayer with gradual strain relief [46].

However, the defective nature of GaN films is still a central problem, and has to be improved for high-performance devices [47]. GaN films contain a significant number of threading dislocations which are mainly generated in the AlN buffer layer [6]. It is thus important to improve the AlN film quality from the viewpoint of reduction of threading

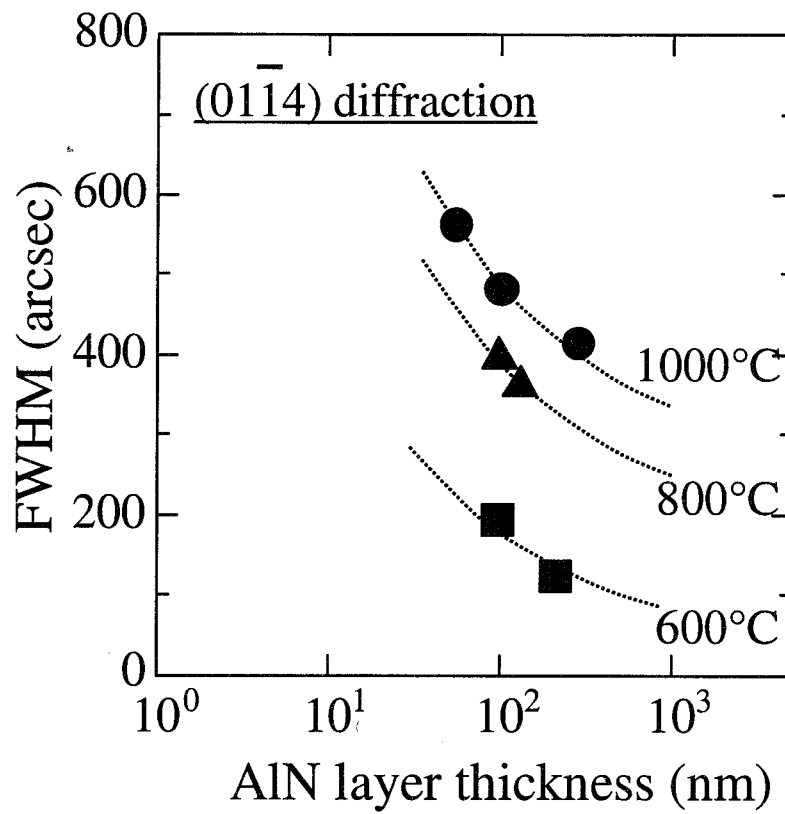


Figure 3.34: Film thickness dependence of (011̄4) diffraction peak linewidth for AlN epilayers grown at 600°C, 800°C, and 1000°C.

dislocations in GaN films.

In this section, the influence of AlN film quality on the properties of subsequently grown GaN epilayers was studied by AFM and HRXRD. The SiC substrates used here were HCl- and Ga/HF/HCl-treated substrates, which lead to 3D and 2D initial nucleation in AlN growth, respectively. As described above, initial 2D growth leads to excellent structural quality of the AlN film, while 3D island growth results in rather poor crystalline quality. Following the deposition of an AlN buffer layer (~ 20 nm) at 1000°C , $1\text{-}\mu\text{m}$ -thick GaN main epilayers were grown at 850°C . During and after GaN growth the RHEED exhibited streak patterns for both samples.

3.5.2 Surface Features of GaN Epilayers

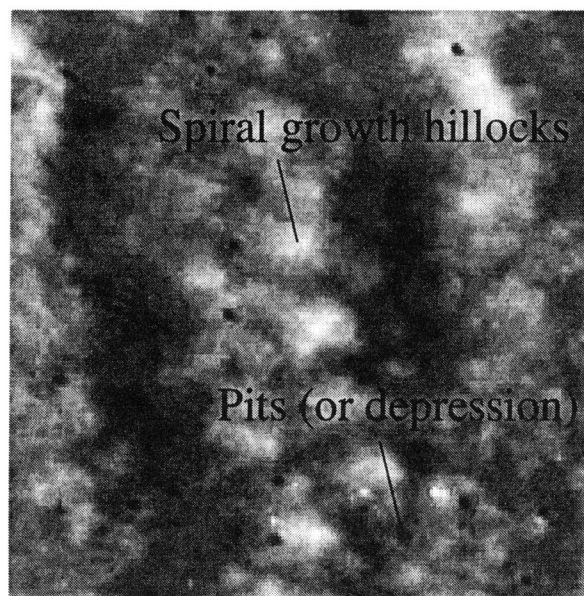
Surface features of GaN epilayers were characterized by AFM. On the HCl-treated substrate [Fig. 3.35(a)], many spiral growth hillocks were observed. Those spiral growth hillocks can be seen around screw-type dislocations under the step-flow conditions [35]. Therefore, the surface morphology suggests that GaN was grown two-dimensionally (step-flow growth mode) and had a relatively smooth surface, however it contained many screw-type dislocations. The density of spiral growth hillocks was approximately 10^9 cm^{-2} , indicative of poor structural quality. Spiral growth hillocks were also observed on the GaN film grown on the Ga/HF/HCl-treated substrate [Fig. 3.35(b)]. It should be mentioned that in this film, the density of spiral growth hillocks was 10^7 cm^{-2} , two orders of magnitude lower compared to the film grown on the HCl-treated substrate. Furthermore, clear step-and-terrace structure could be observed between the hillocks, suggesting that some regions were free of defects. These results agreed with results of defect-selective wet etching [48, 49].

Remarkable reduction of the screw-type dislocation density is probably due to the improved structural quality of the underlying AlN buffer layer. Since spiral growth hillocks also cause substantial thickness variations or surface roughening, those dislocations should be reduced. It is a matter of concern that on the GaN surfaces, some dark spots (or pits) were observed. The presence of surface pits might indicate the existence of other types of dislocations [21].

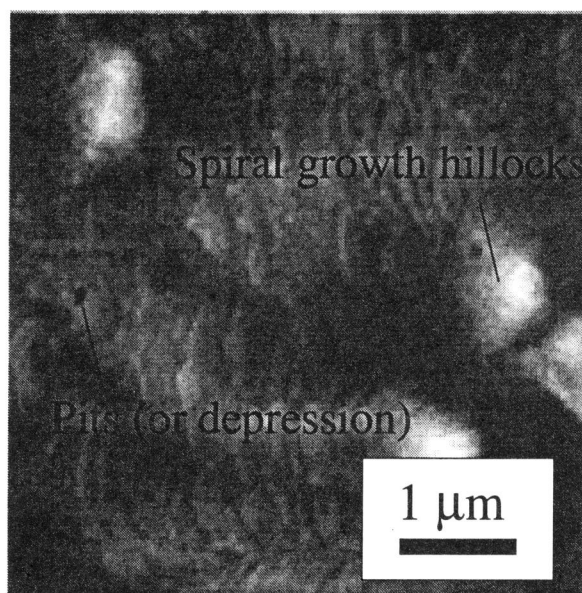
3.5.3 Structural Quality of GaN Epilayers

The structural quality of GaN films grown on HCl- and Ga/HF/HCl-treated substrates was investigated by ω scans of (0002) and (01 $\bar{1}$ 2) diffraction. The linewidths of the (0002) diffraction peak for both GaN films are plotted in Fig. 3.36(a). To check the reproducibility, at least two samples were grown on each substrate. As clearly seen, the linewidths of HCl-treated samples ranged from 200 to 1500 arcsec, significantly larger than those of Ga/HF/HCl-treated samples (less than 200 arcsec). This result indicates the poor crystalline quality of HCl-treated samples, and higher density of screw-type dislocations. It is

Z range: 10 nm
(5 μm $\times$ 5 μm)



(a) on HCl-treated substrate



(b) on Ga/HF/HCl-treated substrate

Figure 3.35: Surface morphologies of GaN films with AlN buffer layers grown on (a) HCl-treated substrate and (b) Ga/HF/HCl-treated substrate.

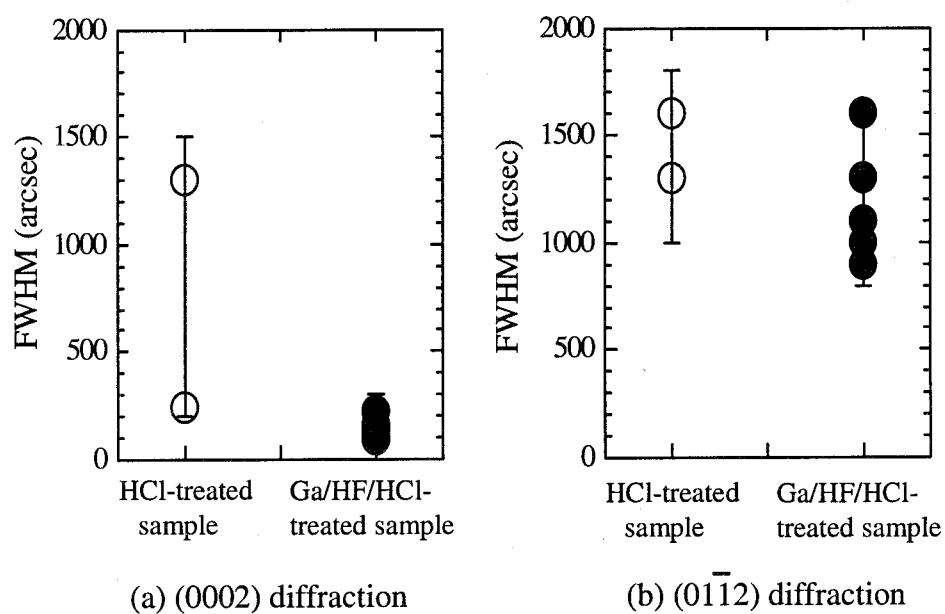


Figure 3.36: Linewidths of (a) (0002) and (b) (01 $\bar{1}2$) diffraction peak for GaN grown on HCl-treated substrates and Ga/HF/HCl-treated substrates.

consistent with the AFM results.

On the other hand, no noticeable differences could be found in the $(01\bar{1}2)$ diffraction data. The linewidths ranged from 900 to 1600 arcsec for both samples as shown in Fig. 3.36(b). It suggests that both GaN films had a similar density of edge-type dislocations. These results were confirmed by the photo-electro-chemical (PEC) etching measurement [50–52]. In the case of AlN growth on SiC substrates, initial 2D growth dramatically reduced the generation of edge-type dislocations by the initial coalescence of 2D nuclei. The defective nature of GaN films is probably related to the initial growth mode of GaN on the AlN buffer layers. Although the structural quality of the AlN buffer layer was successfully improved owing to SiC surface control, the 2.5% lattice mismatch between GaN and AlN is still problematic. Further investigation on growth features at the GaN/AlN interface is absolutely necessary to reduce the structural defect density in GaN films.

3.6 Summary

Initial 2D growth of AlN was realized owing to SiC surface control of not only the step-and-terrace structure with one-unit-cell-height steps, but also the chemical structure, i.e., removal of residual oxygen and realization of a 1/3ML silicon-adsorbed superstructure. Only on the Ga/HF/HCl-treated SiC surface were RHEED intensity oscillations evident from the beginning of AlN growth. It was found that the AlN film with initial 2D nucleation exhibited slower lattice relaxation, which suppressed generation of screw-type dislocations. Furthermore, initial 2D growth dramatically reduced the in-plane misorientation, i.e., density of edge-type dislocations, thanks to the initial coalescence of AlN 2D nuclei.

Kinetics in the initial stages of AlN growth were investigated from the microscopic point of view. RHEED monitoring and AFM characterization revealed the dissolution mechanism of step bunching and the transition from 2D nucleation to step flow. Evolution of surface features during the initial growth stages was characterized, and the effectiveness of surface step control in reduction of SMBs was experimentally demonstrated owing to coherent coalescence of AlN nuclei originating from different terraces.

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Chapter 4

AlN Growth on Off-Axis SiC (0001) and Application for MIS Devices

4.1 Introduction

AlN is expected to be a useful insulator for SiC MIS devices due to its high relative dielectric constant ($\epsilon_{\text{AlN}} = 8.5$) compared to SiO_2 ($\epsilon_{\text{SiO}_2} = 3.9$) [1–5]. Furthermore, the interface between AlN and SiC is expected to be superior to the SiO_2/SiC interface because the lattice mismatch of AlN/SiC is relatively small, 0.9% [6]. In chapter 3, high-quality AlN films were successfully grown on on-axis SiC(0001) substrates by control of the surface structure and the surface chemistry, i.e., Ga/HF/HCl treatment.

In present SiC technologies, homoepitaxy of 4H- or 6H-SiC is normally carried out on substrates inclined by several degrees toward $[11\bar{2}0]$. It has been reported that if the off-cut angle is too small, two-dimensional nucleation of cubic-phase 3C-SiC occurs, resulting in twinned 3C-SiC [7, 8]. For that reason, the use of misoriented substrates, e.g. 3.5° off for 6H-SiC and 8° off for 4H-SiC, has been typical for homoepitaxy of SiC.

In order to fabricate MIS devices utilizing the interface of AlN and SiC epilayers, it is a matter of course that AlN should be grown on off-axis SiC epilayers. However, the literature concerning nitride epitaxy on off-axis SiC(0001) substrates is relatively few, compared to that for on-axis substrates.

With increasing the off-cut angle, the density of surface steps increases accordingly, narrowing the terrace width. In heteropolytypic-epitaxy of 2H nitride on 4H- or 6H-SiC(0001) surfaces, the polytype mismatch at the SiC step edges is one of the significant issues to be solved. Tanaka *et al.* and Aboelfotoh *et al.* revealed by means of cross-sectional HRTEM that AlN films grown on off-axis SiC substrates contained defects originating at step sites on the SiC surface [9, 10]. In chapter 3, the problems related to the stacking mismatch could be solved by SiC surface control, which led to coherent coalescence of AlN nuclei formed on different terraces of the SiC surface. Although SiC surface control was revealed to be very effective, it is still preferable to reduce the density of surface steps.

On the other hand, Xie *et al.* suggested that using off-axis substrates for GaN growth, the dislocation densities of both screw-type and edge-type could be reduced [11]. They examined the density of threading dislocations in GaN films grown on off-axis SiC substrates based on plan-view HRTEM studies, and confirmed that screw-type dislocations were reduced by two orders of magnitude, and edge-type dislocations were reduced by one order of magnitude. Brault and co-workers also found similar results in AlN growth on off-axis SiC substrates [12]. Although they have successfully obtained better structural quality (in view of tilting and twisting) by using off-axis substrates, the surface roughness, on the contrary, drastically increased. The AlN surface was characterized by fairly regular macro-steps, with average height and width of 8-10 and 80-100 nm, respectively [12]. Tanaka *et al.* pointed out that the degree of surface roughness was directly related to the density of surface steps, which was markedly higher on the vicinal surface [9]. Aside from crystalline quality, the surface smoothness of grown films is also one of the important factors for device applications.

To apply an AlN film as a gate insulator for MIS devices, the dielectric properties, i.e., low leakage current and high breakdown field, are also crucial issues. In addition, the electronic properties of the AlN/SiC interface (density of interface traps, channel mobility etc.) should be controlled. Although the AlN/SiC heterostructure is expected to be a promising alternative to SiO₂/SiC MOS structures, the interface characteristics, especially the correlation between the interface structure and electronic properties, have not been understood in detail. The conditions of AlN/SiC interface formation, e.g. the superstructure of SiC surface or initial irradiation by one source flux prior to AlN growth, are thought to affect the interface characteristics.

In this chapter, AlN growth on off-axis SiC substrates is studied from the viewpoints of surface smoothness, structural quality and dielectric properties. Then, electronic properties of the AlN/SiC interface are investigated by means of *in situ* XPS and capacitance-voltage (*C-V*) measurements, and correlations between the interface structure and electronic properties of the interface are discussed.

4.2 Issues in AlN Growth on Off-Axis SiC Substrates

4.2.1 Off-Cut Angle of SiC Substrate

The polytypism of SiC comes from various stacking orders along the hexagonal $\langle 0001 \rangle$ direction, which implies the possibility of polytype mixing in the growth on SiC(0001) faces. Owing to the step-controlled epitaxy proposed in 1987 [13], homoepitaxial growth on hexagonal SiC(0001) surfaces with reasonable crystalline quality for electronic devices could be achieved, where an off-cut angle toward the $[11\bar{2}0]$ direction by a few degrees was introduced to the (0001) substrates [14–20]. Homoepitaxy on SiC(0001) is driven by the step-flow growth mode, while twinned 3C-SiC should result from 2D nucleation since 3C-SiC is energetically preferable at the growth temperature (normally 1500°C) [8].

The introduction of an off-cut angle to SiC(0001) substrates is assumed to strongly affect AlN heteroepitaxy. A slight misalignment between 4 or 6ML-height of 4H- or 6H-SiC and AlN 2ML $\times$ 2 or 3 comes to be a more significant problem compared to on-axis substrates due to the increased surface step density. It will result in misorientation between the AlN growth axis and the *c*-axis of SiC substrate. The misorientation is discussed based on HRXRD studies in this chapter.

4.2.2 Surface Steps of SiC Substrate

In chapter 3, the kinetics in the initial stages of AlN growth on the atomically-flat SiC surface were studied by *in situ* RHEED monitoring and AFM characterization of the surface evolution. The transition mechanism from 2D nucleation to step flow growth was attributed to the reduction of the surface terrace width. When the spacing between steps (or terrace width, L) is longer than the diffusion length of surface adatoms (λ_s), 2D nucleation occurs on the terrace regions. Conversely, if the diffusion length of adatoms is shorter than the terrace width (i.e., $L < \lambda_s$), then the adatoms will be incorporated into the crystal at step edges (step-flow growth).

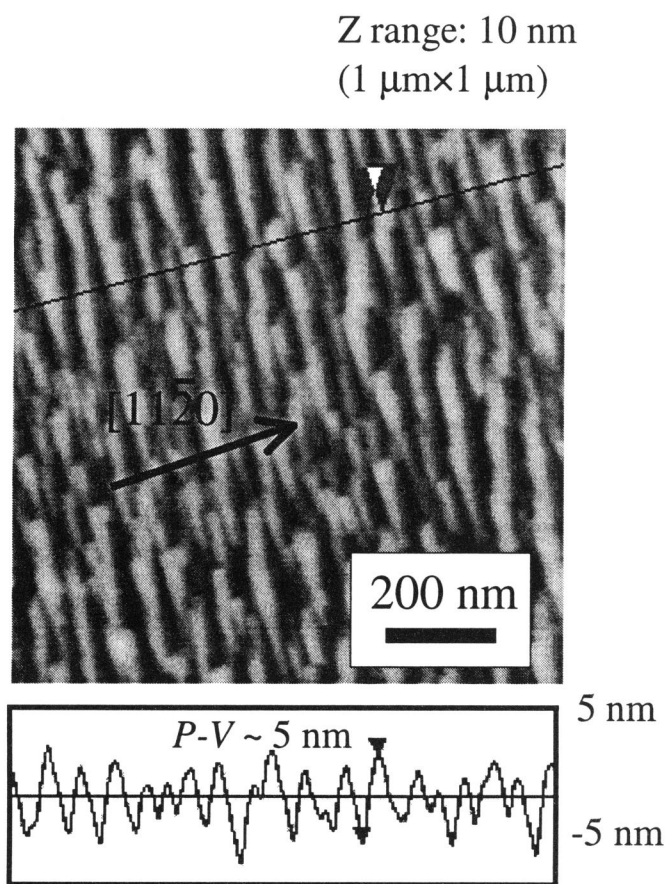
With increasing the off-cut angle, the density of surface steps markedly increases, narrowing the terrace width. For instance, an HCl-treated 4H-SiC substrate with an off-cut angle of 0.3° has one-unit-cell-height steps (4ML: 1.0 nm), and approximately 300-nm-width terraces. In contrast, the terrace width of 4H-SiC with a tilt of 8° pretreated in the same manner is as short as 7 nm. Since the terrace width is less than the diffusion length of adatoms, a step-flow growth mode probably comes to be a dominant mechanism from the beginning of growth on misoriented SiC substrates.

4.3 Surface Features of AlN Epilayers

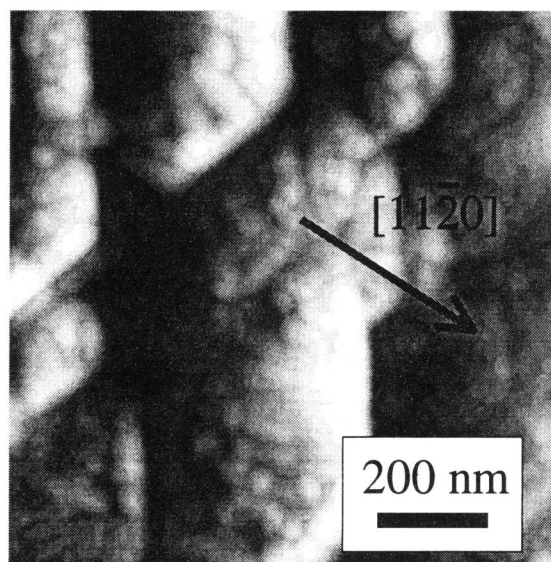
4.3.1 Surface Undulations in High-Temperature Growth

In this work, AlN films were grown on 4H- and 6H-SiC(0001)_{Si} substrates with off-cut angles of 8° and 3.5°, respectively. The off-axis substrates were all tilted toward the [11 $\bar{2}$ 0] direction. The surface preparation was performed in the same manner as for on-axis SiC(0001) substrates described in chapter 3. Accordingly, prior to AlN growth, the ($\sqrt{3} \times \sqrt{3}$)R30° surface reconstruction originating from 1/3ML silicon adatoms was observed in RHEED monitoring.

Figure 4.1 displays surface morphologies of 30-nm-thick AlN films grown at 1000°C on 4H-SiC(0001) 8°off substrates. The surface features obtained in a stoichiometric condition, or effective ratio of Al/N $\sim$ 1 [Fig. 4.1(a)], were quite similar to those found by Brault *et al* [12]. The grown film had fairly regular macro-steps, or macro-undulations along the [11 $\bar{2}$ 0] direction, with a large peak-to-valley (*P-V*) value of approximately 5 nm, and the



(a) Al/N ~ 1



(b) Al/N > 1 (aluminum rich)

Figure 4.1: AFM images of 30-nm-thick AlN films grown at 1000°C on 4H-SiC(0001) 8° off substrates: (a) Al/N ~ 1 and (b) Al/N > 1.

rms roughness was considerably large, about 1.3 nm in a scan size of $1 \times 1 \mu\text{m}^2$. After this, AlN growth in a slightly aluminum-rich condition ($\text{Al}/\text{N} > 1$) was performed. In general for MBE growth of group-III nitrides, a slightly group-III rich condition is considered to be preferable to obtain smooth growth surfaces [21]. Figure 4.1(b), however, showed that even in slightly aluminum-rich conditions, the epilayer did not have a smooth surface, on the contrary it had an even more rough surface (rms roughness ~ 10 nm).

These results completely differ from the case of on-axis SiC substrates. The most striking difference between on-axis and off-axis substrates is the spacing between steps, or the terrace width. Due to the reduction of the terrace width, a step-flow growth mode is thought to be dominant from the beginning of growth. Hence, the difference in initial growth kinetics might cause the different surface features. By analogy to growth on on-axis substrates, lowering the growth temperatures is thought to lead to 2D nucleation instead of step flow since the diffusion length of adatoms is reduced at lower temperatures.

4.3.2 Smooth Surface of Low-Temperature-Grown Epilayers

Next, AlN growth was carried out at 600°C . Figure 4.2 presents surface morphologies of a 30-nm-thick film grown at 600°C on a 4H-SiC(0001) 8°off substrate. The surface roughness dramatically decreased compared to 1000°C growth, i.e., 0.3 nm in a scan size of $1 \times 1 \mu\text{m}^2$. A step-and-terrace surface structure was clearly seen, and most of the step heights were measured to be approximately 0.5 nm, i.e., a double bilayer of AlN ($c = 4.982\text{\AA}$), though some single 1ML steps were also observed. The formation of double bilayer steps is probably due to the consequence of strong anisotropy in the growth rate of type A and type B step edges of 2H-AlN (see Fig. 3.31), which has been described by Xie *et al* [11]. Remarkable improvement in surface morphologies was obtained by lowering the growth temperature from 1000°C to 600°C . Modification of the initial growth kinetics was probably responsible for the superior surface features.

4.3.3 Growth Kinetics on Off-Axis Substrates

Kinetics in the initial stages of AlN growth on the off-axis SiC substrate will now be discussed. With increasing the off-cut angle, the density of surface steps markedly increases, narrowing the terrace width. Hence, it is reasonably assumed that 1000°C growth proceeded partly in a step-flow mode from the beginning of growth (i.e., from the first monolayer on the SiC surface), because the terrace width ($L \sim 7$ nm in 4H-SiC(0001) 8°off) was much smaller than the diffusion length of adatoms (λ_s).

A schematic model of the initial growth kinetics on the off-axis 4H-SiC substrate is illustrated in Fig. 4.3. From the crystallographic point of view, a wurtzite (2H) structure is thermodynamically stable for AlN. Accordingly, 2H-AlN is grown on the terrace region far from the step edges, i.e., 2D nucleation. If terraces of the 4H-SiC surface are terminated

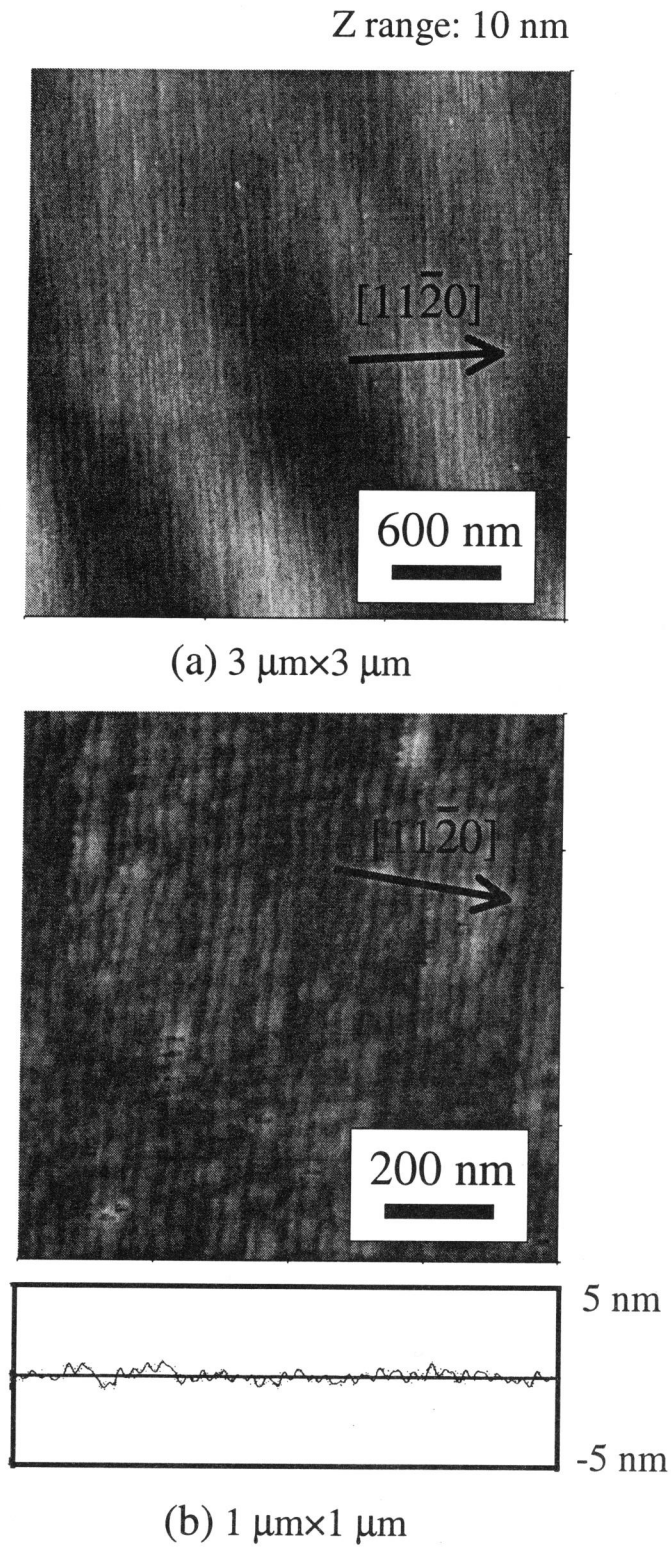


Figure 4.2: AFM images of 30-nm-thick AlN film grown at 600°C on 4H-SiC(0001) 8° off substrate.

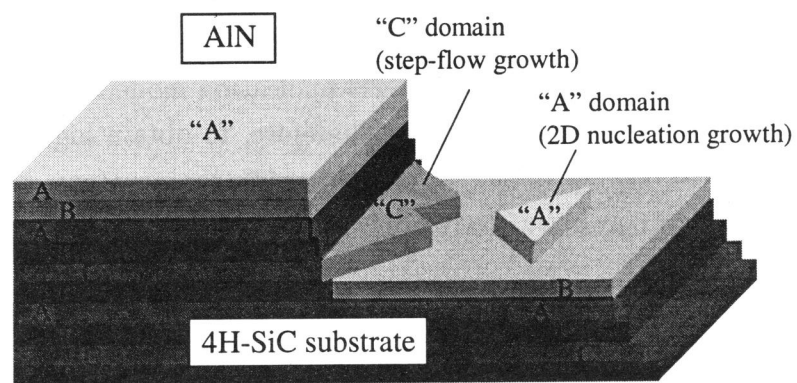


Figure 4.3: Schematic model for initial growth kinetics on off-axis 4H-SiC substrate.

with a stacking sequence of ...CBA, then a BABA AlN 2D nuclei should follow. However, the stacking mismatch between 2H-AlN and 4H-SiC comes to be a problem at the step edges due to step flow from the beginning of growth. At the bunched step edges with one-unit-cell height, the unique configuration of dangling bonds due to the 4H-SiC polytype comes out. It is not impossible to replicate the 4H polytype by step-flow growth even though 2H-AlN is more stable. Surface adatoms are influenced not only by the underlying stacking sequence (...CBA) but also by the bonding configuration at the step edges. In step-flow growth, the latter effect might not be negligible, and the BCBA AlN domain can be formed at the step region.

Consequently, SMBs are generated at the boundaries of terrace region and step region, such as the "A" domain vs. the "C" domain as presented in Fig. 4.3. The initial stacking mismatches near the step edges might explain the surface undulations found for 1000°C growth. This problem did not become obvious in the case of on-axis SiC substrate, because the density of surface steps was much lower, and the spacing between steps was large compared to the case of the off-axis substrate.

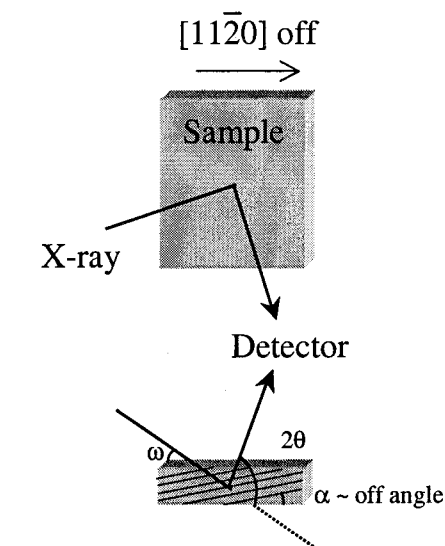
By lowering the growth temperature from 1000°C to 600°C, the surface morphology was remarkably improved. This is because the 2D nucleation mode became more dominant with the reduced diffusion length of adatoms. Therefore, to obtain high-quality AlN films on off-axis SiC substrates, the optimization of the growth temperature, i.e., control of the adatom diffusion length, is necessary.

4.4 Structural Quality of AlN Epilayers

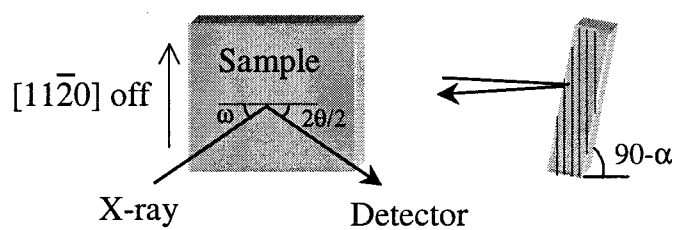
4.4.1 Dependence of Structural Quality on Growth Temperature

The structural quality of AlN films grown on 4H-SiC(0001) 8° off substrates was characterized by HRXRD. Two types of x-ray incidence geometries were performed, and a schematic figures are given in Fig. 4.4. An x-ray incidence geometry parallel to the $[11\bar{2}0]$ off direction is referred to as glancing incidence geometry, because the incident angle is approximately $2\theta/2 - \alpha$ (α : off-cut angle) [Fig. 4.4(a)]. On the other hand, an x-ray incidence geometry perpendicular to the $[11\bar{2}0]$ off direction is referred to as skew geometry due to the tilt (χ) from the off-cut angle [Fig. 4.4(b)].

Figure 4.5 represents HRXRD $2\theta/\omega$ scan profiles for (0002) diffraction. The measured films were grown at (a) 1000°C and (b) 600°C, and the thickness was approximately 50 nm. These profiles were taken in the skew geometry. It should be emphasized that owing to the Ga/HF/HCl treatment, the diffraction peaks could be clearly observed. Without appropriate substrate pretreatment, no diffraction peak for the (0002) plane could be detected for 50-nm-thick films, suggesting poor crystalline structure. The 2θ peak of the AlN film grown at 600°C was located at 35.85°, corresponding to the c -axis lattice constant of 5.006 Å. This value was relatively smaller than that of the 1000°C-grown film (4.995 Å calculated

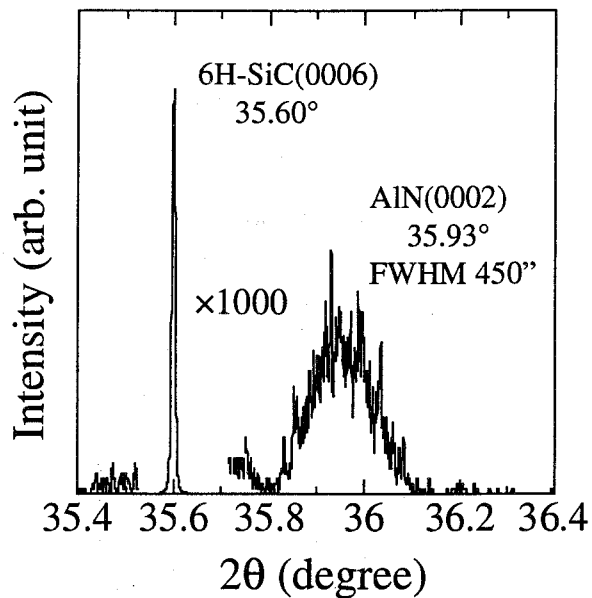


(a) Glancing incidence geometry
(x-ray // [11 $\bar{2}$ 0] off-cut direction)

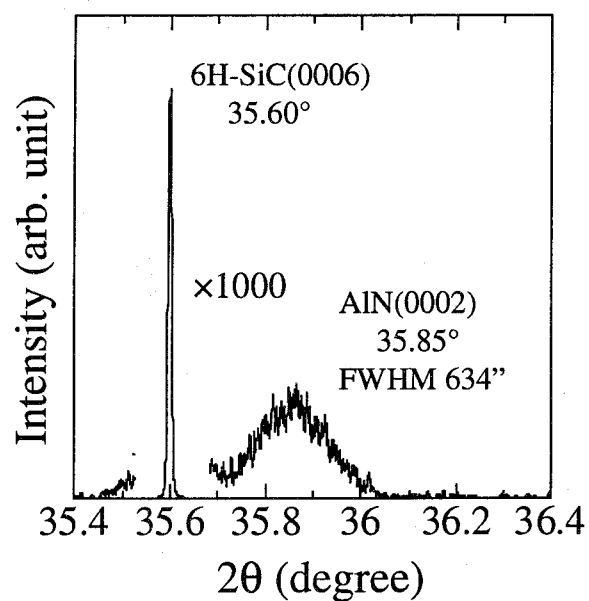


(b) Skew geometry
(x-ray $\perp$ [11 $\bar{2}$ 0] off-cut direction)

Figure 4.4: X-ray incidence geometries for HRXRD measurement: (a) x-ray parallel to [11 $\bar{2}$ 0] off-cut direction (glancing incidence geometry) and (b) x-ray perpendicular to [11 $\bar{2}$ 0] off-cut direction (skew geometry).



(a) 1000°C growth (53.1 nm)



(b) 600°C growth (43.9 nm)

Figure 4.5: HRXRD $2\theta/\omega$ scan profiles of (0002) diffraction for 50-nm-thick AlN films grown at (a) 1000°C and (b) 600°C.

from $2\theta \sim 35.93^\circ$). This result implies that the residual strain in the 600°C-grown film was larger due to the slower lattice relaxation.

The dependence of the c -axis lattice constant on the film thickness is shown in Fig. 4.6. As clearly seen, the lattice relaxation proceeded more slowly at lower growth temperatures. Langer and co-workers also reported that a lower growth temperature could force slower relaxation [22]. Slower lattice relaxation should suppress the generation of misfit dislocations, resulting in improved structural quality of the AlN films. In Fig. 4.6, the c -axis lattice constants of AlN films grown on on-axis substrates are superimposed as a dashed line. It was found that in comparison to on-axis substrates, the lattice relaxation on off-axis substrates proceeded very rapidly. Although it has not been elucidated in detail, the rapid relaxation might be correlated with defect formation at the step edges. Actually, King *et al.* suggested that defects formed at the AlN/SiC interface due to the presence of steps allow AlN films on off-axis substrates to relax more rapidly compared to films on on-axis substrates [23].

Figures 4.7(a) and (b) give ω scan curves of (0002) diffraction for 50-nm-thick films grown at 1000°C and 600°C, respectively. These profiles were also taken in the skew geometry. There was no noticeable difference between 1000°C and 600°C growth. Both curves had extremely small linewidths such as 60 arcsec, suggesting a low density of screw-type dislocations. Thus, regardless of the growth temperatures, the AlN films had excellent structural quality.

4.4.2 Influence of Off-Cut Angle on AlN Film Structure

AlN films grown on off-axis SiC substrates were revealed to have anisotropic crystalline structure. As described above, two types of x-ray incidence geometries were performed, glancing incidence geometry and skew geometry. Diffraction profiles for $2\theta/\omega$ scans were found to be strongly influenced by the geometry. A typical result is given in Fig. 4.8. The sample was a 280-nm-thick AlN film grown on a 4H-SiC(0001) 8° off substrate at 600°C. The diffraction profiles were taken in both the glancing incidence geometry (a),(b) and skew geometry (c). From the results in the glancing incidence geometry, it was revealed that the AlN growth axis was slightly misoriented toward the off-cut direction with respect to the c -axis of the 4H-SiC substrate, and the degree of misalignment ranged from 0.06° to 0.09° .

The orientation relationship between the AlN film and 4H-SiC substrate is shown schematically in Fig. 4.9. Here, the relations of 2θ and ω for AlN and SiC are as follow:

$$2\theta_{\text{SiC}}/2 = \omega_{\text{SiC}} + \alpha \quad (4.1)$$

$$2\theta_{\text{AlN}}/2 = \omega_{\text{SiC}} + \alpha - \beta, \quad (4.2)$$

where α is the off-cut angle of the 4H-SiC substrate ($\sim 8^\circ$), and β is the misorientation angle between the AlN growth axis and the c -axis of the 4H-SiC substrate. For all samples, β corresponded to $0.06 \sim 0.09^\circ$. Brault *et al.* also reported a 0.075° misorientation between

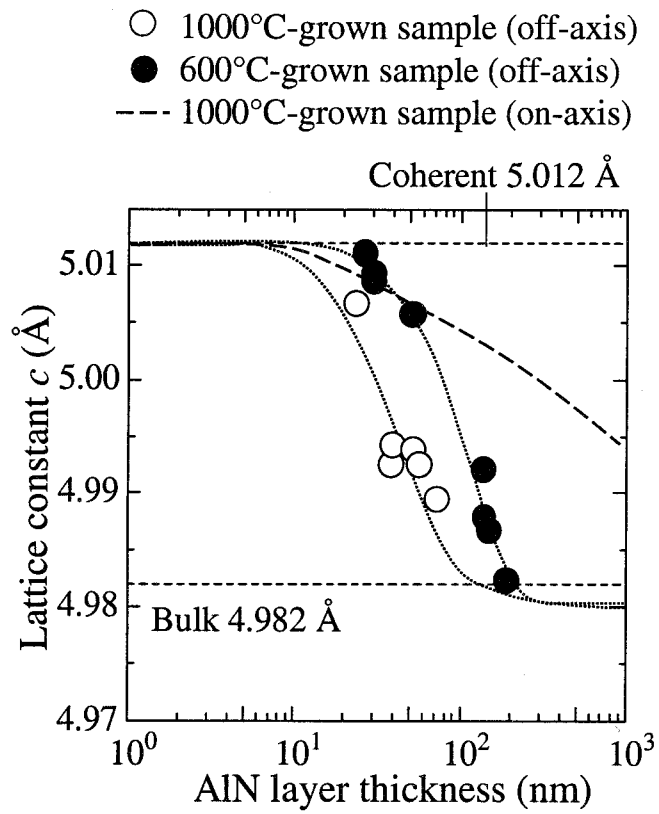
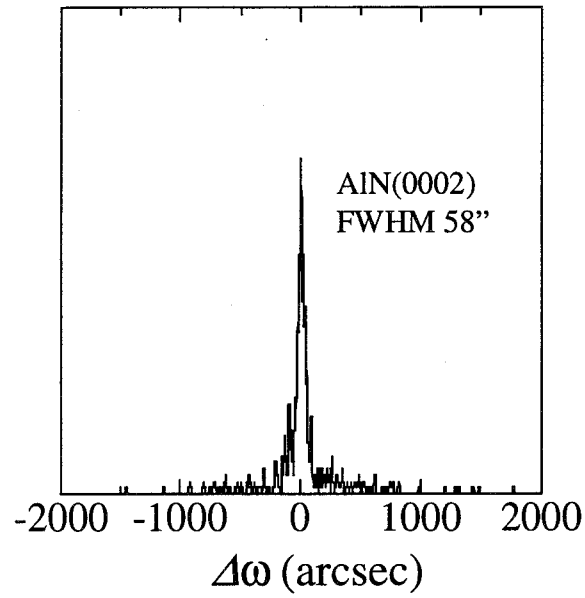
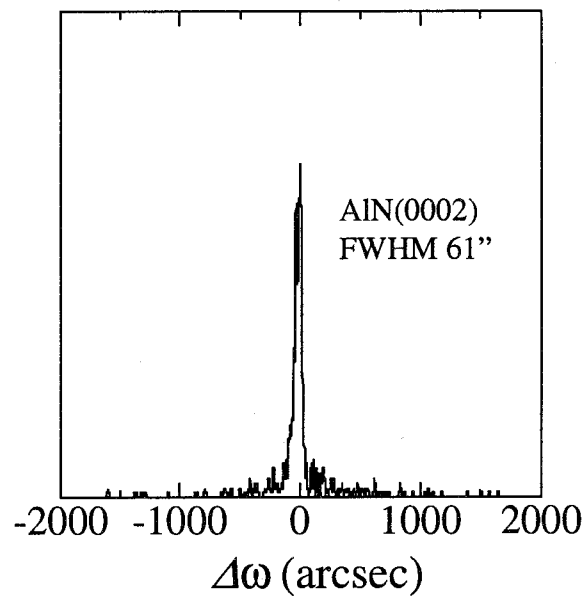


Figure 4.6: Film thickness dependence of c -axis lattice constant for AlN films grown at 1000°C and 600°C. Dashed line is for AlN films grown on on-axis substrates.



(a) 1000°C growth (53.1 nm)



(b) 600°C growth (43.9 nm)

Figure 4.7: HRXRD ω scan profiles of (0002) diffraction for 50-nm-thick AlN films grown at (a) 1000°C and (b) 600°C.

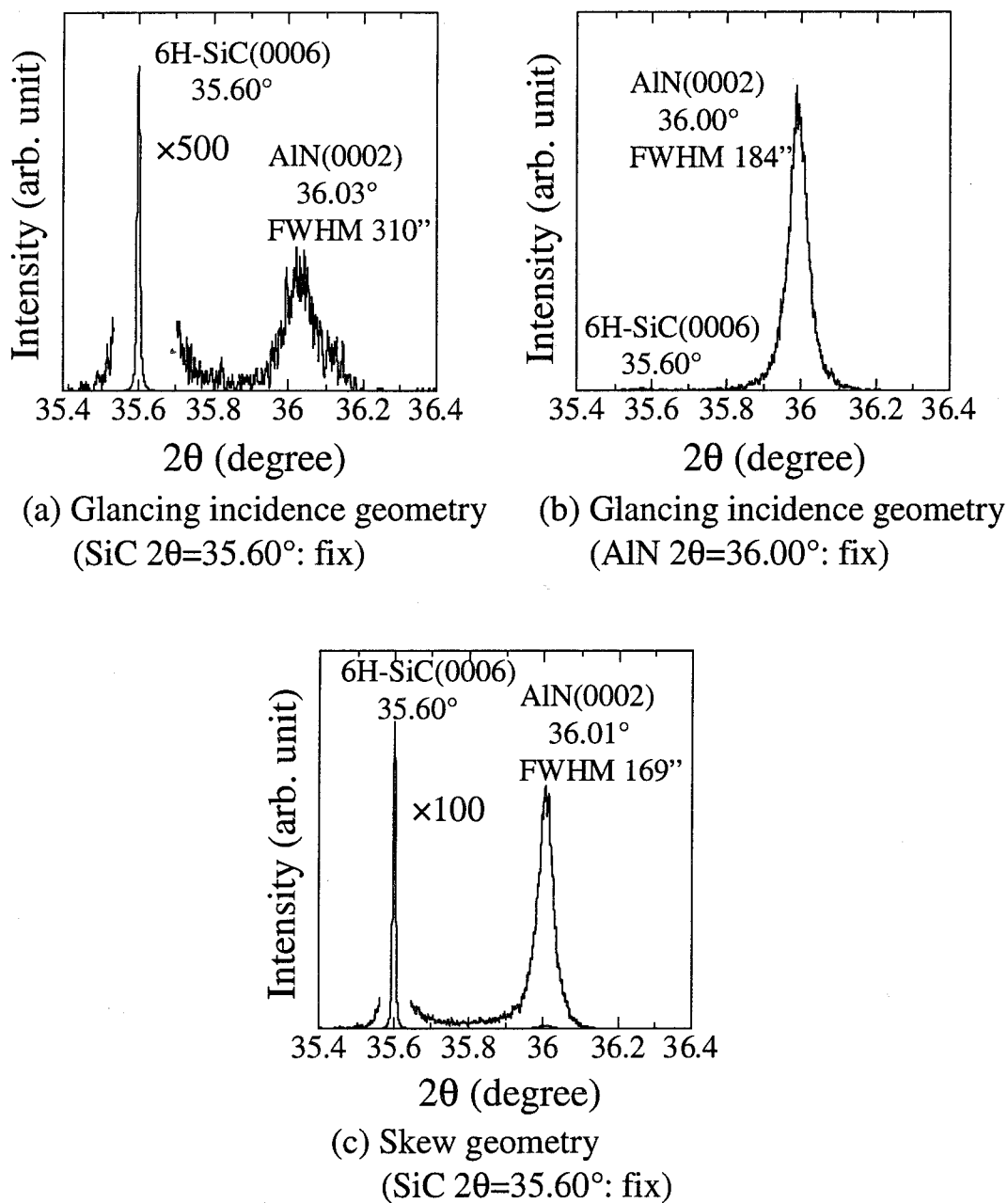


Figure 4.8: HRXRD $2\theta/\omega$ scan profiles of (0002) diffraction for 280-nm-thick AlN film in glancing incidence geometry (a),(b) and skew geometry (c).

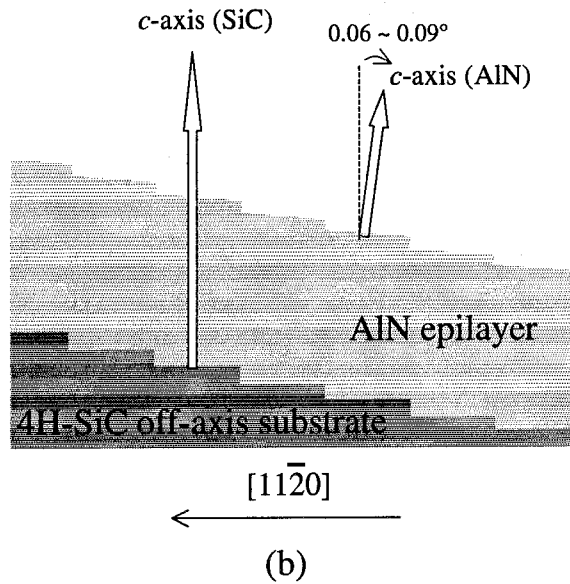
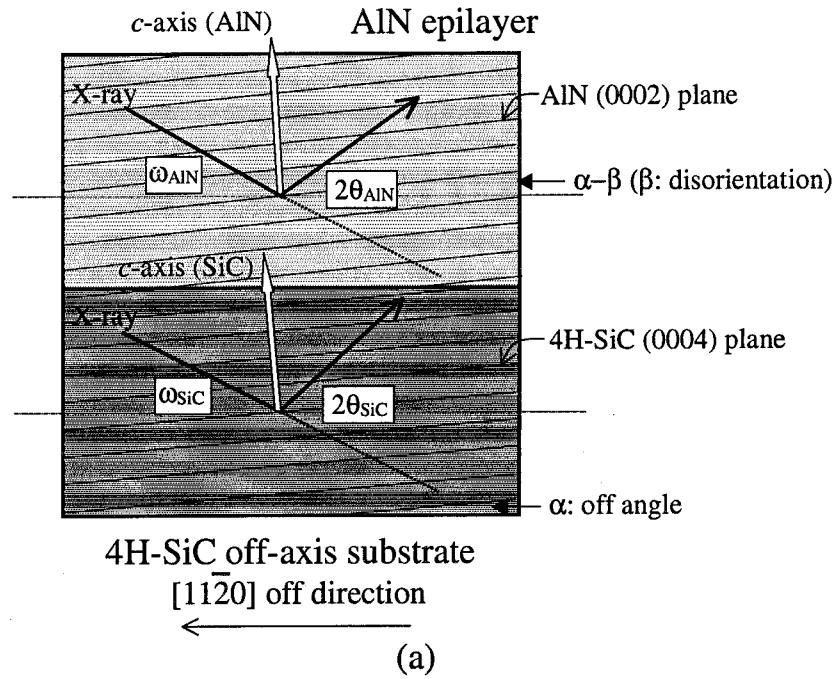


Figure 4.9: (a) Schematic diagram of c -axis disorientation of AlN epilayer toward off-cut direction with respect to c -axis of 4H-SiC substrate. (b) Orientation relationship between AlN film and 4H-SiC substrate.

the AlN growth axis ([0001] direction) and the [0001] axis of SiC substrate, though the off-cut angle of their substrates was 6.5° [12]. They described the slight misorientation of the AlN growth axis is an easy way: (i) to accommodate *c*-axis lattice differences at steps between AlN and SiC (misorientation of 0.088° is estimated for 8° off-cut angle), and/or (ii) to relax part of the in-plane lattice mismatch and thus to reduce the number of dislocations necessary to release the strain.

This slight misorientation between the AlN growth axis and the *c*-axis of SiC substrate is thought to be crucial, and the more rapid lattice relaxation was probably attributed to the larger misorientation of AlN film.

4.5 Dielectric Properties of AlN Epilayers

4.5.1 Band Offset of AlN/SiC Heterostructure

Several detailed studies concerning microstructures at the AlN/SiC interface and the physical defects formed therein have been conducted [24, 25], while relatively few works have been reported regarding the electronic structure of the interface. The valence band discontinuity at the AlN/SiC interface is a fundamental parameter needed to predict and model the electronic properties of the interface. King and co-workers have reported the detailed examination of valence band discontinuity (ΔE_V) at the interface between AlN and 6H-SiC(0001) by using XPS and ultraviolet photoelectron spectroscopy (UPS), and revealed relatively large variations in band offsets [23]. The valence band discontinuity was found to be strongly dependent on the number and types of bonds, i.e., Si-N and/or C-Al, formed at the interface, which was also suggested in the ZnSe/GaAs system [26].

The characterization method used in this work was similar to that of King *et al.* The basic scheme of this approach is to refer the valence band maximum (VBM) energy to a core level (CL) energy from AlN and SiC bulk samples, and then use the measured difference between the two core level energies from a junction between AlN and SiC to determine the discontinuity (see Fig. 4.10).

A thin AlN film (~ 2 nm) was deposited on a 6H-SiC 3.5° off substrate, and the difference between the substrate and epilayer core levels was measured, i.e., $(CL^{6H-SiC} - CL^{AlN})_{\text{interface}}$. As for the energy positions of CLs from 6H-SiC and AlN bulks $(VBM - CL)_{\text{bulk}}$, the reported values listed in Table 4.1 were used [23]. Here, the valence band discontinuity between the AlN epilayer and 6H-SiC substrate is given as (see Fig. 4.10):

$$\Delta E_V(\text{AlN/SiC}) = (CL - VBM)_{\text{bulk}}^{\text{SiC}} - (CL - VBM)_{\text{bulk}}^{\text{AlN}} - (CL^{\text{SiC}} - CL^{\text{AlN}})_{\text{interface}}. \quad (4.3)$$

Figure 4.11 represents XPS profiles for the 2-nm-thick AlN films grown on the 6H-SiC(0001) 3.5° off substrate and on-axis 6H-SiC(0001) substrate. For the off-axis sample (a), the value of Si 2*p* - Al 2*p* was approximately 27.2 eV. The difference between C 1*s* and N 1*s* spectra was about -114.0 eV. From these results, the valence band discontinuity was

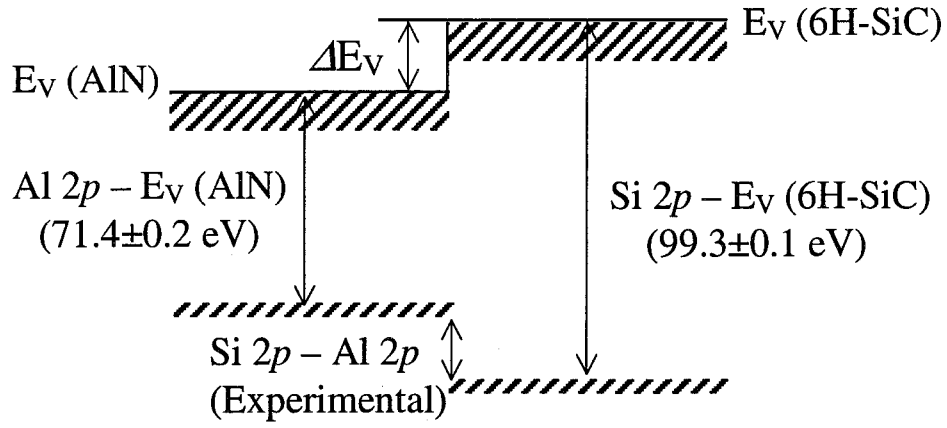
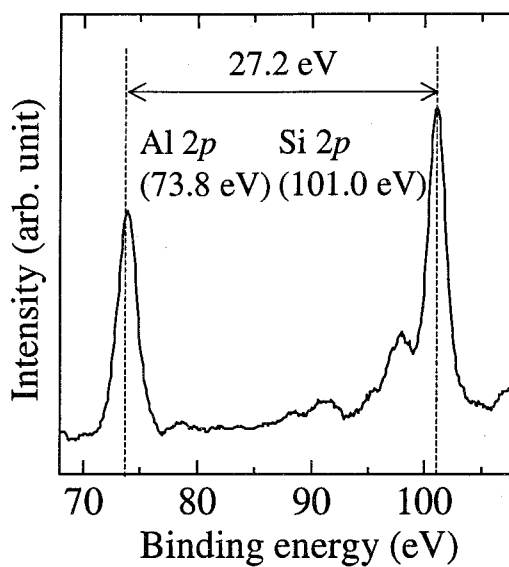


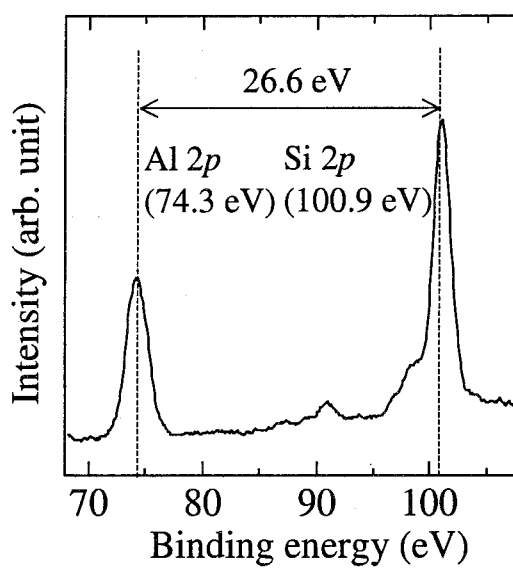
Figure 4.10: Method for calculating valence band discontinuity of AlN epilayer and SiC substrate.

Table 4.1: Si 2*p*, C 1*s*, Al 2*p*, and N 1*s* core levels referenced to SiC and AlN valence band maxima, respectively [23].

CL-VBM	
C1 <i>s</i> - VBM _{SiC}	281.3±0.1 eV
Si2 <i>p</i> - VBM _{SiC}	99.3±0.1 eV
Al2 <i>p</i> - VBM _{AlN}	71.4±0.2 eV
N1 <i>s</i> - VBM _{AlN}	394.7±0.2 eV



(a) AlN(2 nm) / 6H-SiC 3.5° off substrate



(b) AlN(2 nm) / on-axis 6H-SiC substrate

Figure 4.11: XPS spectra (Si 2p and Al 2p) for 2-nm-thick AlN films grown on (a) 6H-SiC(0001) 3.5° off substrate and (b) on-axis 6H-SiC(0001) substrate.

calculated to be 0.7 ± 0.3 eV, which is a small value compared to previous reports ($0.9 \sim 1.3$ eV) [23]. Accordingly, the conduction band discontinuity was deduced to be approximately 2.5 eV by taking the bandgaps of AlN and 6H-SiC to be 6.2 eV and 3.0 eV, respectively (see Fig. 4.12(a)).

The valence band discontinuity of AlN/on-axis 6H-SiC(0001) was found to be slightly larger compared to AlN/off-axis 6H-SiC, and estimated to be 1.0 ± 0.3 eV [Fig. 4.12(b)]. This value was quite similar to that reported by King *et al* [23].

The variation in band offset values is probably due to the different bonding configuration of interface atoms or atomic mixing at the interface. Therefore, the band offset is strongly dependent on the atomic termination or orientation of SiC surface. King *et al.*, however, pointed out that the variation of the valence band discontinuity for off-axis samples may be related to the nature and types of defects generated at the interface due to the presence of steps and strain relaxation [23]. These defects could influence the valence band discontinuity in two different ways: (i) they allow the AlN films grown on off-axis substrates to relax at a thickness less than for on-axis substrates; thus, the observed differences in the valence band discontinuity could be a result of strain. Or (ii) the defects generated at the interface could be charged, and therefore, help to neutralize/balance the charges formed at the (0001) interface due to the unbalanced C-Si-N-Al dipole which occurs along the [0001] direction. This explanation is similar to the cation/anion intermixing proposed by Ferrara and co-workers to neutralize the interface charges [27].

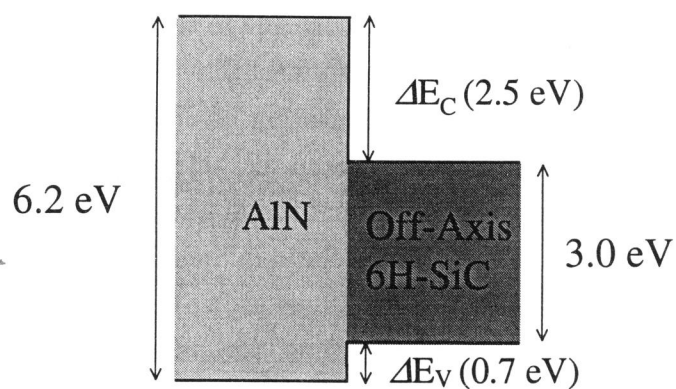
The obtained conduction band discontinuity of 2.0~2.5 eV at the AlN/6H-SiC interface is large enough for MIS device applications even though it is lower than that of 3.0 eV for SiO₂/6H-SiC [28]. The core levels of 4H-SiC are supposed to be equivalent to those of 6H-SiC, therefore, the band offset for AlN/4H-SiC is easily estimated using the bandgap of 3.2 eV for 4H-SiC [29, 30].

4.5.2 Insulating Characteristics of MIS structures

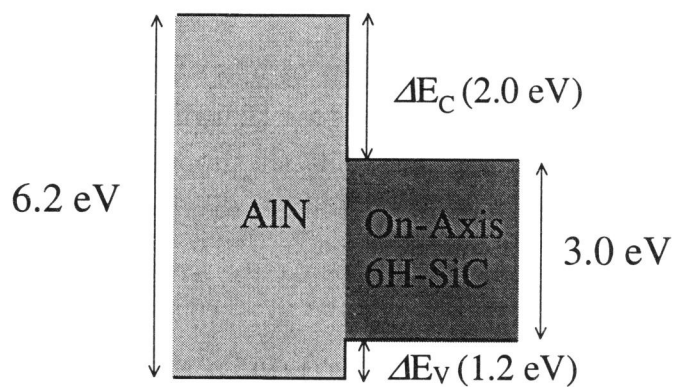
To apply an AlN film as a gate insulator for MIS devices, insulating characteristics of the MIS structures, e.g. leakage current or breakdown field, are significant. The study on MISFETs utilizing the AlN/SiC interface ¹ was reported by Zetterling *et al.*, and showed poor device characteristics due to the large gate leakage current, and noted that the dielectric properties of the AlN gate insulator were crucial for MIS device applications [31].

The dielectric properties of AlN films grown on 6H-SiC(0001) 3.5° off substrates were investigated by using aluminum/AlN/ n^+ -type 6H-SiC MIS structures. 100-nm-thick circular aluminum electrodes (150 μ m in diameter) were deposited on AlN surfaces by vacuum evaporation through a metal mask. Blanket deposition of aluminum was made on the backside of substrate to form a large area ohmic contact. Figure 4.13(a) displays the result of I - V

¹As far as the author knows, this study is the only report on the fabrication and device characteristics of MISFETs utilizing the AlN/SiC interface.

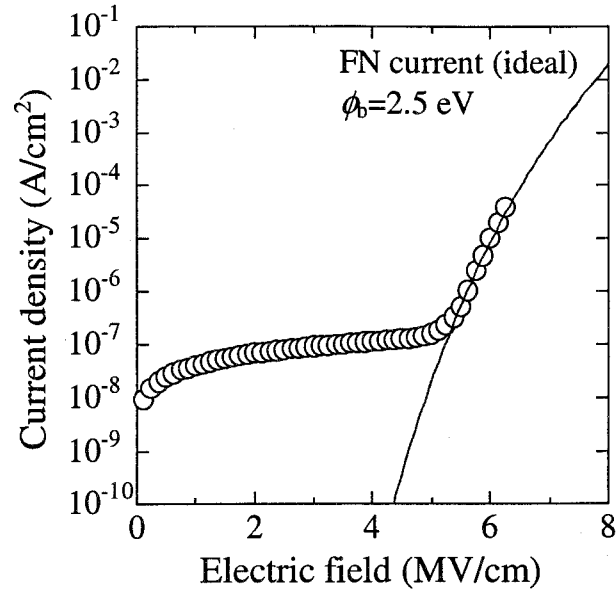


(a) AlN/6H-SiC 3.5° off substrate

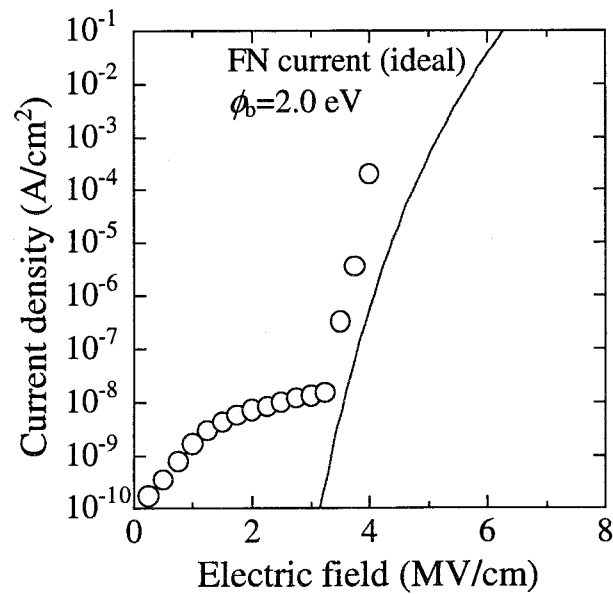


(b) AlN/on-axis 6H-SiC substrate

Figure 4.12: Band diagrams for AlN/6H-SiC(0001) heterostructures: (a) 3.5° off-axis and (b) on-axis.



(a) AlN (25 nm) / 6H-SiC 3.5° off substrate



(b) AlN (25 nm) / on-axis 6H-SiC substrate

Figure 4.13: Insulating characteristics for 25-nm-thick AlN films grown on (a) 6H-SiC(0001) 3.5° off substrate and (b) on-axis 6H-SiC(0001) substrate.

measurement for a 25-nm-thick AlN film grown on a 6H-SiC(0001) 3.5° off substrate. The bias direction was in accumulation mode, i.e., the aluminum circular electrode was biased to positive. The electric field applied to the AlN film was calculated by dividing the applied voltage by the film thickness. Leakage current in the opposite bias direction was smaller than in the accumulation mode.

The insulating characteristics shown in Fig. 4.13(a) were satisfactory for MIS device applications. The resistivity and leakage current density in a low electric field (< 3 MV/cm) were 10^{13} $\Omega\cdot\text{cm}$ and 10^{-8} A/cm², respectively. The ideal curve of Fowler-Nordheim (FN) tunneling current is superimposed in Fig. 4.13(a) using the conduction band discontinuity of 2.5 eV, which was estimated by the XPS measurements. For a relatively high-quality insulator with a low defect density, the FN tunneling current can be observed in a high electric field. The FN tunneling current is expressed as [32]:

$$J_{\text{FN}} = \frac{e^2 m^* E_{\text{AlN}}^2}{8\pi \phi_b m_0} \exp\left(-\frac{8\pi \sqrt{(2em^*)} \phi_b^3}{3hE_{\text{AlN}}}\right), \quad (4.4)$$

where ϕ_b is the barrier height, i.e., the conduction band discontinuity ΔE_C at the AlN/6H-SiC interface, and m^* is the effective electron mass ($0.4m_0$) in AlN [33]. Since the J - E curve beyond 5 MV/cm was quite similar to the ideal curve of FN tunneling current, the observed leakage current in a high electric field might be caused by FN tunneling. Figure 4.13(b) exhibits the J - E characteristics for a 25-nm-thick AlN film grown on an on-axis 6H-SiC(0001) substrate. The leakage current density was as low as 10^{-9} A/cm² below 2 MV/cm, and the resistivity was as high as $10^{13} \sim 10^{14}$ $\Omega\cdot\text{cm}$. Compared to the off-axis sample, the leakage current density was one order of magnitude lower, probably attributed to the lower defect density in the on-axis sample. The measured curve for the on-axis sample was also similar to the ideal curve of FN tunneling current where the barrier height (ϕ_b) of 2.0 eV was applied from the result of XPS measurements. These J - E characteristics also support the variations of band offset between the on-axis and off-axis samples. It should be emphasized that superior crystalline quality of the AlN film leads to excellent dielectric properties. Previous studies reported poor insulating characteristics due to the considerably high defect density in AlN films [34]. The very low breakdown field was exhibited due to the Poole-Frenkel (PF) emission related to defects in the insulator, where $J \propto \exp(E^{1/2})$ [35]. Therefore, improvement in the crystalline quality of AlN epilayers is necessary to achieve highly-insulating properties for practical use.

According to Fukuda *et al.*, in the case of the SiO₂/SiC MOS structure, the current density is almost constant below approximately 6 MV/cm, and then increases rapidly above 6 MV/cm due to FN tunneling, resulting in dielectric breakdown around 10 MV/cm [34]. The SiO₂ yielded by thermal oxidation of SiC has excellent dielectric properties due to the large conduction band discontinuity of 3.0 eV [28]. However, the relative dielectric constant of SiO₂ is low ($\epsilon_{\text{SiO}_2} = 3.9$) compared to that of AlN ($\epsilon_{\text{AlN}} = 8.5$, 2.2 times higher than ϵ_{SiO_2}). It indicates that the channel carriers can be induced in the AlN/SiC interface at a

lower electric field compared to the SiO₂/SiC interface [36]. Therefore, insulators with high dielectric constants are very advantageous for MIS device applications. In Fig. 4.13(a), the breakdown field was more than 6 MV/cm, which corresponded to 13 MV/cm in SiO₂ by Gauss's law:

$$\epsilon_{\text{AlN}} E_{\text{AlN}} = \epsilon_{\text{SiO}_2} E_{\text{SiO}_2}. \quad (4.5)$$

These results suggest that AlN films had sufficient dielectric properties comparable to those of the commonly-used SiO₂.

Thus, it was demonstrated that AlN with sufficiently low defect density is a promising dielectric material, and the obtained results suggest the successful application of AlN as an insulator for SiC MIS devices. To achieve highly-insulating characteristics reproducibly, further improvements in the crystalline quality of AlN film are necessary. Besides misfit dislocations due to the lattice relaxation, the AlN films grown on off-axis SiC substrates also contained many defects originating at step sites on the SiC surface [37]. Hence, it was found difficult to achieve sufficient insulating characteristics compared to AlN films grown on on-axis SiC substrates. Reducing such defects by any means is essential to improve the dielectric properties of AlN films.

4.6 Interface Characteristics of AlN/SiC Heterostructure

4.6.1 Atomic Arrangement at AlN/SiC Interface

For nonisovalent (heterovalent) heterojunctions such as AlN/SiC (III-V/IV-IV), abrupt polar interfaces would be characterized by the occurrence of either oversaturated or undersaturated bonds [10]. It is well known that ideal, abrupt polar interfaces between heterovalent semiconductors suffer from instability problems, as first pointed out by Harrison *et al* [38]. Indeed, if one calculates the electrostatic potential as a function of position along the growth direction, it is found that charge accumulation or depletion at the ideal interface gives rise to a nonzero average electric field that extends throughout the overlayers. Such an electric field could be supported in thin overlayers, but would cause the system to become unstable once the overlayer exceeded a certain thickness. Harrison *et al.* and Stirman *et al.* suggested that charge accumulation or depletion at the interface could be avoided by introducing some measure of atomic mixing in such a way as to compensate III-V and IV-IV bonds [38, 39].

Ponce *et al.* concluded from the results of cross-sectional HRTEM studies that the most favorable atomic arrangements at the abrupt interface between AlN and silicon-terminated SiC(0001) are the intermixed configurations of Si-N and Al-C bonds, which produce no significant changes in the Si-C or Al-N backbond lengths [40]. The image contrast and interplanar distances corresponding to C-N and Al-Si bonds were not observed in their HRTEM studies.

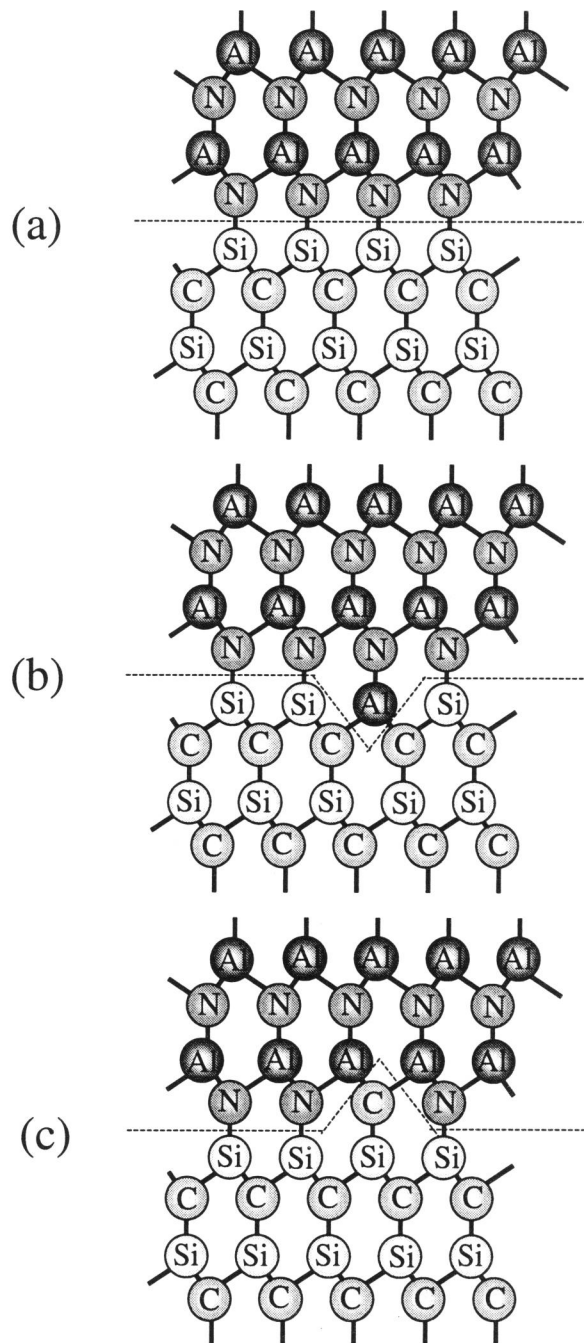
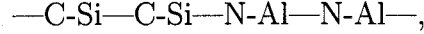


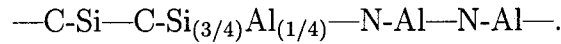
Figure 4.14: Possible atomic arrangements for AlN/SiC interface with (0001) oriented epilayer and substrate.

The possible bonding configurations at the AlN/SiC interface are restricted by the requirement of local charge neutrality. For example, consider the abrupt interface between AlN and SiC(0001), as indicated schematically below (see Fig. 4.14(a)),

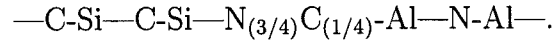


where the interface occurs between silicon and nitrogen layers. (In this notation, the long dash represents the bonds between the widely spaced layers, and the short dash represents the bonds between the closely spaced layers.) Each nitrogen atom contributes $5/4$ of an electron to its bond with silicon, while the silicon atom contributes one electron to this bond. Therefore, there is a local charge excess at the interface of $1/4$ electron per bonds, and so this abrupt interface is not stable.

This charge excess can be relieved by replacing one out of every four silicon atoms with aluminum as shown in the following (see Fig. 4.14(b)):



The aluminum atoms act as acceptors residing on the silicon sublattice of SiC. Alternatively, we could replace one out of four nitrogen atoms with a carbon as shown in the following (see Fig. 4.14(c)):



In this case, the carbon atoms act as acceptors residing on the nitrogen sublattice of AlN.

It should be emphasized that Harrison's arguments for intermixing apply only in the case of thick overlayers [38]; for overlayers which are only a few atomic layers thick, an abrupt (unstable) interface is possible, in principle.

4.6.2 Interface Control in AlN Growth

In contrast to amorphous SiO₂ formed by thermal oxidation of SiC, AlN grown by MBE or other growth methods at high temperatures is commonly a single crystal. The interface between single crystalline AlN and SiC is expected to be superior to the SiO₂/SiC interface because the lattice mismatch of AlN/SiC is as small as 0.9% for the (0001) basal planes (SiO₂/SiC ~ 5%). Unsaturated dangling bonds due to the lattice mismatch are thought to cause electronically-active traps at the interface [41]. Several detailed studies concerning microstructures at the AlN/SiC interface and the physical defects formed therein have been conducted [24, 25], while relatively few works have been reported regarding the electronic structures of the interface.

Tin and co-workers have studied the interface characteristics of MOVPE-grown AlN and 6H-SiC(0001) for MIS device applications [6]. The dependences of the electrical characteristics of MIS structures on the growth conditions were systematically investigated. Their

results demonstrated that the electronic properties of the AlN/SiC interface are very sensitive to variations in the growth procedure. Since interface traps are the product of surface reactions during the initial stages of growth, their number can be controlled by varying the growth procedure. AlN/6H-SiC samples grown directly (without any buffer layers) at a high temperature of 1250°C had the most remarkable C - V characteristics showing low interface state density. They described that the presence of a single crystalline AlN epilayer at the interface helped to reduce the number of interface states. On the contrary, samples grown at a low temperature of 650°C exhibited inferior C - V characteristics. Although the growth procedure utilizing a low-temperature buffer layer has been widely applied in the growth of AlN on SiC, it was obvious that this procedure could not produce an interface with a low interface state density. According to Tin *et al.*, incomplete crystallization of the AlN buffer layer at the interface could contribute to the increased interface state density and interfacial defects [6].

Thus, their results demonstrated that depending on the growth procedure (i.e., growth temperature), the electrical characteristics of MIS structures are remarkably changed. However, they have not discussed the interface structure between AlN and SiC in detail, which is closely correlated with the electronic properties of the interface. Since the AlN/SiC heterostructure is a heterovalent system, the interface bonding configuration probably affects the electronic situation, such as charge accumulation or depletion at the interface.

As Harrison *et al.* pointed out, the instability problems at the interface could be avoided by introducing some measure of atomic mixing in such a way as to compensate III-V and IV-IV bonds [38]. MBE, employed in this work, is a suitable growth method to manipulate the interface structure between AlN and SiC owing to its atomic-scale controllability. In this study, control of the atomic arrangement at the AlN/SiC interface, i.e., artificial manipulation of the interface bonding configuration, was investigated to achieve MIS structures with excellent electrical characteristics.

4.6.3 Pre-Irradiation by Active Nitrogen

As a method to manipulate the interface structure between AlN and SiC, initial growth procedures should be studied in detail. One viable approach is to control surface superstructures by using various adatoms. For instance, a surface structure with carbon adatoms bonded to the uppermost silicon atoms of SiC substrate can compensate III-V and IV-IV bonds at the AlN/SiC interface as schematically presented in Fig. 4.15. Another approach is the control of initial growth sequence, i.e., pre-irradiation by one source flux, which can vary the composition of interface bonds. So far in this work, AlN growth was initiated by simultaneously supplying aluminum and nitrogen species. As for the crystalline quality of AlN epilayers, there were no obvious effects of such pre-irradiation. Up to date, there have been no reports on approaches to manipulate the interface structure between AlN and SiC, and correlations between the interface bonding configuration and interface characteristics

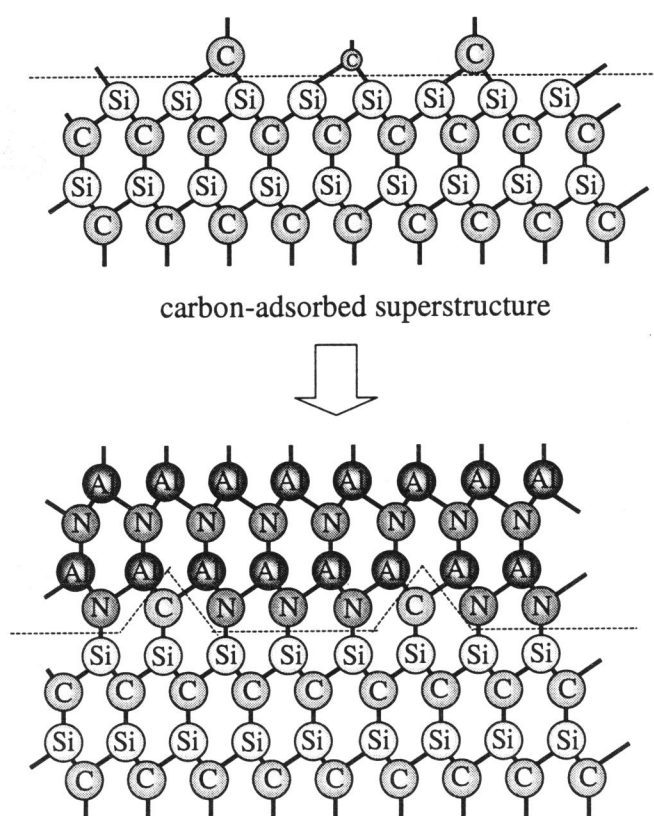


Figure 4.15: Schematic model of atomic mixing at AlN/SiC interface by control of SiC surface superstructure.

have not been understood in detail.

In this work, pre-irradiation by atomic-nitrogen (N^*) was introduced as a method for interface control, and the effects on electronic properties of the AlN/SiC interface were investigated by means of C - V measurements. AlN growth was carried out at 600°C by initiating atomic-nitrogen pre-irradiation for 1 min. AlN films were grown on n-type 4H-SiC(0001)_{Si} 8° off epilayers ($8\text{ }\mu\text{m}$ in thickness). The doping level of the SiC epilayer was approximately $1 \times 10^{16}\text{ cm}^{-3}$. The whole growth procedure except for the pre-irradiation was same as described above.

The influence of atomic-nitrogen irradiation on the chemical structure of 4H-SiC surface was characterized by *in situ* XPS. In this measurement, photoelectrons emitted from the sample surface were collected at the take-off angle of 60° with respect to the surface normal for the sake of more sensitive analysis of surface chemical structure. Figure 4.16 gives the Si 2*p*, C 1*s* and N 1*s* spectra for the 4H-SiC surface without atomic-nitrogen irradiation. The sample was loaded into the XPS chamber through the ultra-high vacuum transfer tunnel after the pretreatment of the 4H-SiC surface in the MBE growth chamber performing all steps except atomic-nitrogen irradiation. The detected peaks were only silicon and carbon-related ones, indicative of no residual oxygen atoms on the surface. The Si 2*p* peak was located at 100.6 eV, corresponding to silicon bonded to carbon atoms [Fig. 4.16(a)] [42]. Although peak deconvolution of the Si 2*p* spectrum was attempted, no other components were distinguished, suggesting that the surface consisted of Si-C bonds. The same result was obtained from the C 1*s* spectrum ($\sim 283.3\text{ eV}$) [Fig. 4.16(b)]. Obviously no signals from nitrogen atoms were detected for the 4H-SiC surface before atomic-nitrogen irradiation [Fig. 4.16(c)].

The Si 2*p*, C 1*s* and N 1*s* spectra for the 4H-SiC surface with atomic-nitrogen irradiation are displayed in Figs. 4.17(a), (b) and (c), respectively. In this case, peak deconvolution of the Si 2*p* spectrum revealed that there were two types of bonds, i.e., Si-C bond (100.6 eV) and Si-N bond (101.6 eV). The existence of Si-N bonds could be also confirmed by the N 1*s* peak evident at 397.5 eV.

Thus, atomic-nitrogen irradiation is thought to form Si-N bonds on the 4H-SiC surface. Therefore, by the pre-irradiation just before AlN growth, the interface structure composed of many S-N bonds is intentionally formed.

4.6.4 Impact of Interface Control on Electronic Properties

The electronic properties of the AlN/SiC interface were investigated using Al/AlN/4H-SiC MIS structures. The C - V characteristics for samples with and without pre-irradiation by atomic-nitrogen were compared to examine the effects of interface control. Figure 4.18 represents high-frequency (1 MHz) C - V curves at room temperature for the samples without the pre-irradiation. The C - V characteristics for all the samples were far from the ideal ones, and exhibited positive flat-band shifts, which originated from negative charges at the

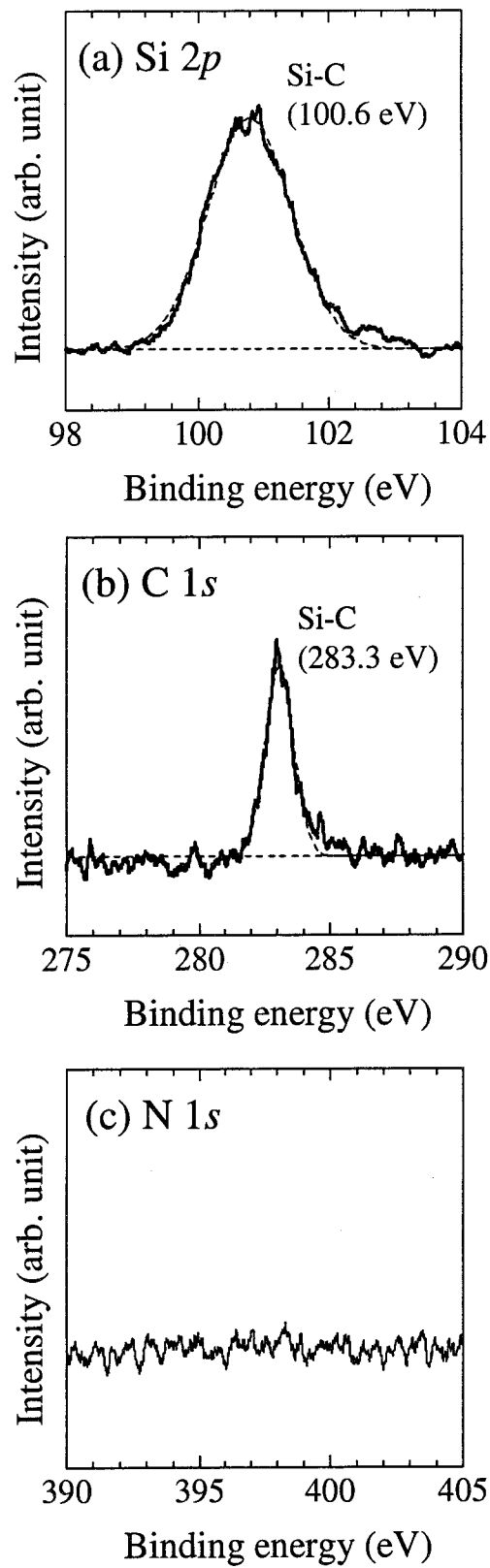


Figure 4.16: XPS spectra for 4H-SiC(0001) surface without atomic-nitrogen irradiation: (a) Si 2p, (b) C 1s, and (c) N 1s.

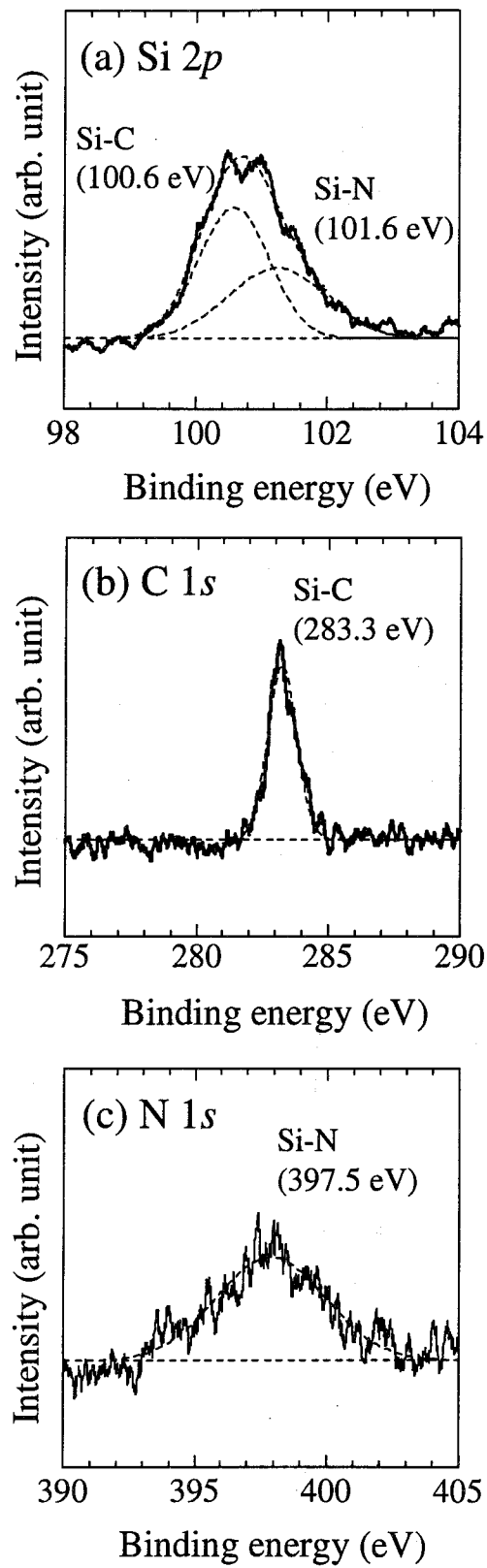
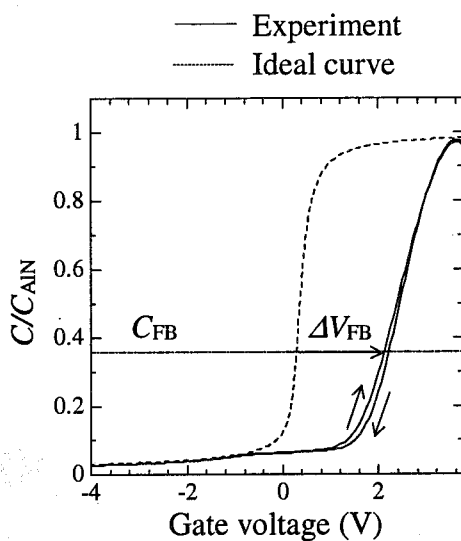
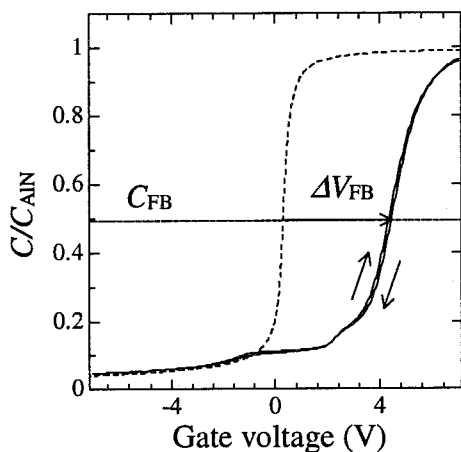


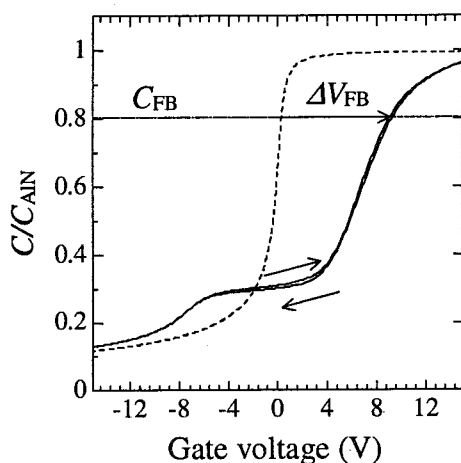
Figure 4.17: XPS spectra for 4H-SiC(0001) surface treated by atomic-nitrogen irradiation: (a) Si 2p, (b) C 1s, and (c) N 1s.



(a) AlN thickness 11.6 nm



(b) AlN thickness 33.3 nm



(c) AlN thickness 60.4 nm

Figure 4.18: High-frequency (1 MHz) C - V characteristics for Al/AlN/4H-SiC(0001) 8° off MIS structures without atomic-nitrogen pre-irradiation.

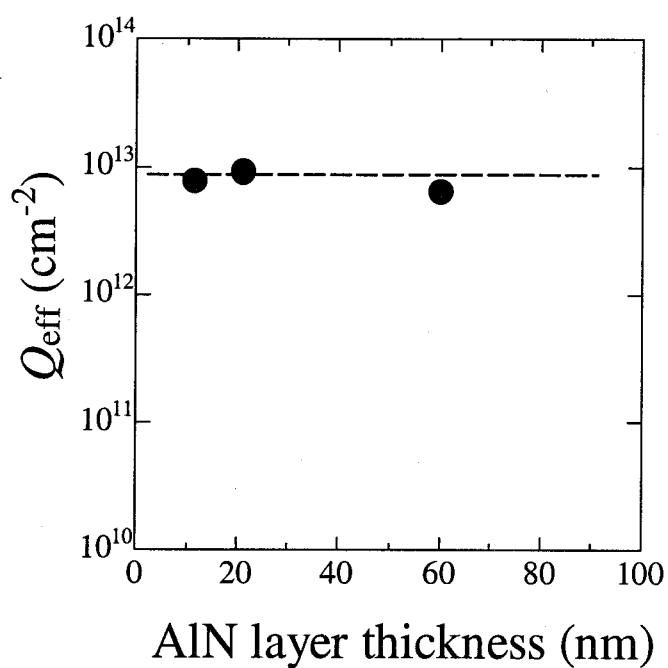


Figure 4.19: Dependence of fixed charge density on AlN thickness (without atomic-nitrogen pre-irradiation).

interface. These fixed charges were probably induced in the interface during the initial stages of growth. The dependence of the fixed charge density on the AlN thickness is given in Fig. 4.19. The fixed charge density (Q_{fixed}) was calculated from the following equation:

$$Q_{\text{fixed}} = -\frac{C_{\text{AlN}}\Delta V_{\text{fb}}}{q}, \quad (4.6)$$

where C_{AlN} is the capacitance of AlN film and ΔV_{fb} is the flat-band-shift voltage. As clearly shown in Fig. 4.19, the density was almost constant, and relatively high, approximately $8 \times 10^{12} \text{ cm}^{-2}$.

As Harrison *et al.* pointed out, such unstable interface structures would be sustained until the overlayer exceeds a certain thickness [38]. Therefore, the negative interface charges are thought to remain at the interface with the AlN thickness less than 60 nm.

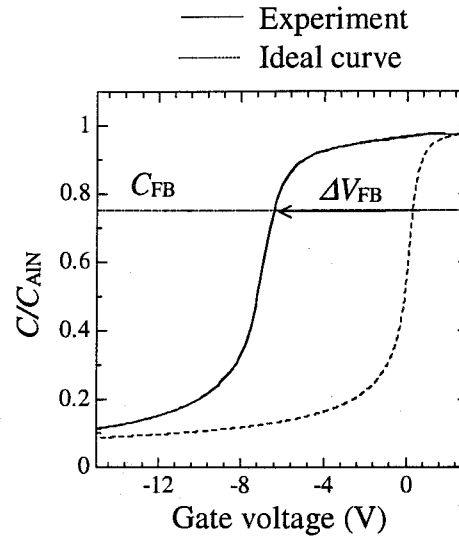
The electronic properties of the AlN/4H-SiC interface changed dramatically with atomic-nitrogen pre-irradiation. Figure 4.20 presents high-frequency C - V characteristics for the samples with the pre-irradiation. For interfaces treated by the pre-irradiation, all the C - V curves exhibited negative flat-band shifts in contrast to interfaces without pre-irradiation. In this case, positive charges were induced in the interface. These fixed charges are thought to be the products of surface reactions during the initial stages of growth.

It is very complicated to elucidate the origin of interface fixed charges. To make this clear, further studies on the mechanism to induce the interface charges are necessary.

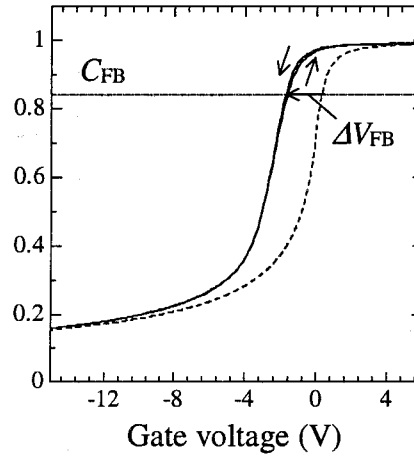
The dependence of fixed charge density on the AlN thickness is shown in Fig. 4.21. It should be emphasized that the fixed charge density reduced remarkably with increasing AlN thickness over 100 nm (from $7 \times 10^{12} \text{ cm}^{-2}$ to $1 \times 10^{11} \text{ cm}^{-2}$). Although the explicit reason for this reduction has not been elucidated yet, it might be attributed to atomic mixing at the interface.

Now, the driving forces to give rise to such intermixing at the AlN/SiC interface are discussed. In our speculation, the reduction of interface charges might be correlated with the lattice relaxation in AlN growth. Figure 4.22 shows the relationship between the lattice relaxation and interface charge density. With increasing AlN thickness, (i) in-plane compressive lattice strain is relaxed, and (ii) misfit dislocations are generated. As for the former, the effect of piezo polarization should be taken into account. In Al-polar AlN films under compressive strain, negative fixed charges are induced at the bottom of the AlN films by the piezoelectric field (E_{pe}). With decreasing the residual strain due to the lattice relaxation, those fixed charges are reduced accordingly (see Fig. 4.23). However, this effect would contradict the results obtained by the C - V measurements, which exhibited the reduction of positive interface charges with increasing AlN thickness.

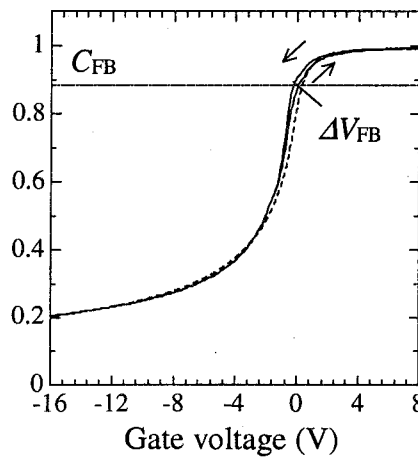
Therefore, generation of misfit dislocations is a more likely explanation for intermixing at the AlN/SiC interface. If misfit dislocations or related defects work as electronically-active traps [41], then they would compensate the positive charges, and neutralize or balance the electronic condition at the interface. However, the C - V curve shown in Fig. 4.20(c) was quite similar to the ideal curve, indicative of excellent interface properties and a low density



(a) AlN thickness 45.0 nm



(b) AlN thickness 142.3 nm



(c) AlN thickness 185.0 nm

Figure 4.20: High-frequency (1 MHz) C - V characteristics for Al/AlN/4H-SiC(0001) 8° off MIS structures with atomic-nitrogen pre-irradiation.

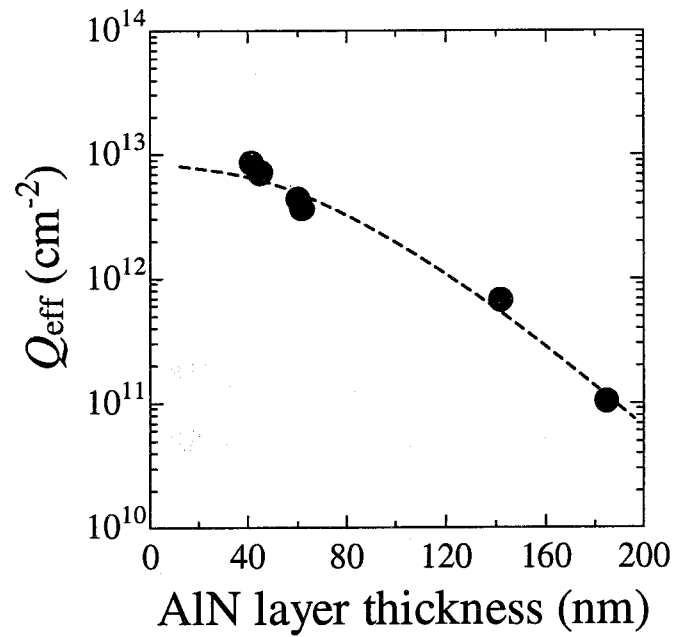


Figure 4.21: Dependence of fixed charge density on AlN thickness (with atomic-nitrogen pre-irradiation).

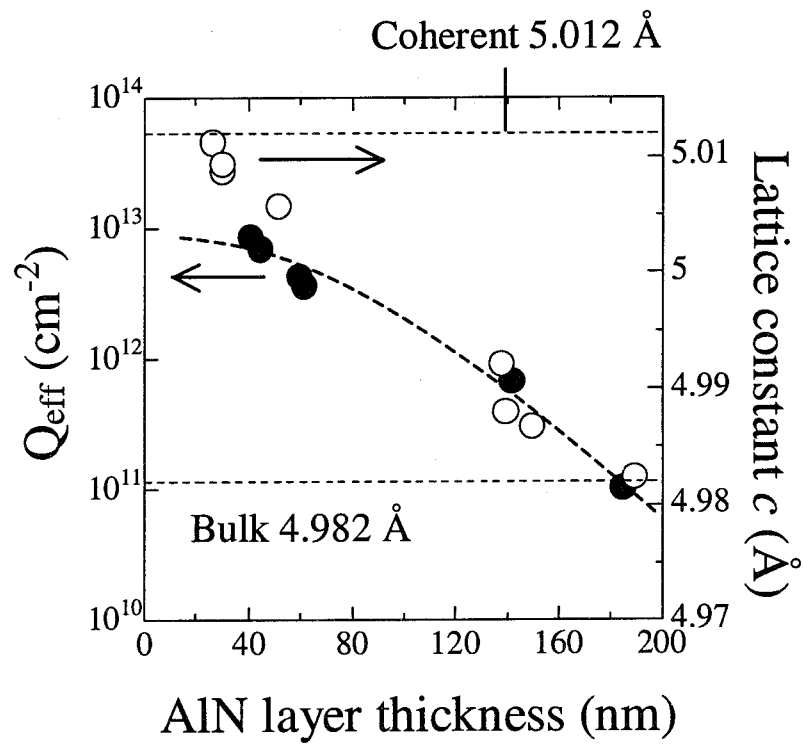


Figure 4.22: Relationship between lattice relaxation and interface charge density.

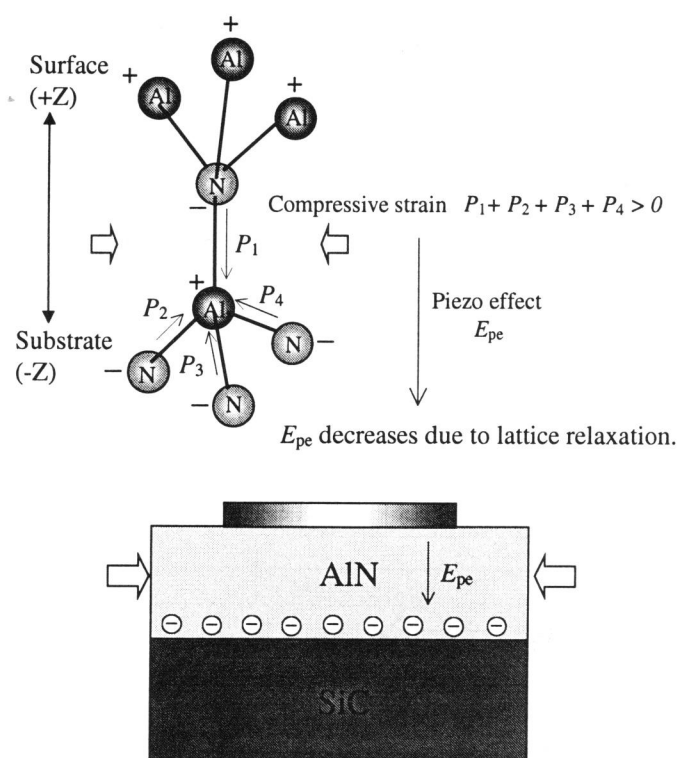


Figure 4.23: Influence of piezo polarization on fixed charges at AlN/SiC interface.

of interface traps. Therefore, further investigations concerning the atomic mixing at the AlN/SiC interface should be performed.

Figure 4.24 presents the energy distribution of the interface state density for AlN/4H-SiC(0001) interfaces estimated by the Terman method. The interface state density (D_{it}) was revealed to be strongly influenced by atomic-nitrogen pre-irradiation. The sample treated by the pre-irradiation had a considerably small interface state density. For the 185-nm-thick AlN films treated by the pre-irradiation, the interface state density was noticeably small, such as $3 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ at $E_{C(4H-SiC)} - 0.2 \text{ eV}$. On the other hand, the interface without the pre-irradiation had relatively high interface state density ($\sim 5 \times 10^{12} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ at $E_{C(4H-SiC)} - 0.2 \text{ eV}$). These results evidently indicate that the pre-irradiation is very effective to reduce the interface state density. Since the interface state density for conventional SiO₂/4H-SiC MOS interfaces is more than $10^{12} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ at $E_{C(4H-SiC)} - 0.2 \text{ eV}$ [29], the AlN/4H-SiC interfaces treated by the pre-irradiation might have superior interface characteristics.

It is worth noting that interface control (i.e. artificial manipulation of interface bonding configuration) strongly affects the electronic properties of the AlN/SiC interface. The results obtained in this work demonstrated that AlN is a promising candidate as an insulator for SiC MIS devices.

4.7 Summary

Remarkable improvement in surface morphologies was obtained by lowering the growth temperature from 1000°C to 600°C, probably due to modification of the initial growth kinetics. A slight misorientation between the AlN growth axis and the *c*-axis of the SiC substrate was found, resulting in more rapid lattice relaxation compared to on-axis substrates.

The conduction band discontinuity of 2.0~2.5 eV for AlN/6H-SiC, which was characterized by XPS, is large enough for MIS device applications. The *J-E* characteristics also supported this estimate of the band offset, and demonstrated that the AlN of low defect density is a promising dielectric material for SiC MIS devices. Although it is lower than 3.0 eV for SiO₂/6H-SiC, the relative dielectric constant of AlN ($\epsilon_{\text{AlN}} = 8.5$) is 2.2 times higher than SiO₂ ($\epsilon_{\text{SiO}_2} = 3.9$), indicating that more channel carriers are induced at the AlN/SiC interface for a same applied electric field.

Control of the atomic arrangement at the AlN/SiC interface, i.e., artificial manipulation of the interface bonding configuration, was investigated to achieve MIS structures with excellent electronic properties. The electronic properties of the AlN/4H-SiC interface changed dramatically with pre-irradiation by atomic nitrogen. Since interface traps are the product of surface reactions during the initial stages of growth, their number can be controlled by varying the growth procedure. Owing to pre-irradiation, a quite small interface state density was obtained, $3 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ at $E_{C(4H-SiC)} - 0.2 \text{ eV}$. Therefore, the obtained results

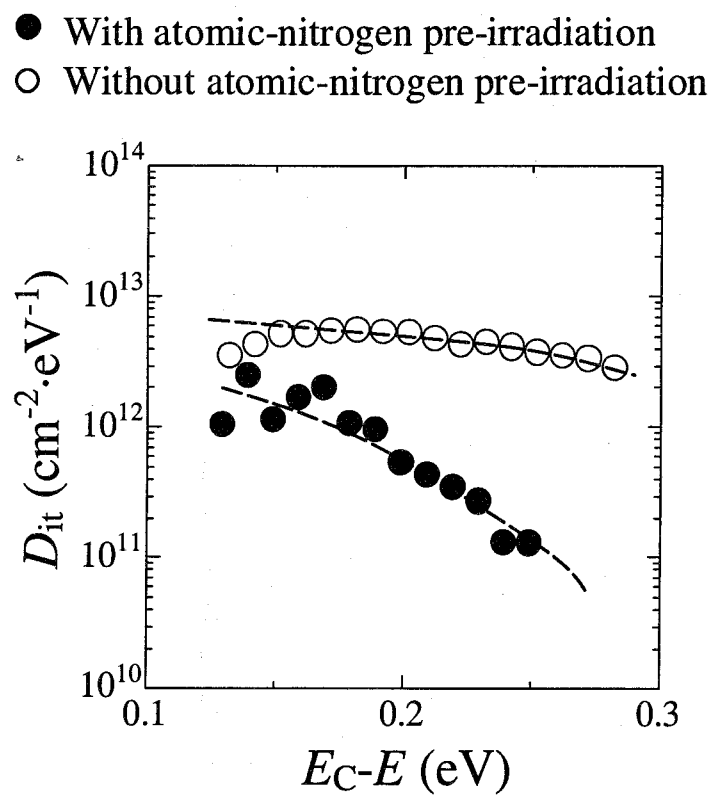


Figure 4.24: Energy distribution of interface state densities for AlN/4H-SiC(0001) interfaces estimated by Terman method. Closed circles and open circles are for samples with and without atomic-nitrogen pre-irradiation, respectively.

suggest the successful use of AlN as an insulator for SiC MIS devices.

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Chapter 5

Polytype Control in AlN Growth on SiC(11 $\bar{2}$ 0)

5.1 Introduction

For heterovalent systems such as AlN/SiC, abrupt polar interfaces would be characterized by the occurrence of either oversaturated or undersaturated bonds, i.e., instability of the interfaces. Charge accumulation or depletion at the polar interfaces could be avoided by introducing some measure of atomic mixing in such a way as to compensate III-V and IV-IV bonds [1, 2]. In chapter 4, control of the atomic arrangement at the AlN/SiC interface, i.e., artificial manipulation of interface bonding configuration, was studied to achieve MIS structures with excellent electrical characteristics.

Another viable approach to solve this instability problem is to choose the AlN growth direction to be a nonpolar $\langle 1\bar{1}00 \rangle$ or $\langle 11\bar{2}0 \rangle$ direction in stead of the polar $\langle 0001 \rangle$ direction (see Fig. 5.1). The nonpolar interface of AlN/SiC is expected to neutralize/balance the charges at the interface due to the equal numbers of Si-N and C-Al bonds.

In current state-of-the-art group-III nitride research, nonpolar films have attracted more and more interests to provide a promising means of eliminating polarization-induced electric fields in devices utilizing heterostructures. [3]. Since nitride films have a wurtzite (2H) structure, strong polarization-induced fields parallel to the $\langle 0001 \rangle$ direction can exist in strained layers [4]. The internal fields, although advantageous for two-dimensional electron gas (2DEG) formation in heterojunction field-effect transistors (HFETs) [5, 6], spatially separate electron and hole wave functions within quantum wells, i.e., the quantum-confined Stark effect (QCSE), resulting in reducing emission efficiency and a redshift in emission energy (see Fig. 5.2) [3, 7].

There have been some reports concerning epitaxial growth of nonpolar nitrides. Ng has demonstrated a remarkable improvement in quantum efficiency with no redshift for GaN/Al_xGa_{1-x}N(11 $\bar{2}$ 0) multiple quantum wells (MQWs) grown on (1 $\bar{1}$ 02) *r*-plane sapphire substrates [3]. Growth of nonpolar (11 $\bar{2}$ 0) *a*-plane GaN or AlN films on sapphire(1 $\bar{1}$ 02)

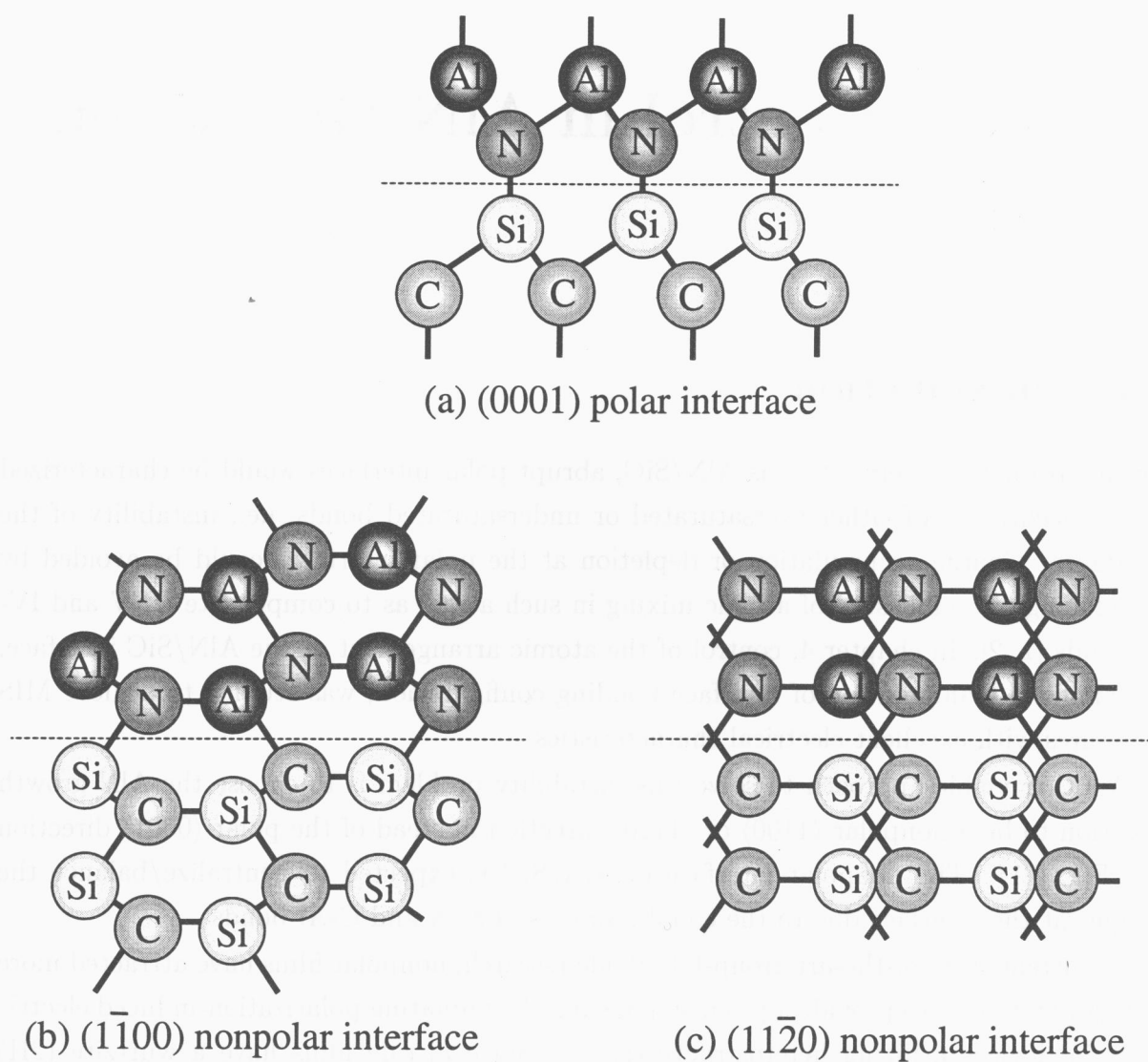
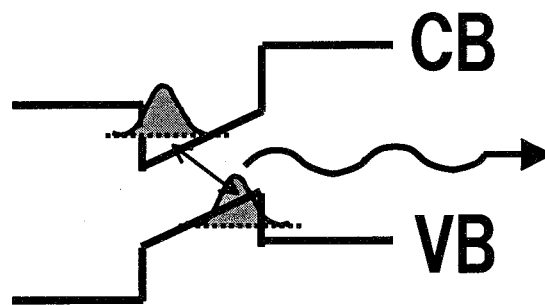
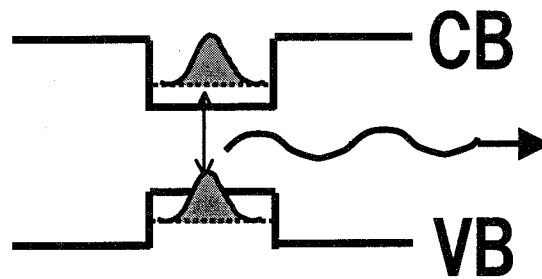


Figure 5.1: Atomic bonding for (a) (0001) interface, (b) (11 $\bar{1}$ 00) interface, and (c) (11 $\bar{2}$ 0) interface.



(a) QW of polar (0001) nitrides



(b) QW of nonpolar nitrides

Figure 5.2: Schematic pictures of wave functions of electrons and holes in (a) polar quantum well with polarization-induced electric fields and (b) nonpolar quantum well.

substrates has been studied extensively [8–15]. As Craven *et al.* pointed out [13], however, the crystalline quality of nonpolar nitride films is still inferior to that of technologically-mature polar (0001) epilayers, and the potential for device quality films has not been realized up to now. The insufficient crystalline quality is attributed to the large structural mismatch between the epilayer and the substrate ((11 $\bar{2}$ 0) *a*-plane vs. (1 $\bar{1}$ 02) *r*-plane).

According to Ng [3], the in-plane orientation relationship between GaN(11 $\bar{2}$ 0) and sapphire(1 $\bar{1}$ 02) is $[0001]_{\text{GaN}} \parallel [\bar{1}101]_{\text{sapphire}}$ and $[\bar{1}100]_{\text{GaN}} \parallel [11\bar{2}0]_{\text{sapphire}}$, resulting in a lattice mismatch of 1.1% along the [0001] axis (layer is under tension) and 16.1% along the [1 $\bar{1}$ 00] axis of GaN (layer is under compression). Also, Dovidenko *et al.* have reported that the lattice mismatch of AlN(11 $\bar{2}$ 0) and *r*-plane sapphire is 2.9% along the [0001] axis and 13% along the [1 $\bar{1}$ 00] axis of AlN [15]. The resulting films contained a high density of planar defects (up to 10^5 cm^{-1}) with the (0001) basal plane and threading dislocations with a density of about 10^{10} cm^{-2} . To obtain high-quality nonpolar films for practical use, exploring more suitable substrates is absolutely necessary.

A nonpolar SiC substrate is a promising candidate owing to its small lattice mismatch with AlN ($\Delta a \sim 0.9\%$, $\Delta c/n \sim 1.15\%$). Stemmer and co-workers reported AlN growth on the (1 $\bar{1}$ 00) prism face of 6H-SiC [16]. Their microscopic investigation using cross-sectional TEM demonstrated that 2H-AlN(1 $\bar{1}$ 00) was grown on the substrate, and the in-plane orientation relationship was found to be $[0001]_{\text{AlN}} \parallel [0001]_{\text{SiC}}$ and $[11\bar{2}0]_{\text{AlN}} \parallel [11\bar{2}0]_{\text{SiC}}$. However, the structural quality of the grown film was not described in detail. In addition, SiC(1 $\bar{1}$ 00) substrates are not commercially available.

On the other hand, SiC(11 $\bar{2}$ 0) substrates have already been commercialized. This is chiefly owing to the recent progress in SiC technology where various superior results have been achieved by using the (11 $\bar{2}$ 0) face (e.g. higher channel mobility in MISFETs) [17–20].

In this work, AlN growth on 4H- and 6H-SiC(11 $\bar{2}$ 0) substrates is studied. 4H- and 6H-SiC substrates have different stacking sequences, i.e., 4H(ABCB $\cdots$) and 6H(ABCACB $\cdots$). Our results demonstrate that the remarkable impact of the SiC substrate polytype on the crystalline structure of the AlN epilayer.

5.2 Polytype Replication from SiC Substrate

The SiC(11 $\bar{2}$ 0) surface has a unique atomic arrangement containing the information of the stacking sequence along the *c*-axis. If an AlN epilayer inherits this arrangement (atomic-template effect), then the polytype of the SiC substrate will be replicated to the epilayer, i.e., 4H- or 6H-AlN. From the crystallographic point of view, however, the wurtzite (2H) structure is the thermodynamically stable phase for AlN. In the (0001) basal plane, 2H-AlN is predominantly grown on the (0001) surface of 4H- or 6H-SiC substrate since the hexagonal close-packed (0001) plane is equivalent for all the polytypes. Only at the step edges containing the information of substrate polytype, problems of stacking mismatch will

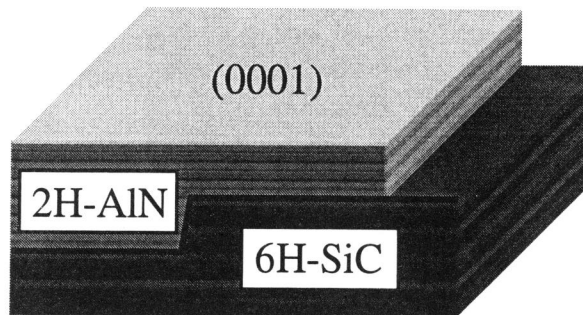


Figure 5.3: Schematic image of 2H-AlN(0001) growth on 6H-SiC(0001) substrate with 6ML-high bunched steps.

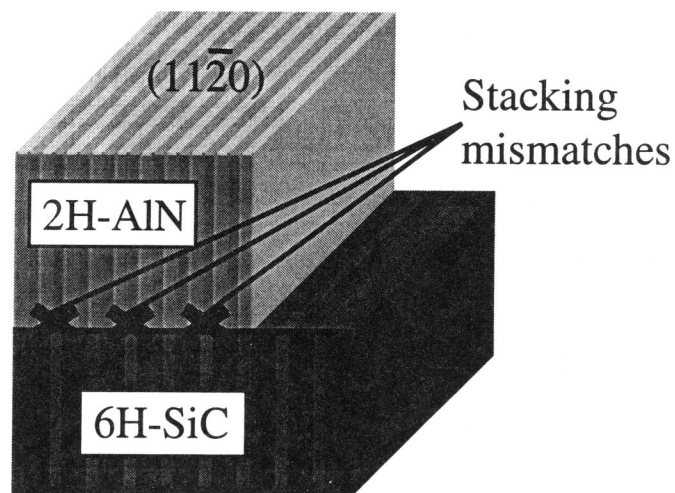
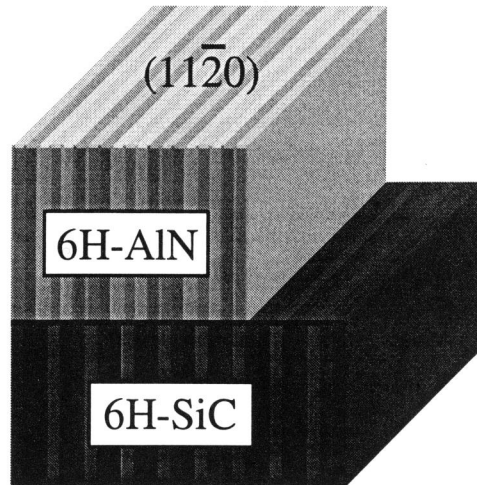
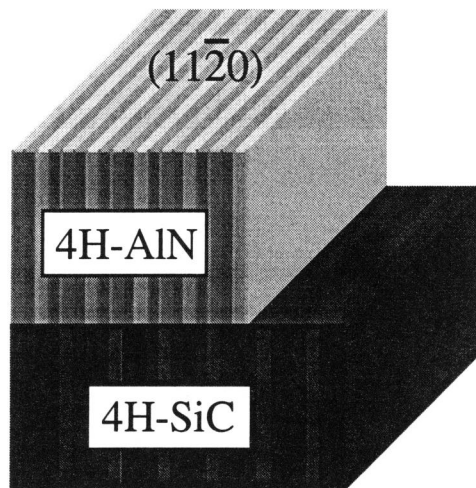


Figure 5.4: Schematic image of 2H-AlN(11 $\bar{2}$ 0) growth on 6H-SiC(11 $\bar{2}$ 0) substrate. Polytypes of epilayer and substrate are mismatched.



(a) 6H-AlN growth on 6H-SiC($11\bar{2}0$) substrate



(b) 4H-AlN growth on 4H-SiC($11\bar{2}0$) substrate

Figure 5.5: Schematic image of polytype replication: (a) 6H-AlN growth on 6H-SiC($11\bar{2}0$) substrate and (b) 4H-AlN growth on 4H-SiC($11\bar{2}0$) substrate.

arise, in particular for the off-oriented SiC(0001) surface where the density of surface steps is high. In this work, owing to SiC surface control, defects related to stacking mismatch were successfully removed (see Fig. 5.3). However, for the (11 $\bar{2}$ 0) face, growth of 2H-AlN on 4H- or 6H-SiC(11 $\bar{2}$ 0) will probably result in the generation of numerous defects at the interface [Fig. 5.4]. Hence, polytype replication from the SiC substrate to the AlN epilayer is essential to obtain epilayers with excellent crystalline quality (see Fig. 5.5). It is worth noting that if the polytype of the SiC substrate is successfully replicated to the AlN epilayer, problems related to stacking mismatch between the epilayer and substrate can be eliminated, which is a major concern in AlN growth on SiC(0001) substrates (see chapter 3 and 4).

5.3 Polytype Mismatch of 2H-AlN Growth on 6H-SiC(11 $\bar{2}$ 0)

5.3.1 Growth Features of 2H-AlN on 6H-SiC(11 $\bar{2}$ 0)

Prior to transferring the substrate into the MBE system, conventional wet chemical treatments were performed (see Chapter 2). It should be mentioned that in this experiment, no additional surface treatments, such as HCl-gas etching or gallium treatment, were conducted, so that growth features on as-received substrates were investigated. AlN growth was carried out at 1000°C under the following conditions: an aluminum beam equivalent pressure of 4.7×10^{-7} Torr, a nitrogen flow rate of 0.5 sccm, and an rf power of 400 W. The same conditions were used for all samples discussed in this chapter. The growth rate under these conditions was 380 nm/h, and the film thickness characterized in this study ranged from 300 nm to 1 μ m.

In situ RHEED monitoring was conducted during AlN growth to investigate the polytype of the AlN film on the 6H-SiC(11 $\bar{2}$ 0) substrate. Figure 5.6(a) shows the diffraction pattern of the substrate just before growth. In view of RHEED indices, the pattern agrees with that of the 6H-SiC(11 $\bar{2}$ 0) face along the [0001] azimuth. In the initial stages of growth, a spotty pattern was observed for several minutes, probably due to 3D island growth. After five minutes or so, the pattern changed to a streak one, indicative of transition to two-dimensional growth. Figure 5.6(b) shows the pattern after the growth along the same azimuth, which corresponded to that of 2H-AlN(11 $\bar{2}$ 0) along the [0001] azimuth (whose theoretical diffraction spots are presented in Fig. 5.6(c)) [8]. The exact epitaxial relationship, i.e., $[11\bar{2}0]_{\text{AlN}} \parallel [11\bar{2}0]_{\text{SiC}}$ and $[0001]_{\text{AlN}} \parallel [0001]_{\text{SiC}}$, was revealed, but the polytype of 6H-SiC was not replicated to the AlN epilayer (2H), in other words, the atomic-template effect of the substrate did not work. This result is similar to that of Stemmer *et al.*, i.e., 2H-AlN growth on 6H-SiC(1 $\bar{1}$ 00) [16].

The microscopic structure of the AlN/6H-SiC(11 $\bar{2}$ 0) interface region was observed by cross-sectional HRTEM. The viewing direction along the $\langle 11\bar{2}0 \rangle$ zone-axis is the most suit-

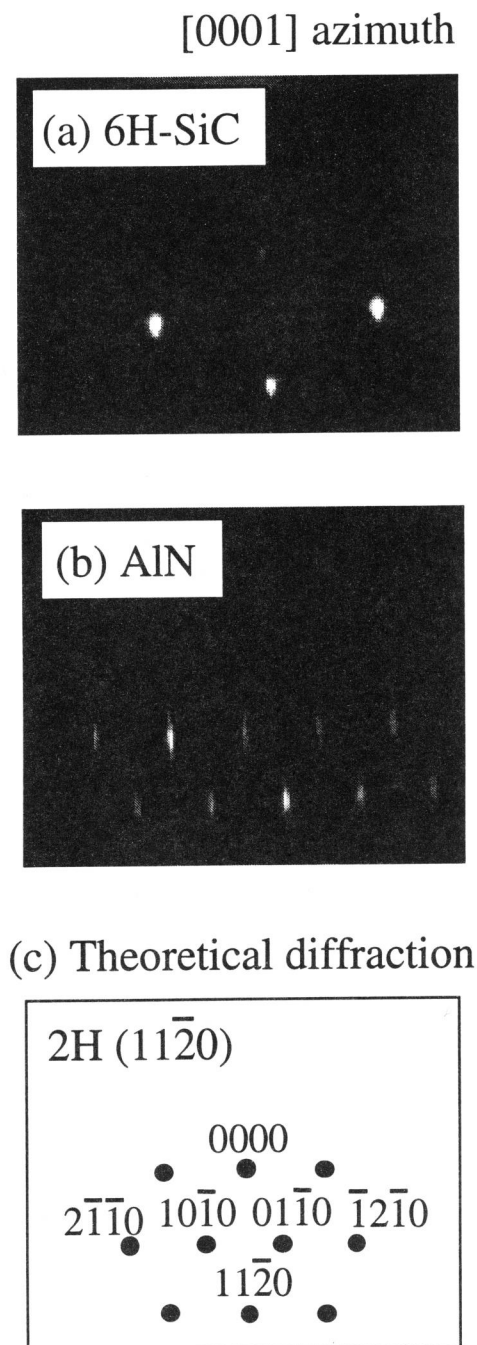
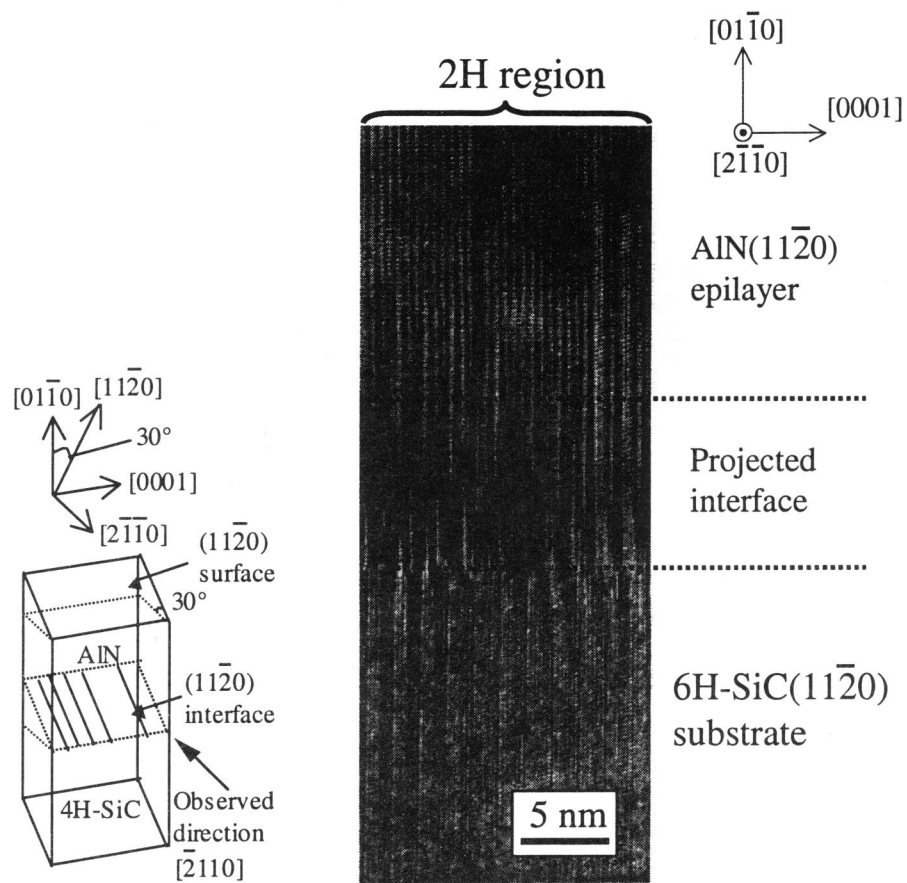


Figure 5.6: RHHED patterns during AlN growth on 6H-SiC(11 $\bar{2}$ 0) substrate along [0001] azimuth: (a) 6H-SiC(11 $\bar{2}$ 0) surface, (b) AlN surface after growth, and (c) theoretical diffraction spots of 2H structure from (11 $\bar{2}$ 0) surface.



(a) Fabricated specimen (b) AlN/6H-SiC(11 $\bar{2}$ 0) interface region

Figure 5.7: (a) Schematic picture of fabricated TEM specimen and (b) lattice image of AlN/6H-SiC(11 $\bar{2}$ 0) interface region.

able for HRTEM studies of hexagonal semiconductors, where the zigzag stacking structure can be seen. To achieve this geometry, a cross-sectional TEM specimen was cut from the wafer with a 30° inclination as shown in Fig. 5.7(a). The specimen was prepared by mechanical thinning and Ar⁺ ion milling. Figure 5.7(b) displays the lattice image of the AlN/6H-SiC(11 $\bar{2}$ 0) heterostructure. In the 6H-SiC substrate region, one set of dark and bright bands corresponds to one unit cell of the 6H structure (1.5 nm). As expected from the analysis of the RHEED pattern, the AlN epilayer was confirmed to have the 2H structure throughout almost the entire region. It should be noted that a considerably disordered region was observed near the 2H-AlN/6H-SiC(11 $\bar{2}$ 0) interface. This disordered region is probably attributed to the polytype mismatch between the AlN epilayer (2H: ABABAB...) and the SiC substrate (6H: ABCACB...), which resulted in the generation of numerous defects.

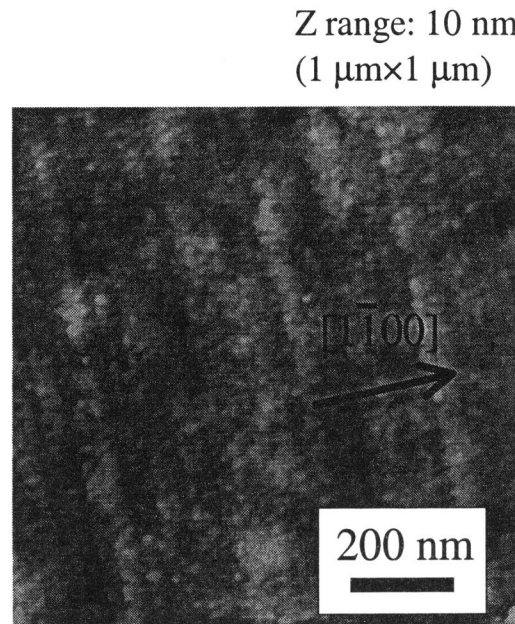
5.3.2 Reduction of Defects using Low-Temperature Buffer Layer

Two-step growth using a 20-nm-thick low-temperature (LT) buffer layer was attempted to improve the structural quality of AlN films. The LT buffer layer was grown at 600°C prior to main growth at 1000°C. Growth procedures utilizing LT AlN or GaN buffer layers have been widely applied in nitride epitaxy on sapphire and SiC(0001) [21–25]. It is well known that such LT buffer layers are effective in promoting 2D lateral growth of subsequent epilayers.

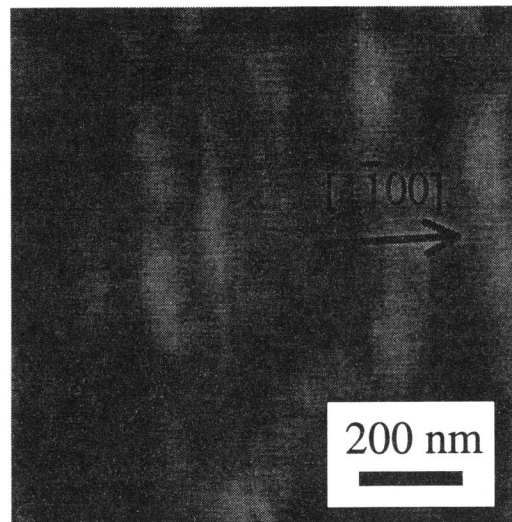
After the deposition of an LT buffer layer, a halo-like RHEED pattern was observed with no evident diffraction, suggesting that the deposited layer was amorphous. Then, the substrate temperature was elevated up to 1000°C for thermal annealing of deposited layer. After annealing for 30 min, the diffraction pattern was bright and spotty. The RHEED indices of this spot pattern were those of the 2H structure, not the 6H structure. Just after main growth, the spot pattern quickly changed to a streak one (2D lateral growth). However, throughout the growth, the RHEED indices did not change, i.e., 2H-AlN was grown even using the two-step growth procedure.

Figures 5.8(a) and (b) present AFM images of 380-nm-thick AlN films grown without and with the LT buffer layer, respectively. The film with the buffer layer had a smoother surface compared to the directly-grown film. The rms roughness in a scan size of 1×1 μm² was 0.6 nm for the film utilizing the buffer layer. As seen in Fig. 5.8(a), many elongated surface defects were found extending along the [1 $\bar{1}$ 00] direction for the directly-grown film. Since these defects were not observed on the substrate, they were probably generated during growth. The density of these defects was somewhat reduced owing to the buffer layer [Fig. 5.8(b)].

Figures 5.9(a),(b) and (c),(d) give XRD 2θ/ω-scan profiles of those films without and with the buffer layer, respectively. Two different x-ray incidence geometries were performed to examine the anisotropy in the crystalline structure. One is perpendicular to the [1 $\bar{1}$ 00]



(a) Without LT buffer layer



(b) With LT buffer layer

Figure 5.8: AFM images of 380-nm-thick AlN films grown (a) without and (b) with LT buffer layer grown on 6H-SiC(11 $\bar{2}$ 0) substrates. In image (b), 20-nm-thick LT buffer layer was grown at 600°C prior to main growth at 1000°C.

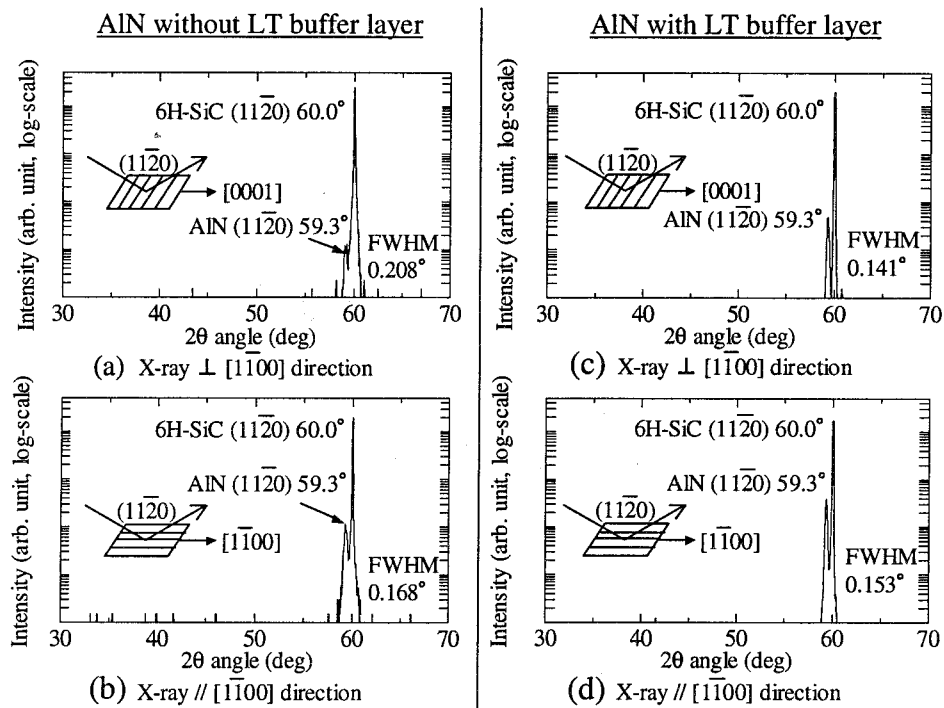


Figure 5.9: XRD $2\theta/\omega$ scan profiles of 380-nm-thick AlN films without [(a),(b)] and with [(c),(d)] LT buffer layer grown on 6H-SiC(11 $\bar{2}$ 0) substrates. (a) and (c) were measured in x-ray incidence geometry perpendicular to $[1\bar{1}00]$ direction, while (b) and (d) parallel to $[1\bar{1}00]$ direction.

direction [(a),(c)] and another is parallel to the [1 $\bar{1}$ 00] direction [(b),(d)]. The diffraction peak from the AlN(11 $\bar{2}$ 0) symmetrical plane ($2\theta \sim 59.3^\circ$) was confirmed for both samples, which supports that the growth axis was [11 $\bar{2}$ 0]. Any diffraction peaks from the AlN(0002) plane ($2\theta \sim 36.0^\circ$) were not detected in the symmetrical diffraction geometries, implying that there was no AlN domain grown toward the [0001] direction. The peak intensities of the film with the buffer layer [(c),(d)] were almost one order of magnitude larger than those without the buffer layer [(a),(b)]. Furthermore, the linewidth of the (11 $\bar{2}$ 0) diffraction peak for the film with the buffer layer was relatively smaller. It definitely suggests that utilizing the buffer layer enhanced the crystalline quality. The diffraction peaks in the geometry perpendicular to the [1 $\bar{1}$ 00] direction [(a),(c)] were considerably weak compared to those in the opposite geometry [(b),(d)], in particular for the film without the buffer layer. Since there was no difference in XRD profiles of 6H-SiC(11 $\bar{2}$ 0) substrate between the two geometries, it is probably attributed to the defects in AlN films, which extend along the [1 $\bar{1}$ 00] direction. These defects are thought to reduce the spatial coherency of the film along the [0001] direction, resulting in weaker diffraction in the geometry perpendicular to [1 $\bar{1}$ 00]. The peak intensity shown in Fig. 5.9(c) was more than 10 times larger than that shown in Fig. 5.9(a). This result suggests that utilizing the buffer layer can suppress generation of defects, which agrees with the AFM images shown in Fig. 5.8.

5.4 Polytype Replication of 4H-AlN growth on 4H-SiC(11 $\bar{2}$ 0)

5.4.1 Growth Features of 4H-AlN on 4H-SiC(11 $\bar{2}$ 0)

The poor structural quality of AlN film grown on the 6H-SiC(11 $\bar{2}$ 0) substrate is chiefly attributed to numerous defects originating from the polytype mismatch between the AlN epilayer (2H: ABABAB $\cdots$) and the SiC substrate (6H: ABCACB $\cdots$). Although the defect density could be reduced to some extent by utilizing the LT buffer layer, it is still far from being acceptable for device applications.

Next, AlN growth on the 4H-SiC(11 $\bar{2}$ 0) substrate, which has a different stacking structure (4H: ABCB $\cdots$) compared to 6H-SiC, was studied, and the impact of the SiC substrate polytype on the crystalline structure of the AlN epilayer was investigated. AlN films were directly grown on as-received 4H-SiC(11 $\bar{2}$ 0) substrates at 1000°C without any buffer layers.

In situ RHEED monitoring was conducted during AlN growth to investigate the polytype of AlN on 4H-SiC(11 $\bar{2}$ 0). The diffraction pattern prior to AlN growth is shown in Fig. 5.10(a), which corresponds to the diffraction from the 4H-SiC(11 $\bar{2}$ 0) surface along the [0001] azimuth. AlN growth was carried out by the same procedure as described above. But in this case, the RHEED indices never changed throughout the growth. Figure 5.10(b) represents the pattern after one hour growth, whose indices were consistent with the the-

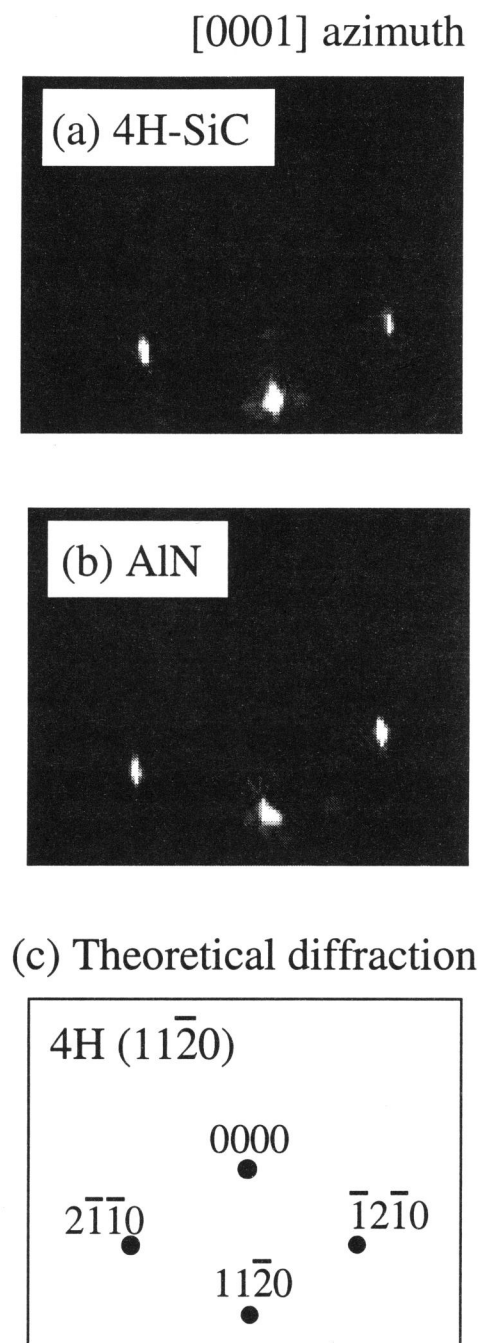


Figure 5.10: RHHED patterns during AlN growth on 4H-SiC(11 $\bar{2}$ 0) substrate along [0001] azimuth: (a) 4H-SiC(11 $\bar{2}$ 0) surface, (b) AlN surface after growth, and (c) theoretical diffraction spots of 4H structure from (11 $\bar{2}$ 0) surface.

oretical diffraction spots of 4H structure shown in Fig. 5.10(c). This RHEED evolution is completely different from that on 6H-SiC(11 $\bar{2}$ 0), and might indicate that the AlN epilayer inherited its polytype from the 4H-SiC substrate.

The microscopic structure of the AlN/4H-SiC(11 $\bar{2}$ 0) interface was characterized by cross-sectional HRTEM. The specimen preparation and viewing direction were same as explained above. Figure 5.11 displays a lattice image of the AlN/4H-SiC(11 $\bar{2}$ 0) heterostructure. The dark and bright bands corresponding to one unit cell (1.0 nm) were seen in the 4H-SiC substrate region, and the same bands could be observed in the AlN epilayer region. It indicates the successful polytype replication from the 4H-SiC substrate to the AlN epilayer, i.e., growth of 4H-AlN. It should be emphasized that the atomic-template effect of the substrate worked well in the growth on 4H-SiC(11 $\bar{2}$ 0), though it did not work effectively for 6H-SiC(11 $\bar{2}$ 0).

5.4.2 Formation Mechanism of Faulted Region

In comparison to the interface for AlN/6H-SiC(11 $\bar{2}$ 0) shown in Fig. 5.7, the interface of AlN/4H-SiC(11 $\bar{2}$ 0) [Fig. 5.11] was not disordered owing to the polytype matching between the epilayer and the substrate. However, some regions were found to be not of the 4H structure, i.e., faulted, and dark lines were observed at the interface (see indications in Fig. 5.11). Since the length of dark lines agrees with $\tan 30^\circ$ (inclination of specimen) $\times$ specimen thickness (20 nm), and the beginning and end are well aligned, these dark lines probably correspond to threading line defects along the $[1\bar{1}00]$ direction at the interface (parallel to the interface). The magnified lattice image of faulted region is given in Fig. 5.12. As clearly seen, the faulted region does not have the 4H structure, but the 2H structure, which is the thermodynamically stable phase for AlN. Since the stacking sequence differed between the faulted region (2H) and the substrate (4H) at the interface, vacancies in the interface atomic sites were generated, which looked the dark lines in the HRTEM image (indications in Fig. 5.11). Thus, the faulted region was related to a planar defect, i.e., stacking fault. The schematic diagram presented in Fig. 5.13 illustrates a possible model for stacking faults.

There are two basic mechanisms by which a stacking fault can be introduced into the film: (i) strain-induced defects (or misfit dislocation) and (ii) growth-related mistakes in the stacking sequence due to faulted nucleation. In our calculation of strain-induced defect density using the *c*-plane space mismatch of 1.15% between AlN and 4H-SiC, it is estimated that one planar defect occurs in every 20 nm (20 unit cell) at the interface ($\sim 5 \times 10^5 \text{ cm}^{-1}$). This calculated density is not consistent with the observed result shown in Fig. 5.11, where the density of stacking faults, i.e., line defects at the interface, was approximately $2 \times 10^6 \text{ cm}^{-1}$. Furthermore, in the former mechanism, the stacking fault should be an extrinsic (or intrinsic) type as shown in Fig. 5.14 [26], which differs from that presented in Fig. 5.13.

Hence, the latter explanation (ii) is a more conceivable mechanism. According to the

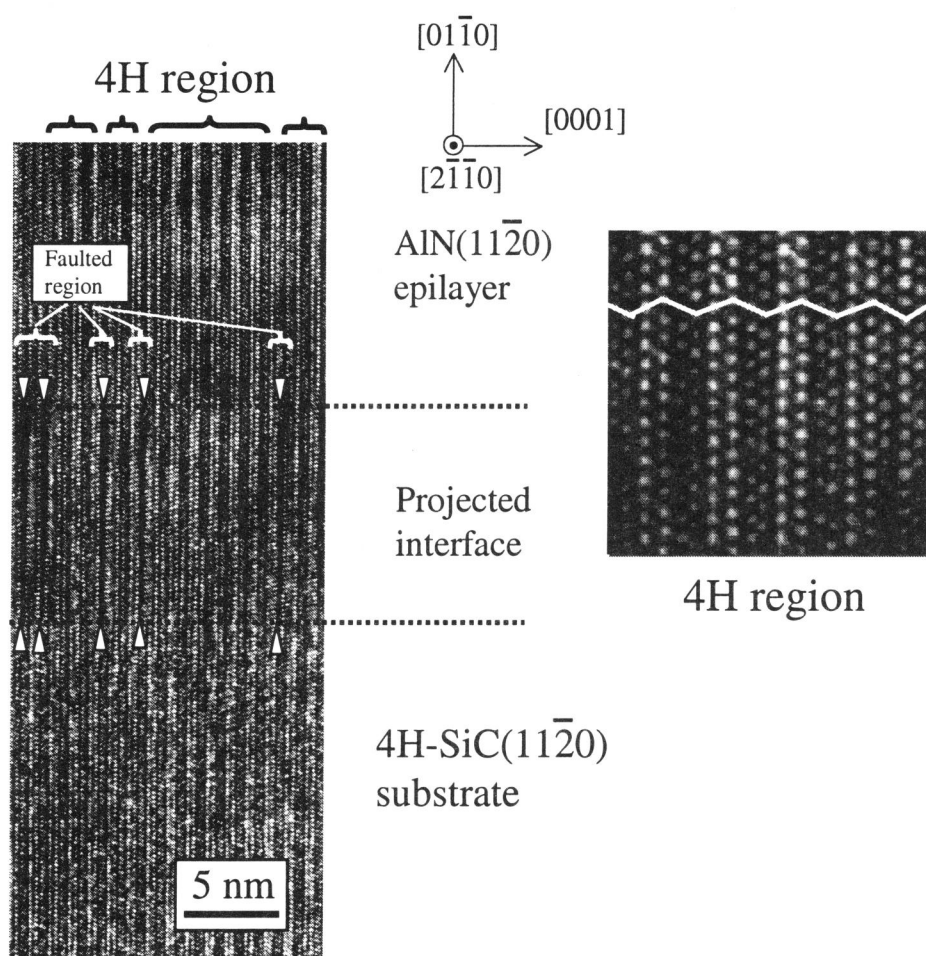


Figure 5.11: Lattice image of AlN/4H-SiC(11 $\bar{2}$ 0) interface region.

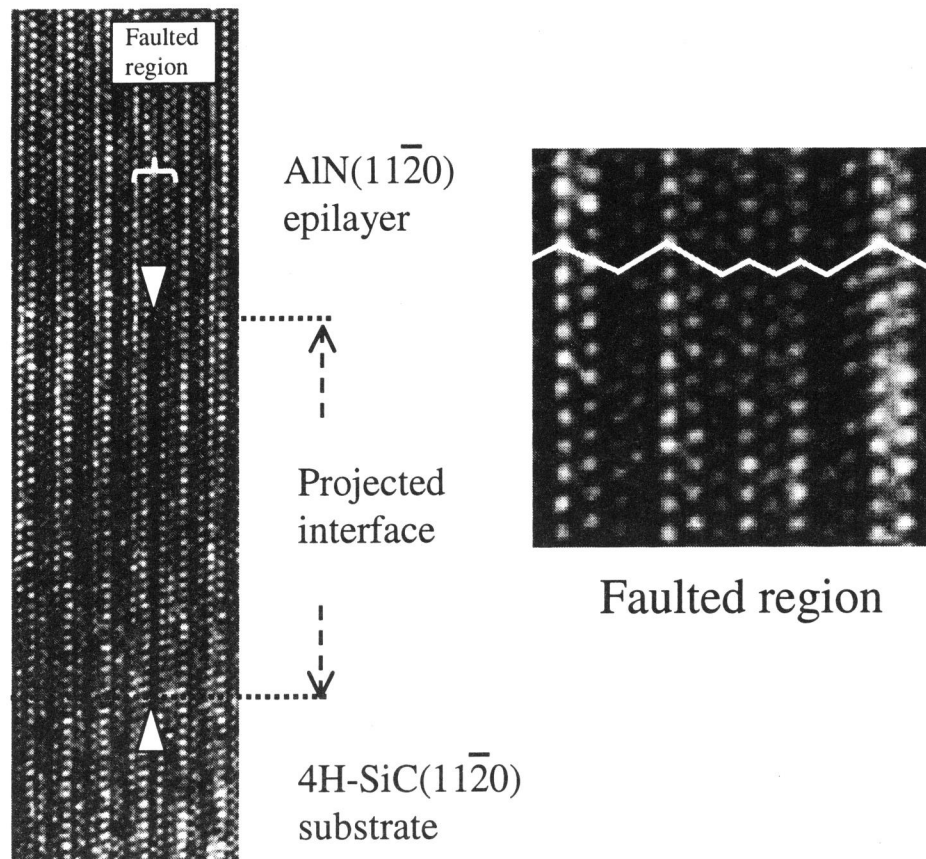


Figure 5.12: HRTEM image of faulted region in 4H-AlN epilayer and threading line defects along $[1\bar{1}00]$ direction at 4H-AlN/4H-SiC interface.

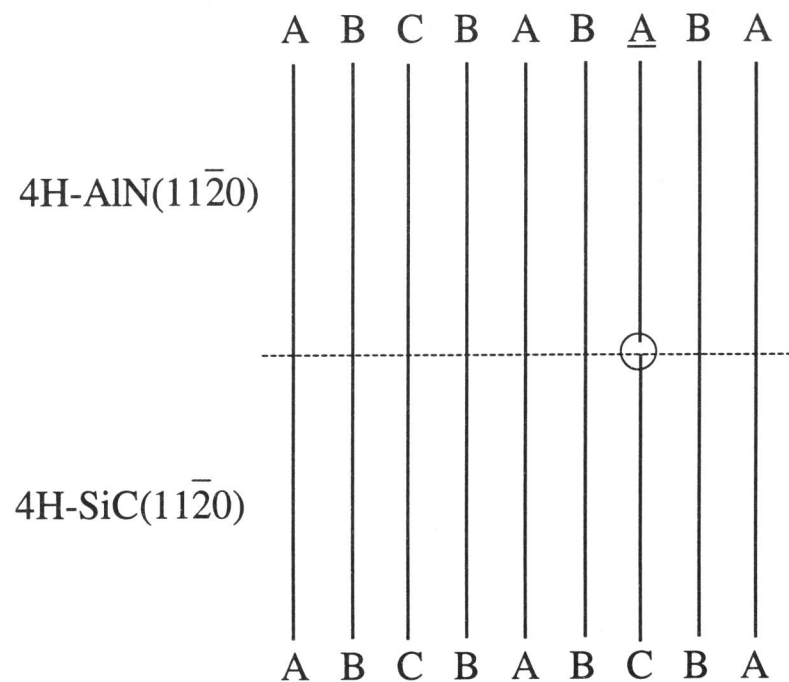


Figure 5.13: Possible model of stacking fault generated in 4H-AlN epilayer grown on 4H-SiC(11 $\bar{2}$ 0) substrate.

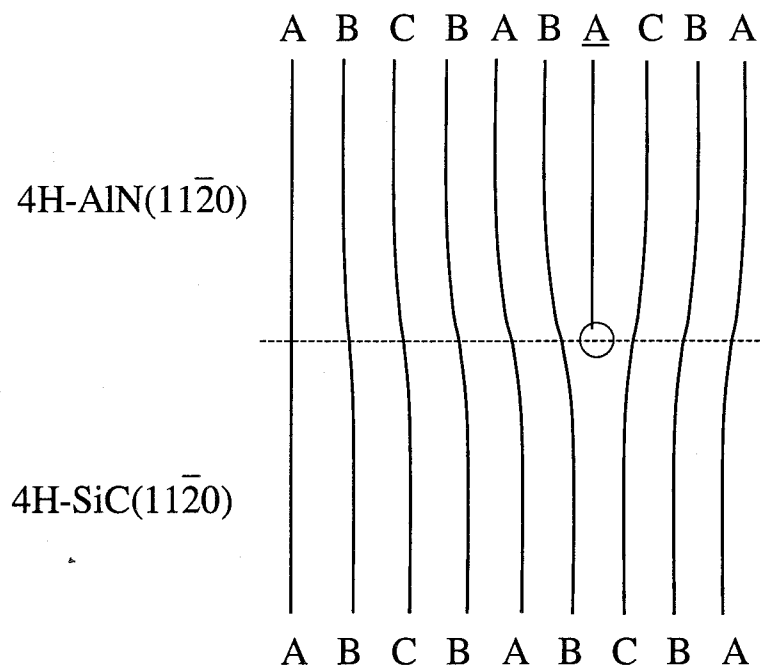


Figure 5.14: Schematic image of extrinsic stacking fault in 4H-AlN epilayer grown on 4H-SiC(11 $\bar{2}$ 0) substrate.

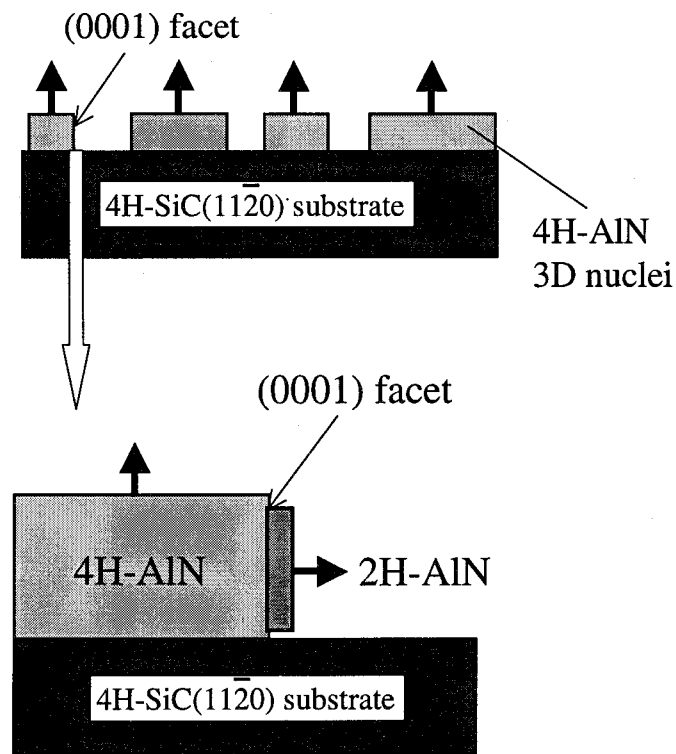


Figure 5.15: Formation mechanism of stacking fault during AlN growth on 4H-SiC(11 $\bar{2}$ 0) substrate.

plan-view TEM studies reported by several groups [13, 15], stacking faults aligned perpendicular to the c -axis were also observed in AlN or GaN(11 $\bar{2}$ 0) films grown on sapphire(1 $\bar{1}$ 02) substrates. Craven and co-workers concluded that stacking faults, commonly associated with epitaxial growth of close-packed planes, most likely originate on the c -plane sidewalls of three-dimensional (3D) islands that form during the initial stages of high temperature growth [13]. The mechanism of stacking fault formation in this study is probably same as reported by Craven *et al.* Figure 5.15 shows the formation mechanism of a stacking fault. In the early stages of growth, 3D nucleation occurs on the 4H-SiC(11 $\bar{2}$ 0) surface. As for the 3D nuclei, their polytype is the 4H structure owing to the atomic-template effect of the substrate. However, once (0001) facets, i.e., c -plane sidewalls, are formed, 2H-AlN will grow on the facets, i.e., lateral growth toward the c direction, resulting in stacking faults. Therefore, to eliminate stacking faults, further optimization of the initial growth conditions will be necessary.

5.4.3 Improvement in Structural Quality by Polytype Matching

Surface morphologies of a 380-nm-thick AlN film grown on a 4H-SiC(11 $\bar{2}$ 0) substrate were investigated by AFM. As exhibited in Fig. 5.16, a considerably smooth surface (rms roughness of 0.3 nm in a scan size of $1 \times 1 \mu\text{m}^2$) was obtained, which is a better result compared to the film grown on the 6H-SiC(11 $\bar{2}$ 0) substrate (see Fig. 5.8(a)). The superior surface features probably reflect excellent crystalline quality.

HRXRD ω scans for the (11 $\bar{2}$ 0) diffraction peak were conducted to examine the impact of polytype matching on the structural quality. As explained above, two different x-ray incidence geometries, parallel and perpendicular to the $[1\bar{1}00]$ direction, were performed to study the anisotropy in the crystalline structure. Figures 5.17(a) and (b) show the ω scan profiles for the 380-nm-thick AlN film grown on the 4H-SiC(11 $\bar{2}$ 0) substrate in those two geometries. There was no large difference in the (11 $\bar{2}$ 0) diffraction between the two geometries. The linewidths exhibited a very small value of 90 arcsec, suggesting noticeably small tilting around the $[11\bar{2}0]$ direction. Figures 5.17(c) and (d) present the ω scan profiles for the 380-nm-thick AlN film directly grown on the 6H-SiC(11 $\bar{2}$ 0) substrate. The diffraction intensity in the x-ray incidence geometry perpendicular to the $[1\bar{1}00]$ direction [Fig. 5.17(d)] was considerably weak compared to that parallel to the $[1\bar{1}00]$ direction [Fig. 5.17(c)]. As described above, the strong anisotropy in the crystalline structure is probably due to numerous stacking faults extending along the $[1\bar{1}00]$ direction, originating from the polytype mismatch of 2H-AlN/6H-SiC(11 $\bar{2}$ 0). From the results of the (11 $\bar{2}$ 0) diffraction, the crystalline quality of the AlN film grown on the 4H-SiC(11 $\bar{2}$ 0) substrate was found to be far superior to that on the 6H-SiC(11 $\bar{2}$ 0) substrate owing to the polytype matching of 4H-AlN/4H-SiC(11 $\bar{2}$ 0).

By using glancing incidence x-ray diffraction (GIXRD), the in-plane, or (11 $\bar{2}$ 0) plane, misorientation in the AlN film was characterized. The rotation angle is precisely determined from the rocking curve for an in-plane reflection in GIXRD [27]. The detailed principle has

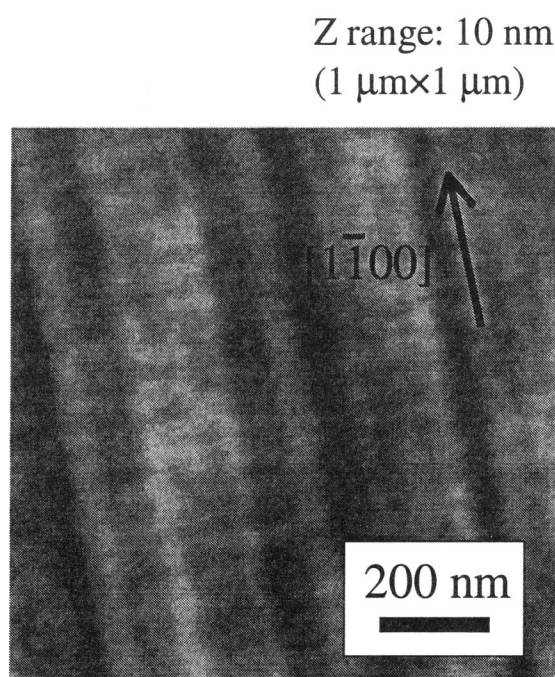


Figure 5.16: AFM image of 380-nm-thick AlN film grown on 4H-SiC(11 $\bar{2}$ 0) substrate.

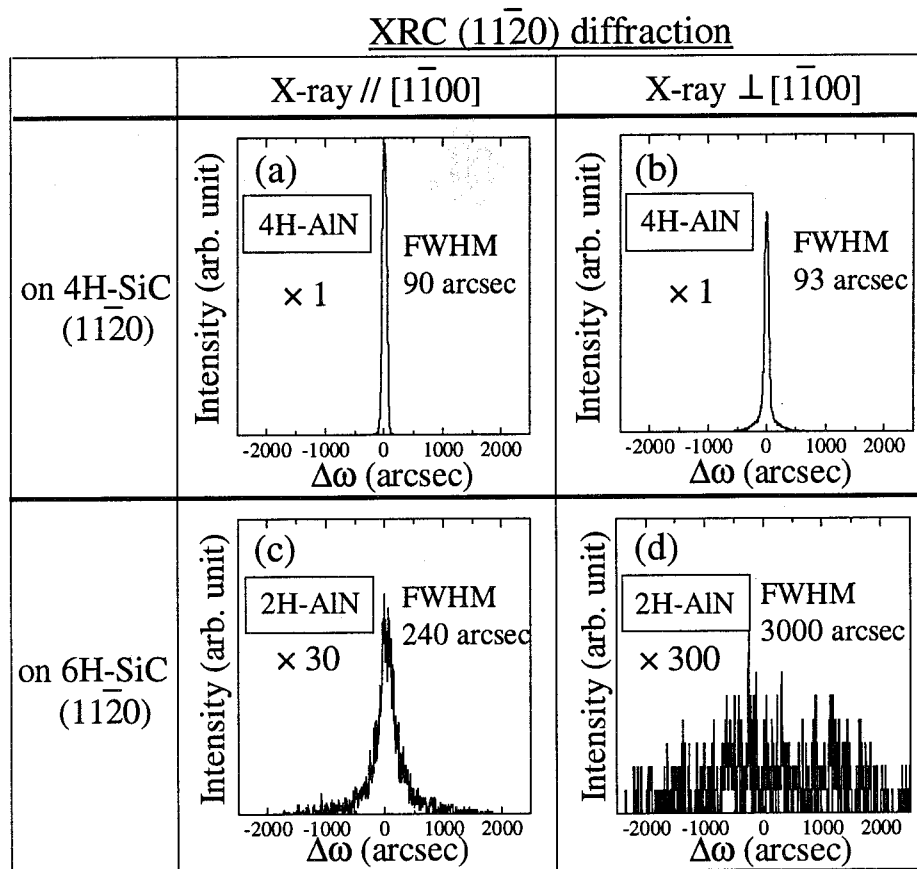


Figure 5.17: HRXRD ω scan of (11 $\bar{2}$ 0) diffraction for 380-nm-thick AlN films grown on 4H-SiC(11 $\bar{2}$ 0) substrate [(a),(b)] and 6H-SiC(11 $\bar{2}$ 0) substrate [(c),(d)]. (a) and (c) were measured in x-ray incidence geometry parallel to [1 $\bar{1}$ 00] direction, while (b) and (d) perpendicular to [1 $\bar{1}$ 00] direction.

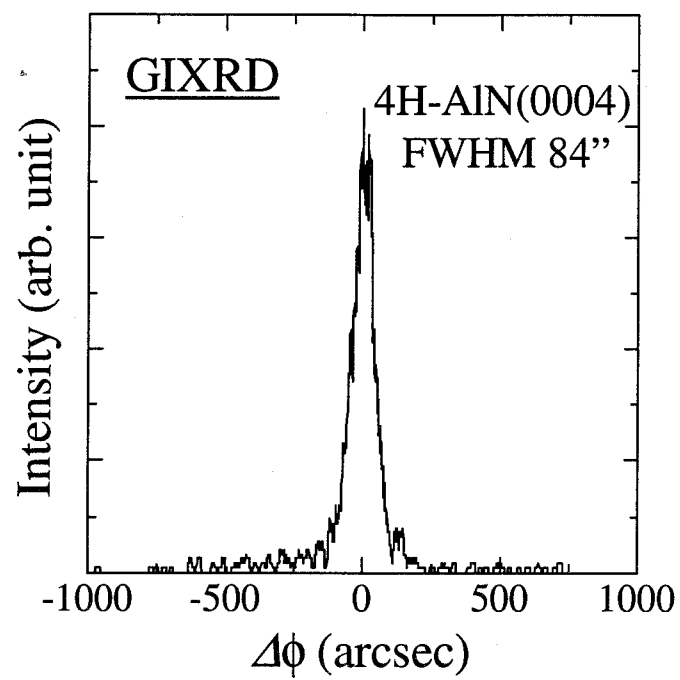


Figure 5.18: GIXRD profile of (0004) diffraction peak for 380-nm-thick 4H-AlN film grown on 4H-SiC(11 $\bar{2}$ 0) substrate.

been described by Segmüller [28]. Since the typical glancing angle was about 0.1° , only diffraction from the upper AlN film was detected. In this measurement, the ϕ scan (rocking curve) of (0002) and (0004) diffraction for the 2H- and 4H-AlN films ($2\theta \sim 36.0^\circ$) was examined. For the AlN film grown on the 6H-SiC(11 $\bar{2}$ 0) substrate, no diffraction peak from the 2H-AlN(0002) plane was detected, indicative of poor crystalline structure (not shown here). On the other hand, for AlN grown on the 4H-SiC(11 $\bar{2}$ 0) substrate, an evident (0004) diffraction peak from the 4H-AlN film was observed. The ϕ scan profile for the (0004) diffraction is shown in Fig. 5.18. The linewidth exhibited a very small value of 84 arcsec, suggesting that the AlN film grown on the 4H-SiC(11 $\bar{2}$ 0) substrate was highly oriented around the [0001] direction (c -axis) as well as the [11 $\bar{2}$ 0] direction (a -axis).

It should be emphasized that crystal imperfections in the AlN film, such as the tilt of the a -axis (tilting) and the rotation of the a -plane (twisting), was greatly diminished by utilizing the 4H-SiC(11 $\bar{2}$ 0) substrate. The excellent crystalline quality of the AlN film is due to the high-quality interface by matching the stacking structure. In the case of 2H-AlN/4H- or 6H-SiC(0001) system described in this work, the rotation of the c -plane was normally larger than the tilt of the c -axis (see Fig. 3.23). Therefore, the perfect polytype matching of 4H-AlN/4H-SiC(11 $\bar{2}$ 0) is expected to reduce structural defects remarkably, and almost the same crystalline quality can be achieved as in homoepitaxy.

5.4.4 Anisotropic Residual Strain in 4H-AlN

The residual strain in AlN films grown on the 4H- and 6H-SiC(11 $\bar{2}$ 0) substrates was investigated by microscopic Raman scattering spectroscopy. Raman spectra were acquired at room temperature using a double grating monochromator and Ar⁺ laser ($\lambda = 488$ nm, 2.54 eV) as a source of excitation. Two different backscattering geometries, $x(y, -)\bar{x}$ and $x(z, -)\bar{x}$, were conducted by polarizing the incident light. Here, Porto's notation is used [29]: x and $\bar{x}$ are the laser incident and scattered directions ([11 $\bar{2}$ 0]), and y or z is the polarization direction of incident light, where y and z are the directions along [1 $\bar{1}$ 00] and [0001], respectively. According to the Raman selection rules, in backscattering configurations of hexagonal nitrides, the observable phonon modes are $A_1(\text{TO})$, $E_1(\text{TO})$ and E_2 . Besides the selection rules, the Raman polarization rules determine the scattering configurations for detecting Raman-active modes. $A_1(\text{TO})$ will be detected in $x(y, y)\bar{x}$ and $x(z, z)\bar{x}$, while $E_1(\text{TO})$ will be observed in $x(y, z)\bar{x}$ and $x(z, y)\bar{x}$. E_2 will be detected only in $x(y, y)\bar{x}$. Table 5.1 summarizes the Raman configurations of allowed modes in hexagonal nitrides [29].

Figure 5.19 shows Raman spectra of a 1- μm -thick AlN film grown on a 6H-SiC(11 $\bar{2}$ 0) substrate. Table 5.2 lists the typical phonon frequencies (cm^{-1}) observed at 300K for 2H-AlN reported by Davydov *et al* [30]. As shown in Fig. 5.19, strong peaks from the SiC substrate appeared in both geometries, while AlN-related peaks were weakly observed. In the $x(y, -)\bar{x}$ geometry, the $A_1(\text{TO})$, $E_1(\text{TO})$ and E_2^H phonon modes were evidently detected. On the other hand, the $A_1(\text{TO})$ and $E_1(\text{TO})$ phonon modes were clearly observed in the

Table 5.1: Raman configurations of allowed modes in hexagonal nitrides.

Configuration	Mode
$x(y, y)\bar{x}$	$A_1(\text{TO}), E_2$
$x(z, z)\bar{x}$	$A_1(\text{TO})$
$x(z, y)\bar{x}$	$E_1(\text{TO})$
$x(y, z)y$	$E_1(\text{TO}), E_1(\text{LO})$
$x(y, y)z$	E_2
$z(y, x)\bar{z}$	E_2
$z(y, y)\bar{z}$	$A_1(\text{LO}), E_2$

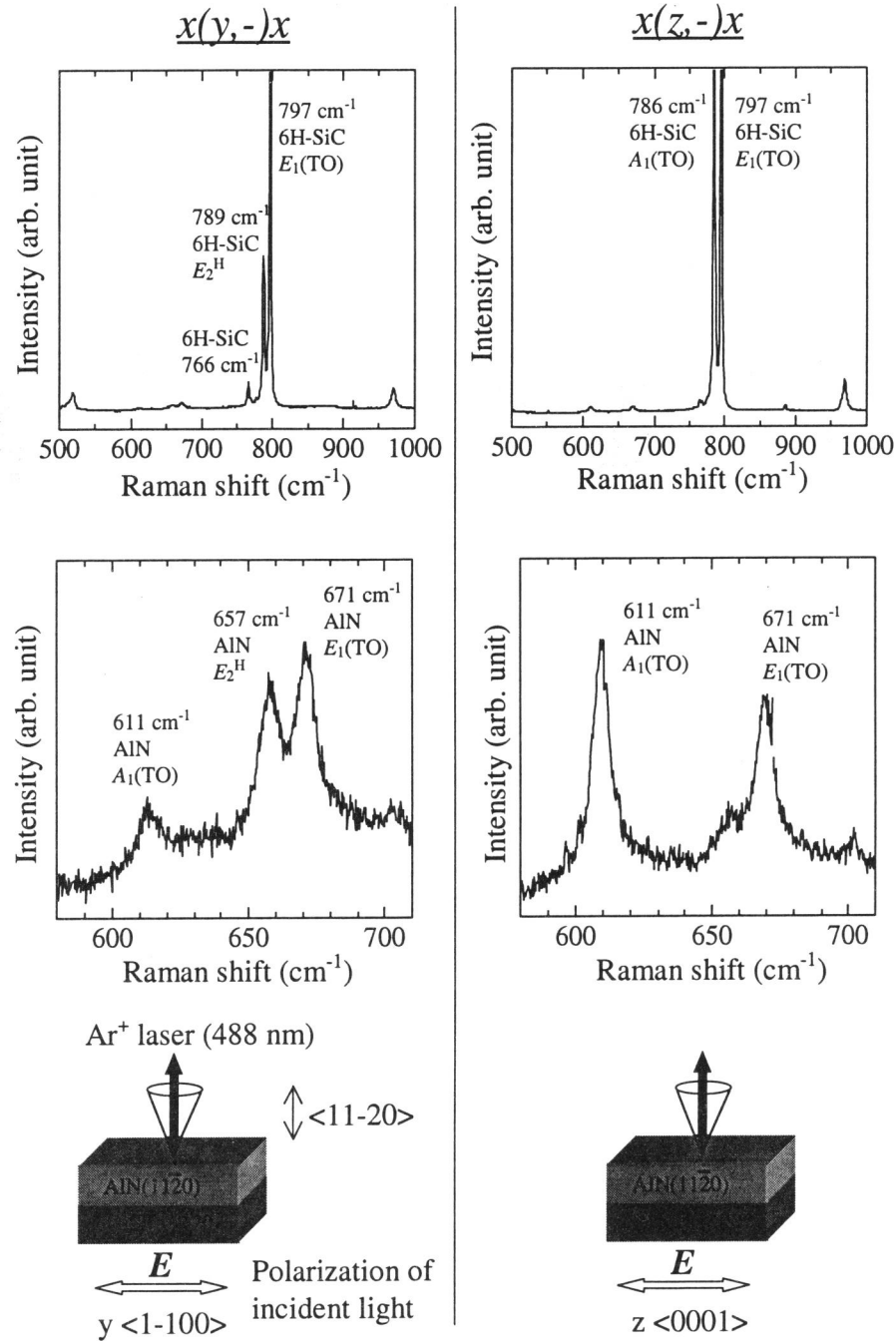


Figure 5.19: Raman spectra for 1- μm -thick AlN film grown on 6H-SiC(11 $\bar{2}$ 0) substrate measured in backscattering $x(y, -)\bar{x}$ and $x(z, -)\bar{x}$ geometries.

Table 5.2: Typical phonon frequencies (cm^{-1}) observed at 300 K for AlN [30].

AlN	
Hexagonal (wurtzite)	
E_2^L	248.6
$A_1(\text{TO})$	611
$E_1(\text{TO})$	670.8
E_2^H	657.4
$A_1(\text{LO})$	890
$E_1(\text{LO})$	912
Substrate	Sapphire
Thickness(μm)	50–70
Cubic (zinc-blende)	
TO	655
LO	902
Substrate	3C-SiC
Thickness (μm)	0.1–0.4

$x(z, -)\bar{x}$ geometry. The $A_1(\text{TO})$, $E_1(\text{TO})$ and E_2^H phonon modes were located at 611 cm^{-1} , 671 cm^{-1} and 657 cm^{-1} , respectively. These phonon frequencies are almost equal to the reported values for bulk 2H-AlN (see Table 5.2). This good agreement suggests that the $1\text{-}\mu\text{m}$ -thick AlN film grown on the 6H-SiC(11 $\bar{2}$ 0) substrate was fully relaxed.

The result for an AlN film grown on 4H-SiC(11 $\bar{2}$ 0) was noticeably different from that on 6H-SiC(11 $\bar{2}$ 0). Figure 5.20 shows Raman spectra for a $1\text{-}\mu\text{m}$ -thick AlN film grown on a 4H-SiC(11 $\bar{2}$ 0) substrate. The $A_1(\text{LA})$ phonon mode from the 4H-SiC substrate was observed at 610 cm^{-1} in both geometries. As shown in $x(y, -)\bar{x}$, the $E_1(\text{TO})$ and E_2^H phonon modes appeared at 665 cm^{-1} and 656 cm^{-1} , respectively. The difference between the $E_1(\text{TO})$ and E_2^H phonon modes was 9 cm^{-1} , which is obviously smaller than that of 2H-AlN ($\sim 13 \text{ cm}^{-1}$) [30]. This result indicates that the E_2^H phonon mode detected in this sample originated from the zone folding of 4H structure, not the 2H structure (see Fig. 5.21), which is consistent with the RHEED and HRTEM studies described above. The $A_1(\text{TO})$ phonon mode was located at 636 cm^{-1} .

The most striking feature in Fig. 5.20 is the extraordinary phonon frequency shifts for the $A_1(\text{TO})$ and $E_1(\text{TO})$ phonon modes compared to bulk 2H-AlN reported by Davydov *et al* [30]. The $A_1(\text{TO})$ phonon mode was shifted positively from 611 cm^{-1} (bulk 2H-AlN) to 636 cm^{-1} ($+25 \text{ cm}^{-1}$). On the other hand, the $E_1(\text{TO})$ phonon mode was shifted negatively from 671 cm^{-1} to 665 cm^{-1} (-6 cm^{-1}). As to the E_2^H phonon mode, it should be taken into account that the zone folding of the 4H structure was different from that of the 2H structure. From these results, the AlN film was found to be under an enormous anisotropic strain. This is a surprising result because the AlN film grown on the 6H-SiC(11 $\bar{2}$ 0) substrate was fully relaxed at the same thickness ($1 \mu\text{m}$). The positive frequency shift for the $A_1(\text{TO})$ phonon mode indicates a compressive strain in the $[1\bar{1}00]$ axis, while the negative frequency shift for the $E_1(\text{TO})$ results from a tensile strain in the $[0001]$ axis.

Gleize and co-workers have reported the experimental values of biaxial stress coefficients K_λ^B ($\text{cm}^{-1}/\text{GPa}$) for AlN [31]. Also, Wagner *et al.* have studied the theoretical values of biaxial stress coefficients using *ab initio* calculations [32]. Table 5.3 lists the reported biaxial stress coefficients for AlN, where the theoretical values are somewhat lower compared to the experimental ones. By using these reported values, the biaxial stress for the AlN film in the present work was estimated. As for the $[0001]$ axis ($E_1(\text{TO})$), the tensile stress is approximately 2 GPa. On the other hand, for the $[1\bar{1}00]$ axis ($A_1(\text{TO})$), the compressive stress was considerably high, about 18 GPa.

These results are thought to reflect the anisotropic lattice (or strain) relaxation between the $[0001]$ direction and the $[1\bar{1}00]$ direction. If the AlN film is grown on the SiC substrate pseudomorphically, the film is under tension in the $[0001]$ axis, and under compression in the $[1\bar{1}00]$ axis due to the lattice mismatch ($\Delta a \sim 0.9\%$, $\Delta c/n \sim 1.15\%$). Since the $[1\bar{1}00]$ axis is in the hexagonal close-packed (0001) plane, it might take more strain energy for relaxation in the $[1\bar{1}00]$ direction compared to the $[0001]$ direction. In the $[0001]$ direction, the strain energy can be relaxed more easily by introducing misfit dislocations. Although the

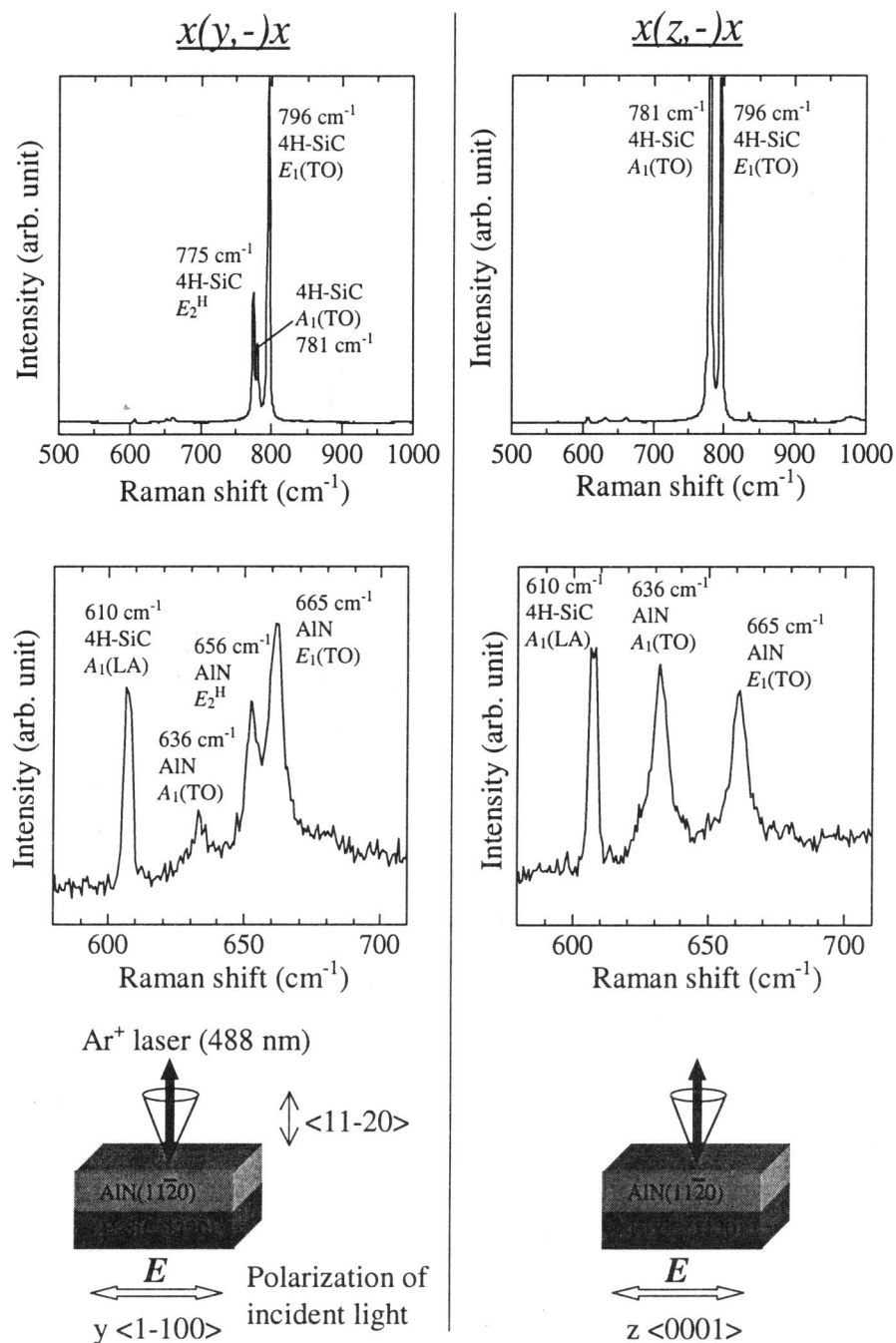


Figure 5.20: Raman spectra for 1- μm -thick AlN film grown on 4H-SiC(11 $\bar{2}$ 0) substrate in backscattering $x(y, -)\bar{x}$ and $x(z, -)\bar{x}$ geometries.

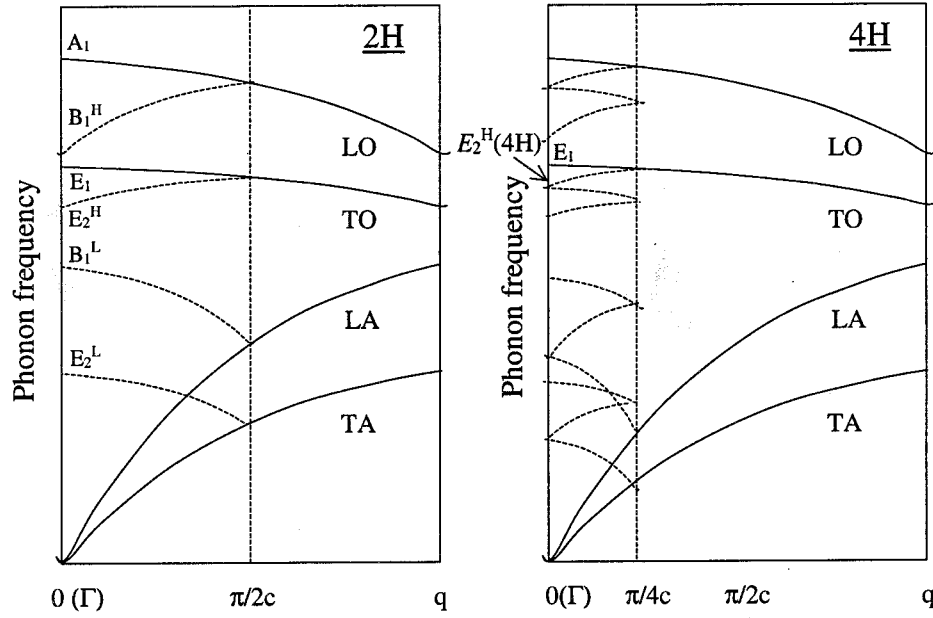


Figure 5.21: Schematic representation of phonon dispersion. Phonon branches along [111] in cubic structure are folded to approximate those of hexagonal structure along [0001].

Table 5.3: Biaxial stress coefficients K_{λ}^B ($\text{cm}^{-1}/\text{GPa}$) for AlN [31, 32].

Mode λ	$A_1(\text{TO})$	$E_2(\text{high})$	$E_1(\text{TO})$	$A_1(\text{LO})$
K_{λ}^B , experimental	2.80 ± 0.57	3.39 ± 0.64	3.01 ± 0.55	1.39 ± 0.28
K_{λ}^B , calculated	2.84	2.56	2.58	2.22

anisotropic relaxation process in the AlN film requires further investigation, the enormous residual strain is thought to result from the excellent interface between 4H-AlN and 4H-SiC(11 $\bar{2}$ 0).

5.5 Summary

AlN growth on 4H- and 6H-SiC(11 $\bar{2}$ 0) substrates was studied. 4H- and 6H-SiC substrates have different stacking sequences, i.e., 4H(ABCB $\cdots$) and 6H(ABCACB $\cdots$). 2H-AlN, which is the thermodynamically stable phase for AlN, was grown on the 6H-SiC(11 $\bar{2}$ 0) substrate, resulting in poor structural quality. In this case, the atomic-template effect of the substrate did not work. A considerably disordered region was observed near the 2H-AlN/6H-SiC(11 $\bar{2}$ 0) interface, attributed to the polytype mismatch. Although the defect density could be reduced to some extent by utilizing an LT buffer layer, it was still unacceptable for device applications.

On the other hand, 4H-AlN, which is a novel polytype for group-III nitrides, was successfully grown on the 4H-SiC(11 $\bar{2}$ 0) substrate due to the atomic-template effect. Owing to polytype replication from the substrate to the epilayer, the interface between 4H-AlN and 4H-SiC(11 $\bar{2}$ 0) was not disordered, and the grown film exhibited superior structural quality.

The perfect polytype matching of 4H-AlN and 4H-SiC(11 $\bar{2}$ 0) is expected to reduce the density of structural defects remarkably, so that almost the same crystalline quality can be achieved as in homoepitaxy.

The reason why the atomic-template effect works in AlN/4H-SiC(11 $\bar{2}$ 0) but not in AlN/6H-SiC(11 $\bar{2}$ 0) has not been elucidated yet. In our speculation, 4H-AlN(11 $\bar{2}$ 0) can be grown on 4H-SiC(11 $\bar{2}$ 0) due to the similar structure of 2H(ABAB $\cdots$) to 4H(ABCB $\cdots$), only one mismatch in every 4ML. On the other side, 2H-AlN(11 $\bar{2}$ 0) is grown on 6H-SiC(11 $\bar{2}$ 0) because of the more dissimilar stacking between 2H(ABABAB $\cdots$) and 6H-SiC(ABCACB $\cdots$), three mismatches in every 6ML.

The results of this study demonstrated that the polytype of the SiC substrate can have a remarkable impact on the crystalline structure of the AlN epilayer.

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Chapter 6

Conclusions

6.1 Conclusions

In this thesis, heteroepitaxial growth of high-quality AlN on SiC was studied using MBE toward the goal of electronic device applications. The interface structure of AlN/SiC (or SiC surface structure) was investigated in detail to obtain AlN epilayers with excellent crystalline quality, and to achieve the AlN/SiC interface with superb electronic properties. Besides the lattice mismatch of 0.9% for the (0001) basal planes, AlN/SiC is a heteropolytypic (2H/4H or 6H) and heterovalent (III-V/IV-IV) system, so that interface control, or tailoring the interface structure, is very important. In heteropolytypic epitaxy of 2H-AlN on 4H- or 6H-SiC(0001) surfaces, the stacking mismatch at the SiC step edges is one of the crucial issues to be solved. In this work, to solve the problems related to polytype mismatch, control of the SiC surface steps was conducted, which led to coherent coalescence of AlN nuclei originating from different terraces of the SiC surface. In the heterovalent system, charge accumulation or depletion at the interface could be avoided by introducing some measure of atomic mixing in such a way as to compensate III-V and IV-IV bonds. In this work, control of the atomic arrangement at the AlN/SiC interface using atomic-nitrogen pre-irradiation was investigated to achieve MIS structures with excellent electrical characteristics. Owing to the pre-irradiation, the electronic properties of the AlN/SiC interface changed dramatically and a noticeably small interface state density was obtained. Also, as another viable approach to solve both the polytype mismatch and the instability problem of polar interface, perfect polytype matching and formation of electronically-stable interface were attempted using nonpolar SiC(11 $\bar{2}$ 0) substrates which has the information of stacking sequence on the surface. 4H-AlN, which is a novel polytype for group-III nitrides, was grown on 4H-SiC(11 $\bar{2}$ 0) substrates by the atomic-template effect of the substrate.

In chapter 3, surface control of the on-axis SiC(0001) substrate was studied to achieve AlN epilayers with excellent crystalline quality. Initial two-dimensional (2D) growth of AlN epilayer was realized owing to surface control of not only the step-and-terrace structure with one-unit-cell-height steps, but also the surface chemistry, i.e., removal of residual oxygen

and realization of a 1/3ML silicon-adsorbed superstructure. It was revealed that the AlN film with initial 2D nucleation exhibited slower lattice relaxation, which suppressed generation of screw-type dislocations. Furthermore, initial 2D growth markedly reduced in-plane misorientation, i.e., the density of edge-type dislocations, thanks to the initial coalescence of AlN 2D nuclei.

Kinetics in the initial stages of AlN growth was investigated from the microscopic point of view. RHEED monitoring and AFM characterization revealed the dissolution mechanism of step bunching and the transition from 2D nucleation to step flow. Evolution of surface features during the initial growth stages was characterized, and the effectiveness of surface step control in reduction of SMBs was experimentally demonstrated owing to coherent coalescence of AlN nuclei originating from different SiC terraces.

The high-quality AlN film grown on the SiC substrate was applied as a buffer layer for GaN growth, and the great impact of AlN film quality on the properties of subsequent GaN epilayers, especially the density of screw-type dislocations, was revealed.

In chapter 4, AlN growth on off-axis SiC(0001) epilayers was studied toward SiC MIS device applications. Remarkable improvement in the AlN surface morphology was obtained by lowering the growth temperature from 1000°C to 600°C, probably due to modification of the initial growth kinetics. The slight misorientation between the AlN growth axis and the *c*-axis of SiC substrate was found, resulting in more rapid lattice relaxation compared to films on on-axis substrates.

The conduction band discontinuity at the AlN/6H-SiC interface was characterized by *in situ* XPS, and found to be 2.0 ~ 2.5 eV, which is large enough for MIS device applications. The *J-E* characteristics also supported this estimate of the band offset, and demonstrated that the AlN with sufficiently low defect density is a promising dielectric material for SiC MIS devices.

Control of the atomic arrangement at the AlN/SiC interface, i.e., artificial manipulation of the interface bonding configuration, was investigated to achieve MIS structures with excellent electrical characteristics. The electronic properties of the AlN/4H-SiC interface changed dramatically with atomic-nitrogen pre-irradiation. Since interface traps are the product of surface reactions during the initial stages of growth, their density can be controlled by varying the growth procedure [1]. Owing to the pre-irradiation, a quite small interface state density was obtained, $3 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ at $E_{C(4H-SiC)} - 0.2 \text{ eV}$. The interface state density for conventional SiO₂/4H-SiC MOS interfaces is more than $10^{12} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ [2] at the energy level, therefore the obtained results suggest the successful use of AlN as an insulator for SiC MIS devices.

In chapter 5, AlN growth on SiC(11 $\bar{2}$ 0) substrates was studied. The nonpolar interface between AlN and SiC(11 $\bar{2}$ 0) would be expected to neutralize/balance the charges at the interface due to the equal numbers of Si-N and C-Al bonds. In the (11 $\bar{2}$ 0) face, polytype replication from the SiC substrate to the AlN epilayer is essential to obtain epilayers with excellent crystalline quality. It is worth noting that if the polytype of the SiC substrate is

successfully replicated to the AlN epilayer, problems related to stacking mismatch between the epilayer and the substrate, which is a major concern in AlN growth on SiC(0001) substrates, can be eliminated.

In this work, AlN growth on 4H- and 6H-SiC(11 $\bar{2}$ 0) substrates was performed. 4H- and 6H-SiC substrates have different stacking sequences, i.e., 4H(ABCB $\cdots$) and 6H(ABCACB $\cdots$). 2H-AlN, which is the thermodynamically stable phase for AlN, was grown on the 6H-SiC(11 $\bar{2}$ 0) substrate, resulting in poor structural quality. In this case, the atomic-template effect of the substrate did not work. A considerably disordered region was observed near the 2H-AlN/6H-SiC(11 $\bar{2}$ 0) interface, attributed to the polytype mismatch. Although the defect density could be reduced to some extent by utilizing an LT buffer layer, it was still unacceptable for device applications.

On the other hand, 4H-AlN, which is a novel polytype for group-III nitrides, was successfully grown on 4H-SiC(11 $\bar{2}$ 0) due to the atomic-template effect of the substrate. Owing to polytype replication from the substrate to the epilayer, the interface between 4H-AlN and 4H-SiC(11 $\bar{2}$ 0) was not disordered, and the grown film exhibited superior structural quality. The perfect polytype matching of 4H-AlN and 4H-SiC(11 $\bar{2}$ 0) is expected to reduce the density of structural defects remarkably, so that almost the same crystalline quality can be achieved as in homoepitaxy.

The reason why the atomic-template effect works in AlN/4H-SiC(11 $\bar{2}$ 0) but not in AlN/6H-SiC(11 $\bar{2}$ 0) has not been elucidated yet. In our speculation, 4H-AlN(11 $\bar{2}$ 0) can be grown on 4H-SiC(11 $\bar{2}$ 0) due to the similar structure of 2H(ABAB $\cdots$) to 4H(ABCB $\cdots$), only one mismatch in every 4ML. On the other side, 2H-AlN(11 $\bar{2}$ 0) is grown on 6H-SiC(11 $\bar{2}$ 0) because of the more dissimilar stacking between 2H(ABABAB $\cdots$) and 6H-SiC(ABCACB $\cdots$), three mismatches in every 6ML. The results of this study demonstrated that the polytype of the SiC substrate can have a remarkable impact on the crystalline structure of the AlN epilayer.

6.2 Outlook for Future Work

Through this work, several aspects in AlN growth on SiC substrates have been clarified. However, there still remain several issues to be solved, and there have emerged some challenges to be accomplished in the future.

- **Generation of edge-type threading dislocations in GaN growth on SiC(0001) substrates with a high-quality AlN buffer layer:**

The high-quality AlN film grown on the SiC substrate was applied as a buffer layer for GaN growth, and the great impact of AlN film quality on the properties of subsequent GaN epilayers, especially the density of screw-type dislocations, was revealed. However, no noticeable improvements in the density of edge-type dislocations were found. Despite the remarkable enhancement of AlN film quality, a considerable density of

edge-type dislocations still remained in subsequent GaN epilayers. In the case of AlN growth on SiC substrates, initial 2D growth dramatically reduced the generation of edge-type dislocations by the initial coalescence of 2D nuclei. Hence, the defective nature of GaN epilayers is probably attributed to the initial growth mode on AlN buffer layers. Although the structural quality of the AlN buffer layer was successfully improved owing to SiC surface control, the 2.5% lattice mismatch between GaN and AlN is still problematic. Further investigation on growth features at the GaN/AlN interface is necessary to reduce the density of structural defects in the GaN films.

- **Dielectric properties of AlN epilayers grown on off-axis SiC(0001) substrates:**

For the AlN films with excellent crystalline quality, satisfactory insulating characteristics were obtained with small leakage current and a high resistivity. However, to achieve reproducible highly-insulating characteristics, further improvements in the crystalline quality of AlN film are necessary. The AlN films grown on off-axis SiC substrates contained numerous defects originating at step sites on the SiC surface. Hence, it was found difficult to achieve sufficient insulating properties compared to AlN films grown on on-axis SiC substrates. Reducing such defects by any means is essential to improve the dielectric properties of AlN films.

- **Advanced control of atomic mixing at the AlN/SiC interface:**

Pre-irradiation by atomic nitrogen was studied intensively as a method to manipulate the interface structure between AlN and SiC. As a result, the electronic properties of the AlN/SiC interface remarkably improved with the pre-irradiation. However, interface fixed charges were found, probably attributed to the occurrence of either oversaturated or undersaturated bonds, i.e., unstable interface structure. One viable approach to solve the instability problem is to control the surface superstructure by using various adatoms. For instance, a surface structure with carbon adatoms bonded to the uppermost silicon atoms of SiC substrate can compensate III-V and IV-IV bonds at the AlN/SiC interface. Thus, tailoring of the AlN/SiC interface and correlations between the interface atomic arrangement and electronic properties are worthy of further study from both the scientific and engineering points of view.

- **Perfect polytype matching in AlN growth on SiC(11 $\bar{2}$ 0) substrates**

Cross-sectional HRTEM investigation on the 4H-AlN/4H-SiC(11 $\bar{2}$ 0) interface revealed that some regions were not of the 4H structure but rather the 2H structure, i.e., faulted. The formation mechanism of the faulted region is probably due to the initial 3D nucleation on the substrate. Once (0001) facets, i.e., *c*-plane sidewalls, are formed in the early stages of growth, 2H-AlN will grow on the facets, i.e., lateral growth toward the *c* direction, resulting in a stacking fault. Therefore, to eliminate stacking

faults, further optimization of the initial growth conditions is necessary. Control of the initial growth conditions might lead to not only high-quality 4H-AlN but also 6H-AlN on 6H-SiC(11 $\bar{2}$ 0) substrates even though the atomic-template effect of substrate is harder to work with this system. Perfect polytype matching of AlN/SiC(11 $\bar{2}$ 0) is expected to reduce the density of structural defects remarkably, so that almost the same crystalline quality can be achieved as in homoepitaxy. Therefore, AlN/SiC(11 $\bar{2}$ 0) is a promising system to realize high-performance polarization-free devices.

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List of Publications

A. Full Length Papers and Letters

1. N. Onojima, J. Suda, and H. Matsunami:
 “Molecular-beam epitaxial growth of insulating AlN on surface-controlled 6H-SiC substrate by HCl gas etching,”
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3. J. Suda, K. Miura, M. Honaga, Y. Nishi, N. Onojima, and H. Matsunami:
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5. N. Onojima, J. Suda, and H. Matsunami:
 “Heteroepitaxial Growth of Insulating AlN on 6H-SiC by MBE,”
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6. N. Onojima, J. Suda, and H. Matsunami:
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7. N. Onojima, J. Suda, T. Kimoto, and H. Matsunami:
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phys. stat. sol. (c) **0** (2003) 2529–2532.
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“Towards High-Quality AlN/SiC Hetero-Interface by Controlling Initial Processes in Molecular-Beam Epitaxy,”
submitted to Mater. Sci. Forum.
11. N. Onojima, J. Suda, T. Kimoto, and H. Matsunami:
“Kinetics of AlN in initial growth stage on surface-controlled SiC(0001),”
in preparation.

B. Conference Proceedings

1. N. Onojima, J. Suda, and H. Matsunami:
“Epitaxial Growth of AlN on 6H-SiC(11 $\bar{2}$ 0) by Molecular-Beam Epitaxy and Effect of Low-Temperature Buffer Layer,”
Mater. Res. Soc. Symp. Proc. **743** (2003) L3.21.
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2. J. Suda, K. Miura, M. Honaga, Y. Nishi, N. Onojima, and H. Matsunami:
“Lattice Relaxation of AlN Buffer on Surface-Treated SiC in Molecular-Beam Epitaxy for Growth of High-Quality GaN,”
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(*Ext. Abstr. Mater. Res. Soc. Fall Meeting*, Boston (MA, USA), 2003.)
3. J. Suda, N. Onojima, T. Kimoto, and H. Matsunami:
“Step-Flow or Layer-by-Layer Growth for AlN on SiC(0001) Substrates,”
to be submitted to Mater. Res. Soc. Symp. Proc.
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C. Related Publications

1. T. Kimoto, Z. Y. Chen, S. Tamura, S. Nakamura, N. Onojima, and H. Matsunami:
“Surface Morphological Structures of 4H-, 6H- and 15R-SiC(0001) Epitaxial Growth
by Chemical Vapor Deposition,”
Jpn. J. Appl. Phys. **40** (2001) 1–5.