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The polarity of AlN films grown on Si(1 1 1)

Vadim Lebedev[a,b,*], Bernd Schröter[a], Gela Kipshidze[b], Wolfgang Richter[a]

[a]*Institut für Festkörperphysik, Universität Jena, Max-Wien-Platz 1, D-07743 Jena, Germany*
[b]*Ioffe Physical-Technical Institute, St. Petersburg 194021, Russia*

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Abstract

The nucleation and subsequent growth of high-quality AlN layers of both crystallographic polarities on nonpolar Si(1 1 1) substrates were investigated. The films were grown by plasma-assisted molecular beam epitaxy. The nucleation conditions of the epitaxial AlN on Si(1 1 1) surface were found to be critical for the formation of the AlN films either with Al- or N-face. The existence of a 7×7-reconstructed Si(1 1 1) surface is also found to be important to provide a proper nucleation and subsequent two-dimensional growth of the AlN (0 0 $\bar{0}$1) and (0 0 0 1) oriented films. The AlN film polarity determination has been performed either ex situ by X-ray photoelectron diffraction or in situ by observing the polarity-dependent surface reconstructions. Finally, the AlN layers of both polarities were characterized by atomic force microscopy to provide information about the surface morphology of the grown films.

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Keywords: MBE; Nitrides; AlN; Polarity; XPD

1. Introduction

Over the last several years, group III nitride-based devices have shown very promising results for possible applications in optoelectronics and high-speed, high-power electronics such as wireless communications. These applications demand large, high-quality substrates with low RF loss. Aluminum nitride on silicon substrates has shown some advantages for these purposes [1,2].

The AlN(0 0 0 1)/Si(1 1 1) heterosystem has shown very promising properties as the basis for surface acoustic wave (SAW) applications [1] and as a template substrate for III-nitride electronics and optoelectronic devices [3]. The integration of group III-nitride optoelectronic devices with the well-developed Si technology may have a number of applications in communication technique [4].

The heteroepitaxial growth of aluminum nitride on silicon is difficult due to a very large misfit of 23.4% usually inducing a three-dimensional growth (3DG) and the formation of a columnar film structure [5]. The large lattice misfit should lead to a high defect density unless the entire misfit is relaxed at the interface. A regular array of misfit

* Corresponding author. Fax: + 49-3641-947442.
E-mail address: lvb@pinet.uni-jena.de (V. Lebedev)

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dislocations at the Si/AlN interface has been visible in transmission electron microscopy (TEM) micrographs published earlier [6]. A geometric analysis shows an approximate 4 : 5 coincidence between Si(1 1 1) and AlN(0 0 0 1) lattices indicating that epitaxy might occur directly on Si(1 1 1) in spite of the significant lattice mismatch.

Likewise, it is well established that the surface and interface properties of the epitaxially grown nitride films depend strongly on the polarity of the layer. A correlation between surface morphology and polarity was clearly observed for the bulk GaN single crystals and for GaN epilayers grown on polar substrates like SiC or ZnO [7,8]. However, the importance of the polar orientation was not so obvious in the case of nitride epilayers grown on nonpolar substrates like Si.

The method of polarity determination also had a great importance in the recent works concerning the growth and characterization of the nitride crystals [8]. In the literature, X-ray diffraction using the anomalous scattering effect, convergent beam electron diffraction (CBED), chemical etching, oxidation or piezoelectric behavior have been used for polarity determination of several polar crystals [8]. X-ray photoelectron diffraction (XPD) has been proved capable of determining the polarity of compound semiconductor surfaces, e.g., of GaN [9], ZnO [10] and 6H–SiC [11]. We used this nondestructive technique to assign the polarity of our aluminum nitride films.

In this paper we report on the MBE growth and polar properties of high-quality AlN films on Si(1 1 1) substrates. It will be shown that the nucleation conditions of AlN films on Si(1 1 1)-7×7 reconstructed surface are critical to form the films of either Al- or N-face polarity.

AlN films polarity determination has been performed either by XPD or by in situ reflection high energy electron diffraction (RHEED) observations of the polarity-dependent surface reconstructions. After the growth, the AlN layers were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD).

2. Experimental details

The AlN films were grown in home-made molecular beam epitaxy system equipped with a radio-frequency plasma source (MPD21, Oxford Applied Research) to supply activated nitrogen.

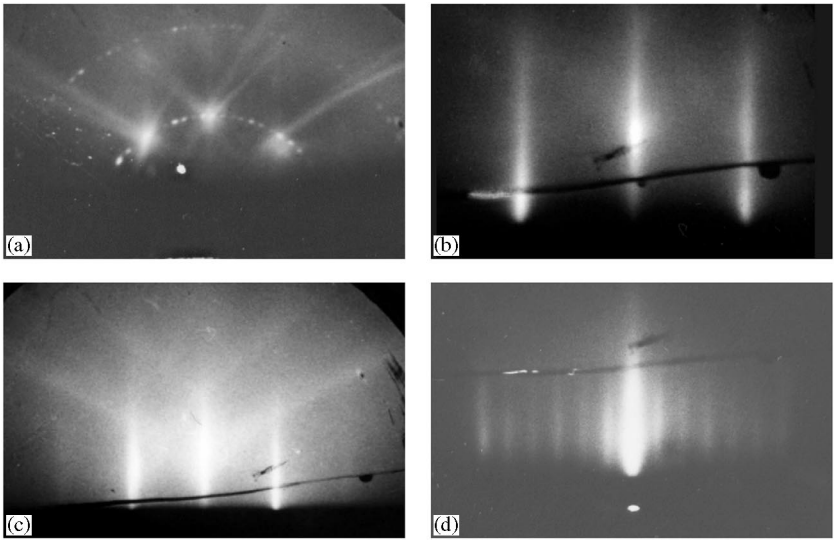

Fig. 1. RHEED patterns of the surface reconstructions for (a) Si(1 1 1))7×7, along [1 1 2] azimuths, and AlN: (b) 1×1, along $\langle 2\,\bar{1}\,\bar{1}\,0\rangle$ azimuths, 1 min after the start, (c) 1×1 along $\langle 2\,\bar{1}\,\bar{1}\,0\rangle$, improvement after the 3DG to 2DG transition, (d) $\times 6$ reconstruction along the $\langle 1\,\bar{1}\,0\,0\rangle$ azimuths during cooling of the specimen down after the growth.

High purity aluminum (6N5) was evaporated from a standard effusion cell. A 10 kV RHEED system was used for monitoring the epitaxial process. The grown sample surfaces were assessed ex situ by a Topometrix TMX-2010 AFM system. The detailed description of the growth and measurement equipment is published elsewhere [5].

p-Type (B-doped, 6.7 $\Omega\,cm^{-1}$) Si(1 1 1) substrates were used in all experiments after a wet chemical cleaning process proposed by Ishizaka and Shiraki [12]. The substrates were annealed under ultrahigh vacuum conditions at temperatures higher than 900°C to remove a thin surface oxide. The surface quality was monitored by RHEED pattern observations. The annealing process was performed until Kikuchi-lines became clearly visible (Fig. 1a). On the clean Si(1 1 1) surface, the 7×7 to 1×1 reconstruction transition was observed at about 830°C [13]. Prior to the epitaxy, a deposition of 2–3 Al monolayers on the clean Si(1 1 1)-7×7 reconstructed surface was performed at lower temperature to prevent the amorphous SiN_x formation.

The growth rate ranged from 120 to 280 nm h^{-1}. The post-growth annealing treatment at 880°C was generally performed in order to increase the structural film quality.

The XPD patterns of Al 2p and N 1s core-level intensities have been measured using Mg K_α (1253.6 eV) and Al K_α (1486.6 eV) radiation for photoelectron excitation. The stepper-motor controlled manipulator was used for angular-dependent measurement of the photoelectrons. The angular resolution of the SPECS hemispherical electron analyzer was 4°. The angle between the X-ray source and the electron analyzer was fixed at 35° and the polar angle between the direction of the analyzer entrance and the normal of the sample surface was varied by rotating the sample holder.

3. Results and discussion

The usual nucleation and subsequent growth procedure consisted of three basic steps: (1) a nucleation of 2–3 strong-stressed AlN monolayers (ML) on a 7×7-reconstructed Si(1 1 1) surface at a temperature lower than the growth temperature, (2) a gradual increasing of the sample temperature to the growth point usually ranging from 860°C to 880°C, (3) a subsequent AlN long-term epitaxy under stable growth conditions.

The first step is peculiar for well-pronounced RHEED pattern streaks from a two-dimensionally growing stressed AlN layer (Fig. 1b). After the formation of 10–12 AlN MLs, the pattern acquires the features more characteristic of 3DG, which points to an increase in roughness of the growing low-temperature layer. Further increase of the substrate temperature to the usual growth point leads to a significant improvement of the RHEED pattern and after approximately 50 AlN MLs the pattern gets more streaky and well pronounced. The growth becomes two-dimensional (2DG) with 1×1 RHEED pattern (Fig. 1c). The corresponding surface roughness, as follows from the AFM measurements (Fig. 2), decreases with an increasing layer

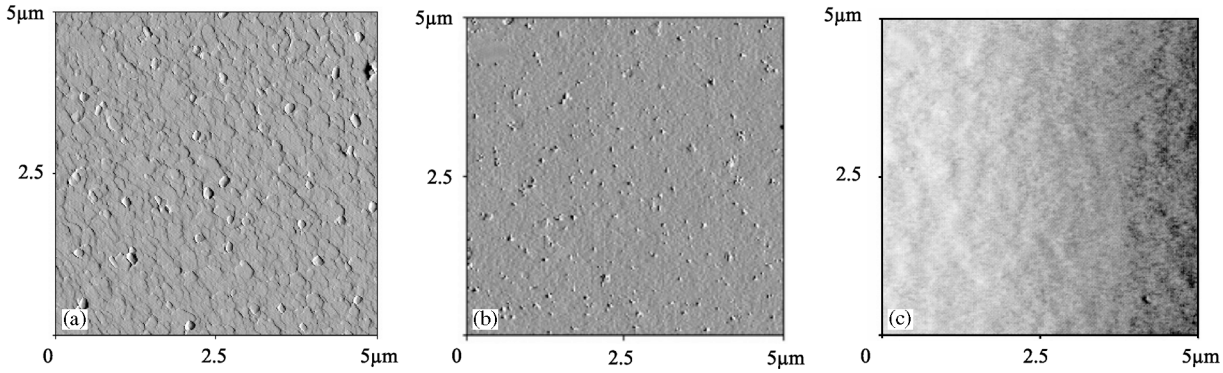

Fig. 2. AFM images of AlN layer surfaces of (a) 50 nm thick film with RMS ~ 9 nm, (b) an improvement of the surface morphology for the thickness of about 200 nm (Al-face, RMS ~ 1.8 nm), (c) 1.1 μm thick layer (N-face, RMS ~ 0.4 nm).

thickness and a typical value of the root-mean-square (RMS) roughness parameter ranges from 9 nm for 50 nm thick films to 0.2 nm for films thicker than 400 nm. From X-ray measurements, the typical value of FWHM (AlN(002), omega-scan) for the 1 μm film is about 0.2°.

An optimization of the initial Al : N flux ratio and substrate temperature for the nucleation process allows avoiding the AlN island formation during the second stage of the growth and thus, to reach a pure 2DG. Such optimization was performed for the AlN nucleation at temperature 800°C and continuous 2DG, in this case, can be explained only by practically full relaxation of the initial lattice misfit on the hetero-interface and only a residual weak stress of the next AlN monolayers can affect the subsequent growth.

If there is no sufficient relaxation of the initial misfit, island formation occurs and an increasing stress energy of the growing layer leads to a transition from 2DG to 3D-like growth. The next transition from 3DG to 2DG may correspond to the coalescence of the AlN islands with a subsequent step controlled overgrowth and can be explained by the rising Al adatoms mobility by a significant substrate temperature increase after the nucleation at low temperature point.

3.1. AlN nucleation on Si(1 1 1) 7 × 7- and 1 × 1-reconstructed surfaces

The reasons for the 2DG of AlN on Si(1 1 1) lie obviously in the atomic arrangement and energetic of the *7 × 7-reconstructed* silicon surface. The Si(1 1 1)-7 × 7 surface has a spatially complex, three-monolayer-deep surface structure [14]. From our viewpoint, it makes this surface favorable for the creation of a new material superstructure with a partial substitution of the substrate adatoms and restatoms by the adsorbed Al and N atoms of the nucleating layer. Then the arrangement of initially adsorbed atoms establishes the regular array of the surface supercells which is responsible for 2DG of the epitaxial layer with its own lattice constant. This also explains the almost full AlN lattice constant relaxation on the distance of 1–2 monolayers from the hetero-interface.

In the high-temperature range the Si(1 1 1) surface loses the spatial structure and 1 × 1 RHEED pattern appears from Si (1 1 1) plane after the phase transition at 830°C. From the experiment, no proper nucleation was observed on the flat Si-1 × 1 surface. Thus, it allows to presuppose that only Si 7 × 7-reconstructed surface provides a sufficient number of advantageous nucleation sites for the proper nucleation and subsequent 2DG of the nitride material.

3.2. Polar properties of AlN epilayers

RHEED studies of AlN films nucleated at different conditions have demonstrated reproducibly either a (1 × 1), (2 × 6) sequence or a (1 × 1), (1 × 3), (3 × 3), (6 × 6) sequence for the AlN RHEED patterns. The subsequent XPD measurements confirmed that the films with a final (2 × 6) and (6 × 6) reconstructions have Al-face and N-face polarity, respectively.

Four types of growth experiments were performed to determine the influence of the nucleation parameters on the formation of either Al- or N-face polarity of the AlN layer.

(i) The experiments of the first group were performed at a nucleation temperature of about 700°C on the annealed Si(1 1 1) 7 × 7 reconstructed surface with a subsequent gradual increase of the substrate temperature to 860–880°C for a long-term epitaxy of thick AlN films. The layers grown on these conditions are unipolar and have N-face polarity demonstrating a smooth surface with RMS ~ 0.4–0.6 nm according to AFM measurement.

(ii) The second group of experiments had a nucleation temperature ranging from 770 to 800°C and a procedure of the subsequent growth similar to (i). These films are unipolar as well and demonstrate Al-face polarity. The surface roughness of these layers (RMS ~ 0.2–0.5 nm) are typically a little lower than for the N-face samples.

(iii) In the third group of experiments, the nucleation temperature range was significantly higher than 830°C (880–900°C) and the nucleation

process on the Si(1 1 1)-1 × 1 surface was investigated. For the epitaxy at these conditions no acceptable surface quality of the AlN films was observed. The XPD measurements show the existence of both AlN polarities with a strong domain structure of the film surface with RMS > 5 nm.

(iv) Finally, the nucleation process initiated with either Al or N* flux was investigated. After 10–20 s of a single flux deposition (2–3 MLs for Al), the second shutter was opened and a normal nucleation of the binary compound followed. For all types of the initiations with either Al or N flux, in a wide temperature range, no intuitively expected N-face or Al-face polarity formation was observed. Thus, as it follows from the experiment, only the nucleation temperature remains the driving force of the Al- or N-face polarity formation of the AlN film.

According to the RHEED measurements, only a small difference in the growth mode for Al- and N-face layers was observed. The longer period of 3D-like growth for N-face films can be explained by the longer time required for the gradual increase of the specimen temperature from the nucleation point to the usual growth temperature. For a thickness more than 400 nm, the films of both polarities show similar surface morphology with a low surface roughness (RMS less than 0.4 nm). These findings do not directly correlate with the GaN data, where the best results in surface and bulk properties of GaN were observed for the Ga-face layers (see Ref. [8]).

The role of the silicon 7 × 7-reconstructed surface in the unipolar AlN layer formation was clearly confirmed by the experimental results, because the nucleation on the relatively flat high-temperature 1 × 1-reconstructed surface leads to a strong domain structure of the film surface and a random polarity nucleation. However, the exact nature of the polar properties of AlN films grown on the Si(1 1 1) surface remains still an open question and requires further theoretical and experimental investigations.

3.3. XPD polarity determination

For AlN, the XPD patterns are obtained by angular-resolved detection of Al 2p and N 1s photoelectron intensities. Due to the strong forward focusing nature of the electron scattering in the energy region near 1 keV, the diffraction pattern is dominated by forward scattering peaks pointing along the low-index directions of nearest-neighbor high-density atomic rows [15]. Thus, information on the atomic structure in real space can be obtained. The situation may be more complicated than in this simple forward-scattering picture because of high-order interference and multiple-scattering effects. Thus, in reality, more complex XPD patterns are usually observed.

We identified the polar sides of aluminum nitride films by comparing the experimentally obtained

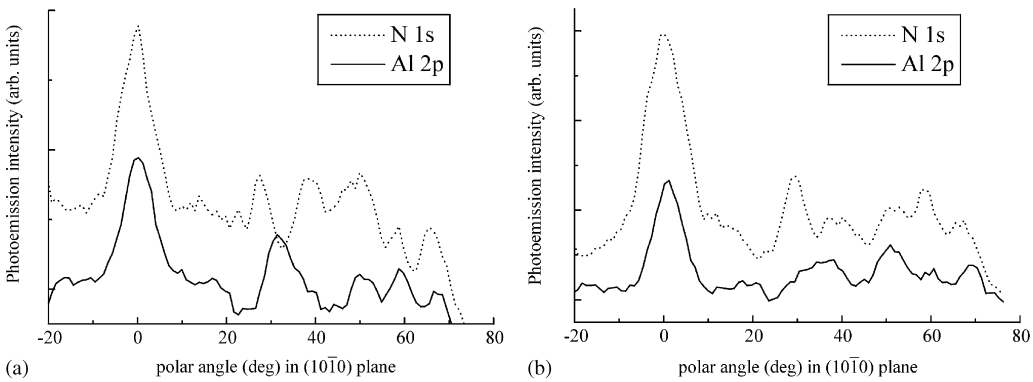

Fig. 3. Experimental polar angle scans of Al 2p and N 1s photoemission intensities with Al K_α excitation in the (1 0 $\bar{1}$ 0) azimuthal plane obtained on AlN films grown on Si(1 1 1) with (a) Al side and (b) N side polarity.

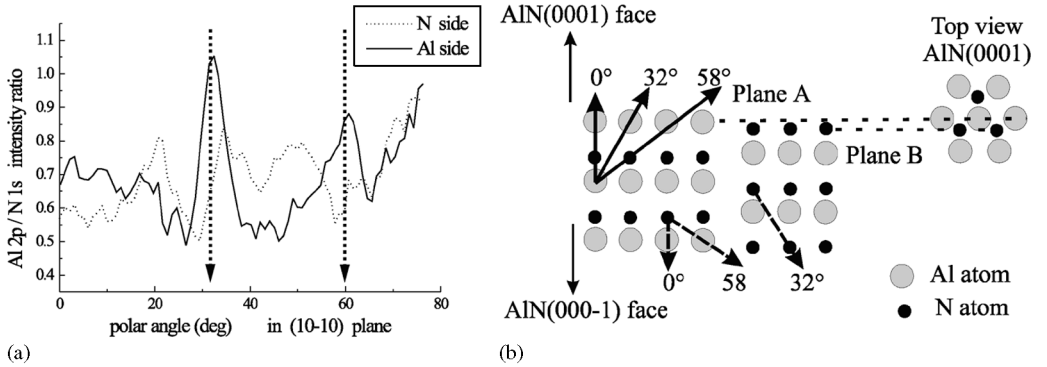

Fig. 4. (a) Experimental polar angle scans of the Al2p/N1s photoemission intensity ratios on both polar sides of AlN in the (1 0 $\bar{1}$ 0) azimuthal plane. The strongest differences between both polarities are measured at polar angles near 32° and 59° which correspond to the next-neighbor directions in the AlN crystal. (b) Geometrical arrangement of Al and N atoms in both {1 0 $\bar{1}$ 0} crystallographic planes A and B. On both polar sides, Al and N atoms are only chemically exchanged.

XPD pattern with those measured for AlN films on both polar sides of 6H–SiC. As it was mentioned in a recent review by Hellman [8], the aluminum side of AlN can be grown on the silicon side of SiC(0 0 0 1) whereas the nitrogen face is on the carbon side. The resulting Al 2p and N 1s diffraction patterns are different for both polar sides. A discussion of the whole diffraction patterns obtained for AlN films with different polarity will be published elsewhere.

Besides AlN films grown on SiC(0 0 0 1) and (0 0 0 $\bar{1}$), we measured more than 20 different samples of AlN films grown on Si(1 1 1). The AlN films grown at definite conditions on 7×7-reconstructed silicon surface have shown XPD patterns which fit exactly into one of the patterns obtained for the AlN films grown on the polar faces of 6H SiC(0 0 0 1) or (0 0 0 $\bar{1}$). A superposition of the diffraction patterns of both polarities was measured on AlN films nucleated at high temperature near 900°C on Si(1 1 1).

Fig. 3 shows the XPD patterns obtained with the high-symmetry (1 0 $\bar{1}$ 0) azimuthal plane. The AlN(0 0 0 1) and (0 0 0 $\bar{1}$) faces have the same crystallographic symmetry and the Al and N atoms have the same geometrical surrounding differing only in the exchange of Al and N atoms. Due to this symmetry, the Al 2p (N 1s) XPD patterns on one polar side would be expected to be similar to the N 1s (Al 2p) patterns on the other side. Although there is some similarity, there are differences, especially at polar angles between 25° and 40° (Fig. 4). These are caused by the different Al and N scattering amplitudes. Aluminum is a stronger electron scatterer than nitrogen. There are pronounced forward-scattering peaks in normal emission (0°), which is the direction of the highest atom density. The Al2p/N1s intensity ratio at 0° is slightly higher (20%) on the Al face reflecting the stronger forward focusing in short-distance next-neighbor directions. On the N-face, nitrogen has the shorter distance to aluminum in a normal direction which results in a higher N 1s intensity.

The strongest differences in photoemission intensities suitable for a quick and unambiguous determination of polarity were found in the (1 0 $\bar{1}$ 0) azimuthal plane at polar angles of 32° and 59° (see Fig. 4). These are the directions of short neighbor distances between the atoms of the same element (32°) and between Al and N atoms (58.5°), respectively. The Al face shows high Al2p/N1s intensity ratios at these crystallographic directions, whereas the N face shows minimum at slightly lower polar angles. Similar differences representing deviations from the simple forward-scattering picture have been observed, especially, for atoms with a low scattering amplitude in compound materials, e.g., carbon in SiC. Multiple-scattering effects have to be considered for interpretation of experimental

diffraction patterns, which is beyond the scope of this paper.

4. Conclusions

In this paper we demonstrated the possibility of the MBE growth of AlN films with both crystallographic polarities on nonpolar Si(111) substrates. The nucleation temperature was found to be responsible for AlN film formation with either Al- or N-face polarity. The role of Si(1 1 1) 7×7-reconstructed surface in the nucleating process was considered. The experimental results allow to conclude that the properties of the 7×7 reconstruction are a key for obtaining the proper nucleation and subsequent 2D-growth of unipolar AlN films on Si(1 1 1) substrates. The role of the 7×7-reconstructed surface peculiarities in nucleation and growth of AlN films with different polar orientation demands further investigations.

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