

A CHEMICAL AND STRUCTURAL STUDY OF THE AlN-Si INTERFACE

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Abstract

Samples of AlN grown on silicon [111] substrates were examined using electron energy loss spectroscopy (EELS) and selected area diffraction (SAD) with high-resolution transmission electron microscopy (TEM) to determine the source of out-of-plane tilts and in-plane rotations of the AlN crystallite at the Si interface. SAD results indicate that the interracial crystallite are sheared along vertical planes, with random, intercrystalline rotation. The interracial phenomena are believed to be the result of Si-Al-N interaction. Analytical experiments show no evidence of silicon nitride formation, witnessed by nitrogen-K peak shape, up to the Si interface. No evidence of substrate-epilayer interdiffusion was observed. Chemical interaction within one monolayer of the interface is therefore suspected as the cause of the epilayer tilts and rotations.

Introduction

The growth of low defect density heteroepitaxial AlN has great implications for optoelectronic and high power devices since the AlN can be used either as device material or as a buffer layer for the overgrowth of other group III-Nitrides. Silicon substrates are particularly attractive for the growth of AlN when considering cost, defect density, available sizes, ease of etching and cleaving and finally the possibility of incorporating III-N devices in VLSI circuits. The current limitations of AlN/Si crystalline quality may stem from interactions occurring at the AlN-Si interface during nucleation, observed in this study using transmission electron microscopy, whereby incipient AlN interracial crystallite are mis-aligned with respect to the substrate.¹ These mis-alignments, witnessed both in and out of the AlN basal plane, are accompanied by a thin amorphous-like region at the AlN/Si interface, and are believed to be a particular feature of III-N/Si growth. Overcoming this errant behavior during subsequent growth, or eliminating these effects entirely would improve epitaxial-layer crystal quality. The focus of the present paper is on the mechanisms giving rise to these features.

Ideally, close-packed planes and directions of the abrupt silicon [111] substrate surface are matched by equivalent planes and directions in the hexagonal AlN epilayer, according to:

$$\begin{aligned} (111)_{\text{Si}} // (0002)_{\text{AlN}} \\ [\bar{1}10]_{\text{Si}} // [11\bar{2}0]_{\text{AlN}} \end{aligned}$$

It has been reported that the close-packed planes between the two layers are randomly tilted away from parallel by $\pm 3-4^\circ$; close-packed directions within these

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planes between the two layers differ randomly by as much as several times this amount.¹ Chemical interactions in the Si-Al-N system appear to be largely responsible for these phenomena. Such interactions, especially those resulting in amorphous compound formation, may disrupt the ideal epitaxial relationship.

In this work, the results of transmission electron microscopy (TEM) involving both high resolution imaging and electron energy loss spectroscopy (EELS) of AlN/Si layers are reported and the relationship between Si-Al-N interactions and the mis-orientation of AlN nuclei is discussed.

Experimental

Single crystal AlN was deposited over Si[111] substrates using reactive molecular beam epitaxy (MBE) and low-temperature metalorganic chemical vapor deposition (MOCVD). Samples for TEM were prepared as in (1). High-resolution TEM imaging was performed at JPL. Analytical microscopy (chemical) was performed both at Berkeley (see Acknowledgments) and at Tempe. At Berkeley, a JEOL 200cx, operating at 200 keV was used with a Gatan PEELS system, functioning with approximately 2.5 V resolution. Sampling diameters were about 0.1 μm . At Tempe, a VGHB501 scanning TEM was used at 100 keV with approximately 1 V resolution and 0.001 μm probe diameter.

Results and Discussion

Figure 1 shows a typical cross-sectional high-resolution TEM image with corresponding electron diffraction pattern. The image shows the out-of-plane tilt and amorphous-like background at the interface that are the subjects of this paper. Apparent in the diffraction pattern is how the tilting of the planes, in this perspective, is confined to the basal planes, and not to the orthogonal (1 $\bar{1}00$)-type planes, as witnessed by the degree of arc for the corresponding reflections. The latter reflections thus remain perpendicular to the AlN/Si interface. These, along with those of (11 $\bar{2}0$)-type, show considerable rotation about the basal plane when viewing the epilayer from above (plan-view), however. Simple tilts and anti-rotations of the hexagonal crystallite seem to be the obvious explanation for the observed images and diffraction patterns, but this would render the vertical planes no longer normal to the silicon surface, and no streaking about the central spot is seen for the $\bar{1}00$ reflections. (Occasionally, however, arcing about the central spot is observed for the vertical planes, indicating simple tilts and rotations for these occurrences.) Distortion of the unit cell is then necessary, but it must be done such that the basal planes are tilted, while the vertical planes remain normal to the silicon surface. This is possible if the unit cell is sheared along these vertical planes. Plan-view samples show these planes to be significantly and randomly rotated about the silicon surface normal. Distortion of the hexagonal unit cell to realize this rotation would again bring the vertical planes away from parallel to the surface normal. It therefore appears likely that the rotation takes place intergranularly. Both the tilting and the rotation are enough to produce the amorphous-like appearance in high-resolution images.

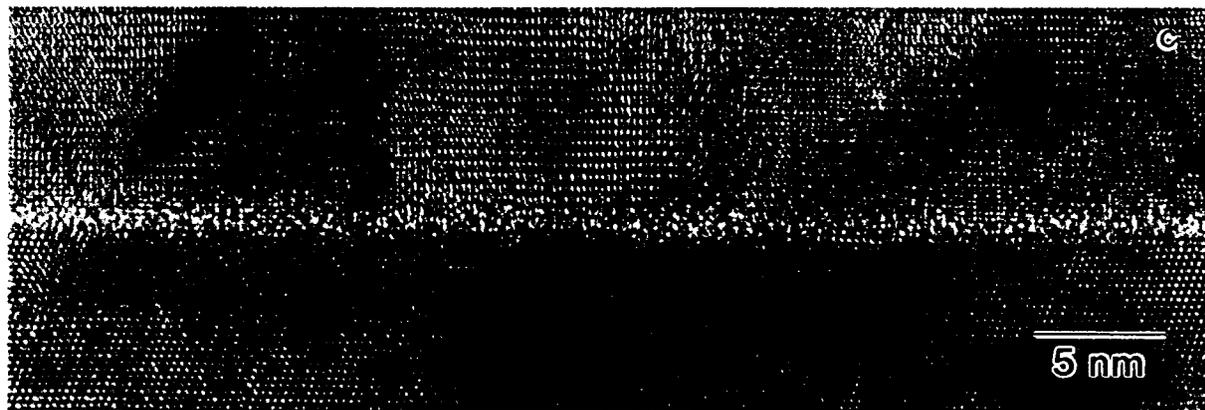
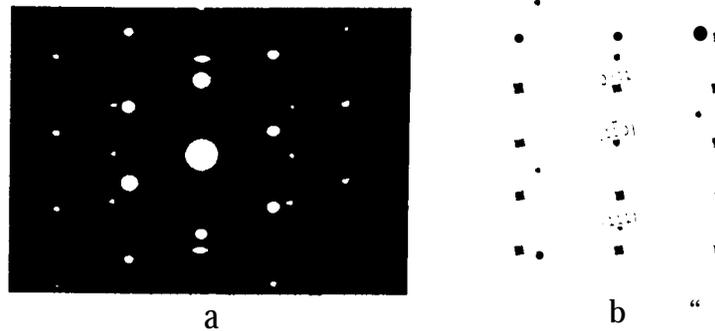


Figure 1: SAD (a), with simulation (b), and corresponding high-resolution TEM cross-sectional image (c), showing interface between silicon (bottom) and AlN (top). Seen, are the diffuse interracial region and AlN crystallite with mis-orientations.

The arrangement at the silicon interface' is such that each crystal is sheared along vertical sets planes and rotation is confined to the interface between the crystallite. This situation suggests the existence of compressive stresses in the nucleating layer, where the tilting of basal planes with larger lattice parameter than that of the substrate yields a projected lattice with more comparable dimensions. Likewise, the rotations may further buckle the epitaxial layer to relieve compressive stress. Compressive stress is not expected for AlN on Si, however. The lattice parameter of AlN is much smaller than that of the silicon substrate, giving a tensile stress in the epitaxial layer. Silicon nitride, on the other hand, can have a hexagonal lattice parameter that is slightly larger than twice that of silicon in the [111] plane. Alpha-Si₃N₄ has a basal-plane lattice parameter of approximately 0.78 nm, and that for the beta phase is around 0.76 nm (about twice the parameter of silicon in the [111] plane).² The former Si₃N₄ phase would then yield the necessary compressive stress.

The accompanying distortion would help to preserve the interracial bonding, while relieving compressive stress. It is therefore likely that, when considering only lattice parameter, the energy expense of distorting the AlN unit cell is lower in magnitude than that for breaking the bond across the AlN/Si interface, and lower than the energy required to initiate an interfacial dislocation. This suggests a quantifiable relationship between the interlayer bonding strength, the energy of distortion, and the dislocation generation energy. However, in addition to lattice

parameter-based stresses, silicon nitride-type bonding would introduce different bond angles.

Like silicon and AlN, the fundamental building block for both alpha and beta silicon nitride idealized bulk structures is the tetrahedron, with Si residing at the center and N at the vertices. Each N is common to three tetrahedra, as opposed to the analogous four for the AlN structure. That is, one structure has three Si around each N, and the other has four Al. It is this difference in the angular distribution of tetrahedra that would provide the necessary distorted template for the observed AlN growth. This may not necessarily require more than a monolayer of silicon nitride to produce the interracial effects observed here. (That the epitaxial structure maintains the directional information of the substrate suggests minimal silicon nitride formation.) It may be that the Si-N bonding across the interface is sufficient for the nitrogen to lower the number of required neighbors at the interface, thus distorting the tetrahedral arrangement and giving bond lengths and directions more toward those of Si_3N_4 . Indeed, as this tilting has been observed to a lesser degree for SiC substrates,³ where the interface is defined by the abrupt termination of the bulk material,⁴ the very presence of the single interracial Si-N bond may be sufficient for this effect. The following examines the extent of Si_3N_4 formation on the present Si substrates.

Figure 2 a-c shows energy-loss spectra obtained with the JEOL 200cx for the nitrogen-K peak for AlN, the AlN/Si interface, and a Si_3N_4 standard, respectively. Examination of the larger peak shapes (particularly the second-largest peak) and intensities for the three spectra shows that no Si_3N_4 -type bonding is evident at the Si interface. The spectra show the 2.5 V resolution to be sufficient for distinguishing between the two bonding situations. The 0.1 μm probe size would not be expected to reveal interracial silicon nitride formation as the relatively small volumes would contribute negligibly to the peak shapes. Figure 3 shows spectra taken using the HB501, utilizing its smaller probe diameter. The similar N-K peak shapes between bulk and interface demonstrate no silicon nitride evidence. Additionally, Si was not found to diffuse into AlN; nor was Al or N found to diffuse into Si. These spectral results show that the chemical interactions responsible for the tilts and rotations of the AlN crystallite are confined to the nearest monolayer to the interface.

Conclusions

It has been shown that the tilts, rotations, and amorphous-like layer reported in (1) consist of shear along vertical planes of the hexagonal unit cell and intergranular rotation of the basal planes. The amorphous-like layer is then the projection of the atomic columns after displacement. Silicon nitride formation was not observed, nor was interdiffusion between the layers at the interface. The influence of the Si-N interracial bond to alter the nearest-neighbor configuration of the first-layer nitrogen atoms is suspected to be the cause of the out-of-plane tilts and in-plane rotations.

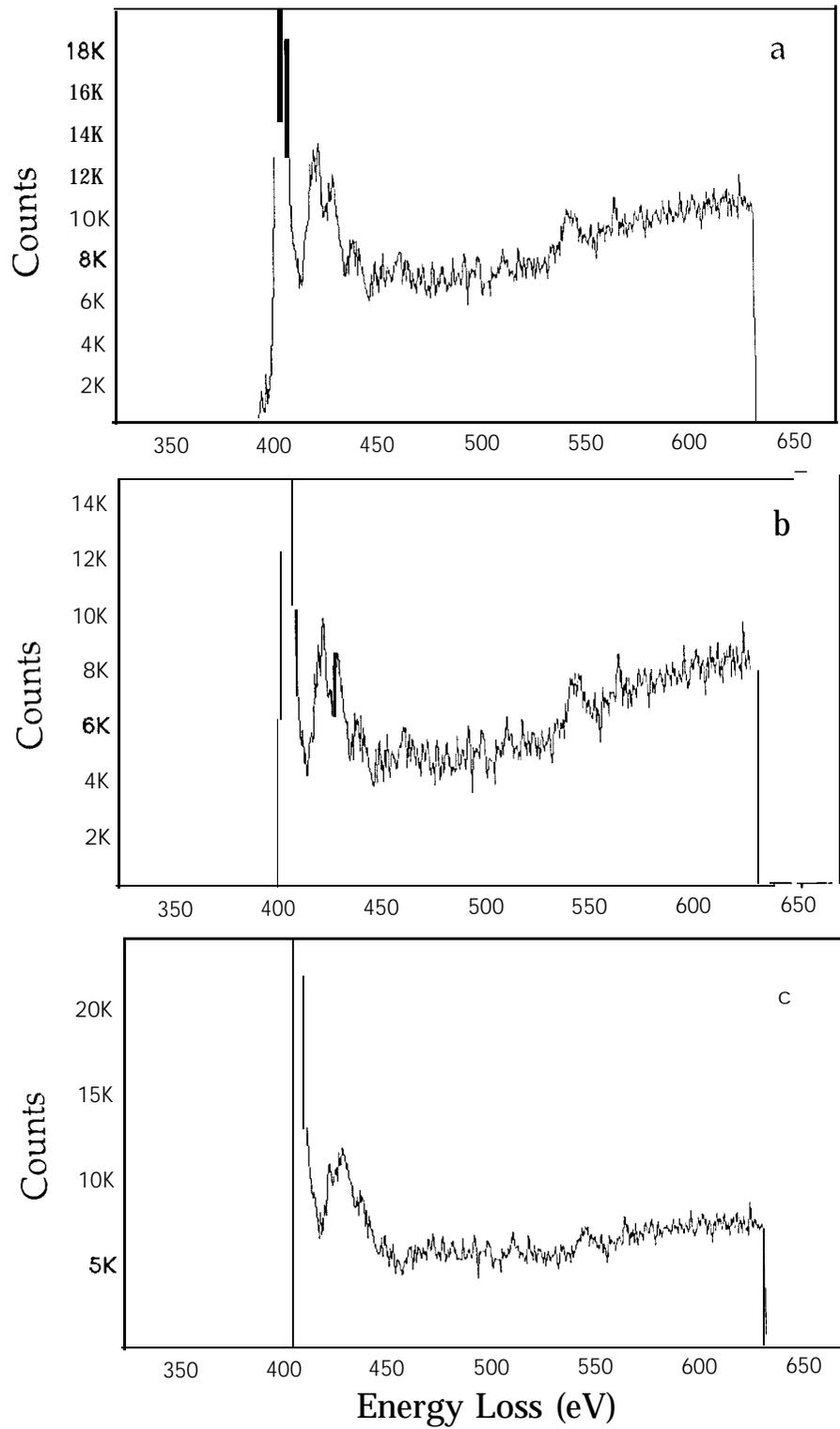


Figure 2: Electron energy loss spectra for nitrogen K (a) in AlN layer, (b) in AlN at Si interface, and (c) in silicon nitride standard.

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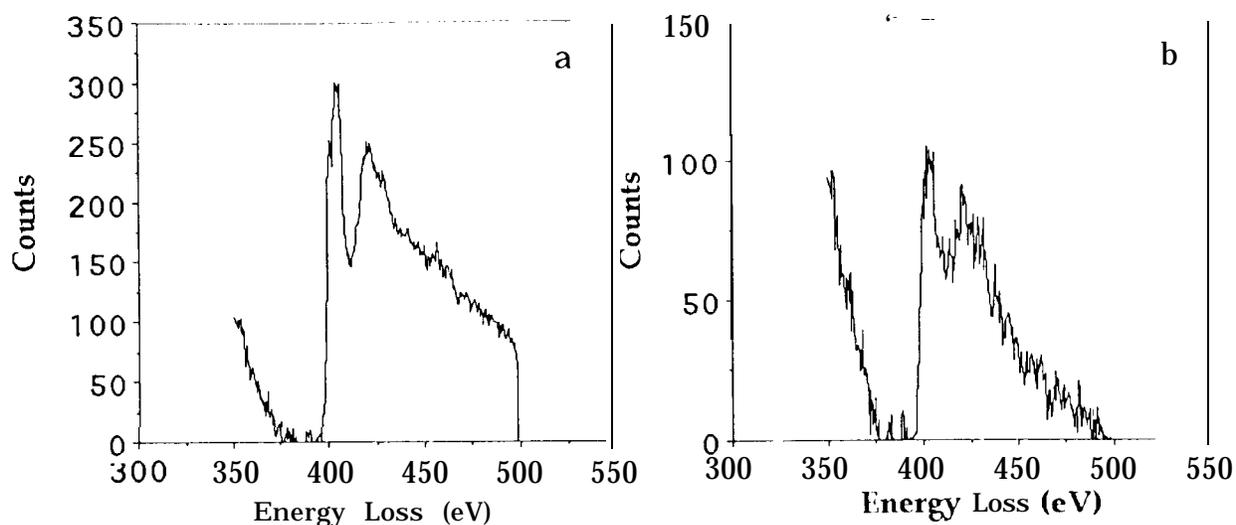


Figure 3: Electron energy loss spectra, showing N-K peaks for AlN layer (a) well away from Si interface and (b) at Si interface, using smaller probe diameter (monolayer scale) than that used in Figure 2. Silicon nitride-type peak is not observed (see Figure 2c).

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