The Properties of Annealed AlN Films Deposited by Pulsed Laser Deposition

K.A. JONES,[1] M.A. DERENGE,[1] T.S. ZHELEVA,[1] K.W. KIRCHNER,[1] M.H. ERVIN,[1] M.C. WOOD,[1] R.D. VISPUTE,[2] R.P. SHARMA,[2] and T. VENKATESAN[2]

1.—U.S. Army Research Lab, 2800 Powder Mill Road, Adelphi, MD 20783.
2.—University of Maryland, Physics Dept., College Park, MD 20742

AlN films deposited on SiC or sapphire substrates by pulsed laser deposition were annealed at 1200°C, 1400°C, and 1600°C for 30 min in an inert atmosphere to examine how their structure, surface morphology, and substrate-film interface are altered during high temperature thermal processing. Shifts in the x-ray rocking curve peaks suggest that annealing increases the film density or relaxes the films and reduces the *c*-axis Poisson compression. Scanning electron micrographs show that the AlN begins to noticeably evaporate at 1600°C, and the evaporation rate is higher for the films grown on sapphire because the as-deposited film contained more pinholes. Rutherford backscattering spectroscopy shows that the interface between the film and substrate improves with annealing temperature for SiC substrates, but the interface quality for the 1600°C anneal is poorer than it is for the 1400°C anneal when the substrate is sapphire. Transmission electron micrographs show that the as-deposited films on SiC contain many stacking faults, while those annealed at 1600°C have a columnar structure with slightly misoriented grains. The as-deposited films on sapphire have an incoherent interface, and voids are formed at the interface when the samples are annealed at 1600°C. Auger electron spectroscopy shows that virtually no intermixing occurs across the interface, and that the annealed films contain less oxygen than the as-grown films.

Key words: AlN, anneal, laser, deposition, spectroscopy

INTRODUCTION

AlN films have been used as encapsulates for annealing ion implanted SiC films,[1–3] a buffer layer for growing GaN films on sapphire[4–8] or SiC,[9] an insulating dielectric,[10–12] and as a thin film resonator.[13] They have been deposited by pulsed laser deposition (PLD),[14–17] organometallic vapor phase epitaxy (OMVPE),[4–11,18] molecular beam epitaxy (MBE),[19,20] chemical vapor deposition (CVD),[21,22] and reactive ion sputtering[23–26] on a variety of substrates. The films often are composed of crystallites highly oriented in the *c* direction.[7–9,15] Their misorientation relative to each other is usually so small, < 1°,[7] that the film is often said to be a single crystal containing a large number of defects frequently designated as stacking mismatch boundaries or microcrystallographic domain boundaries.

Some of the properties that make AlN an attractive material for device processing and/or direct device applications are that it is thermodynamically stable to relatively high temperatures,[27] it is transparent well into the UV because it has a large energy gap (6.2 eV), and the speed of sound through it is higher (5500 m/s) than it is for most materials. These attractive properties have not yet been fully realized, in part, because it is very difficult to grow high quality AlN films. In this paper we explore the possibility of improving the properties of these films with relatively high temperature anneals, and determine the maximum temperature the films can be heated to before they begin to deteriorate.

Using transmission electron microscopy (TEM) and x-ray diffraction (XRD), we examine how the many

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defects are affected by annealing the AlN films in an inert atmosphere at temperatures as high as 1600°C. At this temperature morphological defects created by the evaporation of the AlN are studied with scanning electron microscopy (SEM). The morphological quality of the as grown films is also assessed with SEM. We are also interested in how annealing affects the structure and the chemistry of the interface of the films grown on either SiC or sapphire. We examined the structure using TEM and Rutherford backscattering spectroscopy (RBS), and studied the interface chemistry using Auger electron spectroscopy (AES).

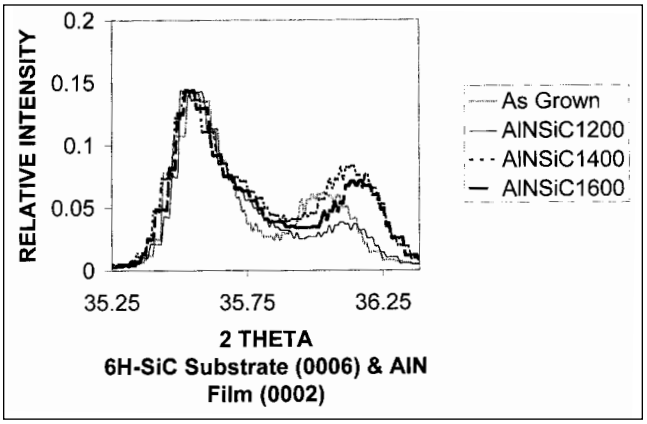
PROCEDURE

The AlN films were deposited on 6H-SiC cut 3.5° off axis and on sapphire substrates by PLD. The 6H-SiC substrates were chemically cleaned in a 10% HF solution, while the sapphire substrates were thermally cleaned during the heating up process. Deposition was done with a KrF excimer laser operating at 248 nm with an energy density of 2 J/cm^2. The base pressure in the system was 3×10^{-8} torr. The film was deposited in an NH_3 background pressure of 5×10^{-5} torr at a substrate temperature of 900°C to a thickness of ~100 nm. The samples were annealed in flowing argon at a pressure of ~400 torr at 1200°C, 1400°C, and 1600°C for 30 min.

An Hitachi S-4500 FE (field emission) SEM operated at 25 keV was used to study morphological changes in the films annealed at the various temperatures. The uncoated films were observed at a 25° tilt to improve the topographic contrast using the in-the-lens secondary electron detector. The structure was examined with a Bruker x-ray diffraction system by recording the position and the shape of the x-ray rocking curves with an emphasis on the (0002) AlN and the (0006) 6H-SiC and sapphire peaks. Spectra were taken at 45 kV and 44 ma. Micrographs were also taken with a JEOL 2010 TEM operated at 200 kV to assess the defect structure of the films and the quality of the substrate-AlN interface. Samples were prepared using the standard "sandwich" procedure, including grinding, polishing, dimpling, and ion milling at the final stage. All images were taken in the bright field imaging conditions. RBS and ion channeling techniques using a well collimated (divergence < 0.01°) beam of 1.5–3.0 MeV He^+ ions were used to examine the quality of the film-substrate interface. The interface was also probed with a PHI 660 SAM (scanning Auger microprobe)/SEM to see if there was carbon buildup at the interface due to the loss of silicon. It was also used to probe the oxygen content of the films. Precautions were taken to minimize the buildup of charge at the sample during the Auger analysis. In particular, the primary electron beam (5 keV) and detection optics were at a 60° angle with respect to the sample normal.

RESULTS AND DISCUSSION

The (0002) x-ray rocking curves for the AlN grown on either SiC or sapphire shown in Fig. 1 are shifted



a

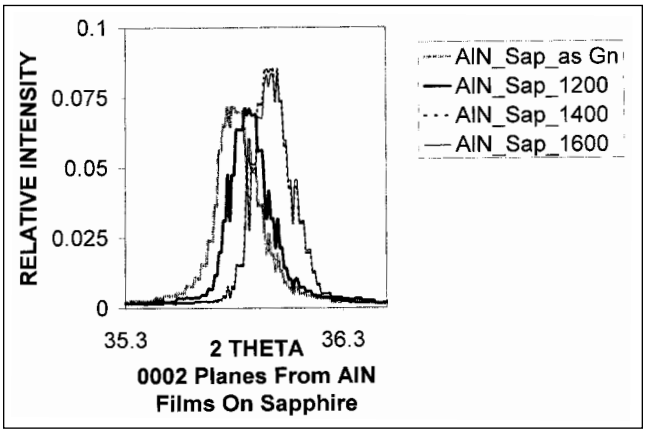


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Fig. 1. X-ray rocking curves of a) the (0002) AlN film and (0006) 6H-SiC substrate, and b) the (0002) AlN film on the sapphire substrate for as-grown samples and samples annealed at 1200°C, 1400°C, or 1600 °C.

to a larger angle as the annealing temperature increases up to 1400°C. This shows that the d-spacing decreases for the (0002) planes. It could be due to an increase in the density of the AlN, or it could be caused by strain relaxation produced by local atomic motion and the subsequent lessening of the Poisson distortion generated by the lattice mismatch. The a-lattice parameter for 6H-SiC (0.3081 nm) is smaller than that of AlN (0.3114 nm), so, assuming that the AlN film grows epitaxially, one would expect the in plane strains in the AlN to be compressive in the as-grown condition. The a-lattice parameter would then lengthen and the c-lattice parameter would shorten when the lattice relaxed. The peak shifts for the growth on sapphire can also be explained by an increase in the density of AlN, but the explanation based on mismatch epitaxy is more complicated, because the nearest neighbor structure is different. In sapphire, α-Al_2O_3, each aluminum atom is bonded to six oxygen atoms, whereas in AlN it is bonded to four nitrogen atoms. Ponce et al.[8] have speculated that at the interface each Al atom is bonded to three oxygen atoms (1/2e) and two nitrogen atoms (3/4e), and they are arranged so that the $[10\bar{1}0]$ AlN direction is parallel to the $[11\bar{2}0]$ Al_2O_3 direction. In these directions the distance between adjacent AlN $(10\bar{1}0)$ (0.2695 nm)

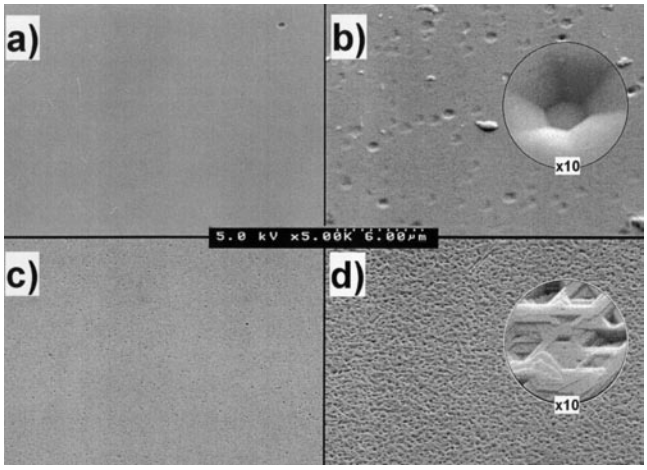

Fig. 2. SEM micrographs of AlN films grown on a) SiC (5Kx), b) SiC and annealed at 1600°C for 30 min (5Kx with a 50 Kx insert), c) sapphire (5Kx), and d) sapphire and annealed at 1600°C for 30 min. (5Kx with a 50 Kx insert).

and Al_2O_3 $(11\bar{2}0)$ (0.2379 nm) planes provides for a 12.5% mismatch. However, if one applies the concept of domain matching epitaxy[15,28] where there are almost nine Al_2O_3 planes for every eight AlN planes,[8,15] the mismatch is only 0.7%. Thus, for either direct epitaxy or domain matching epitaxy, the interplanar spacing in the sapphire is smaller than that of AlN, so the peak shifts can also be explained by relaxation. Unlike SiC, which has the same a-axis thermal coefficient of expansion as AlN (4.15×10^{-6}/K), the larger coefficient for sapphire (7.28×10^{-6}/K)[9,29] could also put the AlN in compression as the sample cools down. Because there is no peak shift between the 1400°C and 1600°C anneals, we conclude that a 1400°C anneal is sufficient for complete relaxation to occur.

That there is atomic motion at the higher annealing temperatures is also supported by the SEM micrographs in Fig. 2. Although virtually no changes were apparent in the surface morphology of the AlN films annealed at 1200°C, some surface roughening appeared on the samples annealed at 1400°C. At 1600°C the surfaces have degraded significantly, as films on both substrates have a number of hexagonal pits that are most likely created by evaporation. In the 50,000x insert for the SiC film an individual pit is shown with six clearly defined sidewalls that are probably identical low energy planes—possibly the $\{1\bar{1}01\}$ planes, which have a low surface energy.[30] Using energy dispersive x-ray spectroscopy (EDX), we confirmed that the flat hexagonal bottom was the SiC substrate; and this was confirmed with atomic force microscopy (AFM) and the knowledge of the film thickness. The film deposited on sapphire and annealed at 1600°C has more pinholes than the equivalent film deposited on SiC. We believe this is due to the as-deposited sample having a rougher surface and therefore more ledges where the atomic processes for evaporation such as the formation of an N_2 molecule can occur. We conclude that the 30 min, 1600°C anneal represents the outer limit of the utility of using AlN as a cap for SiC, and that the AlN should be smooth.

This is consistent with an earlier study in which AFM studies showed that AlN acted as an effective cap for annealing implanted SiC until the annealing temperature reached 1600°C. At this temperature a few rods were formed on the SiC surface after a 15 min anneal, and more were formed after a 30 min anneal.[3] Because the rods are created at the same temperature as the hexagonal pits are formed, and more of them are created when there are more pits, it seems logical to assume they are associated with the preferential evaporation of Si when the SiC at the bottom of the pits is exposed to the atmosphere. However, one would expect pits rather than rods to form on the SiC surface. The fact that rods form, and that they are carbon rich as determined by SEM/EDX,[31] suggests there is considerable atomic mobility on the SiC surface at these temperatures. Capano et al.[32,33] have observed similar phenomena on bare surfaces annealed at high temperatures, where ridges form that are thought to be steps created by the preferential evaporation of silicon.

The RBS channeling and one random spectrum in Fig. 3 are for the AlN films grown on SiC or sapphire

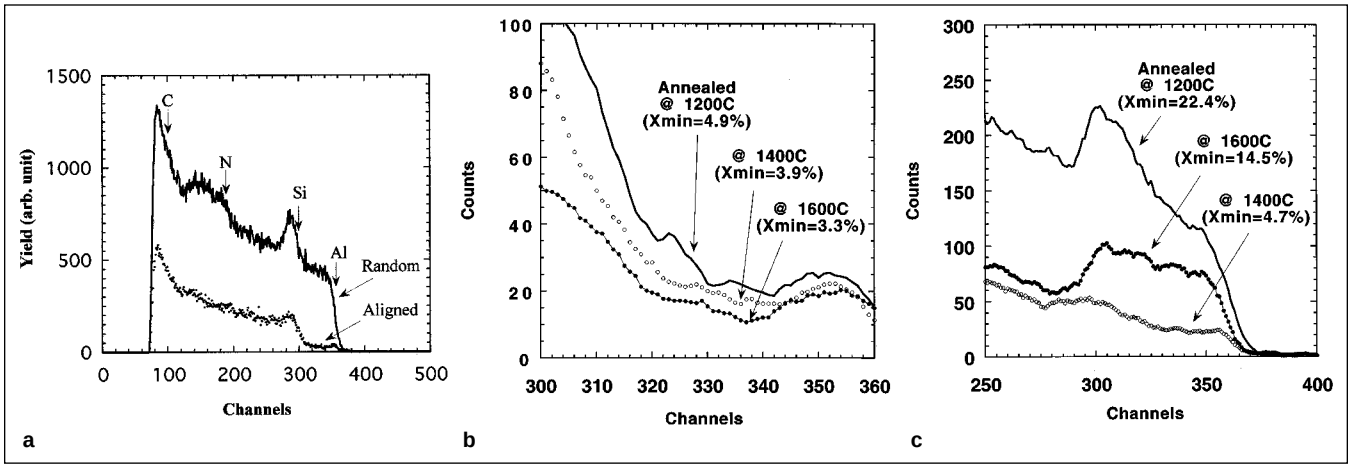

Fig. 3. (a) RBS random and channeling spectra for AlN films on as-grown on SiC. Channeling spectra in the vicinity of the interface peak for AlN films grown on (b) SiC and (c) sapphire and annealed at 1200°C, 1400°C, or 1600°C for 30 min.

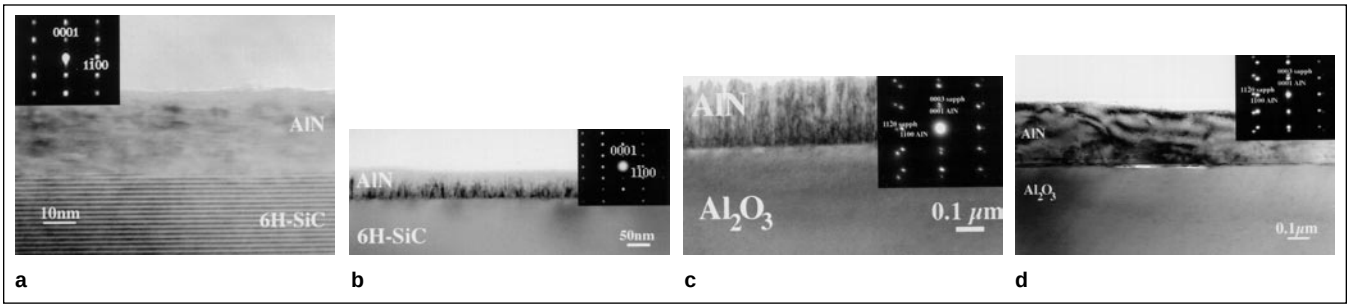

Fig. 4. TEM micrographs of AlN films (a) as-grown on SiC, (b) grown on SiC and annealed at 1600°C for 30 min, (c) as-grown on sapphire, and (d) grown on sapphire and annealed at 1600°C for 30 min.

and subjected to various annealing conditions. The Al and N peaks for the AlN film and the oxygen peak from the sapphire substrate are marked, as is the peak associated with the film-substrate interface. The ratio of the amplitude of the channeling and random spectra, χ_{min}, is smaller for the SiC substrate, suggesting that this interface is more coherent and/or less strained than the one with the sapphire substrate. For growth on the SiC χ_{min} decreases slowly as the annealing temperature increases probably because the atoms can more easily move to reduce the stress at the interface at the higher temperatures. For the sapphire χ_{min} is less at 1400°C than it is at 1200°C, but when the annealing temperature is raised to 1600°C, χ_{min} is larger. The TEM micrographs in Fig. 4d explain one possible reason for this, as some voids have formed at the AlN-sapphire interface after the 1600°C anneal. For the as-grown samples χ_{min} was 6.3% for the SiC substrate and 18.9% for the sapphire substrate. Although the data for the sapphire substrate does not quite fit the trends as χ_{min} for the film annealed at 1200°C is the highest, we attribute this to a small statistical fluctuation.

As seen in Fig. 4, all the AlN films were essentially single crystalline with the c-axis perpendicular to the growth plane. The as-grown film of the 6H-SiC is of good crystallographic quality as revealed by the selective area diffraction (SAD) pattern in the inset, and from the contrast of the micrographs in the imaging mode shown in Fig. 4a. Observations at low magnification (60,000x) of the AlN film show a uniform contrast, which is also a criterion for the high single crystalline quality of the film. The interface with the 6H-SiC substrate is clean and smooth. There are no amorphous phases or precipitates along the observable with the TEM interface line. At higher magnifications (200,000x) the AlN and 6H-SiC lattice fringes reveal a clean and smooth interface as well. The major structural defects in the AlN film are the numerous stacking faults parallel to the interface that are clearly observed from the lattice fringe images in the high resolution (HR) mode. The quality of these PLD grown AlN films is comparable with the structural quality of the best MOCVD grown AlN films we have studied.

The microstructural quality of the film grown on the 6H-SiC substrate and annealed at 1600°C is substantially different, as is seen in Fig. 4b. Observations at low (60,000x) and high (200,000x) magnification reveal a columnar structure composed of crystallographic microdomains with a very small tilt of ~1° between them. The likely driving force for the creation of this structure is the reduction of the interface stress and the number of stacking faults in the as-grown films. Despite the columnar structure, the film appears to be single crystalline, as is revealed by the AlN SAD pattern in the inset. The interface is clean, sharp, and relatively uniformly strained, as is shown in the micrograph.

The film as-grown on sapphire is single crystalline with the commonly observed highly strained state at the AlN-sapphire interface as is shown in Fig. 4c. This is caused by the numerous defects—mainly dislocations and crystallographic microdomains, and the associated microdomain boundaries with their overlapping stress fields.

The film grown on sapphire and annealed at 1600°C exhibits a very high single crystalline quality, as shown by the contrast and SAD pattern in the imaging and diffraction modes in Fig. 4d. The structural defects are localized in the vicinity of the AlN-sapphire interface and are mostly stacking faults and dislocation lines parallel to the interface line. A distinguishing feature of these films is the numerous voids at the AlN-sapphire interface that have a somewhat periodic distribution along the interface. We do not know if the voids are present in the as-annealed sample, or if they are created by preferential ion milling during TEM sample preparation. In either case the periodicity suggests that the voids are a stress release mechanism, as mismatch strain is inherently periodic. Stress relief is more likely to occur in films grown on sapphire, because the strain is larger and the interface bonds are weaker than they are for films grown on SiC. In their growth studies of AlN on SiC and sapphire George et al.[34] also found that bonding across the interface appeared quite different for the two substrates. The excellent single crystalline nature of this AlN film in which the stress has been partially relieved is striking, so it could be a candidate for a compliant substrate.[35]

The AES depth profiles in Fig. 5 are consistent with the TEM micrographs in showing sharp interfaces between the film and the substrate in that the profiles show that there is no intermixing. There is also no indication that SiC decomposed and formed interfacial layers of silicon or carbon. The profiles also show

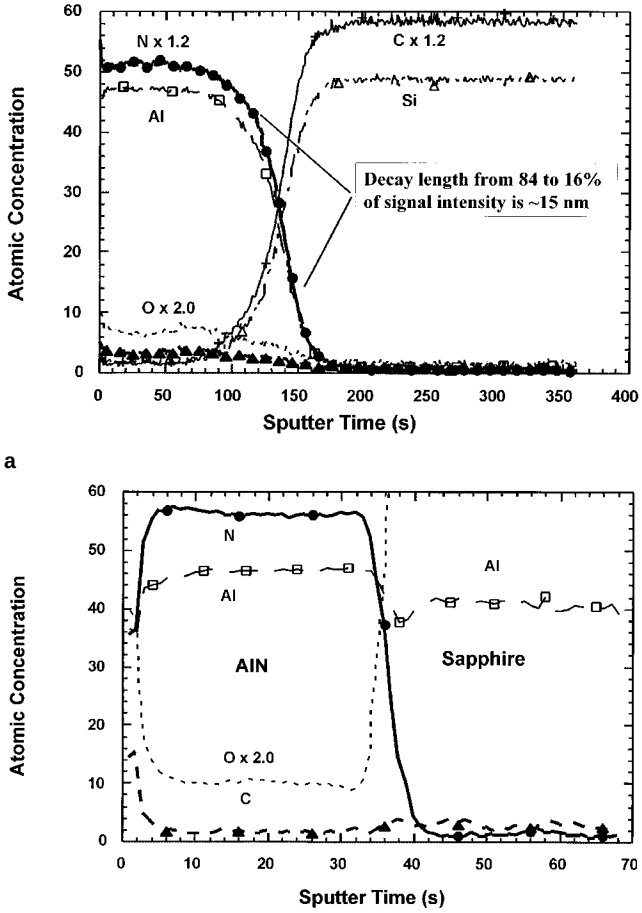

Fig. 5. AES spectra of AlN films grown on (a) SiC or (b) sapphire substrates and annealed at 1600°C for 30 min. (The triangles in (a) are for the original O signal before it was multiplied by 2.)

that the AlN films contain a large amount of oxygen. This probably improves their stability as the vapor pressure of Al_2O_3 [36] is lower than that of AlN[27] at the annealing temperatures, and the AlN readily reacts with oxygen to form Al_2O_3.[37]

CONCLUSIONS

AlN films deposited on (0001) 6H-SiC substrates by PLD have a smooth morphology as determined by SEM, are essentially single crystalline with the same crystallographic orientation as determined by XRD and TEM/SAD, and contain many stacking faults as determined by TEM. The interface is quite highly strained as measured by RBS and TEM, and it is continuous and abrupt as determined by TEM and AES. No discernable changes occur in the surface morphology after a 1200°C anneal for 30 min, but the (0002) AlN x-ray peak shifts to a larger angle indicating that the film has become more dense and/or relaxed somewhat and the Poisson elongation produced by the compressive mismatch strain has been reduced. It is reasonable to assume that the AlN film would be in compression as it would attempt to replicate the SiC substrate, because they have the same planar structure, and the interatomic distance is only 1% larger in AlN. The shift is even larger after the 1400°C anneal, and the shift after the 1600°C anneal is about the same. The reduction in χ_{min} for the interface peak for the RBS spectra also indicates the strain has been reduced. The atomic motion that brings about the reduction in strain, however, produces very little change in the surface morphology until the sample is annealed at 1600°C. For this temperature there are significant changes in the morphology as hexagonal pits, which probably are thermal etch pits, are created in the AlN film. That there is significant atomic motion at this annealing temperature is also shown by TEM micrographs in which the AlN film has a much more columnar structure with grains 3–6 nm in width that are tilted ~1° relative to each other. The interface strain is further reduced, as is indicated by a still smaller value in χ_{min} for the RBS interface peak. TEM micrographs show that the interface remains continuous and sharp, and AES supports this observation as no intermixing of the elements across the interface is observed. AES also shows that there is a relatively large amount of oxygen in the films.

The as-grown AlN film deposited on (0001) sapphire is quite smooth, but it has a few more pinholes in it than the film deposited on the 6H-SiC substrate. It is similar to the as-grown film deposited on the SiC in that it was essentially single crystalline with a *c*-axis orientation, and the interface is sharp with no evidence of intermixing of the elements. It differs in that the structure is more columnar, and the SAD pattern suggests the interface is incoherent; thus, the film did not grow epitaxially in the sense that it did not attempt to replicate the sapphire planar structure. This is not surprising, because AlN does not have the same planar structure as sapphire, Al_2O_3, and the interplanar spacing of Al_2O_3 is much less—0.2379 versus 0.2695 nm. Annealing the films causes them to become more dense and/or to relax and produces the same shifts in the x-ray peaks as were seen when the substrate was SiC. The relaxation process can be explained in the same way as it was for SiC, as the interplanar spacing in the sapphire is smaller. Annealing the films initially reduces the strain at the interface as is indicated by the TEM micrographs and the decrease in χ_{min}. However, χ_{min} is larger after the 1600°C anneal. The reason for this can be seen in the TEM micrographs, where one sees that the films have lifted off the substrate in some regions forming voids. The film annealed at 1600°C also contains many more hexagonal pits than the film deposited on SiC and annealed at the same temperature, probably because the as-grown film contained more pinholes, which can act as nucleation sites for the formation of e.g., N_2, which subsequently evaporates.

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