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NUCLEATION AND GROWTH OF GALLIUM NITRIDE FILMS ON SI AND SAPPHIRE SUBSTRATES USING BUFFER LAYERS

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ABSTRACT

We have investigated the nucleation and growth of gallium nitride (GaN) films on silicon and sapphire substrates using halide vapor phase epitaxy (HVPE). GaN growth was carried out on bare Si and sapphire surfaces, as well as on MOVPE-grown GaN buffer layers. HVPE growth on MOVPE GaN/AIN buffer layers results in lower defect densities as determined by x-ray than growth directly on sapphire. HVPE GaN films grown directly on sapphire exhibit strong near-edge photoluminescence, a pronounced lack of deep level-based luminescence, and x-ray FWHM values of 16 arcsec by an x-ray θ -2 θ scan. The crystallinity of GaN films on sapphire is dominated by the presence of rotational misorientation domains, as measured by xray ω -scan diffractometry, which tend to decrease with increasing thickness or with the use of a homoepitaxial MOVPE buffer layer. The effect of increasing film thickness on the defect density of the epilayer was studied. In contrast, the HVPE growth of nitride films directly on silicon is complicated by mechanisms involving the formation of silicon nitrides and oxides at the initial growth front.

INTRODUCTION

Despite recent technological advances in nitride epitaxy, mechanisms controlling the crystallinity of nitride layers on heteroepitaxial substrates are not well understood. The application of low temperature buffer layers has been shown to dramatically improve the crystallinity of epitaxial GaN on sapphire (1,2); however, the current state of technology for nitride epitaxy still lags well behind that of Si and GaAs. There are several sources of defects in GaN grown on sapphire. Defects in the material are generated, such as threading dislocations, due to lattice mismatch at the heterointerface. The threading dislocation density is expected to decrease with increasing thickness of the film, due to occasional defect annihilation. An additional significant type of defect is the boundary between rotationally misoriented domains within the GaN epilayer. The application of a suitable buffer layer acts to decrease the degree of rotational misorientation in the film (3). The nature and extent of development of the microstructure, dominated by these defects as the film thickness is increased, has not been previously investigated in detail. In this work, we utilize two nitride growth techniques, metalorganic vapor phase epitaxy (MOVPE) growth and halide vapor phase epitaxy (HVPE) growth, to quantify differences in epitaxial GaN arising from the presence of rotational misorientation domains and threading dislocations as a function of film thickness and buffer layer.

From a technological viewpoint, a promising route for the development of GaN substrates is the heteroepitaxial growth of GaN films by rapid growth techniques, such as halide vapor

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phase epitaxy (HVPE), followed by the *in-situ* etch removal of the initial substrate to leave a thick free-standing GaN film. The availability of GaN homoepitaxial substrates would significantly reduce current problems in heteroepitaxial nucleation and eliminate defects arising from differences in the coefficient of thermal expansion between the epilayer and the substrate.

EXPERIMENTAL PROCEDURE

The HVPE technique has been discussed widely in the literature (4,5,6,7). Details concerning our HVPE growth of GaN have been presented elsewhere (8). MOVPE buffer layers and growth studies were carried out in a horizontal MOVPE system, operated at 76 Torr, utilizing trimethylaluminum, trimethylgallium, and ammonia as the reactants. Typical gas velocities were over 30 cm/sec, with cation precursor partial pressures on the order of 0.011 Torr, and a V/III ratio of 1500. Low temperature AlN buffer layers were utilized for MOVPE growths of GaN on sapphire, in accordance with the techniques reported by other researchers (1). For growths of AlN on Si(111) substrates, the Si substrates were initially oxidized, with the oxide removed by HF etch just prior to growth. MOVPE AlN layers were grown on Si(111) using trimethylaluminum and ammonia as the precursors at 1100°C, similar to the method reported by Watanabe *et al* (9).

Both ω -scan (transverse) and θ -2 θ scan (longitudinal) x-ray diffraction geometries were used to characterize the GaN films. The x-ray apparatus was equipped with a four-reflection monochrometer and a three-reflection Si analyzer crystal at the detector. In the ω -scan geometry, the detector was held at a fixed position, and the sample was tilted during the scan. In the θ -2 θ geometry both the sample and detector were moved, with the detector moving at twice the angular velocity of the sample.

RESULTS AND DISCUSSION

The growth rate of GaN, based on the apparent activation energy for growth and the dependence on GaCl partial pressure, previously reported (8), appears to be limited by mass transport of GaCl to the growth front rather than by surface reactions. The growth thickness uniformity was $\pm 8\%$ over a 2.5 cm sample, with a smooth specular surface. Attention to surface cleaning and higher growth rates were found to improve the growth morphology. Higher GaCl partial pressures may increase the rate of nucleation, leading to a higher density of GaN nuclei on sapphire, and transition to the 2-D growth mode at a lower thickness. The theoretical relationship between the heterogeneous nucleation rate and the supersaturation for the general case is widely discussed in the literature (10).

HVPE GaN layers on sapphire were analyzed using X-ray scans in the ω -rocking (transverse) and θ -2 θ rocking geometries (longitudinal). The ω -scan values always exhibit a much broader FWHM to the peak than the θ -2 θ scan (i.e., 636 arcsec versus 16 arcsec for a 110 μ m thick HVPE GaN/sapphire sample). Broadening in the ω -scan is due to composite broadening from both lattice parameter variation and the presence of large angular misorientation domains (mosaic spread) in the epitaxial film. The θ -2 θ scan measures broadening primarily due to variation of the lattice parameter in the material (11). In all samples, regardless of thickness, angular misorientation domains dominate the GaN microstructure. While this conclusion has been reported in the growth of MOVPE GaN, our measurements indicate a similar defect structure in the HVPE-grown materials. The relative magnitude of broadening due to variation

in the c-axis lattice parameter as compared to the effect of the in-plane angular distribution of

GaN domains is demonstrated in Figure 1, which illustrates a reciprocal space map for this material.

Low temperature (7K) photoluminescence studies of thick GaN/sapphire HVPE films obtained with an excitation laser power density of 5 W/cm² possess a negligible amount of yellow luminescence, and very strong near-band transitions at 3.48 eV (FWHM value 10.4 meV). This photoluminescence spectrum has been published elsewhere (8). It is interesting to note that although other HVPE (and MOVPE) samples generally demonstrate strong yellow luminescence



Figure 1: Reciprocal space map for 110 μ m GaN/sapphire, T_{gr}=1050°C (min contour=10^{-0.25} counts, max=10^{3.75} counts, 17 contours)

(12,13,14), the films in this study demonstrate very little luminescence in the 550 nm region. Thus, the lack of yellow luminescence in these samples is not an inherent feature of the HVPE growth technique. Moreover, the x-ray FWHM values of the HVPE materials in this study are not dramatically different from high quality MOVPE GaN, suggesting that the presence of extended defects (such as low angle grain boundaries) are probably not directly responsible for the presence of yellow luminescence.

In many epitaxial systems, the density of threading dislocations and rotational misorientation domains decreases with increasing film thickness (15). X-ray measurements in

the ω scan compared to the θ -2 θ scan geometries were completed for a series of HVPE GaN/sapphire films grown at different thicknesses. The results of this analysis are shown in Figure 2. In the (0002) reflection, the x-ray penetration depth is estimated to be on the order of 20 μm (I/I_=0.1). These thick HVPE layers are well suited for a study of the change in defect structure with thickness. The dominant change in defect structure in the HVPE GaN/sapphire samples with thickness is the angular misorientation of the GaN domains. The variation in the caxis lattice parameter is fairly small and changes little with increasing thickness (θ-20 scan), while the FWHM component attributed to the rotational misorientation





decreases from several thousands of arcsec (ω scan), at low layer thickness, to 300-500 arcsec for layer thickness above 100 μ m (see Figure 2). This result indicates that for all HVPE GaN/sapphire samples the dominant defect structure is the presence of rotational misorientation domains. The contribution to the x-ray peak broadening from these domain or grain boundaries decreases with increasing film thickness, possibly due to ripening growth in the domain size or other routes for annihilation of the extended defects within the domain or comprising the domain boundary.

Based on an analogy to the MOVPE literature, the presence of a suitable buffer layer is expected to significantly reduce the defect density of HVPE GaN layers. To quantify this effect, an MOVPE GaN/AlN/sapphire sample was produced for use as an HVPE buffer layer (starting substrate). The MOVPE buffer layer structure provides a homoepitaxial surface for the initiation of the HVPE growth, eliminating difficulties with the initial nucleation on the sapphire and leading directly to a 2D growth mode. Consequently, samples produced using an MOVPE

GaN/AIN/sapphire substrate for the HVPE growth may result in samples with a reduced defect density. Figure 3 illustrates the ω -scan curves for HVPE GaN films grown on MOVPE GaN/AlN/sapphire buffer layers, as compared with the ω-scan curves for HVPE GaN films grown directly on sapphire as well the initial MOVPE as GaN/AlN/sapphire films. The HVPE GaN film grown on the MOVPE buffer layer exhibits a much smaller FWHM than the thicker HVPE film grown without the buffer layer. The MOVPE process, and specifically the application of a low temperature buffer layer, clearly provides a mechanism for the reduction in the rotational spread of growth domains



Figure 3: X-ray ω -scan curves for GaN as a function of growth technique and buffer layer

at a low film thickness (1,2). The HVPE growth on the MOVPE buffer layer has a higher FWHM and hence higher defect density compared to the MOVPE buffer layer itself. Several possible mechanisms could give rise to this observation. First, due to the large difference in the thermal expansion coefficient between GaN and sapphire, cracks will appear in both the GaN, and possibly the sapphire, upon cooling for GaN layers above ~20 µm in thickness. Significant cracking has been observed in such films. As a result, inhomogeneities and misalignments in the film arising from mechanical cracking can contribute to the measured FWHM of the film. Additionally, some degradation of the MOVPE buffer surface may be occurring prior to the initiation of HVPE growth, due to contamination of the sample during transfer from the MOVPE reactor, or loss of nitrogen from the MOVPE buffer during the HVPE heatup sequence in ammonia. Optimized pre-growth preparation must be developed to fully utilize these GaN buffer layers.

HVPE growths of GaN were also carried out on (111) Si substrates, utilizing a MOVPE AlN buffer or by growth directly on the Si surface. The threefold symmetry of the (111) Si leads to the growth of wurtzite GaN (9). Moreover, Si substrates are of interest because a convenient route exists for removal of the Si substrate in-situ to leave a thick free standing GaN film; e.g., sacrificial etch of the backside of the Si using HCl gas. This approach has the potential advantage of producing free-standing GaN substrates free from strain and cracks induced by differences in the heteroepitaxial coefficient of thermal expansion. Initial attempts to deposit GaN directly on (111) Si resulted in polycrystalline deposition, probably due to either direct nitridization of the (111) Si surface during the HVPE heatup in nitrogen (16) or due to reaction of chlorides in the HVPE system with the Si surface, providing volatile silicon chlorides which subsequently react with ammonia to form silicon nitrides at the epitaxy surface. In fact, the formation of silicon nitride through such volatile silicon chlorides is supported by the highly favorable free energy of formation (-130 kJ/mole SiCl₄ at 1050°C). Additionally, ammonia can react directly with the solid Si surface to form silicon nitrides (17). To alleviate the reactivity of the Si substrate in the HVPE growth environment and provide an improved surface for nucleation, MOVPE AIN buffer layers were deposited on the Si substrates. A key aspect of the AIN/Si deposition was the growth temperature. AIN buffer layers deposited at temperatures of less than 1050°C in this study were not found to be single crystal (also, see ref (9)). However, as observed by other researchers (9), films deposited at temperatures exceeding 1100°C led to epitaxial single crystal growth. The high growth temperature may lead to reduced oxygen contamination of the Si surface through insitu reduction of the Si surface by hydrogen prior to the nucleation of the AIN buffer. AIN buffer layers exceeding a few tenths of microns were found to exhibit cracks with threefold symmetry. Theoretical calculation of the stress in the AIN/Si film (18) indicate a high tensile stress, on the order of 108-109 dynes/cm2 in the AIN film, arising from the difference in the coefficient of thermal expansion between the AlN and Si.

HVPE GaN films deposited on AIN/Si buffers were observed to be smooth and specular except in areas where the AIN buffer layer was cracked. Near the cracked areas, a rough granular morphology was present. Auger analyses confirmed the presence of Ga, N, Si, Al, and O. We postulate that these granular deposits form as a consequence of attack of the exposed Si by HCl, leading to silicon nitrides through the following reactions:

$$Si + xHCl \rightarrow SiCl_{x} + \frac{x}{2}H_{2}$$
$$SiCl_{x} + yNH_{3} \rightarrow SiN_{y} + xHCl + \frac{3y - x}{2}H_{2}$$

CONCLUSIONS

The film properties for GaN grown by the HVPE technique as a function of substrate and buffer layer structure have been examined. The defect structure of the films is found to be dominated by the presence of rotational misorientation domains. Reduction in the defect density is observed with increasing thickness of the HVPE films, primarily due to reduction in the degree of rotational misorientation must be occurring with increasing film thickness. The homoepitaxial nucleation and growth of the HVPE film on a GaN MOVPE buffer layer results in decreased angular spread in the rotational misorientation domains as indicated by the reduced FWHM values in the x-ray ω -scan measurements. The HVPE layers grown on

MOVPE buffers remain structurally inferior to initial MOVPE GaN/AlN/sapphire layers, possibly due to additional complication induced by mechanical fracture in the thick HVPE films. Excellent optical and crystalline characteristics are obtained for the HVPE films on sapphire, with longitudinal x-ray scans of GaN/sapphire indicating a FWHM of 16 arcseconds for a 110 μ m thick film by θ -2 θ scan. The 7K photoluminescence for GaN/sapphire shows strong nearband emission at 3.48 eV with a FWHM value of 10.4 meV. Moreover, no detectable deep level emission was found in PL measurements at modest pump power densities. For HVPE GaN growth on (111) Si substrates, a high temperature AlN/Si MOVPE buffer layers were required to protect the growth surface from silicon nitride formation.

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ABSTRACT

A number of technic work in substrate seedin shown that diamond in roughness. In this wor based 0.1 micrometer di hot-filament chemical v microscopy, scanning profilometry. The result minimal surface roughne permit examination of th at the silicon-diamond in with those prepared u improvement in surface of

INTRODUCTION

Diamond materials i unique thermal, mechan area has been limited b growth of smooth, unif Control of nucleation is adhesion required for o seeding with nanocrysta without any subsequent roughness of 30 nm and powder in water and pl which uses a commerci µm natural diamond pai

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