STRUCTURE OF AIN ON Si (111) DEPOSITED WITH METAL ORGANIC VAPOR PHASE EPITAXY

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ABSTRACT

The surface morphology and structure of AlN deposited by metal organic vapor phase epitaxy (MOVPE) on Si (111) at growth temperatures ranging from 825 to 1175°C was investigated. Transmission electron microscopy (TEM), reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM), and secondary ion mass spectrometry (SIMS) techniques were used to study the resulting film structure. Growth at high temperatures but less than ~1100°C, resulted in a wire texture with some degree of in-plane alignment with (0001)_{*AIN*} //(111)_{*Si*}, <1010>_{*AIN*} // <211>_{*Si*}, and <1120>_{*AIN*} // <110>_{*Si*}. Deposition at temperatures greater than 1100°C results in single crystal films consisting of domains 60 nm across with an aspect ratio near unity. Growth below 1100°C leads to degraded crystal quality with the grains developing random rotational misalignments around the AlN [0001] axis. Growth at lower temperatures produces islands elongated along the [1120] direction. At the growth temperature of 825°C, the aspect ratio of the islands increased to 3 and a width of 25 nm. Cross-sectional TEM reveals that these islands are faceted due to slow growth on the {1101} planes.

INTRODUCTION

Nitride-based III-V materials have been receiving attention due to their ability to lase in the green and blue spectral regions. However, these materials are difficult to fabricate. The strong bonding of N_2 and low nitrogen solubility in molten Ga results in very high nitrogen overpressures during crystallization of a nitride crystal from the melt. These difficulties have prevented the production of useful GaN bulk crystals. Lack of a single-crystal nitride substrate requires devices to be made through heteroepitaxial growth. GaN and AlN also have a coefficient of thermal expansion, lattice constant and crystal structure different from other III-V semiconductors. Nitrides therefore need to be grown on a substrate different from those normally used for compound semiconductor growth, such as GaAs or InP.

The highest quality materials have used either silicon carbide or sapphire substrates [1,2]. These materials can be expensive and limited in size. Additionally, the lattice mismatch to these substrates is quite large and even the highest quality materials contain a high concentration of lattice mismatch related structural defects. Silicon substrates have been successfully used for nitride growth. A Si (111) substrate will have the required hexagonal surface symmetry. The low cost and availability of this substrate makes it an attractive alternative to silicon carbide and sapphire substrates.

Previous work using Si substrates centered upon growth of AlN and GaN. Much of this work was done in ultra-high vacuum (UHV) using molecular beam epitaxy (MBE) or sputtering to produce the layers [3,4]. Single crystal films could be grown under optimized conditions. As with most nitride heteropitaxial growth, the films contained a dense network of structural defects.

Direct growth of GaN on Si (111) is difficult due to poor film nucleation, however single crystal AlN buffer layers have been grown directly on Si (111) [5]. The optimization of AlN

growth on Si (111) was carried out using metal organic vapor phase epitaxy (MOVPE). In MOVPE growth, the metal organic precursor, trimethyl aluminum, and ammonia are carried to the growth surface in a hydrogen carrier gas. The precursors undergo a series of chemical reactions, which can take place both in the gas stream and on the substrate. These reactions result in a growth surface possessing a distribution of organic compounds and deposited film species. On the other hand, the UHV-based techniques only deliver the specific inorganic film species. MOVPE films could therefore have different material properties due to the modified surface kinetics.

A possible limitation in the MOVPE process is the purity of the gas sources. Impurities may be present in the reactor from a variety of sources. Contaminants in the source materials, reaction by-products and real as well as 'virtual' leaks can all lead to unwanted chemical impurities in the growing film. Virtual leaks are the slow release of impurities, such as water, absorbed on internal reactor and gas line surfaces. The virtual leaks are largely due to air exposure during installation or sample exchange. These impurity sources contain notably different contaminants. Most of the air is quickly removed, but the surface adsorbed water tends to persist in the system for extended periods. The gas source-based impurities are metal alkoxides and reaction byproducts from the decomposition of the metalorganic specie. These contaminants are complex metalorganic molecules that may decompose and yield C impurities in the growing film.

During MOVPE growth of most III-V materials, the requirements on the oxygen or water content in the reactor are relaxed because of the volatility of III-V oxides within a H₂ ambient at high temperatures. Alternatively, Si readily forms surface oxides in the presence of trace amounts of oxygen or water, a process that was studied by Ghidini and Smith [6]. Higher temperatures were found to promote oxide desorption. At the high temperature of 1000°C, the partial pressure of water within the reactor must be less than 10^{-4} Torr to have an oxide-free Si surface. This constraint is a significant practical limitation to growth upon Si substrates.

AlN growth was studied here at growth temperatures between 825 and 1175°C. Under these conditions, the maximum allowable water vapor pressure in the reactor tolerated before surface silicon oxides will form range from 5×10^{-7} to 5×10^{-2} Torr. The Si substrates initially received a brief dilute HF dip prior to sample loading. A 2.5 minute anneal at 1175°C in hydrogen was performed to initiate each sample with hopefully identical oxide-free Si surfaces. Growth was carried out for 30 min. with a V/III ratio of 10000 at a reactor pressure of 76 Torr, which resulted in films 200 to 300 nm in thickness. To probe the influence of reactor chemistry, an additional sample was grown at 1125°C with the ammonia flow rate doubled.

The samples were analyzed for chemical, structural, and surface defects, using *ex situ* reflection high energy electron diffraction (RHEED), transmission electron microscopy (TEM), surface ion mass spectrometry (SIMS), and atomic force microscopy (AFM).

RESULTS AND DISCUSSION

AFM analysis was performed in both contact and tapping modes. The samples were populated by a dense network of small islands as shown in Figure 1. The island size is comparable to the size of a standard AFM probe, requiring detailed measurements to confidently image these features. The surface morphology contains small islands as shown in Figure 1. Samples grown above 1100°C have rounded features. At lower growth temperatures, the islands become elongated with widths decreasing from 60 to 25 nm. The variations in the island aspect ratio and relative orientation was determined and are given in Figure 2. The island lateral growth rate varies with in plane crystal direction. At high temperatures, the islands have an aspect ratio near 1 resulting in a flat angular orientation. Below 1100°C the islands extend preferentially in the $[11\overline{2}0]$ directions.

Figure 3 presents cross sectional images of the islands obtained from TEM and AFM. The island sidewalls are inclined nearly 60 degrees from the $[01\overline{1}0]$ direction, which identifies the



diffraction from both Si and AlN. The diffraction patterns were obtained by TEM-selected area diffraction and obtained on the 1125, 1025, and 925°C samples.



sidewall facet as a $\{1\overline{1}01\}$ plane. The extension of the sidewall indicates this to be a slow growth crystal face. This same preferential faceting and growth rate variation has been observed during epitaxial lateral overgrowth of GaN [7,8].

Both RHEED and TEM were used to examine the microstructure of the samples. The diffraction patterns in Figure 1 exhibit a clear transition in structure at 1100°C. For growth temperatures greater than 1100° C, the following in plane film orientations were determined: $(0001)_{AIN} //(111)_{Si}$, $<10\overline{10}>_{AIN} //<\overline{2}11>_{Si}$, and $<11\overline{2}0>_{AIN} //<\overline{1}10>_{Si}$. At temperatures below 1100°C, the diffraction patterns indicate a textured, polycrystalline structure. The absence of the (0002) ring in these diffraction patterns indicates that very few if any of the grains have their [0002] axis inclined from the Si [111] axis. Identical behavior at 1100°C has been noted in work by Watanabe et al. and Weeks et al [5,2]. Plan view TEM dark-field micrographs indicate that the average grain sizes in these textured samples are 50, 36, and 35 nm for growth temperatures of 1175, 1075, and 925°C respectively.



Figure 3. An AFM line scan and cross section TEM images of the surface structure of the films detailing the faceted $\{1\overline{1}01\}$ planes. There is good correspondence between the TEM and AFM determined surface roughness.

Doubling the ammonia flow rate during growth at 1125°C was found to greatly deteriorate the sample quality. The RHEED image of this sample appeared very similar to the sample grown at 825°C. Additionally, the island distribution was also comparable to the samples grown at low temperature. This observation indicates that increasing the ammonia flow rate has similar effects on sample structure as lowering the growth temperature. The ammonia is known to have a high water concentration, which would lead to increased oxygen incorporation at high ammonia flow rates.

Impurity incorporation during AlN growth was determined through SIMS measurements of the samples grown at 1125 and 1075°C. Both samples exhibit significant amounts of carbon at the substrate interface. These SIMS measurements are complicated by the surface roughness, however the carbon and oxygen found at the surface do extend deep into the AlN layer. The bulk of the films were found to contain oxygen with the sample grown at 1075°C having three times more oxygen than the sample grown at 1125°C.

The microstructure of all the films is characterized by small grains whose interiors are largely free of defects as determined from TEM. Growth above 1100°C results in films with grains aligned to the Si substrate. Below a growth temperature of 1100°C the grain structure loses this epitaxial relationship but retains an overall texture. The angular variation increases with decreasing growth temperatures. The loss of epitaxy at lower growth temperatures was initially thought to be caused by the oxidation of the Si surface prior to growth. The trimethyl aluminum source can also contain low levels of oxygen contaminants, which could lead to the high oxygen

content of these films. A high oxygen content would obscure any oxygen signal which might be originating from SiO_2 at the interface. Surface roughness also complicates and degrades the depth resolution in the SIMS measurement.

Surface kinetics can also play a role in determining epitaxy and physical structure. Surface transport is dependent on the growth temperature, surface adsorbed species and existing surface structure. Independent of contamination issues on the Si surface, such factors can play a fundamental role in the determination of the microstructure. The observed grain size and wire texture are attributed to surface transport during film nucleation. At higher temperatures the increased surface diffusion results in the formation of few large, stable nuclei. Furthermore, the high temperatures allow the nuclei to homogeneously orient themselves with the Si substrate in a low energy configuration. This conclusion accounts for the results obtained with UHV deposition, where a reduction in growth temperature below a critical value produced an identical degradation of crystal structure to wire texture [3]. However, this temperature occurred at 700°C under UHV sputtering instead of the 1100°C found for the MOVPE deposition reported here and also by Watanabe et al [5]. The chemical species present during MOVPE growth, may limit surface diffusion similar to a reduction in temperature. Thus to surmount the limited surface diffusion, the temperature must be increased from 700 to 1100°C during MOVPE growth.

CONCLUSIONS

The physical structure of MOVPE-grown AlN on Si (111) is sensitive to both the temperature and V/III ratio. The films are characterized by granular structures. Single crystal films are observed above 1100°C at a V/III ratio of 10000. Below 1100°C, the AlN grains are not epitaxial but exhibit a preferred texture. The surface contains a network of faceted islands exhibiting slow growth on $\{1\,\overline{1}\,01\}$ planes. The differential growth rate of the island facets yields nominally round islands at a growth temperature of 1175°C and islands with an aspect ratio near 3 at 825°C.

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