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Nucleation of AlN on the (7×7) Reconstructed Silicon (1 1 1) Surface

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The (7×7) reconstructed (1 1 1) surface of silicon is found to be an excellent surface for the nucleation of epitaxial aluminum nitride, despite the +23.4% misfit in the AlN/Si system. AlN nucleated above the (7×7) to (1×1) transition temperature (830°C) is found to contain 30° misoriented grains, while films nucleated below the transition temperature are single orientation. Optimized aluminum nitride films grown on (7×7) silicon surfaces make excellent substrates for GaN heteroepitaxy.

1 Introduction

GaN FET's have shown very promising results [1] [2] [3] for possible applications in high-speed, high-power applications such as wireless communications. These applications demand substrates with good thermal conductivity and low RF loss. Silicon substrates offer some intriguing advantages for these applications. Although the thermal conductivity is not as high as in silicon carbide, silicon substrates can actually outperform silicon carbide in heat removal because micromachining techniques for silicon are well developed. The availability of large, high quality Si substrates presents many manufacturing advantages, and the importance of substrate cost is difficult to over-emphasize.

The disadvantages of Si as a substrate for GaN hetero-epitaxy have been daunting. The +20.5% misfit [a] has led people to conclude that growth of GaN directly on silicon was not likely to work well. In addition, the thermal expansion misfit between GaN and Si may lead to cracking in films grown at high temperatures.

Several attempts have been made to grow GaN on Si using intermediate layers. For example, GaAs [5], oxidized AlAs [6], and SiC [7] [8] buffer layers have all been investigated. More recently, several groups have made remarkable progress on earlier work [9] using AlN buffer layers grown directly on the Si (1 1 1) surface [10] [11]. Similar techniques were recently used to fabricate a blue LED in GaN grown on a silicon substrate [12].

In this paper, we will report on our optimization of AlN buffer layers for growth of GaN. We find that the most critical parameter is the nucleation temperature for the AlN layer. The best nucleation conditions are found just below the (7×7) to (1×1) surface reconstruction transition temperature for the Si surface. We briefly discuss properties and cracking of thick GaN films grown on the highest quality buffer layers.

2 MBE Growth

An RF-coupled nitrogen plasma source from SVT Associates was used to obtain active nitrogen for AlN nucleation. The plasma pressure was 300mTorr, and the RF power was 450W. The tip of the source is mounted about 40 cm from the substrates. Under these conditions, AlN growth rates in excess of 900Å/hr result in films with Al precipitates. The Al flux for the nucleation experiments described here was set close to be close to this maximum.

Radiatively heated 75mm diameter n- and p-type Si (111) substrates were used. They were mounted on In-free wafer holders, and outgassed in ultra high vacuum at 700°C before putting them in the MBE chamber. The oxide is blown off by heating the samples to 900° in vacuum. Our best results are obtained by using the silicon wafers directly out of the package, with no cleaning. Reflection high energy electron diffraction (RHEED) using a 7.5kV beam is used to study the structure of the surfaces. We observe that SiC islands are formed at temperatures above 800°C by reaction with background CO gas if the surface is prepared by dipping in HF. Carbide formation may depend on the cleanliness of the vacuum system which may thus affect the quality of the AlN epitaxy.

After thermal removal of the oxide, we use RHEED to check for the transition temperature between the (7×7) and (1×1) surface reconstructions. Figure 1a shows the (7×7) RHEED pattern at about 5° below the transition temperature. (The differential is measured by the substrate heater thermocouple.) Figure 1b shows the (1×1) pattern observed when the substrate is five degrees above the transition. In the literature, this transition is reported to occur at 830°C. [13] We use the measured transition temperature as a calibration point for our substrate heater thermocouple. We then adjust the substrate temperature to the starting temperature we have chosen (about 25° below the (7×7) transition seems to be optimum), and turn the substrate manipulator so that the substrate is facing away from the plasma source and source furnaces. We then open the nitrogen valve and light the plasma. The aluminum shutter is then opened, and the substrate is turned to face the sources. Under optimal conditions, the RHEED pattern for AlN appears immediately and is streaky, as shown in figure 1c. Early on, we tried pre-coating the silicon substrate with Al before starting the plasma to prevent Si_3N_4 formation, but we found that the Al rapidly disappeared upon heating to growth temperatures.

After five minutes of growth at the nucleation temperature, RHEED streaks are typically well developed, as shown in figure 1d. The substrate temperature is then raised to 875°C , where the remainder of the AlN layer is grown. If AlN growth is continued, the RHEED pattern becomes extremely sharp, as shown in figure 1e. When the Al flux is shut off, reconstructions briefly appear in the AlN RHEED pattern, first $(\sqrt{3}\times\sqrt{3})R30°$, then (3×3) and finally back to (1×1).

We studied the effects of the AlN nucleation temperature on the subsequent growth. We first tried nucleation at 500°C. The AlN RHEED pattern was initially diffuse, but it sharpened upon immediate ramping to the growth temperature. Increasing the nucleation temperature to 800° led to improved RHEED patterns. At a nucleation temperature of about 850°C, a second set of streaks was observed in the initial the RHEED pattern, consistent a 30° rotated orientation variant.

Ammonia was used as a nitrogen source to grow thick layers of GaN on the AlN buffer layers. The NH_3 flow rate was 2 sccm, the substrate temperature was about 800°C, and the GaN growth rate was 0.6µm/hr. At the end of such a growth, we observe streaky GaN RHEED patterns, and on cooling in vacuum, we observe 2x reconstructions if a small amount of gallium is applied, as shown in figure 1f. This reconstruction has been associated with the Ga face of GaN [14].

For comparison, we tried nucleating GaN without the AlN buffer. The RHEED pattern was amorphous at the start of growth, and subsequent GaN growth was polycrystalline. We also tried growing AlN on Si (1 0 0) substrates. As expected from symmetry considerations, 30° rotated orientation variants were observed.

X-ray diffraction was used to study the variation of microstructure in GaN films with different AlN nucleation steps. Figure 2 shows azimuthal ϕ scans of the GaN $(1\,0\,\bar{1}\,2)$ peak for 4 different samples. The bottom data set shows the results for a film with optimum AlN nucleation. Notice the sharp peaks at 0 and 60°, and note the absence of intensity at 30°. The orientation relationship for the 0 and 60° peaks is $GaN(0\,0\,0\,1)\|Si(1\,1\,1)$ and $GaN[1\,0\,\bar{1}\,0]\|Si[2\,\bar{1}\,\bar{1}]$, which is the relationship widely reported in the literature [15]. A film nucleated at a slightly higher temperature has a small peak at 30° and broad peaks at 0 and 60°. A film nucleated at 500°, then ramped, has wide peaks at 0 and 60° but no intensity at 30°. Finally, a film grown on (1 0 0) silicon has broad peaks every 30°, as expected by symmetry.

The film nucleated at 500°C was further studied by cross-section transmission electron microscopy (TEM) (see figure 3). A high density of defects at the AlN/Si interface is observed; many defects are eliminated across the thickness of the AlN, but those that remain appear to continue into the GaN layer. The interfaces are smooth and free of second phases such as Si_3N_4.

In situ cathodoluminescence of the AlN films using the RHEED gun showed blue luminescence. Thick AlN films are insulating except when aluminum precipitates are present. When an n-type silicon wafer is used, a p-n junction, presumably due to diffusion of aluminum [16], is formed on the surface of the silicon wafer; I-V characteristics from these junctions showed an open circuit voltage of 0.5V under room lighting and good rectifying behavior. Room temperature photoluminescence measurements showed band-edge and impurity-related emission in GaN films grown on both sapphire and on AlN buffered (1 1 1)Si.

Thick (>1.5µm) GaN films grown on Si crack. The amount of cracking varies widely, with crack-free areas ranging from 1µm x 1µm in our worst films and up to 500µm × 500 µm in our best films. The factors which determine the extent of cracking are not understood. We have not observed cracking in AlN films grown on (1 1 1) silicon; but we have not grown AlN films thicker than 1µm.

3 Discussion

Our results suggest that the (7×7) surface reconstruction of the silicon (1 1 1) surface may play a role in the nucleation of AlN. There are a number of reasons this could occur. One possibility is that the stability and relative inertness of the reconstructed surface makes the (7×7) a better surface to nucleate on. At higher temperatures, mobile Si adatoms may react more easily with nitrogen atoms. Alternatively, the (7×7) surface may just offer advantageous nucleation sites for AlN nucleation. Another possibility is that the (7×7) presents a *high-order lattice match* to AlN.

The misfit of AlN on Si is +23.4% in the orientation that we observe to be dominant. Although the 30° mis-oriented orientation gives a -28.7% misfit for AlN, a 3:2 lineup reduces the misfit to +6.9%. [15] This orientation is suppressed at temperatures where the 7×7 is stable. An examination of the structure of the (7×7) surface, [17] shown schematically in figure 4, shows that its large unit cell has several sites where extra GaN planes (i. e. edge dislocations) can be favorably accomodated. The 14Si:17GaN match shown schematically in figure 4 results in a +1.6% mismatch, small enough to support lattice-matched growth. [b]

4 Conclusion

(7 × 7) Si (1 1 1) surfaces nucleate surprisingly well-oriented AlN (0 0 0 1) epitaxial films under plasma-MBE conditions. More detailed studies of the interface may reveal the mechanism behind this miracle. Better understanding of cracking in GaN films could thus lead to widespread practical applications for GaN and AlN epitaxial films on silicon in low-cost electronic and opto-electronic devices.

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[a] This paper fallows the convention of Matthews [4] by calculating the misfit as (difference in lattice constant)/(film lattice constant).

[b] The term “pseudomorphic” seems a stretch in this situation, perhaps a term like “pseudometric” mightbe appropriate.

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FIGURES

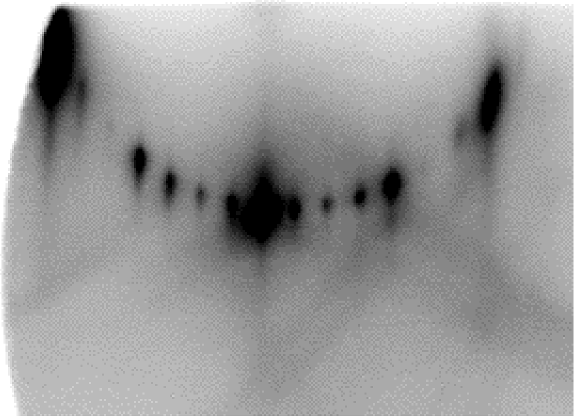

Figure 1a. Reflection high-energy electron diffraction (RHEED) from a clean Si (111) surface at 825°C, showing the (7×7) surface reconstruction. All the RHEED patterns are displayed as negative images for clarity.

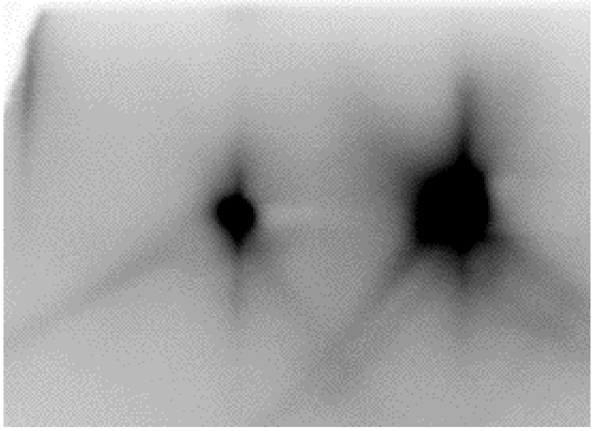

Figure 1b. RHEED from the clean Si (111) surface at 835°C

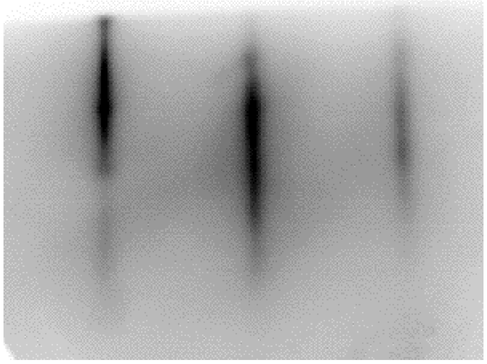

Figure 1c. AlN nucleated 25° below the (7×7) transition, 45 seconds after start of growth.

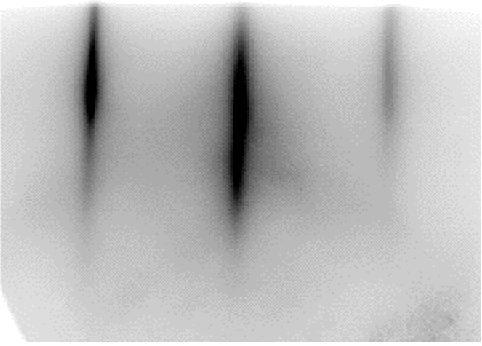

Figure 1d. 6 minutes after start of growth; substrate temperature has been ramped to ~875°C

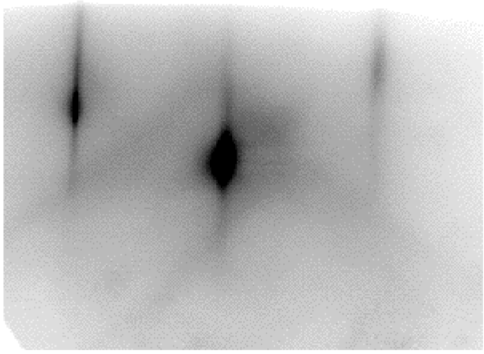

Figure 1e. End of 2 hour growth ~2000Å AlN.

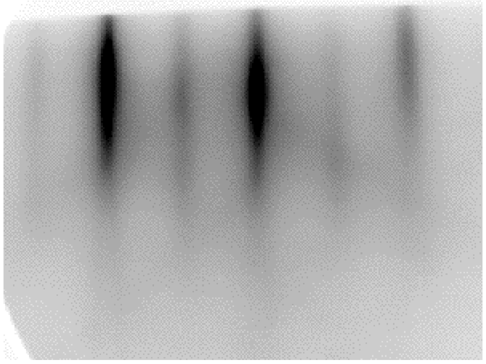

Figure 1f. On cooling after growth of ~1µm GaN on AlN buffer layer. The 2× reconstruction is thought to be characteristic of Ga-face material.

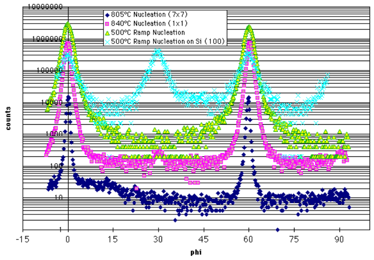

Figure 2. Azimuthal x-ray diffraction scans on the GaN $(1\,0\,\bar{1}\,2)$ peak. for four different GaN/Si samples.

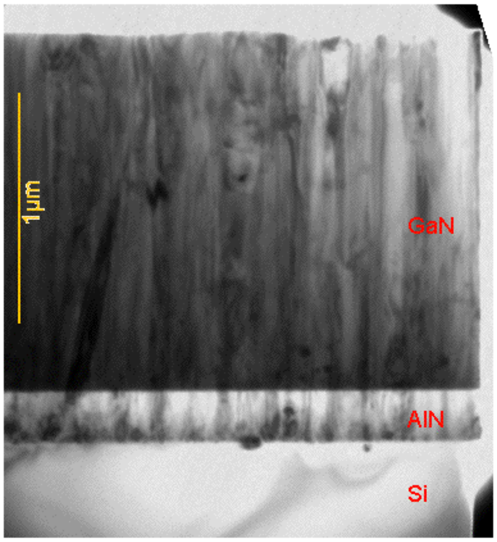

Figure 3. TEM micrograph of a GaN/AlN/Si sample. The AlN was nucleated at 500°C and ramped immediately to 875°C for growth of the 2200Å thick buffer layer.

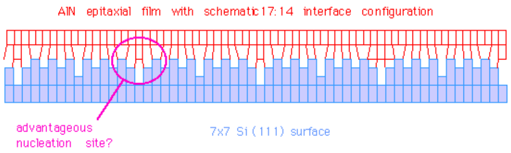

Figure 4. Illustration of 17:14 lattice matching on the 7×7 reconstruction of the (1 1 1) Si surface.