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Effect of Interface Manipulation for MBE Growth of AlN on 6H-SiC

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ABSTRACT

AlN layers were grown on 6H-SiC(0001) by molecular beam epitaxy using ammonia as the nitrogen source. Clean (√3x√3)R30° SiC surfaces was prepared by in-situ annealing alone and also by in situ annealing consisted of followed by Si deposition and subsequent annealing. The surface morphology of the AlN films observed by AFM was significantly changed by the nucleation procedure. When the AlN growth was initiated with Al flux exposure on a SiC surface prepared by thermal annealing, the surface roughness of the AlN was significantly reduced. Two-dimensional growth of AlN was observed with reflection high-energy electron diffraction from the very beginning. Atomically flat AlN surfaces with a RMS-roughness of ~0.3 nm were obtained. On the other hand, when film growth was initiated with an ammonia flux exposure on a Si rich SiC surface, a high density of bumps was observed. The bumps seemed to originate from SiN_x formation at the heteroepitaxial interface. It was found that control of the Si composition and the V/III ratio at the growth interface is crucial for the AlN film quality.

INTRODUCTION

Because single crystal III-nitride substrates are not commercially available, heteroepitaxial film growth is required to obtain large area surfaces for optoelectronic devices based on these materials. The control of the hetero-epitaxial interface between the epitaxial layer and the substrate is one of the key issues to achieve device quality group-III nitride films. Sapphire has been the most commonly used substrate - despite the fact that its lattice constant and thermal expansion coefficient are quite different from those of any of the nitrides. On the other hand, SiC has several advantages over the sapphire as a nitride growth substrate. These include a small lattice mismatch, similar thermal expansion coefficients, a large thermal conductivity, the feasibility of similar cleavage planes, and the availability of a conductive substrate. In spite of these potential advantages, the quality of III-nitride films grown on SiC substrates is not significantly better than those grown on sapphire substrates [1-2]. One aspect that may contribute to the poor quality of the films is the properties of the SiC substrate surface. As-received commercial SiC substrates usually contain not only dislocation and micropipes, which originate in the bulk crystal of the substrate but also a high density of ridges and scratches which result from the lapping and polishing process. Obtaining polished surfaces with small roughness is difficult at least in part because of the physical hardness and chemical inertness of SiC. It has recently been reported that hydrogen etching can effectively remove the ridges and scratches on commercially polished surfaces [3-5]. In addition, in-situ annealing with a Si or Ga flux is also effective for removing surface contaminants and the native oxide layer. It is anticipated that a similar process will be necessary to clean the hydrogen etched surfaces [6-7]. To date, growth of GaN films directly on SiC usually leads to island growth and highly defective films. To avoid this problem, a thin AlN layer can be used as a buffer layer prior to the growth of device quality GaN layers [8].

In this study, we investigated the impact of engineering of the AlN/SiC interface on the quality of the AlN film growth. The engineering approaches include SiC surface cleaning procedures and variation of the nitride growth initiation. The growth of AlN is achieved using molecular beam epitaxy (MBE). It was found that the process of Al exposure prior to AlN growth on $(\sqrt{3}\mathrm{x}\sqrt{3})\mathrm{R}30°$ SiC prepared without excess Si is most favorable to achieve an atomically flat AlN surface. On the other hand, excess Si on the SiC surface results in a high density of bumps on the AlN surface.

EXPERIMENTAL PROCEDURE

The substrates were n-type 6H-SiC$(0001)_{\mathrm{Si}}$ wafers obtained from Cree Research Inc. As-received substrates were etched with a 10:1 HF acid solution to remove the thermally grown oxide layer. Tungsten was deposited on the back of the substrates to assist in radiative and electron bombardment heating. After tungsten deposition, the substrates were degreased and exposed to a vapor from an 10:1 HF buffered oxide etch to remove the remaining oxide [9]. The samples were then introduced into the custom nitride MBE growth system through a load lock chamber. The MBE system was coupled to an Auger electron spectroscopy (AES) analysis chamber and a photo emission electron microscope (PEEM) system [10]. The PEEM was excited with UV light from a mercury arc lamp. The 5.1 eV high energy cutoff of the Hg lamp will excite electrons more readily from regions with lower thresholds for photo-electron emission. This effect can be used to observe the Si coverage and uniformity on SiC surfaces after thermal cleaning.

An electron beam evaporator was used to provide Si flux for the SiC substrate cleaning. The sample surface was monitored by reflection high energy electron diffraction (RHEED) during the SiC cleaning and AlN growth. Sample heating consisted of radiative heating from a tungsten filament and electron bombardment. The substrate temperature was measured using an optical pyrometer. Al (99.999%) was provided by a cold lip single-filament effusion cell with the cell temperature of 1170°C. A quartz oscillator was used to monitor the nominal Si and Al beam fluxes.

Purified ammonia (99.99994%) was used for the N source. A variable leak valve was used to control the ammonia flow rate, and the background pressure of the growth chamber was monitored and controlled in the range of 1×10^{-6} to 1×10^{-5} Torr. AlN films were grown at ~900°C. The growth rate was approximately 0.1μm/hr. Atomic force microscopy (AFM) was used to evaluate the surface roughness.

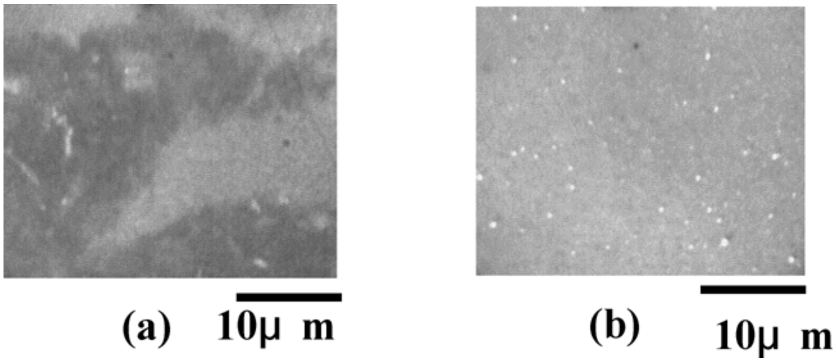

Figure 1 *PEEM images of the (√3 x √3)R30° SiC surface after (a) room temperature Si deposition (`1.5nm) followed by in situ annealing and (b) in situ annealing of the as-loaded etched surface. For the two surfaces, the Si LVV/C KLL ratio in the differentiated AES spectra were (a) 4.38 and (b) 1.4, respectively. The speckles in (b) originate from particles generated in the PEEM chamber.*

RESULT AND DISCUSSION

The (√3x√3)R30° SiC surface was routinely produced by a procedure that involved Si deposition at room temperature followed by in situ, high temperature annealing [10]. After ex-situ cleaning of the SiC surface, a weak (1x1) RHEED pattern was observed, while a considerable amount of oxygen was detected on the surface by AES. The sample was then exposed at room temperature to a Si beam from the electron beam evaporator. A very slow deposition rate of less than 0.1 Å/sec was used for ~10 minutes until the (1x1) RHEED pattern disappeared. The nominal thickness of the Si deposition was ~15Å. The substrate temperature was then elevated at ~950˚C and held for ~5 minutes until a clear (√3x√3)R30° RHEED pattern appeared. The Auger spectrum showed no detectable oxygen peak. The peak-to-peak ratio of the differentiated AES line of the Si LVV and C KLL (Si/C ratio) was typically around 4.0. This value is larger than the 2.21 value reported by Starke et al. for the (√3x√3)R30° 4H-SiC(0001) [11]. The cause for the discrepancy is likely due to non-uniform coverage of the Si. To explore this effect the sample surfaces were observed in situ with PEEM. As shown in the PEEM image in Figure 1(a), bright areas indicate either a (1x1) or (√3x√3)R30° reconstruction both of which have estimated photo-threshold values of 5.06 eV [12]. The dark areas, which were not excited by the UV-photons, are ascribed to regions of (3x3) reconstruction, which has an estimated photo-threshold energy of 6.1 eV [12].

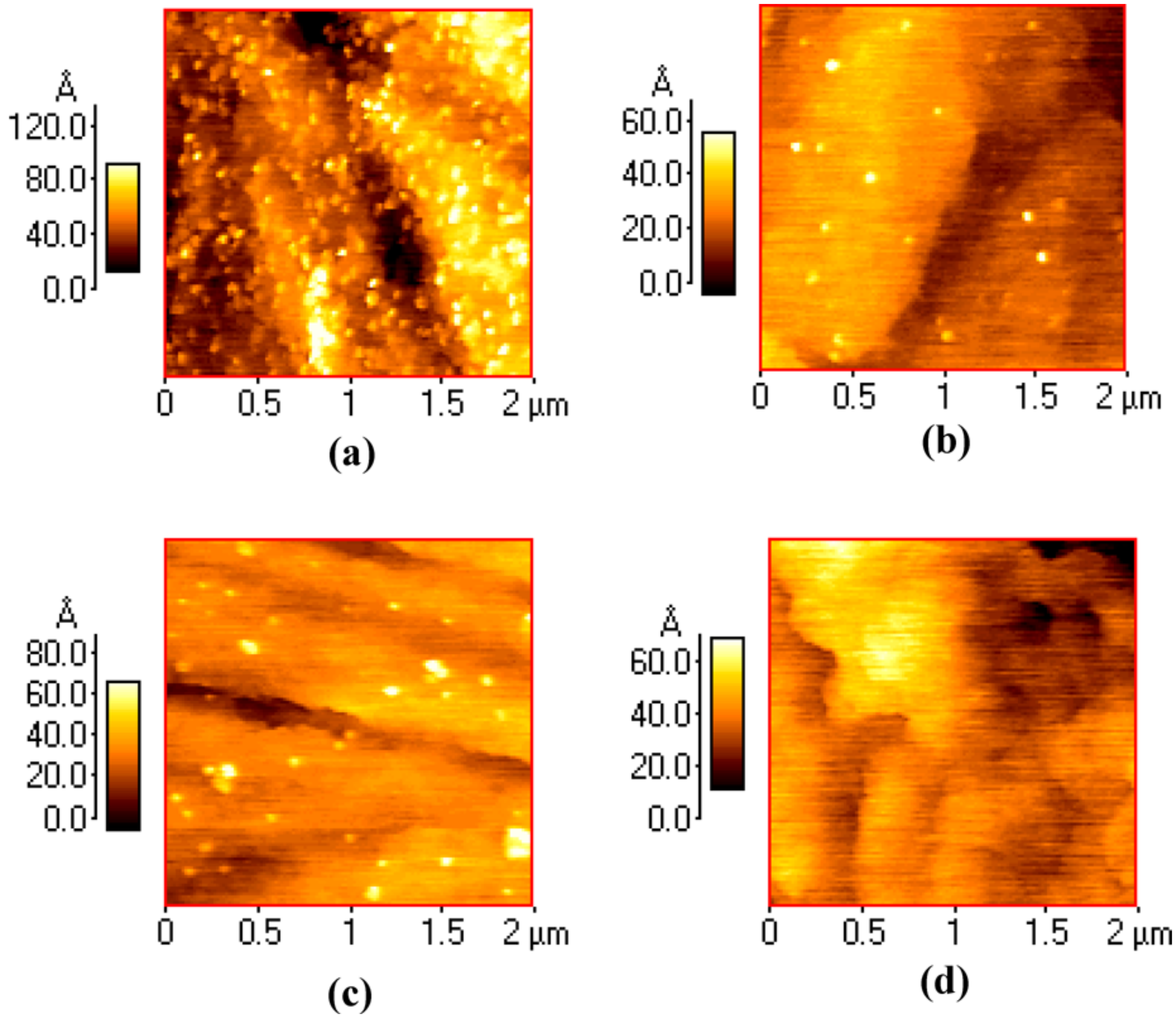

Figure 2 *AFM images of the AlN film surface on (√3x√3)R30° SiC. For (a), (b) the SiC surfaces were Si-rich and for (c), (d) the surfaces were C-rich. For (a), (c) AlN growth was initiated with* NH_3 *exposure, and for (b), (d) AlN growth was initiated with Al exposure.*

A (√3x√3)R30° reconstructed SiC surface could also be prepared through a process which involved simple thermal cleaning of the etched surface at ~950°C. There was no Si exposure step in this process. In this case, the Si /C ratio was ~1.4 and the PEEM image showed a bright uniform surface, which could be indicative of a uniform (√3x√3)R30° reconstruction on the surface. Because the photo-threshold of the 1x1 surface exhibits a similar photo-threshold value, we cannot exclude the possibility of the presence of some (1x1) regions. Using this process, the oxygen peak was again below the AES detection limit. In the following text, these different (√3x√3)R30° SiC surfaces prepared with and without Si deposition are designated as Si-rich (√3x√3)R30° SiC or C-rich (√3x√3)R30° SiC, respectively, for the sake of convenience. Previous studies have suggested that the regions with a (√3x√3)R30° reconstruction should be attributed to a surface with

Si adatoms at the T_4 site on the Si-face of SiC(0001) [13].

AlN layers with a thickness of ~50nm were grown using several different nucleation procedures on these (√3x√3) R30° SiC surfaces. When AlN growth was initiated using an NH_3 flux exposure prior to the growth on the Si-rich (√3x√3)R30° SiC surface, the initial streaked RHEED pattern gradually changed to a spot pattern. As shown in Fig. 2a, the AFM image displayed a high density of bumps ($> 3x10^9$ cm^{-2}). In contrast, when the growth was initiated with an Al flux exposure on the Si-rich (√3x√3)R30° SiC surface, the bump density was decreased by about one order of magnitude, and the surface roughness was also reduced (Fig 2(b)). A streaked (1x1) RHEED pattern, which is an indication of 2-dimensional growth, was observed from the very beginning of the growth. Auger spectra of this sample indicated a small amount of Si on the AlN surface. The excess Si at the heteroepitaxial surface decreased depending on the film thickness and disappeared at a thickness of ~100nm. It is possible that the excess Si segregated on the growth surface and was also possibly incorporated into the AlN film. We suggest that the bumps on the AlN surface are related to the strong bonding between Si and N. While N atoms should form bonds with Si atoms at the topmost layer of a uniform Si face SiC(0001) surface, the excess Si may lead to Si-N bonds which could form SiN_X polycrystals at the heteroepitaxial interface. In contrast, initiating the growth with an excess of Al seemed to prevent or at least reduce this SiN_x formation.

In contrast, the bumps were not observed when the AlN growth was initiated with Al exposure on the C-rich (√3x√3)R30° SiC surface (Fig. 2(d)). An atomically smooth surface was observed with a root mean square (RMS) roughness of ~0.3nm. This value was obtained on the terrace area between polishing scratches. In this case, no Si segregation was detected. A clear (1x1) streaked RHEED pattern was observed during the entire growth. On the other hand, when the growth is initiated with an NH_3 flux exposure on the C-rich (√3x√3)R30° SiC, bumps were again detected on the AlN surface with a density of $\sim 1x10^8$ cm^{-2} (Fig. 2(c)). This result may be anticipated since the nominal C-rich (√3x√3)R30° $SiC(0001)_{Si}$ surface should still exhibit the T_4 Si adatoms. It has been suggested that carbon segregation may exist in the faulted boundaries of SiC for the case of the (√3x√3)R30° $SiC(0001)_{Si}$ surface [13].

The $\omega/2\theta$ x-ray rocking curve scans of the above mentioned four samples showed a full width of at half maximum (FWHM) of about 360 arcseconds. No significant difference was observed between the samples. Further improvement of the FWHM may be possible by growing AlN on hydrogen etched SiC surfaces which remove polishing damage and exhibit a terrace and step structure with full unit cell steps [4].

CONCLUSIONS

The impact of engineering of the AlN/SiC interface was investigated using MBE. The interface engineering included SiC surface cleaning procedures and nitride growth initiation processes. It was found that Al exposure prior to the AlN growth on a nominal C-rich (√3x√3)R30°

SiC surface promoted two-dimensional growth, and resulted in atomically flat AlN surfaces with an RMS-roughness of ~0.3 nm. On the other hand, NH_3 exposure prior to the AlN growth on nominal Si-rich (√3x√3)R30° SiC surfaces resulted in three-dimensional growth and the formation of a high density of bumps ($>3x10^9cm^{-2}$). These bumps seemed to originate from SiN_x formation at the heteroepitaxial interface. It was found that control of the Si composition and V/III ratio at the growth interface is crucial for the AlN film quality.

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