**Mechanism for persistent hexagonal island formation in AlN buffer layer during growth on Si (111) by plasma-assisted molecular beam epitaxy**

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The characteristics of structure and morphology of AlN grown by a growth interruption method on Si (111) with plasma-assisted molecular beam epitaxy are investigated. It is found that the growth interruption method would improve the surface flatness of the AlN layer without the formation of Al droplets. However, AlN hexagonal islands were present and persistent throughout the entire growth owing to effective strain relaxation and Eherlich-Schowebel barrier effect of preexistent surface islands grown on higher terraces of the Si substrate. The density of threading dislocations underneath the hexagonal islands is much less than elsewhere in the film, which is presumably due to dislocation annihilation during the island growth process. © 2007 American Institute of Physics.

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In recent years, there has been increasing interest in producing high quality AlN films because, being a compound semiconductor with a hexagonal wurtzite structure and a wide energy band gap of 6.2 eV, AlN has many potential applications in optoelectronic devices, especially in UV emitters. In addition, AlN is also becoming important for its action as an effective buffer layer for GaN growth with superior quality on Si (111) substrates. Previous growth experiments, with either molecular beam epitaxy (MBE) or metal organic chemical vapor deposition, have shown that the growth under Al-rich conditions leads to a two-dimensional (2D) growth with higher crystalline quality, but often accompanying the formation of Al droplets. In contrast, under N-rich conditions, excess N adatoms at the surface significantly reduce the mobility of Al adatoms and resulting in three-dimensional (3D) growth. The intermediate growth regime for AlN of better crystalline quality and flat surface without Al droplets is very narrow. On the other hand, it is well known that growth interruptions and migration enhanced epitaxy techniques are useful for improving the interface flatness for GaAs growth as well as the surface morphology and crystal quality for nitride epilayer growth. These techniques have also been shown to be promising in regard to enhancing the external efficiency of GaN-based light emitting diodes. Nevertheless, recent results obtained from AlN/sapphire (0001) (Ref. 10) and GaN/AlN/Si (111) (Ref. 11) heterostructures showed that the inversion domains caused by initial inclined surface planes at the interface of the AlN and the substrate resulted in the hexagonal pyramid-shaped hillocks formation on the surfaces. To the contrary, by employing a growth interruption with plasma-assisted MBE (PAMBE), we report on the formation of AlN hexagonal surface islands on Si (111), which are persistent throughout the entire growth and distinctive from the previously reported hillocks. These persistent surface islands consist of much fewer dislocations and maintain the same number density over the entire thickness range up to 180 nm. The formation of the persistent islands was found to be related to the rough Si surface and was enhanced by strain relaxation and the Eherlich-Schowebel barrier effect. The perfect hexagonal persistent islands can serve as ideal templates for nanostructure material growth.

AlN layers were grown on n-type Si (111) substrates by a Veeco/Applied-EPI 930 PAMBE. Prior to the epitaxy, Si (111) 7 × 7 clean surface was observed at 750 °C by heating the substrate at 860 °C for 30 min. The AlN layer was grown at 850 °C under an Al-rich condition with the growth interrupted method, where the Al and N shutters close for 1 min after 5 min growth at the same growth temperature. The AlN layers were characterized by atomic force microscopy (AFM) (Seiko SPA400). The microstructures of the AlN layers were characterized by transmission electron microscopy (TEM) to examine the formation mechanism of the persistent hexagonal islands. TEM images were acquired at 200 keV with a field emission TEM (JEOL 2100F) equipped with a Gatan imaging filter. The micro-Raman scattering experiments were carried out at room temperature using a Jobin Yvon Labram HR spectrometer in a Z(Y,Z)-backscattering geometry with 50 mW incident power. A 100× microscope objective was used to focus the 532 nm laser beam onto the sample.

Due to a large lattice mismatch and a large interfacial energy between AlN and Si (111), the AlN/Si (111) heteroepitaxial growth would be expected to follow Volmer-Weber (VW) growth mode for nucleation and coalescence of 3D islands in the early growth stage. The microstructural evolution should include nucleation of discrete islands, is-

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land growth, island impingement, and coalescence. Figure 1(a) shows an AFM image of the AlN layer consisting of coalesced and homogeneously distributed islands for the thickness of 40 nm with the roughness of 1.85 nm. During this period, reflection high-energy electron diffraction exhibit a spotty pattern (not shown), consistent with the nature of 3D islands. As the thickness increased to 180 nm, the initial VW islands would undergo grain growth with higher lateral growth compared to vertical growth, followed by coalescence of the AlN grains to form a continuous film under the Al-rich conditions. The AlN layer exhibited a 2D layer by layer growth, as shown in Fig. 1(b) with the roughness reduced to 0.38 nm. Notably, some pronounced AlN hexagonal surface islands were still persistent on the AlN layer surfaces even after other islands had coalesced. From a cross sectional imaging study (shown later in Fig. 2), the AlN persistent islands appeared as soon as the growth started and the aspect ratio increased with increasing growth time, indicating that the characteristics of these persistent islands must be distinctive from other nucleated 3D islands leading to the higher growth rate. The density of the AlN persistent islands is about $10^7$ cm$^{-2}$ throughout the entire growth. On the contrary, when AlN layers were grown under an Al-rich condition without using the interrupted growth method, the Al adatoms would be held to the surface by weak and delocalized metallic Al–Al bonds, which form a liquidlike film on the surface and reduce the energy barrier for the surface migration of N atoms. Thus, the N adatoms gained higher surface diffusion length and could move to preferable incorporation sites, resulting in a smooth 2D growth morphology as well as yielding excess Al accumulation on the surface, which would promote the formation of Al droplets with the roughness of 0.72 nm. This means that all accumulation of nonincorporated and nonevaporated Al droplets would dissociate during the growth interruption process and attach to the existing AlN persistent hexagonal islands. However, the hexagonal islands were always persistent on the surface and independent of the interrupted process.

Figure 2(a) shows a cross sectional TEM dark-field image from the 40 nm thick AlN layer sample taken with an exact 0002 two-beam condition. The thinner AlN layer is discontinuous and consists of (0001)-oriented AlN islands. The image demonstrates that 3D islands nucleate on the substrate and grow up to 100 nm in size before island impingement and coalescence to a continuous film. There is no amorphous layer at the interface with the substrate, but the AlN/Si (111) interface is not flat and steps with different heights have been determined. Moiré fringes with a spacing of 1.2 nm along the (0002) can also be seen in Fig. 2(a) due to the interference of the lattices of the AlN layer with those of the Si substrate, implying that the interface is rough. Upon the heat pretreatment at 860 °C for 30 min before AlN epitaxy, round grains were found to dominate the rough surface of the Si substrate with an average diameter of about 30 nm (not shown), which is consistent with the step size in Fig. 2(a). This phenomenon has been reported previously. Figure 2(b) shows the elemental maps from the Si/AlN interface by the three-window technique with energy-filtered TEM. Figure 2(b) shows that the AlN and Si have a sharp interface, without obvious elemental intermixing. It is also evident that the AlN persistent island nucleates on a higher Si terrace, accompanied by a nonzero displacement along the 0002 growth direction, which leads to the formation of the persistent islands. The big contrast between the persistent islands and other coalesced islands must be related to the Eherlich-Schowebel (ES) barrier effect. During the growth, the mean diffusion length of Al adatoms is much higher than the distance between the nucleus of the persistent islands and the excess Al adatoms preferentially attach to those islands due to the ES barrier effect, which creates an effective uphill gradient. As expected, after the coalescence process is complete, the ES barrier effect has a great impact on the vertical growth rate of the persistent islands. In addition, the adatoms deposited near the persistent islands prefer sticking to the ascending steps and therefore some holes develop near the islands, as shown in Fig. 1(b). Finally, the persistent islands grow in 3D, linearly with the growth time, however, in the absence of Al droplets or additional AlN island nucleation.

Figures 3(a) and 3(b) are TEM two-beam dark-field images using $g=0002$ and $g=11 \rightarrow 20$, respectively, obtained from the cross sectional AlN layer of 180 nm thickness. From Fig. 3(a), there are no columnar defects between the island and adjacent regions. Therefore, the formation of the AlN hexagonal islands is different from the hexagonal pyramid-shaped hillocks due to inversion domains. Using the well-known $g, b=0$ invisibility criterion, we can identify the threading dislocations in Figs. 3(a) and 3(b) as type c and type $a$, respectively. Figure 3 also reveals that the threading dislocation density exhibits a remarkable difference between
the persistent island and other regions. The threading dislocation density remains high throughout the thickness range at the regions other than the island. However, the density of the threading dislocations is highest near the AlN/Si interface and then decreases sharply toward the subinterface underneath the persistent island due to a dislocation annihilation mechanism. The plausible mechanism can be rationalized as the redirection of the threading dislocation by the different growth rates between the persistent island and the surroundings, leading to the formation of dipole half loops by the intersection of the threading segments of opposite sign and finally to a significant dislocation density reduction (the mechanism was shown in the supporting materials), which has been proposed previously.\(^{17,18}\) The Moiré fringes with a spacing of 1.8 nm, as indicated in Fig. 3(a) and 1.1 nm in Fig. 3(b), imply that the persistent island has a small tilt of about 7.2° away from the AlN matrix as a result of the accommodation of the orientation mismatch due to the different growth modes involved with the persistent island and the surroundings.

Raman scattering is employed to obtain information about strain involved in the sample. The \(E_2\) (high) mode of an AlN film near 656 cm\(^{-1}\) could provide a clear signature for biaxial stress within the basal plane of AlN.\(^{19}\) A room temperature Raman spectrum of the 180 nm thick AlN film consisting of persistent islands is shown in Fig. 4. As seen in the spectrum, the broad peak containing \(E_2\) (high) mode can be decomposed into two peaks, located at 656.6 and 653.7 cm\(^{-1}\), which are assigned to originate from the AlN film and the persistent islands, respectively. The \(E_2\) (high) mode of the AlN film at 656.6 cm\(^{-1}\) indicates a small residual strain in the AlN films. However, the tensile strain in the persistent islands is evidenced by the shift of the \(E_2\) (high) mode to 653.7 cm\(^{-1}\). The persistent AlN islands exhibit a higher tensile stress than the AlN layer due to much fewer dislocations underneath for strain relaxation, which also contributes to the high growth rate, and becoming taller islands as a means of reducing the strain. The strain relaxations in the persistent AlN islands could reduce the island edge diffusion barrier.\(^{20}\) Therefore, adatoms can easily migrate to the preexistent persistent island edges and eventually form larger islands.

In summary, the interrupted method would improve the surface flatness of the AlN layers to avoid the Al droplets formation under an Al-rich growth condition. The formation of AlN hexagonal islands is strongly induced by strain relaxation and ES barrier effect of preexistent surface islands grown on the higher terraces of the Si substrate. The density of threading dislocations underneath the hexagonal islands is much less than elsewhere in the film, which is presumably due to dislocation annihilation during the island growth process. These hexagonal islands might serve as the ideal templates for further growth of nanostructure devices.

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