Effect of Trimethyl-aluminum Preflow on The Structure and Strain Properties of AlN Films

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Abstract: We studied the effects of trimethyl-aluminum (TMAI) preflow on the properties of AlN films grown on (0001) sapphire substrates via metalorganic chemical vapor deposition using high-temperature treatments. Short TMAI preflow treatments had little effect on the surface morphology of the AlN films, but hexagonal islands appeared on the surface when the TMAI preflow time increased. As the preflow time increased, the crystalline quality decreased and the stress state of the AlN films also changed. The origin of this stress behavior can be explained through a combination of extrinsic stress and intrinsic stress.

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1 Introduction

Recently high quality AlN films have received a great deal of attention because of their attractive physical properties such as a wide bandgap (6.2 eV) strong piezoelectricity and good thermal and chemical stability\textsuperscript{[1-4]}. Because of these properties AlN films have many promising applications. For example they can be used to fabricate deep ultraviolet emitting devices\textsuperscript{[5-7]} z-band surface acoustic wave devices\textsuperscript{[8]} and high power and high temperature electronic devices\textsuperscript{[9]}. However AlN films are usually grown heteroepitaxially on sapphire, Si or SiC because of the lack of homoepitaxial substrates. At present sapphire is the most commonly used substrate for AlN and several groups have reported high-quality AlN grown on sapphire via metalorganic chemical vapor deposition (MOCVD)\textsuperscript{[10-14]}. However the crystalline quality and polarity of high-temperature (HT) AlN are very sensitive to the initial growth conditions. For example a rough HT-AlN film with an N-polar or mixed polar surface usually forms when HT-AlN is grown on nitried sapphire\textsuperscript{[15-16]}. However smooth HT-AlN films can be obtained if the AlN film has an Al-polar surface that has benefited from optimized initial growth conditions. Therefore to obtain high crystalline quality and Al-polar MOCVD-grown HT-AlN careful control of the initial growth conditions is required. In this experiment we systematically investigated the effect of trimethyl-aluminum (TMAI) preflow on the structure and strain properties of AlN films grown on (0001) sapphire substrates. Our results show that the crystalline quality and strain properties of the AlN films were strongly affected by the TMAI preflow.

2 Experiments

The AlN epilayers were grown on c-plane sapphire substrates in a horizontal low-pressure AIX 200/4 RF-S MOCVD reactor. TMAI and NH\textsubscript{3} were used as the Al and N precursors respectively. Prior to AlN growth the sapphire substrate was thermally cleaned at 1 100 °C in a hydrogen environment for 10 min. Then the temperature was decreased to 950 °C and TMAI preflow was performed on the samples for 0, 20, 60 s (the samples were marked as A, B, C and D respectively). Following the TMAI preflow a thin AlN nucleation layer with a thickness of about 25 nm was deposited at 950 °C. Finally an ~ 1 μm HT-AlN film was grown at 1 300 °C. All of the samples were grown with identical growth parameters other than their differing TMAI preflow time. The entire growth process was monitored in situ via a light reflectance measurement at a wavelength of 405 nm. The surface morphology was investigated via scanning electron microscopy (SEM, JEOL-JSM 6500F). The structural properties and stress state of the AlN layers were investigated via high-resolution X-ray diffraction (HR-XRD, D8 Discover, Bruker, Germany).

3 Results and Discussion

Fig. 1 shows the changes in reflectance at 405 nm over the entire growth process. It can be seen that the reflectivity sharply increases during TMAI preflow. This suggests that thin Al interlayers with thicknesses that varied from sample to sample formed on the sapphire substrate. From Fig. 1 it can be seen that the oscillation amplitude of the reflectance curves also changed during the growth of the nucleation layer and the HT-AlN. Without TMAI preflow (sample A) the reflectance of the HT-AlN during growth first weakened and then became strong. This means that the growth process for HT-AlN without TMAI preflow transitions from an island growth mode to a quasi-layer-by-layer growth mode. For sample B the reflectance of the HT-AlN during growth increased until a steady-state situation was reached. This means that the growth process for
Fig. 1 Reflectance during the growth of the 1-μm-thick AlN films on the sapphire substrates with TMAI preflow time for 0 (A) 2 (B) 20 (C) 60 s (D).

HT-AlN with a 2 s TMAI preflow transitions from a state in which the adjacent islands meet and coalesce to form a continuous smooth layer to a quasi-layer-by-layer growth mode. For sample C (20 s) the reflectance of the HT-AlN during growth was stable. This means that the growth process for HT-AlN with a 20 s TMAI preflow begins and remains in a quasi-layer-by-layer growth mode. For sample D (60 s) the reflectance of the HT-AlN during growth was also stable, but the oscillation amplitude was smaller than that of the other three samples in steady state. This suggests that the surface of sample D may have been worse than those of the other three samples.

The surface morphology of the HT-AlN films was measured via SEM (Fig. 2). The TMAI preflow time for the samples shown in Fig. 2 are 0 (a) 2 (b) 20 (c) 60 s. The SEM results show that sample B have smoother surface than the other samples. This indicates that optimizing TMAI preflow time can improve the two-dimensional growth of the AlN films because molten aluminum can protect the sapphire surface from nitridation and thus Al-polar HT-AlN was deposited on the sapphire substrate. A smooth surface can be obtained if the AlN film has an Al-polar surface. However, a TMAI preflow time that is too long will lead to a rough surface. For sample D we believe that the metal-deposition patterns are those of aluminum because the substrate was pretreated with TMAI for a long time.

The subsequent NH3 treatment during AlN growth could not completely react with the aluminum that had been preflowed on the substrate. Consequently the aluminum is on the substrate. If the duration of the aluminum pre-seeding is too long, aluminum will accumulate on the substrate in quantities that are too large to facilitate the formation of a smooth layer. Subsequent AlN growth will not have a two-dimensional growth mode and will form a discontinuous and rough surface.

In all of the samples a strong peak related to the AlN (0002) plane was observed at a diffraction angle (2θ) of 36°. The (0002) and (1012) full width at half maximum (FWHM) values in the XRD traces of all samples are shown in Fig. 3. Both the (0002) and (1012) FWHM values increase with the TMAI preflow time, which means that the TMAI preflow causes the AlN crystal quality to deteriorate. The TMAI preflow results in disruptions in the alignment of the nuclei thus it produces many more sub-grains during the growth of the nucleation layer.
The high density of NL sites leads to an immediate transition to a two-dimensional growth mode [20-22].

To investigate the effect of TMAl preflow on the strain properties of the films, we measured the lattice parameters $a$ and $c$ for the four samples using HR-XRD. We used HR-XRD $2\theta-\omega$ scans of the symmetric (002) and asymmetric (102) peak positions. We calculated the parameters using:

$$c = \frac{\lambda}{\sin\theta_{002}}$$

$$d_{102} = \frac{\lambda}{2\sin\theta_{102}} a = \frac{cd_{102}}{\sqrt{3c^2 - 4}}$$

where $\lambda$ is the X-ray radiation wavelength and $\theta_{002}$ and $\theta_{102}$ are the angular positions of the symmetric (002) and asymmetric (102) peaks. The measurement error for the lattice parameter is approximately 0.0001 nm.

Then the in-plane biaxial stress ($\sigma$) in the AlN film can be calculated as follows:

$$\sigma = \left( C_{11} + C_{12} - 2 \frac{C_{23}^2}{C_{33}} \right) \epsilon_{ss}$$

where $\epsilon_{ss}$ is the in-plane biaxial strain which can be obtained using the measured $a$ and $c$ value from the unstrained material. $C_{ij}$ are the independent components of the elastic stiffness tensor ($C_{ij}$). The values for $C_{ij}$ were taken from those reported by Wright ($C_{11} + C_{12} = 538$ GPa $C_{13} = 113$ GPa $C_{33} = 370$ GPa). The measured values differ from the standard values for AlN ($a_0 = 0.31127$ nm $c_0 = 0.49817$ nm).

The lattice parameters and in-plane biaxial stress were measured at room temperature for each sample shown in Fig. 4 (a) and Fig. 4 (b). The measured values differ from the standard values for AlN ($a_0 = 0.311$ 27 nm $c_0 = 0.498$ 17 nm). The calculated stress values for samples A, B, C, and D were $-0.256$, $0.121$, $1.025$, and $-0.979$ GPa respectively. We observed that the strain was dependent on the TMAl preflow time. For samples B and C, $a$ for AlN was greater than that of the standard values and $c$ was smaller than that of the standard values. The inverse was true for samples A and D. Meanwhile, the in-and out-of-plane strains for all of the samples were different from one other.

In the heteroepitaxial process the conditions that determine the actual stress are very complex. Many simple models decompose the stress into the intrinsic stress and the intrinsic stress. We attribute lattice mismatch and thermal expansion mismatch between the AlN film and the sapphire substrate to the extrinsic stress. The AlN/sapphire epitaxial system has the following relationship:

$$\alpha_{AlN} = 6.3 \times 10^{-6}/K$$

Therefore, the lattice mismatch will be $-0.9\%$ which corresponds to a compressive stress of about $-5$ GPa. The thermal mismatch can be calculated with the following formula:

$$\epsilon_{th} = \Delta T (\alpha_{AlN} - \alpha_{sapphire})$$

where $\epsilon_{th}$ is the strain induced by the thermal mismatch and $\Delta T$ is the difference between the ambient temperature and the growth temperature. $\alpha_{sapphire} = 7.5 \times 10^{-6}/K$ and $\alpha_{AlN} = 6.3 \times 10^{-6}/K$ are the thermal expansion coefficients of sapphire and AlN respectively. In our experiments the growth temperature was fixed at 1 300 °C and the thermal mismatch stress was found to be $-0.75$ GPa (compressive stress). Thus, for the AlN sample, the
extrinsic stress is constant at about $-5.75 \text{ GPa}$ (compressive stress).

According to the Volmer–Weber model\textsuperscript{26}\\textsuperscript{1} intrinsic stress is a tensile stress and is introduced by the surface energy reduction associated with grain boundary formation during island coalescence\textsuperscript{27-28}. Because the energies of dislocations are proportional to the square of the Burgers vectors\textsuperscript{1} the grain boundary energies increase sharply and become misaligned with the substrate. This results in broadening in the symmetric scans. The TMAl preflow results in more misalignment among the nuclei and the coalescence of many more sub-grains in the AlN films as discussed above. The coalescence of these small sub-grains produces flat films\textsuperscript{1} but the sub-grains tend to be slightly misaligned with respect to one another. Therefore\textsuperscript{1} total grain boundary energy increases. Therefore\textsuperscript{1} the intrinsic stress increases with the TMAl preflow time. However\textsuperscript{1} the three-dimensional growth mode in sample D did not allow for complete coalescence. The tensile stress is attributed to grain coalescence. Therefore\textsuperscript{1} in sample D\textsuperscript{1} the tensile stress is small. Consequently\textsuperscript{1} the actual stress in sample D is compressive stress.

4 Conclusion

In summary\textsuperscript{1} AlN epilayers with different TMAl preflow time grown on c-plane sapphire substrates by MOCVD have been studied. It is found that the structural and strain properties of the AlN films are strongly affected by the TMAl preflow time. The suitable TMAl preflow time can make the smooth surface of the AlN films but too long TMAl preflow time causes rough surface with hexagonal islands. XRD results show that the AlN crystal quality decreased with the increase of TMAl preflow time which perhaps is due to TMAl preflow resulting in more tilt of the nuclei. The samples with 0 s and 60 s TMAl preflow in-plane stress was tensile stress and out-plane stress was compressive stress; the inverse was true for the samples with 2 s and 20 s TMAl preflow. The combination of extrinsic stress and intrinsic stress play a key role for this stress behavior which can be controlled by adjusting the TMAl preflow time.

References:


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