Enhanced crystalline quality of non-polar a-plane AlGaN epitaxial film grown with Al-composition-graded AlGaN intermediate layer

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Abstract

The non-polar a-AlGaN epitaxial film was successfully grown on the semi-polar r-sapphire substrate by metal-organic chemical vapor deposition technique. An Al-composition-graded AlxGa1−xN (x = 0.0 to 1.0) intermediate layer with varying film thickness from 260 to 695 nm was deposited between the high-temperature AlN layer and the non-polar a-AlGaN epitaxial film to enhance the morphological and crystalline quality. The non-polar a-AlGaN epitaxial films were investigated by using atomic force microscopy (AFM), high-resolution x-ray diffraction, photoluminescence (PL) spectroscopy and the Hall effect measurement techniques. The characterisation results indicate substantial improvements in surface morphology and crystalline quality for the non-polar a-AlGaN epitaxial film grown by adding an Al-composition-graded AlGaN intermediate layer. The surface roughness measured from AFM and the defect-related emission (yellow band) relative to the near-band-edge emission from PL spectra were decreased significantly by optimizing the layer thickness of the Al-composition-graded AlGaN layer. A relatively low background carrier concentration down to −4.4 × 10^{17} cm^{−3} was achieved from Hall effect measurement for the non-polar a-AlGaN epitaxial film.

Introduction

AlGaN-based III-nitrides are promising materials to make deep-ultraviolet light emitting diodes (DUV-LEDs) and laser diodes (LDs) in the light emission wavelength ranged between 210 and 365 nm. The AlGaN-based DUV-LED can be used to inactivate microorganisms and has many potential applications such as water filtration, resin hardening, and sterilization [1]. The most commonly used material for making DUV-LEDs is the polar AlGaN grown on (0001) c-plane sapphire substrate. However, in the polar AlGaN material there is the so-called quantum-confined Stark effect (QCSE) due to the spontaneous- and piezoelectric-polarization. This QCSE bends the energy band structure [2–4], leading to a substantial reduction in the carrier recombination and thus the efficiency of light emitting devices [5].

Although the QCSE is eliminated in the non-polar a-AlGaN epitaxial film, owing to the strong anisotropy in the growth rate, the crystalline quality and surface morphology of the non-polar a-AlGaN epitaxial film are generally much poorer than its polar counterpart. In fact, the non-polar a-plane AlGaN epitaxial film usually demonstrates high density of surface pyramidal defects and strong crystalline anisotropy produced in the epitaxial growth process [6, 7]. Therefore, it is very difficult to grown non-polar a-AlGaN epitaxial thin film with high crystalline quality either by using molecular beam epitaxy (MBE) or metal–organic chemical vapor deposition (MOCVD) technique [8–10]. Because of the big difference in lattice parameter between the high Al concentration non-polar AlGaN epitaxial films and the r-plane sapphire substrate, there is always a development tendency for the basal planes stacking faults and the strong crystallographic anisotropy to be generated in the epitaxial growth process of the non-polar a-AlGaN epitaxial films with an undulating surface morphology [11].
Thus, the growth of non-polar $a$-AlGaN epitaxial films with high crystalline quality [12] will play a vital role in the development of the non-polar AlGaN-based DUV-LEDs.

So far, numerous techniques have been developed to enhance the crystallinity and surface smoothness of the non-polar $a$-AlGaN epitaxial films. Among them, different intermediate films [13–15] and patterned-sapphire substrates (PSSs) have been used to enhance the crystalline quality of the non-polar GaN and AlGaN thin films and AlGaN-based LEDs [16–18]. In spite of these efforts, even today it is still an arduous task to improve the surface morphology and the crystalline quality of the non-polar $a$-AlGaN layers.

In this study the Al-composition-graded AlGaN intermediate layer with various thicknesses was used for the growth of the non-polar $a$-AlGaN epitaxial films by MOCVD technique on the semipolar $r$-sapphire substrate. The optical and structural properties have been characterized by using high-resolution x-ray diffraction (HR-XRD), room temperature photoluminescence (RT-PL) spectroscopy, and atomic force microscopy (AFM). The characterization results show that with the insertion of the Al-composition-graded AlGaN intermediate layer with an optimized thickness, the non-polar AlGaN epitaxial films with relatively smooth surface morphology and high crystalline quality were achieved.

**Experimental**

The growth of the non-polar $a$-AlGaN epitaxial film on the 2-inch semipolar $r$-sapphire substrate was performed by using vertical chamber MOCVD system at low pressure (~40 Torr). The TMAI (trimethylaluminum), TMGa (trimethyl-gallium), and NH$_3$ (ammonia) were used as the MO sources for Al, Ga, and nitrogen, respectively. Hydrogen (H$_2$) was used as carrier gas, as have been described elsewhere [19, 20]. Prior to the growth, the semipolar $r$-sapphire substrate was treated in the H$_2$ atmosphere at a high temperature of 1,060 °C to remove surface contaminants. Following the H$_2$ cleaning process, nitridation treatment was applied in the NH$_3$ ambient at 1,050 °C with a flow rate of 2,400 sccm. The temperature was raised to 1,130 °C and a 200 nm-thickness high-temperature AlN (HT-AlN) buffer layer was grown. Afterward, an Al-composition-graded AlGaN intermediate layer with varied thickness was deposited at a high temperature of 1,145°C. Finally, the non-polar $a$-AlGaN epitaxial film was grown on the Al-composition-graded AlGaN intermediate layer at 1,160 °C. Four samples named as samples A1, A2, A3 and A4 were grown to study the impacts of the insertion of the Al-composition-graded AlGaN intermediate layer on the crystalline quality and surface morphology of the non-polar $a$-AlGaN epitaxial films. The schematic diagram of the multilayers structure is shown in figure 1. The growth parameters for the four samples used in this study were the same except for the thickness of the Al-composition-graded AlGaN intermediate layer, which varied from 260 to 695 nm.

The crystalline quality was investigated by using x-ray rocking curve (XRC). The Al composition and the crystal orientation of the non-polar $a$-AlGaN epitaxial film samples were determined by using HR-XRD and a simulation software, while the RT-PL was carried-out to characterize the optical properties. Furthermore, the
surface morphology was characterized with AFM by probing a scanning area of $5 \times 5 \mu m^2$. All the samples were cut into $1 \times 1$ cm$^2$ pieces for Hall measurement. The Hall effect measurement was performed by using the Van der Pauw method under a magnetic field of 0.35 T and the Ohmic contact was indium to evaluate the electrical properties.

**Results and discussion**

The HR-XRD $2\theta$-{$\omega$} scanning curve for sample A1 is shown in figure 2. The two distinct XRD peaks at $2\theta = 57.64^\circ$ and $59.28^\circ$ correspond to the same (11\overline{2}0) diffraction plane for the non-polar \textit{a}-AlGaN and \textit{a}-AlN buffer layer, respectively. The Al composition of the non-polar \textit{a}-AlGaN epitaxial film in sample A1 was estimated to be 23\% based on the XRD peak position. The Al compositions for other three samples A2-A4 have also been determined to be nearly 23 \%. By taking into account the strong structural anisotropy in the non-polar \textit{a}-AlGaN epitaxial film, the x-ray rocking curves (XRCs) were measured to investigate the crystalline quality. The XRCs for sample A1-A4 at an azimuth angle of $\varphi = 0^\circ$ and $90^\circ$ parallel to [0001] and [1\overline{1}00] directions are shown in figures 3(a) and (b), respectively. The full width at half maximum (FWHM) values of XRCs for the non-polar \textit{a}-Al$_{0.23}$Ga$_{0.77}$N epitaxial film samples A1-A4 were measured and summarized in table 1. Figure 3(a) shows that the FWHM value along [0001] diffraction direction at $\varphi = 0^\circ$ gradually decreased from 2,404 arcsec to
1,569 arcsec as the thickness of the Al-composition-graded AlGaN intermediate layer increased from 260 nm for sample A1 to 695 nm for sample A4. However, the FWHM value of XRC increased again to 1,663 arcsec for sample A4 when the layer thickness further increased to 695 nm. Furthermore, as shown in figure 3(b), the smallest FWHM value was obtained for sample A3 measured along [1100] diffraction direction at \( \varphi = 90^\circ \), implying that the thickness of the Al-composition-graded AlGaN intermediate layer has a significant impact on the crystalline quality of the \( a \)-AlGaN epitaxial films. This result demonstrates that the insertion of the Al-composition-graded intermediate layer between the HT-AlN buffer layer and non-polar \( a \)-plane (11\( \bar{2} \)0) \( Al_{0.23}Ga_{0.77}N \) epitaxial film directly links to the dislocations density as a result of the variation in the inserted intermediate layer thickness. The interaction between different types of defects and dislocations could also be triggered by the insertion of the Al-composition-graded intermediate layer. In other words, with the optimization of the intermediate layer thickness, the defect density and the threading- and screw-dislocations can be decreased, resulting in an improved crystalline quality of the non-polar \( a \)-AlGaN epitaxial film [8, 21–23]. For the samples with any other intermediate layer thickness, the densities of defects and dislocations could be increased, leading to the degradation in crystalline quality [19, 24].

The effects of intermediate layer thickness variation on the optical properties of the non-polar \( a \)-AlGaN epitaxial films were characterized by the RT-PL spectroscopy. As shown in figure 4, the near-band-edge emission (NBE) peaks in the RT-PL spectra for all samples are close to 330 nm, corresponding to a 23 % Al concentration, which is the same as that obtained from the HR-XRD measurement. Although the NBE peak may be overlapped with the basal stacking faults (BSF)-related emission peak as reported in the literature [25], they are hardly resolved in the RT-PL spectra. In figure 4, the yellow band (YB) emission peaks are observed for all samples. In the AlGaN-based materials, the defects-induced deep energy level recombination centers might be responsible for these YB emissions. The YB emission peak at 620 nm in figure 4 is ascribed to various defects-related emissions due to gallium vacancies \( (V_{Ga}) \), oxygen substitution on nitrogen sites \( (O_N) \), and the \( V_{Ga}O_N \)
The ratio of NBE to YB peak intensity ($I_{\text{NBE}}/I_{\text{YB}}$) is calculated for all the RT-PL spectra of four samples shown in figure 4. The intensity ratio ($I_{\text{NBE}}/I_{\text{YB}}$) decreases with increasing film thickness of intermediate layer except for sample A4 as summarized in table 1. This result shows that the crystalline quality of the non-polar AlGaN films is directly linked to the defects-related emission band. In fact, it was found that sample A3 has the highest crystalline quality and relatively least defect emission intensity. This phenomenon implies that the deep energy level recombination centers caused by the defects in the Al-composition-graded intermediate layer might have a vital role in generating the YB emission and strong impact on the crystalline quality of the topmost non-polar $a$-plane ($11 \bar{2}0$) Al$_{0.23}$Ga$_{0.77}$N epi-layer.

The surface morphology was characterized by atomic force microscopy (AFM) for all the non-polar $a$-AlGaN epitaxial films as shown in figure 5. It can be seen clearly that samples A1 and A4 demonstrate a much rougher surface than samples A2 and A3. In fact, the root-mean-square (RMS) value decreases from 18.1 nm for sample A1 to 3.5 nm for sample A3 as the thickness of the Al-composition-graded intermediate layer increases from 260 nm for sample A1 to 540 nm for sample A3. However, the RMS value increases rapidly to 13.3 nm as the thickness of the Al-composition-graded intermediate layer further increases to 695 nm for sample A4. This fact indicates that the crystalline quality and the surface morphology of sample A3 are the best among the four samples used in this study. In other words, both the crystalline quality and the surface morphology can be significantly improved by carefully optimizing the intermediate layer thickness. Moreover, as shown in figures 5(e) and (f), the dense pyramidal type features are observed in the surfaces of samples A1 and A4. These pyramidal features are distributed along the $c$-direction due to the strong anisotropy in the growth rate of the non-polar $a$-AlGaN and the diffusion rate of Al atoms [28]. A significant reduction in pyramidal features on the
surfaces of samples A2 and A3 reflects that the insertion of the Al-composition-graded AlGaN intermediate layer with optimized thickness is effective to decrease the anisotropy in the atomic distribution distance for Ga and Al atoms. As a result, it becomes relatively easy for Ga and Al atoms to move to their favorable lattice cite to combine with nitrogen atoms, thereby improving the crystalline quality and the surface morphology.

Figure 6 illustrates the background electron concentration (BEC) obtained from Hall effect measurements and the RMS values from AFM measurement as a function of the thickness for the Al-composition-graded AlGaN intermediate layer. The lowest BEC of the non-polar and the RMS values from AFM measurement as a function of the thickness for the Al-composition-graded AlGaN intermediate layer. It is well known that the unwanted high BEC is usually due to the oxygen impurities that act as the donors to the GaN-based epitaxial film although the first principle calculation result shows that oxygen will undergo a DX transition in Al0.6Ga0.4N for x > 0.3, which will behave like an acceptor [29]. The decrease in BEC can be attributed to the reduction in the density of VN (nitrogen vacancy) which is the primary natural source of the carrier in GaN epitaxial film [30].

Conclusions

The non-polar a-plane (11 20) AlGaN epitaxial films with an Al concentration of ~23% were successfully grown on the semipolar r-sapphire substrates with the insertion of the Al-composition-graded intermediate layers. The impact of the insertion of the Al-composition-graded AlGaN intermediate layer on the crystalline quality, optical property, and surface morphology of the non-polar a-plane (11 20) AlGaN epi-layers was thoroughly investigated. It was found that by carefully optimizing the thickness of the inserted Al-composition-graded AlGaN intermediate layer, both the crystalline quality and surface morphology of the non-polar a-AlGaN epitaxial film could be improved significantly. It was also revealed that the PL intensity ratio of the NBE and the YB was strongly dependent on the thickness of the Al-composition-graded intermediate layer. These results indicate that the insertion of the Al-composition-graded AlGaN intermediate layer with an optimized thickness is very effective method to grow the non-polar a-AlGaN epitaxial film with high crystalline quality and smooth surface morphology, which is the key material for the fabrication of the non-polar AlGaN-based UV-LEDs in the future.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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