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Room temperature growth of semipolar AlN $(1\bar{1}02)$ films on ZnO $(1\bar{1}02)$ substrates by pulsed laser deposition

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Semipolar AlN $(1\bar{1}02)$ films have been prepared on ZnO $(1\bar{1}02)$ substrates by employing room temperature (RT) grown AlN layers using pulsed laser deposition. The use of the RT-AlN layer suppresses the interfacial reactions between AlN and ZnO and makes it possible to take full advantage of the nearly lattice matched wurtzite substrates. The FWHM values of XRCs of semipolar AlN $(1\bar{1}02)$ films were 1180 arcsec and 1620 arcsec for symmetric $1\bar{1}02$ diffraction and in-plane $11\bar{2}0$ diffraction, respectively. These results indicate that the use of the RT-AlN layers and the ZnO substrates would be quite attractive for fabrication of high efficiency UV light emitting devices.

Group III nitride-based light emitting devices grown on semipolar planes have attracted increasing attention due to their potential for significant reduction in the undesirable effects of built-in electric fields [1, 2]. In fact, various research groups have demonstrated GaN/InGaN based light emitting devices fabricated on $(10\bar{1}3)$, $(10\bar{1}1)$, and $(11\bar{2}2)$ planes [3, 4]. Among the group III nitrides, AlN is especially promising for the fabrication of ultraviolet solid-state light sources such as light emitting diodes and laser diodes [5], because it has a direct wide band gap of 6.1 eV [6] and high thermal conductivity of 285 W/mK [7]. It has also been pointed out that semipolar and nonpolar plane AlN films improve the light extract efficiency from the surface, compared with conventional *c*-plane AlN films [8]. However, little work on the epitaxial growth of semipolar AlN films has been reported due to a lack of an appropriate substrate for semipolar growth. Although it is known that semipolar AlN $(11\bar{2}2)$ can be grown on *m*-plane sapphire substrates, sapphire has different symmetry and large lattice mismatch with AlN. Therefore, the AlN film suffers from a high density of threading dislocations and the incorporation of other crystallographic orientations [9].

ZnO is quite promising as a substrate material for the epitaxial growth of semipolar AlN, because AlN and ZnO share the same crystal structure (wurtzite) and their lattice mismatch is quite small. In addition, recent progress in the hydrothermal growth technique has made it possible to fabricate high quality ZnO single crystals with large diameters [10]. However, a serious problem exists with the use of ZnO substrates, concerning the formation of interfacial layers at elevated temperatures that negates the advantages of the crystalline properties [11]. To solve this problem, the development of a low-temperature growth technique for AlN is highly desirable. Recently, we have demonstrated that the use of pulsed laser deposition (PLD) allows us to dramatically reduce the growth temperature for group III nitrides [12–14]. In fact, we have demonstrated that low temperature growth by PLD improves the crystalline quality of the group III nitrides grown on lattice matched substrates such as SiC and ZnO, and found that such improvement can be attributed to the suppression of the introduction of misfit dislocations [15, 16]. We have also demonstrated the epitaxial growth of polar and nonpolar AlN films on ZnO substrates using the room temperature growth technique [17, 18]. In this letter, we report on the epitaxial growth of semipolar AlN $(1\bar{1}02)$ films on ZnO $(1\bar{1}02)$ substrates using the room temperature (RT) PLD technique for the first time, and investigate their structural properties.

We used mechanochemically polished 10×5 mm^2 ZnO $(1\bar{1}02)$ substrates. The root mean square (RMS) surface roughness of the substrate estimated from a 5×5 µm^2 atomic force microscope (AFM) image was as low as 0.2 nm. The substrates were degreased with ethanol and then introduced into an ultra high vacuum (UHV) PLD chamber with a background pressure of 2.0×10^{-10} Torr. Before the initiation of film growth, the substrates were annealed at 850 °C in the chamber for 30 min in order to remove the remaining contaminants from the substrate surfaces. The growth of AlN was performed in the PLD chamber at the substrate temperatures of RT and 900 °C. KrF excimer laser (COMPex 110, Coherent Inc.) pulses ($\lambda = 248$ nm, $\tau = 20$ ns) were used to ablate an Al target (99.999% purity) at an energy density of approximately 3 J/cm^2 and a pulse repetition rate of 30 Hz. Nitrogen was supplied through an rf plasma radical generator (UNI-Bulb, Veeco) operated at 400 W at a pressure of 6.0×10^{-6} Torr. Characterization of the AlN films was carried out using *in-situ* reflection high-energy electron diffraction (RHEED), electron backscattering diffraction (EBSD), AFM and high-resolution X-ray diffraction (HRXRD). All the X-ray diffraction measurements were performed with a BRUKER AXS D8 Discover X-ray diffractometer. We also performed grazing incidence X-ray reflectivity (GIXR) measurements to determine the film thickness, surface roughness and interfacial roughness between AlN and ZnO by curve fitting of the experimental data using Fresnel equation.

The RHEED image for the 200 nm thick AlN film directly grown on ZnO $(1\bar{1}02)$ at 900 °C exhibits a dim pattern (solid lines) with similar diffraction pattern for the substrates and spots (dashed lines) with different spacings as shown in Fig. 1(a). The superimposition of two different RHEED patterns indicates the coexistence of several AlN orientations. In order to determine the crystallographic orientations involved, we performed EBSD measurements. A {0001} pole figure for this sample shown in Fig. 1(b) exhibits two dominant peaks indicating the existence of the 180° rotational domain of AlN $(1\bar{1}02)$. EBSD measurements also have revealed the coexistence of a cubic AlN domain, in agreement with the spots in Fig. 1(a). This phenomenon is probably caused by the interfacial reactions between AlN and ZnO which occur at the growth temperatures above 500 °C [17]. In order to suppress the interfacial reactions between AlN and ZnO, we reduced the growth temperature down to RT. Figure 1(c) shows that the RHEED pattern for AlN grown on ZnO $(1\bar{1}02)$ at RT is the similar diffraction pattern to that for the substrate, which indicates single crystalline AlN $(1\bar{1}02)$.

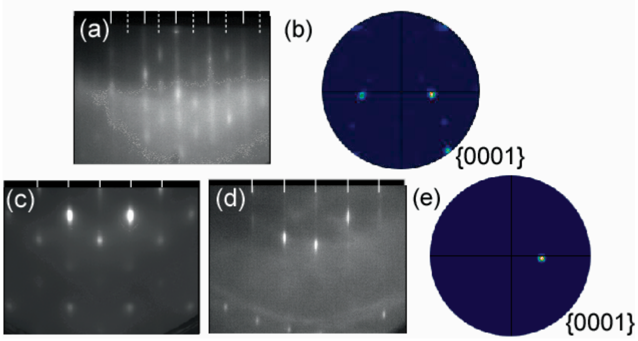

Figure 1 (online colour at: www.pss-rapid.com) RHEED patterns and {0001} EBSD pole figures for (a), (b) AlN directly grown on the ZnO substrate at 900 °C, (c) RT-AlN layer, and (d), (e) AlN grown on a RT-AlN buffer layer at 900 °C. The incident electron beam is parallel to the $[11\bar{2}0]$ direction of the ZnO substrate.

GIXR measurements have revealed that the hetero-interface between a 50 nm thick RT-AlN layer and ZnO substrates is quite abrupt with the interfacial layer thickness of less than the detection limit (0.3 nm). This result indicates that reduction in growth temperature down to RT suppresses the interfacial reactions between AlN and ZnO. It was also found that AlN films can be epitaxially grown at 900 °C on the RT layers without causing degradation of the AlN/ZnO hetero-interface. The RHEED pattern for a 250 nm thick AlN layer grown at 900 °C with this technique exhibited sharp streaks, as shown in Fig. 1(d). The {0001} pole figure for this sample shown in Fig. 1(e) indicates that the film grown at 900 °C with this technique contained no rotational domains. These results make a striking contrast with those for AlN directly grown on ZnO at 900 °C. This contrast suggests that the ZnO surface is vulnerable to chemical species at the initial stage of film growth, but that the AlN/ZnO hetero-interface is quite stable once it has been formed.

Figure 2 shows an AFM surface image of 250 nm thick AlN $(1\bar{1}02)$ films fabricated with this technique. The surface of this sample was quite smooth and the RMS surface roughness over this 1×1 µm^2 picture was 1.2 nm. We did

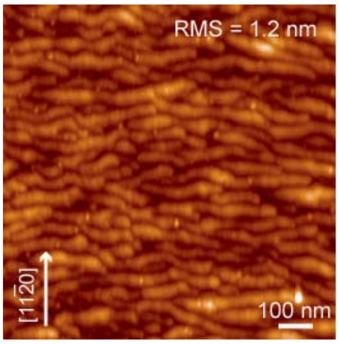

Figure 2 (online colour at: www.pss-rapid.com) AFM surface image of 250 nm thick AlN $(1\bar{1}02)$ film with elongated morphology along *c*-axis direction.

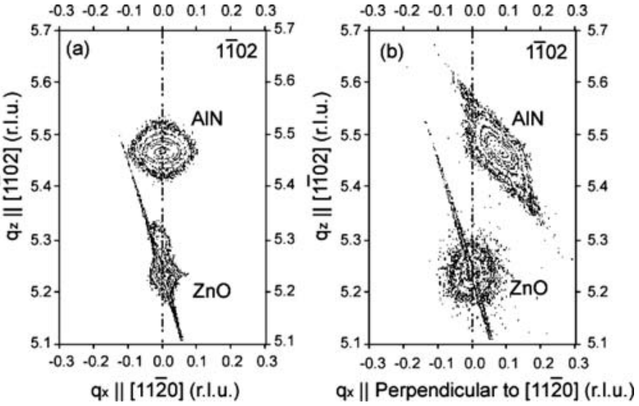

Figure 3 Symmetric RSMs around $1\bar{1}02$ diffraction with X-ray incidence on (a) the plane containing [$1\bar{1}02$] and [$11\bar{2}0$] directions and (b) the ($11\bar{2}0$) plane.

not observe any striped morphologies perpendicular to the *c*-axis, which are believed to be related to basal stacking faults, as reported for nonpolar or semipolar GaN and AlN films [19, 20].

In order to investigate the details of the crystallographic orientation, reciprocal space mapping (RSM) measurements were performed. Symmetric RSMs around $1\bar{1}02$ diffraction, with X-ray incidence on the plane containing [$1\bar{1}02$] and [$11\bar{2}0$] direction and the ($11\bar{2}0$) plane are shown in Fig. 3(a) and (b), respectively. In Fig. 3(a), peaks for ZnO and AlN are located at the same position in the q_x, [$11\bar{2}0$] direction. On the other hand, in Fig. 3(b), the peak for AlN is shifted towards a higher value in the q_x direction which is perpendicular to [$11\bar{2}0$]. These results indicate that the [$1\bar{1}02$] direction of AlN is misoriented towards *c*-axis by 0.87° from the [$1\bar{1}02$] direction of ZnO. This tilting of the AlN films can be attributed to the formation of a small angle boundary at the hetero-interface caused by the lattice mismatch between AlN and ZnO. Further investigations are necessary to clarify this point. In order to investigate the crystallinity of AlN ($1\bar{1}02$) films prepared with this technique, we performed X-ray rocking curve (XRC) measurements. The full width at half maximum (FWHM) value of the symmetrical AlN $1\bar{1}02$ diffraction, measured by setting the detector and the source in the ($11\bar{2}0$) plane, was 1180 arcsec as shown in Fig. 4(a). We also measured the AlN $1\bar{1}02$ diffraction by setting the detector and the source in the plane containing [$1\bar{1}02$] and [$11\bar{2}0$] directions, but the FWHM value obtained was slightly larger (2000 arcsec). This discrepancy in FWHM values of the XRCs has also been reported for *m*-plane AlN [18] and is believed to be due to the anisotropy in a crystallographic tilting and/or lateral correlation lengths of mosaic blocks. The in-plane XRC was also investigated for this sample as shown in Fig. 4(b). We have found that the FWHM value of XRCs for $11\bar{2}0$ diffraction was 1620 arcsec.

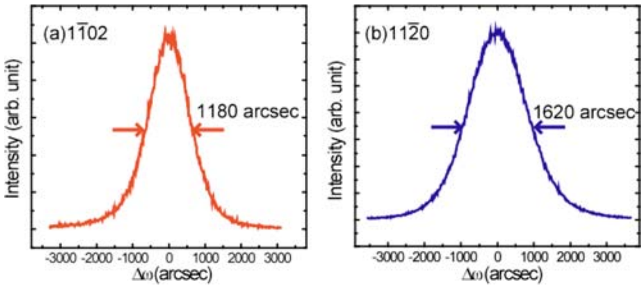

Figure 4 (online colour at: www.pss-rapid.com) X-ray rocking curves for (a) symmetrical $1\bar{1}02$ diffraction and (b) in-plane $11\bar{2}0$ diffraction.

In summary, we have succeeded in the epitaxial growth of semipolar AlN ($1\bar{1}02$) films on ZnO ($1\bar{1}02$) substrates by employing PLD RT-AlN layers. We have found that the use of a RT-AlN layer suppresses the interfacial reaction between AlN and ZnO and makes it possible to take full advantage of the nearly lattice matched wurtzite substrates. The FWHM values of XRCs for semipolar AlN ($1\bar{1}02$) films were 1180 arcsec and 1620 arcsec for symmetric $1\bar{1}02$ diffraction and in-plane $11\bar{2}0$ diffraction, respectively. These results indicate that the use of RT-AlN buffer layer and ZnO substrates would be quite attractive for the fabrication of high efficiency UV light emitting devices.

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