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Semipolar Single-Crystal ZnO Films Deposited by Low-Temperature Aqueous Solution Phase Epitaxy on GaN Light-Emitting Diodes

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Low-temperature aqueous solution deposition has been used for the first time to produce epitaxial ZnO layers on the semipolar $(10\bar{1}\bar{1})$ surface of bulk GaN substrates and LEDs. Although the ZnO films have single in-plane and out-of-plane orientations, which are nominally the same as those of the $(10\bar{1}\bar{1})$ GaN substrate, the ZnO lattice is observed to be slightly tilted with respect to that of the substrate. A $(10\bar{1}\bar{1})$ light-emitting diode using an epitaxial ZnO film as a transparent current-spreading layer achieved a high external quantum efficiency of 48%.

Due to their high efficiency, long life, and lack of toxic components, light-emitting diodes (LEDs) based on GaN are leading candidates to replace conventional incandescent lighting.[1,2] However, continued improvements in efficiency, and or reductions in cost will be critical for the success of GaN LED technology. Currently, most commercial GaN LEDs are fabricated through heteroepitaxial growth of *c*-plane GaN on non-native single-crystal substrates, e.g., sapphire or SiC. However, the spontaneous polarization of Wurtzite GaN, as well as piezoelectric polarization caused by heteroepitaxial lattice strain, can lead to an internal electric field oriented parallel to the *c*-axis of the LED. For an LED structure grown on a *c*-plane-oriented wafer, this electric field causes the energy bands in the quantum wells to slant. The resulting spatial separation of the electron and hole wave functions, known as the quantum confined Stark effect (QCSE), leads to a decrease in radiative recombination, and thus, a lower internal quantum efficiency (IQE). By eliminating or reducing this effect, nonpolar and semipolar orientations of GaN for LEDs should allow for higher IQEs to be achieved.[3] Although the potential benefits of nonpolar and semipolar GaN LEDs have been known for some time, the recent availability of bulk and free-standing GaN substrates, which can be cut and polished into numerous orientations, has greatly increased interest in non-*c*-plane devices.[4]

Semipolar devices have demonstrated potential to improve the IQE of GaN LEDs,[5] but maximizing external quantum efficiency (EQE) still requires additional measures to increase light extraction from the device. Numerous techniques have been used to extract more of the light produced in LEDs, but some of the simplest and most widely used are based on the addition of transparent current-spreading layers.[6] As the name suggests, these layers spread current over the device, increasing the area and uniformity of the light-generating region. To allow the light generated to be extracted from the device, current-spreading layers are usually composed of semitransparent thin metal films, e.g., 5 nm Ni + 10 nm Au,[7] or a transparent conductive oxide, e.g., indium tin oxide (ITO),[8] zinc oxide (ZnO),[9] etc. ZnO is an especially attractive transparent conductive oxide because of its low cost relative to ITO, and the fact that its similar crystal structure allows for low-strain epitaxial growth on GaN. Single-crystal epitaxial films should display higher mobility and increased transparency compared with polycrystalline films due to the lack of grain boundary scattering. With an optical band gap of 3.3 eV, ZnO is transparent to the entire visible spectrum, but can display significant n-type conductivity even when only unintentionally doped. Another potential advantage over other current-spreading layers is the fact that ZnO can be both synthesized and wet-etched in aqueous solutions under relatively mild conditions. Thompson *et al.* previously demonstrated that a current-spreading layer consisting of epitaxial ZnO deposited from low-temperature aqueous solution could improve the power output of *c*-plane GaN LEDs by over 90% compared with a Ni–Au current-spreading layer.[10] In this report, we demonstrate that low-temperature aqueous deposition can also be used to produce epitaxial semipolar ZnO films that can function as highly effective current-spreading layers on $(10\bar{1}\bar{1})$-oriented GaN LEDs.

The $(10\bar{1}\bar{1})$ bulk GaN substrates used were supplied by Mitsubishi Chemical. To fabricate the LEDs used, a multi-layer homoepitaxial (In,Ga,Al)N structure was deposited by atmospheric pressure metal organic chemical vapor deposition (MOCVD). The epi-structure consisted of a 1-µm-thick Si-doped n-type GaN layer, followed by the active region, which consisted of 3 periods of alternating 20 nm unintentionally doped GaN and 3 nm 15–20% InGaN layers. On top of the last quantum well, a single 16 nm Mg-doped layer was deposited, followed by a 16 nm, Mg-doped, 15% AlGaN electron-blocking layer, a 50 nm Mg-doped p-type GaN layer, and finally, a 10 nm Mg-doped p^+ GaN contact layer.

It was found that epitaxial $(10\bar{1}\bar{1})$ oriented ZnO films could be deposited on bulk GaN substrates, or on GaN-based LEDs, using a low-temperature aqueous solution method similar to those previously reported for *c*-plane growth.[11,12] However, it was discovered that when using $(10\bar{1}\bar{1})$ substrates, a coalesced film could be deposited without a separate nucleation, or "seeding", step and without solution additives to modify the morphology. In contrast, without a separate nucleation step and the addition of citrate ions to the growth solution, similar conditions for growth on *c*-plane GaN result in uncoalesced epitaxial ZnO needles. Figures 1(a) and 1(b) show scanning electron micrographs of the ZnO structures that resulted from identical growth conditions on (0001) and $(10\bar{1}\bar{1})$ bulk GaN substrates, respectively. In this case, ZnO was deposited using a pH 12, 0.5 M NH_3 solution saturated with dissolved ZnO, which was prepared in the manner described in previous

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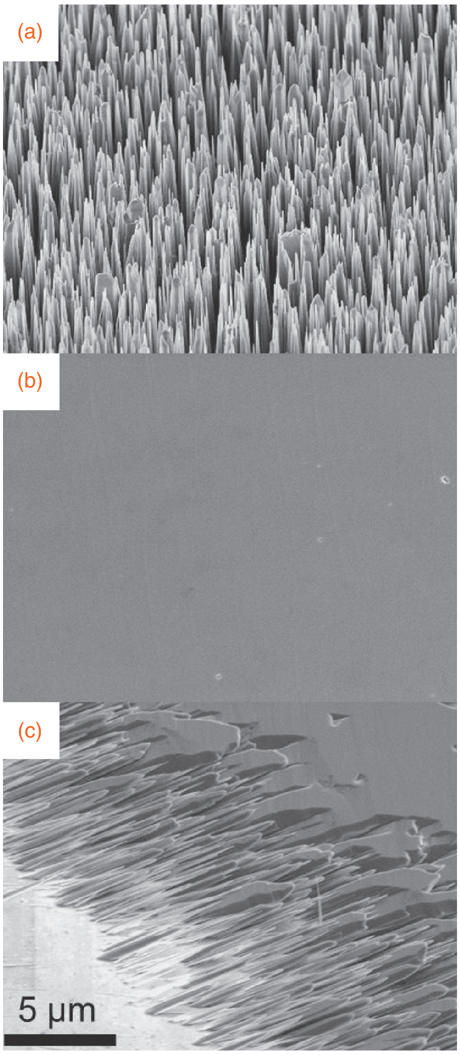

Fig. 1. Representative SEM images showing the ZnO morphology resulting from identical growth conditions on (a) (0001) and (b) $(10\bar{1}\bar{1})$ GaN substrates. An uncoalesced region of the same $(10\bar{1}\bar{1})$ film from (b) is shown in (c).

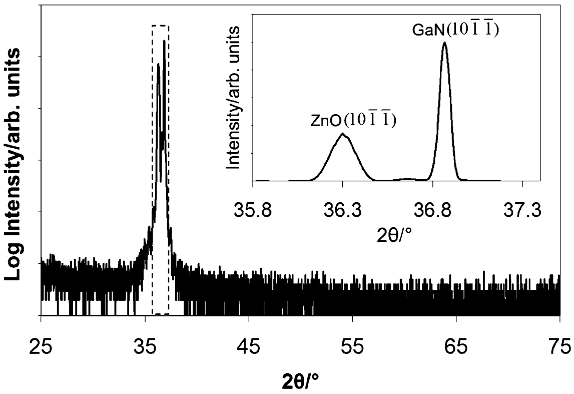

Fig. 2. 25–75° 2θ–ω XRD scan plotted with log scale intensity showing only the $(10\bar{1}\bar{1})$ of ZnO and GaN. The inset shows a higher resolution scan of the ZnO and GaN $(10\bar{1}\bar{1})$ peaks on a linear scale.

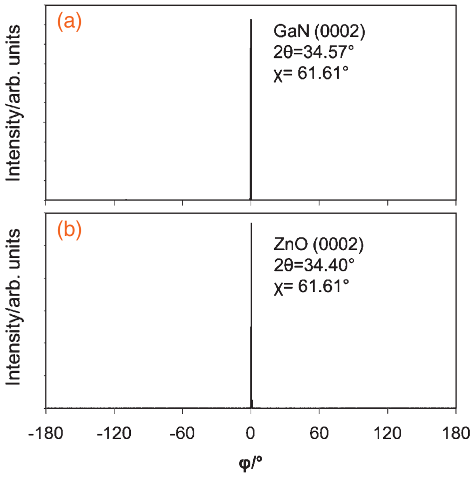

Fig. 3. 360° φ scans showing the alignment of the (a) GaN (0002) and (b) ZnO (0002) XRD reflections.

reports.[12,13)] The substrates were suspended in 25 ml of the solution in a sealed vessel that was then placed in a 90 °C oven for 18 h. From these images, one may guess that the ZnO growth mechanism is very different on the $(10\bar{1}\bar{1})$ substrate. However, by examining the edge of a region where growth was prevented by the sample holder, as shown in Fig. 1(c), we see that that individual ZnO crystals still grow with the same acicular morphology seen on the (0001) substrate. As with growth on a (0001) surface, the fast growth in the c-direction results in needle-shaped crystals. A continuous film appears to form not by layer-by-layer growth, but by coalescence of these individual ZnO needles. However, while the needles on the (0001) substrate grow perpendicular to the surface, the needles grown on the $(10\bar{1}\bar{1})$ substrate are inclined from the surface normal by ~62°. Based solely on this geometry, needles of the same density and aspect ratio on a $(10\bar{1}\bar{1})$ surface would be expected to coalesce into a film with only factor of cos(62°), or about half, the growth needed on a (0001) surface. This geometric effect explains why growing fully coalesced films on $(10\bar{1}\bar{1})$ substrates does not require a high nucleation density or enhanced growth perpendicular to the c-direction, which in a c-direction growth have previously been provided by a separate seeding step and by citrate ions in the growth solution, respectively.[14,15)]

The epitaxial nature and crystal quality on the ZnO films were characterized by X-ray diffraction performed using a Phillips X'Pert MRD Pro diffractometer. As seen in Fig. 2, the $(10\bar{1}\bar{1})$ peaks for ZnO and GaN were the only reflections observed in an on-axis 2θ-scan, indicating that the ZnO film is phase pure and has the same out-of-plane orientation as the GaN substrate. An off-axis 360° φ-scan of the ZnO (0002) peak, shown in Fig. 3, displayed a single in-plane orientation matching that of the substrate. The lattice parameters for ZnO and GaN calculated from their respective (0002) and $(10\bar{1}\bar{1})$ 2θ peaks are $a_{\mathrm{ZnO}} = 3.245$, $c_{\mathrm{ZnO}} = 5.210$, $a_{\mathrm{GaN}} = 3.187$, and $c_{\mathrm{GaN}} = 5.185$ Å, which closely match the expected values. Although both the in-plane and out-of-plane orientations of the ZnO film nominally correspond with those of the GaN substrate, high-resolution ω-scans of the $(10\bar{1}\bar{1})$ peaks of ZnO and GaN reveal that the ZnO planes are tilted with respect to that of the substrate. By performing orthogonal ω-scans with the sample tilting towards the a-directions and c-directions, as shown respectively in Figs. 4(a) and 4(b), we see that the peak shift is

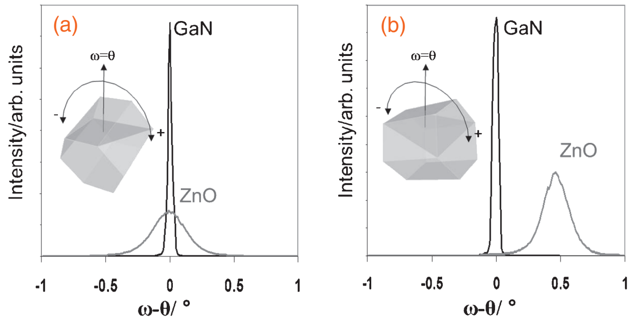

Fig. 4. XRD ω rocking curves of the ZnO($10\bar{1}\bar{1}$) reflection of sample 4 obtained by rocking towards the (a) *a*-directions and (b) *c*-directions of the GaN substrate.

approximately 0.4° towards the c^+ projection. Lattice tilt has previously been shown to occur as a misfit strain release mechanism in semipolar $Ga_{1-x}In_xN$ and $Ga_{1-x}Al_xN$ films on GaN.[16] A similar mechanism may be occurring here, but further examination is needed to characterize the nature of the ZnO lattice tilt.

To test the effectiveness of the epitaxial ZnO as a transparent current-spreading layer, a thicker film was prepared by multiple depositions on an LED epistructured wafer. First, a thinner than normal film was deposited using the same pH 12, 0.5 M NH_3 growth solution described above, but with only a short 2 h heating in a 90 °C oven. This film was then annealed in 20% O_2–80% N_2 at 500 °C for 15 min using a rapid thermal annealer. The annealing of a thin first layer was utilized to improve film adhesion in order to avoid delamination of the entire ZnO film, which would occasionally occur when depositing thicker layers. A second and then a third deposition, with fresh growth solution and 18 h in a 90 °C oven each time, were performed to achieve the final ZnO thickness. After ZnO deposition, devices were fabricated using standard GaN LED processing techniques. The ZnO was patterned by a photoresist masked wet-etch with dilute HCl. The $2 \times 0.5\,\mathrm{mm}^2$ device mesas were formed by a Cl_2 inductively coupled plasma (ICP) dry-etch. The metal contact pads were deposited by electron beam evaporation. The backside of the wafer was roughened for enhanced light extraction using the technique described by Zhao *et al.*[17] Individual devices were removed from the wafer by scribing and cleaving.

For electrical and light output measurements, a device was packaged in the vertical stand transparent LED architecture recently reported by Pan *et al.*[18] The light output power and external quantum efficiency, obtained by integrating sphere detector measurements, are shown in Fig. 5. Using pulsed current injection with a 1% duty cycle, the device output 27 mW of power at a current density of $2\,\mathrm{A/cm}^2$ and 276 mW at $35\,\mathrm{A/cm}^2$. A maximum EQE of 48% was measured at $1\,\mathrm{A/cm}^2$, with the EQE then decreasing to 27.5% at the highest current density measured, $35\,\mathrm{A/cm}^2$. Due to the small size of the bulk ($10\bar{1}\bar{1}$) GaN substrate, it was not possible to compare the performance of the LED using the epitaxial ZnO current-spreading layer with a control device using an ITO current-spreading layer from the same substrate. The light output and EQE of the device using the ZnO were lower than results previously published for a similarly packaged ($10\bar{1}\bar{1}$) device using an ITO current-spreading layer.[17] However, the potential differences in the performance of these devices related to substrate and the MOCVD run to run variations necessitate further tests to determine the performance of aqueous solution deposited ZnO relative to ITO current-spreading layers.

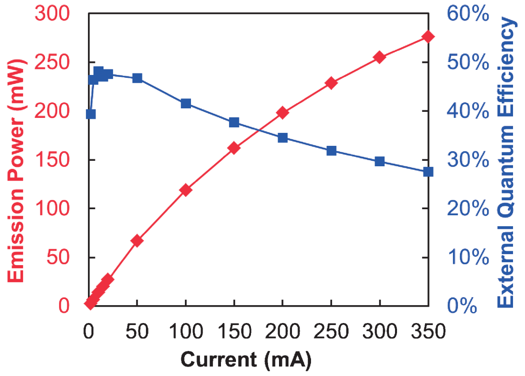

Fig. 5. Light emission power and external quantum efficiency of a semipolar ($10\bar{1}\bar{1}$) LED using an epitaxial ZnO current-spreading layer deposited from low-temperature aqueous solution. Measurements were performed under pulsed current conditions (1% duty cycle).

In conclusion, we have demonstrated that low-temperature aqueous deposition can be used to produce epitaxial ZnO films on the ($10\bar{1}\bar{1}$) surface of GaN single crystal substrates and LEDs. Because of the tendency for ZnO produced by this method to grow fastest in the *c*-direction, simple geometry allows coalesced films to be formed on ($10\bar{1}\bar{1}$) substrates under conditions that result in ZnO needles on a (0001) surface. The ZnO films display good epitaxial crystal quality, but the ($10\bar{1}\bar{1}$) lattice planes of the ZnO are observed to be tilted by ~0.4° in the *c*-direction projection with respect to those of the GaN. When used as a transparent current-spreading layer for a semipolar ($10\bar{1}\bar{1}$) LED, an epitaxial ZnO film helped enable high values for light output power and EQE. These results indicate that aqueous solution deposited epitaxial ZnO films appear promising as current-spreading layers for semipolar GaN LEDs, but more work will be necessary to analyze and optimize performance, as well as understand the nature of the epitaxial interface.

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