Heteroepitaxy of ZnO on GaN and its implications for fabrication of hybrid optoelectronic devices

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ZnO thin films have been grown heteroepitaxially on epi-GaN/sapphire (0001) substrates. Rutherford backscattering spectroscopy, ion channeling, and high resolution transmission electron microscopy studies revealed high-quality epitaxial growth of ZnO on GaN with an atomically sharp interface. The x-ray diffraction and ion channeling measurements indicate near perfect alignment of the ZnO epilayers on GaN as compared to those grown directly on sapphire (0001). Low-temperature cathodoluminescence studies also indicate high optical quality of these films presumably due to the close lattice match and stacking order between ZnO and GaN. Lattice-matched epitaxy and good luminescence properties of ZnO/GaN heterostructures are thus promising for ultraviolet lasers. These heterostructures demonstrate the feasibility of integrating hybrid ZnO/GaN optoelectronic devices. © *1998 American Institute of Physics.*
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Wide band gap materials such as GaN and its alloys (GaAlN, GaInN, and AlGaInN) have been a focal point of research in semiconductors and optoelectronics since the demonstration of high quality GaAlInN based optoelectronic heterostructures, ultrahigh brightness blue–green light emitting devices, ultraviolet (UV) detectors, short wavelength laser diodes, and high-temperature high-power operating devices.[1] Another material analogous to GaN is ZnO which has a room temperature band gap of 3.3 eV and wurtzite structure (see Table I). It is also being considered as a promising material for UV and blue light emitting devices.[2–7] The interesting features of ZnO are: (1) a large exciton binding energy[2] (60 meV) which may be useful for efficient UV laser applications based on stimulated emission due to the recombination of excitons at room temperature ($KT=25$ meV), (2) low power thresholds for optical pumping at room temperature,[3] and (3) tunable band gap from 2.8 to 3.3 eV and 3.3 to 4 eV by alloying with CdO and MgO, respectively.[4] The optically pumped lasing in the ZnO bulk crystals was studied by Hvam *et al.*[5] and more recently by Reynolds *et al.*[3] Room temperature optically pumped lasing in epitaxial ZnO films grown on sapphire (0001) was demonstrated recently by groups of Kawasaki and Koinuma[6] and Bagnall *et al.*[7]

To date the epitaxial ZnO films have been reported on sapphire, which has a poor structural and lattice match to ZnO (Table I). Although high quality epitaxial ZnO films on sapphire have been reported by various groups[6–8] including ours,[9] as-grown films are known to contain a high density of defects (mainly threading dislocations) near the interface due to the large lattice mismatch (~16.7%) between sapphire and ZnO. To our knowledge, there is only one report on the growth of ZnO on small lattice mismatched (5.5%) SiC substrate.[10] No buffer layer approach has been developed so far for the ZnO epitaxy on sapphire. In this letter, we report details of growth and characterization of ZnO epitaxy on high quality GaN buffer layers on sapphire (0001). These films grown on epi-GaN/sapphire by PLD were found to be single crystalline due to the match of stacking order and a low lattice misfit (1.9%) between GaN and ZnO as compared to those grown directly on sapphire.

Two PLD chambers, one for oxides[9] and the other for nitrides,[11] evacuated by turbomolecular pumps to a base pressure of 1×10^{-8} Torr were used for the thin film growth and fabrication of metal-oxide/nitride heterostructures.[11] In this study, 0.1–1.5 μm thick high quality epitaxial GaN buffer layers on sapphire (0001) substrates grown by either PLD or metal-organic chemical-vapor deposition (MOCVD) were used as template for ZnO epitaxy. The ZnO films were grown at a substrate temperature ranging from 500 to 750 °C and an oxygen partial pressure of $10^{-5}-10^{-4}$ Torr. To avoid the oxidation of the GaN surface, initial deposition of ZnO up to a thickness of about 20 Å was carried out at the reduced oxygen pressure (10^{-6} Torr).

Figure 1 shows x-ray diffraction (XRD) ''$\theta-2\theta$'' angular scans for the 5000 Å thick ZnO film grown on GaN/sapphire (0001). The results show only {000*l*} family of

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TABLE I. The structural, optical and thermal properties of ZnO, GaN and sapphire.

Material	Crystal structure	Lattice constant (Å)	Energy gap (eV)	Exciton binding energy (meV)	Thermal expansion coefficient (/°K)	Thermal conductivity (W/cm K)
ZnO	Wurtzite	$a=b=3.249$ $c=5.206$	3.3	60	6.51×10^{-6} 3.02×10^{-6}	0.60
GaN	Wurtzite	$a=b=3.186$ $c=5.178$	3.4	28	5.59×10^{-6} 7.75×10^{-6}	1.35
Sapphire (α-Al_2O_3)	Corundum/ rhombohedral	$a=b=4.758$ $c=12.99$	-	-	7.50×10^{-6} 8.50×10^{-6}	0.50

planes of ZnO, GaN and sapphire indicating that the ZnO/GaN heterostructure is strongly c-axis oriented normal to the sapphire (0001) plane. The XRD rocking curve full width at half maximum (FWHM) for the ZnO and GaN films was found to be 3 arcmin. The *in-plane* alignment of the heterostructures was investigated by using XRD Φ scans. The *in-plane* epitaxial relationship in these heterostructures was found to be ZnO $[10\bar{1}0] \| GaN [10\bar{1}0] \| Al_2O_3 [11\bar{2}0]$. The FWHM of $(10\bar{1}1)$ peak for both ZnO and GaN was about 15 arcmin.

The nature of epitaxial growth and the quality of the ZnO films on GaN were investigated by ion channeling technique and high resolution transmission electron microscopy (HRTEM). Figure 2 shows the aligned and random backscattering spectra for the epitaxial ZnO film grown on GaN/sapphire. The aligned spectrum shows a large reduction of the backscattered yield indicating the single crystalline nature of the ZnO film. The minimum yield near the surface region is $\sim$1%–2%. It is worth noting that the peak seen due to a large density of misfit dislocations near the interface of ZnO/sapphire[9] is small in the case of ZnO/GaN. The dechanneling analysis shows that the dislocation densities near the ZnO/GaN and ZnO/sapphire interfaces are $2\times10^8/cm^2$ and $4\times10^9/cm^2$, respectively. Figure 3 shows the HRTEM lattice image and selective area electron diffraction (SAED) pattern of ZnO/GaN interface. These results show that the lattice planes of ZnO are perfectly aligned with those of GaN and the interface is fairly sharp. It means high quality ZnO films can be grown pseudomorphically up to a critical thickness, t_c, using following equation[12]

$$t_c=\frac{(b\cos\lambda)}{2f}\left\{1+\left[\frac{(1-\nu/4)}{4\pi(1+\nu)\cos^2\lambda}\right]\ln(t_c/b)\right\}, \qquad (1)$$

where ν is the Poisson's ratio (0.38), b is the dislocation Burgers vector, f is the lattice misfit between the substrate and the epilayer (0.019), and λ is the angle between the Burgers vector and the direction in the interface, normal to the dislocation line ($\lambda=\pi/3$). Considering the bulk lattice constants, the estimated t_c for ZnO on GaN is about 70 Å. However, our recent studies of ZnO growth using reduced oxygen pressure conditions[13] indicate that the "a" parameter of ZnO film can be compressed by 1.2% which leads to further reduction of lattice misfit to 0.7% between ZnO and GaN. Using these growth conditions, we can fabricate coherently strained ZnO epilayers up to $t_c\sim300$ Å on GaN. In addition, since the HRTEM confirms the suitability of a GaN buffer layer for ZnO growth, a perfectly lattice matched GaInN system[14] can also be an ideal candidate for ZnO overlayer growth for obtaining t_c more than 300 Å. The surface morphology characterized by atomic force microscopy indicates relatively smoother ZnO epilayers on GaN (rms roughness $\sim$50 Å) compared to those of ZnO films grown on sapphire (rms roughness $\sim$130 Å).

Figure 4(a) shows cathodoluminescence (CL) spectrum obtained at 8 K for 5000 Å ZnO epilayer grown on epi-GaN/sapphire. For comparison, we also show 8 K CL spectra obtained for a 0.5 μm epi-ZnO layers grown directly on sapphire (0001) [Fig. 4(b)] and 1.5 μm thick MOCVD grown epi-GaN/sapphire [Fig. 4(c)]. The CL spectra for ZnO film on GaN/sapphire demonstrate distinct peaks due to the free A exciton and $D^{\circ}X$ bound exciton. In additions to this, the CL spectra show pronounced features due to the donor-acceptor pair transitions at 3.32 eV with phonon replicas at 3.25 and 3.18 eV. From the CL studies, we also note: (1) FWHM of a free A-exciton line width is about 20 meV which is comparable to that of device quality GaN film, (2) under identical conditions of excitation, we see a fivefold

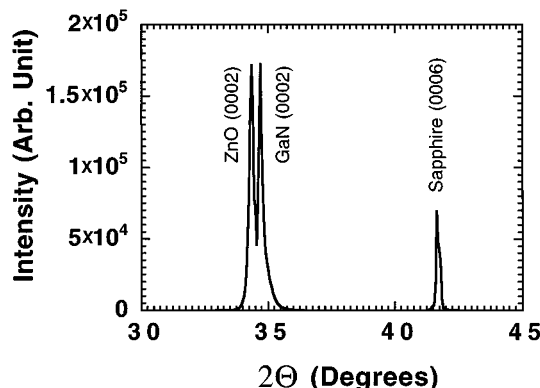

FIG. 1. X-ray diffraction "$\theta-2\theta$" scan of the epi-ZnO/GaN/sapphire (0001) heterostructure.

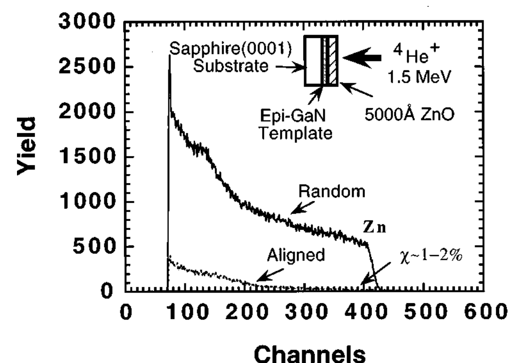

FIG. 2. Random and aligned Rutherford backscattering spectroscopy of an epitaxial ZnO film grown on epi-GaN/sapphire substrate.

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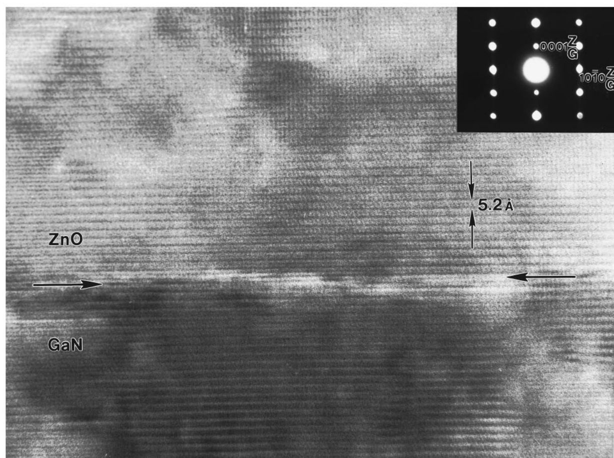

FIG. 3. HRTEM lattice image and the corresponding SAED pattern of ZnO/GaN interface.

increase in the free exciton peak in 0.5 μm thick ZnO epilayer when grown on GaN versus the highest quality 1.5 μm thick GaN film on sapphire (0001). Note that the *n*-type doping concentrations in the PLD ZnO and MOCVD GaN are $2\times10^{17}/\mathrm{cm}^3$ and $1\times10^{16}/\mathrm{cm}^3$, respectively, (3) a substantial decrease in exciton peak for the ZnO film grown without a buffer layer, and (4) the absence of green band luminescence (which is associated with the structural defects in ZnO[15]) for ZnO/GaN/sapphire which is otherwise seen in the ZnO film grown directly on sapphire.

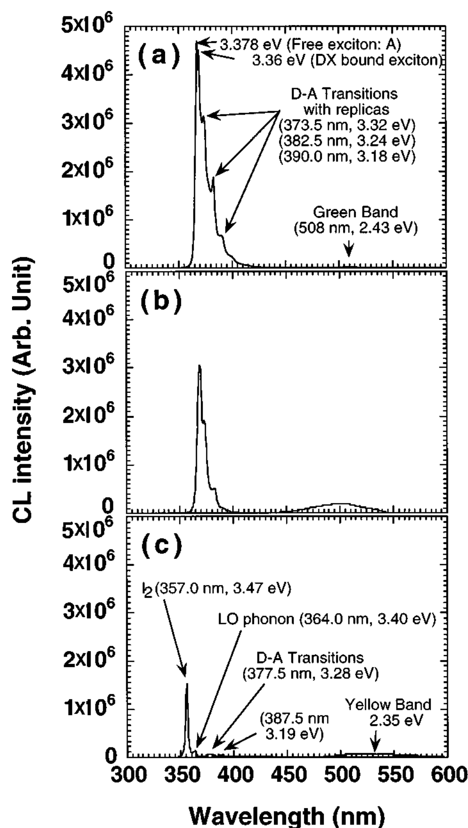

FIG. 4. Low temperature (8 K) CL spectra taken under identical excitation conditions for (a) 0.5 μm thick epi-ZnO/GaN/sapphire, (b) 0.5 μm thick epi-ZnO/sapphire, and (c) 1.5 μm thick MOCVD GaN film grown on sapphire (0001).

Due to their lattice matching epitaxy, thermal and optical compatibility, the ZnO/GaN heterostructures on sapphire may be useful for fabrication of the hybrid optoelectronic devices exploiting advantages of both ZnO and GaN. Recently Mamdani *et al.*[16] have demonstrated high optical quality epitaxial GaN films on ZnO crystals by molecular beam epitaxy (MBE). It means that under MBE and PLD growth conditions, high quality ZnO/GaN and GaN/ZnO heterostructures can be integrated on sapphire. Another interesting feature of thick GaN buffer layer for ZnO is its high thermal conductivity which may be beneficial for ZnO thin film lasers. At this juncture, we feel optimistic about the possibility in fabrication of novel *p*-*n* junctions based on *n*-type ZnO (Al or Ga doped) and *p*-type GaN (Mg-doped) semiconductors for light emitting devices.

In conclusion, we have fabricated high quality epitaxial ZnO/GaN heterostructures on sapphire. These heterostructures showed a substantial improvement in the crystalline quality, defect density, and the luminescence properties. In addition, the matching of stacking order, thermal and optical properties, and the compatibility of these heterostructures with sharp interfaces provide new opportunities for the fabrication of hybrid ZnO/GaN optoelectronic devices on sapphire.

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