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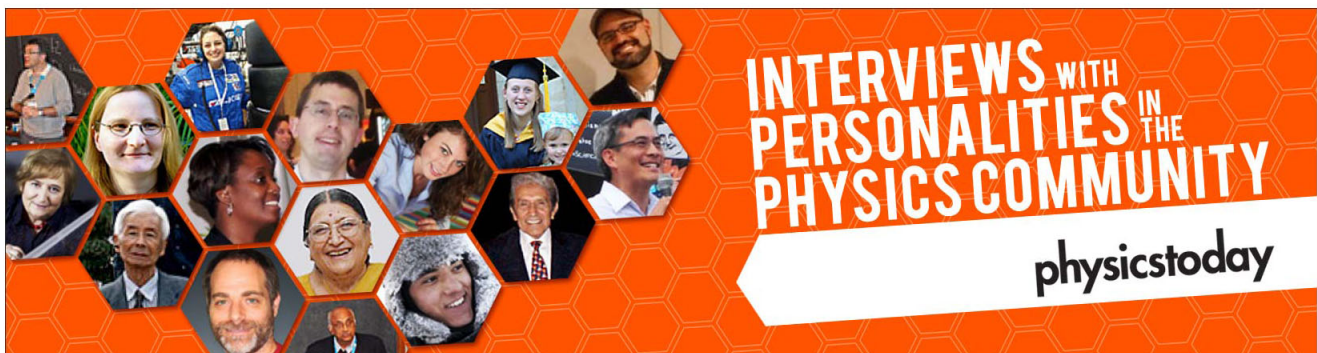
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GaN epitaxy on thermally treated c-plane bulk ZnO substrates with O and Zn faces

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ZnO is considered as a promising substrate for GaN epitaxy because of stacking match and close lattice match to GaN. Traditionally, however, it suffered from poor surface preparation which hampered epitaxial growth in general and GaN in particular. In this work, ZnO substrates with atomically flat and terrace-like features were attained by annealing at high temperature in air. GaN epitaxial layers on such thermally treated basal plane ZnO with Zn and O polarity have been grown by molecular beam epitaxy, and two-dimensional growth mode was achieved as indicated by reflection high-energy electron diffraction. We observed well-resolved ZnO and GaN peaks in the high-resolution x-ray diffraction scans, with no Ga_2ZnO_4 phase detectable. Low-temperature photoluminescence results indicate that high-quality GaN can be achieved on both O- and Zn-face ZnO. © 2004 American Institute of Physics. [DOI: 10.1063/1.1690469]

ZnO is considered as a promising substrate for GaN epitaxy due to its stacking order match, close lattice match and, to some extent, thermal expansion match. Moreover, ZnO can be wet chemically processed and removed easily. Furthermore, due to good conductivity of ZnO, contacts can be formed on both faces of the grown structure to reduce current crowding, which exacerbates the efficiency of high power light-emitting diodes and lasers.^{1,2} Planar defects such as stacking mismatch boundaries (SMB), and inversion domain boundaries (IBD) are inevitable for GaN grown on non-wurtzite substrates such as sapphire and SiC.³ Due to the lack of large area and affordable GaN bulk substrates, alternative approaches such as ZnO, which is the only isomorphous substrate for GaN epitaxy, are being explored. Mixed success for GaN epitaxy on ZnO effort has already been noted in the past.⁴⁻⁸ However, the surface preparation has been mentioned as the main reason for the less than satisfactory results.⁴⁻⁶ Wet etching is widely employed in surface preparation of many substrates such as sapphire. However, both acid and alkali solutions can attack ZnO severely which makes wet etching for surface preparation of ZnO substrates undesirable. The surface damage on ZnO from the chemical mechanical polishing (CMP) must be removed prior to use as a substrate in order to achieve growth of high quality GaN and its alloys.

In this letter we report that a high-temperature thermal treatment can render both O and Zn face of basal plane ZnO surfaces atomically flat and ideal for epitaxial growth of GaN. Although the present work is limited to GaN growth on both Zn and O faces of ZnO, the method is equally applicable for homoepitaxy of ZnO and related compounds, which are gaining a good deal of popularity due in part to reports of *p*-type ZnO.⁹ The ZnO substrates were obtained

from Cermet, Inc. Both oxygen-terminated (000 $\bar{1}$) direction (oxygen face), and zinc-terminated (0001) direction (zinc face) were used. After 3 h annealing at 1050 °C in the breadth of angels, atomic force microscopy (AFM) images revealed that all the surface damage from the CMP was removed, leaving atomically flat and terrace like features on both O- and Zn-face ZnO, as shown in Fig. 1. Further experiments demonstrate that such thermal treatment is effective not only to remove surface damage from CMP, but also

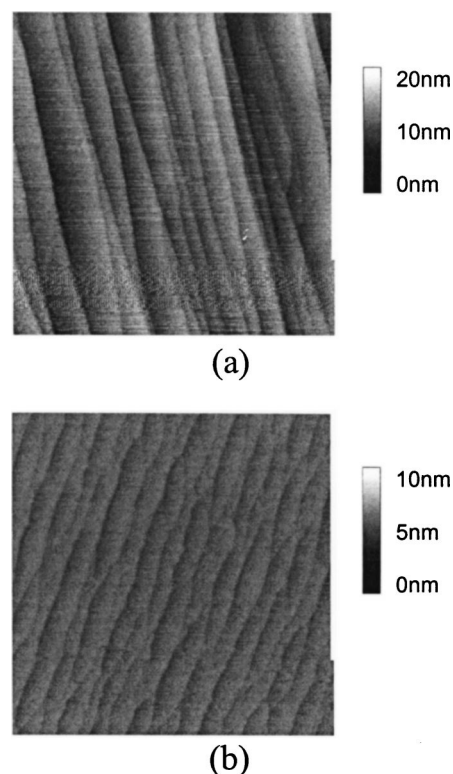


FIG. 1. AFM images ($2 \times 2 \mu\text{m}$) of ZnO surface after annealing at 1050 °C (a) O-face ZnO (b) Zn-face ZnO.

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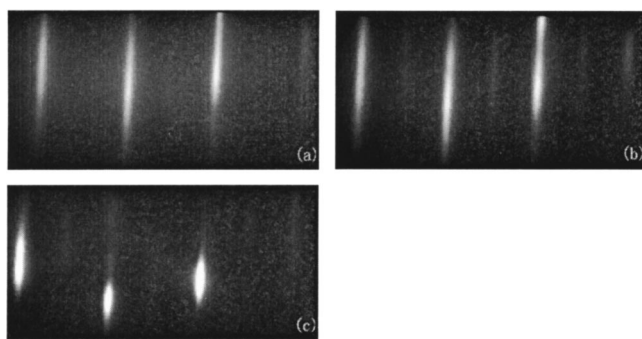


FIG. 2. RHEED pattern of GaN/ZnO (a) during growth (on Zn-face ZnO) (b) cooling down to 350 °C (on Zn-face ZnO) (c) cooling down to 350 °C (on O-face ZnO).

to remove chemically induced damage, such as forming gas annealing.

GaN epitaxy on such thermally treated ZnO substrates was performed by a molecular beam epitaxy (MBE) system, which employs both radio-frequency (rf) plasma enhanced nitrogen and ammonia as active nitrogen sources. Due to the reactivity between ZnO and ammonia, first a thin low-temperature GaN buffer layer was grown with rf nitrogen plasma in order to initiate the GaN growth. Then the substrate temperature was raised and the main GaN layer was grown under a Ga-rich (N limited) condition under typical GaN growth conditions. The rf nitrogen flux was such that as to maintain a growth rate of 0.3 $\mu\text{m/h}$. Reflection high energy electron diffraction (RHEED) was used to monitor the GaN quality *in situ*. A sharp and streaky RHEED pattern was maintained through the entire growth procedure on both Zn- and O-face ZnO, which is an indication of two-dimensional growth mode. This is a marked improvement in the RHEED image, compared with earlier results,⁷ which we attribute to the surface preparation mentioned earlier. Without such surface preparation, the RHEED patterns of the ZnO substrate are typically composed of weak and broken diffraction lines, and the RHEED patterns on the surface of grown GaN layers are also typically broken with poor resultant layer quality. Upon cooling the substrate temperature down to 350 °C a clear 2×2 RHEED reconstruction can be found on both Zn and O terminated ZnO (Fig. 2), which is an indication of Ga-polarity GaN grown on ZnO.

In general, two different bonding configurations are possible between the interfacial GaN on ZnO. On the Zn face, the possibilities are Zn–Ga bonds or Zn–N bonds and on the O face they are O–Ga or O–N bonds. Since both GaN and ZnO are polar materials, from electrostatic and bond strength considerations, the Zn (triply bonded to the O layer below) N bonds and the Ga–O (triply bonded to the Zn layer below) bonds are most likely. This would imply that Zn- and O-face substrates would lead to Ga- and N-polar GaN, respectively. However, our RHEED observations indicate that GaN layers are of Ga-polarity irrespective of the substrate polarity, i.e., 2×2 reconstruction on GaN upon cooldown grown either way. In an overly simplistic picture, one might be tempted to conclude that on the O-face ZnO, the O–N bonds form for polarity consistency. Moreover, one can also forward the argument that O–Ga covalent radii is larger than that for O–N bonds which would lead to stronger interfacial bonding

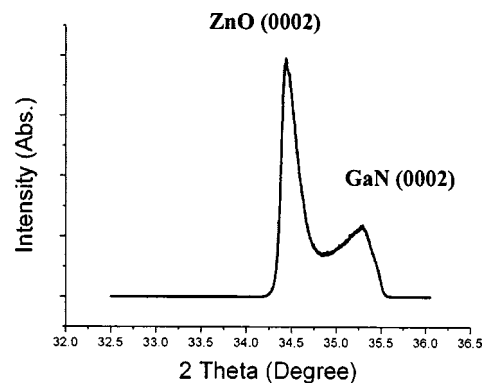


FIG. 3. XRD θ – 2θ scan of GaN/ZnO on Zn-face ZnO.

for the latter pair. However, this simplistic model assumes static interfaces. It is very likely that several monolayers near the surface of ZnO could dynamically participate in atomic exchange and a more detailed investigation of the interface is warranted to be certain about the mechanism(s) leading to Ga-polarity GaN regardless of the substrate polarity.

According to earlier reports,⁷ the spinel structure Ga_2ZnO_4 oxide can be easily formed between ZnO and Ga, as has been confirmed by x-ray diffraction (XRD) θ – 2θ scans. Using a low temperature GaN buffer layer allowed us to avoid deleterious reactions, at least to the extent that can be discerned by our high resolution XRD scan. Indeed, only GaN and ZnO peaks can be resolved, as shown in Fig. 3. Growth on Zn- and O-face ZnO gave identical XRD results. Gil *et al.*¹⁰ have built a theoretical model employing the Pikus and Bir Hamiltonian to fit the energy shift of the valence and conduction bands, taking into account the relaxation arising from thermal and lattice mismatch strain. They pointed out from optical measurements that the GaN grown on sapphire and on ZnO is under compressive strain while that grown on SiC is under tensile strain. The thermal strain (ϵ_{th}) is

$$\epsilon_{th} = [\Delta a_l(T) - \Delta a_s(T)] / \Delta a_s(T),$$

where $\Delta a_l(T)$ and $\Delta a_s(T)$ are the variation of the lattice parameter between the growth temperature and room temperature for GaN layers and substrates, respectively.⁸ The calculation of ϵ_{th} using the temperature dependence of thermal expansion coefficient indicates that the thermal strain of GaN/ZnO is negative and GaN/SiC is positive, while the absolute value for GaN/ZnO is smaller. This indicates that thermal strain of GaN/ZnO should be compressive while that of GaN/SiC should be tensile. These are in good agreement with our optical measurements where the exciton peak of GaN/ZnO was very slightly blueshifted while that for GaN/SiC is redshifted. It should be noted that in the latter case a net compressive strain instead of tensile strain has been reported by some groups^{11,12} which is most probably due to incomplete relaxation of the misfit. In GaN/ZnO the lattice mismatch is smaller (1.9%) than GaN/SiC (3.54%), so it is reasonable that thermally induced strain dominates over the misfit strain.

Ammonia was also used as the N source after the ZnO surface was protected by an initial GaN layer grown with rf nitrogen plasma. Compared with the layers grown by rf nitrogen, the surfaces for the GaN layers grown with ammonia

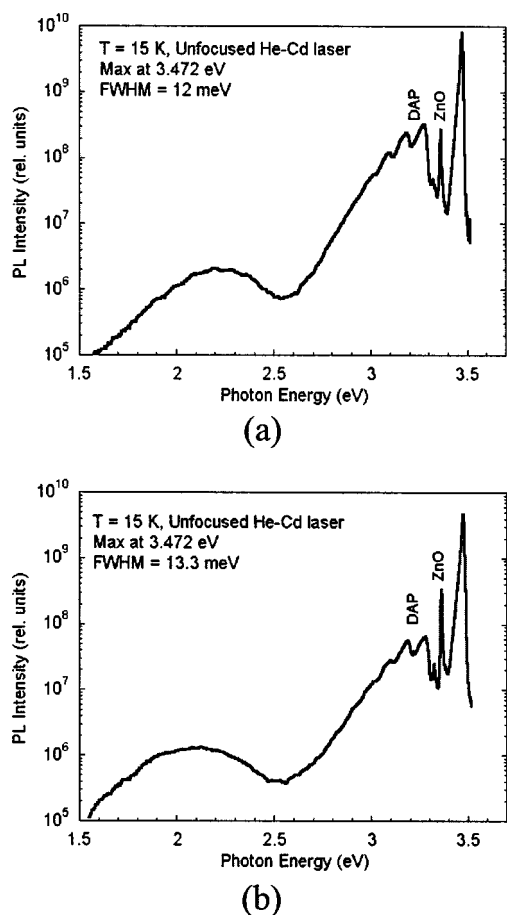


FIG. 4. Low-temperature PL spectra of GaN grown on ZnO with ammonia as N source (a) on O-face ZnO (b) on Zn-face ZnO.

are rougher, which is typical of ammonia regardless of the substrate employed, probably due to the high mobility of species afforded by ammonia on the surface, in part due to complex dissociation processes and presence of H. (If ammonia induces a high surface mobility, it would lead to a smoother or rougher surfaces depending on the growth conditions, particularly the growth temperature.) GaN with better optical quality, as judged by photoluminescence (PL), was achieved by using ammonia as the N source when grown at the temperature of 690 °C. Figure 4 shows the PL spectra of GaN grown on Zn and O faces of ZnO at 15 K. Compared to our typical GaN layers grown on sapphire and SiC in similar growth conditions, GaN grown on ZnO (both on Zn and O faces) demonstrated very high radiative efficiency (up to 20%) and weak yellow luminescence. The V_{Ga} -donor complex, isolated^{13,14} or bound to structural defects such as dislocations¹⁵ or SMB¹⁶ is believed to be the major source for yellow luminescence. The higher radiative efficiency and weaker yellow luminescence in GaN/ZnO compared to other substrates thus may evidence a reduction in defect density. The smallest full width at half maximum (FWHM) for the dominant GaN exciton peak at 15 K was 12

meV for GaN on O-face ZnO and 13.3 meV for that on Zn-face ZnO. Several earlier reports^{5,7,8} indicated that GaN grown on O-face ZnO was better. The present results demonstrate that by careful controlling the growth parameters and using the new surface preparation method, the same good quality GaN can be achieved on Zn-face as well.

In summary, we prepared ZnO substrates with atomically flat surfaces, exhibiting terrace-like features following high temperature annealing, for GaN growth by MBE. RHEED patterns showed that two-dimensional epitaxial growth of GaN can be achieved on these thermally treated ZnO substrates. To the extent that can be determined by high-resolution XRD results, no phase reactions have been found which imply that the surface of ZnO can be protected from the reaction with either Ga or ammonia by employing a low temperature rf-nitrogen GaN buffer layer. The XRD method resolved the GaN diffraction from that of ZnO. Low temperature PL results show that GaN layers with similar optical quality can be achieved on both O- and Zn-face annealed ZnO substrates.

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