Comparison of nanostructure characteristics of ZnO grown on GaN and sapphire

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(Received 22 August 2005; accepted 10 January 2006; published online 1 March 2006)

The immature developments of *p*-type ZnO and ZnO-related ternary or quaternary compound and the small lattice mismatch between ZnO and GaN stimulate interest in the hybrid growth of ZnO and GaN. In this research, we compared the nanostructures and optical properties of two ZnO thin-film samples grown under the same conditions but on different underlying materials (sapphire and GaN). With the high growth temperature of 450 °C, both samples show domain structures. However, in contrast to the sample of ZnO on sapphire, the sample of ZnO on GaN starts with smaller domains (a few tens of nanometers in width) of almost vertical boundaries at the interface and evolves into larger domains (around 100 nm in width). The 30° twist of the basal plane in ZnO with respect to its underlying sapphire does not occur in the sample of ZnO on GaN. Within a domain of ZnO on sapphire, misfit and threading dislocations can be periodically observed along the interface with the separation of about 8 nm. The transition of the lattice structure across the interface between ZnO and GaN was quite smooth, indicating the high heterojunction quality in this sample. The x-ray diffraction results showed that the crystalline quality of ZnO on GaN is slightly better than that of ZnO on sapphire. However, based on the thermal quenching behavior of integrated photoluminescence intensity, we estimated that the optical quality of the two samples is about the same. © 2006 American Institute of Physics. [DOI: [10.1063/1.2174121](https://doi.org/10.1063/1.2174121)]

I. INTRODUCTION

The large three-dimensional (3D) exciton binding energy (60 meV) in ZnO guarantees the effective exciton radiative recombination for light-emitting device applications at room temperature.¹ The exciton binding strength can be even stronger when a ZnO/MgZnO quantum well structure is formed.² Besides free exciton (FX) recombination, in high-quality ZnO crystals, the emission of biexcitons (XX) has also been observed at low temperatures.³ With increasing XX binding energy in a quantum well structure, emission of XX at room temperature becomes possible. Because the recombination rate of a XX is larger than that of FX, XX emission at room temperature implies the possibility of even higher efficiency in the light-emitting devices based on ZnO. Recently, significant progress in ZnO crystal quality has been made. Besides the nanostructures such as nanotubes,^{4,5} nanorods,^{6,7} and nanowalls,⁸ high-quality ZnO thin films have been grown with molecular beam epitaxy,^{9,10} metal-organic chemical vapor-phase deposition (MOCVD),^{11–13} pulsed-laser deposition,^{14,15} and sputtering.^{16,17} Light-emitting devices based on ZnO homostructures and heterostructures have been reported.^{18–20}

However, for implementing an efficient ZnO-based light-emitting device, several difficulties need to be overcome first, including the reliable *p*-type ZnO and high-

quality ZnO-based ternary or quaternary compounds (such as MgZnO and ZnCdO). Although the implementations of *p*-type ZnO have been reported (e.g., Refs. 21–23), recipes for reliable fabrications of *p*-type ZnO and *p*-type MgZnO need to be assured. In this situation, the hybrid growth of ZnO- and GaN-based compounds has been considered.²⁴ A light-emitting diode based on the ZnO/GaN hybrid growth has been reported.²⁵ The idea of the hybrid growth is stimulated not only by the aforementioned difficulties in ZnO growth, but also by the small lattice mismatch between ZnO and GaN (only 1.89%). With the almost lattice-match condition and the more mature nitride growth and process technologies, the combination of ZnO- and GaN-related compounds can lead to device implementations of a larger variety.

Nevertheless, so far the study on the heterostructures of ZnO and GaN is still quite rare. The crystal quality of ZnO grown on GaN is still not well understood yet. Also, the optical properties of the II-VI ZnO on III-V GaN represent many interesting research topics. In this research, we compare the material nanostructures and basic optical properties of a ZnO thin film grown on a GaN template with those of a ZnO thin film grown on sapphire substrate. The nanostructures are demonstrated with the scanning electron microscopy (SEM), x-ray diffraction (XRD) technique, and high-resolution transmission electron microscopy (HRTEM). The comparison shows quite interesting differences in the nano-

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structures near the interfaces of the underlying layers although their basic optical qualities are similar. This paper is organized as follows. In Sec. II, we describe the sample growth conditions and the operation conditions of HRTEM, XRD, and optical characterization. The surface morphologies of the samples and the XRD results are discussed in Sec. III. Then, in Sec. IV we present and discuss the images of HRTEM of these samples. The results of optical characterization are shown in Sec. V. Finally, conclusions are drawn in Sec. VI.

II. SAMPLE PREPARATION AND EXPERIMENTAL CONDITIONS

The two MOCVD-grown ZnO thin-film samples were grown with MOCVD with 6 Torr in pressure and 450 °C in temperature for 90 min. The growth pressure and temperature were chosen based on the optimized conditions for growing high-quality ZnO thin films on sapphire.²⁶ Sample A was grown on a GaN template and sample B was grown on (0001) sapphire substrate. The GaN template includes a GaN nucleation layer of 25 nm in thickness, grown at 535 °C, on (0001) sapphire substrate and then a GaN layer of 2 μm in thickness, grown at 1070 °C. In growing ZnO, oxygen gas and diethyl zinc [$\text{Zn}(\text{C}_2\text{H}_5)_2$, DEZn] were used as precursors, and nitrogen was used as carrier gas for the DEZn. For both samples, O_2 flow was 30 SCCM (standard cubic centimeter per minute), N_2 was 5 SCCM, and temperature of DEZn was 4 °C.

The HRTEM investigations were performed using a Philips Tecnai F30 field-emission electron microscope using an accelerating voltage of 300 kV and a probe forming lens of $\text{Cs}=1.2$ mm. The current density focused onto the samples was estimated to be lower than 16 A/cm². In the XRD measurements, we used a Bede D1 system with a four-bounce channel-cut Si (220) monochromator, delivering a $\text{Cu } K\alpha_1$ line of wavelength $\lambda=0.154\,056$ nm. Although no analyzer crystal is used, a resolution of about 15 arc sec can be achieved. In optical characterization, photoluminescence (PL) was measured with the excitation of a HeCd laser at 325 nm. The samples were placed in a cryostat for temperature-dependent measurements.

III. SCANNING ELECTRON MICROSCOPY AND X-RAY DIFFRACTION RESULTS

Figures 1(a) and 1(b) show the SEM images of samples A and B, respectively. Spiral growth mode leading to domain structures can be clearly seen in both samples. Although the scale sizes of the domains in the two samples are about the same at around 100 nm, their surface morphologies are quite different. In sample B, the spiral growth extends outward from the spiral axis at the top to form a shape like a flower in full blossom. However, in sample A, the spiral growth seems to be parallel to the axis or tilted inward to form a shape like a flower bud.

Figure 2 shows the Φ -scan XRD patterns of the two samples, including three curves for (a) ZnO grown on GaN (sample A), (b) ZnO grown on sapphire (sample B), and (c) the sapphire substrate of sample B. The XRD patterns of

FIG. 1. SEM images of samples A (a) and B (b).

FIG. 2. Φ -scan XRD patterns of the two samples, including three curves for (a) ZnO grown on GaN (sample A), (b) ZnO grown on sapphire (sample B), and (c) the sapphire substrate in sample B.

FIG. 3. ω -scan XRD patterns of the two samples.

ZnO in the (11-24) plane in Figs. 2(a) and 2(b) show the same basal plane orientation. However, the sapphire pattern shows a 30° twist of the basal plane with respect to ZnO. The 30° relative twist between ZnO and the underlying sapphire substrate has been reported.¹³ It results from the large mobility of Zn atoms at the high growth temperature such that they can select sites for reducing the large ZnO/sapphire lattice-mismatch-induced strains. By rotating the hexagonal basal plane by 30° , the strain is reduced and the ZnO crystal quality is improved. However, this twist does not occur in ZnO grown on GaN simply because of the small lattice mismatch between the two compounds. Figure 3 shows the ω -scan patterns of the (0002) plane in the two ZnO samples. One can see that both samples have reasonably good qualities. However, ZnO on GaN has the smaller rocking width (1256 vs 1562 arc sec), indicating a higher crystalline quality in sample A.

It is noted that the domain structures in both samples with the spiral growth mode may include crystalline twist of essentially random nature. A parameter of such a twist-type imperfection in crystalline can reflect the quality of a ZnO

FIG. 4. FWHMs in ω scans of the (0002), (10-15), (10-14), (11-24), and (10-12) planes with their respective inclination angles. The dashed curves represent the fitting curves.

FIG. 5. Large-scale TEM images of samples A (a) and B (b), showing domain structures.

sample. An effective method for determining the orientation spread of imperfect crystalline with XRD has been demonstrated.²⁷ In this method, the full width at half maximum (FWHM) values in ω scans at different inclination angles are used to fit an equation of this scan width for obtaining the average twist angle. Figure 4 shows the FWHMs in ω scans of the (0002), (10-15), (10-14), (11-24), and (10-12) planes with their respective inclination angles. The fitting curves are also shown in Fig. 4 with the dashed curves. The fitting of those data leads to the average twist angles of 0.5123° and 0.6534° for ZnO grown on GaN and sapphire, respectively. The comparison between these two values also implies that the crystalline quality of ZnO on GaN is slightly better than that on sapphire and is consistent with the result in Fig. 3.

IV. IMAGES OF TRANSMISSION ELECTRON MICROSCOPY (TEM)

Figures 5(a) and 5(b) show the large-scale TEM images of samples A and B, respectively. From such a cross-sectional view, both samples demonstrate rodlike domain structures. The average lateral domain sizes of the two

FIG. 6. A HRTEM image of sample A near the interface showing the smaller-domain structures and vertical boundaries.

samples are about the same, on the order of 100 nm. The clear dark line almost along the c axis in the GaN layer of sample A represents a threading dislocation. The threading dislocation does not significantly affect the growth of ZnO on it. A close look at the image of sample A reveals that near the GaN surface, smaller domains of a few tens of nanometers in width exist. Such smaller-domain structures extend for around 100 nm along the growth direction, after which the larger-domain structures at the size order of 100 nm are formed by connecting smaller domains.

Figure 6 shows a typical smaller-domain structure near the interface of GaN. It is interesting to see the vertical domain boundaries extending from the interface. The lateral domain size is in the range of 10–30 nm and the domain gap is about 10 nm. Although not very clear, some crystalline structures exist in the gap regions. From the statistics of a few similar HRTEM images, a quasiperiodic pattern can be observed. The ZnO compound was grown with such a vertical domain structure for around 100 nm. Beyond that, they become connected to form larger domains. Such a smaller-domain structure was not observed in sample B. In this sample, the larger domains of around 100 nm in size extend from the sapphire surface to the top of the sample. The major cause for the formation of the smaller-domain gaps in sample A is unclear. They may exist for relaxing the built strains.

Figures 7(a) and 7(b) show the finer images near the interfaces of samples A and B, respectively. The vertical boundary structures can again be seen in sample A. It seems that between boundary lines, different domains have different sample thicknesses. Such a contrast may be due to the spiral-mode growth in which the thinner region in the image represents a crystal portion behind the thicker region. The almost vertical boundaries shown in Figs. 5(a), 6, and 7(a) indicate the parallel spiral sheets along the axis. This observation is consistent with the surface morphology in Fig. 1(a). On the contrary, such clear boundaries within a domain in sample B are not observed. In this sample, misfit defects are periodically formed along the interface for releasing the built strains, as indicated with the arrows in Fig. 7(b). The separation between two neighboring misfit dislocations is around 8 nm. Note that the line patterns in both ZnO and GaN in Fig. 7(a) confirm the same orientation of their basal planes; whereas the line pattern in ZnO versus the dot pattern in sapphire in Fig. 7(b) confirms the 30° twist of the basal plane of ZnO with respect to sapphire.

FIG. 7. HRTEM images of samples A (a) and B (b) near the interfaces, showing a domain gap in sample A and misfit dislocations in sample B.

Figures 8(a) and 8(b) show the atomic-scale images of samples A and B, respectively, near the sample top surfaces. The crystal qualities of the two samples are essentially quite good. However, regions of dislocations can be seen in sample A, as exemplified by the circled region in Fig. 8(a). On the other hand, in sample B, quasiperiodic threading dislocations, separated by around 8 nm, can be seen. Two of them are observed in Fig. 8(b), as indicated with arrows. Figures 9(a) and 9(b) show the fine-scale HRTEM images of samples A and B, respectively, near the interfaces. The two images were chosen to cover the regions within individual domains in the samples such that no domain boundaries can be seen. Here, we can observe clearly the interface quality. The transition of the lattice structure across the interface between ZnO and GaN was quite smooth, indicating the high heterojunction quality in this sample. On the other hand, the

FIG. 8. HRTEM images of samples A (a) and B (b) near the ZnO top surfaces, showing the essentially good crystalline qualities of the two samples.

different HRTEM patterns between ZnO and sapphire in sample B are due to the 30° twist of the basal plane. Figure 9(a) implies that the heterostructure quality in the hybrid growth of ZnO and GaN can be quite high.

V. COMPARISON OF OPTICAL PROPERTY

Figure 10 shows the temperature-dependent PL spectra of sample A. Those of sample B are similar and not shown in this paper. Figure 10 demonstrates typical PL behaviors in a high-quality ZnO sample.²⁸ At 10 K, the peak near 3.36 eV corresponds to donor-bound exciton (D^0X). That near 3.37 eV beyond 40 K corresponds to FX. Also, the evolving peak around 3.3 eV beyond 60 K is due to the contributions of donor-acceptor pair (DAP) and one-LO-phonon-assisted FX emission (LO phonon energy about 70 meV). Below 40 K, excitons are mainly trapped by neutral donors. Because of the thermal energy, excitons are thermalized into free states to form the FX peak beyond 40 K. This peak becomes dominating and starts to redshift due to the thermal effect beyond 80 K. Beyond 140 K, the thermal energy is larger than the binding energy (8–10 meV) of a neutral do-

FIG. 9. Fine-scale images of samples A (a) and B (b) near the interfaces, showing the high-quality heterojunction of sample A.

nor and hence FX and D^0X become mixed.²⁹ When the room temperature is approached, the complex of FX and D^0X mix with the contributions of DAP and one-LO-phonon-assisted FX emission. In this situation, DAP may be thermalized into the emission level of the conduction band-neutral acceptor transition.

FIG. 10. Temperature-dependent PL spectra of sample A.

FIG. 11. Integrated PL intensities of the two samples as functions of temperature.

Figure 11 shows the integrated PL intensities of the two samples as functions of temperature. The thermal quenching rate of the integrated PL intensity is usually used to represent the density of nonradiative recombination center in a sample.³⁰ In Fig. 11, although the integrated PL intensities of sample B are slightly higher than those of sample A at most temperatures, the two curves are almost coincident, indicating that the two samples have about the same photon emission efficiency. In other words, in spite of the large lattice mismatch between ZnO and sapphire, the 30° basal plane twist can reduce the effective lattice mismatch and lead to quite high material and optical qualities. Meanwhile, the optimized condition for ZnO growth on sapphire can lead to high quality ZnO on GaN. Nevertheless, the optimized condition for ZnO growth on GaN still requires further investigation. Note that although the interfacial nanostructures of the two samples are quite different, their optical properties are mainly controlled by the crystalline qualities in the upper layers of the ZnO thin films. As discussed above, due to either the basal plane twist or the small lattice mismatch between ZnO and the underlying layers, the crystalline qualities of the upper ZnO layers in both samples are quite high. Therefore, their optical properties are similar.

VI. CONCLUSIONS

In summary, we have compared the nanostructures and optical properties of two ZnO thin-film samples of the same growth conditions but on different underlying materials. With the high growth temperature, both samples showed domain structures. However, different from the sample of ZnO on sapphire (sample B), the sample of ZnO on GaN (sample A) started with smaller domains (a few tens of nanometers in width) of almost vertical boundaries at the interface and evolved into larger domains (on the order 100 nm in width). The 30° twist of the basal plane in ZnO with respect to its underlying sapphire in sample B did not occur in sample A of ZnO on GaN. Within a domain of sample B, misfit and threading dislocations could be periodically observed along the interface with the separation of about 8 nm. The transition of the lattice structure across the interface between ZnO and GaN was quite smooth, indicating the high heterojunc-

tion quality in sample A. The x-ray diffraction results showed that the crystalline quality of ZnO on GaN was slightly better than that of ZnO on sapphire. However, based on the thermal quenching behaviors of integrated photoluminescence intensity, we estimated that the optical qualities of the two samples were about the same.

ACKNOWLEDGMENTS

This research was supported by National Science Council of Taiwan, The Republic of China, under the Grant Nos. NSC 93-2210-M-002-006 and NSC 94-2215-E-002-015, and by U.S. Air Force under the Contract Nos. AOARD-04-4026 and AOARD-05-4085.

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