Effects of MgO buffer annealing on optical and electrical quality of P-MBE grown ZnO films on c-sapphire

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Abstract. Zinc oxide (ZnO) has been attracting much attention because of its potential applications in photonic and optoelectronic devices. In this present study, we investigated the effect of MgO buffer annealing on the optical and electrical quality of P-MBE grown ZnO films on c-sapphire with MgO buffer layer. The optical quality was observed by low-temperature PL (photoluminescence) measurement in the near band edge emission region measured at 10K and at 77K. The emission line located at 3.368eV dominates the spectrum in both samples (ZnO with and without MgO buffer annealing) at 10K and 77K. This emission can be divided into two peaks, 3.367eV and 3.363eV and assigned as I2 (ionized donor bound excitons emission) and I4 (Hydrogen donor related emission), respectively. The relative intensity of these donor bound exciton to free exciton emission of the sample without MgO buffer annealing is greater than that of the sample with MgO buffer annealing. Comparison of the PL spectra of ZnO with and without annealing revealed that the intensity of free exciton emission from the sample with MgO buffer annealing is twice of that from the sample without annealing. We also found that the intensity of deep-level broad emission is reduced by about 1/3 by MgO-buffer annealing. Hence, the decrease of deep level emission intensity and the increase of free exciton emission intensity by annealing of MgO buffer corresponds to the reduction of defects of the ZnO film. The PL properties also suggest that there are fewer nonradiative recombination centers in ZnO layers with MgO buffer annealing than those in ZnO layers grown without MgO buffer annealing. The electrical quality was measured by room temperature Hall measurements. We found that the samples have a background n-type carrier concentration. The ZnO samples with MgO buffer annealing has a carrier concentration of 1.17x1017 cm-3 and Hall mobility of 120 cm2/V.s, while the ZnO sample without MgO buffer annealing has a carrier concentration of 2.63 x 1016 cm-3 and Hall mobility of 105 cm2/V.s. The improvement of electron mobility of ZnO films by MgO buffer annealing is due to a decrease in dislocation density. We conclude that annealing of MgO buffer layer increases the optical and electrical quality of the ZnO films. These results agree with the structural quality as observed by HRXRD.

1. Introduction

ZnO is a direct band gap semiconductor (Eg=3.37 eV at RT) with a wurtzite structure. A unique property of ZnO is its large exciton binding energy, 60 meV, which is about three times larger than that of ZnSe or GaN. Reports on the lasing mechanisms of ZnO have shown that ZnO is a promising photonic material for exciton devices in the wavelengths ranging from blue to ultraviolet [1][2][3].
High-quality ZnO is a prerequisite for ZnO-based optical device applications. Up to now, challenges of moving toward device applications are the difficulty in achieving high crystal quality of ZnO, as well as the difficulty in controlling p-type conductivity. On the other hand, controlling the crystalline defects in naturally n-type ZnO is the critical issue to obtain p-type ZnO.

Low price high-quality c-sapphire has been extensively used as a substrate for ZnO epitaxy or deposition in many growth techniques. Among growth techniques, P-MBE has shown high controllability to grow high-quality ZnO layers [4][5]. Because of the large lattice misfit between ZnO and c-sapphire (18%) and the formation of 30° rotated domains, ZnO layers grown on c-sapphire showed rough surface morphology and poor crystalline quality [5][6].

The use of a buffer layer is the most widespread technique used in heteroepitaxy. To overcome the problems caused by the large mismatch between ZnO and a c-sapphire substrate, the growth of double buffer layers consisting of low-temperature MgO and ZnO buffer followed by high-temperature annealing has been utilized with success by P-MBE [7][8]. Consequently, the growth of high temperature (HT) ZnO is dominated by layer-by-layer growth, the formation of 30°-rotated domains is completely suppressed, and the dislocation density is reduced. However, the dislocation density still remains high, in particularly edge dislocation (higher than 5×10^9 cm^-2) [9]. Therefore, further reducing of the ZnO dislocation density is crucial for device applications. Buffer growth parameters such as thickness, growth temperature, and its annealing, and growth rate should be precisely controlled. So far, most studies on the quality of ZnO films have been addressed on the structural quality of the ZnO film. But only a few studies focussed on the optical and electrical quality of the ZnO films.

2. Experiment

In this experiment, we prepared ZnO sample grown on c-sapphire with annealed and un-annealed low-temperature MgO/ZnO buffer layer before ZnO growth. The c-sapphire substrate was degreased in acetone and methanol in an ultrasonic cleaner followed by rinsing in deionized water. The substrate was then chemically etched in an H2SO4 (96%): H3PO4 (85%) = 3:1 solution. Prior to growth, the substrate was thermally cleaned at 750 °C in the preparation chamber for 1 hour. The substrate was then treated in an oxygen plasma at 650 °C for 30 minutes in the growth chamber to produce an oxygen-terminated c-sapphire surface. The sample structure is ZnO/ZnO-buffer/MgO-buffer/c-sapphire. The buffer layers were grown under optimum growth temperature; at 490 °C for MgO buffer and 500 °C for ZnO buffer. ZnO buffer was annealed at 750 °C for 5 minutes. High-temperature ZnO layers were then grown at 700 °C. In the case of ZnO layers grown with MgO buffer annealing, the MgO buffer was annealed at 800 °C for 25 minutes. ZnO layers were then characterized by high-resolution x-ray diffraction (HRXRD), Photoluminescence (PL), and Hall measurements.

3. Result and Discussion

ZnO film has been successfully grown on c-sapphire with MgO/ZnO double buffer layer. AFM measurement revealed that that the ZnO films show a smooth surface morphology. Structural quality addressed by HRXRD measurement also shown that the ZnO films have a good crystalline quality. The surface roughness of the ZnO layers is 0.6 nm and 0.3 nm while step height (terraces size) average 0.2 nm (94 nm) and 0.3 nm (245 nm) for the ZnO films without and with MgO buffer annealing, respectively. Here we note that annealing of LT-MgO buffer at high temperature enhanced the surface migration of adatoms, leading to the formation of larger terraces on the surface and smoother surface morphology of ZnO layer. [10]

The crystalline quality of ZnO layers was addressed by HRXRD. FWHM values of (0002) (10-11) rocking curves (in arcsec) are 18 (1076) and 22 (843), respectively for ZnO layers grown on an LT-MgO buffer and on an annealed LT-MgO buffer. Nearly the same low FWHM values of (0002) scans for these two samples implies low screw dislocation density in both [10]. A much broader (10-11) reflection than (0002) reflection implies the present of a high density of edge-type dislocations. Note that all types of dislocations (edge, screw, and mixed) broaden the (10-11) reflection, whereas the (0002) reflection is only sensitive to screw and mixed type dislocations[11][12]. Furthermore, the
FWHM values of the (10-11) scan of the ZnO layer grown on annealed MgO buffer is smaller than that grown on an LT-MgO buffer, indicating much lower edge dislocation density.

3.1. Optical Quality
For further insight into the quality of the ZnO layers, we investigated the optical properties by PL measurement. Figure 1 shows low-temperature PL spectra of the samples with and without MgO-buffer annealing in the near band edge emission region measured at 10K (a) and at 77K (b). The spectra were normalized by the free exciton-A emission intensity for clarity. The emission line located at 3.368eV dominates the spectrum in both samples at 10K. This emission can be divided into two peaks, 3.367eV and 3.363eV and assigned as I2 (ionized donor bound excitons emission) and I4 (Hydrogen donor related emission), respectively [13]. Note that these lines are clearly resolved into two lines at 77K in the sample with annealing as shown in Figure 1 (b). The intensity of I2 is greater than that of I4 in both samples. In the donor bound excitons region [9], another relatively weak emission which is assigned as I8 or I9 (Gallium or Indium donor related emission) [13] was also observed at around 3.358eV. It can be seen that the relative intensity of these donor bound excitons to free exciton 96 emission of the sample without MgO buffer annealing is greater than that of the sample with MgO buffer annealing. It might be related to different impurity incorporation or formation of native defects in the samples.

![Figure 1. Photoluminescence spectra at low temperature. (a)T=10K (b)T=77K. Solid line: ZnO with MgO-buffer annealing; dotted line: is ZnO without MgO-buffer annealing. The spectra are normalized with respect to FX(A) emission.](image)

At the lower energy region, a sharp emission located at 3.335eV and longitudinal optical (LO) phonon assisted bound exciton emission were observed in both samples. For the temperature dependence of PL spectra (data is not shown here), the intensity of the emission line at 3.335eV reduces like donor bound excitons with increasing temperature. Accordingly, this line can be attributed to exciton nature. Kato et al. [14] reported the origin of this emission is neutral acceptor bound exciton (Ian) emission from PL spectra of epitomical layers on a-sapphire grown by MBE. On the other hand, Laves et al. [15] assigned the exciton emission line at 3.335eV to exciton bound to structural defects.
(DBX) emission from CL in experiments on as-grown and annealed bulk samples. In the present case, the intensity of the 3.335eV line in ZnO film with MgO buffer annealing is greater than that without annealing, that is, the intensity increases even though the dislocation density is lower. Considering this point, it is appropriate to assign this line to neutral acceptor bound excitons, in this case, though the origin of the acceptor is still unknown. At 77K, free exciton-A emission located at 3.374eV becomes dominant instead of donor bound excitons. The free exciton-B emission appears at 3.380eV with 6 meV energy spacing to the free exciton-A emission. LO-phonon replica of the free exciton emission clearly appeared at 3.312eV, 3.239eV, and 3.166eV. As each spectrum of excitonic emission lines can be resolved, the emission lines from the sample with MgO buffer annealing have narrower spectral width compared to those of ZnO without MgO buffer annealing. This indicates better crystal quality of ZnO film with MgO-buffer annealing [16].

![Figure 2](image.png)

**Figure 2.** Room temperature PL spectra of ZnO layer grown with and without MgO buffer annealing

Figure 2 shows room temperature PL spectra of ZnO films grown with and without MgO-buffer annealing. The free exciton emission at 3.31eV and a broad deep-level emission at around 1.75eV were observed in both the samples. Comparison of the PL spectra of ZnO with and without annealing revealed that the intensity of free exciton emission from the sample with MgO buffer annealing is twice of that from the sample without annealing. We also found that the intensity of deep-level broad emission is reduced by about 1/3 by MgO-buffer annealing. Generally, the deep level luminescence of ZnO originates from oxygen vacancies and some impurity related complexes in ZnO films [12]. Hence, the decrease of deep level emission intensity and the increase of free exciton emission intensity by annealing of MgO buffer corresponds to the reduction of defects of the ZnO film. This agrees with the structural characterization which shown a reduction of dislocation density of the ZnO films from 5.3x10⁹ cm⁻² to 1.9x10⁹ cm⁻² by MgO-buffer annealing [10]. The PL properties suggest that there are fewer nonradiative recombination centers in ZnO layers with MgO buffer annealing than those in ZnO layers grown without MgO buffer annealing.

In order to gain further insight into the correlation between the structural and optical properties, Figure 3 provides a plot of structural properties represented by XRD against optical properties represented by PL intensity for ZnO samples grown on c-sapphire with and without MgO buffer. Broadening of 1110 Ω scan can be correlated to the presence of an edge, screw, and mixed dislocations while PL intensity can be correlated to the 99 presence of non-radiative channels generated by the defects in the crystal. Figure 3 clearly shows that decreasing FWHM of 10-11 Ω scan is followed by increasing PL intensity. This feature directly implies a correlation between the structural and optical quality of the ZnO films.
3.2. Electrical Quality
Room temperature Hall measurements show that the samples have a background n-type carrier concentration. The ZnO samples with MgO buffer annealing has a carrier concentration of $1.17 \times 10^{17}$ cm$^{-3}$ and Hall mobility of 120 cm$^2$/V.s while the ZnO sample without MgO buffer annealing has a carrier concentration of $2.63 \times 10^{16}$ cm$^{-3}$ and Hall mobility of $10^5$ cm$^2$/V.s. The improvement of electron mobility of ZnO films by MgO buffer annealing is due to a decrease in dislocation density. Here, the edge dislocations introduce acceptor centers along the dislocation line, which capture electrons from the conduction band of an n-type semiconductor [17]. The dislocation line becomes negatively charged, and a space charge is formed around it which scatters electrons, thus reducing their mobility [18]. It should be noted here that the mobility of ZnO decreases as carrier concentration (n) decreases, in contrast to the behavior in most another semiconductor, in which mobility continues to rise as n falls. The same phenomenon was also observed in GaN grown on Al2O3 with the concentration below about $10^{17}$-$10^{18}$ cm$^{-3}$ [19][20]. This phenomena can be explained by considering charged dislocation scattering, in which below a certain n, dislocation scattering dominates, while above a value of n, ionized-impurity (or defect) scattering is more important [21].

4. Conclusion
We have investigated the effect of MgO buffer annealing on the optical and electrical quality of P-MBE grown ZnO films on c-sapphire with MgO buffer layer. Optical quality observed by low-temperature PL measurement in the near band edge emission region at 10K and 77K revealed that the emission line located at 3.368eV dominates the spectrum in ZnO samples with and without MgO buffer annealing at 10K and 77K. This emission can be divided into two peaks, 3.367eV and 3.363eV and assigned as $I_2$ (ionized donor bound excitons emission) and $I_1$ (Hydrogen donor related emission), respectively. Comparison of the PL spectra of ZnO samples revealed that the intensity of free exciton emission from the sample with MgO buffer annealing is twice higher than that from the sample without annealing. We also found that the intensity of deep-level broad emission is reduced by about 1/3 by MgO-buffer annealing, which corresponds to the reduction of defects of the ZnO film. The PL properties suggest that there are fewer nonradiative recombination centers in ZnO with MgO buffer annealing than those in ZnO grown without MgO buffer annealing. The electrical quality measured by room temperature Hall measurements found that the samples have a background n-type carrier concentration. The ZnO sample with MgO buffer annealing has a carrier concentration of $1.17 \times 10^{17}$ cm$^{-3}$ and Hall mobility of 120 cm$^2$/V.s while the ZnO sample without MgO buffer annealing has a carrier concentration of $2.63 \times 10^{16}$ cm$^{-3}$ and Hall mobility of $10^5$ cm$^2$/V.s. The improvement of electron mobility of ZnO films by MgO buffer annealing is due to a decrease in dislocation density. We conclude that annealing of MgO buffer layer increases the optical and electrical quality of the ZnO films. The results agree with the structural quality as observed by HRXRD.
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