Metal-organic vapor phase epitaxial growth of high-quality ZnO films on $Al_2O_3(00\cdot1)$

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High-quality ZnO thin films were grown epitaxially at 250–550 °C $Al_2O_3(00\cdot1)$ substrates using low-pressure metalorganic vapor phase epitaxy. The reactants for the growth were diethylzinc and oxygen. Growth temperature, one of the important experimental parameters for epitaxial layers, was optimized. The films grown at 500 °C exhibited good crystallinity and strong ultraviolet absorption and emission. Photoluminescence spectra of the films showed a dominant excitonic emission with a weak deep level emission. More importantly, a strong stimulated emission peak was observed even at room temperature.

I. INTRODUCTION

Much attention has been paid recently to ZnO for short-wavelength photonic device applications since it has a direct band gap energy of 3.3 eV at room temperature.[1] Due to its large exciton binding energy of 60 meV,[2] ZnO has demonstrated strong excitonic emission in the ultraviolet (UV) range even at room temperature.[3] The exciton binding energy is twice as large as that of GaN, the most popular material for blue lasers. In addition, the band gap energy of ZnO can be extended to 4 eV by adding Mg or Mn and narrowed to 2.8 eV by alloying with CdO.[4] Furthermore, ZnO can be grown at 500 °C, hundreds of degrees lower than gallium nitride, which enables the growth of ZnO on Si and glass substrates.[5]

For ZnO film growth, numerous deposition techniques including sputtering, pulsed laser deposition (PLD), molecular beam epitaxy (MBE), and metalorganic vapor phase epitaxy (MOVPE) have been employed.[6–8] Among these techniques, MBE has yielded high quality ZnO epilayers which have shown good crystallinity and strong room-temperature excitonic emission.[3,7] Meanwhile, stimulated emission from MOVPE-grown ZnO has not yet been reported, which may result from the difficulty in growing high-quality ZnO films by MOVPE. This contrasts with the successful MOVPE growth of high-quality GaN and its alloys.[9] In the MOVPE of ZnO films, the films have been generally grown by chemical reaction between dimethylzinc (DMZn) or diethylzinc (DEZn) and O_2 or H_2O.[10] However, the Zn precursors are highly reactive with oxygen and water vapor so that pre-reaction in the gas phase occurs easily, resulting in the formation of white powders and degradation of film quality.[11] In this research, the pre-reaction was significantly reduced since the films were grown at low pressure in a cold-wall reactor with two separate inlets for the reactant. Using this MOVPE growth technique, high-quality ZnO films were grown on $Al_2O_3(00\cdot1)$ substrates as determined by x-ray diffraction and optical characterization.

II. EXPERIMENTAL PROCEDURE

The ZnO layers were grown on $Al_2O_3(00\cdot1)$ substrates using a horizontal-type MOVPE system. For the film growth, DEZn and oxygen were employed as the reactants, and argon as the carrier gas. The flow rates of oxygen and DEZn used were in the range of 20–50 sccm and 1–5 sccm at a bubbler temperature of 10 °C, respectively. The growth temperature investigated in this research ranged from 250 to 550 °C. To prevent premature reaction of the reactants, the O_2 gas line was separated from the main gas manifold line, and the pressure in the reactor during growth was kept at 5 torr.

Film thicknesses were measured using both surface profilometry and cross-sectional scanning electron microscopy. For surface profilometry measurements, ZnO layers were deposited with a thin substrate fragment placed on the substrate corner. The typical thickness of the films grown for 1 h was 1–1.5 μm.

As-grown ZnO films were highly transparent and specular. For optical characterization of the films, UV transmission and photoluminescence (PL) techniques were employed. The transmission of the films was measured with a two-beam spectrometer. Prior to the

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measurements, a background correction was performed over the optical scan range of 300 to 1200 nm. The transmission spectra of the films were obtained by subtracting substrate spectra from the film/substrate spectra.

PL measurements were performed using a pulsed nitrogen laser (337 nm) or a continuous wave (cw). He–Cd laser (325 nm) as the excitation source. Film luminescence was measured with a detection system equipped with a photomultiplier and a photon counter. For the spectroscopic measurements, both the detection system and a grating monochromator were computer controlled. A typical scan range was 2.0–3.5 eV with an instrumental resolution of 0.1 nm. For low-temperature measurements, the samples were cooled with a He Displex system.

III. RESULTS AND DISCUSSION

The crystal structure and film orientation of the as-grown films were investigated using Θ–2Θ scans of x-ray diffractometry (XRD). Typically, ZnO films grown at 250–550 °C were epitaxially grown on $Al_2O_3(00\cdot1)$. As shown in Fig. 1, the XRD data of ZnO films exhibited a 2Θ peak at 34.47°, which corresponds to the (00·2) peak of ZnO. Figure 1 also indicates that the crystallization temperature of ZnO films was as low as 250 °C.

X-ray rocking curve measurements were carried out to determine the degree of film alignment perpendicular to the substrate. Figure 2(a) shows a typical XRD rocking curve of as-deposited ZnO films grown at 500 °C. The rocking curve was measured at the (00·2) reflection of the ZnO films. As shown in Figure 2(a), an XRD rocking curve of ZnO grown at 500 °C exhibits a full width at half-maximum (FWHM) of 0.19°, which indicates high crystallinity of the ZnO film. The FWHM value is narrower than the previous value of 0.25° of MOVPE-grown ZnO on an *r*-plane sapphire substrate.[11]

The degree of in-plane alignment in the films was further examined using XRD pole figure analysis. A ZnO crystal with a *c*-axis orientation possesses 6-fold symmetry. Thus, six poles should appear in the pole figure if it has a homogeneous in-plane alignment. As presented in Fig. 2(b), the six poles, separated one from another by 60°, are evident in the pole figure of the ZnO film. The 60° rotational symmetry clearly indicates that the ZnO film was grown epitaxially with homogeneous in-plane alignment.

Growth temperature is one of the most important parameters in the growth of high-quality epitaxial films. The effect of growth temperature on the crystallinity of ZnO films was investigated using XRD rocking curve measurements. As shown in Fig. 3, growth temperature up to 500 °C resulted in decreasing the rocking curve

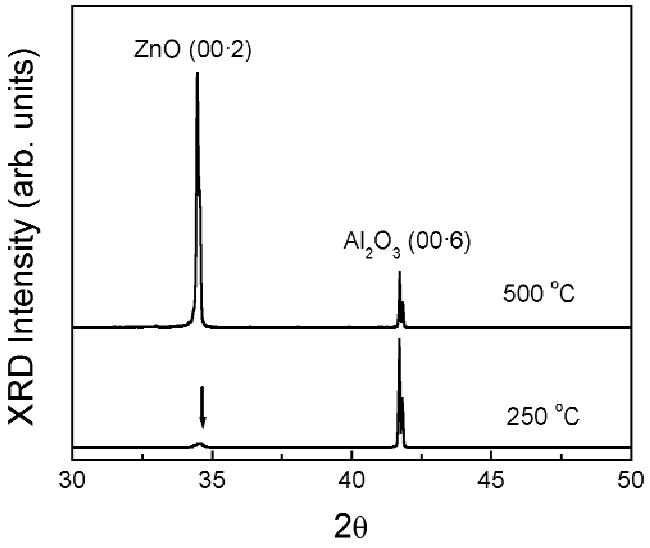

FIG. 1. 1. XRD Θ–2Θ scan results of ZnO films grown at 250 and 500 °C. The XRD data exhibits a 2Θ peak at 34.47°, which corresponds to the (00·2) peak of ZnO.

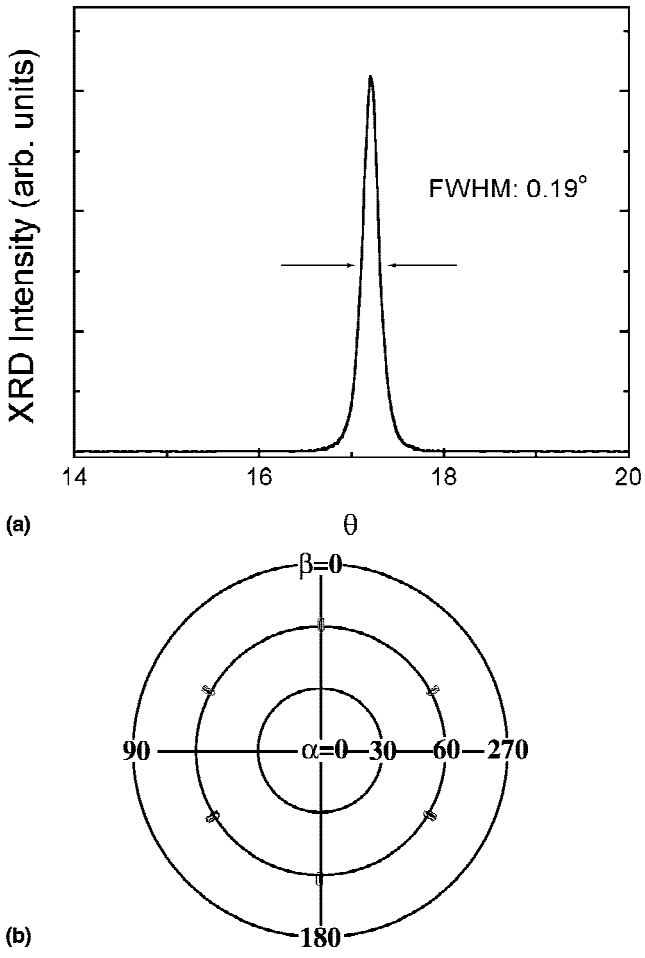

FIG. 2. (a) Typical x-ray rocking curve and (b) pole figure of a ZnO film grown on $Al_2O_3(0001)$ at 500 °C using MOVPE. The ZnO film shows a narrow FWHM and 6-fold symmetry.

FWHM values. This indicates that films grown at higher growth temperatures up to 500 °C show better alignment along the *c* axis.

UV transmission measurements were carried out for optical characterization of the films. The optical absorbance was obtained from the optical transmittance of the ZnO films grown on double-side polished Al_2O_3 (00·1) substrates. Figure 4 shows the spectral dependence of the absorbance, which indicates low optical absorption in the visible region. The absorbance in the UV region increased abruptly near 3.2–3.3 eV, resulting from a band-to-band transition. In this transition, UV absorption occurs due to the excitation of electrons from the filled valence band to the conduction band.

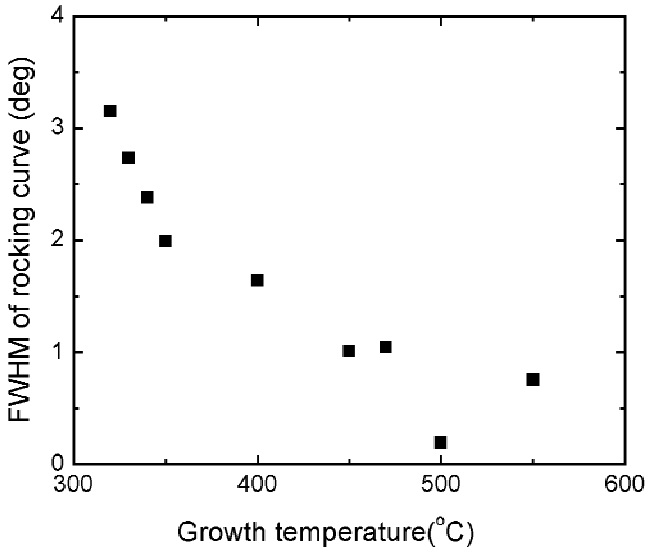

FIG. 3. XRD rocking curve results of ZnO films grown at different temperatures. The FWHM of the rocking curves decreases with increasing the growth temperature up to 500 °C.

Based on the UV absorbance measurements, the band gap energy of the films was calculated from the spectral dependence of the absorbance. By plotting $\alpha^2 E^2$ versus. E (α: absorbance, E: incident photon energy) and extrapolating the linear position of the curves to plotting $\alpha^2 E^2 = 0$, the band gap of the films is 3.24 eV, similar to the value of 3.2 eV previously reported by Kumar *et al.*[12]

Figure 5 shows a typical low temperature PL spectrum measured at 15 K. The 325 nm line of a He–Cd laser was used to illuminate the ZnO films grown at 500 °C. As shown in Fig. 5, the dominant emission peak of the ZnO film was observed at 3.364 eV, which is tentatively attributed to the exciton transition (I_2) bound to neutral donors. Narrow emission due to the excitons was usually observed in the low-temperature PL spectra of ZnO bulk crystals and MBE-grown films.[13,14] The exciton peak of the MOVPE-grown film showed a FWHM value of 7 meV, comparable to 6 meV (11 K) from ZnO grown on *r*-Al_2O_3, 1.5 meV (2 K) from bulk ZnO, and 8.9 meV (4.2K) from ZnO grown on GaN/SiC.[11,13,14]

In addition to the dominant exciton peak, a deep level emission band centered at 2.0 eV was also observed as indicated by an arrow in Fig. 5. The origin of the deep level emission is not yet clearly identified but it is presumably associated with structural defects or impurities. As shown in Fig. 5, the present MOVPE-grown film exhibited extremely weak deep level emission. The

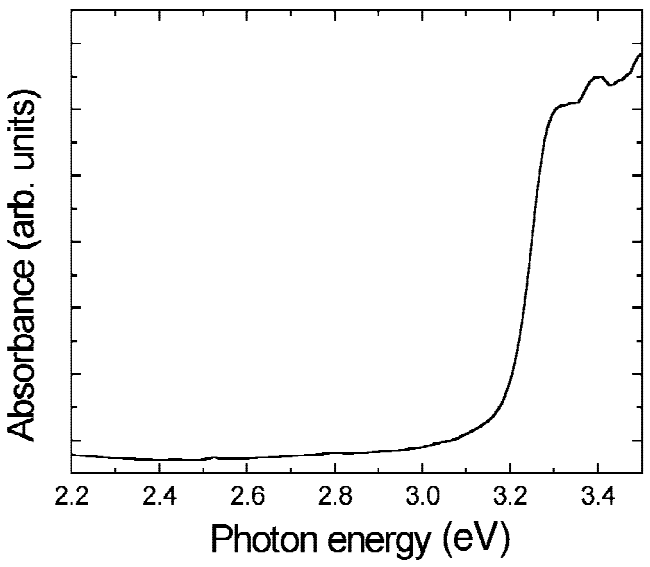

FIG. 4. Room-temperature absorbance spectrum of ZnO. The absorbance spectrum shows a low absorbance in the visible region and strong UV absorption at 3.2–3.3 eV.

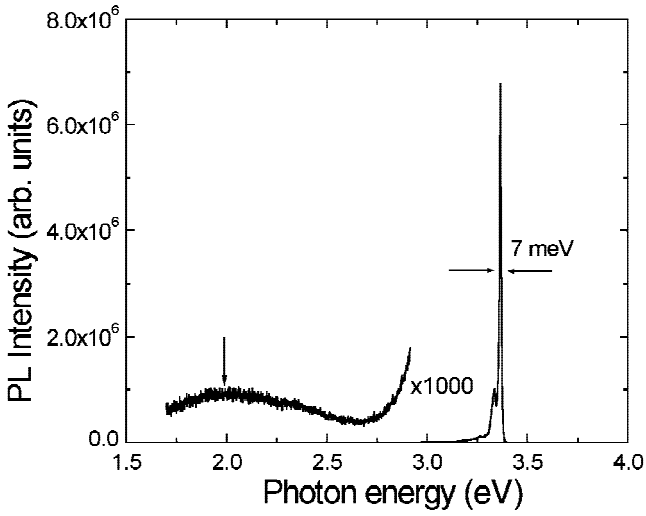

FIG. 5. PL spectrum of ZnO at 15 K. The PL spectrum was measured at 15 K using the 325 nm line of a He–Cd laser. A dominant emission peak was observed at 3.364 eV with a very weak deep level emission at 2.0 eV as indicated by an arrow. The near-band-edge emission is tentatively attributed to a neutral donor-bound exciton peak.

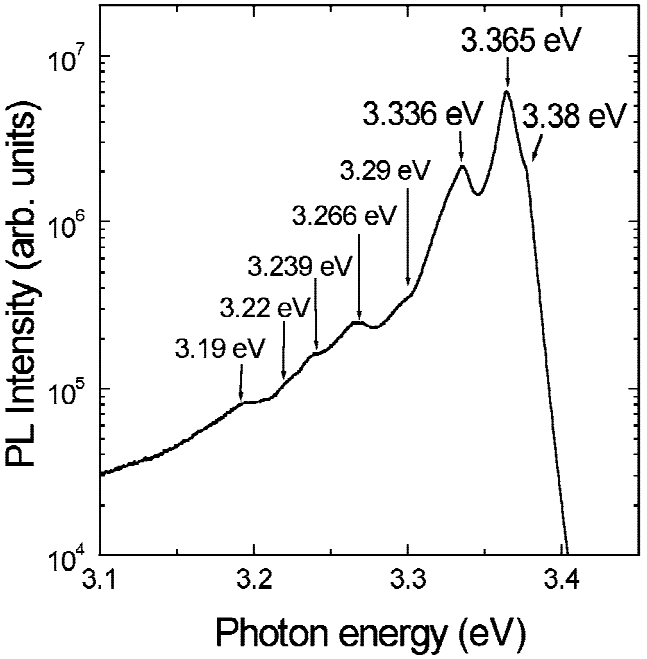

FIG. 6. High-resolution PL spectrum at 15 K. The PL spectrum shows five apparent peaks at 3.365, 3.336, 3.266, 3.239, and 3.192 eV and three shoulders at 3.38, 3.29, and 3.22 eV.

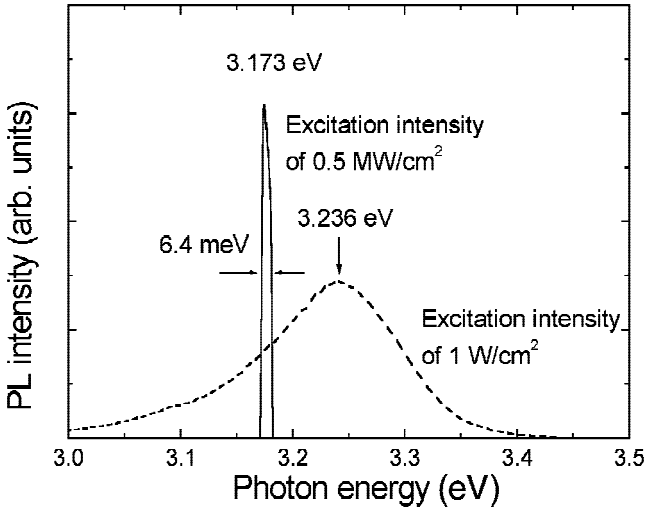

FIG. 7. Room-temperature PL spectra of ZnO grown at 500 °C. The PL spectra were measured using different excitation intensities of 1 W/cm^2 and 0.5 MW/cm^2. A broad peak was observed at 3.236 eV for the low excitation intensity. For the high excitation intensity of 0.5 MW/cm^2, however, a strong and narrow emission was observed at 3.173 eV.

intensity ratio of band-edge emission to deep level emission is about 6700, while ZnO grown by MBE has a ratio of around 100–500.[15] The sharp excitonic emission and weak deep level emission indicate that the MOVPE-grown film is of high quality.

High-resolution PL spectra were measured to determine the origin of the near-band-edge (NBE) emission. As shown in Figure 6, it is evident that the NBE emission at 15 K is composed of five apparent peaks at 3.365, 3.336, 3.266, 3.239, and 3.192 eV and three shoulders at 3.38, 3.29, and 3.22 eV. The dominant peak at 3.365 eV is tentatively ascribed to the exciton transition (I_2) bound to neutral donors since a similar peak has been observed at 3.365, 3.363, 3.36, and 3.360 eV for bulk single crystals and MOCVD, PLD, MBE-grown films, respectively.[6,11,13,15] Another peak at 3.336 eV is tentatively attributed to the exciton transition bound to neutral acceptors or deep donors. Compared with the previous report, the weak shoulder at 3.38 eV is presumably due to a transition from free excitons.[6,15]

Meanwhile several weak peaks and shoulders are also observed at 3.1–3.3 eV. In particular, they have a regular interval of 72 ± 2 meV, which almost coincides with the theoretical value calculated by Klingshirn.[16] Hence, the shoulders at 3.29 and 3.22 eV might be longitudinal optical phonon replicas of the bound exciton peak at 3.365 eV, and the peaks at 3.266 and 3.192 eV are tentatively attributed to longitudinal optical phonon replicas of the bound exciton peak at 3.336 eV. The shoulder at 3.29 eV is due to the free exciton peak at 3.38 eV.

Figure 7 shows typical room-temperature PL spectra of MOVPE-grown ZnO, which were measured using different excitation sources of a cw He–Cd laser (a 325-nm line with an excitation intensity of 1 W/cm^2) and a pulsed nitrogen laser (a 337 nm line with an excitation intensity of 0.5 MW/cm^2). As shown in Fig. 7, a broad peak was observed at 3.236 eV when the 325-nm line with a low excitation intensity of 1 W/cm^2 illuminated the films. For the high excitation intensity of 0.5 MW/cm^2, however, a strong and narrow emission was observed at 3.173 eV. The FWHM of the emission is 6–7 meV. Since a similar peak was observed at 3.175–3.181 eV from MBE-grown films, the peak is tentatively attributed to the exciton-exciton scattering process.[3] To our knowledge, this is the first observation of stimulated emission from MOVPE-grown ZnO. The strong excitonic emission from the MOVPE-grown ZnO film strongly suggests that MOVPE can be used to grown high-quality epitaxial ZnO films for highly efficient light emitters.

IV. CONCLUSIONS

In conclusion, high-quality ZnO thin films were grown on Al_2O_3(00·1) substrates using low-pressure MOVPE. Films grown at the optimized growth temperature of 500 °C showed strong UV absorption at 3.22–3.24 eV and a dominant excitonic emission at room temperature. From the PL spectra measured at 15 K, a dominant PL emission peak was observed at 3.364 eV with a FWHM of 7 meV. More importantly, room-temperature PL

spectra measured with an excitation intensity of 0.5 MW/cm^2 exhibited a strong stimulated emission peak at 3.173 eV with a FWHM of 6 meV.

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