Deposition of ZnO thin films on (100) γ-$LiAlO_2$ substrate

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Optical properties for ZnO thin films grown on (100) γ-$LiAlO_2$ (LAO) substrate by pulsed laser deposition method were investigated. The *c*-axis oriented ZnO films were grown on (100) γ-$LiAlO_2$ substrates at the substrate temperature of 550 °C. The transmittance of the films was over 85%. Peaks attributed to excitons were shown in absorption spectra, which indicated that thin films had high crystallinity. Photoluminescence spectra with the maximum peak at 540 nm were observed at room temperature, which seemed to be ascribed to oxygen vacancy in the ZnO films caused by diffusion of Li from the substrates into the films during the deposition.

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The resurgence in the study of ZnO continues. The now ready availability of good–quality single crystals and films[1,2] and discovery of lasing action in the materials[3] have generated new life in an old material. A direct semiconductor with a gap energy of 3.3 eV[4], ZnO is in the position of being able to offer a challenge to GaN in the blue laser market[5]. The advantages of ZnO are the high quality of the material and the large exciton binding energy (60 meV). The large exciton binding energy allows lasing action to occur even at room temperature (RT)[4,6]. γ-$LiAlO_2$ (LAO) crystal has numerous important applications in optical device owing to its crystal structure. The lattice mismatch between GaN, ZnO and γ-$LiAlO_2$ is only 1.4%, 3%, respectively. Recently, M-plane GaN free of electrostatic fields and GaN thick film ($\sim$ 40 μm) are successfully grown on (100) γ-$LiAlO_2$[7−9], this makes (100) γ-$LiAlO_2$ more attractive as a promising substrate for GaN, ZnO epitaxial growth.

In this study, we successfully prepared high crystallinity ZnO thin films on (100) LAO by pulsed laser deposition (PLD) technique which can preserve stoichiometry of compound materials from target to thin film, and then investigated the crystallinity of ZnO films by X-ray diffraction (XRD) and the optical properties such as transmittance, optical band gap and photoluminescence (PL) spectra.

Sintered ceramic target of ZnO (99.999%) was used for the PLD of ZnO thin film. (100) LAO was employed as the substrates. KrF excimer laser operating at 248-nm and 20-ns duration time was used as light source for the ablation of the target. The energy density of the focused laser beam irradiated on the target was about 5 J/cm^2 with a laser repetition rate of 5 Hz. The working pressure was maintained at 150 mTorr by a flowing oxygen stream. Prior to the deposition, the substrate (LAO) was cleaned in ultrasonator with acetone, ethanol and deionized water for 10 minutes in sequence. In order to attain the best ZnO films, the substrate temperatures were kept on at 400, 550 and 700 °C during the deposition, respectively. Each deposition process was of 1 h at 150 mTorr oxygen pressure in the chamber for the purpose of attaining about 200-nm thick films and reducing defects such as interstitial Zn and oxygen vacancy, then cooled down to RT. The crystal structures of ZnO films were investigated by XRD using Cu K_α radiation. The absorption spectra were measured by a UV/VIS spectrophotometer (Model V-570, JASCO) at RT. PL spectra were recorded using xenon arc lamp as the excitation source. The excitation wavelength was 365 nm and the spectral resolution was 0.5 nm. All spectra were measured at RT.

The film thickness determined from cross-section scanning electronic microscopy (SEM) is illustrated in Fig. 1. Zhao *et al.*[10] reported that the film thickness only depended on deposition time, the average deposition rate is about 3.5 nm/min. In this experiment, we also find that with the same deposition time (1 h), the films grown at different substrate temperature (400, 550 and 700 °C) have almost the same thickness (about 200 nm). So Fig. 1 shows one micrograph for the film thickness.

Figure 2 shows the X-ray θ-2θ scan patterns of ZnO films deposited on (100) LAO substrates at different

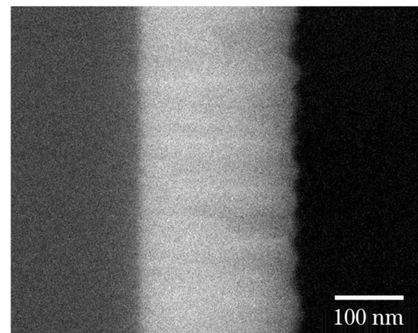


Fig. 1. Cross-section SEM morphology of ZnO films deposited on (100) LAO substrates at 400, 550 and 700 °C.

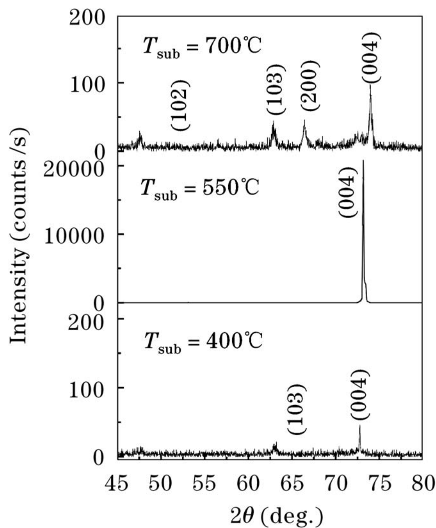


Fig. 2. XRD spectra obtained from ZnO films deposited at the substrate temperatures of 400, 550 and 700 °C at fixed oxygen pressure of 150 mTorr.

temperatures, respectively. In the XRD spectra, the (200) diffraction peak ($2\theta = 34.64°$) of LAO substrate is located very near the (002) peak ($2\theta = 34.44°$) of ZnO film, therefore (004) peak of ZnO film located at about 72.8° was examined. The XRD pattern of $T_{\rm sub} = 400$ °C clearly reveals the polycrystalline characteristic of ZnO film, this means that the ZnO film crystallizes at 400 °C, but without preferred orientation. As the substrate temperature increases to 550 °C, the (004) diffraction peak becomes very strong while other peaks almost vanish in the range of 45—80 degrees. However, when the $T_{\rm sub}$ rises to 700 °C, the intensity of (004) peak decreases dramatically while other peaks such as (102), (103) appear, and the film becomes polycrystalline without preferred orientation again. It is manifested that the substrate temperature ($T_{\rm sub}$) plays an important role for obtaining high-quality ZnO thin films. Low substrate temperature results in the low surface migration of adatom, so it is difficult to attain highly preferred orientation. On the other hand, the high substrate temperature probably destroys the arrangement of atoms and causes the Li diffusing into ZnO film, so the quality of film becomes bad. Our present work shows that highly c-axis oriented ZnO film can be grown by PLD on LAO substrate at the optimized growth temperature of about 550 °C.

The crystallinity of ZnO films was also investigated by measuring the transmittance, the absorption and the optical band gap. The transmittances of ZnO films grown at the substrate temperature of 400 °C were about 80% in the wavelength range of 400—800 nm. While the transmittance of ZnO films at 550 and 700 °C is over 85% in the same wavelength range. The substrate absorption had already been eliminated. The fall of transmittance was very sharp near absorption edge, which indicates high crystallinity. As a direct band gap semiconductor, ZnO film has an absorption coefficient (a) obeying the following relation for high photo energies ($h\gamma$)[11]

$$a^2 = A(h\gamma - E_{\rm g}),$$

where $E_{\rm g}$ is the optical band gap of thin film, and A is a constant. The a can be calculated from the following equation

$$T = \exp(-ad),$$

where T is the transmittance and d is film thickness. The variations of a^2 versus $h\gamma$ in the fundamental absorption region are plotted in Fig. 3(a), and $E_{\rm g}$ can be evaluated by extrapolation of the linear part to "$a = 0$". The optical band gap values of films grown at 400, 550 and 700 °C are determined to be about 3.25, 3.22 and 3.22 eV, respectively. For stoichiometric ZnO films, the optical band gap is known to be about 3.24 eV. Therefore, the obtained optical band gaps demonstrate the high crystallinity of the ZnO films on LAO grown at the temperature of 400, 550 and 700 °C. Besides, in absorption spectra at RT shown in Fig. 3(b), excitonic absorptions are clearly visible for ZnO films fabricated at 550 and 700 °C. Excitonic absorption spectra are observed in the films at 550 and 700 °C even though the absorption spectra do not split into two or more peaks. This is also sufficient to display that the crystallinity of ZnO films fabricated at 550 °C is so high that inhomogeneity-induced broadening effect obscuring the observation of excitonic peak at RT can be suppressed.

The PL spectra at RT, the important characteristic in ZnO film, were measured for ZnO films with high crystallinity. Figure 4 shows the PL spectra excited by 365 nm measured at RT for the ZnO films fabricated at 400—700 °C. PL spectra of ZnO on LAO at 550 and 700 °C with a peak at around 540 nm were observed. Moreover, as the substrate temperature increases, the peak intensity increases greatly. However, ZnO on LAO at 400 °C and ZnO on sapphire at any substrate temperature have no peak. It is manifested that the peak is associated with the substrate and the substrate temperature ($T_{\rm sub}$). It is well known that the emission peak at 540 nm is commonly attributed to radiation emission at interstitial Zn and oxygen-vacancy related defects[12]. Considering in terms of the deep level emission, Li must diffuse into the

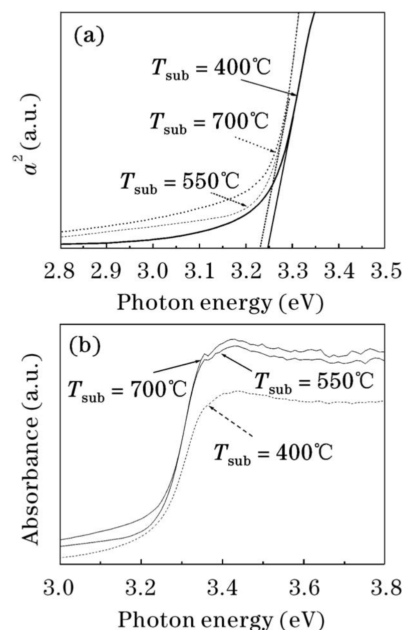


Fig. 3. Optical band gaps (a) and measured absorption spectra (b) for ZnO films deposited on the substrate (LAO) at RT.

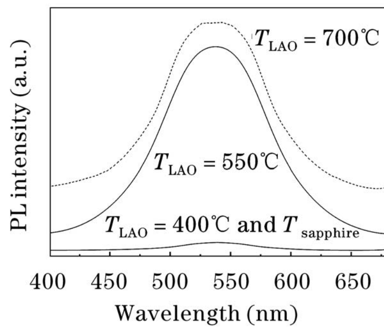
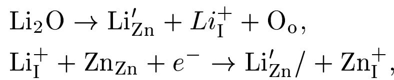


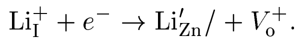
Fig. 4. PL spectra obtained at RT for ZnO films on the substrate(LAO).

ZnO films from the substrate in the course of the deposition. Moreover, the higher the temperature is, the more Li diffuses into ZnO film. Tabata *et al.* reported that when $LiNbO_3$ substrate was annealed in vacuum, the deposition of Li and O from substrate was observed from around 400 °C and the rate of deposition was increased rapidly from around 500 °C[12]. When LAO substrate was annealed over 700 °C in air or oxygen atmosphere, the lithium volatilized severely, and formed more lithium vacancies in LAO crystal[13]. According to the Refs. [14,15], Li doping into ZnO process was



$$\mathrm{Li_2O} \rightarrow \mathrm{Li}'_{\mathrm{Zn}} + Li_{\mathrm{I}}^{+} + \mathrm{O_o},$$
$$\mathrm{Li}_{\mathrm{I}}^{+} + \mathrm{Zn_{Zn}} + e^{-} \rightarrow \mathrm{Li}'_{\mathrm{Zn}}/ + \mathrm{Zn}_{\mathrm{I}}^{+},$$

or



$$\mathrm{Li}_{\mathrm{I}}^{+} + e^{-} \rightarrow \mathrm{Li}'_{\mathrm{Zn}}/ + V_{\mathrm{o}}^{+}.$$

When $\mathrm{Li}'_{\mathrm{Zn}}$ represents lithium on Zn lattice site, $\mathrm{Li}_{\mathrm{I}}^{+}$ represents lithium in interstitial position, $\mathrm{O_o}$ represents oxygen on lattice site, $\mathrm{Zn}_{\mathrm{I}}^{+}$ represents zinc in interstitial position, and V_{o}^{+} represents oxygen vacancy. Accordingly, as Li diffuses into ZnO film, the number of Zn in interstitial site or oxygen vacancy increases. This could enhance the intensity of deep level emission related to interstitial Zn and oxygen vacancy. Thus, it is supposed that the PL spectra observed for the ZnO films on LAO substrates are caused by oxygen deficiencies or interstitial Zn ions, resulted from the diffusion of lithium atoms from the substrate into ZnO films. So we can conclude that the great stress in ZnO film on LAO at high substrate temperature was caused by the lithium diffused into ZnO films. On the other hand, it had been recently reported that Li-doped ZnO film showed ferroelectric behavior. Ferroelectricity has to do with a nonlinear electro-optic effect[16−18]. Therefore Li-doped ZnO film, produced by virtue of the diffusion of Li from LAO substrates, enables to supply another method capable of developing new ZnO optical devices.

In summary, ZnO thin films prepared at 550 °C by PLD exhibited preferential *c*-axis orientation, perpendicular to the (100) LAO substrates. when the T_{sub} rises to 700 °C, the high substrate temperature destroys the arrangement of atom and causes the Li diffusing into ZnO film. Then the film becomes polycrystalline without preferred orientation. The crystallinity was very high enough to display the excitonic peak in absorption spectra at RT. PL spectra related to oxygen vacancy were measured at RT. The PL spectra are supposed to be owe to the penetration of Li atoms in substrate constituents into the ZnO films during the deposition.

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