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Epitaxial growth of ZnO films on (100) and (001) γ-$LiAlO_2$ substrates by pulsed laser deposition

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Abstract Structural and optical properties were investigated for ZnO films grown on (100) and (001) γ-$LiAlO_2$ (LAO) substrates by pulsed laser deposition method. According XRD results, it is intuitionistic that (100) LAO is suitable for fabricating high quality ZnO film, while (001) LAO is unsuitable. The FWHM of XRD, stress in film and FWHM of UV PL spectra for ZnO films on (100) LAO show a decreasing with increasing substrate temperature from 300 to 600 °C. ZnO film fabricated at 600 °C has the greatest grain size, the smallest stress (0.47 Gpa) and PL FWHM value (~85 meV). This means that the substrate temperature of 600 °C is optimum for ZnO film deposited on (100) LAO. Moreover, it was found that the UV PL spectra intensity of ZnO film is not only related to the grain size and stoichiometric, but also depends on the stress in the film.

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Introduction

One important advantage of ZnO is that it is a II–VI semiconductor of wurtzite structure with a wide direct-band-gap of 3.3 eV [1] at room temperature. Wide and direct band gap semiconductors are interest for blue and ultraviolet optical devices, such as light-emitting diodes and laser diodes [2–4]. The other notable advantage of ZnO is its high exciton binding energy (60 meV) at room temperature, which is much higher than that of ZnS (20 meV) and GaN (21 meV). This makes ZnO an ideal material to realize room temperature excitonic devices. Many techniques and various substrates have been used to deposit ZnO films. Among these techniques such as magnetron sputtering [5], chemical vapor deposition (CVD) [6], metalorgnic vapor phase epitaxy (MOVPE) [7], sol-gel [8], spray pyrolysis [9], and pulsed laser deposition (PLD) [10, 11], the PLD technique is more useful in obtaining high quality thin films of metal oxide materials. The plasma fabricated by the pulsed laser ablation is very energetic, and its mobility can be easily controlled through changing processing parameters. For these practical reasons, PLD technique has been wildly applied for fabricating high quality thin films. Among the various substrates such as sapphire, silicon, GaAs, $LiNbO_3$ (LN) or $LiTaO_3$ (LT) and glass [10, 12, 13], the lattice mismatch between ZnO and LN (or LT) is the smallest, but still over 9%. The large lattice mismatch between ZnO and these substrates result in high-dislocation densities and residual stress, which seriously affect the optical and electrical performance of the fabricated devices. It was found that γ-$LiAlO_2$ (LAO) is a promising substrate for ZnO film growth due to its small lattice mismatch (~3%), chemical and thermal stability, and potential ease of separation [14].

In this study, we first report the study on the difference between the ZnO films grown on (100) and (001) LAO substrates by pulsed laser deposition. XRD and PL spectra are used to evaluate the substrate temperature effects on the properties of ZnO thin films on (100) LAO substrate.

Experimental

Sintered ceramic target of ZnO (99.999%) was used for fabricating ZnO thin film by PLD. The (100) and (001) LAO wafers were 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 mm Torr by a flowing oxygen stream. Prior to the deposition, the substrates (LAO) were cleaned in ultrasonator with acetone for 10 min. In order to attain the best ZnO films, the substrate temperatures were kept on at 300, 400, 500, 600 and 700 °C during the deposition, respectively. Each deposition process lasts 1 h at 150 mm Torr oxygen in the chamber for the purpose of attaining about 200-nm thick films and reducing defects such as interstitial Zn and oxygen vacancy. After deposition, the films were investigated by X-ray diffraction (XRD) with a Cu target and a monochronmator at 40 kV and 300 mA. The optical properties of the ZnO thin films were characterized by photoluminescence with a He–Cd laser as a light source using an excitation wavelength of 325 nm (Hole: 100 μm, Time: 1 s). All spectra were measured at room temperature.

Results and discussion

Figure 1(a) is the XRD patterns of ZnO films on (100) LAO deposited at 300–700 °C. Only (002) and (004) peaks of ZnO can be seen in the patterns except the peaks belonging to the LAO substrate. The former locates around 34.4° and the latter around 72.6°. This means that ZnO films fabricated on (100) LAO at 300–700 °C show highly preferred *c*-axis orientation. On the other hand, the films deposited on the (001) LAO show quite different XRD patterns as shown in Fig. 1(b), although the corresponding films on (100) and (001) LAO are fabricated under the same conditions. The intensity of (002) diffraction peak of ZnO on (001) LAO decreases sharply as the substrate temperature increases, and finally the (002) peak almost vanishes in the background. It is intuitionistic that (001) LAO cannot act as the substrate for fabricating high quality ZnO film according to the above the XRD results. The main reason is the large lattice and thermal expansion mismatch with ZnO.

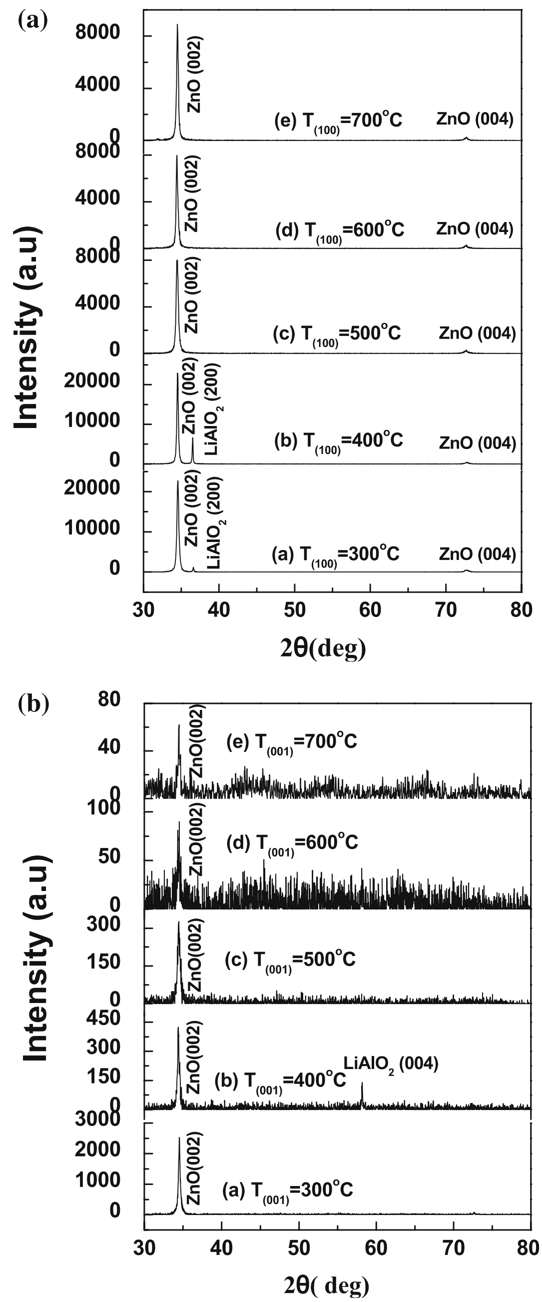

Fig. 1 (**a**) XRD spectra of ZnO films grown on (100) LAO at different substrate temperature in fixed oxygen pressure of 150 m Torr. (**b**) XRD spectra of ZnO films grown on (001) LAO at the same condition

The biaxial stress in ZnO films can be calculated by the following equation [15]

$$\sigma = -453.6 \times 10^{9}((C - C_{o})/C_{o}) \quad (1)$$

where σ is the biaxial stress in ZnO film, C_0 (0.5213 nm) is the lattice constant for bulk ZnO [16], and C is the measured one for the film. Figure 2 shows the FWHM of ZnO (002) and the stress in the films obtained at different substrate temperatures. The FWHM value decreases dramatically as the substrate temperature is up to 400 °C. Then it decreases slightly when the substrate temperature continues increasing from 400 to 600 °C. ZnO film fabricated at 600 °C has the lowest FWHM of about 0.241°. However, as the temperature is over 600 °C, the FWHM increases again. Small FWHM corresponds to the large average grain size. The FWHM curve in Fig. 2 suggests that the ZnO film can be grown to be large grain size in the temperature range of 400–600 °C. The interesting phenomenon observed here is that the average grain size of ZnO film becomes small when the substrate temperature exceeds 600 °C. According to Fig. 2, the biaxial stresses in ZnO films deposited on (100) LAO in the temperature range of 300–700 °C are tensile. The stress decreases monotonously with the substrate temperature increases from 300 to 600 °C. As the substrate temperature is up to 600 °C, the stress reaches the lowest value of 0.47 Gpa. When the substrate temperature continues increasing, the stress increases greatly. These results of the FWHM and the stress demonstrate that the film on the (100) LAO can grow to be large size under the two conditions, the first is the relatively high substrate temperature (600 °C), the second is relatively low film stress (0.47 Gpa). When substrate temperature exceeds 600 °C, the film stress increases sharply, and the coalescent film may crack due to large stress and subsequently the average grain size becomes small. The reason why the film stress increases with increasing substrate temperature may lie on the lithium diffusion from the substrate to the ZnO film, and on that such diffusion may change the lattice matching between substrate and the film.

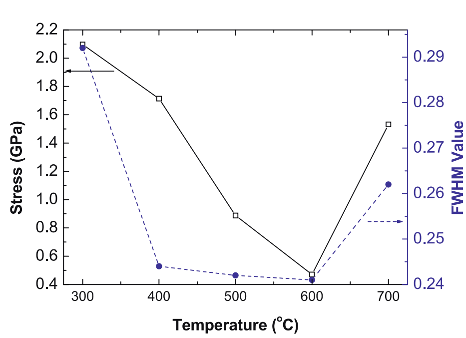

Fig. 2 Stress (□) and FWHM (●) of the films versus the substrate temperature

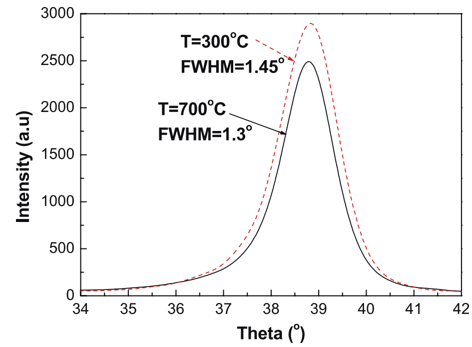

Fig. 3 X-ray rocking curve for ZnO films fabricated on (100) LAO at 300 °C and 700 °C, respectively

As shown in Fig. 3, the FWHMs of the (004) rocking curves of the ZnO films deposited at 300 and 700 °C substrates are almost the same. This implies that the change of the substrate temperature and the film stress seems not to affect obviously the degree of preferred orientation of the film. From the XRD spectrum analyses, the substrate temperature of 600 °C is optimum for ZnO film deposited on (100) LAO under 150 mm Torr oxygen pressure by PLD, which is also proved by PL spectra. Figure 4 shows the PL spectra of ZnO films fabricated at 300–700 °C. The shape of the spectra, unlike to those reported by others [17], is featured by a strong emission near UV but almost no defect-related deep level emission in visible region. It means that ZnO films fabricated on (100) LAO by PLD has high UV luminous efficiency and good optical properties, namely the ZnO films at 300–700 °C keep good stoichiometry.

Shionoya et al. [18] has reported that UV PL intensity is not only dependent upon the textured grain size but also upon the stoichiometry of ZnO. In the present work, though ZnO films fabricated at 400, 500 and 600 °C have similar grain size and stoichiometry, the UV PL intensity of ZnO film deposited on the 600 °C substrate is about twice as large as that of ZnO

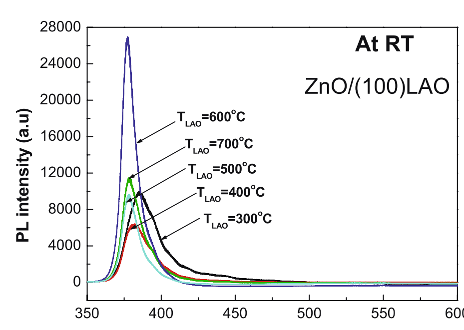

Fig. 4 Room temperature photoluminescence spectra of ZnO film deposited on (100) LAO at different temperature

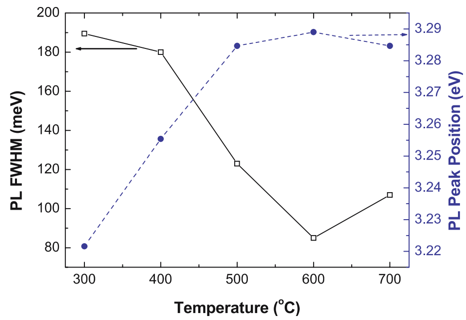

Fig. 5 PL intensity (□) and PL FWHM (●) versus substrate temperature

films deposited on 400 or 500 °C substrates. Therefore, one can argue that one more important factor, which affects the UV PL intensity, exists besides the textured grain size and stoichiometry.

Figure 5 shows the change of the PL FWHM and the PL peak position against the substrate temperatures. The UV emission peak position shifts slightly towards the shorter wavelength with increasing substrate temperature in the range of 300–600 °C. The UV PL FWHM decreases monotonously with the substrate temperature increases from 300 to 600 °C. ZnO film deposited on 600 °C substrate has the narrowest PL FWHM value of 85 meV, which is narrower than the value of 140 meV reported recently by Fan et al. [10] obtained on Si by PLD and that of 98 meV reported by Ye [19] obtained on sapphire by MOCVD. It is clear that the curve shape of PL FWHM in Fig. 5 is similar to that of the stress in Fig. 2, this suggests that the stress in film is closely related to the PL FWHM, namely, the more important factor affecting the UV PL intensity may be the stress in ZnO film.

Conclusions

We have fabricated ZnO films on (100) and (001) LAO at the substrate temperatures of 300–700 °C in the oxygen pressure of 150 m Torr by pulse laser deposition. Although the corresponding films on (100) and (001) LAO are fabricated under the same conditions, ZnO films fabricated on (100) LAO at 300–700 °C show highly preferred *c*-axis orientation, while the intensity of (002) diffraction of ZnO on (001) LAO decreases sharply as the substrate temperature increases, and finally the (002) peak almost vanishes in the background. The FWHM of XRD, stress in film and FWHM of UV PL spectra for ZnO films on (100) LAO show a decreasing with increasing substrate temperature from 300 to 600 °C. ZnO film fabricated at 600 °C has greatest grain size, smallest stress (0.47 Gpa) and PL FWHM value (~85 meV). This means that the substrate temperature of 600 °C is optimum for ZnO film deposited on (100) LAO. It was found that the UV PL spectra intensity of ZnO film is not only related to the grain size and stoichiometric, but mainly depends on the stress in the film. Moreover, the FWHM of UV PL spectra strictly decrease as the stress in ZnO films decreases.

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