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Substrate effects of ZnO thin films prepared by PLD technique

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Abstract

ZnO thin films are prepared on the glass, GaAs (100), Si(111), and Si(100) substrates at different temperatures by the pulsed laser deposition (PLD) method. X-ray diffraction (XRD) measurements indicate that the substrate temperatures of 200–500, 200–500, 300–500, and 300–500 °C are the optimized conditions of crystalline for the glass, GaAs (100), Si (111), and Si (100) substrates, respectively. In spite of the films deposited on the different substrates, the films always show (002) orientation at the optimized conditions. Photoluminescence (PL) results indicate that the thin films fabricated at the optimized conditions show the intense near band PL emissions. The optimized conditions for PL are 500, 500, 400–500, and 500 °C for glass, GaAs (100), Si (111), and Si (100) substrates, respectively.

Keywords: Films; Optical properties; Substrate effects; X-ray methods; ZnO

1. Introduction

Since the late eighties the pulsed laser deposition has been verified as a versatile technique for deposition of various materials including ferroelectrics, amorphous diamond and other ultra hard phases, polymers, compound semiconductors, and non-crystalline materials especially for metal oxide materials.[1] Among the several characteristics that distinguish PLD from other film growth techniques are its simplicity, the in-situ processing of the multi-layer heteo-structures by using the multiple targets, and stoichiometric deposition etc. II–VI semiconductors are attractive in acoustic, electronic, and optical applications such as surface acoustic wave (SAW), acousto-optic, piezo-optic and photoelectric devices in particular, and voltage photophosphorescent devices.[2] ZnO is a novel photonic material with the properties similar to those of GaN. It has the direct band gap of 3.3 eV at room temperature, the large exciton binding energy of 60 meV, and the high melting temperature of 2248 K. Since the wide applications of GaN, these properties similar to GaN make ZnO a potential candidate material for the optical devices such as light emitting diodes (LEDs) and laser diodes (LDs). So ZnO related materials have received considerable attentions in the recent years.[3–6] In order to develop ZnO thin films with high quality for devices with good performance, it is necessary to clarify the roles and the effects of additives, the different conditions of growth, and the substrate types. This will result in different microstructures suitable for the different applications.[7–9] Since ZnO thin films are highly c-axis oriented, the self-textured ZnO films can be synthesized easily on all substrates such as glass, GaAs, and Si etc. In this paper we report on the structural and optical properties of ZnO thin films fabricated on the glass, GaAs (100), Si(111), and Si(100) substrates at different temperatures by PLD technique. In this study, XRD and PL are used to evaluate the temperature and the substrate effects on the properties of ZnO thin films, since it is essential to evaluate the film quality for the device applications.

2. Experiment

In the chamber of the PLD system, there are four target holders on one carousel and one substrate holder. The substrate holder is usually located at the opposite position to one of the target holders. KrF excimer laser ($\lambda = 248$ nm, $\tau = 25$ ns) is used for the ablation of the ZnO target at the energy density of about 1 J/cm^2. The strong absorption of 248 nm laser radiation by the tar-

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get produces an intense plasma plume in front of the target surface. The ablated material is then deposited on the substrate kept at 50 mm away from the target.

The high purity ZnO powder (99.99%, Aldrich Chem. Co., Inc) is used in the experiment. The disk-shaped specimen of 10 mm in diameter and 2 mm in thickness is obtained by the uniaxial pressing at 100 MPa, followed by the cold iso-static press at 200 MPa. The disk-like ZnO is sintered at 600 °C for 2 h and at 1200 °C for 4 h in order to condensate the target. In this study, the experiment conditions are as follows; the repetition frequency of the laser is 5 Hz, the deposition time is 30 min, the ambient O_2 pressure is 200 mTorr, and the temperature of the substrate varies from room temperature to 600 °C.

The structures of ZnO thin films are studied by (XRD) measurements (D/MAX 2100H, Rigaku, Japan, 40 kV, 30 mA) using the Cu$K\alpha_1$ radiation with $\lambda = 1.54056$ Å. PL measurements are carried out by the excitation of the He–Cd laser with 325 nm with an output power of 30 mW at room temperature. All optical measurements are performed in air as the reference. The emitting light from the sample is focused into the entrance slit of a spectrometer that has a spectral grating of 1200 grooves/mm, and it is picked up by PMT. A cutoff filter is used to suppress the scattered laser radiation. The cutoff wavelength of the filter at the ultraviolet side is about 340 nm.

3. Results and discussion

Fig. 1 shows XRD patterns of ZnO thin films fabricated at different substrate temperatures (T_s) on glass (A), GaAs (100) (B), Si (111) (C), and Si (100) (D) substrates. It is found that the substrate temperature T_s plays an important role in determining the structure of ZnO thin films. To assess the quality of the thin films, the full width at half maximum (FWHM) is measured by omega scan and is shown in the insets of Fig. 1(A),(B),(C), and (D), respectively. It is found that FWHM values of (002) ZnO at 34.42° are around 0.2°, which means the high quality of the thin films fabricated by PLD.

Fig. 1(A) shows XRD patterns of ZnO thin films on the glass substrates. It is clear that the film deposited at T_s higher than 100 °C has a polycrystalline structure, with (002) preferred orientation. While the thin film fabricated at room temperature has an amorphous nature. As T_s is increased to 500 °C the preferred orientation of (002) shows a further increase in the peak intensity. It is found that FWHM increases at first, but

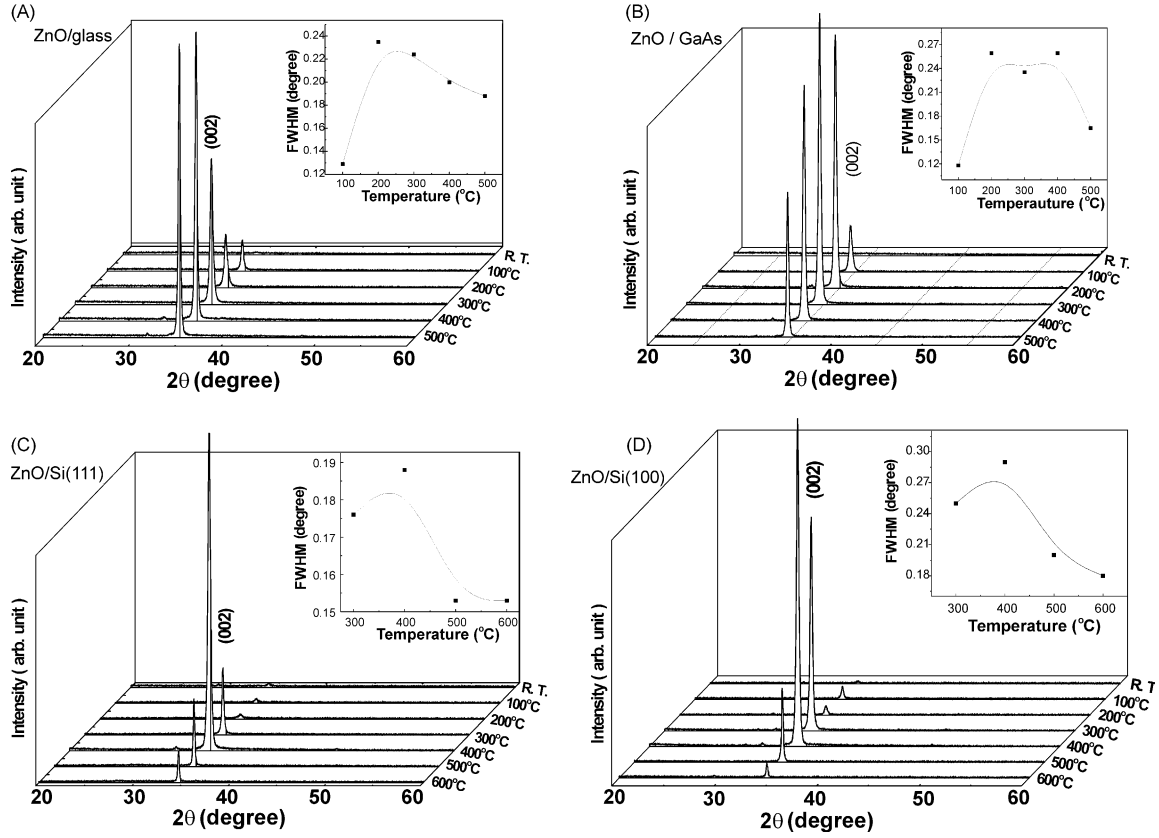

Fig. 1. XRD patterns of ZnO thin films grown at different temperatures on glass (A), GaAs (100) (B), Si (111) (C), and Si (100) (D) substrates.

it decreases with T_s in the following, as shown in the inset of Fig. 1(A). FWHM reaches its maximum when the thin film is fabricated at 200 °C. While FWHM is correlated with the grain size D by Scherrer formula,[10]

$$D = \frac{0.9\lambda}{\beta\cos\theta_0} \quad (1)$$

λ is the radiation wavelength, θ is the Bragg angle of (002) peak, and β is FWHM value. From XRD results on the glass substrates, we conclude that T_s of 200–500 °C is good for crystalline.

Fig. 1(B) shows XRD patterns of ZnO thin films on GaAs (100) substrates. The thin film fabricated at room temperature shows the amorphous structure that is the same as the one on the glass substrate. The (002) orientation appears at the fabrication temperature of 100 °C. The (002) orientation is enhanced when T_s is increased from 100 to 300 °C. When T_s surpasses 300 °C, the film becomes clearly less oriented, with a resulting decrease in the (002) peak intensity. The variation of FWHM with T_s is shown in the inset of Fig. 1(B). The same behavior as the thin films on the glass substrates is found. One difference is that FWHMs of the thin films fabricated at 200, 300, and 400 °C are nearly the same. It is found that the fabrication temperature of 200–500 °C is a good condition for crystal structures.

Fig. 1(C) and (D) show XRD patterns of ZnO thin films on Si (111) and Si (100) substrates, respectively. The (002) orientation in the thin films that are fabricated at high temperature and at low temperature almost disappears. The variations of FWHM on T_s are shown in the insets of Fig. 1(C) and (D). The same behavior as that on glass and on GaAs substrates is found in the thin films deposited on Si (111) and Si (100) substrates. In the case of Si (111) substrate, the thin film fabricated at the temperature of about 400 °C shows the strongest diffraction peak, and simultaneously the largest FWHM is observed in this thin film. It means the thin film fabricated at 400 °C has the smallest grain size. In the case of Si (100) substrates, the thin films fabricated at 300–500 °C show the intense diffraction peaks. The thin film fabricated at 400 °C also exhibits the largest FWHM.

XRD results indicate that the c-axes of the grains become uniformly perpendicular to the substrate surface at the optimized temperatures. It is suggested that the surface energy of (002) plane is the lowest in the ZnO crystal.[11] Grains with the lower surface energy will become larger as the film grows. Then the growth orientation develops into one crystallographic direction of the lowest surface energy. This means that the (002) texture of the film may be easily formed. T_s is crucial in that the low substrate temperature results in the low surface migration of adatoms, while the high substrate temperature causes the adatoms to re-evaporate from the film surface. The ZnO wurtzite structure makes the film grow in (002) preferred orientation on all substrates at the optimized growth temperature.

Fig. 2(A),(B),(C), and (D) shows the PL spectra of ZnO thin films on different substrates. Note that PL results of the thin films fabricated at room temperature,

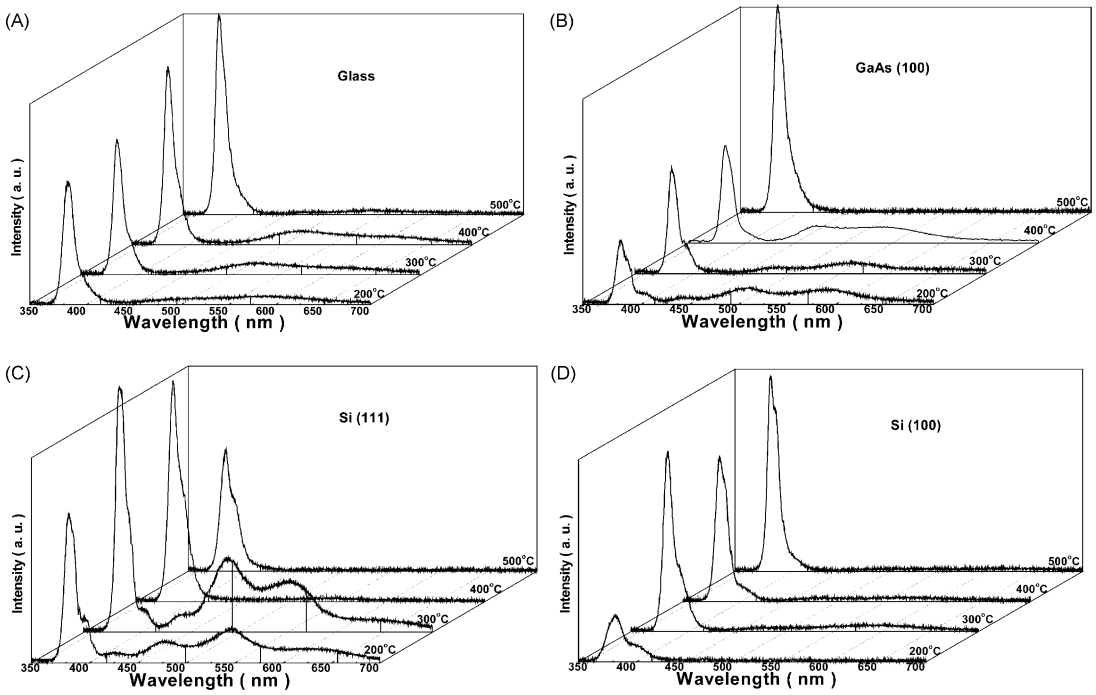

Fig. 2. PL spectra of ZnO thin films fabricated at different temperatures on different substrates.

100, and 600 °C are not shown here. Fig. 2(A) shows PL of ZnO thin films on the glass substrates. Near band emissions are found in all thin films, however, the intensity increases with T_s. We have to mention here that the slit size of spectrometer for measuring the thin film fabricated at 500 °C is only 1/5, 1/6, and 1/6 compared with that for the thin film fabricated at 400, 300, and 200 °C, respectively. There are small broad green-yellow emissions in the thin films fabricated at 200, 300, and 400 °C. However, only a little green emission is observed in the thin film fabricated at 500 °C, which indicates its good quality.

Fig. 2(B) shows PL results from GaAs (100) substrates. The thin film fabricated at 500 °C shows the most intense near band emission without green one. The thin films fabricated at 400, 300, and 200 °C show small broad green and yellow emissions. The slit size of the spectrometer for the thin film fabricated at 500 °C is only 1/20, 1/20, and 1/40 compared with those of the thin films fabricated at 400, 300, and 200 °C, respectively. This result indicates that 500 °C is good for PL.

PL results of the thin films deposited on Si (111) substrates are plotted in Fig. 2(C). All ZnO thin films on Si (111) show the intense near band emissions. However, only the thin films fabricated at 200 and 300 °C show broad green emissions. The thin films fabricated at 400 and 500 °C do not show green emissions, which means the good quality of the thin films. This indicates that the substrate temperature between 400 and 500 °C is the best condition for PL.

From PL results of ZnO thin films on Si (100) substrate as shown in Fig. 2(D), the strong near band with a little green emission are found in the thin films fabricated at 200, 300, and 400 °C, however, the green emission of the thin film fabricated at 500 °C is invisible. As shown in Fig. 2(D), the peak intensities of the thin films fabricated at 300, 400, and 500 °C are nearly the same. This indicates that the thin film fabricated at 500 °C is of good quality.

4. Conclusions

ZnO thin films are prepared on the glass, GaAs(100), Si(111), and Si(100) substrates at different temperatures by PLD method. XRD and PL are used to characterize ZnO thin films. XRD results indicate that the substrate temperatures of 200–500, 200–500, 300–500, and 300–500 °C are the good conditions for crystalline for the glass, GaAs (100), Si (111), and Si (100) substrates, respectively. In spite of the films on the different substrates, the films always show (002) orientation at the optimized conditions. The thin films fabricated at the optimized condition show the intense near band PL emission. As results, the optimized conditions are 500, 500, 400–500, and 500 °C for the glass, GaAs (100), Si (111), and Si (100) substrates, respectively.

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