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Aging and Annealing Effects of ZnO Thin Films on GaAs Substrates Deposited by Pulsed Laser Deposition

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Abstract. Zinc oxide (ZnO) thin films were deposited on GaAs (100) substrates at different temperatures in the pulsed laser deposition (PLD) system. From the measurements of X-ray diffraction (XRD) at room temperature, 300–500°C were found to be good condition for the crystallization of the thin films. From the photoluminescence (PL) measurements, 500°C was found to be the optimized temperature for its optical property. Samples grown at 100, 200, 300, and 400°C showed near band-edge (NBE) emissions and deep-level emissions. The intensity of deep-level emissions decreased as time goes on, which is believed to originate from oxygen vacancies or zinc interstitials in thin films. While for the sample grown at 500°C, bright NBE emissions were observed at room temperature, and no deep-level emissions observed. This means that the high-optical-quality thin film was grown at 500°C. At the same time, annealing process of ZnO thin films grown at room temperature was carried out in PLD chamber. It was found that the annealing temperature of 600°C has strong effects on its PL. Aging and annealing effects in ZnO thin films grown on GaAs substrates by PLD were observed for the first time.

Keywords: ZnO thin films, pulsed laser deposition, aging effect, annealing effect

1. Introduction

As a wide band gap semiconductor, Zinc oxide (ZnO) is one of the most interesting II–VI compounds with a wide direct band gap of 3.3 eV at room temperature [1]. The optical properties of ZnO were studied as early as 1960s [2, 3], but the extensive studies of ZnO thin films have been carried out in the past years. It has been used for applications, such as transparent conductive films, solar cell windows, bulk acoustic wave devices, piezoelectric transducers, gas sensors, and ultravioloet light emitting/detecting technology [4–7]. The crystal structure of ZnO is the same as that of GaN, and the optical properties are similar to each other [8]. While GaN is known to be a good material for the fabrication of optical devices, such as light emitting diodes (LEDs) or laser diodes (LDs). The similarity of the properties between ZnO and GaN makes ZnO one of the most promising materials for photonic devices in the ultraviolet range. The exciton binding energy of ZnO (60 meV) is larger than that of GaN (25 meV) at room temperature. This is another advantage ZnO has over GaN for the exciton-related device applications. As a wide band gap semiconductor, ZnO is a relatively hard material. The strength of the Zn-to-O bond is larger than that of Ga-to-N bond. The hardness of ZnO, its resistance to mechanical stress, and its high melting temperature are features that could conceivably expand the lifetime of devices. So ZnO related materials have received considerable attention [9–15].

Various techniques have been used to fabricate textured and epitaxial thin films, including sol-gel, sputtering, chemical vapor deposition, pulsed laser deposition (PLD), and molecule beam epitaxy methods. Among so many techniques, however, PLD method has been proved to be a very excellent one for growth of oxide materials. Because the plasma created by the pulsed laser is very energetic. The growth is easily

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controllable by changing the experimental parameters. Many researchers reported that ZnO thin films deposited on various substrates by different techniques showed bright NBE emission at about 379 nm, while some researchers reported the green-yellow emission at about 500 nm. Most of them explained that the green-yellow emission originated from oxygen vacancies, zinc interstitials or zinc vacancies, however, as far as we know, no group reported how the green-yellow emissions change as time goes on.

In this report, ZnO thin films on GaAs (100) substrates were fabricated by PLD at different temperatures. X-ray diffraction (XRD) and photoluminescence (PL) measurements were carried out to characterize thin films. Through PL measurements at different dates after the deposition, the aging effects were observed. To find the annealing effects of thin films deposited at room temperature, thin films deposited at room temperature were annealed at different temperatures in PLD chamber. Aging and annealing effects of ZnO thin films deposited on GaAs substrates are reported, and their mechanisms are discussed.

2. Experiment

In our PLD system, there are four target holders on one carrousel and one substrate holder inside the chamber. The substrate holder is located at the opposite position to one of the target holders. The dimensions of the target and the substrate holder are 25 and 50 mm in diameter, respectively. A KrF excimer laser (Lambda Physik, Germany, $\lambda = 248$ nm, $\tau = 25$ ns) was used for the ablation of ZnO target at an energy density of about 1 J/cm^2. The strong absorption of 248 nm laser radiation by the target produced an intense plasma plume in front of the target surface. The ablated material is then deposited on GaAs substrates kept at 50 mm away from the target.

The high-purity ZnO powder (99.99%, Aldrich Chemical Company, Inc, USA) was used in this experiment. Disk-shaped specimen of 10 mm in diameter and 2 mm in thickness was obtained by uniaxial pressing at 100 MPa, followed by the cold iso-static press at 200 MPa. The disk-like ZnO was sintered at 600°C for 2 hours and at 1200°C for 4 hours in order to densify the target. In our system, the experiment parameters were described in our previous papers [16–18]. Briefly, during the thin film fabrication the conditions were as follows; repetition rate of the laser was 5 Hz, deposition time was 30 minutes, the background O_2 pressure was 200 mTorr, and the substrate temperature was varied from room temperature to 500°C.

In order to find the annealing effects, ZnO thin films were deposited at room temperature and annealed at various temperatures (100, 200, 300, 400, 500, and 600°C, respectively) for 30 minutes in the PLD chamber. During the annealing, the oxygen pressure inside the chamber was kept constant of 10 Torr. The annealing process includes 3 steps. First, increased the substrate temperature from room temperature to the desired annealing temperature in 10 minutes; second, annealed the thin film at desired temperature for 30 minutes; third, after annealing the thin film was cooled naturally down to room temperature for measurements. An X-ray diffractometer (D/MAX 2100H, Rigaku, Japan) using CuK$_{\alpha 1}$ radiation ($\lambda = 1.5405$ Å) was used to study the crystalinity of ZnO thin films. The excitation source for PL measurements was a He-Cd laser operating at 325 nm with an output power of 30 mW. The scattered light from the sample was focused into the entrance slit of a monochromator and it was picked up by a photo multiplier tube (PMT). A cutoff filter was used to suppress the scattered laser radiation. The cutoff wavelength of the filter at the ultraviolet side was 340 nm. To measure the aging effect, PL measurements were carried out at different dates after deposition. The samples were put in air for aging effect measurements. All measurements were carried out at room temperature.

3. Results and Discussion

3.1. Structural Properties

To evaluate the crystal quality, ZnO thin films deposited on GaAs substrates by PLD were characterized by XRD. The X-ray θ-2θ curves for thin films deposited at different tem-peratures are shown in Fig. 1. It is found that the substrate temperature plays an important role in determining the crystal quality of ZnO thin films. The thin film deposited at room temperature shows an amorphous nature. The samples deposited at the temperatures higher than 100°C show the preferred ZnO (002) orientation. This means that ZnO thin films on GaAs substrates deposited by PLD are of high qualities. While the intensity of ZnO (002) peak of the thin film fabricated at 100°C is much lower than those of the thin films deposited at higher temperatures. This means that the substrate temperature higher

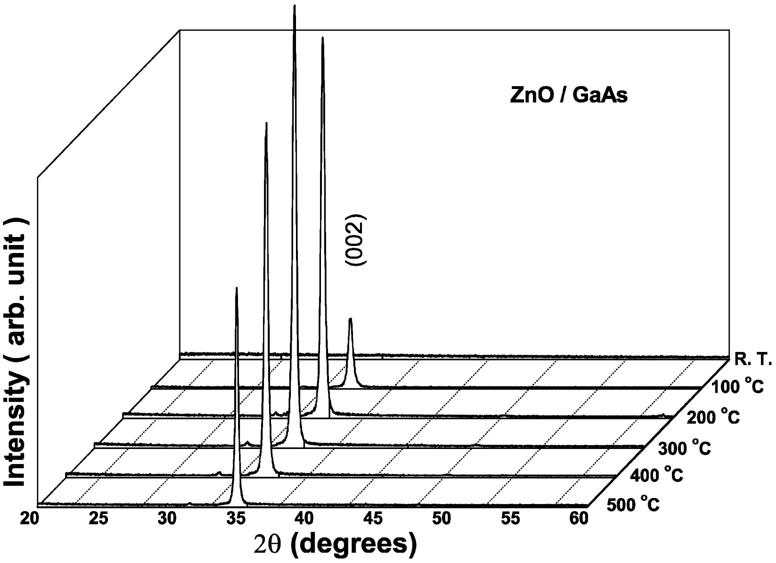

Fig. 1. XRD patterns of ZnO thin films deposited at different temperatures on GaAs (100) substrates.

than 200°C is good for crystal quality. And the peak intensity of the thin film deposited at 500°C is also small compared with those of the thin films deposited at 300 and 400°C. This is believed to be caused by the thickness variation of the thin film.

The temperature dependence of the crystal quality of thin films can be explained mainly by the mobility of the particles at different temperatures. At room temperature, the adatoms with low surface mobility will be located at different positions within the substrate. The low mobility of the adatoms prevents the crystallization of the thin film, so the thin film is of amorphous nature at room temperature. At the temperatures higher than 400°C, ZnO thin film is difficult to deposit, so the intensity of XRD signal will be small compared with those of the thin films deposited at the optimized temperatures. This can be verified by scanning electron microscope (SEM) investigations.

3.2. Aging Effects

Figure 2 shows PL spectra of ZnO thin films deposited on GaAs substrates at different temperatures (100, 200, 300, 400, and 500°C) just after deposition. From this result, near band edge (NBE) emissions at around 380 nm are observed in all thin films. Interestingly, thin films deposited at 100, 200, 300, and 400°C show deep-level emissions at around 430–570 nm. However, the thin film deposited at 500°C shows the most intense near band emission without deep-level ones. This indicates that, although the thickness is small compared with the thin films deposited at 300 and 400°C, the high-quality thin film was successfully deposited at 500°C. Roughly, the intensity of NBE emission increases with increasing growth temperature. The intensity of NBE emission of the thin film deposited at 100°C is much lower than others. This is consistent with the low intensity of XRD ZnO (002) peak. The peak intensity of NBE emission of the thin film deposited at 500°C is much higher than that of the thin film deposited at 400°C, the intensity surpasses the maximum range of PMT. We have to mention here that, the slit size of the spectrometer for PL measurement of the thin film fabricated at 500°C is only 1/20, 1/20, 1/40, and 1/80 compared with those of the thin films fabricated at 400, 300, 200, and 100°C, respectively. This result indicates that 500°C is an optimized condition in depositing ZnO thin film on GaAs substrate by using PLD technique.

To investigate the aging effects of ZnO thin films, we measured PL spectra of ZnO thin films one year later. The PL spectra are shown in Fig. 3. It is found that the deep-level emissions in thin films deposited at 200, 300, and 400°C disappear. So we conclude that the deep level emissions originate from oxygen vacancies or zinc interstitials. As time goes on, oxygen vacancies or zinc interstitials in the thin film are slowly compensated. In PL spectrum of the thin film

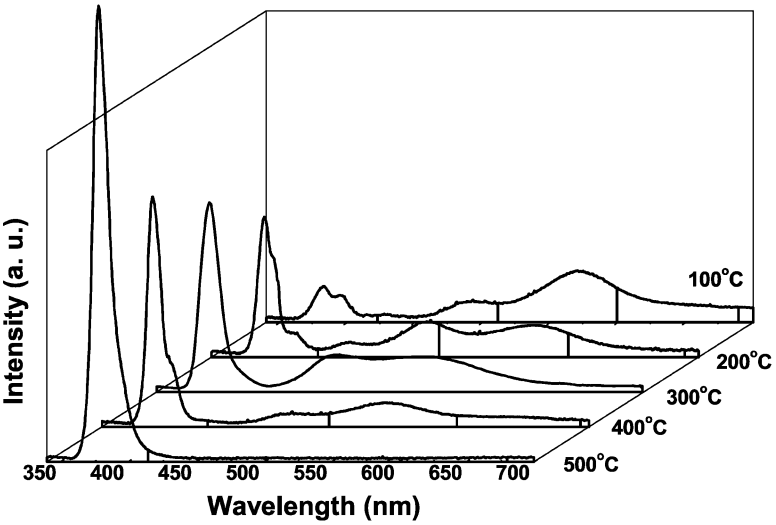

Fig. 2. PL spectra of ZnO thin film deposited at different temperatures on GaAs substrates just after deposition.

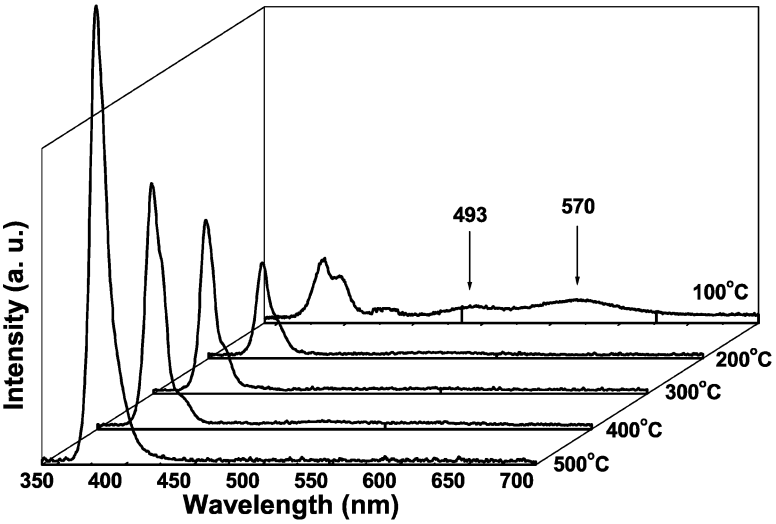

Fig. 3. PL spectra of ZnO thin films measured one year later.

deposited at 100°C, the intensity of the deep level emission peak decreases, but it is still visible. This indicates that, there are more defects in the thin film deposited at low temperature.

3.3. Annealing Effects

To find the annealing effects of ZnO thin films deposited on GaAs substrates, the thin films were deposited at room temperature and annealed at different temperatures in PLD chamber. Figure 4 shows PL spectra of ZnO thin films annealed at different temperatures in PLD chamber. The thin film deposited at room temperature shows small peak at around 500–600 nm and no NBE emission found, which is believed to be from the amorphous nature of the thin film. When the thin films were annealed at 100 and 200°C, the adatoms in the thin film will be slowly crystallized. So the thin films show the peak located at around 535 and a shoulder at around 625 nm, and the intensity of this peak increases with increasing annealing temperature.

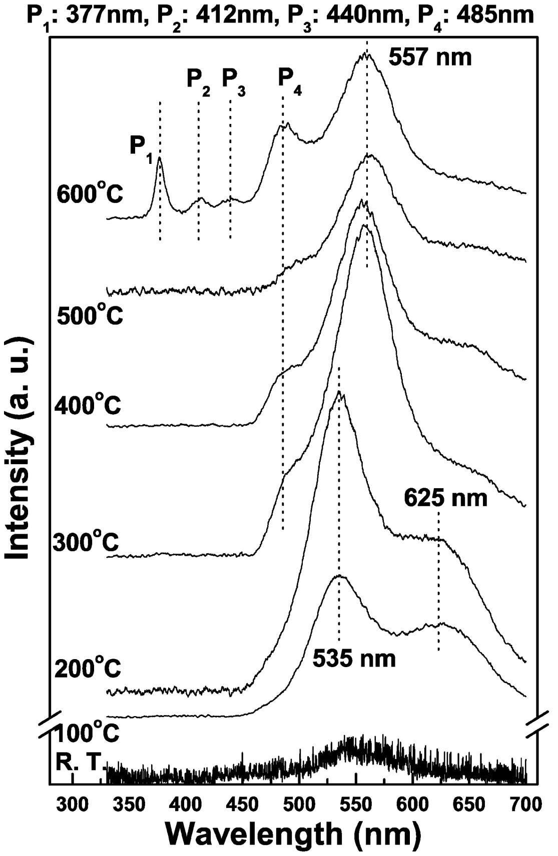

Fig. 4. PL spectra of ZnO thin films deposited at room temperature and annealed at different temperatures in PLD chamber.

According to the literatures, the peak and the shoulder maybe originate from oxygen vacancies or zinc interstitials, which is unclear so far.

When the thin film was annealed at the temperature higher than 200°C, the shoulder at around 625 nm disappears and the peak of 535 nm shifts to 557 nm. The intensity of the peak located at 557 nm decreases with increasing annealing temperature, which is caused by decreasing the defect centers in the thin films. Another shoulder at around 485 nm appears. Abrupt changes take place in the thin film annealed at 600°C. The peak located at 557 nm still exists but the intensity decreases. The shoulder at around 485 nm existed in the thin films annealed at 300, 400 and 500°C appears to be one peak, and small peaks around 412 and 440 nm are also observed. The most interesting thing is that NBE emission at around 377 nm is observed in the thin film. This means that the quality of the thin film was greatly improved.

According to this result, annealing in chamber affects the intensity of the green-yellow-red emissions at around 485–625 nm, the quality of the thin film was improved when it was annealed at 600°C. Note that the annealing results in the chamber are quite different from those of thin films deposited at different temperatures, but we believe that it is caused by the limitation of the annealing time. If the annealing time is long enough (for example, 24 hours or 2 days), the PL results are supposed to be similar with each other. This is exciting for practical applications, because it means that, the quality of thin film deposited at room temperature can be greatly improved by post-annealing process in the PLD chamber.

4. Conclusions

In conclusion, PLD technique was used to deposit ZnO thin films on GaAs (100) substrates at different temperatures. The structural and optical properties of ZnO thin films were studied. By XRD measurements, the substrate temperature higher than 300°C was found to be the optimized experimental condition for the crystallization of thin film. The PL spectra revealed that, NBE and deep-level emissions were observed in the thin films grown at 100, 200, 300, and 400°C, while the thin film deposited at 500°C showed NBE emission without deep-level ones. Through PL results of the thin films measured one year later, the aging effects were observed in thin films deposited at 100, 200, 300, and 400°C. The intensity of the deep-level emissions decreases as time goes on. This is believed to originate from the compensation of the oxygen vacancies or zinc interstitials in thin films.

The annealing effects of ZnO thin film grown at room temperature were studied. It is found that annealing at the temperatures lower than 500°C has little effect on PL. However, PL of the thin film annealed at 600°C changes much, and the quality of the thin film is greatly improved. The aging and annealing effects in ZnO thin films grown on GaAs substrates by PLD were observed for the first time.

Acknowledgments

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