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Studies of ZnO Thin Films On Sapphire (0001) Substrates Deposited by Pulsed Laser Deposition

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Abstract. ZnO thin films are deposited on sapphire (0001) substrates at different temperatures in the pulsed laser deposition (PLD) system. By measurements of X-ray diffraction (XRD), atomic force microscopy (AFM), and Photoluminescence (PL) at room temperature, fabrication temperatures higher than 400°C is found to be the optimum condition for the structural and optical properties of ZnO thin films. With the increase of the fabrication temperature, the grain size becomes bigger and the thin film becomes more homogeneous. In order to get the high-quality ZnO thin film at low temperature, ZnO thin films are deposited at room temperature and annealed in a rapid thermal annealing (RTA) system. It is found that the optical property of the thin film can be greatly improved by annealing in RTA system.

Keywords: ZnO thin films, pulsed laser deposition, rapid thermal annealing, photoluminescence

1. Introduction

There has been a surge of interest in the growth of high-quality thin films. Zinc oxide (ZnO), like other transparent conducting oxides, is an important material for next-generation short-wavelength optoelectronic devices. It has been used for applications, such as transparent conductive films, solar cell windows, and surface acoustic wave devices [1–4]. The crystal structure and optical properties are similar to that of GaN [5], 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 (24 meV) at room temperature, giving advantages over GaN for the exciton-related device applications. So, ZnO related materials have received considerable attention in recent years [6–16].

ZnO thin films can be grown by various deposition techniques, including sol-gel, CVD, and MBE methods etc. Among so many techniques, however, PLD method is found to be an excellent one for the growth of ZnO thin films because the plasma created by the pulsed laser is very energetic and its density is easily controllable by changing the experimental parameters. As a versatile method, PLD is widely used in fabricating metal oxide thin films and the related materials. To realize device applications, an important issue is to fabricate high-quality thin films. PLD method has been regarded to have the potentiality to grow high-quality thin films at relatively low substrate temperatures compared with other techniques.

The purpose of this study is to find the structural and optical properties of ZnO thin films on sapphire (0001) substrates prepared by different methods. ZnO thin films are processed in two ways; one is that high-quality ZnO thin films are deposited at different temperatures

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in PLD system, the other is that ZnO thin films are deposited at room temperature in PLD system and annealed at different temperatures in RTA system. XRD, AFM and PL measurements are carried out to characterize the thin films.

2. Experiment

The explanation of our experiment setup was described in our former papers [9, 10, 12, 13]. Briefly, KrF excimer laser ($\lambda = 248$ nm, $\tau = 25$ ns) is used for the ablation of ZnO target at an energy density of 1 J/cm^2. The strong absorption of 248 nm laser radiation by the target produces an intense plasma plume in front of the target surface. The ablated material is then deposited on sapphire substrates kept at 50 mm away from the target. The dimension of the substrate is 12 mm × 12 mm.

The high-purity ZnO powder (99.99%, Aldrich Chemical Company, Inc, USA) is used in the experiment. 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 hours and at 1200°C for 4 hours in order to densify the target. In our experiment, the optimum experiment parameter was described in our previous papers [13–16]. So, during the thin film fabrication the conditions are as follows; the repetition rate of the laser is 5 Hz, the deposition time is 30 minutes, the background O_2 pressure is 200 mTorr, and the temperature of the substrate varies between room temperature and 600°C. To find the annealing effect of ZnO thin films, ZnO thin films are deposited at room temperature and annealed in RTA system at different temperatures.

X-ray diffractometer (D/MAX 2100H, Rigaku, Japan) using CuK$_{\alpha 1}$ radiation ($\lambda = 1.5405$ Å) is used to study the structure of ZnO thin films. The surface morphologies of thin films are investigated by a scanning probe microscope (SPA-400, Seiko Instrument, Japan). The excitation source used in PL measurements is a He-Cd laser operating at 325 nm with an output power of 30 mW. The emitting light from the sample is focused into the entrance slit of a monochromator, 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 340 nm. All measurements are carried out at room temperature.

To find the rapid annealing effects, ZnO thin films are deposited at room temperature and annealed in RTA system at different temperatures (100, 200, 300, 400, 500, and 600°C, respectively). The annealing processes include 3 steps; the first step is to increase the temperature from room temperature to the desired annealing temperature in 1 minute; the second step is to anneal the sample for 15 minutes; the third step is to cool down the samples to room temperature in 3 minutes. We have to note here that, when we anneal samples at the temperatures higher than 400°C, ZnO thin films evaporated. So, when we anneal the samples at the temperatures higher than 400°C, we change the time for the first step. The time of the first step for samples annealed at 400, 500, and 600°C are 3, 5, and 10 minutes, respectively. The oxygen pressure inside the RTA chamber is 1 atm.

3. Results and Discussion

3.1. Effects of Growth Temperature

3.1.1 Crystal Quality. ZnO thin films deposited by PLD on sapphire (0001) substrates are characterized by XRD to evaluate the crystal quality. XRD patterns of thin films deposited at different temperatures are shown in Fig. 1. It is found that all thin films show the preferred (002) orientation, however, the growth temperature also plays a role in determining the crystal quality. XRD intensity of (002) peaks of thin films grown at 400, 500, and 600°C are similar. However, when the substrate temperature is lower than 400°C, the intensity of (002) peak increases with increasing growth temperature. To evaluate the crystal quality, the rocking curve of (002) peak is measured. The inset of Fig. 1 shows the rocking curve of the thin film deposited at 400°C. The full width at half maximum (FWHM) is 0.18°. FWHMs of thin films deposited at 400, 500, and

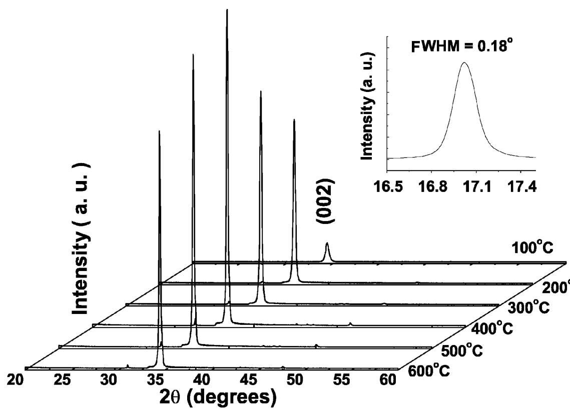

Fig. 1. XRD patterns of ZnO thin films deposited at different temperatures on sapphire (0001) substrates.

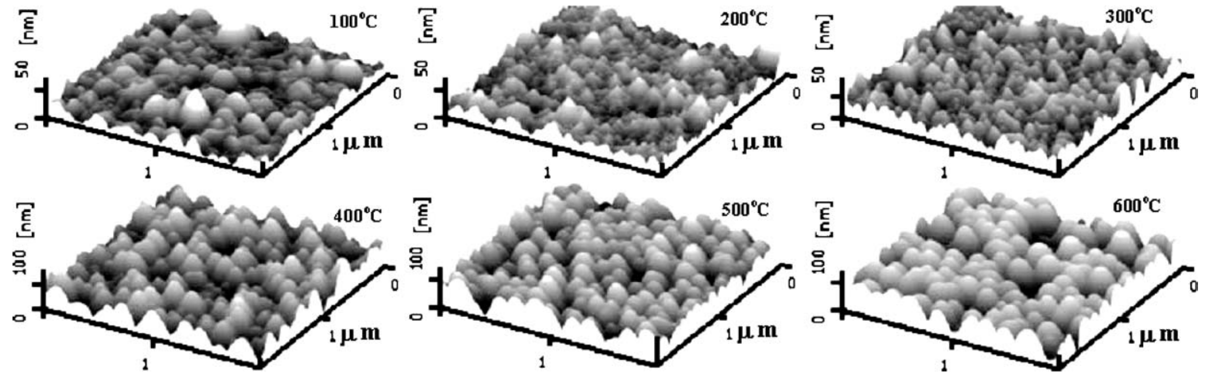

Fig. 2. AFM images of ZnO thin films deposited at different temperatures on sapphire (0001) substrates.

600°C are similar. While FWHMs for thin films that deposited at 100, 200, and 300°C are 8.5°, 2°, and 0.5°, respectively. This means that the temperature higher than 400°C is optimum condition for the crystal quality on sapphire substrate.

3.1.2 Surface Morphology. The surface morphologies of thin films are investigated by SPA-400 in AFM mode. Figure 2 shows AFM images of ZnO thin films deposited at different temperatures. It is found that the surface morphology is strongly dependent on the growth temperature. With increasing growth temperature, the grain size evidently becomes larger and more homogeneous. However, the average roughness becomes bigger. RMS values are 87, 79, 119, 276, 218, and 294 Å for a scanning area of 2 μm × 2 μm for thin films deposited at 100, 200, 300, 400, 500, and 600°C, respectively. Note that the height scale of AFM images of ZnO thin films deposited at 100, 200, and 300°C is 50 nm, and that for ZnO thin films deposited at 400, 500, and 600°C is 100 nm.

3.1.3 Luminescent Property. PL measurements are also carried out at room temperature to study the luminescent properties of thin films. Figure 3 shows PL spectra of ZnO thin films deposited at different temperatures (100, 200, 300, 400, 500, and 600°C) on sapphire (0001) substrates. Near band edge (NBE) emissions at around 380 nm are found in all thin films, this means that high quality ZnO thin films on sapphire substrates deposited by PLD. To find the differences of NBE emissions, NBE emission peaks are shown in the inset of the figure. With the increasing of the growth temperature, the intensity of NBE emissions increases. However, the peak of NBE emission shifts from 382 to 378 nm. This shift is believed to originate from the strain stress inside the thin film.

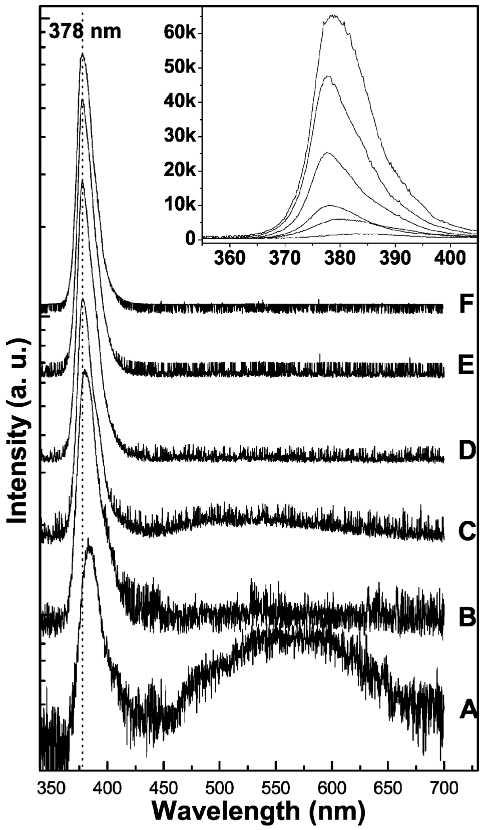

Fig. 3. PL spectra of ZnO thin films deposited at different temperatures on Sapphire (0001) substrates. **A**, **B**, **C**, **D**, **E**, and **F** represents the PL of ZnO thin films deposited at 100, 200, 300, 400, 500, and 600°C, respectively.

To evaluate the optical quality of thin films deposited at different temperatures, FWHM values are also calculated. FWHM values at 380 nm are calculated to be 180, 151, 115, 95, 96, and 94 meV for thin films that deposited at 100, 200, 300, 400, 500, and 600°C, respectively. It is found that FWHMs of NBE emission become narrower with increasing growth temperature from 100 to 400°C, but FWHM values are same for thin films deposited at the temperatures higher than 400°C. These are the best quality ZnO thin films reported in the literature [17–19]. The narrow FWHM indeed suggests a narrow size distribution of the thin film, as also evident from AFM images. When the quality of ZnO thin films is relatively poor, the grain size has a larger distribution, leading to a broader PL band. When the quality of the thin film improved, the grain size becomes larger and more homogeneous, resulting in a narrower FWHM.

It is remarkable that, the deep-level emissions of the thin film deposited at 100°C in the visible range is comparable with its NBE emission. However, the thin films deposited at the temperatures higher than 400°C do not show deep-level emissions. Most of researchers reported that PL spectra of most ZnO samples showed NBE emission accompanied by a broad visible luminescence, and the visible deep-level emission from ZnO seems to be '*intrinsic*' in nature. However, our results indicate that the quality of ZnO thin films deposited at temperatures higher than 400°C on sapphire substrates by PLD is quite excellent.

3.2. *Effects of Rapid Thermal Annealing*

According to our previous works, high-quality ZnO thin films can be grown on glass, GaAs, and Si substrates by PLD at the optimized experimental conditions [9–16]. To obtain high-quality ZnO thin films, the growth temperature of ZnO thin films in PLD should be higher than 400°C. However, the high growth temperatures often cause problems at the film substrate interface. On the other hand, it can save much time and more convenient if the high-quality thin film can be achieved by annealing in RTA after the deposition at low temperature. In order to get high-quality ZnO thin films at low temperature, we try to deposit ZnO thin films at room temperature and anneal them in RTA system. In this paper we report for the first time the properties of ZnO thin films grown at room temperature with a post-deposition RTA treatment.

3.2.1 Effects on Crystal Structure and Surface Morphology. There is no much difference of XRD patterns between ZnO thin films grown at room temperature and the ones annealed at different temperatures in RTA. This means the crystal structure is not greatly improved during annealing in RTA system. AFM images of ZnO thin films deposited at room temperature and annealed at different temperatures in RTA system have little difference, so we don't show them here. The average roughness is about 147, 200, 152, 165, 142, and 139 Å for a scanning area of $2 \times 2\ \mu$m for thin films annealed at 100, 200, 300, 400, 500, and 600°C, respectively.

The effect of rapid thermal annealing on crystal structure and surface morphology is not so evident. Because the surface energy of (002) plane is the lowest in ZnO crystal, the rough crystal structure of ZnO thin film is easily formed at all temperatures. However, the low growth temperature will lower the ordering of the perfect structure of ZnO thin film, which leads to the decrease of the intensity of XRD peak. With the increase of the growth temperature, the structure of ZnO thin film becomes more perfect. As result, XRD peak becomes intenser. Concurrently, when the thin film with lower ordering is annealed, the structure will become perfect. However, because the improvement of the rough structure is more difficult compared with the growth, so the annealing process needs much longer time to get perfect structure.

3.2.2 Effects on PL. Figure 4 shows PL spectra of ZnO thin films deposited at room temperature and annealed in RTA system at different temperatures (100, 200, 300, 400, 500, and 600°C) on sapphire (0001) substrates. The thin film deposited at room temperature shows NBE emission accompanied by broad deep-level emissions. When the thin films are annealed at 100 and 200°C in RTA, the deep-level emissions disappear. However, the annealing seems no effect on NBE emissions. When the thin film is annealed at 300°C, NBE emission is greatly improved and no deep-level ones are observed. When thin films are annealed at 400 and 500°C, NBE emission around 380 nm is observed to be improved, but the intensity of NBE emission is smaller than that annealed at 300°C. At the same time, the small deep-level emission reappears. When the thin film is annealed at 600°C, NBE emission is improved a little, but the broad deep-level emissions become stronger than NBE emission.

From the results of RTA annealing effects, we conclude that, although RTA process does not change the lower ordering of ZnO structure much, the optical

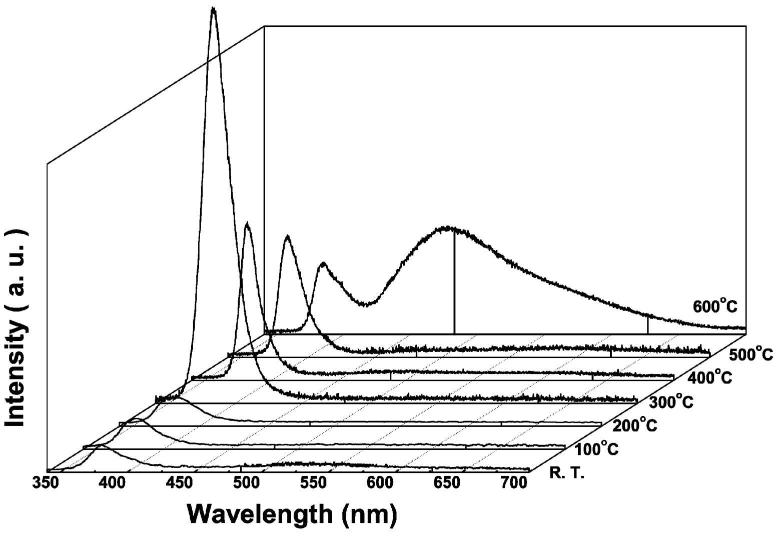

Fig. 4. PL spectra of ZnO thin films deposited at room temperature and annealed at different temperatures in RTA system.

properties of ZnO thin films deposited at room temperature can be greatly improved. The annealing speed is very important in improving the quality of the thin film. If the annealing speed is low, the quality cannot be greatly improved. If the annealing speed is too high, the thin film will be broken because of the stress inside the thin film.

In order to find the effect of the annealing gas, the oxygen and nitrogen gas are used respectively. However, it seems that the results of thin films annealed in oxygen and nitrogen are same.

4. Conclusions

In conclusion, PLD technique is used to deposit ZnO thin films on sapphire (0001) substrates at different temperatures. The structural and optical properties of ZnO thin films are studied. It is found that the substrate temperature higher than 400°C is necessary for good structural and luminescent properties. AFM images indicate that, with increasing growth temperature, the grain size increases and the thin film becomes more homogeneous. However, the average roughness becomes bigger. The intensity of NBE emissions increases with increasing growth temperature.

ZnO thin films are deposited at room temperature and annealed at different temperatures in RTA system. It is found that annealing in RTA can greatly improve the optical properties of ZnO thin films. It means that by annealing ZnO thin film deposited at room temperature, high-quality ZnO thin films can be achieved.

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