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Optical properties of As doped ZnO thin films prepared by pulsed laser deposition technique

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Abstract

ZnO thin films are deposited on glass substrates at adapted experimental conditions during the pulsed laser deposition (PLD). The as-deposited thin films are attached by GaAs wafers and annealed at different temperatures and for different times. Transmittance and photoluminescence (PL) are measured to evaluate the As doping. With increasing annealing temperature and annealing time the transmission of films in the VIS range decreases. The band gap energies are determined by a linear fit of the absorption edge. In PL spectra, two PL emission peaks are found in all samples, one is the near band edge emission, and the ether is green emission. The annealing decreases the intensity of the green emission. The aging is found in ZnO thin films by PL measurements. As time goes on, the green emission peak decreases, and the near band emission peak is enhanced because of the decrease of oxygen vacancies in thin films.

Keywords: Annealing; Films; Impurities; Optical properties; ZnO

1. Introduction

Zinc oxide is one of the most interesting II-VI compound semiconductors with a wide direct band gap of 3.3 eV at room temperature.[1] It has been used for many applications, such as, transparent conductive films, solar cell windows, and bulk acoustic wave devices.[2–5] The similarity of the properties between ZnO and GaN makes ZnO one of the most promising materials for photonic devices in the ultraviolet range, 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 binding energy of the exciton of ZnO (60 meV) is larger than that of GaN (25 meV) at room temperature, giving advantage over GaN for the exciton-related device applications. So ZnO related materials have received considerable attention.[6–9]

Many techniques have been used to deposit epitaxial and textured ZnO films, including CVD, MBE, and PLD methods etc. As a versatile method, PLD is widely used in fabricating metal oxide thin films and related materials. Particularly for the integration of semiconductors with emerging technologies based on metal oxides and other multi-component materials, PLD may be the best alternative.[10] ZnO thin films are deposited by PLD at adapted oxygen pressures and substrate temperatures, and post-annealing processes are executed by attaching GaAs wafers for different annealing temperatures and times. Aging and annealing effects on optical properties of thin films are reported and discussed.

2. Experimental

In the PLD system, there are four target holders on one carrousel and one substrate holder. The angle between the target normal and the laser beam is about 45°. The substrate holder is located at the position (adjustable) where the center of the plasma plume arrives. The dimensions of the target and the substrate holder are about 25 and 50 mm in diameter, respectively. KrF excimer laser radiation ($\lambda = 248$ nm, $\tau = 25$ ns) is 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 produces an intense plasma plume in front of the target surface. The ablated

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material is then deposited on the glass substrate at 50 mm distance from the target.

High purity ZnO powder (99.99%, Aldrich Chemical Company, Inc, USA) is used in the experiments. Disk-shaped specimens of 10 mm in diameter and 2 mm in thickness are obtained by the uniaxial pressing at 100 MPa, followed by the cold iso-static press (CIP) 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 densify the target. During the thin film deposition the conditions are as follows; the repetition frequency of the laser is 5 Hz, the deposition time is 30 min, the background O_2 pressure is 200 mTorr, and the temperature of the substrate is 400 °C. The sizes of the glass substrates used are about 12 mm in square. After deposition GaAs wafers are tightly attached to the surfaces of the ZnO thin films by clips and annealed at different temperatures and for different times in air in an oven. The samples are cooled naturally down to room temperature for optical measurements.

The optical transmittances at the normal incidence are measured by double-beam optical spectroscopy using a spectrophotometer (Cary-5, Varian, Australia) in the UV-VIS-NIR range (300–900 nm). In PL measurement the excitation source is a He-Cd laser (325 nm) with an output power of 30 mW. 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 photo-multiplier tube (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. All of the optical measurements are performed at room temperature. To measure the aging, the as-deposited ZnO thin film is put in air for six months for investigations.

3. Results and discussion

The transmittances of ZnO thin films on the glass substrates annealed at different temperatures and times by attaching tightly a GaAs wafer are shown in Fig. 1. The films show the different optical transmission in the VIS with increasing annealing temperature and annealing time. As the transmittance of the thin film becomes lower, the as-deposited thin film shows the highest transmittance. The dependence on annealing temperature and time may be explained by the diffusion of impurities. The conditions of the larger annealing temperatures and annealing times result in more Ga and As ions to penetrate into the thin films, which decreases its transmittance. While the concentrations of Ga and As ions in the thin film are different, the concentration of As is about 10 times larger than that of Ga, which has been proved by Ryu et al.[11]

From the transmittance result, the band gap energies of the thin films can be also calculated. Assuming the

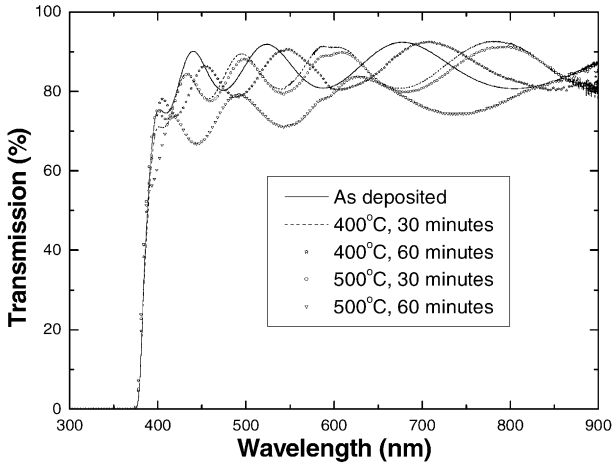

Fig. 1. Transmittance of ZnO thin films deposited at the adapted experimental condition of 400 °C, 200 mTorr and annealed at different temperatures and times attached by GaAs wafer.

absorption coefficient $\alpha \sim$- Ln (T) corresponding to the direct band gap of the Wurtzite structure, a plot of $[\alpha^*(h\nu)]^2$ versus the photon energy $h\nu$ yields in the sharp absorption edge for the high quality films by a linear fit. The optical band gap energies determined from the obtained transmittance spectra are shown in Table 1. The band gap energy increases when the annealing time extends from 30 to 60 min at 400 and 500 °C, respectively. Compared with the band gap energy of ZnO single crystal (3.3 eV), the band gap energies of the pure ZnO thin films decrease by a small amount.

Fig. 2 shows PL spectra obtained at room temperature for ZnO thin films annealed at different temperatures and times on the glass substrates. All samples show UV near band edge emission and the broad green emission. Two emission lines are found in the green emissions, and their intensity is larger than that of the near band emission. The near band edge emission of the as-deposited thin film has no distinguishable change compared with those annealed at different temperatures and times. That means the annealing does not improve the crystal quality. But the annealing affects the broad green emission. The as-deposited sample exhibits the strongest green emission compared with the annealed ones. As we know, the green emission originates from the oxygen vacancies or zinc interstitials. The annealing may diminish the concentration of oxygen vacancies in

Table 1
The band gap energies of ZnO thin films annealed at different temperatures and times attached by GaAs wafer. (unit: eV)

Temp	Time		
	As-Deposited	Anneal 30 min	Anneal 60 min
400 °C	3.27	3.28	3.29
500 °C	3.28	3.29	3.29

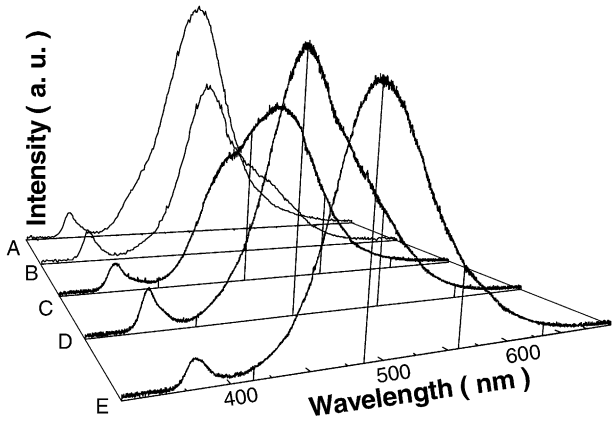

Fig. 2. PL spectra of ZnO thin films fabricated at the adapted experimental condition of 400 °C and annealed at 400 °C for 30 min (B), at 400 °C for 60 min (C), at 500 °C for 30 min (D), and at 500 °C for 60 min (E) attached by GaAs wafer. Curve A shows the PL for a as-deposited thin film.

the thin films, which decreases the intensity of the green emission. With increasing the time of annealing at definite temperature (400 or 500 °C), the intensity of the green emission is lowered. As the annealing time goes on, the oxygen molecules will slowly penetrate the thin films and decrease the concentration of oxygen vacancies in the thin films. Another phenomenon is that the intensity of the green emission of the thin film annealed at the temperature of 500 °C is stronger than that of ZnO thin film annealed at 400 °C. Also its intensity is lower than that of the as-deposited thin film. The annealing will improve the concentration of oxygen vacancies in the thin films. However, the improvement at 500 °C is lower than that at 400 °C. So the intensity of the green emission of the thin films annealed at 500 °C is stronger than the one annealed at 400 °C.

Fig. 3 shows PL results of ZnO thin films at different date after fabrication. The data in curve A is measured two weeks later after the fabrication of the sample. The data in curve B is measured four months after the fabrication. And the data in curve C is measured six months after the fabrication of the sample. Interestingly, an aging effect is found in the sample. All data show two peaks. One is the near band emission at about 379 nm, the other is the green emission at about 500 nm. For convenience a parameter ρ is defined, which is the peak intensity ratio of the near band emission and the green emission. The value ρ is about 1/10, 6/1, and 15/1 for the curves A, B, and C, respectively. It is found that the intensity of the near band emission becomes high as time goes on. However, the intensity of the green emission becomes weak as time goes on. The green emission is thought to originate from the oxygen vacancies. The concentration of the oxygen vacancies slowly decreases after the deposition by the penetration of oxygen molecules. So the green emission becomes weak. As the concentration of the oxygen vacancies decreases, the structure of ZnO becomes more perfect with few defects. As a result, the near band emission becomes more intense.

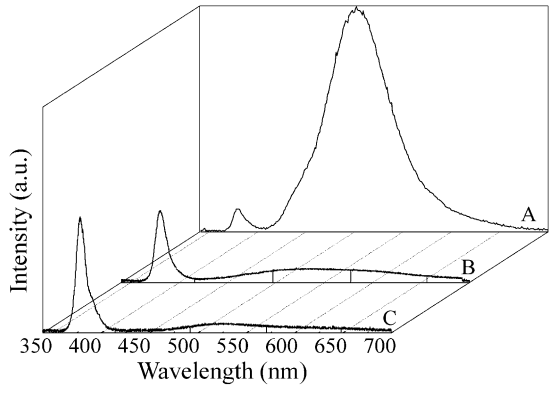

Fig. 3. Aging effect of PL spectra of ZnO thin film deposited at 400 °C. The curve A stands for PL of the as-deposited ZnO thin film, the curve B for PL measured four months after fabrication, and the curve C for PL measured six months after the fabrication.

4. Conclusions

ZnO thin films on glass substrates are deposited at adapted experimental conditions (the substrate temperature of 400 °C and the oxygen pressure inside the chamber of 200 mTorr) in a PLD system. The as-deposited ZnO thin films on the glass substrates attached by GaAs wafer are annealed at different temperatures and times. The transmittances of samples are measured by optical spectroscopy. It is found that the higher the annealing temperature is and the longer the time is, the transmission in the visible range decreases. From the absorption edge of the transmittances, the band gap energies of the samples annealed at different temperatures and times are calculated. The band gap energy is very similar to that of ZnO single crystal.

PL measurements are carried out for ZnO thin films. The annealing clearly affects the green emission. At the annealing temperature of 400 °C, the intensity of the green emission decreases with increasing annealing time. The same phenomenon is found in thin films annealed at 500 °C. The green emission results from oxygen vacancies. The extended annealing times compensate oxygen vacancies in thin films to decrease the green emission. The green emission decreases and the near band emission is enhanced as time goes on.

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