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Journal of the European Ceramic Society 24 (2004) 1869–1872
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Band gap energy of pure and Al-doped ZnO thin films

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Abstract

Pulsed laser deposition (PLD) technique is used to deposit pure and Al-doped ZnO thin films at different temperatures on glass substrates. From the transmission data from optical spectroscopy the band gap energy E_g of the films is derived. The dependences of E_g on the deposition temperatures of the pure and Al-doped ZnO films are different. The band gap energy of the pure ZnO increases and saturates with temperature. However, E_g of Al-doped ZnO shows an exponential decrease. Refractive indices of 1.9–2.1 in the VIS are determined by the spectroscopic ellipsometry (SE). Photoluminescence (PL) data reveal the strong near band emission by increasing the deposition temperature.

Keywords: Films; Optical properties; Pulsed laser deposition; ZnO

1. Introduction

In the past decades, many techniques have been employed in the deposition of thin films. Chemical vapor deposition (CVD),[1] atomic layer epitaxy (ALE),[2,3] vapor phase epitaxy (VPE)[4] and molecular beam epitaxy (MBE) are among them.[5,6] Nowadays, pulsed laser deposition (PLD) technique has been realized to be more useful in growing high quality thin films of metal oxide materials compared with other techniques because of its good features.[7] The system is simple hardware, atomic-layer control achieved by adjusting the laser fluence and the pulse repetition rate, and has the possibility of in situ processing of the multi-layer hetero-structures by using the multiple target arrangements. The plasma created by the pulsed laser radiation is very energetic and its density can be easily controlled by changing the processing gas pressure inside the chamber. For these practical reasons, PLD technique has been extensively employed for the preparation of the high quality thin films of multi-component metal-oxide ceramics in the past several years.[8]

As one promising metal-oxide material in the semiconductor field due to its potential properties, ZnO has received considerable attention in the recent years.[9–11] ZnO is a wide band-gap material with an energy gap of 3.3 eV and the large exciton binding energy of 60 meV at room temperature.[12] Its band structure and optical properties are very similar to those of GaN, which is known to be a good material for the fabrication of the optical device, such as light emitting diodes (LEDs) and laser diodes (LDs). These properties of ZnO similar to GaN indicate that ZnO is one of the promising materials in these applications. In this report, pure and Al-doped ZnO thin films are deposited at different temperatures by PLD. The crystalline and the optical properties of the films are presented and discussed.

2. Experimental

There are four target holders on one carousel and one substrate holder inside the chamber in the PLD system. The angle between the target normal and the laser beam is about 45°. The substrate holder is located at the right 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 the pure and Al-doped ZnO target (2 wt.% of Al) at an energy density of about 1 J/cm^2. The stainless steel vacuum chamber is evacuated by a turbo molecular pump to the base

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doi:10.1016/S0955-2219(03)00490-4

pressure at about 10^{-7} Torr. 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 deposited on the substrate kept at 50 mm away from the target.

High purity ZnO powder (99.99%, Aldrich Chemical Company, Inc., USA) is used in this work. To dope Al, 2 wt.% Al is mixed with ZnO powder in the planetary milling for 4 h using a plastic container without balls. 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 isostatic 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 densify the target. ZnO disk is attached to the target holder by the epoxy resin, and the substrate is cleaned carefully and attached to the substrate holder. During the thin film deposition, the conditions are as follows; the repetition rate of the laser is 5 Hz, the oxygen pressure inside the chamber is 200 mTorr, the deposition time is 30 min, and the temperature of the substrate is between room temperature and 500 °C. The resulting thickness of the thin film is about 500 nm.

The structures of ZnO thin films are studied by X-ray diffraction using X-ray diffractometer (D/MAX 2100H, Rigaku, Japan, 40 kV, 30 mA) using the Cu$K\alpha_1$ radiation with $\lambda = 1.54056$ Å. The optical transmittance at normal incidence is measured by optical spectroscopy using a double-beam spectrophotometer (Cary-5, Varian) in the UV-VIS-NIR (300–900 nm).

The excitation source used in PL 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 that has a spectral grating of 1200 grooves/mm and picked up by a photomultiplier 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. For the sample fabricated at 500 °C, the slit size of the monochrometer decreases to 1/5, 1/6, 1/6, 1/20, and 1/20 times compared with the slit size that is used for measuring PL of the samples fabricated at 400, 300, 200, 100, and room temperature, respectively.

To calculate the refractive index, SE (Jobin-Yvon UVISEL, UK) measurements are carried out at the incident angle of 56° and in the spectral range 0.7–3.2 eV with 0.02 eV steps. All the optical measurements are performed in air.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows XRD patterns of the pure ZnO thin films deposited at different temperatures. It is found that the intensity of (002) orientation increases with the deposition temperature, but the diffraction peak disappears when ZnO is deposited at room temperature. The same behavior in Al-doped ZnO thin films is investigated. The samples grown at low temperatures have an amorphous nature, but the samples grown at higher temperatures show (002) preferred orientation. This result indicates that 400–500 °C is the adapted deposition condition for the growth of ZnO thin film on glass substrates by PLD.

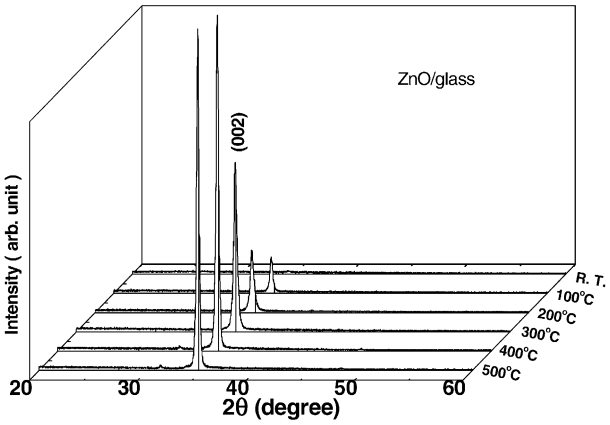

Fig. 1. XRD patterns of pure ZnO thin films deposited at different temperatures.

3.2. Transmittance

The room temperature transmittance of pure ZnO thin films deposited at different temperatures is shown in Fig. 2(a). The films show 85–90% optical transmission in the visible range, which is important for applications. Assuming the absorption coefficient $\alpha \sim -\mathrm{Ln}(T)$ 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 versus temperature as determined from the obtained transmittance spectra are shown in the inset of Fig. 2(a). Interestingly, the band gap energy of the pure ZnO thin films increases with temperature and saturates at high temperatures. Compared with the band gap energy of ZnO single crystal (3.3 eV), the band gap energy of the pure ZnO thin films is somewhat smaller. The small variation of the band gap energy is assumed to result from the defects in ZnO thin films.

Fig. 2(b) shows the transmittances of Al-doped ZnO thin films deposited at different temperatures. The temperature dependence of the band gap energies of Al-doped ZnO is different from that of the pure ZnO, a nearly exponential decay with temperature is found. The exponential decay might be explained by the composition variation of the films as a function of the

growth temperature.[13] The band gap energy of Al-doped ZnO deposited at any temperature is larger than that of the bulk ZnO, which is believed to be Burstein–Moss effect because of the doping by Al. ZnO is naturally n-type material, and the Fermi level will be inside of the conduction band by ξ_n when it is doped with Al. Since the states below ξ_n in the conduction band are filled, the absorption edge should shift to the higher energy by ξ_n. The optical band gap of Al-doped ZnO thin films ranging from 3.32 to 3.77 eV is higher than those of 3.25 to 3.28 eV obtained for pure ZnO thin films.

3.3. Photoluminescence

Fig. 3 shows the PL spectra obtained at room temperature for pure ZnO thin films. PL results are found to be strongly dependent on the deposition temperature. All the samples show UV emission of the near band edge, but the intensity of the peak increases with the deposition temperature. The strong near band emission of the sample deposited at high temperature indicates its good quality. There are also broad green–yellow emissions comparable with the near band emission in the samples deposited at low temperatures. This is believed to result either from oxygen vacancies or from interstitial zinc ions. PL spectra of Al-doped ZnO thin films are quite different. Al-doped ZnO thin films show quite broad emission bands, which is believed to originate from impurities in the thin films.

3.4. Refractive index

The procedure of modeling and fitting to determine the refractive index n is based on the procedure by Kim.[14] Accordingly the refractive index can be expressed by the single oscillator Sellmeier dispersion relation[15]

$$n^2(\lambda) = A + B\frac{\lambda^2}{\lambda^2 - \lambda_0^2}, \quad (1)$$

where $A + B$ is the same as n_∞^2 and n_∞^2 is the refractive index in the long wavelength limit. B is a measure of the oscillator strength, and λ_0 is the resonance wavelength.

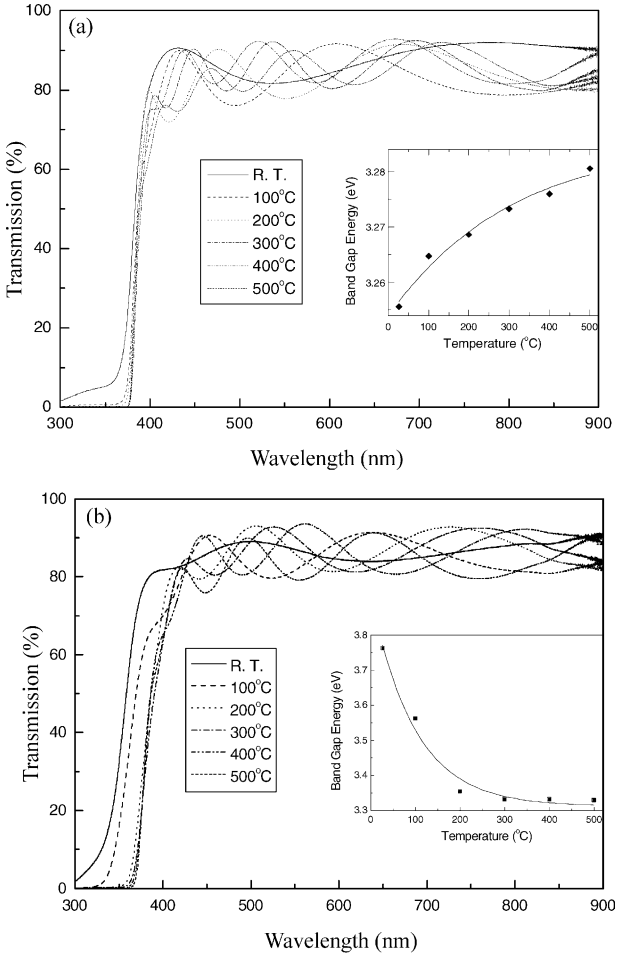

Fig. 2. Optical transmission spectra of pure (a) and Al-doped (b) ZnO thin films on glass substrates deposited at different temperatures.

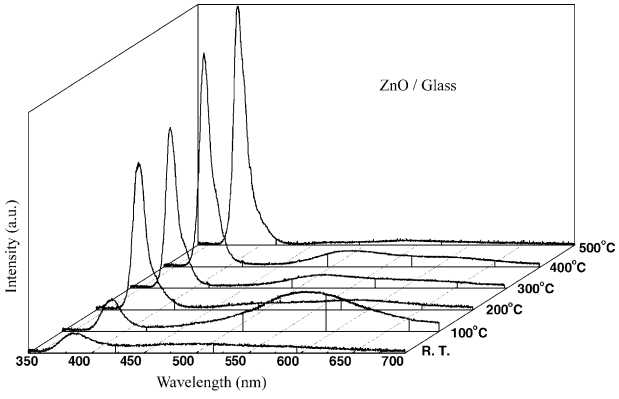

Fig. 3. PL spectra of pure ZnO thin films deposited at different temperatures.

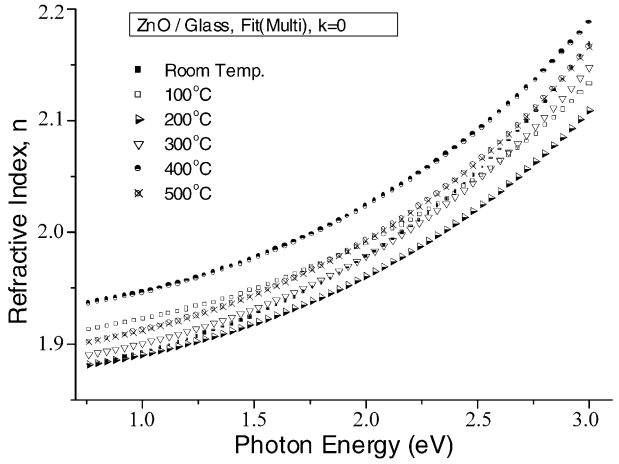

Fig. 4. Refractive index versus photon energy for pure ZnO thin films deposited at different temperatures.

For the three-phase system with one homogeneous layer between an ambient medium and the substrate, the refractive index of the film can be expressed by three constants A, B, and λ_0. In this work, a three-film model with two additional layers (surface and interface layer) with void fractions (F_v) is adopted to reflect the structural inhomogeneities.

The refractive indices from the theoretical fitting of the ellipsometric angles (Δ and Ψ) of the samples are plotted in Fig. 4. As can be seen the refractive index in the visible wavelength range is in the reasonable range of 1.9–2.1, corresponding to polycrystalline ZnO thin films. The optical functions of ZnO thin films have shown the normal dispersion of the refractive index in the visible range. The curves obtained by the ellipsometric data are in the 0.7–3.0 eV range.

4. Conclusions

Temperatures of 400–500 °C result in high-quality crystalline thin films during deposition on glass substrates. From the transmission data by optical spectroscopy, the band gap energies are derived by a linear fit. An increase and saturation behavior with deposition temperature is found in the pure ZnO, but an exponential decay is found in Al-doped ZnO. Band gap energies of the pure ZnO are very close to those of ZnO single crystal, but band gap energies of Al-doped ZnO grown at low temperatures are much larger than those of ZnO single crystal, which is believed to result from the Burstein–Moss effect. The refractive index of ZnO thin films as derived by SE is in the range of 1.9–2.1 in the VIS. PL results show a strong near band emission in thin films, therefore PLD is very suitable in depositing ZnO thin films compared with other techniques.

Acknowledgements

The authors would like to thank financial support by Electronic Ceramics Center (ECC) of Dongeui University founded by Korea Science and Engineering Foundation (KOSEF), Ministry of Science and Technology (MOST) and Busan Metropolitan City Government.

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