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Photoluminescence and absorption in sol–gel-derived ZnO films

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Abstract

Highly *c*-axis-oriented ZnO films were obtained on corning glass substrate by sol–gel technique. The characteristics of photoluminescence (PL) of ZnO, as well as the exciton absorption in the absorption (UV) spectra are closely related to the post-annealing treatment. The difference between PL peak position and the absorption edge, designated as Stokes shift, is found to decrease with the increase of annealing temperature. The minimum Stokes shift is about 150 meV. The decrease of Stokes shift is attributed to the decrease in carrier concentration in ZnO film with annealing. X-ray diffraction, surface morphology and refractive index results indicate an improvement in crystalline quality with annealing. Annealed films also exhibit a green emission centered at ~520 nm with activation energy of 0.89 eV. The green emission is attributed to the electron transition from the bottom of the conduction band to the antisite oxygen O_{Zn} defect levels.

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Keywords: Zinc oxide; Thin films; Sol–gel; Photoluminescence; Absorption; Stokes shift

1. Introduction

ZnO, a II–VI compound semiconductor, has emerged as a promising material to be used in exciton-related optical devices because of its large band gap of 3.37 eV [1] at room temperature and large exciton-binding energy of 60 meV [2]. ZnO is a semi-conducting, photo-conducting and piezoelectric material had widely used as transparent electrodes in solar cells [3], active channel in thin film transistor [4], varistors, chemical and gas sensors. ZnO films have also been widely used as bulk acoustic devices and surface acoustic wave (SAW) devices [5]. Recently, ZnO gained much attention of the research community of the ease of tailoring of its optical and electrical properties using doping and find applications in the areas of spintronics, p–n junction, short wavelength optoelectronic devices [6]. ZnO films can be deposited by variety of deposition techniques, such as sol–gel process [7], spray pyrolysis [8], molecular beam epitaxy (MBE) [9], chemical vapor deposition (CVD) [10] and sputtering [11]. The properties of ZnO thin films are much influenced by not only the growth methods, but also by post-annealing process parameters; therefore, it is important to study the influence of annealing on the properties of ZnO films. The large exciton-binding energy permits excitonic recombination well above room temperature. Exciton provides a sensitive indicator of material quality [12]. Photoluminescence (PL) is very sensitive to the quality of crystal structure and to the presence of defects. The green luminescence from high-quality undoped ZnO film dominates the defects-related part of PL spectrum.

A pronounced exciton absorption peak in the UV spectra is related to the exciton effect phonon interactions, strain, doping which also broaden or shift the absorption edge and influence the optical constant near the band gap

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[13]. In this paper, Zinc oxide films have been obtained by spin coating using sol–gel process. The PL and absorption spectra are measured as a function of annealing temperature. The crystalline quality of the film is judged from X-ray diffraction (XRD) patterns, surface morphology and refractive index.

2. Experimental

The solutions were prepared by dissolving 0.6 M zinc acetate "$Zn(CH_3COO)_2 \cdot 2H_2O$" (Purity 99.95%) in anhydrous methanol and the monoethylinamine (MEA) was added to the stable sol in the ratio (r) of MEA/zinc acetate as 1. This resulted a change of pH value from 6.4 without MEA to 10.6 with MEA. The alkaline nature of the sol has been reported to help the growth of ZnO films. The clear solutions were used for deposition after 48 h of aging. The films were deposited on corning glass (7059) substrate using spin coating technique. Prior to the coating the substrates were cleaned ultrasonically, first in acetone, and subsequently in methanol for 10 min each. They were further cleaned with ion-exchanged distilled water for 20 min, dried in nitrogen and kept in an oven at 80 °C for 30 min. The films were dried on a hot plate at 300 °C for 10 min. This process was repeated several times to deposit films of desired thickness. The films were annealed in air for 1 h at different temperatures (400–600 °C) at the rate of 4 °C/min. and subsequently cooled in air. The thickness of the films was measured by the DEKTECK^{3-ST} surface profilometer and was found to be ~0.18 μm. The dependence between annealing temperature and the physical structure of the films (crystalline structure and microstructure) was investigated by the XRD patterns of the films using by Cu K_α (= 1.54056 Å) radiation (XRD Riggaku). The current and voltage of XRD was maintained at 20 A and 40 V, respectively during the measurement. Topographical information of the film was obtained by atomic force microscopy using SPI 3700/SPI 300; Seiko instruments Co., Tokyo, Japan. The optical properties of the deposited films were investigated using dual beam UV–vis spectrophotometer (Shimatzu UV 336) in the wavelength range 190–1500 nm. Spectroscopic Ellipsometry (SE) measurements were performed with a rotating-analyzer ellipsometer (Woollam Inc., VASE model) at an incident angle of 70° in the energy range of 1–5 eV at room temperature on ZnO films grown on corning glass substrate and annealed at different temperatures. The optical emission studies on ZnO films were made by PL spectroscopy using 325 nm beam of He–Cd laser at room temperature.

3. Results and discussion

3.1. Structural properties

The XRD spectra shown in the Fig. 1 reveal the influence of post-annealing treatment in the temperature range of 300–600 °C on the structure of the ZnO thin films. It is clear that the entire films exhibit highly preferred orientation with c-axis perpendicular to the substrate surface. Essentially, only (0 0 2) phase is observed in all the films, indicating high crystalline quality in the film.

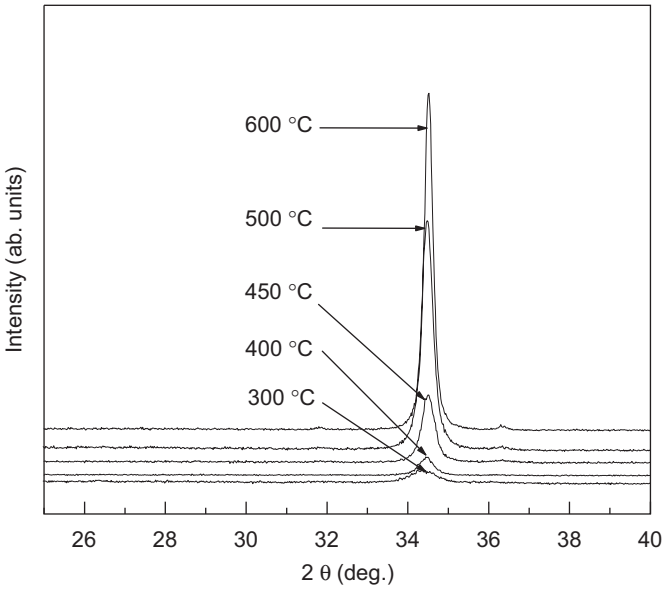

Fig. 1. X-ray diffraction patterns of ZnO films at different annealing temperatures.

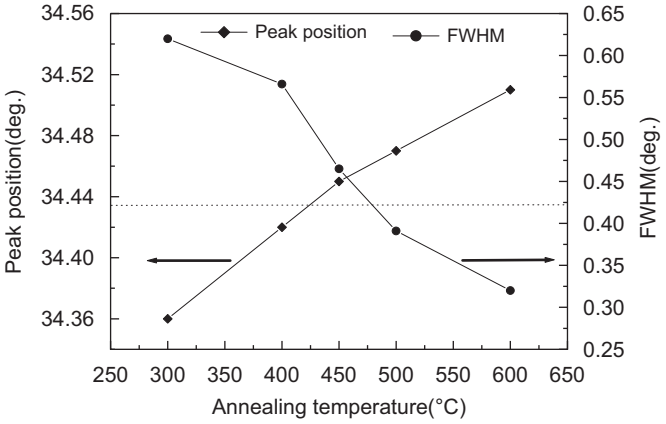

Fig. 2. X-ray diffraction peak position and FWHM of ZnO films at different annealing temperatures.

Fig. 2 shows the (0 0 2) XRD peak position of ZnO films as a function of annealing temperature. XRD (0 0 2) peak position for as grown ZnO film is at 34.36°, which is lower than the corresponding bulk value at 34.43°. It is observed that with increase in annealing temperature, up to 450 °C, the peak position shifts towards the powder value. Further annealing at higher temperature (>450 °C), the (0 0 2) peak position again starts to deviate from the powder value but in the opposite direction, indicating change in the direction of stress. The peak position at lower value indicates a tensile stress in the film. The residual stress along c-axis tends to lower the length of c-axis. During annealing treatment these crystallites gain enough diffusion/activation energy and small crystallites migrate to relatively equilibrium sites in the