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Review

Structural and luminescent characteristics of non-stoichiometric ZnO films by various sputtering and annealing temperatures

Po-Tsung Hsieh[a,*], Ying-Chung Chen[a], Kuo-Sheng Kao[b], Chih-Ming Wang[c]

[a]*Department of Electrical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan*
[b]*Department of Computer and Communication, Shu-Te University, Kaohsiung, Taiwan*
[c]*Department of Electrical Engineering, Cheng Shiu University, Kaohsiung, Taiwan*

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Abstract

ZnO thin films were prepared by reactive RF magnetron sputtering at various deposition temperatures. They were annealed in oxygen ambient at various annealing temperatures. The microstructures and photoluminescence characteristics of ZnO films were investigated. The grain size of the ZnO thin film that was deposited at room temperature (RT) after annealing exceeded that of the film that was deposited at 500 °C. Excess Zn atoms were considered to be present in the ZnO film that was deposited at RT, so the film was non-stoichiometric ZnO. No visible emission of either of the ZnO films deposited at the two temperatures was observed before annealing. Following annealing at high temperature, the green emission from the ZnO film that was deposited at RT was stronger than that of the film that was deposited at 500 °C. The relationship between the non-stoichiometry of the thin film and the visible emission was discussed. The luminescent centers that correspond to green emission are defects; the concentration of defects was higher in the ZnO thin film that was deposited at RT than in the film that was deposited at 500 °C.

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Keywords: Sputtering; II–VI semiconductors; Photoluminescence; Annealing and defects

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*Corresponding author. Tel.: +886 7 5254121; fax: +886 7 5254015.
E-mail address: ycc@mail.ee.nsysu.edu.tw (Y.C. Chen).

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1. Introduction

Potential applications of ZnO in electronic and optoelectronic fields have attracted much interest because of its excellent electrical, optical and piezoelectric properties. ZnO has a wide band gap of 3.3 eV and high efficiency as a low-voltage phosphor material [1]. Normally, ZnO crystallites have a hexagonal wurtzite lattice with mean lattice constants of $a = 3.25$ Å and $c = 5.206$ Å [2]. Recently, thin films of ZnO have attracted substantial interest because of their use in numerous optoelectronic devices, such as short wavelength light emitting diodes [3] and transparent electrodes [4].

Many methods can be adopted to fabricate ZnO thin films, such as spray pyrolysis, metal organic chemical vapor deposition (MOCVD), sputtering and molecular beam epitaxy (MBE) [5–9]. Sputtering is convenient for the deposition of semiconductor thin films and promotes the formation of a homogeneous large area [10].

The photoluminescence (PL) of ZnO film is worthy of study because it provides valuable information on the quality and purity of the film, and thus on its optical properties [11]. The PL spectra of a ZnO film are normally obtained in the ultraviolet (UV) and visible emission bands. The UV emission band is known to be caused by band-to-band transition and free excitons transition [12]. In a preliminary study [13], a more stoichiometric ZnO thin film, which was fabricated by sputtering, exhibited stronger UV emission. The luminescent mechanism of visible light emission is still being debated. However, most related studies [14–16] have addressed the relationship between the defects and visible light emission. According to Bhaumik et al., the defects that are generated during the preparation of ZnO thin film may result in a non-stoichiometric ZnO film [2]. In this investigation, the ZnO film was prepared at various deposition and annealing temperatures to yield a non-stoichiometric ZnO film, which emits in the visible region. The effects of sputtering and annealing temperatures on the structural and PL characteristics of ZnO thin film were investigated.

2. Experiments

The reactive RF magnetron sputtering system is utilized to deposit the ZnO thin film on the SiO_2/Si substrates at substrate temperatures of room temperature (RT) and 500 °C. SiO_2 to a thickness of 1000 Å was deposited on Si substrates by low-pressure chemical vapor deposition (LPCVD) to increase the adhesion between the ZnO film and the Si substrate. A piece of metallic zinc with a diameter of 2-in, a thickness of 0.25 in and 99.99% purity was used as the target. After the vacuum chamber was evacuated to below 10^{-5} torr, oxygen (O_2) and argon (Ar) gases with an $O_2/O_2+\mathrm{Ar}$ ratio of 21% were introduced into the chamber as the gaseous atmosphere during sputtering. The working pressure was 5 mtorr; the sputtering power was 100 W, and the sputtering time was 1 h. The ZnO thin films with the thickness of 1.7 and 4 μm were obtained as the ZnO thin films were deposited at 500 °C and RT by sputtering. After sputtering, the as-grown samples were annealed in a sealed ULVAC MILA-3000 rapid thermal annealing furnace (RTA) in an atmosphere of oxygen at temperatures of 700, 800 and 900 °C. The heating rate was 6 °C/s and the dwell time was 1 h.

The crystalline and surface structures of the film were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD measurements were made using Cu-K α radiation to analyze the orientation of the ZnO films. The diffraction angle 2θ was scanned from 30° to 60° at 0.05° per second. A Philips XL-40FEG field emission scanning electron microscope (FESEM) was used to investigate the surface and grain structures of ZnO films. The PL characteristics of ZnO films were measured using a Jobin-Yvon T64000 Micro-PL/Raman Spectroscope. A He–Cd laser with a wavelength of 325 nm at a power of 20 mW is used an as excitation light source. The laser beam was transmitted through variable attenuators. An Olympus BX41 microscope with a 40× object lens was used to focus and collect the laser beam and the PL emissions. All of the measurements were made at RT.

Table 1
The related serial numbers of different processing parameters

	Sputtering temperature	Annealing temperature
S1	500	–
S2	500	700
S3	500	800
S4	500	900
S5	RT	–
S6	RT	700
S7	RT	800
S8	RT	900

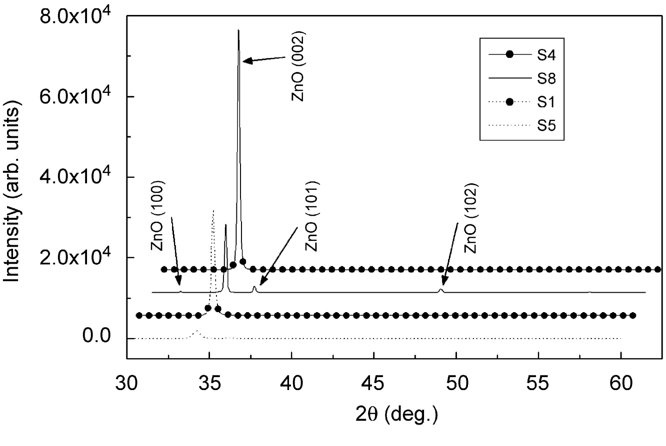

Fig. 1. XRD patterns of ZnO under different sputtering and annealing temperatures.