Physica B 405 (2010) 2526–2529

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

# Effects of the annealing environment on green luminescence of ZnO thin films

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ARTICLE INFO

*Article history:*
Received 17 February 2010
Accepted 8 March 2010

*Keywords:*
Photoluminescence
Zinc oxide
Defects
Annealing
Green emission

ABSTRACT

The effects on visible light emission of ZnO thin films annealed by various annealing conditions were investigated. Based on the photoluminescence (PL) properties, stronger green light emission of ZnO thin films was obtained as annealing in oxygen than in other atmospheres. The green light emission increased in intensity with the increased annealing temperature and the strongest green light emission stood at the temperature of 800 °C. According to the structural analyses, ZnO films show a preferred (0 0 2) orientation peak and the crystalline became better through annealing process. The surface morphologies became closer to the hexagonal shape and also became denser as annealing in oxygen. Mechanism analysis of PL shows that green emission band should be derived from the defects, which is greatly related to oxygen concentration during annealing, formed in ZnO films. The relationship between green luminescence and oxygen concentration in ZnO thin films was discussed.



## 1. Introduction

Zinc oxide is one of the most interesting II–IV compound semiconductors because of its electrical, optical, and piezoelectric properties, which make it suitable for many applications [1]. Comparing to other wide band-gap semiconductors, ZnO posses higher quantum efficiency and higher exciton energy [2,3]. Therefore, ZnO is potential for many applications in optoelectronic devices, such as light emitting diodes (LED), photodetectors, and electroluminescence devices [4]. Some articles also discussed optical pumped stimulated emission and lasing of ZnO thin films [5–8]. Therefore, it is essential to investigate the photoluminescence (PL) characteristics for the fabrication of optoelectronic devices and valuable information on the quality of the materials can also be provided [9]. Generally, there are several luminescence bands for ZnO in the UV and visible regions [10–12]. It is known that UV emission could be caused by the exciton transition and transition between conduction band and valence band [13–15]. However, the physical mechanisms behind visible light emission in ZnO are still in controversy. Several articles have illustrated various visible luminescence bands attributed to the defects related to deep level emission, including oxygen vacancies, interstitial oxygen, zinc vacancies, and interstitial zinc [7,16–18]. Therefore, it is important to investigate the luminescent mechanism caused by the defects of ZnO thin films since they are the key factors of obtaining the visible luminescence.

Many fabricating methods for preparing ZnO thin films were proposed. Among the deposition techniques, the most commonly used technique is sputtering because of its possibility to obtain good orientation and uniform films [19]. As reported, many structural morphologies and PL characteristics of ZnO deposited by sputtering technology were discussed and the luminescence mechanism was also investigated [4,13,14]. However, according to Lim et al. [19], the PL characteristics of ZnO thin films are more dependent on the post-annealing process than on the growing method. Annealing process conditions such as annealing temperatures, process time, and atmosphere may have significant influence on the structural formation and PL properties of ZnO films [20,21].

In the preliminary work, we have successfully deposited ZnO thin films on $SiO_2$/Si substrate and investigated the photoluminescence characteristics with different sputtering parameters [22]. In this study, efforts for post-annealing process of ZnO thin film under various temperatures and atmospheres using annealing furnace are presented. The physical property and the luminescent characterization of annealed ZnO films are investigated.

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doi:10.1016/j.physb.2010.03.021

## 2. Experimental

ZnO thin film was deposited on the $SiO_2$/Si substrate with the optimal sputtering parameters based on better PL intensity by using reactive RF magnetron sputtering technique. ZnO film was deposited for 1 h and the thickness was around 2 μm. After deposition, as-grown ZnO films were annealed under various temperatures of 700–900 °C and various atmosphere of ambient atmosphere, oxygen, and nitrogen by using thermal annealing furnace with the dwelling time of 1 h. After annealing, the sample was naturally cooled down to room temperature in the furnace.

Crystalline orientations of the ZnO films were presented by X-ray diffraction (XRD), which was made on a Siemens D-5000 diffractometer using Cu-Kα radiation. The diffraction angle $2\theta$ scans from 30° to 60° and the scanned speed was 0.05° per second. The surface structures were observed by scanning electron microscopy (SEM) on Philips XL-40FEG field emission scanning electron microscopy. The different luminescent characteristics of ZnO films under different annealing conditions were measured by the PL measurement, which was performed on a JOBIN-YVON T64000 Micro-PL/Raman Spectroscopy. He–Cd laser with a wavelength of 325 nm and power of 30 mW is used as the excitation light source. The receiving time for collecting the luminescence of ZnO thin films was fixed at 10 s. All the measurements were performed at room temperature.

## 3. Results and discussion

Fig. 1(a)–(d) shows the SEM morphologies of as-grown ZnO thin films and annealed in oxygen atmosphere at 700–900 °C. It is clearly demonstrated that the morphology of as-deposited ZnO film is constructed by many individual conical islands, as shown in Fig. 1(a), and it seems to be in melting state. This formation may be resulted from the substrate temperature of 500 °C during sputtering, Zn atoms could gain more kinetics and bond with oxygen atoms more easily since the melting point of Zn is 419.5 °C. The inset figure shows the cross section of as-grown ZnO thin film. The crystallites of the films are columnar and perpendicular to the plane of the substrate. Fig. 1(b)–(d) illustrate the surface morphologies of ZnO films annealing in oxygen atmosphere under 700, 800, and 900 °C. As compared to Fig. 1(a), the conical islands disappeared, the grain size and boundaries of ZnO films seemed to be larger and more apparent with the increase of annealing temperatures, respectively. Moreover, the grains were clearer and the shape of some grains was close to the hexagon. According to Minami et. al., the chemical component of as-grown ZnO films prepared by sputtering method was nonstoichiometric and usually with Zn-excess [21]. The excess Zn atoms may exist between ZnO–ZnO grain boundaries. During annealing, excess Zn atoms were melted and bonded with oxygen atoms existing in the atmosphere with high temperature. ZnO grain located on the surface of the thin film adsorbed oxygen atoms and the grain became larger. In order to investigate the effects on ZnO thin films with various oxygen concentrations as annealing, ambient atmosphere, and nitrogen were used for annealing. The surface morphology of ZnO films annealed in ambient atmosphere, as shown in Fig. 1(e), revealed apparent hexagonal grain shape and the grain size was smaller than that annealed in oxygen. Fig. 1(f) presents SEM morphologies of ZnO films annealed at 800 °C in nitrogen. It was clarified that ZnO film annealed in nitrogen exhibited scraggy surface structure and each grain showed round type instead of the hexagonal formation shown in Fig. 1(c). The phenomenon may be resulted from different annealing atmosphere. When ZnO thin films were annealed in nitrogen, it drove away the adsorbed oxygen molecules. This situation was similar to the phenomenon of desorption of adsorbed vapors from material surface on nitrogen flushing [19]. As a result, ZnO grains in round type may be caused by the lack of oxygen. Based on the above discussion, the situation was considered to be owing to the insufficiency of oxygen atoms in the chamber during annealing.

Fig. 2 presents the X-ray diffraction patterns for as-grown ZnO film and annealed in oxygen at 800 °C and shows the dominant (0 0 2) diffraction peak at $2\theta = 34.5°$. No diffraction peak of Zn or other elements was detected and the existence of (0 0 2) diffraction peak reveal that ZnO was purely deposited with a well-defined crystal orientation. As annealed at high temperatures, the intensity

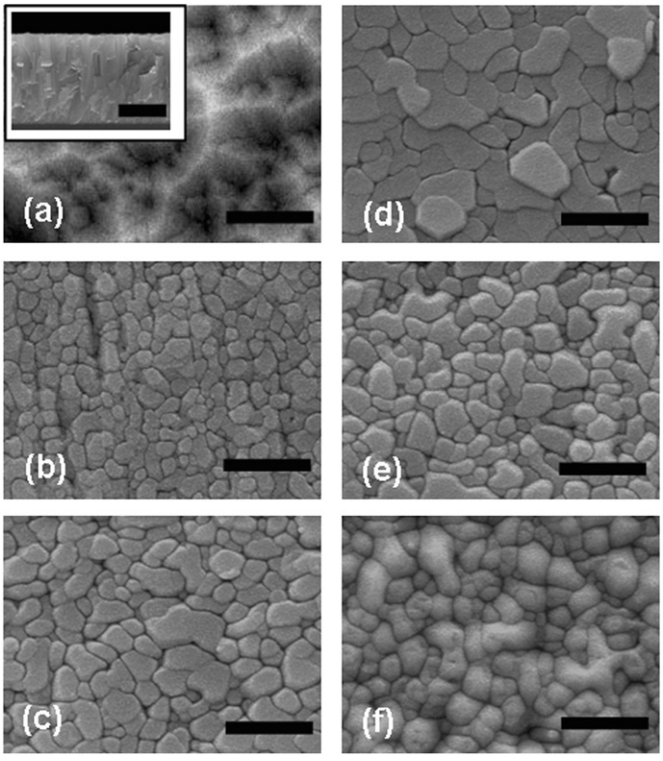


**Fig. 1.** SEM morphologies of (a) as-deposited ZnO films (the inset figure is the cross section image) and annealed at (b) 700 °C in $O_2$, (c) 800 °C in $O_2$, (d) 900 °C in $O_2$, (e) 800 °C in air, and (f) 800 °C in nitrogen (the scale bar is 500 nm).

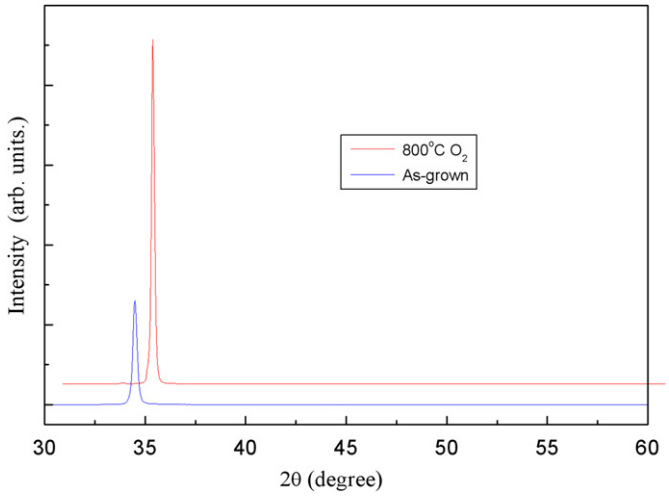


**Fig. 2.** XRD diffraction peaks of as-deposited and annealed ZnO films in $O_2$ at 800 °C.