Available online at www.sciencedirect.com
ScienceDirect
Journal of Luminescence 128 (2008) 297–300
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Structural and PL properties of Cu-doped ZnO films

Xingping Peng[a,c,*], Jinzhang Xu[b], Hang Zang[a], Boyu Wang[b], Zhiguang Wang[a]

[a]*Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou 73000, PR China*
[b]*School of Nuclear Science and Technology, Lanzhou University, Lanzhou 73000, PR China*
[c]*School of Physical Science and Technology, Lanzhou University, Lanzhou 73000, PR China*

Received 22 October 2006; received in revised form 16 July 2007; accepted 17 July 2007
Available online 18 September 2007

Abstract

Cu-doped ZnO films with hexagonal wurtzite structure were deposited on silicon (1 1 1) substrates by radio frequency (RF) sputtering technique. An ultraviolet (UV) peak at ~380 nm and a blue band centered at ~430 nm were observed in the room temperature photoluminescent (PL) spectra. The UV emission peak was from the exciton transition. The blue emission band was assigned to the Zn interstitial (Zn_i) and Zn vacancy (V_{Zn}) level transition. A strong blue peak (~435 nm) was observed in the PL spectra when the α_{Cu} (the area ratio of Cu-chips to the Zn target) was 1.5% at 100 W, and ZnO films had *c*-axis preferred orientation and smaller lattice mismatch. The influence of α_{Cu} and the sputtering power on the blue band was investigated.

Keywords: ZnO films; Cu-doped; XRD; Photoluminescence; RF sputtering

1. Introduction

ZnO is one of the most important II–IV compound semiconductors with many applications, such as ultraviolet (UV) light-emitters, varistors, transparent high-power electronics, surface acoustic wave devices, piezoelectric transducers, gas-sensing, window materials for display and solar cells, and so on [1–3].

ZnO has a wide band gap (~3.37 eV at room temperature) and high exciton binding energy (60 meV), which assure more efficiently excitonic emission at room temperature or high temperature [4,5]. Besides, it can be prepared at a lower temperature. Owing to these properties, ZnO has attracted increasing attention as a promising candidate material for potential applications in optoelectronic devices [4–9]. The emission properties of undoped and doped ZnO films have been widely studied [7–11].

In this paper, Cu-doped ZnO films had been deposited by radio frequency (RF) sputtering technique. A UV peak at ~380 nm and a blue emission band centered at ~430 nm were observed in the photoluminescent (PL) spectra at room temperature. The mechanism of blue emission band and the influence of Cu-chips on the structural and PL properties of samples were investigated and discussed.

2. Experimental details

High-purity Zn target (>99.99%, 100 mm in diameter) and silicon (1 1 1) substrates were used in the experiments. The distance between target and substrate was 50 mm. Before loading into the RF sputtering chamber, the silicon substrates were ultrasonically cleaned with acetone and alcohol in sequence, then dipped into the diluted HF solution (5%) to remove a native oxide layer on them, and finally rinsed with distilled water and dried in nitrogen. The sputtering chamber was evacuated to 5×10^{-3} Pa prior to the introduction of the $Ar–O_2$ gas mixture. The partial pressure ratio of oxygen, working pressure, deposited time and substrate temperature were fixed at 0.4, 2 Pa, 1 h, and 400 °C, respectively. The sputtering power was varied in the range of 100–200 W. In order to change the content of copper in the deposited ZnO films, Cu-chips were equably spread on the Zn target and the relative sputtering area

*Corresponding author. School of Physical Science and Technology, Lanzhou University, Lanzhou 73000, PR China. Tel.: +86 931 4969036; fax: +86 931 8272100.
E-mail address: pengxp@lzu.edu.cn (X. Peng).

0022-2313/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jlumin.2007.07.016

ratio of Cu-chips to the Zn target (α_{Cu}) varied in the range of 0–3%.

The structures of the Cu-doped ZnO films were characterized by using Rigaku Dmax 2400 XRD (Cu Kα, $\lambda = 0.1542$ nm). The PL spectra of the samples were measured at room temperature by using rf-5301 fluorescent spectrophotometer excited by wavelengths of 340 nm.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD pattern of the Cu-doped samples at 150 W. The six diffraction peaks of ZnO films appeared at $2\theta = 31.81°$, 34.46°, 36.27°, 47.54°, 56.60°, and 62.87°, which are corresponding to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), and (1 0 3) planes of ZnO films, respectively. The results indicated that ZnO films with hexagonal wurtzite structure were prepared by doped Cu-chips by using RF sputtering technique. The (0 0 2) diffraction peak was the strongest one when α_{Cu} was 1%. While α_{Cu} reached to 2.5%, the (0 0 2) diffraction peak of the samples was the weakest, and its intensity decreased 90%. The (0 0 2) peak values of the four samples were 34.32°, 34.24°, 34.36°, and 34.08°, respectively, which were smaller than that of the strain-free ZnO powder samples (34.43°). The lattice constant c of the samples, which could be calculated by Bragg formula, was 0.5222, 0.5233, 0.5216, and 0.5257 nm, respectively. The mismatch of the four samples is 0.3%, 0.5%, 0.2%, and 1.0% [12], respectively. With the increasing of α_{Cu}, the full width at half maximum (FWHM) of the (0 0 2) peak became wider and the orientation poorer. Especially, the samples had the high c-axis orientation and small mismatch when α_{Cu} was 1%.

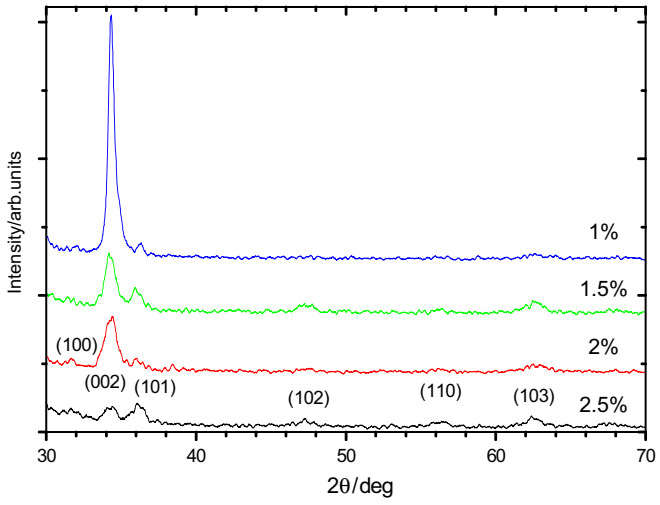

Fig. 1. The XRD pattern of Cu-doped ZnO films for various α_{Cu} at 150 W.

3.2. PL properties

Fig. 2 shows the PL spectra of Cu-doped ZnO films prepared at 150 W. A UV peak at ~380 nm (~3.26 eV) and a blue emission band at ~430 nm (~2.88 eV) were observed. A stronger blue double-peak which is located at ~410 nm (~3.03 eV) and ~438 nm (~2.83 eV) was observed in PL spectra when α_{Cu} was 2.5%. The UV emission peak came from the exciton transition [4–7]. When α_{Cu} was 1%, the intensity of blue emission band was weaker than that of undoped ZnO films. With the increasing α_{Cu}, the intensity of blue band became stronger, reached the maximum when α_{Cu} was 2.5%, and then decreased. The blue emission center shifted to shorter wavelength. The relationship of the blue band center and intensity versus α_{Cu} was shown in Fig. 3.

The blue emission might come from the intrinsic defects or/and Cu impurity. Zn interstitial (Zn_i) and oxygen vacancy (V_O) are main donor defects while Zn vacancy

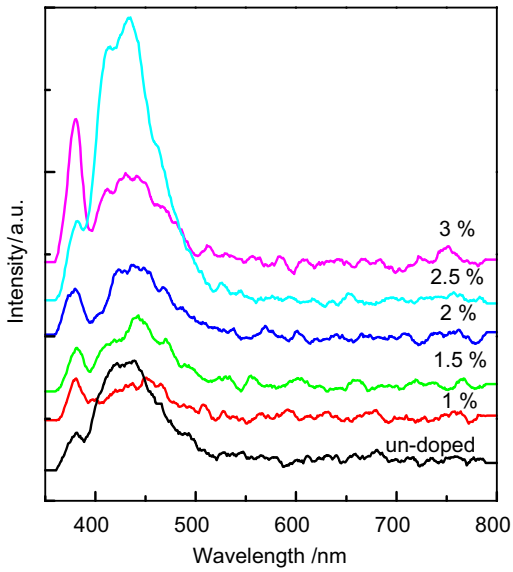

Fig. 2. The PL spectra of various α_{Cu} Cu-doped ZnO films at 150 W.

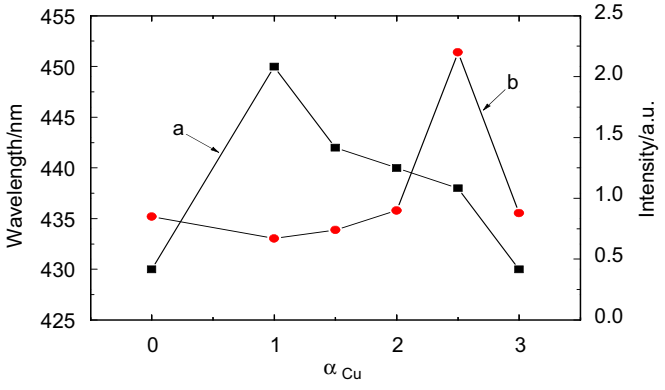

Fig. 3. The relationship of the blue band center (a) and intensity versus α_{Cu} (b).