Enhanced photoluminescence properties of Al doped ZnO films

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Abstract. Al doped ZnO films are fabricated by radio frequency magnetron sputtering. In general, visible emission is related to various defects in ZnO films. However, too much defects will cause light emission quench. So it is still a controversial issue to control appropriate defect concentrations. In this paper, based on our previous results, appropriate Al doping concentration is chosen to introduce more both interstitial Zn and O vacancy defects, which is responsible for main visible emission of ZnO films. A strong emission band located at 405 nm and a long tail peak is observed in the samples. As Al is doped in ZnO films, the intensity of emission peaks increases. Zn interstitial might increase with the increasing Al^{3+} substitute because ZnO was a self-assembled oxide compound. So Zn interstitial defect concentration in Al doped ZnO films will increase greatly, which results in the intensity of emission peaks increases.

1. Introduction

ZnO materials with both wide band gap (~3.37 eV) and large exciton binding energy (~60 meV) is an ideal material for optoelectronic devices [1]. It can also be applied to ultraviolet lasers, solar cells, laser diodes, transparent conductive contacts, thin film transistors and emitters [2]. Optical properties of ZnO have been investigated for a long time. Rao et al. [3] explained the role of defects in photoluminescence (PL) properties of ZnO. Hwang et al. [4] elucidated the surface plasmon resonance effects on enhancing the UV response in p-Si/n-ZnO heterojunction photodetectors. Tabib et al. [5] revealed a high density of defects in ZnO nanocrystals which are mainly oxygen vacancies. Rao et al. [6] integrated different ZnO nanostructures into white light-emitting diodes to improve quality in angular CCT uniformity. Shatnawi et al. [7] observed a strong correlation between the magnetic and optical behavior of the Co-doped ZnO nanoparticles.

In general, visible emission is related to various defects in ZnO films. As above mentioned, different methods are used to introduce defects to improve visible emission of ZnO. However, too much defects will cause light emission quench. So it is still a controversial issue to control appropriate defect concentrations. In this paper, based on our previous results [8], appropriate Al doping concentration is chosen to introduce more both interstitial Zn and O vacancy defects, which be responsible for main visible emission of ZnO films.

2. Experimental details

The samples are deposited on glass substrates by radio frequency and direct current magnetron co-sputtering. High-purity Al and ZnO targets (≥ 99.995%) are used in the experiment. The sputtering chamber is evacuated to 6×10^{-5} Pa before introducing Ar and O_2 mixed gas. Note that the substrate

rotation rate during sputtering process is maintained at 10 rpm. ZnO film is carried out in the growth ambient with O_2:Ar=15:25 (sccm) at room temperature (RT) and the sputtering power of 100 W is used during sputtering for 1 h. In addition, Al target is direct current co-sputtered at voltage of 150V and current of 0.15 A. To further improve the crystal quality and photoluminescence properties, the samples are annealed in 2×10^{-4} Pa vacuum at 350℃ for 1 h. Then the heated system is suddenly switched off and cooled down to room temperature.

X-ray diffraction (XRD) patterns of the samples are studied using a D/Max-2400 X-ray diffractometer. Scanning electron microscopy (SEM) images of the samples are characterized by a JEOL JSM-7600F field emission scanning electron microscope. Transmittance and absorption spectra are measured by a Jasco V-570 UV/VIS/NIR spectrophotometer. PL properties of the samples are measured by a FluoroMax-3 fluorescence spectrometer. All spectra are measured at room temperature.

3. Results and discussion

Figure 1 shows XRD patterns of ZnO (a) and Al doped ZnO films (b). A strong ZnO (002) diffraction peak centered at 34.38°, which is smaller than that of standard ZnO powder (2θ=34.42° [9]), is observed in ZnO films. This indicates that compressive stress is introduced in the ZnO film. As Al is doped in ZnO films, ZnO (002) peak shifts to 34.60°, as shown in the inset of figure 1. A tensile stress is formed in Al doped ZnO film. This indicates that Al atoms may incorporate interstitially or replace Zn atomic sites substitutionally in the ZnO hexagonal lattices. Compared with ZnO film, the full width at half maxima (FWHM) of the (002) peak in Al doped ZnO increased, implying that crystal quality is deteriorated after Al incorporation.
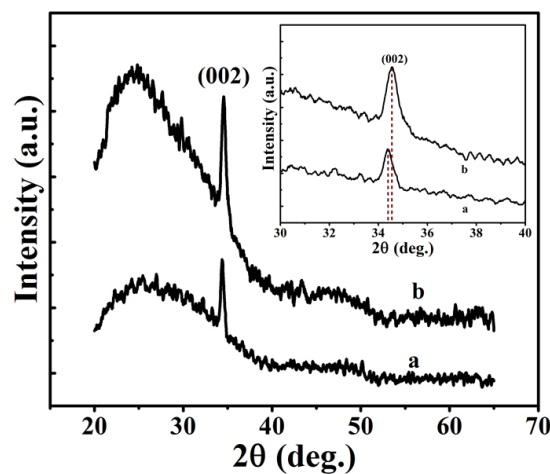
Figure 1. XRD patterns of ZnO (a) and Al doped ZnO films (b). The inset is the corresponding enlarged view.
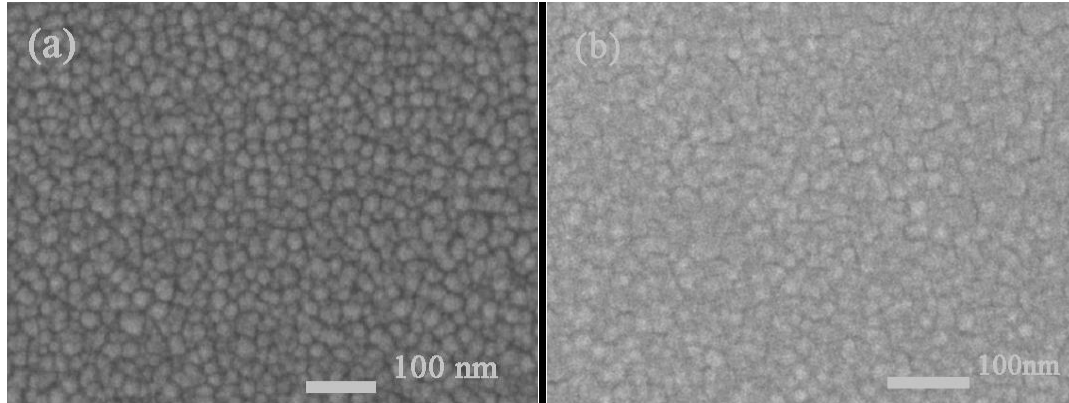
Figure 2 presents SEM images of ZnO (a) and Al doped ZnO films (b). Dense and irregular ZnO nano particles are observed in ZnO film. As Al is doped in ZnO films, ZnO nano particles become regular and even. This can be ascribed to compressive stress is introduced in the ZnO film, while a tensile stress is formed in Al doped ZnO film.

Figure 3 displays transmission spectra of ZnO (a) and Al doped ZnO films (b). It is clear that a transmittance of over 80% in the visible range of all the samples is obtained. It shows an excellent shoulder peak at 354 nm in ZnO film. As Al is doped in ZnO films, average transmittance increases and shoulder peak disappears.

Figure 4 illustrates $(ahv)^2$ vs hv plots of ZnO (a) and Al doped ZnO films (b). In order to calculate the direct optical band gap of samples, we used the Tauc relationships follows [10]:

$$\alpha h v = A\left(h v - E_g\right)^{\frac{1}{2}} \tag{1}$$
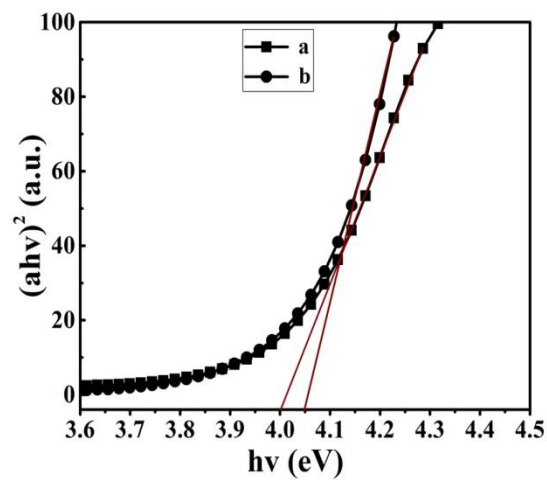
Where α is the absorption coefficient, A is a constant, h is Planck's constant, v is the photon frequency, E_g is the optical band gap. E_g values are 4.00 and 4.05 eV for ZnO and Al doped ZnO films, respectively.

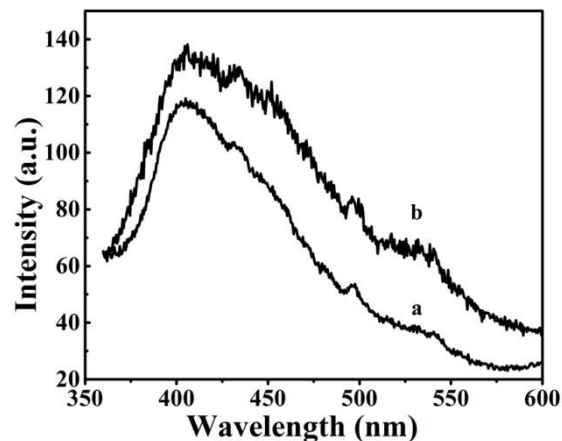**Figure 2.** SEM images of ZnO (a) and Al doped ZnO films (b).
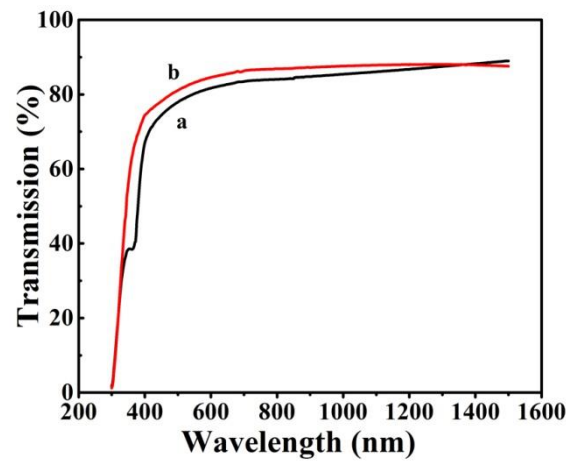
Figure 3. Transmission spectra of ZnO (a) and Al doped ZnO films (b).

Figure 4. $(ahv)^2$ vs hv plots of ZnO (a) and Al doped ZnO films (b).

Figure 5 depicts PL spectra of ZnO (a) and Al doped ZnO films (b). A strong emission band located at 405 nm and a long tail peak is observed in the samples. As Al is doped in ZnO films, the intensity of emission peaks increases.

The origin of the defect-related PL emission has been investigated for a long time. Several different hypotheses have been proposed, however, they are still under investigation. As Al is incorporated in ZnO, Al^{3+} may replace Zn^{2+} ions sites substitutionally in the ZnO hexagonal lattices because the radii of Al^{3+} (0.053 nm) is less than that of Zn^{2+} ions (0.074 nm). Zn interstitial might increase with the increasing Al^{3+} substitute because ZnO is a self-assembled oxide compound [11]. So Zn interstitial defect concentration in Al doped ZnO films will increase greatly, which results in the intensity of emission peaks increases. Interstitials Zn and oxygen vacancies are main donor defects while Zn vacancies and interstitials oxygen are main acceptor defects in intrinsic ZnO [12]. Kohan et al. [13] have calculated the energy levels of defects in ZnO thin films by the full-potential linear muffin-tin orbit method. The luminescence center observed in this work agrees quite well with Kohan's theoretical calculation. Therefore, the blue emission band is assigned to the electron transition from the Zn interstitial levels to the top of the valence band.

Figure 5. PL spectra of ZnO (a) and Al doped ZnO films (b).

4. Conclusions

Al doped ZnO films are fabricated by radio frequency magnetron sputtering. Based on our previous results, appropriate Al doping concentration is chosen to introduce more both interstitial Zn and O vacancy defects, which is responsible for main visible emission of ZnO films. As Al is doped in ZnO films, crystal quality is deteriorated, average transmittance increases and optical band gap decreases. In addition, the intensity of emission peaks increases. In ZnO film, a strong emission band located at 405 nm and a long tail peak is observed in the samples. As Al is doped in ZnO films, the intensity of emission peaks increases. The enhanced mechanism is discussed. The luminescence center observed in this work agrees quite well with previous theoretical calculation. Therefore, the blue emission band is assigned to the electron transition from the Zn interstitial levels to the top of the valence band. This work may help the development of advanced photoelectric devices based on ZnO materials.

References
[1]   Godlewski M, Guziewicz E, Kopalko K, Luka G, Lukasiewicz MI, Krajewski T, Witkowski BS

and Gierałtowska S 2011 *Low Temp. Phys.* **37** 235-240

[2] Ding J J, Wang M Q, Zhang X Y, Ran C X, Shao J Y and Ding Y C 2014 *Appl. Phys. Lett.* **105** 233106

[3] Rao T P, Goswami G K and Nanda K K 2014 *J. Appl. Phys.* **115** 213513

[4] Hwang J D, Wang F H, Kung C Y, Lai M J and Chan M C 2014 *J. Appl. Phys.* **115** 173110

[5] Tabib A, Bouslama W, Sieber B, Addad A, Elhouichet H, Férid M and Boukherroub R 2017 *Appl. Surf. Sci.* **396** 1528-1538

[6] Rao L S, Tang Y, Li Z T, Ding X R, Li J S, Yu S D, Yan C M and Lu H G 2017 *Optics Express* **25** A432-A433

[7] Shatnawi M, Alsmadi A M, Bsoul I, Salameh B, Alnawashi G A, Al-Dweri F and El Akkad F 2016 *J. Alloys Compd.* **655** 244-252

[8] Chen H X, Ding J J, Wang X M, Wang X J, Chen G X and Ma L 2016 *Optical Materials* **62** 505-511

[9] Chen Y, Bagnall D M, Koh H J, Park K, Hiraga K, Zhu Z and Yao T 1998 *J. Appl. Phys.* **84** 3912-3918

[10] Girtan M and Folcher G 2003 *Surf. Coat. Technol.* **172** 242-250

[11] Ding J J, Ma S Y, Chen H X, Shi X F, Zhou T T and Mao L M 2009 *Physica B* **404** 2439-2443

[12] Zhang S B, Wei S H and Zunger A 2001 *Phys. Rev. B* **63** 075205

[13] Kohan A F, Ceder G and Morgan D 2000 *Phys. Rev. D* **61** 15019