Structural and optical properties of Zn-doped β-Ga_2O_3 films*

Yue Wei(岳伟), Yan Jinliang(闫金良)†, Wu Jiangyan(吴江燕), and Zhang Liying(张丽英)

School of Physics, Ludong University, Yantai 264025, China

Abstract: Intrinsic β-Ga_2O_3 and Zn-doped β-Ga_2O_3 films were prepared using RF magnetron sputtering. The effects of the Zn doping and thermal annealing on the structural and optical properties are investigated. In comparison with the intrinsic β-Ga_2O_3 films, the microstructure, optical transmittance, optical absorption, optical energy gap, and photoluminescence of Zn-doped β-Ga_2O_3 films change significantly. The post-annealed β-Ga_2O_3 films are polycrystalline. After Zn doping, the crystallization deteriorates, the optical band gap shrinks, the transmittance decreases and the UV, blue, and green emission bands are enhanced.

Key words: transparent conductive oxides; Zn-doped β-Ga_2O_3; optical transmittance; optical band gap; photoluminescence

DOI: 10.1088/1674-4926/33/7/073003 **PACC:** 7360F; 7855; 4225B

1. Introduction

A need for ultraviolet transparent conductive oxide (UV TCO) films has recently emerged for use as antistatic electric layers of the phase masks used for photolithography and as transparent electrodes for UV optoelectronic devices[1, 2]. Development of UV TCO thin films is a challenge from a material science point of view because materials with a wider band gap tend to exhibit smaller conductivity. Conventional TCOs such as ZnO are opaque for the deep-UV light (< 300 nm) due to a narrow band gap (3.4 eV). New TCO materials need to be explored in order to improve ultraviolet transparency. There are several difficulties in fabricating deep-UV transparent films. Since the position (scaled from the vacuum level) of the conduction band bottom is relatively high, the donor levels tend to become deep levels. Introduction of the shallow donor levels into the compounds for efficient release of electrons into the conduction band is more difficult than in narrow gap oxides. This significantly reduces the number of candidate materials for deep-UV TCOs. β-Ga_2O_3 is a wide band (4.8 eV) intrinsic insulator[3−6] and can be changed to n-type semiconductor by doping[7]. It is suitable for the next generation of optoelectronic devices operating at ultraviolet wavelength.

β-Ga_2O_3 films with n-type conductivity up to 8.2 S/cm were reported by Orita in 2002[1]. Kiyoshi reported that the photoluminescence of the β-Ga_2O_3 could be improved by Si doping[8]. The Si-doped β-Ga_2O_3 and Sn-doped β-Ga_2O_3 behave as the n-type semiconductor because of donor impurity and oxygen deficiency[9]. To prepare β-Ga_2O_3 based semiconductor optoelectronic devices, P-type β-Ga_2O_3 films are needed. As one of group IIB elements，Zn could be a potential dopant for β-Ga_2O_3. The radius of Zn^{2+} is similar to Ga^{3+}, thus Zn atom can substitute Ga atom efficiently. To the best of our knowledge, few reports have been published on the structural and optical properties of Zn-doped Ga_2O_3 thin films, especially by means of magnetron sputtering.

In this article, the intrinsic Ga_2O_3 and Zn-doped Ga_2O_3 films are prepared using RF magnetron sputtering, the effects of the Zn doping and thermal annealing on the structural and optical properties of the films are investigated.

2. Experiment

The Zn-doped β-Ga_2O_3 films (2 wt%) were deposited on Si (111) and UV transparent quartz (JGS1) substrates by RF magnetron sputtering a Ga_2O_3 ceramic target at the power of 70 W in a Ar/O_2 (1 : 1) mixture atmosphere for 4 h. Before deposition, the quartz glass substrates were ultrasonically cleaned in acetone and alcohol, rinsed in deionized water and subsequently dried in flowing nitrogen gas. The sputtering chamber was evacuated to a base pressure of 6×10^{-4} Pa. The thickness of the films is about 320 nm. The films were prepared at room temperature (RT) and then annealed in vacuum for 2 h at 800 ℃. The crystal orientation, photoluminescence, optical transmittance and optical absorption of the samples were characterized using X-ray diffraction (D/MAX2500V) with a Cu-Kα radiation source, a fluorescence spectrometer (RF-5301) and a double beam spectrophotometer (TU1901) by taking the glass substrates into consideration.

3. Results and discussion

3.1. Crystal structure

The XRD patterns of intrinsic β-Ga_2O_3 films and Zn-doped β-Ga_2O_3 films deposited on Si substrate and post-annealed in vacuum are shown in Fig. 1. Two predominant peaks Si (111) and β-Ga_2O_3 (111) are observed. It means that the post-annealed intrinsic β-Ga_2O_3 and Zn-doped β-Ga_2O_3 films are polycrystalline and the Ga atoms are substituted by the Zn atoms without changing the crystal structure. The intensity of the β-Ga_2O_3 (111) peak becomes weak after Zn doping

* Project supported by the National Natural Science Foundation of China (No. 10974077), the Natural Science Foundation of Shandong Province, China (No. 2009ZRB01702), and the Shandong Province Higher Educational Science and Technology Program, China (No. J10LA08).

† Corresponding author. Email: yanjinliang@yahoo.cn

Received 1 January 2012, revised manuscript received 14 February 2012

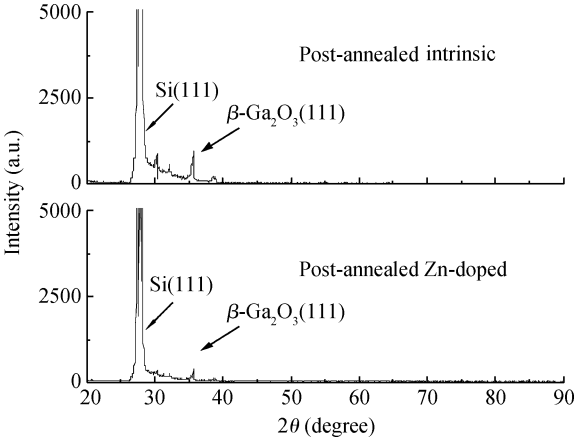

Fig. 1. XRD patterns of intrinsic β-Ga_2O_3 films and Zn-doped β-Ga_2O_3 films deposited on a Si substrate and post-annealed in vacuum at 800 ℃ for 2 h.

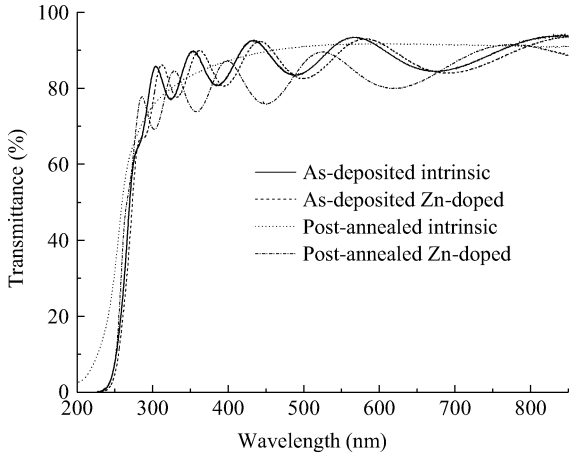

Fig. 2. Optical transmittance of as-deposited β-Ga_2O_3 films and post-annealed β-Ga_2O_3 films.

which indicates that the crystallization deteriorates. The position of the β-Ga_2O_3 (111) peak shifts from 35.69° to 35.66° because of the different radius of Zn^{2+} and Ga^{3+} (Zn^{2+}: 0.074 nm, Ga^{3+}: 0.062 nm).

3.2. Optical properties

The optical transmittance of as-deposited β-Ga_2O_3 films and post-annealed β-Ga_2O_3 films is shown in Fig. 2. The as-deposited films show high transparency in the visible region with an average transmittance above 90% and an excellent transmittance of more than 75% in the UV region (300–400 nm). Before annealing, the Zn-doped films have a slightly low transmittance. After annealing, the transmittance of Zn-doped films decreases obviously in the UV and visible region. It means the Zn dopant is activated by annealing.

The optical absorption of β-Ga_2O_3 films before and after annealing is shown in Fig. 3. All the films have a sharp absorption edge in the deep UV region. Before annealing, the absorption of the films increases after Zn doping. After annealing, the absorption decreases obviously for the intrinsic films and increases for the Zn-doped films. The near-edge absorption appears in the post–annealed Zn-doped β-Ga_2O_3 films, which

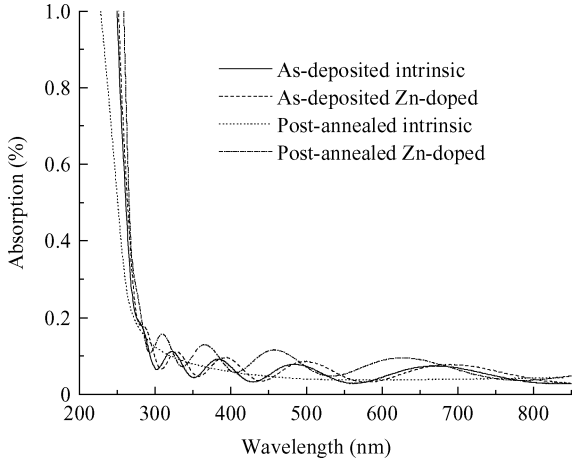

Fig. 3. Optical absorption of as-deposited β-Ga_2O_3 films and post-annealed β-Ga_2O_3 films.

indicates that the doped Zn atoms are activated effectively after annealing and act as acceptors. Thus, the states of Zn acceptors in the band gap of Zn-doped β-Ga_2O_3 films should be responsible for the near-edge absorption. The near-edge absorption represents transitions from singly ionized Zn acceptors to the conduction band bottom or from singly ionized Zn acceptors to deep level donors such as oxygen vacancy (V_O) or intrinsic defects[10]. The appearance of absorption of as-deposited Zn-doped films means that the Zn dopant is not activated before annealing, therefore, the increase of the absorption of post-annealed Zn-doped films should be mainly attributed to the activation of Zn dopant.

The optical band gaps of Zn-doped β-Ga_2O_3 films are estimated by extrapolating the linear portion of the square of absorption coefficient against photon energy using Eq. (1).

$$(\alpha h\nu)^2 = A(h\nu - E_g). \quad (1)$$

Here A is a constant. Before annealing, the obtained optical band gaps of the intrinsic β-Ga_2O_3 and the Zn-doped β-Ga_2O_3 films are 4.90 eV and 4.87 eV, shown in Fig. 4(a). It indicates that the Zn dopant could reduce the forbidden band gap as a result of lattice mismatch or stress. The optical band gaps of the post-annealed intrinsic β-Ga_2O_3 and Zn-doped β-Ga_2O_3 films are 5.1 eV and 4.80 eV, shown in Fig. 4(b). As shown in Fig. 1, the crystallization of the intrinsic β-Ga_2O_3 films is improved after annealing and some defect states in the forbidden band are reduced, thus the optical band gap is expanded. For the Zn-doped β-Ga_2O_3 films, the obvious change of the optical band gap should be attributed to the efficient activation of the Zn dopant which introduces the acceptor energy levels on the top of the valence band after annealing.

3.3. Photoluminescence

Room temperature photoluminescence (PL) spectra of post-annealed intrinsic β-Ga_2O_3 films and Zn-doped β-Ga_2O_3 films are shown in Fig. 5, in which the green emission, the UV emission and the blue emission can be observed. The intensity of the emission systematically increases after Zn doping. For intrinsic β-Ga_2O_3 films, the UV emission and blue emission could be divided into four Gaussian peaks which are located at

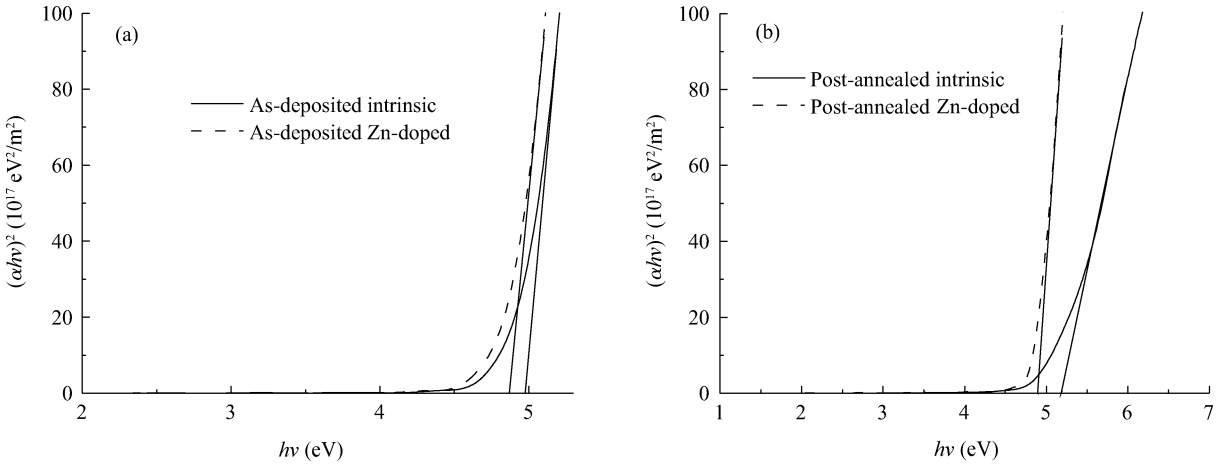

Fig. 4. (a) Optical band gap of as-deposited intrinsic β-Ga_2O_3 films and Zn-doped β-Ga_2O_3 films. (b) Optical band gap of post-annealed intrinsic β-Ga_2O_3 films and Zn-doped β-Ga_2O_3 films.

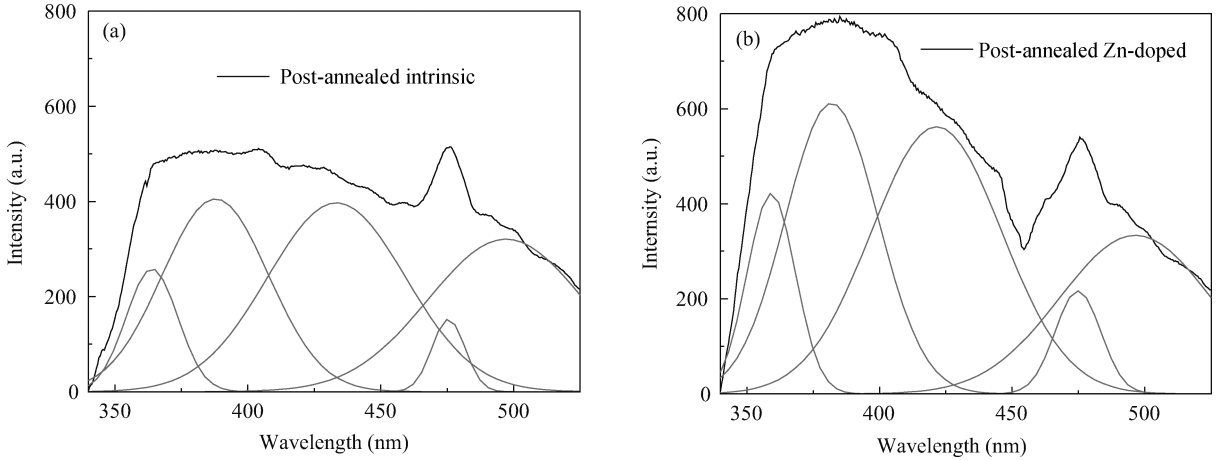

Fig. 5. Photoluminescence spectra of (a) post-annealed intrinsic β-Ga_2O_3 films and (b) Zn-doped β-Ga_2O_3 films.

364 nm, 391 nm, 427 nm and 476 nm. At the same time, the green emission peak is located at 497 nm. The positions of the peaks change slightly after Zn doping.

The UV emission could be attributed to the recombination of self-trapped excitons[11]. Blue luminescence is associated with the recombination of a trapped electron in a donor with a trapped hole in an acceptor. Oxygen vacancies V_O^X or Ga interstitials Ga_i^X are proposed as donors[12, 13]. The gallium-oxygen vacancy pairs $(V_O, V_{Ga})'$ are proposed as acceptors. These donor-acceptor pairs can form trapped excitons resulting in the blue emission according to the following process: $(V_O, V_{Ga})^X + V_O^X \rightarrow (V_O, V_{Ga}) + V_O^\bullet + h\nu$[13]. Moreover, Zn substituting Ga $(Zn_{Ga})'$ should be another acceptor, so the blue luminescence is greatly enhanced when the $(Zn_{Ga})'$ concentration increases after Zn doping. The broad green band emission which is located at 497 nm is generated by the radial recombination of a photo-generated hole in V_{Ga} or V_{Ga} : V_O and Zn_{Ga} with the electron in ionized V_O.

4. Conclusion

The structural and optical properties of the intrinsic β-Ga_2O_3 films and the Zn-doped β-Ga_2O_3 films are discussed before and after annealing. The transmittance of the as-deposited Zn-doped β-Ga_2O_3 films is comparable to that of the as-deposited intrinsic films. The absorption of the as-deposited Zn-doped β-Ga_2O_3 films is higher than that of the as-deposited intrinsic ones. After annealing, both the intrinsic β-Ga_2O_3 films and the Zn-doped β-Ga_2O_3 films are polycrystalline. The average absorption decreases for the intrinsic films and increases significantly for the Zn-doped films. Three characteristic emission bands are observed, the UV emission and the blue emission are enhanced after Zn doping.

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