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Preparation and Properties of Zn-doped β-Ga_2O_3 Films

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Abstract: β-Ga_2O_3 is a wide band gap semiconductor with a band gap of $E_g \approx 5.0$ eV, which has potential optical and optoelectronic applications. The intrinsic β-Ga_2O_3 and Zn-doped β-Ga_2O_3 films were prepared on Si (111) and UV transparent quartz substrates using RF magnetron sputtering. The optical transmission, optical absorption, structural property, photoluminescence were measured using a double beam spectrophotometer, X-ray diffractometer, fluorescence spectrometer. The effects of the Zn doping and thermal annealing on the structural and optical properties were investigated. The post-annealed β-Ga_2O_3 films are polycrystalline. In comparison with the intrinsic β-Ga_2O_3 films, the intensity of the Zn-doped β-Ga_2O_3 (111) peak becomes weak, the crystallization deteriorates, the (111) peak position shifts from 35.69° to 35.66°. For the post-annealed Zn-doped β-Ga_2O_3 films, the optical band gap shrinks, the transmittance decreases, the absorption increases, the near-edge absorption appears, and the UV, blue, green emission bands are enhanced. It means that the doped Zn atoms are activated effectively after annealing and act as acceptors.

Key words: Zn-doped β-Ga_2O_3; Optical transmittance; Optical band gap; Photoluminescence

CLCN: O484.4; O472.3 **Document Code**: A **Article ID**: 1004-4213(2012)10-1242-5

0 Introduction

A need for ultraviolet transparent conductive oxide (UV TCO) films has recently emerged for use as antistatic electric layers of phase masks for photolithography and as transparent electrodes for UV optoelectronic devices[1-2]. Development of UV TCO thin films is a challenge from the 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 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 TCO. 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 optoelectronic devices operating at ultraviolet wavelength.

β-Ga_2O_3 films with n-type conductivity up to 8.2 S. cm^{-1} were reported by Masahiro 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

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properties of the films are investigated.

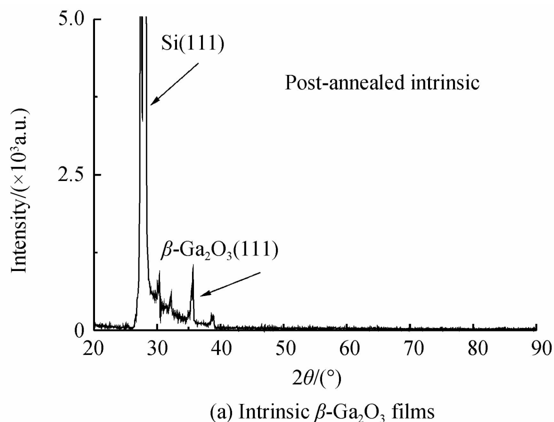
1 Experiment

The β-Ga_2O_3 films and 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 and a Zn-doped 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 320nm. 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 (Y-2000) with Cu-Kα radiation source, fluorescence spectrometer (RF-5301) and double beam spectrophotometer (TU1901) by taking the glass substrates into consideration.

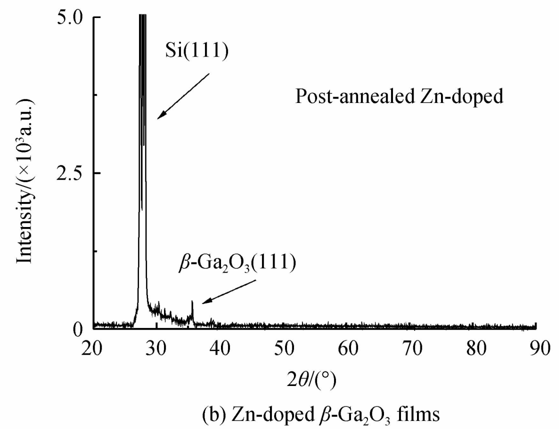
2 Results and discussion

2.1 Crystal structure

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 which indicates that the crystallization deteriorates. The position of β-Ga_2O_3(111) peak shifts from 35.69°



(a) Intrinsic β-Ga_2O_3 films



(b) Zn-doped β-Ga_2O_3 films

Fig. 1 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 at 800℃ for 2 h

to 35.66° because of different radius of Zn^{2+} and Ga^{3+} (Zn^{2+}: 0.074 nm, Ga^{3+}: 0.062 nm).

2.2 Optical properties

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 more than 75% in the UV region (300～400 nm). Before annealing, the Zn-doped films have a slight 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.

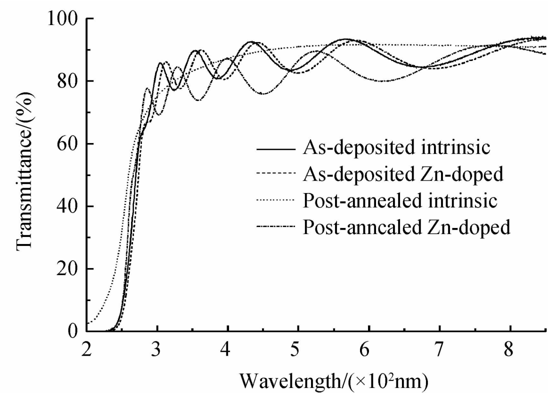


Fig. 2 Optical transmittance of as-deposited β-Ga_2O_3 films and post-annealed β-Ga_2O_3 films

Optical absorption of β-Ga_2O_3 films before and after annealing is shown in Fig. 3. All the films have 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 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.

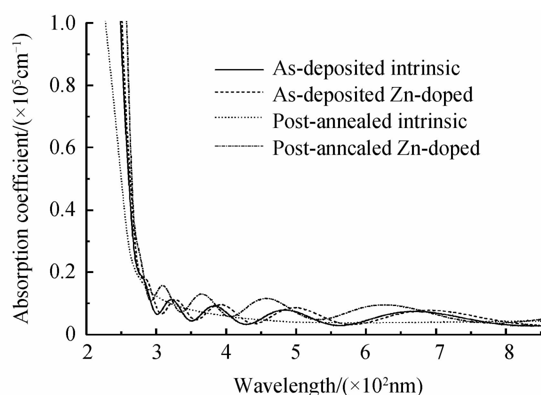


Fig. 3 Optical absorption of as-deposited β-Ga_2O_3 films and post-annealed β-Ga_2O_3 films

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 equation (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 film 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 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.

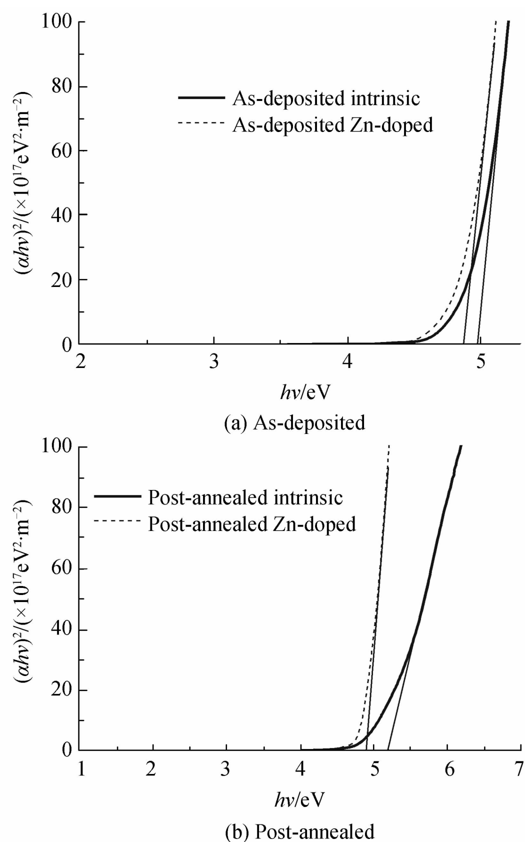
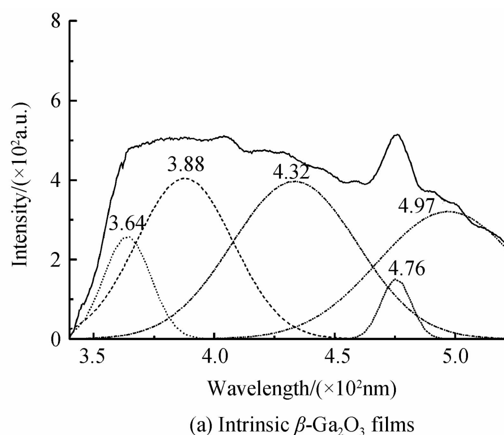
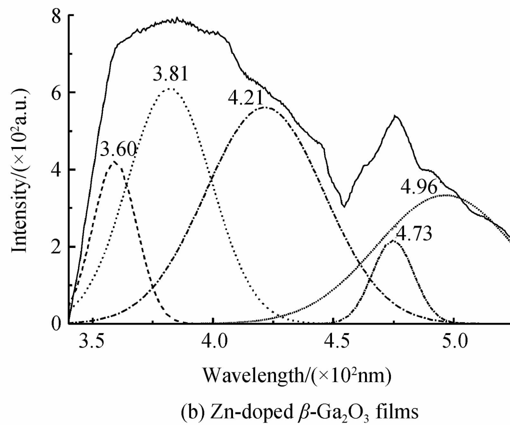


Fig. 4 Optical band gap of intrinsic β-Ga_2O_3 films and Zn-doped β-Ga_2O_3 films

2.3 Photoluminescence

Room temperature photoluminescence 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 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 364 nm, 391 nm, 427 nm and 476 nm. At the same time, the green emission peak is located at 497 nm. The positions





(b) Zn-doped β-Ga_2O_3 films

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

of the Gaussian peaks corresponding to Zn-doped β-Ga_2O_3 films are located at 360 nm, 381 nm, 421 nm, 473 nm and 496 nm, which 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 $V_O^{\times}$ or Ga interstitials $Ga_i^{\times}$ 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[13]

$$(V_O, V_{Ga})^{\times} + V_O \rightarrow (V_O^{\times}, V_{Ga}) + V_O^{*} + h\nu \quad (2)$$

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.

3 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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Zn 掺杂 β-Ga_2O_3 薄膜的制备和特性研究

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摘　要：β-Ga_2O_3 是一种宽带隙半导体材料，能带宽度 $E_g \approx 5.0$ eV，在光学和光电子学领域有广泛的应用．用射频磁控溅射方法在 Si 衬底和远紫外光学石英玻璃衬底制备了本征 β-Ga_2O_3 薄膜及 Zn 掺杂 β-Ga_2O_3 薄膜，用紫外-可见分光光度计、X 射线衍射仪、荧光分光光度计对本征 β-Ga_2O_3 薄膜及 Zn 掺杂 β-Ga_2O_3 薄膜的光学透过、光学吸收、结构和光致发光进行了测量，研究了 Zn 掺杂和热退火对薄膜结构和光学性质的影响．退火后的 β-Ga_2O_3 薄膜为多晶结构，与本征 β-Ga_2O_3 薄膜相比，Zn 掺杂 β-Ga_2O_3 薄膜的 β-Ga_2O_3(111)衍射峰强度变小，结晶性变差，衍射峰位从 35.69°减小至 35.66°．退火后的 Zn 掺杂 β-Ga_2O_3 薄膜的光学带隙变窄，光学透过降低，光学吸收增强，出现了近边吸收，薄膜的紫外、蓝光及绿光发射增强．表明退火后 Zn 掺杂 β-Ga_2O_3 薄膜中的 Zn 原子被激活充当受主．

关键词：Zn 掺杂 β-Ga_2O_3；光学透过；光学带隙；光致发光