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Preparation and photoluminescence studies of high-quality AZO thin films grown on Zno buffered Si substrate

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ABSTRACT

Al-doped ZnO (AZO) films were deposited by radio frequency (RF) reactive magnetron sputtering. The effects of buffer layer, annealing temperature and atmosphere on the structure, crystallinity and optical properties of epitaxial AZO films were investigated. The XRD results indicate that AZO thin films deposited on buffer layer has a better *c*-axis preferentially oriented growth than AZO films without buffer layer, and a better crystal quality can be obtained by an appropriate annealing process. The PL spectra show excellent UV/vis light-emitting characteristics: 387 nm, 424 nm, 463 nm and 506 nm. The intensities of the UV/vis peaks change when AZO films are annealed in oxygen or vacuum at different temperatures. The origin of the UV/vis emissions is discussed and the photoluminescence mechanism of AZO films is suggested.

1. Introduction

Zinc oxide (ZnO) is a transparent semiconductor with natural n-type conductivity, which is widely used as transparent conducting film (TCO) in semiconductor industry due to its low cost as well as its excellent electrical, optoelectronic, luminescent properties and nontoxicity [1–3]. The origin of nature n-type conductivity for ZnO is believed mainly due to intrinsic point defects like oxygen vacancy (V_O) and zinc interstitial (Zn_i). There have been many efforts to improve the electrical and optical properties of ZnO films by doping Al, B, In or Ga, the conductivity of ZnO films can be enhanced with control of intrinsic defects or the appropriate extrinsic dopants (Al, Ga, F, B, etc.) [1,4]. Among these dopants, Al is most promising to achieve high-quality Al-doped ZnO (AZO) film. Al is an efficient n-type dopant for realizing high-quality films with high conductivity, ultraviolet/blue light emission and high visible light transmittance [5,6]. Further more, AZO films are very important as substrates for deposition of the gold nanoparicles for nonlinear optics [7].

The direct growth of ZnO film on Si substrates may introduce large residual stress because of the different thermal expansion coefficients. Lattice mismatch between ZnO films and Si substrates make the growth of high-quality ZnO thin films particularly difficult [8]. Several researchers research the growth of epitaxial ZnO thin films by introducing hetero-buffer layers (such as SiO_2, GaN) and ZnO homo-buffer layer. We attempt to grow high-quality AZO thin films with excellent white light emission by introducing ZnO homo-buffer layers between AZO and Si substrates.

In this paper, AZO thin films are deposited on ZnO buffer layers by RF magnetron sputtering. The effects of buffer layer, annealing temperature and annealing atmosphere on the structure, morphology, crystallinity and optical properties of AZO thin films are investigated in detail.

2. Experimental

AZO thin film was deposited on ZnO buffer layers from a high-purity Zn target (99.9999%, 60 mm in diameter). Al foils (99.9%) were pasted to Zn target. The film growth was carried out at a sputtering pressure of 2 Pa while flowing Ar gas at 18 sccm and O_2 gas at 10 sccm. The substrate was fixed at 300 °C the sputtering power was 100 W. Here, the ZnO buffer layer was coated by RF magnetron sputtering on a p–Si (100) substrate. The settings used during the buffer layer growth were a substrate temperature of 300 °C, RF power of 60 W, pressure of 1 Pa. For comparison, AZO film without buffer layer was deposited under the similar conditions. In order to investigate the effect of annealing temperature and atmosphere on crystallinity and photoluminescence properties of AZO thin film, four identical AZO films with ZnO buffer layer

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and AZO thin films deposited on non-buffered substrate were subsequently annealed in vacuum or oxygen at temperature of 400 °C and 500 °C for 1 h, respectively.

The microstructure of the AZO thin films was investigated by XRD (D/Max-2400, λ=0.1541 nm). The surface morphologies were observed by SEM (JSM-6701F). The optical properties and crystal defects were examined by photoluminescence (PL) (RF-5301, the spectral resolution of the PL is 1 nm).

3. Results and discussion

3.1. Effect of ZnO buffer layer on the morphology and microstructure of AZO films

Fig. 1 presents the SEM images of AZO thin films deposited on Si substrate and ZnO buffered substrates, respectively. It can be seen that the AZO thin films are composed of countless ZnO grains and the surface of AZO thin films are rough. The results demonstrate that AZO films can be successfully grown on Si substrates with ZnO buffer layer. The AZO thin film grown on ZnO buffered Si substrate shows a clearer granular growth feature, and the average grain size shown in Fig. 1(b) are bigger than the sample without buffer layer.

Fig. 2(a) shows the typical EDS pattern of AZO thin film. The Al doping concentration is about 2.36 at%. Fig. 2(b) displays the XRD patterns of the two AZO thin films. The results indicate that AZO films deposited on buffer layer has a better preferential orientation along *c*-axis. Comparing with AZO film grown on non-buffered substrate, the (002) diffraction peak of AZO film grown on buffered substrate narrows obviously, indicating the crystallite size becomes bigger. Furthermore, 2θ for (002) peak of AZO film grown on buffered substrate has slightly right shift. Such a result was also observed by Ri et al., which is attributed to compressive stress [9]. The average grain sizes of AZO thin film grown on the non-buffered and ZnO buffered substrates are estimated to be about 13.4 nm and 18.4 nm, respectively. The results suggest that the crystalline quality of AZO film can be improved greatly due to the introduction of compliant ZnO buffer layer. ZnO buffer layer may relax partial stress induced by large crystal lattice and thermal mismatch between AZO film and Si substrate. Moreover, increase in crystallite size can reduce grain boundary scattering and leads to a decrease in surface roughness [1]. Low surface roughness increases the transmittance of AZO thin film, resulting in less light scattering. The crystallinity of AZO thin film grown on the ZnO buffered substrates is better than that of non-buffered.

3.2. Effect of annealing temperature and atmosphere on crystallinity and PL properties of AZO films

Fig. 3 shows XRD patterns of AZO thin films annealed in vacuum and oxygen atmospheres at different annealing temperatures. Polycrystalline nature of the sample is confirmed. The crystalline films show highly *c*-axis preferentially orientation. All the diffraction peaks coincide well with standard data profile of the hexagonal wurtzite ZnO phase (JCPDS No. 36–1451).

Fig. 4 depicts PL spectra of the AZO films on ZnO buffered substrates. Two asymmetric peaks (395 nm and 468 nm) are observed. The peaks of each AZO film can be Gaussian divided into four components: a strong near-band-edge emission (NBE) at 387 nm, a violet peak located at about 424 nm, a blue peak located at 463 nm and one green peak located at about 506 nm.

The luminescence mechanism of AZO films has been investigated for a long time. The UV emission is usually considered as the characteristic emission of ZnO, which is attributed to the band-edge transition or the recombination of free excitons through an exciton–exciton collision process [10]. Fig. 4 shows that there are significant changes in NBE UV emission with annealing in different environments. Intensity of the NBE peaks increases with increasing annealing temperature either annealed in oxygen or vacuum, as shown in Fig. 4(b) and (d). As reported by Zeng et al., the increasing UV emission corresponds to the crystallinity of ZnO particles [11]. Higher annealing temperature in our experiment is benefit to the crystallinity of ZnO particles, which leads the enhancement of UV emission.

For AZO films annealed in oxygen or vacuum, the intensity of the violet peak reduces with increasing annealing temperature. For AZO films annealed in oxygen, the intensity of the blue/green peak decrease with increasing annealing temperature. Intensities of the two visible emission of AZO films annealed in vacuum increase with increasing annealing temperature.

The visible emission (violet/blue/green emission) are universally considered to be associated with the intrinsic or extrinsic defects in ZnO, such as oxygen vacancies (V_O), zinc vacancies (V_{Zn}), oxygen atoms at zinc position in crystal lattices (O_{Zn}) and Zn interstitials (Zn_i) [12]. Prabakar et al. [13] observed a violet peak appeared about 2.97 eV, which was attributed to radiation transition related interface traps existing at grain boundaries. According to the report from Jin et al. [14], the violet luminescence is due to the defect level transition in grain boundaries of AZO films. Interface traps exist in the depletion regions of ZnO–ZnO grain boundaries, and the level of the interface trap has been found to be about 0.33 eV below the conduction band edge. Therefore, the violet peak is probably due to defects in radiation-induced interface-trap formation. The PL intensity of violet emission decreases with increasing annealing temperature, which may be ascribed to the decrease of grain boundary defects of AZO thin films.

AZO films show strong blue/green luminescence peaks located

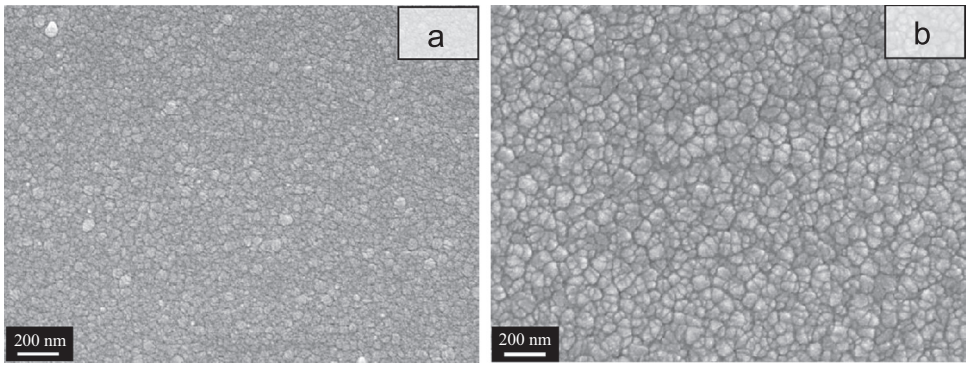

Fig. 1. SEM images of AZO thin films deposited on (a) Si substrates and (b) ZnO buffered substrates.