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Influence of post-annealing atmosphere on microstructure, optical and electrical properties of zinc cadmium oxide films deposited by DC and RF magnetron co-sputtering

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ABSTRACT

Zinc cadmium oxide ($Zn_{1-x}Cd_xO$) films were deposited on quartz substrates by direct current (DC) and radio frequency (RF) reactive magnetron co-sputtering and the influence of post-annealing atmosphere on their microstructure, optical and electrical properties were investigated by X-ray diffraction (XRD), optical absorbance, photoluminescence (PL) and Hall measurements. Results indicate that the band gap (E_g) of all $Zn_{1-x}Cd_xO$ films annealed in different atmospheres are smaller than that of the undoped ZnO, the observed shifts in E_g being 0.43, 0.37 and 0.32 eV for the $Zn_{1-x}Cd_xO$ films annealed in argon, oxygen and vacuum, respectively. Hall measurement results indicate that all $Zn_{1-x}Cd_xO$ films annealed in different atmospheres show the n-type conduction, but the $Zn_{1-x}Cd_xO$ film annealed in vacuum has low resistivity and high concentration, which has room-temperature resistivity of 1.59 Ω cm and carrier concentration of 2.07×10^{17} cm^{-3}. Compared with $Zn_{1-x}Cd_xO$ films annealed in oxygen and argon, $Zn_{1-x}Cd_xO$ film annealed in vacuum has the best crystal quality, luminescence and electrical properties. The influencing mechanism of the post-annealing atmosphere on the electrical and optical properties of the $Zn_{1-x}Cd_xO$ film is discussed.

1. Introduction

ZnO is an II–VI compound semiconductor with a wide direct band gap of 3.37 eV at room temperature [1]. It has an exciton binding energy of 60 meV larger than that of Ga–N and high exciton emission efficiency. Due to these features, it can be used for optoelectronic devices such as light-emitting diodes (LEDs) and laser diodes (LDs) operating in the visible and ultraviolet region, etc [2]. In order to design ZnO- based optoelectronic devices, an important step is the realization of band-gap engineering to create barrier layers and quantum wells in device heterostructure. The band gap of ZnO can be engineered by cationic (Cd^{2+} or Mg^{2+}) substitution, which is a versatile tool to tune structural, electrical and optical properties [3]. For narrowing the band gaps, CdO with rocksalt structure will be an appropriate candidate which has a narrow band gap of 2.38 eV [4]. Alloying with CdO, the band gap of ZnO can be modulated and the luminescence of $Zn_{1-x}Cd_xO$ alloy films can cover the UV to green spectrum [5]. Therefore, the $Zn_{1-x}Cd_xO$ alloy is also important and useful to construct appropriate ZnCdO-related heterostructures or quantum well structures, which are the key elements in ZnO-based optoelectronic devices [6].

Currently, the $Zn_{1-x}Cd_xO$ alloy films have been prepared by various physical and chemical deposition techniques, such as metal organic chemical vapor deposition (MOCVD) [7,8], molecular beam epitaxy (MBE) [9], magnetron sputtering [10,11] and pulse laser deposition, et al. [6,12]. Among these techniques, the magnetron sputtering has some distinctive advantages. For example, it is cost-effective for the growth of ZnO films with different dopant sources on various substrates. And the magnetron sputtering is a widely used and versatile technique that allows us to monitor the growth by controlling relevant parameters such as the sputtering power, sputtering time, substrate temperature, sputtering gas, and sputtering target, etc. So far, many $Zn_{1-x}Cd_xO$ alloy films prepared by direct current (DC) or radio frequency (RF) magnetron sputtering have been reported [13–15], but the $Zn_{1-x}Cd_xO$ alloy films grown by DC and RF reactive magnetron co-sputtering technique are rarely reported. So in this work, the $Zn_{1-x}Cd_xO$ films were prepared by DC and RF reactive magnetron co-sputtering technique with Zn and Cd metal targets, respectively. When the $Zn_{1-x}Cd_xO$ films were prepared by DC and RF

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reactive magnetron co-sputtering technique, the Zn, Cd and O atoms can reach the substrate separately, and the $Zn_{1-x}Cd_xO$ films were formed through reaction between Zn, Cd and O atoms, so crystal quality of deposited $Zn_{1-x}Cd_xO$ films would be better than that of films deposited by RF magnetron sputtering with ceramics target or films deposited by DC magnetron sputtering with alloy target.

In addition, post-annealing greatly affects the film properties, such as crystal quality, electrical and optical properties. Post-annealing treatment by various atmospheres, such as oxygen, hydrogen, air, nitrogen, or in vacuum, is usually considered as an essential and effective technique to improve the electrical and optical properties [16]. The effects of post-annealing on the properties of films in various atmospheres are different, and the as-grown films grown by the same processing annealed in different atmosphere usually have different changing behaviors. A limited literature is available on the detailed study related to effect of annealing atmosphere on optical and electrical properties of $Zn_{1-x}Cd_xO$ films. In the present work, the $Zn_{1-x}Cd_xO$ films were prepared by DC and RF reactive magnetron co-sputtering technique and post-annealed in vacuum, oxygen and argon atmosphere, respectively. Meanwhile, the influence of post-annealing atmosphere on microstructure, optical and electrical properties of $Zn_{1-x}Cd_xO$ films was studied in detail.

2. Experimental procedures

$Zn_{1-x}Cd_xO$ thin films were prepared on quartz substrates using mixture of oxygen and argon as sputtering gas by DC and RF magnetron co-sputtering technique. The targets are a Zn (99.99%) metal target and a Cd (99.99%) metal target placing at two different target seats. The quartz substrates were cleaned in an ultrasonic bath with acetone, ethanol, and deionized water for 15 min sequentially at room temperature, and then washed using deionized water. The vacuum chamber was evacuated to a base pressure of 2×10^{-4} Pa, and then sputtering gases, high purity 30 sccm O_2 (99.99%) and 30 sccm Ar (99.99%), were introduced with a constant total pressure about 3.0 Pa. The DC power of Zn metal target was fixed to 80 W and the RF power of the Cd target were fixed to 90 W. The loaded target was continuously presputtered for 10 min to remove any surface contamination of the target. The substrates temperature was held at 773 K during the films deposition and the deposition time of 90 min was maintained for all samples, then annealed for 60 min at 773 K under 10^{-3} Pa vacuum, 3×10^2 Pa oxygen and 3×10^2 Pa argon ambient in a tube furnace, respectively. To prevent pollution, a quartz tube was inserted into the furnace and the films were placed in a quartz boat.

Crystal structure of the samples were characterized by X-ray diffraction (Japan Rigaku D/max-ga X-ray diffractometer) using Cu$K\alpha$ (λ=0.15406 nm) and transmission electron microscope (TEM-2100). Chemical state of elements in the $Zn_{1-x}Cd_xO$ films were detected by X-ray photoelectron spectroscopy (XPS) (ESCALAB MARK II, VG Inc.) using an Al $K\alpha$ as x-ray source. *All narrow scan spectra showed a peak shift due to the electrostatic charging of the surface layer. It was corrected considering the increment registered on the surface C–C/C–H peak position, with respect to the literature value of* 284.6 eV. The room-temperature absorbance measurement was performed using an UV–VIS–near infrared (NIR) spectrophotometer (UV-3101PC). Photoluminescence (PL) measurement was performed at room temperature by the excitation from a 325 nm He–Cd laser. The electrical properties were detected by Hall effect measurements in the Van der Pauw configuration using an electrical transport property measurement system (Lake shore 7600 Hall) at room temperature.

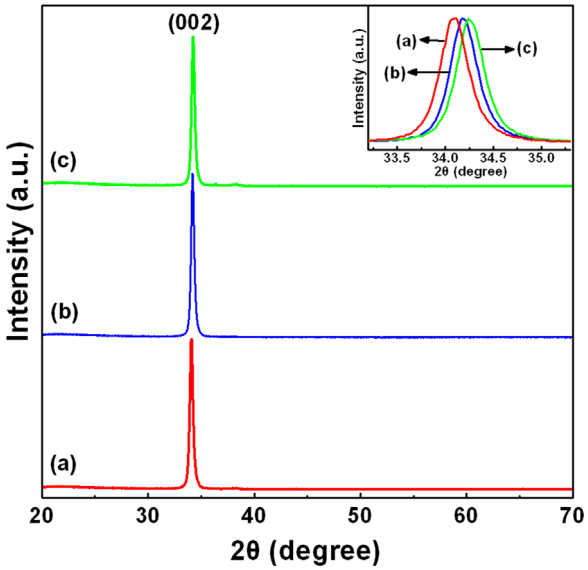

Fig. 1. X-ray diffraction patterns of $Zn_{1-x}Cd_xO$ films annealed in (a) argon, (b) oxygen and (c) vacuum atmosphere after deposition. The insets show the XRD patterns of $Zn_{1-x}Cd_xO$ films in a diffraction angle 2θ between 33.2° and 35.3°.

3. Experimental results and discussions

Fig. 1(a)–(c) shows the XRD patterns of the $Zn_{1-x}Cd_xO$ films annealed in argon, oxygen and vacuum atmosphere, respectively. As shown in Fig. 1, only one strong diffraction peak was observed at 34.08°, 34.17° and 34.23°, respectively, which is attributed to the diffraction of (002) plane of ZnO (ICDD card#79-0206) with hexagonal wurtzite structure. And no other impurity phases (e.g., Cd, or CdO) are detected, indicating that all films are of wurtzite structure with (002) preferential orientation. It is found that the (002) peak of all films shift toward the low angle side compared to that of the standard ZnO (34.42°). It is an indication of increment in the lattice parameter c of all $Zn_{1-x}Cd_xO$ films annealed at different atmosphere. The variation is attributed to the Cd^{2+} incorporation into ZnO lattice, because the ionic radius of Cd^{2+} (0.97 Å) is larger than that of Zn^{2+} (0.74 Å) [4]. It was observed from the inset that the diffraction angle shift of (002) peak for the $Zn_{1-x}Cd_xO$ films annealed in argon atmosphere is the biggest, and the diffraction angle shift of (002) peak for the $Zn_{1-x}Cd_xO$ films annealed in vacuum atmosphere is the smallest. It is concluded that the Cd content in $Zn_{1-x}Cd_xO$ films annealed in argon atmosphere is the most, while the Cd content in $Zn_{1-x}Cd_xO$ films annealed in vacuum atmosphere is the least. In addition, the full-width at half-maximum (FWHM) obtained from the (002) peak in the XRD profile are 0.34°, 0.33° and 0.32° for the $Zn_{1-x}Cd_xO$ films annealed in argon, oxygen and vacuum atmosphere, respectively. It indicates that compared with the $Zn_{1-x}Cd_xO$ films annealed in argon and oxygen atmosphere, the $Zn_{1-x}Cd_xO$ films annealed in vacuum atmosphere has the best crystal quality.

In order to identify the chemical states of Cd element doped in $Zn_{1-x}Cd_xO$ film, XPS measurement is performed for the $Zn_{1-x}Cd_xO$ film annealed in vacuum atmosphere. To avoid the effects of surface contamination, the $Zn_{1-x}Cd_xO$ film is cleaned by Ar^+ ion bombardment for 120 s prior to XPS measurement. *In the XPS spectrum, the presence of peak for* C1s *at approximately* 284.6 eV *is served as the internal standard for calibrating the binding energy.* The high-resolution scan XPS spectra of the O1s, Zn2p and Cd3d from the $Zn_{1-x}Cd_xO$ film and their fitted curves are shown in Fig. 2(a)–(c). Fig. 2(a) shows the O1s XPS spectrum of the $Zn_{1-x}Cd_xO$ film. As reported in literature [17], the broad and asymmetric nature of the peak is due to various coordinations of