Journal of Alloys and Compounds 663 (2016) 107–115

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Co-doped ZnO dilute magnetic semiconductor thin films by pulsed laser deposition: Excellent transmittance, low resistivity and high mobility

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ARTICLE INFO

Article history:
Received 7 October 2015
Received in revised form
28 November 2015
Accepted 13 December 2015
Available online 17 December 2015

Keywords:
Co-ZnO
Pulsed laser deposition
Electrical properties
Role of oxygen vacancies

ABSTRACT

The 120-nm-thick Co-doped ZnO (CZO) dilute magnetic semiconductor films were grown by pulsed laser deposition at various substrate temperatures (T_s) of 100–700 °C. During the film's growth, Ar or O_2 or Ar/O_2-mixed gas atmosphere was used. Hall measurements indicate the CZO films prepared in Ar atmosphere possess the lower resistivity. Then, the microstructural, optical, electrical and magnetic properties of the CZO films deposited in Ar atmosphere were investigated in detail. For the deposition in Ar atmosphere, the lowest resistivity of 4.30×10^{-2} Ω-cm appeared in the 400 °C-grown CZO film since it had more oxygen vacancies with 0 charge state (V_O^0). As the T_s was raised to 100–300 °C, the CZO films had low mobilities of 5.1–10.7 cm^2/V. This is attributed to the formation of oxygen vacancies with 2+ charge state (V_O^{2+}), resulting from the appearance of lattice distortions in these films. A significant relaxation of lattice distortion occurred in the 400 °C-grown CZO film, causing the efficient reduction in the amount of V_O^{2+}. Therefore, the 400 °C-grown film had a relatively high mobility of 21.0 cm^2/V. With increasing the T_s to 400–700 °C, the transmittances (@450 nm) of 84.1%–95.8% were obtained in the CZO films. Furthermore, the saturation magnetization values of 100, 400 and 700 °C-grown CZO films were 2.74×10^{-5}, 3.37×10^{-5} and 5.33×10^{-5} emu, respectively. These results suggest the CZO films are highly potential for spintronic and optoelectronic applications, especially for the 400 °C-grown film.

1. Introduction

Recently, dilute magnetic semiconductors (DMSs), that are non-magnetic semiconductors doped with a few magnetic ions, have been studied extensively for microelectronic applications via the spin characteristics and the charge of carriers [1,2]. To prepare the DMSs, the main doped metal elements consist of Mn, Co and Fe [3–5]. By accurately controlling the spin and electron charges, the DMSs can be widely applied for next generation spintronic devices. On the other hand, ZnO transparent conductive oxide (TCO) is a direct and wide band gap (3.37 eV) semiconductor and possesses the luminescence ability in UV region, which can be used for many optoelectronic applications consisting of solar cells, flat-panel displays and light emitting diodes (LEDs) [6–10]. Thus, novel functions can be obtained in ZnO-based spintronic devices such as spin-field effect transistors and spin LEDs [11,12].

Among various magnetic elements doped into ZnO, Co metal is a promising material since the Co-doped sample can exhibit a remarkable magnetization per Co ion for very low substitutions. Up to present, Co-doped ZnO (CZO) thin films and nanostructures have been prepared by several techniques including sputtering [13], sol–gel [14,15], spin-coating [16], solvothermal [17], ultrasonic spray [18,19] and pulsed laser deposition (PLD) [20–22]. Compared with other techniques, PLD is more useful for the growth of epitaxial ZnO-based thin films because its atomic-layer control can be achieved through the adjustment of laser repetition rate. Moreover, during the PLD process, the source particles possess high energy which can enhance the surface mobility of the ad-atoms.

At present, most researches of ZnO-based DMSs focused on the improvement of magnetic characteristics. However, the TCO-related properties [23] such as electrical resistivity, mobility and transmittance are usually neglected in ZnO-based DMSs. Although several ZnO-based DMSs with good magnetic characteristics have

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http://dx.doi.org/10.1016/j.jallcom.2015.12.101
0925-8388/

been proposed, the higher electrical resistivity or the lower transmittance also occurred in these materials. This will confine the optoelectronic applications of ZnO-based DMSs.

In this study, the 120-nm-thick CZO thin films were prepared by PLD using a KrF excimer laser. During the PLD growth, the pure Ar or pure O_2 or Ar/O_2-mixed gas was introduced into the growth chamber at various substrate temperatures (T_s) ranging from 100 to 700 °C. The structural, electrical, optical and magnetic properties of CZO films have been analyzed in detail. By adjusting the gas atmosphere and the T_s, the optimum growth conditions of CZO films can be achieved. The PLD-CZO films proposed in our work would possess good magnetic characteristic, excellent transmittance, low electrical resistivity and high mobility. This suggests the CZO films can be applied for both spintronic and optoelectronic devices.

2. Experimental

In this research, CZO thin films were prepared on c-plane (001) sapphire substrates by PLD (PLD/MBE-2000, PVD products). The KrF excimer laser ($\lambda = 248$ nm) was put in the deposition system, and the pulsed duration of 25 ns was employed to ablate the CZO target. Moreover, the energy fluence and the repetition rate of KrF laser are set at 600 mJ/pulse and 2 Hz, respectively. During the film's growth, a stoichiometric ceramic CZO target with a composition of 95 at% ZnO and 5 at% Co was used. By using a resistive heater, the T_s can be raised from 100 to 700 °C. The distance between the substrate and the target was maintained at 8 cm. After pumping the growth chamber to a base pressure, the 15-sccm pure Ar or pure O_2 or Ar/O_2-mixed gas was introduced, and the working pressure was kept at 2×10^{-3} torr. The CZO films were fixed at 120 nm in thickness.

Crystal structures and qualities of CZO films were characterized by double-crystal X-ray diffraction (XRD). Microstructures of these films were analyzed by transmission electron microscopy (TEM). Room temperature photoluminescence (PL) measurements for CZO films were performed by employing a He–Cd laser with 325 nm as an excitation source. Cross-sectional images of the samples can be observed both by scanning electron microscopy (SEM) and TEM. Hall measurements were used for electrical properties of CZO films, and the UV–Vis system was employed to obtain their transmittance spectra. Compositions of CZO films were recorded using X-ray photoelectron spectroscopy (XPS) for quantitative analysis, and the magnetic characteristics were measured by a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Fig. 1a and b displays the XRD patterns of CZO films deposited at various T_s of 100–700 °C in Ar and O_2 atmospheres, respectively. We can observe all samples present the CZO(002), CZO(004) and sapphire(006) diffraction peaks, and there is no peak with other planes in the CZO films, indicating these films possess a single crystalline phase. The CZO(002)-family peaks existed in these films can be ascribed to the preferred stacking along (001) plane with the lowest surface free energy on the sapphire surface [24]. Additionally, when the Ar atmosphere was used, the full width at half maximum (FWHM) values of rocking curves at CZO(002) of the films grown at 100, 200, 300, 400, 500, 600 and 700 °C were measured to be 2.87°, 1.861°, 1.358°, 0.926°, 0.464°, 0.381° and 0.298°, respectively. Meanwhile, in O_2 atmosphere, the FWHM values of rocking curves at CZO(002) of the films prepared at 100, 200, 300, 400, 500, 600 and 700 °C were 3.86°, 3.49°, 3.07°, 0.70°, 0.462°, 0.340° and 0.206°, respectively. Obviously, the crystal quality of the PLD-CZO film was improved with increasing the T_s. The average crystalline grain size (L) can be evaluated by the following Scherrer formula [25].

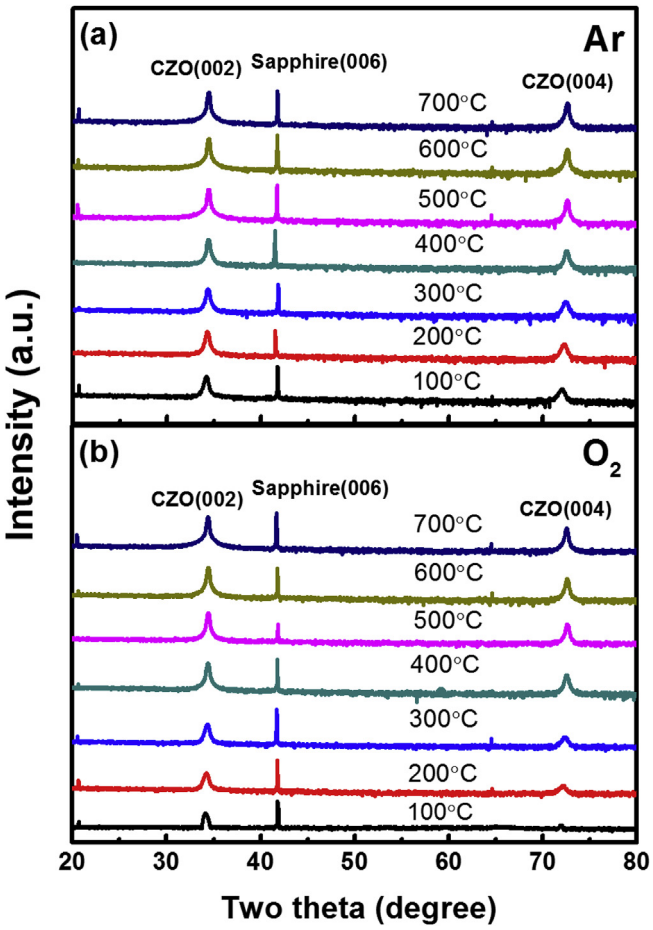

Fig. 1. XRD patterns of CZO films grown at various T_s (100–700 °C) in (a) Ar and (b) O_2 gas atmospheres.

$$L = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the X-ray wavelength, β is the FWHM value of XRD rocking curve and K is a constant of 0.9 related to the crystallite shape. The FWHM values of rocking curves at CZO(002), corresponded d-spacing values of CZO(002) peaks and average crystalline grain sizes for CZO films grown at 100–700 °C in Ar and O_2 atmospheres were summarized in Tables 1 and 2, respectively. It can be found the average grain size of the CZO film deposited in Ar atmosphere increased from 3.18 to 30.61 nm with increasing the T_s from 100 to 700 °C. Moreover, by introducing the O_2 atmosphere,

Table 1
The FWHM values of rocking curves at CZO(002), corresponded d-spacing values of CZO(002) peaks and average crystalline grain sizes for CZO films prepared at various T_s in Ar atmosphere.

Sub. temp. (°C)	FWHM (degree)	D-spacing (Å)	Grain size (nm)
100	2.87	2.620	3.176
200	1.861	2.613	4.899
300	1.358	2.607	6.715
400	0.926	2.604	9.849
500	0.464	2.602	19.656
600	0.381	2.603	23.938
700	0.298	2.602	30.607