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Full Length Article

Investigation of material properties and defect behavior in In-doped CdO films

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In-doped CdO ($In_xCd_{1-x}O$) thin films were prepared by magnetron sputtering and characterized in detail. Results indicated that the electron mobility improves with small amount of In doping (x = 0.012) to CdO, but then decreases with further In addition. It was proposed that the initial increase in mobility is because the oxygen vacancy concentration decreases and the grain size increases, and that the later degradation is due to the increased scattering by the In ions and the decreased grain size. It was also observed that the carrier concentration, while generally increased with the addition of the In donors, decreases with high amount of In doping (x = 0.072). It was proposed that this is because the solubility limit of In in CdO film is reached and excess In ions form non-conducting In-oxide clusters. It was observed that the In doping widens the energy band gap of CdO film via the Burnstein-Moss effect and the Vegard's rule.

1. Introduction

Recently, cadmium oxide thin films have attracted considerable attention to take advantage of their high electrical conductivity and the exceptionally high electron mobility [1–3], for various optoelectronic applications such as plasmon lasers, transistors, sensors, and information storage [4,5]. It has been reported that the optoelectronic properties of CdO could be controlled and improved by doping with different foreign metallic ions [6–8]. Among the doped CdO films, the In-doped CdO is generally regarded as the most suitable material as the In has a similar ionic radius with that of Cd [9].

It has been reported that the In-doping introduces extra electrons to the CdO lattice, leading to the improvements in electrical properties and the increased optical band gap due to the Burstein–Moss effect, without critically affecting the optical transmission [10]. It is also demonstrated that the refractive index and extinction coefficient are closely correlated with the In doping concentration [11]. It has been reported that an electric resistivity (ρ) of 5.95 $\times 10^{-5}\ \Omega$ cm and an electron mobility of 96 $cm^2\ V^{-1}\ s^{-1}$ may be obtained with properly doped (3.9 wt%) InCdO film [8], much improved numbers than those of the InSnO films ($\rho \sim 1.3 \times 10^{-4}\ \Omega$ cm) and the GaZnO films ($\rho \sim 2.1 \times 10^{-4}\ \Omega$ cm) [12,13].

It is known that the crystalline quality and the behavior of various defects are key parameters affecting the electrical and optical properties of films [4] and details of the phenomena need to be clarified to understand and thereby improve the properties. Unfortunately, there are little studies in the literature reporting the detailed defect behavior within the InCdO films. Most researchers largely limited their focus on the effects of doping concentration on property itself, such as the electrical conductivity, the transmittance and the band gap [8,11].

In this work, the optical, structural, and electrical properties of the reactive magnetron-sputtered $In_xCd_{1-x}O$ films with different In composition are characterized in detail. The behavior of various defects and the possible role of the crystalline structure are proposed, within the In-doped CdO films.

2. Experimental

The $In_xCd_{1-x}O$ films were deposited on quartz substrates by radio frequency (RF) magnetron sputtering at room temperature. The chamber pressure was maintained at 0.67 Pa and the RF power was fixed at 75 W. The thickness of the oxide $In_xCd_{1-x}O$ films was fixed at 400 nm, as confirmed by the scanning electron microscopy

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(SEM) observation. Detailed conditions for the sputtering has been reported in the previous work [13].

The electrical properties were characterized by a 4-point probe system (Changmin Tech, CMT-SR2000) and a Hall measurement system (M/N #7707_LVWR, LAKE SHORE CRYOTRONICS INC., USA). The crystalline quality of the CdInO was examined by a high-resolution X-ray diffractometer (XRD, X'pert PRO, Philips, Eindhoven, Netherlands) and the film morphologies by a field-emission SEM (FE-SEM, JSM-6710F JEOL, Japan). The X-ray photoelectron spectroscopy (XPS, VG Multilab 2000) was applied to characterize the chemical state of the elements within the films. Elemental compositions of the films were analyzed by the inductively coupled plasma optical emission spectroscopy (ICP-OES) and the In composition (x_{In}) in the $In_xCd_{1-x}O$ films was analyzed to be 0.012, 0.024, 0.043 and 0.072. The optical transmittance of the deposited films was measured using an UV–visible spectrophotometer (VARIAN Technologies, USA). The calibration of the spectrophotometer was performed against a quartz substrate as a reference.

3. Results and discussion

Fig. 1 shows effects of the In concentration (x_{In}) on the electrical properties of the $In_xCd_{1-x}O$ films. It is observed that the carrier concentration gradually increases with the In addition from 2.4×10^{20} cm^{-3} at $x_{In} = 0.0$ to 1.8×10^{21} cm^{-3} at $x_{In} = 0.043$ and then decrease with further increase in the In concentration, to 1.4×10^{20} cm^{-3} at $x_{In} = 0.072$. The electron mobility also initially increases from 65 $cm^2\,V^{-1}\,s^{-1}$ at $x_{In} = 0.0$ to 97 $cm^2\,V^{-1}\,s^{-1}$ at $x_{In} = 0.012$ and then decrease, to 36 $cm^2\,V^{-1}\,s^{-1}$ at $x_{In} = 0.072$. As a result, the electrical resistivity drastically decrease with addition of ∼1% In (from $3.9 \times 10^{-4}\,\Omega\,cm$ at $x_{In} = 0.0$ to $9.0 \times 10^{-5}\,\Omega\,cm$ at $x_{In} = 0.012$), maintain an almost constant value with further In addition and then slightly increase with higher amount of In-doping (from $5.2 \times 10^{-5}\,\Omega\,cm$ at $x_{In} = 0.043$ to $1.2 \times 10^{-4}\,\Omega\,cm$ at $x_{In} = 0.072$). It is mentioned that the electrical measurements were repeated with several sets of samples and the data points in Fig. 1 represent results from four to five samples.

It is quite interesting to observe the simultaneous increase in the carrier concentration and the electron mobility as a result of the addition of a small amount ($x_{In} = 0.012$) of In to CdO. In general, the mobility is known to decrease with the doping, as the foreign impurities introduce extra lattice strains and carrier scattering.

It is believed that the observed increase in the mobility in the InCdO film with $x_{In} = 0.012$ may be attributed to the reduction in the oxygen vacancy (V_O) concentration. It has been previously reported that the oxygen vacancies in the InCdO films are donors

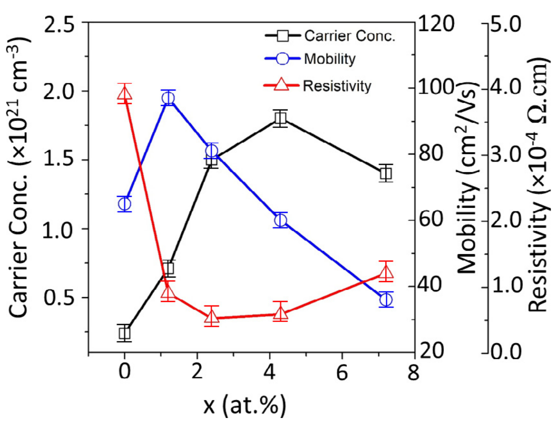

Fig. 1. Effects of In doping on the electrical properties of the $In_xCd_{1-x}O$ films.

and their formation energy increases with increasing Fermi energy (E_F) [4]. As the In donor doping would increase the E_F, it is suggested that the concentration of the oxygen vacancies ($[V_O]$) would be reduced as a result of the In doping [4].

To clarify if the [Vo] is indeed reduced in the In-doped CdO films, the XPS measurement was performed. Fig. 2 shows the XPS O 1s core level peaks for the CdInO films with different In composition. In Fig. 2a–c, it is observed that the O 1s peaks are asymmetric and the deconvolution of the peaks yields four contributions attributable to different chemical states of oxygen. The lowest binding energy peak at 528.7 eV (O1) is known to be due to the O^{2-} ions normally surrounded by the Cd ions in the cubic CdO structure [14], and the higher binding energy peak at 530.5 eV (O2) is from the O^{2-} ions in the oxygen-deficient regions within the metal oxide matrix (oxygen vacancies) [15,16]. The peaks at 531.3 eV (O3) and 532.1 eV (O4) have been attributed to the loosely bound oxygens on the surface of InCdO films, belonging to a specific species containing C-O and/or H-O compounds [14–17].

The curve fitting of the O 1 s core level peaks was conducted and the area of the four peaks were estimated from the fitted curves. The area ratio $A_{O2}/(A_{O1} + A_{O2})$ is shown in Fig. 2d as a function of the In composition, where A_{O1} represents the O1 peak area and A_{O2} the O2 peak area. In Fig. 2d, it is clearly observed that the $A_{O2}/(A_{O1} + A_{O2})$ ratio decreases with increasing In composition, indicating that the [Vo] in the InCdO films indeed decreases with the In doping.

The plan-view FE-SEM images of the InCdO films with various x_{In} are shown in Fig. 3, which indicates that the grain size of the films initially increases (from 66.7 nm at $x_{In} = 0$ to 76.9 nm at $x_{In} = 0.012$) and then decrease to 18.5 nm at $x_{In} = 0.072$. As the grain boundaries also act as the scattering centers for the electron movement, the increased grain size in the $In_{0.012}Cd_{0.988}O$ film would be another mechanism responsible for the improved mobility.

In Fig. 4, XRD spectra of the InCdO films, it is observed that all the XRD peaks may be assignable to the cubic CdO. It is also seen that the films show a preferential growth along [220] direction at low indium concentration but the (1 1 1) peak becomes stronger

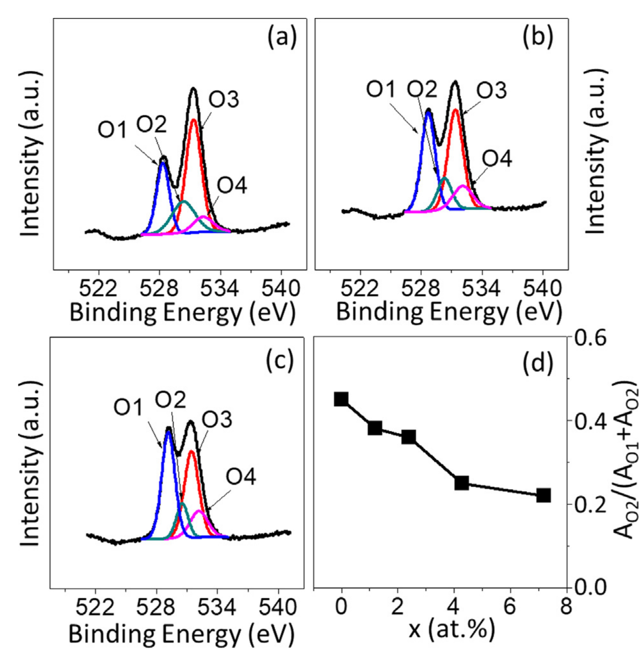

Fig. 2. High resolution XPS O 1s peaks of the $In_xCd_{1-x}O$ films with different In compositions, (a) pure CdO, (b) $x_{In} = 0.043$, and (c) $x_{In} = 0.072$. (d) shows the area ratios, $A_{O2}/(A_{O1}+A_{O2})$, as a function of the In composition.