Materials Science and Engineering B 212 (2016) 96–100

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Defects-related optical properties of $Zn_{1-x}Cd_xO$ thin films

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ARTICLE INFO

Article history:
Received 9 April 2016
Received in revised form 14 July 2016
Accepted 5 August 2016
Available online 12 August 2016

Keywords:
Transparent conductive oxide
ZnO
Coating
Photoluminescence

ABSTRACT

We present a systematic investigation on the structural and optical properties of $Zn_{1-x}Cd_xO$ thin films produced by spray pyrolysis. X-rays diffraction patterns show polycrystalline films grown preferentially along [002] direction and the incorporation of Cd in wurtzite ZnO without secondary phases up to $x = 0.25$. Above this concentration, the presence of secondary cubic phases indicates Cd-rich segregation, which is corroborated by optical transmittance/absorbance measurements. At low Cd concentrations, the optical bandgap energy decreases with the increasing of Cd, describing a nearly linear relation with slope 18.4 meV per% of Cd. Photoluminescence measurements show preferential defects emissions around 500 nm, associated with carrier localized and delocalized levels, which can be attributed to the presence of defects due to growth conditions and Cd incorporation.

1. Introduction

Transparent conducting oxides (TCO) are well-studied materials due to their real applicability on devices as transparent electrodes, displays, optical waveguides, gas sensors [1–3]. Accordingly, bandgap engineering in these wide bandgap materials is a current topic due to use of light emitters in visible optical range. Furthermore, doping or progress on ternary alloys play a fundamental part in this technological development. The high transparency of ZnO in the visible range associated with the large exciton binding energy (60 meV) and its optical emission in the near UV-range provide a suitable matrix to be used on ternary alloys. In addition, an interesting system to be considered to form an alloy is the CdO, a higher conductivity oxide. For these purposes, $Zn_{1-x}Cd_xO$ represents an attractive system with an optical window between 3.4 eV (ZnO) to 2.26 eV–2.46 eV (CdO) [4,5].

However, the crystalline structural mismatch between both materials (wurtzite ZnO and cubic CdO) emphasizes the role of defects in high Cd concentration in ZnO alloy. These defects create typical levels in the bandgap, which can deeply modify the optical emission properties of $Zn_{1-x}Cd_xO$. Nevertheless, these changes can also be useful for some specific applications in optoelectronic devices.

In addition, despite the transparency of ZnO coatings provides good results on top of silicon solar cells, there is a loss of efficiency associated to the absorption of near-ultraviolet light due to lattice thermalization. The extra-intensity available for a silicon photovoltaic in this optical range ($\lambda < 550$ nm) is around 30–36% in different solar spectra (AM1-1.5) [6]. The main mechanism explored to take advantage of this energy is the down-conversion mechanism, that usually employs rare-earth ions with a quantum yield larger than 1 [7]. A similar proposal with quantum yield less than 1 is the down-shifting process, in which one photon with higher energy is converted into another one with lower energy that is more efficiently absorbed by the cell. For this mechanism, the employment of defects-related optical emission in a transparent electrode oxide thin film can be used to improve the efficiency of conventional solar cells.

Additionally, the spray pyrolysis technique is a low-cost and versatile method to grown thin films based on the pulverization of a solution on a hot substrate. The main parameters in this technique are related to the employed precursors by their molarity in the liquid solution and their pyrolysis temperature. With an appropriate choice, it is possible to grown quality polycrystalline films on top of several substrates at moderate temperatures. We employed this route to obtain $Zn_{1-x}Cd_xO$ thin films. This work shows the effect of Cd introduction in ZnO in concentrations up to $x = 0.75$ and compare with a pure CdO film. The structural and optical properties present interesting results, which intend to be useful in photovoltaic and light-emitters applications.

2. Material and methods

In order to have an overview about the $Zn_{1-x}Cd_xO$ alloy, thin films with different Cd concentrations x were grown by spray pyrolysis method using aqueous solution containing zinc acetate

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http://dx.doi.org/10.1016/j.mseb.2016.08.002
0921-5107/

dihydrate and cadmium acetate dihydrate in appropriated ratio. The 0.01 M solution was carried by compressed air at 1kbar and pulverized on top of glass substrates at 330 °C. As the temperature drops to 250 °C, the flux is interrupted and the layers are annealed up to 330 °C. After that the cycle restarts. We attribute the formation of $Zn_{1-x}Cd_xO$ to the dehydration of bound water followed by the decomposition and oxidation of Zn or Cd $(CH_3COO)_2$ with liberation of CO_2 and H_2O, as reported for NiO growth [8]. The thicknesses of the produced films are around 1 μm.

The structural properties were characterized by X-rays diffraction (XRD), performed with an X-ray diffractometer Shimadzu model XRD-6000 employing Cu K_α line with wavelength 1.5406 Å. Optical transmittance/absorption measurements were analyzed with a spectrophotometer Agilent Cary 5000 UV–vis-NIR, with the samples at room temperature. The optical emission of films were investigated by photoluminescence spectroscopy measured as a function of temperature in the range 15–300 K, using the 325 nm line from a HeCd laser as an excitation source. The emission was monitored by an Ocean Optics spectrometer (model USB4000-UV–Vis/200 μm slit) in the range 350–1000 nm.

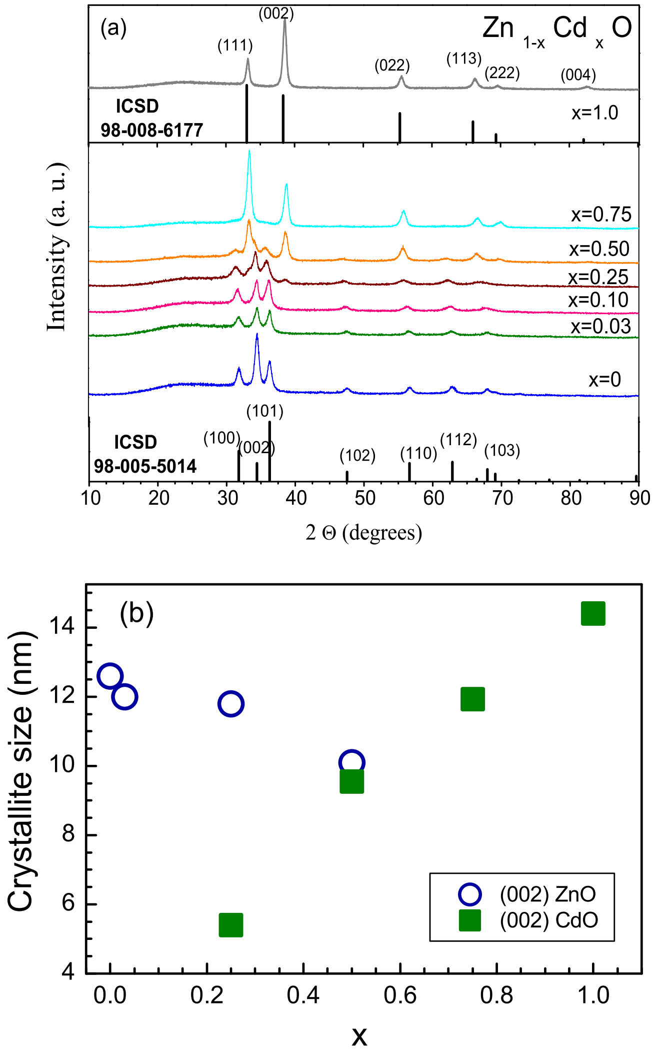

Fig. 1. (a) XRD data for $Zn_{1-x}Cd_xO$ films. Diffraction peaks from CdO are evident for $x \geqslant 0.25$. (b) Variation of crystallite size obtained through Bragg peak (0 0 2) using Scherrer equation as a function of Cd content x.

3. Results and discussion

Fig. 1(a) displays the X-ray diffraction (XRD) patterns of the polycrystalline $Zn_{1-x}Cd_xO$ films at room temperature. The standard ZnO and CdO diffraction peaks indicate the formation of hexagonal wurtzite and the cubic crystalline structures, respectively. The intense XRD peaks suggest good crystallinity for binaries samples with preferential growth along [0 0 2] direction. It can be noticed from XRD data that the samples with low concentration of a third-element ($x \leqslant 0.10$ and $x \geqslant 0.75$) are single-phase, indicating the effective substitution of Zn atoms by Cd atoms in the wurtzite structure [9] and replacement of Cd atoms by Zn atoms in the cubic structure, respectively. Samples with intermediate concentrations (x = 0.25 and 0.50) present a secondary phase. However, it is observed that the relative intensity of the peak corresponding to the reflection in (1 1 1) plane of CdO increases when x decreases from x = 1.0 to x = 0.50. A similar behavior has also been reported by Helen et al. [10] and it was attributed to the imperfection in crystalline structure by the excess of Zn incorporation into CdO lattice structure. The crystallite size (*D*) of the $Zn_{1-x}Cd_xO$ was estimated by Scherrer equation at the Bragg peak (0 0 2),

$$D = \frac{0.94\lambda}{FWHM\ cos\theta_B}, \tag{1}$$

where λ is the wavelength of used radiation, θ_B is the Bragg diffraction angle, and *FWHM* is the full width at half maximum in radians.

Fig. 1(b) shows the dependence of crystallite size *D* as a function of Cd concentration x, where open circles and closed squares indicate the *D* values obtained from (0 0 2) peak characteristic of ZnO and CdO phases, respectively. The crystallite size decreases from 12.6 nm (ZnO) to a minimum value at 10.1 nm ($Zn_{0.5}Cd_{0.5}O$), which reveals that the increasing of Cd concentration into ZnO introduces a compressive strain [11]. In the opposite, the crystalline quality and crystallite size also decrease with incorporation of Zn into CdO, comparing CdO (*D* = 14.5 nm) and $Zn_{0.75}Cd_{0.25}O$ (*D* = 5.4 nm). The degradation of the film crystallinity can be attributed to the dissimilarity of CdO cubic structure and ZnO wurtzite structure as well as the phase separation for $Zn_{1-x}Cd_xO$ alloys [12].

Thus, a better understanding about the Cd-incorporation effects in ZnO films can be remarked in the Fig. 2(a), which shows the optical transmittance spectra as a function of x, measured at room temperature. The samples present broad transmittance windows with $T \geqslant 75\%$ for wavelengths decreasing (increasing energy) from 800 nm up to the band edge absorption. The absorption edge progressively redshifts from 370 nm to 500 nm for concentration varying from x = 0 to x = 0.25 with increase in Cd concentration. For x values higher than 0.25, the transmittance curves are independent of Cd concentration and we attribute this fact to a formation of cadmium-rich phases, as noticed from X-ray diffractograms in Fig. 1. Therefore, the correlation between structural (XRD) and optical (transmittance) characterizations indicates significant phase segregation in $Zn_{1-x}Cd_xO$ for $x \geqslant 0.25$.

The optical bandgap (E_g) of a semiconductor is related to the optical absorption coefficient (α) and the incident photon energy ($h\nu$) by Tauc equation [13]:

$$\alpha h\nu = C_1(h\nu - E_g)^n \tag{2}$$

where C_1 is a proportionality constant, *n* is 2, 3, 1/2, and 3/2 for indirect allowed, indirect forbidden, direct allowed, and direct forbidden transitions, respectively and E_g is the bandgap energy. The bandgap E_g can be estimated by plotting the optical absorption versus the photon energy. The absorption coefficients were calculated by means of the Beer-Lambert law, considering that the absorbance of the films is the predominant effect for the transmittance attenuation and the reflectance was assumed to be negligible. The extrapolations