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Optical, electrical and structural properties of indium-doped cadmium oxide films obtained by the sol–gel technique

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Abstract

Indium-doped cadmium oxide films were obtained by mixing cadmium oxide and indium oxide precursor solutions by the sol–gel technique. The indium atomic concentrations in solution (x) studied were 0, 2, 5 and 10 at%. The films were sintered at two different sintering temperatures (T_s) 350 and 450 °C, and after that annealed in a 96:4 N_2/H_2 gas mixture atmosphere at 350 °C. X-ray diffraction patterns showed that all films sintered at $T_s = 350$ °C only consisted of cadmium oxide crystals. The films sintered at $T_s = 450$ °C consisted of cadmium oxide crystals also; however, for the highest indium atomic concentration (10 at%) the formation of cadmium indate oxide crystals was evident. All films show high optical transmission (>85%) and an increase of the direct band gap value from 2.4 to 3.1 eV, as the indium atomic concentration in solution increases. The minimum resistivity value obtained was $6.3 \times 10^{-4}\,\Omega$ cm for the films with $x = 5$ at%, $T_s = 450$ °C and annealed at 350 °C.

Keywords: Cadmium oxide; Indium oxide; Thin films; Sol–gel; Transparent conductor oxide

1. Introduction

CdO thin films have great technological interest due to their high-quality electrical and optical properties. Doped CdO films, as multicomponent oxides films constituted of CdO, have been used in several applications: photovoltaic devices [1,2], gas sensors [3], phototransistors and diodes [4], etc. Different methods have been adopted to deposit these films such as metalorganic chemical vapor deposition (MOCVD) [5], sputtering [6], electron beam evaporation [7] and sol–gel [8,9] among others. However, there are few works reported in the literature with respect to CdO films obtained by the sol–gel technique, a fact rather surprising due to the several advantages that the sol–gel technique presents [10]. Among the impurities used as doping agents for CdO films are fluorine [1,8,9,11], aluminum [12], tin [2,13] and indium [2,5,7]; with indium, it has been possible to reach resistivity values of $6 \times 10^{-5}\,\Omega$ cm [5,7]. In the case of solar cells and diodes fabrication, high values of ionic radii of impurities are important in doping in order to decrease impurity diffusion towards the p–n junction. In this way, tin and indium are better doping materials than fluorine and aluminum.

In this work, indium-doped CdO thin films were obtained starting from a simple precursor solution by the sol–gel method. The main objective was to increase the conductivity and band gap energy value of the films, without detriment to their high optical transmission.

2. Experimental

The indium-doped cadmium oxide precursor solution was prepared starting from cadmium oxide and indium oxide precursor solutions obtained separately. The procedure employed for the preparation of the cadmium oxide precursor solution was similar to the one previously reported [8], only the molar concentration of methanol was changed. The cadmium oxide precursor solution was prepared using cadmium acetate (1 mol), methanol (33 mol), glycerol (0.2 mol) and triethylamine (0.5 mol). With respect to the indium precursor solution, this one was

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prepared starting from indium acetate (1 mol), 1-propanol (90 mol), lactic acid (9 mol) and deionized water (135 mol). The procedure was simple; lactic acid was added to the indium acetate and after that a solution consisting of 1-propanol and deionized water was incorporated. The solution was stirred constantly for 2 h until a transparent solution was obtained. The indium-doped cadmium oxide precursor solution was obtained mixing both precursor solutions at room temperature (RT) using several volumetric proportions, which were calculated to obtain the indium concentrations of 0, 2, 5 and 10 at% in solution.

The films were deposited on glass substrates, at RT by the dipping method, 24 h after the preparation of the final solution. The withdrawal speed was 3.0 cm/min. All the films were thermally pre-treated at 100 °C and sintered at two different sintering temperatures of 350 and 450 °C, in both cases in an air atmosphere for 1 h. Finally, they were annealed in a 96:4 N_2/H_2 gas mixture, at an annealing temperature of 350 °C for 1 h, also.

Due to the fact that the viscosity of the precursor solution decreases as higher volume of indium precursor solution is added, and the dipping number was different for each indium concentration in the solution, the thicknesses were between 1000 and 2500 Å.

The thickness of the films was measured by means of a profilometer (Sloan Dektak II), after removal of a step-like portion of them with diluted HCl. The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-2100 diffractometer ($CoK\alpha_1$ radiation, 1.78899 Å), employing a thin film attachment. The ultraviolet–visible (UV–vis) spectra of the films were measured on a Perkin-Elmer Lambda-2 spectrometer, in the 300–1100 nm wavelength range. The transmission was measured using a non-coated glass in the reference beam. The resistivity was measured by the conventional four-aligned probe method using a Loresta-6P model MCP-T600 equipment. This parameter was also measured by current–voltage measurements in accordance with the standard Van der Pauw configuration. Hall effect measurements were carried out in an Ecopia, model HMS-3000 using a magnetic field of 0.5 T. Indium contacts were used in the electrical measurements with the exception of the four-probes method. All the characterization was carried out at RT.

3. Results and discussion

XRD patterns of the CdO films and indium-doped CdO films are displayed in Fig. 1a and b, for the two sintering temperature values of 350 and 450 °C, respectively. The films sintered at $T_s = 350$ °C only show the cubic crystalline structure of the cadmium oxide with five characteristic peaks assigned to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes. The intensity of the peaks decreases and the full-width at half-maximum (FWHM) increases as the indium content increases; both these observations are very evident for the film with high indium content (10 at%). This behavior can be associated with the presence of indium–cadmium compounds in the amorphous phase and with a diminishing of the cadmium oxide grain size. With respect to the CdO films sintered at $T_s = 450$ °C, they show a similar behavior to the films sintered at $T_s = 350$ °C; however, the presence of a shoulder in the CdO (1 1 1) peak to lower 2θ values could be attributed to a new compound. Fig. 2a shows only the XRD patterns of the CdO films doped with indium at 10 at%. By means of a Gaussian deconvolution of the above-mentioned peak (Fig. 2b), the

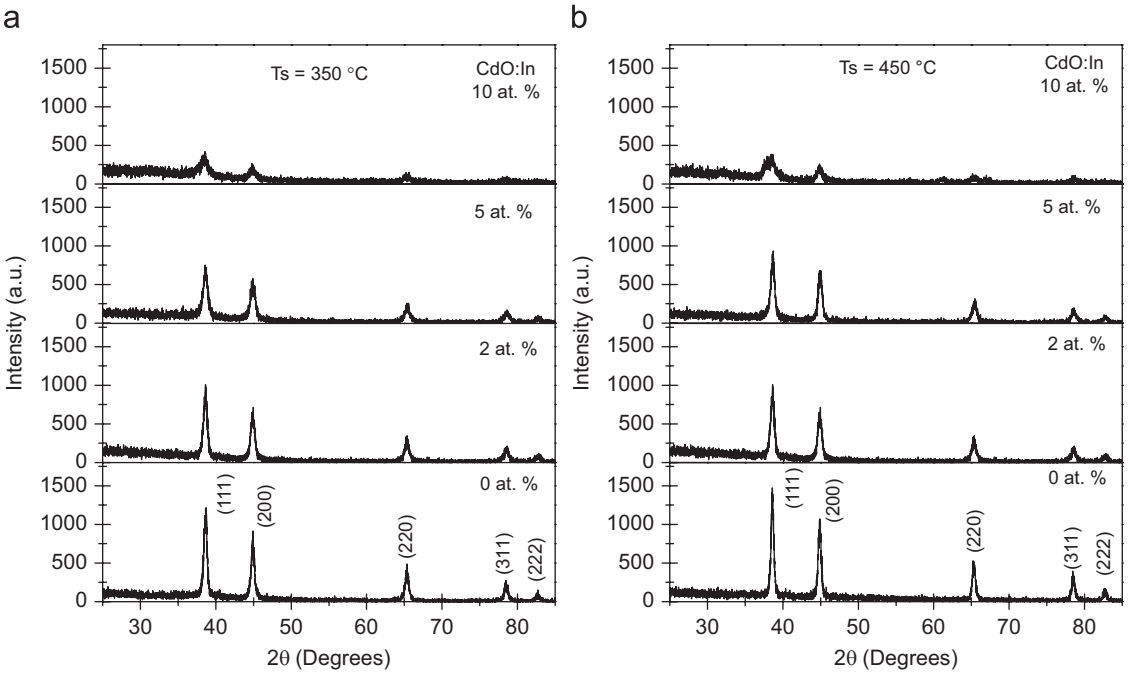

Fig. 1. XRD patterns of the CdO films and indium-doped CdO films sintered at (a) $T_s = 350$ °C and (b) $T_s = 450$ °C.