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Dependence of electrical and optical properties of sol–gel prepared undoped cadmium oxide thin films on annealing temperature

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Abstract

The effect of the annealing temperature (T_a) on the optical, electrical and structural properties of the undoped cadmium oxide (CdO) thin films obtained by the sol–gel method, using a simple precursor solution, was studied. All the CdO films annealed in the range from 200 to 450 °C are polycrystalline with (111) preferential orientation and present high optical transmission >85% for wavelengths above 500 nm. The resistivity decreases as T_a increases until it reaches a value of 6×10^{-4} Ω cm for T_a=350 °C. For higher temperatures the resistivity experiences a slight increase. Images obtained by atomic force microscopy show an evident incremental change of the aggregate size (clusters of grains) as T_a increases. The grain size also increases when T_a increases as observed in data calculated from X-ray measurements.

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1. Introduction

Thin films of transparent conductive oxides (TCO) such as zinc oxide, indium–tin oxide, tin oxide and cadmium oxide (CdO) have been extensively studied because of their use in semiconductor optoelectronic device technology [1–3]. Among the films of oxides mentioned, those of CdO have received less attention because of their relatively narrow energy band gap (~2.6 eV and ~2.1 eV direct and indirect band gap, respectively) [4]. However, these films show higher mobility values ($\mu\sim216$ cm^2 V^{-1} s^{-1} [5]), which are necessary for high-conductivity TCO materials, especially when low free-carrier absorbance is desired.

Undoped and doped CdO thin films have been obtained by different techniques such as reactive sputtering (RS) [6–8], ion beam sputtering [9], activated reactive evaporation [10], chemical bath deposition [11,12], spray pyrolysis [13,14], metalorganic chemical vapor deposition [5,15], and sol–gel (SG) [4]. For undoped CdO films, the resistivity values of 2 to 20×10^{-4} Ω cm are obtained for those deposited by sophisticated techniques such as reactive sputtering and metal organic chemical vapor deposition, whereas for simpler techniques such as chemical bath deposition and SG, resistivity values are obtained between 10^{-3} to 10^{-2} Ω cm.

In this work, we present the results obtained for undoped CdO thin films deposited by the sol–gel method starting from simpler precursor solution than previously reported [4]. The new solution is based on cadmium acetate dehydrate, methanol, glycerol and triethylamine, without the addition of water. The structural, optical and electrical properties of the films were studied as a function of the annealing temperature (T_a) in the 200 to 450 °C range. The CdO films show high transparency and resistivity values which are within the lowest value ranges obtained by more sophisticated techniques.

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2. Experimental details

The CdO precursor solution was prepared by the following procedure: 7 ml (half the volume used) of methanol were added to 2 g (7.5 mmol) of cadmium acetate dehydrate. In order to obtain a transparent solution, slow constant stirring was required. Subsequently, 0.11 ml (1.5 mmol) of glycerol was added. A solution consisting of the remaining 7 ml of methanol and 0.52 ml (3.75 mmol) of triethylamine was prepared separately, and subsequently added with constant stirring to the transparent solution prepared initially. No additional water was added to the mixture. The procedure was done entirely at room temperature (RT). The resulting solution was completely colorless and transparent, and only a slight turbidity appeared 12 days after its preparation. All reagents were analytical grade and used as received.

The films were grown at RT, by the multiple-dipping method on glass slides as substrates. The withdrawal speed was 1.2 cm/min. The films were thermally pre-treated at 100 °C and then subjected to an annealing process at temperatures of 200 to 450 °C (at 50 °C intervals). Both treatments were carried out in an open atmosphere for 1 h, afterwards, the oven was turned off. The samples were kept inside the oven until RT was reached. The thickness of the films was determined by means of a profilometer with 1 nm of vertical resolution (Sloan Dektak II), after removing a portion of the film with diluted HCl to make the step. X-ray diffraction (XRD) studies were carried out in a Rigaku D/max-2100 diffractometer ($Cu-K_{\alpha 1}$ radiation, 1.5406 Å), using a thin-film attachment. The resistivity, mobility and carrier concentration were obtained from Hall measurements, which were performed at RT under a 0.5 Tesla magnetic field intensity, in accordance with the standard Van der Pauw configuration. Silver paste was used for the electric contacts. The resistivity was also measured by the conventional four aligned probe method using a Loresta-6P, model MCP-T600. The ultraviolet-visible 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 glass as reference. The surface morphology of the films was analyzed on a SPC-400 Park Scientific Instruments atomic force microscope (AFM), using a 10-μm scanner.

3. Results and discussion

The films are uniform, transparent, crack free and present good adherence. The thickness dependence on the number of coatings (cycles of dipping) for the film annealed at 350 °C is shown in Fig. 1. As can be seen in Fig. 1, after the first coating the thickness of the layers increases linearly (~24.5 nm/layer) with the number of dips, such lineal behavior is characteristic of the sol–gel process [16]. The difference of the thickness resulting from the first layer (44 nm), as compared to the thickness of the subsequent ones, is due to differences in the surface tension between glass/solution and CdO film/solution. For this work, we used seven coatings, and the thickness was in the 180–190 nm range. This range of thickness was used because we have observed that above 120 nm the resistivity does not depend on the thickness. The fitted relationship between the thickness (τ) and the number of cycles (n) is: $\tau = [(24.5 \pm 0.8)\ \text{nm}] * n + (19.6 \pm 0.6)\ \text{nm}$.

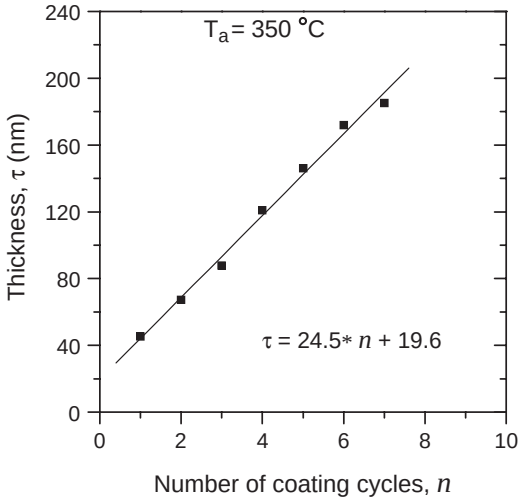

Fig. 1. Thickness (τ) versus number of coating cycles (n) for the sample with T_a=350 °C. The relationship included in the figure represents a linear fit between τ and n.

Typical XRD patterns of undoped CdO films are shown in Fig. 2 (for T_a equal to 200, 300 and 450 °C). The patterns reveal the presence of pure polycrystalline CdO thin films, with a NaCl cubic structure and with a small preferential orientation in the plane (111) for all the T_a. It is important to mention also that when the T_a increases the relative intensity of the peaks is maintained and their full width at half maximum (FWHM) decreases. The fact that the FWHM decreases is indicative of the improvement of the crystalline quality. Using Scherrer's formula and the FWHM of the three diffraction peaks, corresponding to (111), (200) and (220) crystalline planes, the grain size was calculated for the different annealing temperatures. In Fig. 3, the average grain size is shown as a function of the annealing temperature. From the figure, it can be seen that the grain size increases from 20 to 27 Å, when the T_a increases. A similar behavior can be seen in AFM images (Fig. 4), where the aggregate size increases significantly when T_a rises, up to an approximate average value of 150 nm in diameter for the films annealed at 450 °C. It is clear from both AFM and grain size results, that the aggregates consist of several crystalline grains.

The resistivity values for the films as a function of T_a are shown in Fig. 5. The resistivity decreases approximately one order of magnitude as the T_a increases, from 200 to 350 °C, reaching a minimum value of $6 \times 10^{-4}\ \Omega$ cm. For higher