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The importance of the methanol content in the precursor solution, on the physical properties of cadmium oxide thin films prepared by the sol–gel method

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ABSTRACT

Undoped and fluorine doped cadmium oxide films were obtained by the sol–gel technique, starting from a simple precursor solution constituted of: cadmium acetate, methanol, glycerol and triethylamine and only for doped samples, ammonium fluoride as the fluoride source. Due to the methanol content used is higher with respect to the other reagents, variations in this parameter affect the viscosity and gelation time of the precursor solution, giving as result changes in the thickness. The importance of the methanol content in the growing solution on the structural, morphological, optical and electrical properties of the films is reported. Higher thickness was obtained for lower methanol content, in the range 33–46 mol, in the growing solution. Largest growing rate was obtained when the methanol content in the precursor solution was 33 mol. The films showed good characteristics for their use as transparent conductive films in solar cells.

1. Introduction

CdO thin films have been of interest as transparent electrode and window material in the manufacture of solar cells. Different types of simple heterojunction solar cells have been studied: CdO/crystalline-Si [1], CdO/CdTe [2–5], CdO/Cu_2O [6], CdO/CuGaInSe [7] and CdO/ITO in dye-sensitized solar cells, where the CdO has been employed in place of TiO_2 [8]. As well, CdO films can be obtained by several techniques, such as, reactive sputtering [9–11], activated reactive evaporation [3,12], chemical bath deposition [13], spray pyrolysis [14], rapid thermal oxidation [1], sol–gel [15–18] and recently In, Sn, Al and Ti doped CdO films deposited by pulsed laser technique [19–22]. In order to diminish the cost of the solar cells, it is important to use simple and cheaper deposition techniques. The sol–gel technique satisfies these requests, however it has the disadvantage that films with higher thickness must be obtained with higher coatings number.

In this work, the results in undoped and fluorine doped CdO films deposited by sol–gel technique, with higher deposition rates than the ones previously reported by us, are reported [5,17]. The films were obtained, starting from precursor solutions with different methanol contents (solvent reagent). CdO films deposited at higher deposition rates present the structural, optical and electrical properties appropriate for their use in solar cells.

2. Experimental details

The undoped and fluorine doped CdO precursor solutions were prepared following the procedure previously reported by the authors [16,17]. For the undoped CdO precursor solution, four methanol contents were used: 33, 37, 41 and 46 mol, with respect to 1 mol of cadmium acetate. 46 mol of methanol concentration was already used in a previous work with good results. The glycerol/cadmium acetate and trietylamine/cadmium acetate ratios were fixed at 0.2 and 0.5, respectively. The fluorine doped CdO precursor solution was only made with methanol contents of 33 mol (which resulted with the highest deposition rate) and 46 mol, and with fluorine content in solution of 5 at.%. Ammonium fluoride was used as fluorine source. The films were deposited 24 h after the precursor solution was made. The films were obtained by the multiple-dipping method on glass slides as substrates, at room temperature, and with a withdrawal speed of 1.2 cm/min. Films with coats from 1 to 7 were prepared with the objective to determine the deposition rate. All films were first thermally pre-treated at 100 °C and subjected to a sintering thermal treatment at 350 °C, in both cases in an open atmosphere for 1 h. A set of undoped CdO films with methanol content of 33 mol (and with seven coats) and fluorine doped CdO films, only, were subsequently annealed at $T = 350\,°C$ in a 96/4 N_2/H_2 gas mixture for 1 h, with the objective to decrease the resistivity values. The thickness of the films was measured by means of a Sloan Dektak profilometer. The surface morphology of the films was observed by scanning electron microscopy (SEM) with a Jeol 35C instrument, the energy used was 25 keV. The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-2100 diffractometer ($CuK_{\alpha 1}$ radiation, 1.5406 Å), using a thin film attachment. The transmission spectra were obtained using a PerkinElmer Lambda-2 spectrophotometer with a non-coated glass in the reference beam. The resistivity of the films was measured by the conventional four aligned probe method using a Loresta-GP, model MCP-T600.

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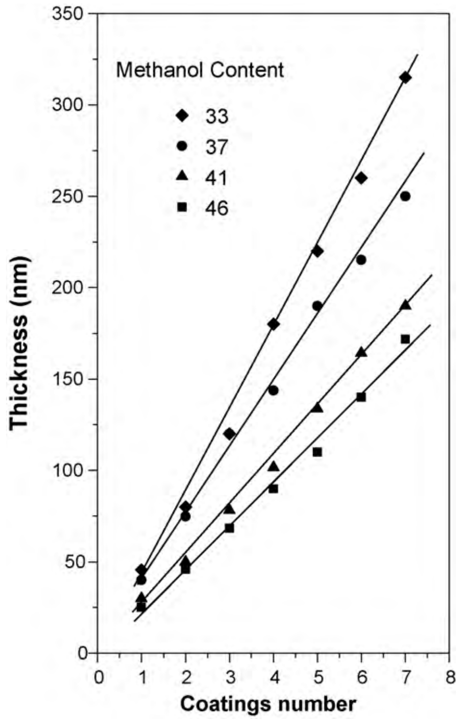

Fig. 1. Thickness (τ) versus coatings number (n) for the undoped CdO films obtained with different molar contents of methanol in the precursor solution.

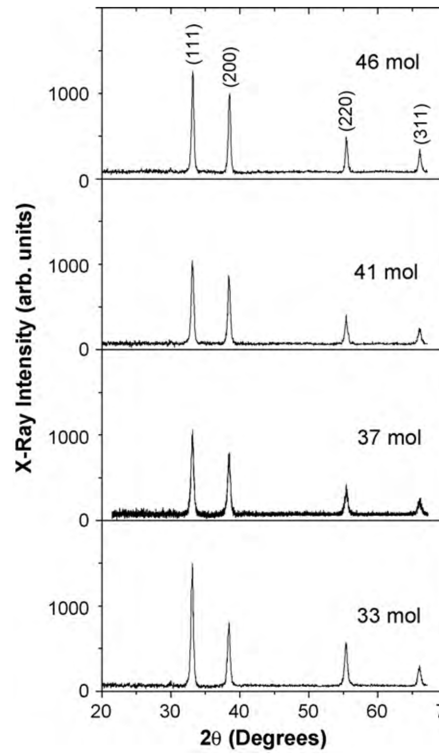

Fig. 2. XRD patterns of undoped CdO films, obtained at different methanol contents in the precursor solution.

3. Results and discussion

3.1. Undoped CdO films (without annealing)

All films are uniform and have a good adherence to the substrate. Fig. 1 shows the average thickness of the films versus the coatings number, for each of the methanol contents studied. The highest deposition rate is obtained for the precursor solution with 33 mol of methanol; films with thickness ~400 nm can be obtained with nine coatings starting from this solution. Precursor solutions with lower methanol content (23 mol) were prepared, however, the films obtained using this solution are whitish. The result that the larger methanol content the lower thickness can be originated by the fact that the larger methanol content the minor amount of cadmium acetate in the growing solution, consequently, minor CdO-reagent in contact with the substrate.

XRD patterns of the CdO films with seven coats are shown in Fig. 2. All films are polycrystalline with cubic phase, type NaCl. The four peaks observed are assigned to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes. A light preferential orientation in the (1 1 1) plane is observed for the films with lowest methanol content in the precursor solution (33 mol). The grain size was calculated with the full-width at half-maximum (FWHM), the θ position of the four main diffraction peaks and using the formula given in the reference [23]. The average grain size of the films as a function of the methanol content is shown in the Fig. 3. It can be seen that the highest grain size (~28 nm) is obtained for the films deposited starting from the precursor solution with highest deposition rate i.e. with a methanol content of 33 mol. SEM images of the undoped CdO films with 7 coats (Fig. 4), reveal how dense films and spherical-type aggregates are obtained for all methanol contents. The film with 33 methanol content shows the highest aggregate size, whereas, the films with higher methanol content show more uniform aggregate size. It is clear from the crystalline grain size values obtained from XRD and aggregate size from SEM images, that the aggregates consist of several crystalline grains and that the film with 33 mol of methanol has the highest quantity of crystalline grains. On the other hand, we think that the aggregate size plays a main role in the crystalline grain size i.e. if the aggregate size is higher we expect a higher crystalline grain size with respect to films with lower aggregate sizes. A crystalline grain can increase its size when has a major number of neighbor grains. The increase of the crystalline grain size was also observed with the sintering temperature [17]. The transmission spectra of the films for the different methanol contents studied are shown in Fig. 5. All films have high transmission practically around 80% for wavelengths higher or equal to 500 nm and an absorption edge without change. The little change of transmission observed in these films is attributed to changes de thickness of around 200 Å. The resistivity of the films as a function of methanol content and coatings number is shown Fig. 6a. The resistivity decreases as the number of coats increases, and tends

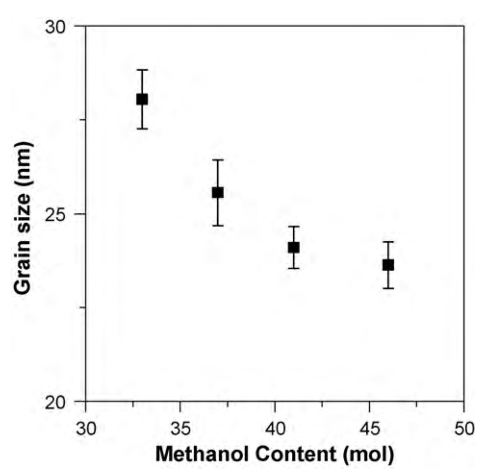

Fig. 3. Grain size of undoped CdO films versus methanol content in the precursor solution (films with 7 coats).