



# 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.

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## 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<sub>2</sub>O [6], CdO/CuGaInSe [7] and CdO/ITO in dye-sensitized solar cells, where the CdO has been employed in place of TiO<sub>2</sub> [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.

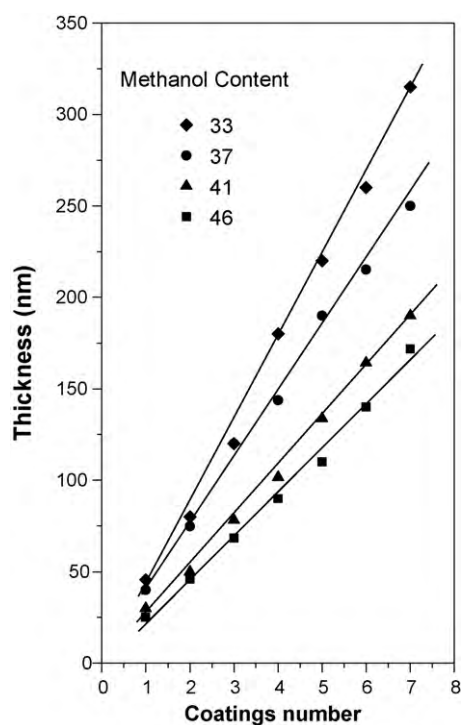
In this work, the results in undoped and fluorine doped CdO films deposited by sol–gel technique, with higher deposition rates than the ones previously reported by us, are reported [5,17]. The films were obtained, starting from precursor solutions with different methanol contents (solvent reagent). CdO 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 triethylamine/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  $T=350\text{ °C}$  in a 96/4 N<sub>2</sub>/H<sub>2</sub> 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<sub>α1</sub> 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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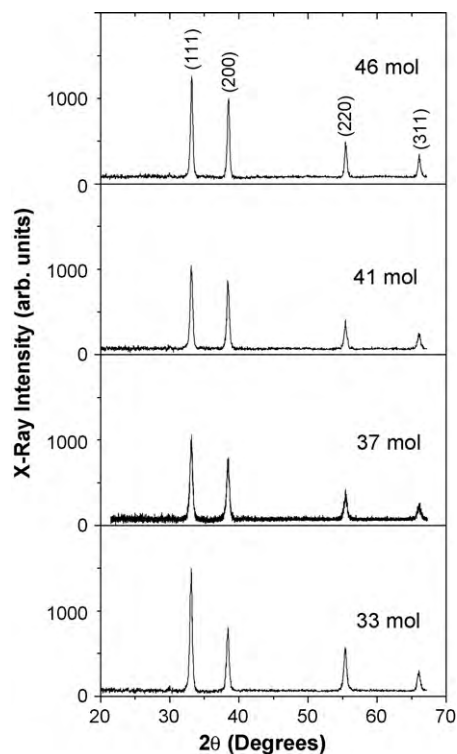
**Fig. 1.** Thickness ( $\tau$ ) versus coatings number ( $n$ ) for the undoped CdO films obtained with different molar contents of methanol in the precursor solution.

### 3. Results and discussion

#### 3.1. Undoped CdO films (without annealing)

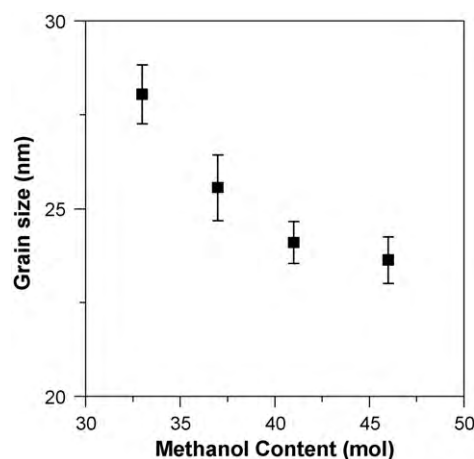
All films are uniform and have a good adherence to the substrate. Fig. 1 shows the average thickness of the films versus the coatings number, for each of the methanol contents studied. The highest deposition rate is obtained for the precursor solution with 33 mol of methanol; films with thickness  $\sim 400$  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  $\theta$  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 ( $\sim 28$  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



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

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).

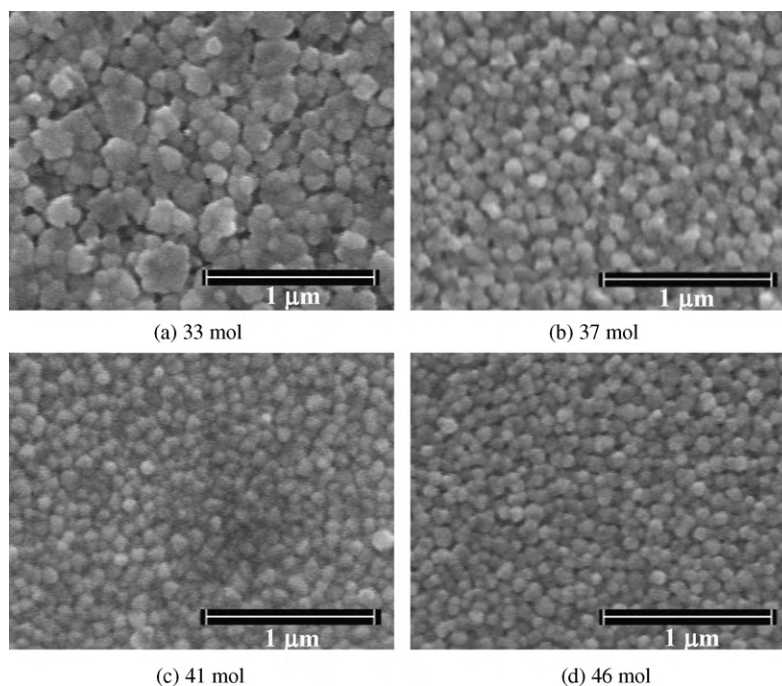


Fig. 4. SEM images of the undoped CdO films, for the four methanol contents studied in the solution precursor.

to be approximately constant after a critical thickness is reached, which is a common characteristic of material in thin films. From this figure, it can be seen, that the methanol content does not have significant effect on the resistivity, the values are within the same order of magnitude. However, in general, the resistivity decreases when thickness increases as can be observed in Fig. 6(b) for the methanol content of 33%. Changes of this type have been observed in ITO films [24]. The average resistivity value of the films with 7 coats for the four different methanol contents is  $1.5 \times 10^{-3} \Omega\text{-cm}$ . It is important to point out that these films have not been still annealed in any reactive nor inert atmosphere neither doped, with both lower resistivity values can be obtained [17].

### 3.2. Fluorine doped CdO films

XRD spectra of fluorine doped CdO films are shown in Fig. 7. The spectra are very similar to the ones obtained for undoped CdO films. These do not show the presence of any fluorine compound in according with it previously reported [17]. The crystalline grain

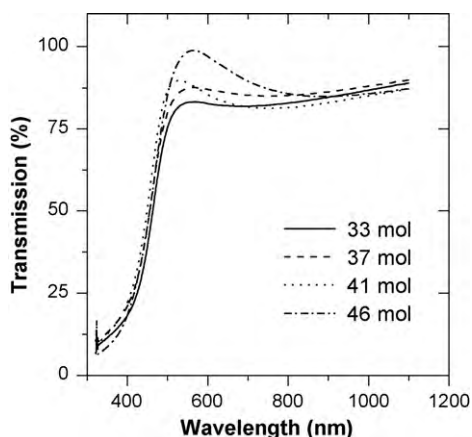


Fig. 5. Transmission spectra of the undoped CdO films for the different methanol content studied.

size was also calculated with the same procedure that it used for undoped films. The crystalline grain size diminishes around 0.8% for both methanol contents.

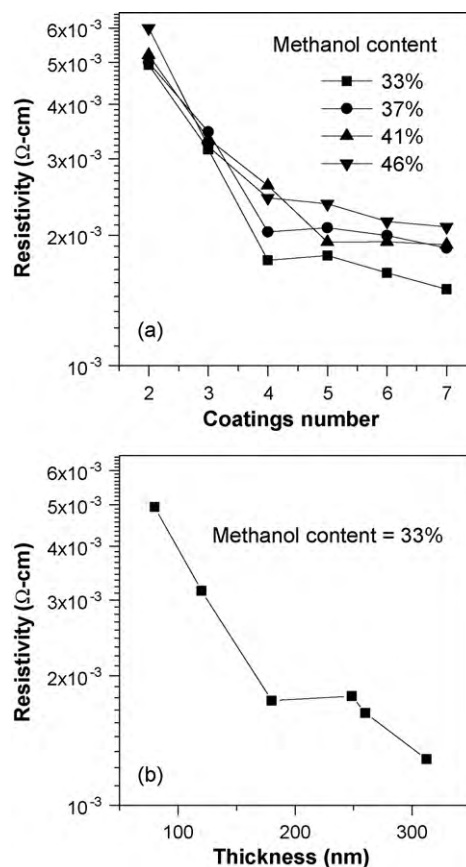


Fig. 6. Resistivity values of the undoped CdO films as a function of: (a) coatings number and (b) the methanol content in the precursor solution.

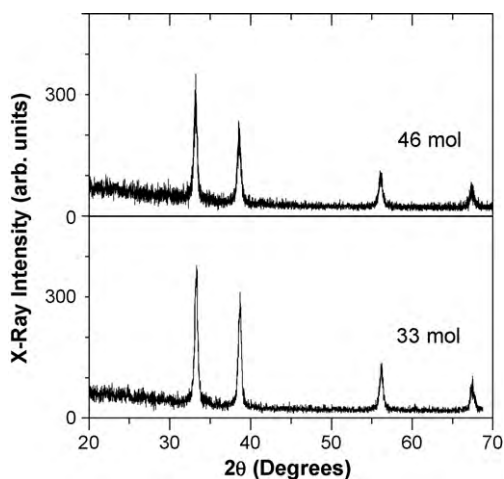


Fig. 7. XRD patterns of fluorine doped CdO films, obtained at methanol contents of 33 and 46 mol, in the precursor solution.

The resistivity of the CdO films can be diminished when the films are doped with fluorine [17]. Fluorine doped CdO films were obtained starting from the undoped precursor solution with the highest (33 mol of methanol) and lowest (46 mol of methanol) deposition rates. The films were doped with fluorine at a concentration of 5 at.% and annealed in a 96/4N<sub>2</sub>/H<sub>2</sub> gas mixture, because we have previously found that these conditions are optimal [17]. Fig. 8 shows the average thickness of the fluorine doped CdO films obtained with no annealing (NA) and with annealing (WA), as well as, the average thickness of the undoped CdO films (NA), as a function of the coatings number for films obtained starting from precursor solutions with methanol content of 33 and 46 mol. In the case of 33 mol, the doped films exhibit a decrease of the deposition rate, which can be associated to the fact that denser films and with lower crystalline grain size and aggregate are obtained when the fluorine is incorporated in the precursor solution [17]. As well, the annealing treatment provokes a diminishing of the thickness of the films. In the case of undoped and doped CdO films with methanol content of 46 mol (the lowest deposition rate), it can be seen that the doped films with the lowest methanol content (33 mol) keep the highest deposition which is similar to the undoped CdO films.

SEM images of the fluorine doped CdO films are shown in Fig. 9, for films constituted of one (a) and seven (b) coatings respectively. The films with lower coatings number show lower aggregate size than the films with a higher coatings number in accordance with that observed for the undoped films. As well, the effect of the fluorine on the decrease of the aggregated size can be observed from Fig. 9b and Fig. 4. Spectra transmission of the undoped and doped films are shown in Fig. 10, the presence of the fluorine does not

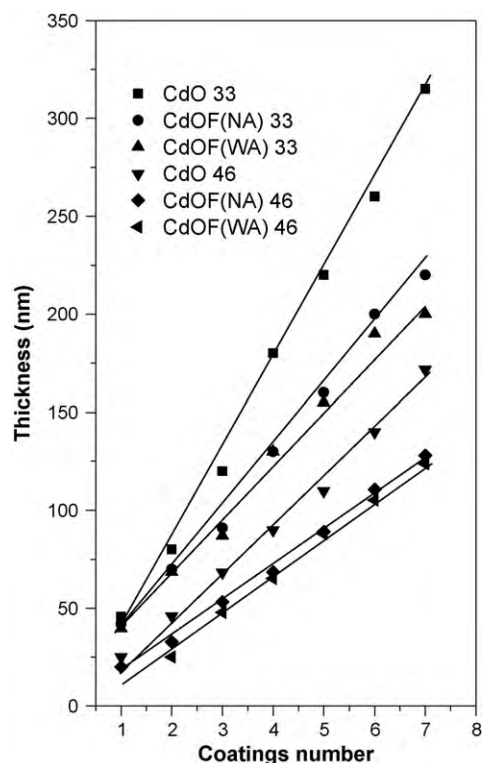


Fig. 8. Thickness as a function of coatings number. Undoped and F doped CdO films with methanol contents of 33 and 46 mol. Films with no annealing (NA) and with annealing (WA).

influence negatively their transmission. The shift observed of the absorption edge into lower wavelengths with the fluorine presence, previously observed by the authors [17], is attributed to the Moss-Burstein effect.

Even though, the deposition rate decreases due to the fluorine presence, the films obtained starting from a precursor solution with methanol content of 33 mol have a higher deposition rate with respect to the films obtained with other methanol contents. These films keep their high transmission (Fig. 5) and a lowest resistivity value of  $6 \times 10^{-4} \Omega\text{-cm}$  [17], due to the doping.

CdO:F/CdTe type solar cells were obtained before for our group [5], the thickness of the CdO:F film was of 0.42  $\mu\text{m}$ , which was obtained starting from 16 coatings. With the results shown in this work, it is possible to obtain CdO:F films with a thickness of 0.42  $\mu\text{m}$  starting from only 7 coatings and with a higher withdrawal speed, of 6 cm/min. The films are uniform, transparent, crack free and present good adherence.

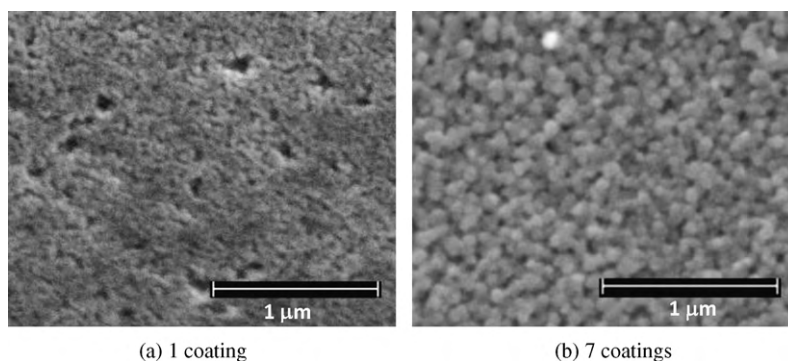
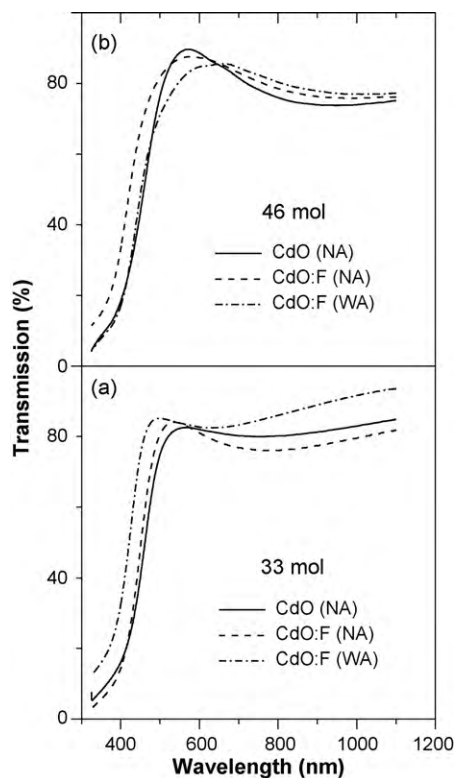


Fig. 9. SEM images of fluorine doped CdO films starting from: (a) 1 coat and (b) 7 coats, and with 33 mol of methanol content.



**Fig. 10.** Transmission spectra of the undoped and doped CdO films (CdO:F) with no annealing (NA) and with annealing (WA) in a 96/4N<sub>2</sub>/H<sub>2</sub> gas mixture. These films have a thickness of ~1250 Å.

#### 4. Conclusions

By changing the methanol content in the growing solution for the CdO undoped and F doped CdO films were prepared by sol–gel method. The fundamental participation of methanol concentration in the growing solution was analyzed. In the range 33–46 mol in the growing solution, the 33 mol content in the precursor solution shows the highest deposition rate is observed. These films have the structural, optical and electrical properties requested for their use

as transparent electrodes in solar cells with the advantage that a lower coatings number leading to higher thicknesses.

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