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Mechanical and Tribological Properties of CdO+SnO₂ Thin Films Prepared by Sol-gel

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Abstract

We report the mechanical and tribological properties of transparent conductive oxide CdO+SnO₂ coatings. The films were deposited on glass substrates by the sol-gel technique using, as precursor solution, a mixture of CdO and SnO₂ solutions obtained at room temperature. Depending on the Sn atomic concentration percentage values the X-ray diffraction patterns show three types of films constituted of i) CdO + Cd₂SnO₄, ii) Cd₂SnO₄ and iii) Cd₂SnO₄+ CdSnO₃ crystals. Reciprocal microfriction tests revealed that films with Cd₂SnO₄ phase have friction values in the range 0.48 to 0.51 and a low wear rate of $\sim 5 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. Nanoindentation tests have shown an increment of the elastic modulus from 50 GPa for CdO + Cd₂SnO₄ films to 90 GPa for Cd₂SnO₄ films, while the hardest coating was the one constituted by Cd₂SnO₄ crystals with $H=5.7 \text{ GPa}$, comparable to the hardness and elastic modulus reported for ITO films.

Keywords: Transparent Conductive Oxides, Mechanical properties, Cadmium Tin Oxide, Friction Coefficient, Nanoindentation.

1. Introduction

Solar cell technology requires the development of new thin film materials with low electrical resistivity and high optical transmittance. In addition, it is desirable that the films have also a good mechanical and tribological behavior to resist contact load and shear stresses during the processing and packaging, and a good adhesion to the substrate in order to successfully design a solar cell. If the mechanical and tribological behavior is not taken into account, it could bring profitability problems: premature delamination or loss of efficiency originated from scratches by handling will decrease the estimated lifetime of the solar panel, which implies economic losses due to the replacement manufacturer's warranty. [1].

To date, indium tin oxide (ITO) is the most popular transparent conductive oxide (TCO) despite of its high cost. To overcome this limitation, new materials such as Zn₂SnO₄, Cd₂SnO₄, CdIn₂O₄, SnO₂, and ZnO have received greater attention. Their low electrical resistivity, high carrier

concentration, and high optical transmittance in the visible region of the solar spectrum make them a good alternative for their use as transparent electrodes in photovoltaic, flat-panel displays, electrochromic devices and active electrodes in photo-electrochemical solar cells [2]. In particular, Cd_2SnO_4 (CTO) deposited by sputtering has been recently tested as a TCO in a CdTe polycrystalline based thin-film solar cell with a total-area efficiency of 16.5% [3]. CTO thin films have been grown using different techniques such as spray pyrolysis [4], pulsed laser deposition [5], sputtering [6], MOCVD [7] and sol-gel [8, 9]. In addition to monitoring the electric and optical properties through careful control of the processing parameters, there is a growing demand for investigating the mechanical and tribological properties of TCO films because the contact loading during processing or packaging can significantly degrade the performance of devices [1].

Nowadays, nanoindentation is probably the most prominent technique used in nanomechanics to investigate and characterize the mechanical properties of the materials in the sub-micron scale. Nanoindentation tests has been used to study the elastic–plastic and fracture properties of TCO's (such as Ga-doped ZnO, ITO, AZO, etc.) on flexible substrates such as PET [10, 11, 12] and rigid substrates such as glass [10, 13, 14, 15, 16] and Si [17]. Interestingly, there are no reports about the mechanical or tribological properties of the mixed $\text{CdO}+\text{SnO}_2$ system.

In the present work, we study the mechanical and tribological performance of $\text{CdO}+\text{SnO}_2$ thin films deposited by sol gel with different tin atomic percentages in the precursor solution around the stoichiometry of Cd_2SnO_4 .

2. Experimental

2.1 Sample preparation

Thin films of the mixed $\text{CdO}+\text{SnO}_2$ system were deposited on corning-glass-2947 substrates using a mixture of cadmium oxide and tin oxide precursor solutions obtained separately, after a method previously reported by the authors [18]. Both precursor solutions were mixed at room temperature (RT), at different tin atomic concentration percentages in solution (X) in a range around the stoichiometry of the Cd_2SnO_4 . The X values studied were 16, 25, 29, 33, 36 and 40 at.%. The cadmium oxide precursor solution was prepared using cadmium acetate ($(\text{CH}_3\text{COO})_2\text{Cd}\cdot 2\text{H}_2\text{O}$) (1 mol), methanol (33 mol), glycerol (0.2 mol) and triethylamine (0.5

mol). The SnO₂ precursor solution was prepared starting from stannous chloride (SnCl₂·2H₂O) (1 mol), ethanol (40 mol), glycerol (0.20 mol) and triethylamine (0.10 mol). Lactic acid (0.4 mol) was added to the mixture of both solutions in order to obtain a transparent final precursor solution. The films were deposited by the multiple-dipping method 24 h after the preparation of the precursor solution with a withdrawal speed was of 2.0 cm/min. Films of the single precursor oxides, CdO and SnO₂, were also deposited using the same experimental conditions. All the films were first thermally pretreated at 100°C and then subjected to a sintering treatment at 550°C, in both cases in air atmosphere for 1 h. The films, consisting of seven coats, were highly transparent, homogeneous and with good adherence to the substrate [18].

2.2 Structural Characterization

The crystal structure of the films was analyzed by a Rigaku Ultima IV diffractometer (CuKα1 radiation, 1.5406 Å). The thickness of the films was measured by using an optical profiler Bruker Contour GT-K0. Atomic force microscopy operated at 23 °C and relative humidity less at 2% was used to obtain the surface roughness average (Ra).

2.3 Nanoindentation and friction-wear testing

The nanoindentation tests were performed by a Hysitron Triboindenter TI-950 equipped with a Berkovich type diamond tip. Sixteen indentations with spacing of 5 microns were made on the films surface at 300 μN load; this load produces a penetration depth of about 10% of the thickness. Elastic modulus and hardness were obtained from load-displacement curves applying the Oliver and Pharr Method [19]. The influence of the diamond indenter to the reduced modulus data was decoupling using:

$$E_2 = \frac{E_r \cdot E_1 \cdot (1 - \nu_2^2)}{E_1 - E_r \cdot (1 - \nu_1^2)} \quad (1)$$

where, E_1 and ν_1 are elastic modulus and Poisson's ratio for the diamond tip, with values of 1140 GPa and 0.07 respectively, ν_2 is the Poisson's ratio for the film with value of 0.25 for TCO's [15], E_r is reduced elastic modulus from Oliver and Pharr analysis and E_2 is the elastic modulus of the film.

For the friction-wear tests, the Hysitron Triboindenter was equipped with a 90° diamond conical tip of 5.06 μm radius of curvature. In the reciprocal-mode test, the applied load was 100 μN , the length of the track was 5 microns and the test was run during 12 cycles to evaluate the evolution of the friction and wear. The friction coefficient μ was calculated using $\mu = FF/L$, where FF is the friction force and L is the applied load while the wear rate was obtained using Archard's equation [20].

3. Results and discussion

3.1 Structural characterization

The optical, electrical and structural properties of the films are already reported by the authors in a previous work [18], where it is shown that the films with only sintering treatment have high transparency ($T > 85\%$) and resistivity values of $10^{-2} \Omega \text{ cm}$.

X-ray diffraction patterns show three types of films (figure 1): i) For $X < 29 \text{ at.}\%$, the films are a mixture of $\text{CdO} + \text{Cd}_2\text{SnO}_4$ crystals, ii) For $X = 29 \text{ at.}\%$ and $33 \text{ at.}\%$ the films are constituted of only Cd_2SnO_4 crystals and iii) For $X > 33 \text{ at.}\%$, the films are a mixture of $\text{Cd}_2\text{SnO}_4 + \text{CdSnO}_3$ crystals [18]. The Cd_2SnO_4 crystallite size, calculated from the full-width at half-maximum (FWHM) data of the main diffraction peaks of the Cd_2SnO_4 using the Scherrer's formula [21], is in the 10–40 nm range. The biggest grain size value was obtained for the films only constituted of Cd_2SnO_4 . The thicknesses of the films resulted $340.0 \pm 14 \text{ nm}$, $244.0 \pm 10 \text{ nm}$, $223.0 \pm 1.6 \text{ nm}$, $247.0 \pm 5.1 \text{ nm}$, $205.0 \pm 10 \text{ nm}$, $281.0 \pm 5.8 \text{ nm}$ for the films from $X = 16$ to $40 \text{ at.}\%$, respectively. For the CdO and SnO_2 films the thickness is $250.0 \pm 8.3 \text{ nm}$ and $312.5 \pm 11 \text{ nm}$, respectively.

Fig. 1 XRD patterns of six films with different tin atomic concentration percentages in solution (X). For $X < 29$ at.% there is a mixture of CdO and Cd_2SnO_4 structures. For $X = 29$ at.% and 33 at.% only the stoichiometric phase of Cd_2SnO_4 is obtained. At tin concentration higher than $X=33$ at.% result in a mix of $\text{Cd}_2\text{SnO}_4 + \text{CdSnO}_3$ crystals

3.2 Mechanical properties

3.2.1 Nanoindentation tests

Load-displacement curves for tin atomic concentration $X=16$ at.%, 29 at.% and 40 at.% films are shown in figure 2 together with load-displacement curves of CdO and SnO_2 films. From these curves is it observed that the film at $X=29$ at. % (pure Cd_2SnO_4 crystals), present mechanical properties comparable to SnO_2 film, while the CdO and 16 at.% Sn films show the lower mechanical properties. As it is known, usually the mechanical properties of crystalline solids are dominated by their microstructure [22], as it will be shown also for our films.

Due to different mechanical response of the CTO's films reported in this work, some films had a penetration depth that exceeded the 10 percent of their thickness when were indented at 300 μN : the maximum penetration depth was 17% of thickness for the films with $X=16$ at.%. To avoid overestimation (film softer than substrate) or underestimation (film harder than substrate) of the mechanical properties, the method proposed by Zhuo and Prorok [23] was applied by making

sixteen indentations on the films surface with varying loads from 300 μN to 1400 μN . This method requires to know the mechanical properties of the substrate (corning glass), which were evaluated from nanoindentation load-displacement curves, giving values of $H = 6.3 \pm 0.2$ GPa and $E = 74.8 \pm 0.8$ GPa. Figure 3 shows the elastic modulus and hardness values for each film as a function of the tin atomic concentration. As it is shown in figure 3b, the elastic modulus evaluated by using the Zhuo and Prorok method does not change the behavior and values of E obtained by Oliver and Pharr, thus the mechanical properties will be discussed from Oliver and Pharr results for loads of 300 μN .

Fig. 2 Nanoindentation load-displacement curves for SnO_2 and CdO films, and for films from the mixed system with tin atomic concentrations $X = 16$ at.%, 29 at.% and 40 at.%

Figure 3 demonstrates that there is a correlation between the structural and the mechanical properties. For the film with $X=16$ at.%, where a combination of CdO and Cd_2SnO_4 crystals are present, figure 1 shows that the peaks are wide and with low intensity, indicating poor crystalline quality. In this film the mechanical properties are poor, with a low hardness of 1.8 ± 0.3 GPa and elastic modulus of 50.9 ± 0.8 GPa. A deconvolution analysis of the main diffraction peak (figure 4) gives a contribution of 25% for CdO and 75% for Cd_2SnO_4 crystals. For the film with $X=25$ at.% the crystalline quality increase as well as the hardness and elastic modulus, reaching values of 4.9 ± 0.1 GPa and 82.1 ± 1.3 GPa, respectively. The deconvolution of the main peaks for the 25

at.% film gives only 10% of CdO compound. The decrease of CdO compound seems to provoke a better mechanical behavior, given by the strong influence of the Cd₂SnO₄ crystals. When the cubic spinel Cd₂SnO₄ crystals is completely formed (X=29 at.%), the hardness and elastic modulus increase to 5.7±0.1 GPa and 88.9±1.4 GPa, respectively. The thickness of this film was the lowest in all the series (223 nm), indicating that the density is higher for the Cd₂SnO₄ compound. For X=33 at. %, a deterioration of the mechanical properties is observed; although the Cd₂SnO₄ stoichiometry is satisfied, the increase of thickness (247 nm) with respect to the X=29 at.% film indicates that the good distribution of the crystals with cubic spinel phase start to loose, probably due to the presence of amorphous components of Cd-Sn-O which is manifested with a fall of the (311) peak intensity. For X=36 at.% and X=40 at.%, a further decrease in H and E is observed, reaching values of 3.4±0.3 GPa and 80.8±2.9 GPa respectively. This deterioration in the mechanical properties is probably associated to the presence of Cd₂SnO₃ compounds.

Fig. 3 a) Hardness and b) Elastic modulus as a function of Sn concentration. The arrows indicate the mechanical properties of CdO and SnO₂ films (precursor oxides) deposited under the same conditions. In b) the filled diamond symbols in the elastic modulus indicates the corrected values after applying the Zhou and Prorok method. No significant deviations from results for indentations at 300 μ N using Oliver and Pharr method are observed

The mechanical properties reported in this work for Cd₂SnO₄ thin films (X=29 at.%) are comparable to the properties reported for ITO. Kaiyang Zeng et al. [15] reported elastic modulus values of 100 $\pm$ 13 GPa and hardness values of 6.5 $\pm$ 1.6 GPa for ITO films grown by magnetron sputtering with thickness of 250 nm. The elastic modulus values obtained for our films are also similar to values previously reported for other TCO's as TiO₂ [13] deposited by sol-gel.

Fig. 4 Main diffraction peaks for CdO and Cd₂SnO₄ in X=(16, 25 and 29) at.% films

3.3 Friction-Wear test

Figure 5 shows the wear profile obtained for 16 at.%, 25 at.% and 29 at.% on the virgin surface (continuous black line) and profiles after 3, 5, 7, 9 and 12 cycles. Although the length of the wear track was 5 microns, only the data within the central zone of 4 microns were used to evaluate μ and wear to avoid spurious contributions due to accumulation of material in the track borders. It

is observed that for the films at X=16 at.% the wear rate is higher than the wear for films constituted by pure Cd_2SnO_4 crystals.

Fig. 5 Profiles obtained simultaneously during the friction-wear test for $\text{CdO}+\text{Cd}_2\text{SnO}_4$ (X=16 at.% and X=25 at.%) and Cd_2SnO_4 (X=29 at.%) films. The virgin surface is the continuous black line while the dashed profiles are after 3 (...), 5 (---) 7 (-.-.-.-.-), 9 (-.-.-.-.-) and 12 cycles (thin continuous black)

The evolution of μ for all the films shown in figure 6 were simultaneously recorded with the wear data displayed in figure 5 and figure 7. For X=16 at.% the wear rate increases as the number of cycles increase, being the one who shows the more severe damage. This film also has the worst mechanical properties; this behavior can be associated to the high concentration of CdO compound present in the film (25% of CdO). The roughness measured as a function of the cycles (figure 8) also shows that the X=16 at.% film has the highest roughness value (6 nm), given place to detachment of particles from the film during the wear test which has influence on the tribological properties, acting like a lubricant and decreasing the friction coefficient. Topography analysis from AFM images (figure 9) shows that the aggregate size for the films at X=16 at.% compare to the film at X=29 at.% conserves a relationship of 10:1. On the other hand, for the films at 25 at.% the wear rate felt almost to zero, and even when the Cd_2SnO_4 crystals start to dominate, the μ increases from 0.46 to 0.57. This increase in μ can be due to the lower roughness

(figure 8) which produce an increase in the contact area between the indent and the surface [24]. For the films with X=29 at.% and 33 at.% with the only presence of Cd_2SnO_4 crystals, the wear rate values are around of $5 \times 10^{-5} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$, which means that the diamond tip penetrates only ~ 1 nm during all the experiment. The friction coefficient is stable with values of ~ 0.48 for X=29 at.% while a slight fall from ~ 0.52 to ~ 0.50 is observed for X=33 at.%, probably due to detachment of particles which cause a lubricant effect [24]. This argument is consistent with the worsening of the mechanical properties, due probably to the presence of amorphous components of Cd-Sn-O which is manifested with a decrease of the (311) peak intensity. Topography analysis (figure 9b) for X=29 at.% reveals a homogeneous surface with roughness of 1.44 nm. The same behavior was observed for the film at 36 at.%, even when there is presence of a mix phase constituted of $\text{Cd}_2\text{SnO}_4 + \text{CdSnO}_3$ crystals. The most stable μ values as the number of cycles increases correspond to the films at 29 at.%, 33 at.% and 36 at.%, with values of ~ 0.48 , ~ 0.51 and ~ 0.46 , respectively. For the film at X=40 at.% the wear rate increased with the cycles to values of $\sim 200 \times 10^{-5} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$ while the friction coefficient was almost constant in 0.53. The increment in wear was expected due to the low mechanical properties ($E=80.8 \pm 2.9$ GPa and $H=3.4 \pm 0.3$ GPa) which is associated to the presence of CdSnO_3 crystals.

Fig. 6 Friction coefficient (μ), as a function of the number of cycles for all films

From our experiments we can conclude that the best mechanical and tribological properties correspond to the films with $X = 29$ at.%, which are films constituted only by Cd_2SnO_4 crystals. These films present the highest H and E values, very low wear rate and a stable friction coefficient. This behavior is similar to the observed for ITO thin films deposited by sputtering onto glass substrate, where the films with high crystallinity show the best mechanical properties [25]. Interestingly, we have recently shown that these films with $X = 29$ at.% also present the best optical and electrical properties for their use as transparent electrodes in solar cells [18].

Fig. 7 Wear as a function of the cycles for all the films

Fig. 8 Roughness average (R_a), as a function of the number of cycles for all films

Fig. 9 AFM topography images for a) $X=16$ at.% and b) 29 at.%

4. Conclusions

Nanoindentation and friction-wear test were made on thin films of the mixed $\text{CdO}+\text{SnO}_2$ system deposited by the sol-gel technique. The results show that the films containing only Cd_2SnO_4 crystals (tin atomic concentration percentages in solution $X=29$ at.%) have the best mechanical properties with values of 5.7 ± 0.1 GPa for hardness and 88.9 ± 1.4 GPa for elastic modulus,

comparable to ITO films. These films also have low wear rate, and a stable friction coefficient. We have also found that the presence of CdO and CdSnO₃ crystals in the films have a negative influence in their mechanical and tribological properties. The Cd₂SnO₄ sol gel films, which are already known for having similar electrical and optical properties than ITO films, have a good potential in the manufacturing of solar cells. The simplicity and economy of the technique used in their preparation and the good mechanical and tribological properties make these films good candidates as transparent conductive oxides, because they will probably resist the contact load and shear stresses during the processing and packaging.

Aknowlegments

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