SnO_2:F thin films deposited by RF magnetron sputtering: effect of the SnF_2 amount in the target on the physical properties

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SnO_2:F thin films were prepared by RF magnetron sputtering onto glass substrates using SnF_2 as fluorine source. The films were deposited under a mixed argon/hydrogen atmosphere at a substrate temperature of 500°C. The X-ray diffraction shows that polycrystalline films were grown with a phases mixture of SnO_2 and SnO. The optical transmittance is between 80 and 90%. The physical properties of the films suggest that SnO_2 thin films grown with small SnF_2 content in the target can be considered as candidates for transparent electrodes.

Keywords: F-doped tin oxide; transparent conducting oxide; RF magnetron sputtering; transparent electrodes.

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1. Introduction

Transparent conducting oxide (TCO) thin films have important applications in the opto-electronics field as transparent electrodes in photovoltaic conversion due to their optical and electrical properties [1]. The tin oxide (SnO_2) is one of the metal-oxide semiconductors commonly used in such devices because it has high transmittance in the visible spectrum (400-700 nm) and low resistivity. If SnO_2 were completely stoichiometric it would be an insulator or at most an ionic conductor [2]. However, this material is never stoichiometric and presents oxygen deficiencies. These vacancies are responsible for available electrons in the conduction process. Even a perfectly stoichiometric SnO_2 crystal can behave as a conductor generating oxygen deficiencies by heating of the sample or by chemical doping.

SnO_2 films can be prepared by different techniques, such as spray pyrolysis [3], chemical vapor deposition (CVD) [4], laser evaporation [5], electron beam evaporation [6] and sputtering [7]. Sputtering technique offers low production cost, a relevant factor for industrial applications [8]. In the present work F-doped SnO_2 films (SnO_2:F) were deposited by RF reactive magnetron sputtering. We report on the influence of the nominal concentration of fluorine in the target on the structural, topography, optical and electrical properties of the SnO_2:F films.

2. Experimental details

2.1. Sample preparation

SnO_2 thin films were deposited on glass substrates by RF magnetron sputtering using targets with different amounts of SnF_2 and SnO_2 in a mixed atmosphere of argon/hydrogen, containing 97% Ar and 3% H. We introduce a small percentage of hydrogen in order to create a reactive atmosphere, when using a pure argon atmosphere insulating SnO_2 films were obtained. The targets were fabricated from SnO_2 and SnF_2 powders with a purity of 99.99%, varying the SnF_2 weight (wt) concentration in the different targets from 1, 7, 10 to 15 wt%. The powders were mixed in a ball mill for 6 hr and then were pressed at 4 tons into a plunger with a diameter of 1 inch. The substrate temperature was 500°C. The background pressure in the deposition chamber was 10^{-5} Torr. For the growth the power at the target was maintained at 50 W and the substrates were located 7 cm below the target. The growth time in all cases was 1 hr. The samples were labeled according to the SnF_2 amount in the target (see Table I).

2.2. Sample characterization

The crystalline structure was determined by X-ray diffraction (XRD), in a Siemens D5000 diffractometer, using the Cu-Kα line (λ = 1.5406 Å). The topography studies were performed by AFM, using a ThermoMicroscope Autoprobe CP Research (Veeco Instruments) in contact mode. Film thicknesses were measured by a profile meter KLA Tencor P15. The transmittance spectra were obtained using an UV-Vis Perkin Elmer Lambda 25 spectrophotometer. The electric characterization was made by measurements of sheet resistance (R_s), using the four-point probe method [9] applying the corresponding geometric correction factors.

3. Results and Discussion

3.1. Structural properties

Figure 1 shows the XRD patterns of SnO_2:F films grown by RF magnetron sputtering. It can be seen that all samples pre-

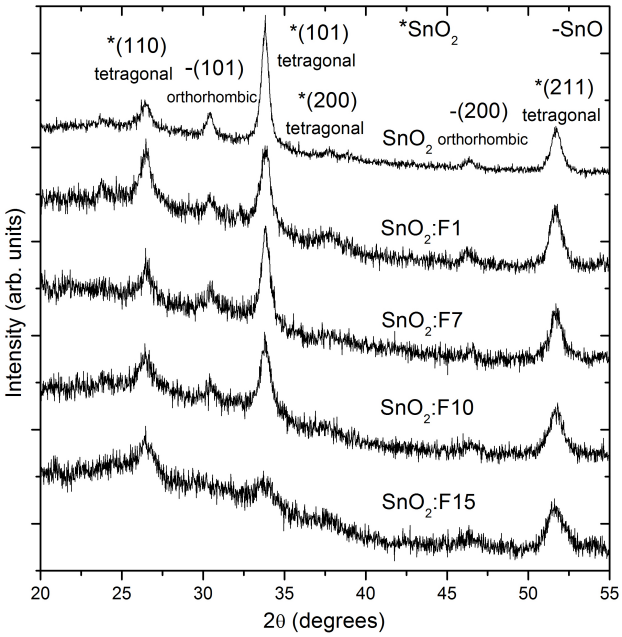

FIGURE 1. XRD patterns of a SnO_2 film and four SnO_2:F films with different SnF_2 percentage in weight in the target.

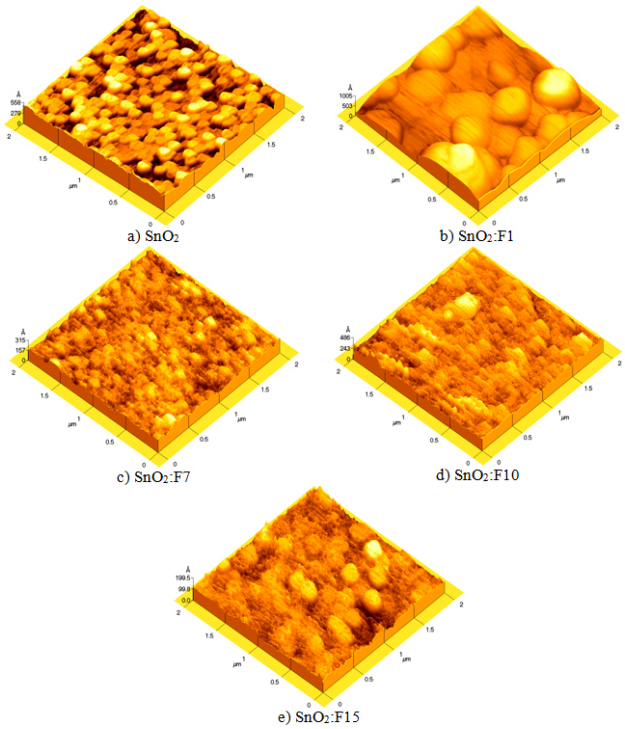

FIGURE 2. AFM images of the SnO_2:F thin films grown by RF sputtering.

sent six peaks located at 26.42°, 30.40^o, 33.82°, 37.80°, 46.28° and 51.70°. The peaks located at 26.42°, 33.82°, 37.80° and 51.70° correspond to the tetragonal phase of SnO_2 and the diffraction planes are (110), (101), (200) and (211), respectively. The peaks at 30.40° and 46.28° correspond to the SnO orthorhombic and the diffraction planes are (101) and (200), respectively. The peaks were indexed using the powder diffraction files 41-1445 (SnO_2 tetragonal) and 24-1242 (SnO orthorhombic). Tin oxide films with a mixture of phases of SnO_2 and SnO are usually obtained by sputtering [10]. It is important to mention that diffraction peaks of the films present a slight shift with respect to reference cards, which indicates that probably there residual strain in the films. These residual strain may be due to the presence of different phases. In the diffractograms it can be also seen that when the SnF_2 amount in the target increases the films lose crystalline quality.

According to Fig. 1, for SnF_2 amounts in the target between 1 and 10% the diffraction patterns are very similar. However for the sample SnO_2:F15, deposited with a SnF_2 content of 15 wt% the pattern indicates a strong decrease in the crystalline quality. The diffraction peaks became broader and less intense. This result suggests that SnO_2:F thin films with better physical properties are those grown with smaller amounts than 15 wt% of SnF_2 in the target.

3.2. Atomic force microscopy characterization

Figure 2 exhibits the SnO_2 thin films surface morphology images obtained by AFM (2×2 μm). The Fig. 2a) shows the morphology of an undoped SnO_2 film, which presents circular shape grains with an average size of 132 nm. The surface of SnO_2:F1 sample (Fig. 2b) has larger grains of around 500 nm. The SnO_2:F7 and SnO_2:F10 samples, Figs. 2c-d) respectively, present grains of arbitrary shape and many grain boundaries. Fig. 2e) shows the surface of the SnO_2:F15 sample, which has few grains with circular shape with an average diameter of 181 nm. We believe that the increase of grain boundaries in SnO_2:F7, SnO_2:F10 and SnO_2:F15 samples may be due to the formation of Sn-F complexes. The boundaries between grains play a significant role in the scattering of carriers in polycrystalline thin films [11], so it is important to obtain thin films with large grain size and few grain boundaries. The rms roughness (see Table I) of the undoped SnO_2 sample has a value of 4.91 nm, the rms roughness increases to a value of 7.10 nm for the sample with 1 wt% of SnF_2 in the target and for amounts greater than 1% the rms roughness decreases. Surface morphology of transparent electrodes is an important factor in order to achieve improvements in some applications such as photovoltaic conversion and flat displays, it is known that lower roughness of the films is a parameter linked with the efficiency of CdTe thin-film solar cells [12,13]. The rms roughness values obtained in this work are similar to those reported in the literature by other authors [6,13,14].

3.3. Optical properties

Transmittance measurements were performed as a function of the wavelength to determine the effect of fluorine incorporation on the optical properties of the SnO_2:F films. Fig. 3 shows the transmittance spectra for representative undoped and F-doped SnO_2:F films. The average transmittance in the visible region is shown in Table I, the transmittance values

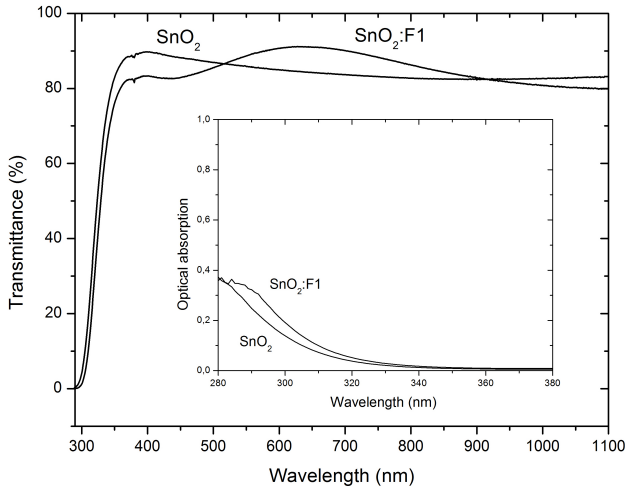

FIGURE 3. Optical transmittance and absorption of a SnO_2 and SnO_2:F1 films. In the visible region the transmittance of SnO_2:F films is between 80 and 90%.

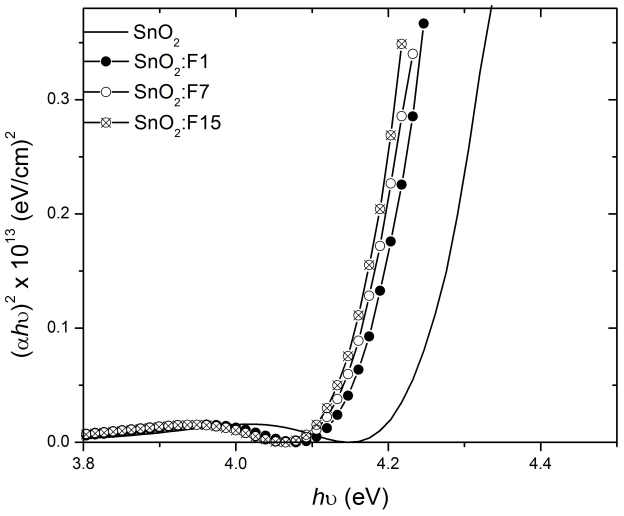

FIGURE 4. Bandgap calculations of SnO_2:F films.

were between 80 and 90%, thus we conclude that the obtained films are highly transparent in the visible region. In the inset of the Fig. 3 the optical absorption as a function of the wavelength was graphed for representative undoped and F-doped SnO_2 films. The absorption coefficient (α) was calculated using the relation [15]:

$$T = (1 - R)^2 \exp(-\alpha d), \quad (1)$$

where: T is the transmittance, R is the reflectance and d is the film thickness. The average thickness of films was 103 nm $\pm$ 5%. The reflectance was calculated from the relation: $T + R + A = 1$, where A is the absorbance. By plotting $(h\upsilon\alpha)^2$ vs $h\upsilon$ the bandgap value (*Eg*) was estimated [16], as shown in the Fig. 4. The undoped SnO_2 film has a bandgap of 4.24 eV, while that for the SnO_2:F1 sample is 4.16 eV (see Table I), observe that the bandgap of the SnO_2 films decreased from 4.24 to 4.13 eV. These E_g values are within the range of those reported in the literature [2]. We believe that the incorporation of F^- ions in the lattice gives rise to donor levels in the SnO_2 bandgap causing the conduction band to extend which reduces the bandgap.

TABLE I. Physical properties of the SnO_2:F thin films grown by RF sputtering.

Sample	SnF_2 in the target (wt%)	*Eg* rms roughness (nm)	T (%)	Resistivity (eV)	(Ωcm)
SnO_2	0	4.91	4.24	85	0.211
SnO_2:F1	1	7.10	4.16	88	3.1×10^{-3}
SnO_2:F7	7	3.80	4.14	84	0.29
SnO_2:F10	10	3.08	4.14	87	1.13
SnO_2:F15	15	3.70	4.13	85	1.23

3.4. Electric characterization

The resistivity values are displayed in Table I. There is a strong dependence between the SnF_2 amount in the target and the resistivity. The resistivity of the SnO_2 sample has a value of 0.211 Ωcm, the resistivity decreases to 3.1×10^{-3} Ωcm for a 1 wt% of SnF_2 in the target and for a quantity greater than 1 wt% the resistivity increases. The initial decrease in resistivity is expected due to the incorporation of fluorine ions in the SnO_2 structure. Thus, the initial reduction in the resistivity can be attributed to an increase in the free carriers concentration due to the substitutional incorporation of F^- ions instead of O^{2-} ions [13]. For SnF_2 amounts greater than 1 wt%, the free carrier concentration saturates and the mobility decreases probably due to the formation of Sn-F complexes in the grain boundaries causing an increase in the resistivity [13]. Stjerna *et al.*, [17] obtained a resistivity of 2.8×10^{-3} Ωcm after doping with fluorine their SnO_2 films by RF reactive sputtering using an atmosphere with low content of CF_4 as fluorine source, this value is in the range to that reported in this paper. However, we believe that using a solid dopant in the target has advantages over a reactive atmosphere.

4. Conclusions

Polycrystalline and low roughness SnO_2:F films were obtained by RF magnetron sputtering using SnF_2 as fluorine source. The structural analysis performed indicates that the films have tetragonal and orthorhombic crystallographic phases. The SnO_2:F thin films are highly transparent in the visible region of the electromagnetic spectrum, the transmittance of these films was found between 80 and 90%. The lowest resistivity value was 3.1×10^{-3} Ωcm and corresponds to a SnF_2 amount of 1 wt% in the target. This film is highly transparent and presents low roughness. We conclude, based

on the results, that the SnO_2:F1 films have potential as transparent electrodes for photovoltaic applications.

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