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Effect of Processing on the Electrical Properties of Spray-Deposited SnO_2:F Thin Films

[1]Shadia J. Ikhmayies and [2]Riyad N. Ahmad-Bitar
[1]Department of Physics, Faculty of Basic Science, Applied Science Private University, Amman, Jordan
[2]Department of Physics, Faculty of Science, University of Jordan, Amman, Jordan

Abstract: Highly transparent SnO_2:F thin films were produced by the Spray Pyrolysis (SP) technique to be used as forcontacts in the home made CdS/CdTe solar cells. Films of thickness 100-200 nm were prepared at substrate temperatures in the range 380-480°C. To improve the electrical properties of the films, annealing in nitrogen atmosphere at 400°C and etching by HNO_3 were tried. The resistivity of the films was calculated from the I-V plots which are all linear. It had significantly decreased after annealing, but slightly decreased after HNO_3-etching alone. The improvement in the electrical properties was accompanied by an improvement in the X-Ray Diffraction (XRD) spectra and an increase in the grain size as shown by the scanning electron microscope (SEM) images. The annealing period needed to obtain the lowest resistivity was longer for films prepared at lower substrate temperatures.

Key words: Thin films, annealing, doping, spray pyrolysis, solar cells

INTRODUCTION

Tin oxide is a crystalline solid with a tetragonal crystal lattice. It is a widegap, non stoichiometric semiconductor and behaves more or less as a degenerate n-type semiconductor with a low n-type resistivity ($\approx 10^{-3}$ Ω.cm)[1]. Tin oxide can exist in two structures belonging to direct and indirect optical transitions, with different bandgaps; a direct band gap that ranges from 3.6 to 4.6 eV[2] at room temperature and indirect bandgap of about 2.6 eV[3]. An important property of tin oxide is that it is the most chemically stable in atmospheric ambient[1,4] amongst the other metal oxides.

Transparent conducting tin oxide films are of considerable interest for solar-energy conversion applications. They are used in thin film solar cells as a window material and as an electrode to collect the charge in CdS/Cu_2S[1], CdS/CdTe[5] and amorphous silicon solar cells[1]. In addition to solar cell technology, tin oxide has also been used in fabrication of gas sensors due to the sensitivity of its surface conductance to gas adsorption[2, 6].

The electrical conductivity of these films can be enhanced by appropriate doping. It has been established that F-doped tin oxide films have higher conductivity, optical transmission and infrared reflection than the tin oxide films prepared with other dopants[7]. Tin-oxide thin films have been prepared by several methods: reactive sputtering[8], evaporation[9], chemical vapour deposition[9,10], dip coating[11] and spray pyrolysis[2,5,6]. Of these methods the spray pyrolysis represents the less expensive alternative, since it can produce large area, high-quality and low cost thin films [2]. Doping with Sb, Cl, Br and F has been achieved by adding a suitable compound of the dopant to the spray solution.

The purpose of this work is to improve the electrical properties of the spray deposited SnO_2:F thin films to be suitable as forecontacts in the home made CdS/CdTe solar cells. Highly transparent SnO_2:F thin films which were produced at substrate temperatures in the range 380-480°C were annealed in nitrogen atmosphere at 400°C or etched by HNO_3. The electrical properties of the films were investigated through the I-V plots which are linear and the resistivity was calculated from the slopes. Since electrical properties are related to structural properties, the XRD spectra and SEM images of the films were recorded to see the effects of the aforementioned treatments on the crystal growth and grain size.

EXPERIMENTAL PART

Stannous chloride $SnCl_2.2H_2O$ was used in making the precursor solution for SnO_2 thin films. Hydrofluoric acid HF (40%) was used as the doping material. A

Corresponding Author: Shadia J. Ikhmayies, Department of Physics, Faculty of Basic Science, Applied Science Private University, Amman, Jordan

Small amount of hydrochloric acid HCl (about 36% HCl) was added to improve the solubility and water was added as a source of oxygen.

The solution was made by dissolving 5.0×10^{-2} moles of $SnCl_2.2H_2O$ with 5.71×10^{-2} moles of HF in 45 mL of methanol, 40 mL of distilled water and 10 mL of HCl. The ratio of fluorine ions to tin ions in the solution was approximately the same as Gordillo *et al.*[6], that is 1.14. This ratio was chosen because they found that the optimum concentration of fluorine ions to tin ions in the precursor solution made from $SnCl_2$ and HF was 1.1.

The substrates which are ordinary glass with dimensions 2.5×6×0.1 cm^3 were cleaned first by dipping in distilled water to remove the dust and then they were ultrasonically cleaned in methanol for at least 15 min. Finally they were soaked in distilled water and polished with lens paper. The pretreatment of the substrates was carried out to facilitate nucleation on the substrate surface. Presence of contamination on the substrate surface is one of the reasons of the appearance of pinholes.

The spray rate was usually in the range 15-18 mL min^{-1}. The optimum carrier gas pressure for this rate of solution flow was around 5 kg cm^{-2}. At lower pressures, the size of the solution droplets becomes large, which results in the presence of recognized spots on the films and then less transparency. This situation increases the scattering of light from the surface and then reduces the transmittance of the films.

The substrate temperatures for SnO_2:F thin films was taken in the range 380-480°C. Lower substrate temperatures resulted in smaller grain size[5], larger resistivity and incomplete crystal growth in the films.

A solution made of 1 mL of nitric acid HNO_3 (Assay 69 to 72%) and 100 mL of distilled water was used to etch the SnO_2:F thin films. The films were rinsed in this solution for 20 s, where gas bubbles were seen on the surface of the film during the etching process. Finally the films were rinsed in distilled water and dried with air drier. This solution is slightly effective in improving the conductivity of the films.

Silver was used as the contact material for SnO_2:F thin films. Two strips were deposited on the surface of the film by vacuum evaporation. The strips are of thickness around 0.4 μm, length of 1 cm, width of 1 mm and separation of 2-3 mm.

The films were annealed in nitrogen atmosphere at 400°C by using the annealing system described in[5]. The transmittance of the films was measured by using a double beam Shimadzu UV 1601 (PC) spectrophotometer with respect to a piece of glass of the same kind of the substrates. X-ray measurements were made with a Philips PW1840 Compact x-ray diffractometer system with Cu K_α (λ = 1.5405 Å) and the SEM images were taken by a LEITZ-AMR 1000A scanning electron microscope.

RESULTS AND DISCUSION

Highly transparent polycrystalline SnO_2:F thin films were spray-deposited at substrate temperatures T_s = 380-480°C. The transmittance of two films with different film thickness was shown in Fig. 1 in the wavelength range λ = 290-1100 nm.

As the figure shows the transmittance is as high as more than 90% for both films. The presence of interference maxima and minima is an indication of the uniformity of the films. The minima were used to estimate the film thickness. The polycrystalline nature of the films was evident in the XRD spectra (Fig. 4) and the SEM images (Fig. 5).

The effects of annealing in nitrogen atmosphere at 400°C and etching by HNO_3 on the electrical properties of the films were investigated.

Effect of annealing: To improve the electrical properties of the as-deposited SnO_2:F thin films, they were annealed in nitrogen atmosphere at 400°C for different periods of time. Annealing had significantly decreased the resistivity of the films. In Fig. 2a the I-V characteristics are shown for a film of thickness about 100 nm prepared at T_s = 400°C. Its resistivity had

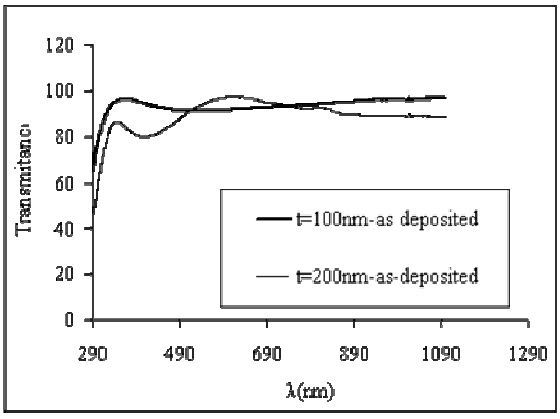


Fig. 1: The transmittance of two as-deposited SnO_2:F thin films of different thickness

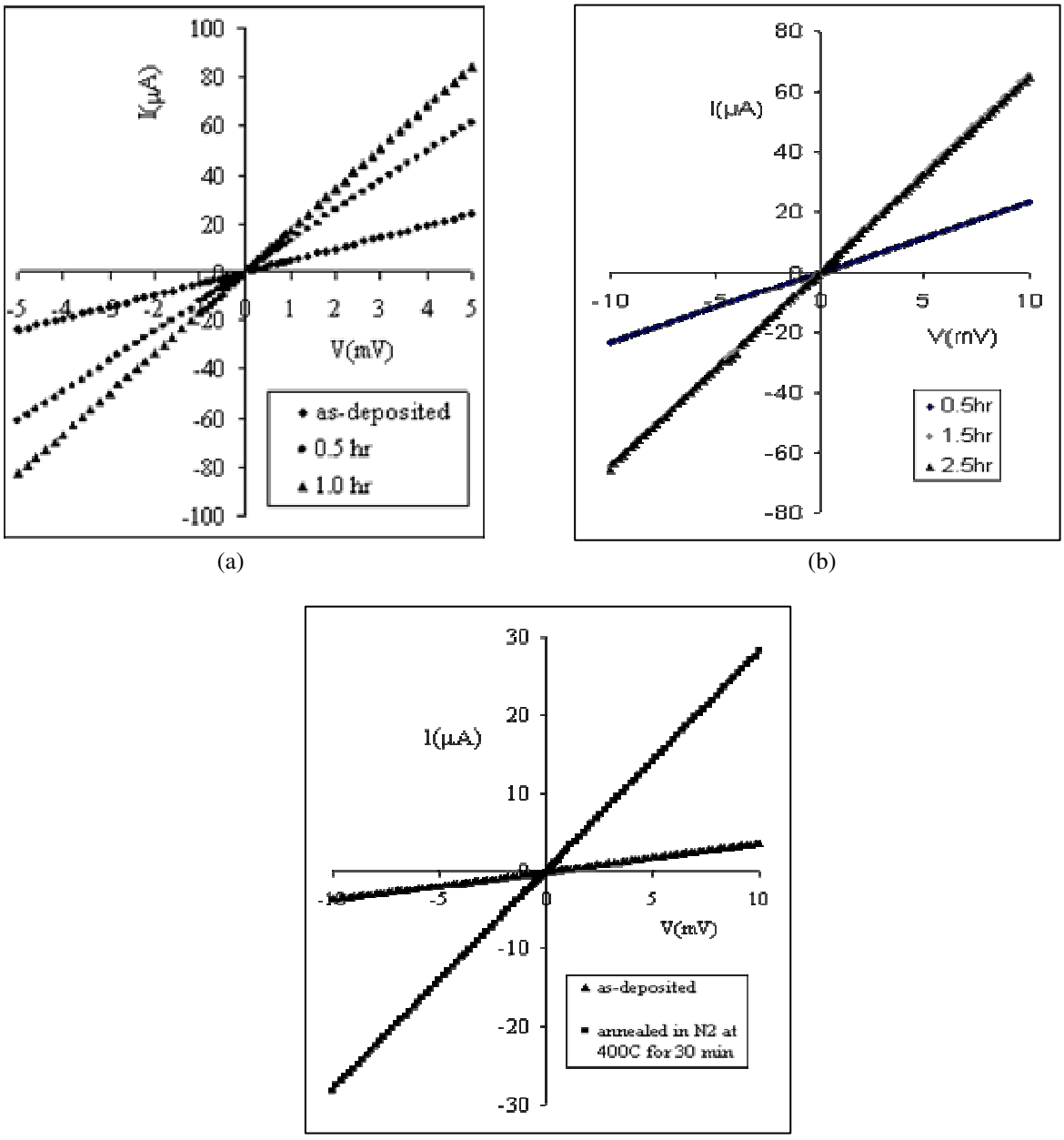


Fig. 2: (a) The effect of annealing on the I-V curves of a SnO_2:F thin film of thickness about 100 nm deposited at T_s = 400°C. (b) The effect of the annealing period on the I-V curves of a SnO_2:F thin film deposited at T_s = 400°C. (c) The effect of the annealing period on the I-V curves of a SnO_2:F thin film deposited at T_s= 480°C

decreased after 0.5 h annealing period from 1.59×10^{-1} Ω.cm to 2.1×0^{-2} Ω.cm, or by a factor of 7.6. But after 1.5 or 2.5 h annealing periods (Fig. 2b) the resistivity had decreased to 7.72×10^{-3} Ω.cm, or a decrease by a factor of 20.6. No improvement occurs after the 1.5 h annealing period. The decrease in the resistivity is accompanied by an enhancement in the crystal growth as shown in the XRD spectra (Fig. 3b) and a considerable increase in the grain size as shown in the SEM images (Fig. 4b).

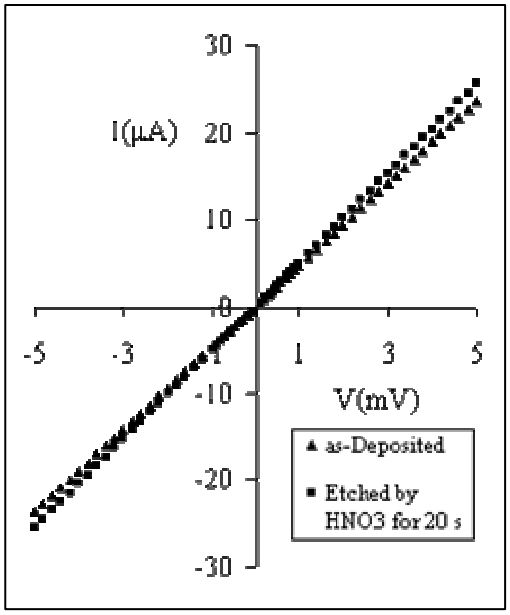


Fig. 3: The effect of HNO_3 etching on the I-V curves of SnO_2:F thin films of thickness about 200 nm prepared at substrate temperature of 480°C

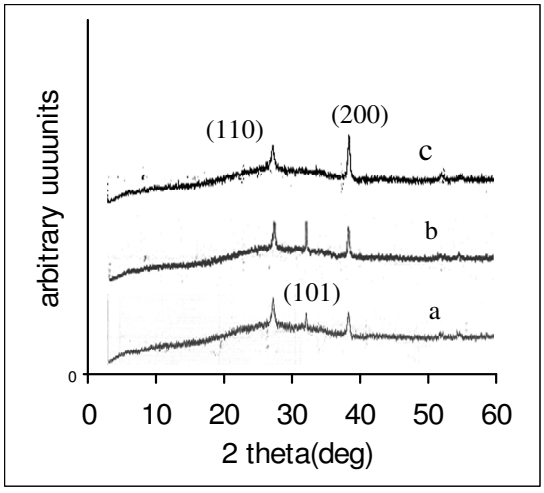
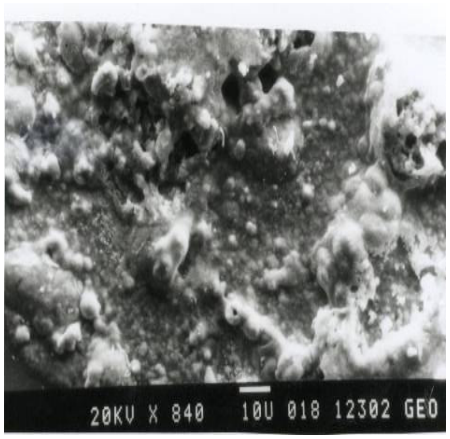


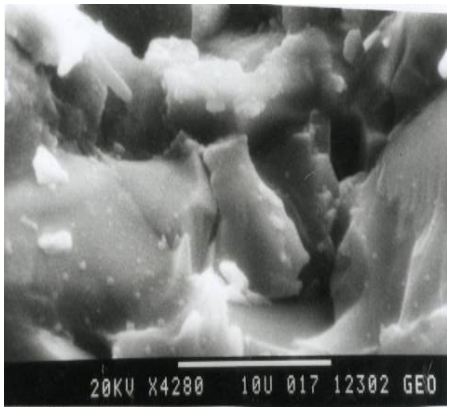
Fig. 4: X-ray diffraction spectra of SnO_2:F thin films. (a) As-deposited. (b) Annealed in nitrogen at 400°C and (c) Etched in HNO_3 then annealed at 400°C

In Fig. 2c the I-V curves were taken for a film of thickness 200 nm deposited at 480°C. The resistivity had decreased from 2.11×10^{-2} Ω.cm for the as deposited film to 7.5×10^{-3} Ω.cm after annealing the film for half an hour or a decrease by a factor of 2.8,

(a)



(b)



(e)

Fig. 5: L SEM images of SnO_2:F thin films. (a) As-deposited. (b) Annealed at 400°C for 30 min and (c) Etched by HNO_3 in distilled water, then annealed at 400°C in N_2 for 30 min

but it had decreased to 5.96×10^{-3} Ω.cm after annealing the film for 1 h a decrease by a factor of 3.5. So better

results where obtained for the film deposited at 480°C. That is it needs a shorter annealing period and a smaller value of the resistivity could be obtained. This can be explained by saying that; larger grain size is obtained at higher substrate temperatures and the crystal growth is more complete in this case[5, 12].

Effect of HNO_3 etching: The as-deposited films were etched with HNO_3 in distilled water (1:100 by volume). This had slightly improved the electrical properties of the films (Fig. 3). The resistivity of a film of thickness 200 nm had decreased from 2.02×10^{-2} Ω.cm for the as-deposited film to 1.87×10^{-2} Ω.cm for the etched film. The slight decrease in the resistivity may be due to the removal of a surface layer by HNO_3, since it is an oxidizing agent and gas bubbles were observed on the surface of the film during etching.

CONCLUSIONS

The effects of annealing in nitrogen atmosphere at 400°C and HNO_3 etching on the electrical properties of SnO_2:F thin films were studied by investigating the I-V characteristics of the SnO_2:F thin films. Annealing in nitrogen atmosphere is effective in decreasing the resistivity of the films, but etching decreases it slightly. The effect of the annealing period was also studied. It is found that as the substrate temperature increases the required annealing period to get the best results becomes less. There is a certain limit of the annealing period after which annealing becomes ineffective. This limit is achieved when the crystal growth becomes complete. The improvement in the electrical properties was accompanied by a slight enhancement of the crystal growth and a considerable increase in the grain size as shown by the XRD spectra and the SEM images.

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