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Effect of solvent ratio on the properties of highly oriented sprayed fluorine-doped tin oxide thin films

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Abstract

Transparent conducting thin films of F:SnO_2 have been deposited onto preheated glass substrates by a spray pyrolysis technique using pentahydrate stannic chloride ($SnCl_4 \cdot 5H_2O$) and ammonium fluoride (NH_4F) as precursors and mixture of water and propane-2-ol as solvent. The concentration of $SnCl_4 \cdot 5H_2O$ and NH_4F is kept fixed and the ratio of water and propane-2-ol solvent in the spraying solution is varied. A fine spray of the source solution using air as a carrier gas has grown films of thickness up to 995 nm. Optical absorption, X-ray diffraction, Van der Pauw technique for measurement of a sheet resistance and Hall effect measurements at room temperature for determination of carrier density and conductivity have been used. The as-deposited films are of polycrystalline SnO_2 with a tetragonal crystal structure and are preferentially having orientation along the (200) direction with texture coefficient as high as 6.16. The average grain size for the as-deposited sample is found to be of the order of 44 nm. The films have moderate optical transmission (up to 70–85% at 550 nm). The figure of merit (ϕ) values vary from $1.95 \cdot 10^{-3}$ to $35.68 \cdot 10^{-3}$ Ω^{-1}. The films are heavily doped, degenerate and exhibit *n*-type electrical conductivity. The lowest sheet resistance (R_s) for the optimized sample is 5.1 Ω. The films have a resistivity of $5.43 \cdot 10^{-4}$ Ω cm and mobility around 7.38 cm^2 V^{-1} s^{-1}.

Keywords: Transparent conducting oxide thin films; Tin oxide; Spray pyrolysis; Van der Pauw technique; Hall effect

1. Introduction

The simultaneous occurrence of high optical transparency in the visible region and high electrical conductivity is not possible in an intrinsic stoichiometric material. The only way to obtain good transparent conductors is to create electron degeneracy in a wide band gap (greater than 3 eV) oxide by controllably introducing non-stoichiometry and/or appropriate dopants [1]. SnO_2 has a tetragonal structure, similar to the rutile structure with the wide energy gap of $E_g = 3.67$ eV, and behaves as an *n*-type semiconductor [2]. These conditions are very conveniently obtained in SnO_2 thin films, prepared by a number of deposition techniques. Numerous techniques for depositing fluorine-doped tin oxide (FTO) have been employed [3–10]. Among these spray pyrolysis is well suited for the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings [11]. Organic solvents like methanol and ethanol are typically used in spray pyrolysis of transparent conducting oxides (TCO). There are few reports on the synthesis of ITO films wherein a methanol/water (volume ratio 9:1) as organic/aqueous solvent mixture was used [12]. Further it has been observed that the optical transmission of SnO_2 films could be increased by the addition of few drops of oxalic acid to the spray solution [13].

It has been observed that the electrical properties of FTO thin films strongly depend on the deposition conditions [2]. Hence to achieve a better control over the physical properties of these films, systematic investigations over each process parameter are needed. It is found that [14], the sprayed FTO thin films are highly oriented along the [200] direction. The preferred growth remained predominant irrespective of the substrate temperature, thickness and quantity of spraying solution, wherein the solution composition required to deposit good quality thin films is kept constant. In order to check whether one can control the growth mechanism through the solvent (water/propane-2-ol)

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composition, FTO thin films are deposited using different solvent (water/propane-2-ol) ratios in the present investigation. The concentration of [$SnCl_4 \cdot 5H_2O + NH_4F$] is kept fixed and by changing the volumetric proportions of water to propane-2-ol in the spraying solution, solvent ratio is changed. Dependence of film growth rate, optical, structural, and electrical transport properties on solvent composition has been studied and discussed.

2. Experimental

Spray pyrolysis involved the spraying of a precursor solution through a pneumatic nozzle onto a substrate located on a temperature controlled heating plate. The apparatus has been described elsewhere in detail [15]. Stannic chloride, ammonium fluoride, oxalic acid, and solvent (propane-2-ol) obtained from Loba Chemie, Mumbai were used. Doubly distilled water was used throughout the experimentation. $SnCl_4 \cdot 5H_2O$ was diluted with double distilled water. When the ammonium fluoride (NH_4F) salt diluted with water was added in this solution to affect 20% fluorine doping, the resulting solution was turbid. To remove turbidity, 24 ml of 0.01 M oxalic acid was added to it [14]. This forms the stock solution. Bhardwaj et al. [13] reported that, in order to improve the optical transmission of FTO films, a few drops of oxalic acid need to be added to the stock solution. The final spraying solution (20 ml) was made by mixing stock solution (10 ml) and solvent (water plus propane-2-ol) 10 ml. Resulting concentrations of $SnCl_4 \cdot 5H_2O$ and NH_4F in the spraying solution were turned out to be 0.81 M and 1.51 M respectively. The FTO films were deposited by varying water to propane-2-ol ratio in the volumetric proportions as 10:0, 8:2, 6:4, 4:6, 2:8 and 0:10 and the deposits obtained are designated respectively as 10W, 8W2P, 6W4P, 4W6P, 2W8P and 10P. The air pressure of 1.5 kg cm^{-2} and spray rate of 5 ml min^{-1} was kept constant throughout the experiment. The chromel–alumel thermocouple, connected to a temperature controller was used to record the temperature of the substrates, which were maintained at 475 °C. This temperature is known to be the optimal for formation of $F:SnO_2$ films [14]. It was observed that at this temperature when the metallic solution was sprayed onto a hot substrate, pyrolytically decomposed good quality $F:SnO_2$ thin films were formed. These films were then allowed to cool at room temperature and further used for optical, structural, morphological and electrical characterizations.

UV–VIS spectrophotometer (Systronics, Model 119) was used to investigate the optical properties. The transmission spectrum was recorded at room temperature with normal incidence in the wavelength range 300–850 nm. The crystal structure of the as-deposited thin films was determined by Philips X-ray diffractometer model PW-1710. The surface morphology of the films, grain size and distribution of grains were examined by JEOL, Japan make scanning electron microscope (SEM) model JSM-6360. The morphology of the deposited films was further examined by using atomic force microscopy (AFM). The scans were performed with 2 μm × 2 μm and 50 μm × 50 μm scanner. The contact mode AFM images of the films were obtained using JEOL, JSPM-4200 scanning probe microscope. The electrical parameters like resistivity (ρ), sheet resistance (R_s), carrier concentration (n_D) and mobility (μ) at room temperature were determined using the Van der Pauw method [16,17] with a Hall effect setup supplied by Scientific Equipments, Roorkee, India. A specially designed Hall probe on printed circuit board (PCB) was used to fix the samples. Silver paste was employed to ensure good electrical contacts.

3. Results and discussion

3.1. Optical absorption

The FTO thin films deposited by spray pyrolysis as described previously were investigated for optical absorption in the visible and near IR-regions using UV–VIS spectrophotometer. Since absorption was measured for the film deposited on glass substrate, it was necessary to measure the absorption by the glass plate prior to the deposition of FTO film. This spectrum was subtracted from the spectrum obtained with FTO film deposited over the glass to get the actual transmission of FTO film. Fig. 1 shows the transmission versus wavelengths for the FTO film prepared with only water and propane-2-ol is about 70% and 85% respectively at 550 nm. Acosta et al. [10] have observed the transmittance of 85% for the tin oxide doped with 20% F. It is seen from the plots that all the films prepared with a high amount of propane-2-ol are highly transparent over 500–1000 nm. From the plot one can notice that the transmission of such films is strongly affected by the solvent variation. The films show moderate optical transmittance between 70 and 85% at 550 nm.

Fitting the observed transmittance data with the calculated one, given by Eq. (1), the thickness of the FTO film was estimated [18].

$$T = \frac{t_1^2 t_2^2}{(1 + 2r_1 r_2 \cos 2\delta_1 + r_1^2 r_2^2)} \times \frac{n_2}{n_0} \quad (1)$$

where $r_1 = \frac{n_0 - n_1}{n_0 + n_1}$, $r_2 \frac{n_1 - n_2}{n_1 + n_2}$, $t_1 = \frac{2n_0}{n_0 + n_1}$, $t_2 = \frac{2n_1}{n_1 + n_2}$ and

$$\delta = \frac{2\pi n_1 d}{\lambda}$$

n_0, n_1 and n_2 are respectively refractive indices of air, SnO_2 and glass, d the film thickness and λ wavelength of incident electromagnetic radiation. The variation of thickness of the deposited

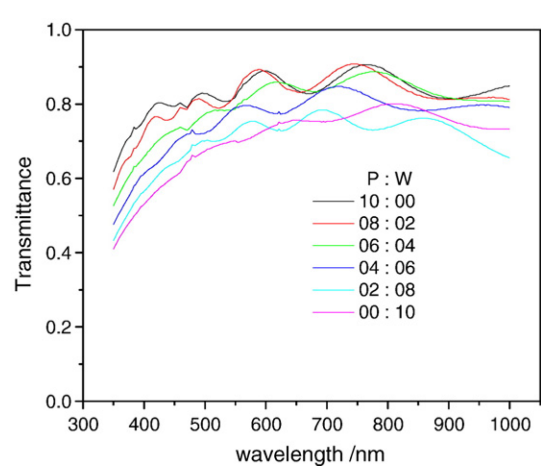

Fig. 1. The transmission versus wavelengths plots of $F:SnO_2$ thin films prepared with different ratios of water and propane-2-ol.