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Aquo-organic sol-based F-doped SnO_2 (Sn:F = 90:10) coatings on glass

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An aqueous precursor of F-doped SnO_2 was prepared starting with hydrated Sn (IV) chloride, ammonium fluoride and water. Polyvinyl alcohol (mol. wt. 22 000), a sol stabilizer, was used for better adherence to the glass substrate. Both the dipping and the spinning techniques were used to deposit layers of different thickness (from 200 to 650 ± 10 nm). Air drying and subsequent curing at ca. 450 °C in air yielded a tetragonal cassiterite phase of SnO_2 and a tetragonal Sn phase. The percentage of visible transmission of the spin-coated samples was relatively high (ca. 80 %). Incorporation of polyvinyl alcohol into the aqueous precursor minimized etching by fluoride ions, as revealed by SEM pictures. The surfaces of the developed films seemed to be porous, and the spin-coated sample was relatively less porous. The refractive index (RI) of the dip-coated samples was in the range 1.650–1.803, while the spin-coated samples had RI values in the range 1.670–1.823. The sheet resistance of the spin-coated films was in the range 3.3–1300 kΩ /□, and 1.4 – 2500 kΩ /□ in the case of dip coated samples.

Key words: *fluorine-doped tin oxide; sol-gel; SEM; polyvinyl alcohol*

1. Introduction

Thin films of SnO_2, In_2O_3 and their doped forms possess high transparency in visible and high electrical conductivity [1–4]. Fluorine-doped tin oxide films also yield high conductivity [4, 5]. These films can be produced by various deposition methods [6, 7]. Chemical vapour deposition (CVD) [7] has been exploited in the commercial production of F-doped SnO_2. The latest developments in sol-gel science and technology yield a simple method of film deposition [8, 9]. Indium tin oxide (ITO) and Sb-doped SnO_2 coatings on glass produced by sol-gel processing [10–13] have been intensively investigated, but the results concerning sol-gel F-doped tin oxide coatings on glass are scanty. As precursors for F-doped SnO_2 (FTO) coatings contain fluoride ions, there is a large probability of surface etching. Our previous work [14] discussed

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severely corroded surface features of FTO developed from precursors having no organic binders. Polyvinyl alcohol (PVA), which acts as an organic binder, is partially resistant to fluoride ions. Therefore PVA may be used to overcome the corrosion problem. This work is an attempt to learn about FTO coatings prepared from precursors containing fluoride ions and an organic binder.

2. Experimental

Preparation of precursor sol. SiO_2 precursor sol of 7 wt. % equivalent silica in a mixture of 1-propanol and 2-butanol was prepared from tetraethylorthosilicate (TEOS). The details of preparation are given elsewhere [15].

The starting materials of the FTO precursor sols were $SnCl_4 \cdot 5H_2O$ (Loba Chemie, 98%), and aqueous HF solution (E. Merck India Ltd, 40%, GR). $SnCl_4 \cdot 5H_2O$ was initially dissolved in ethanol. The required amount of HF solution (Sn:F = 90.0:10.0) was then added to the above salt solution. Next, 2 wt. % aqueous solution of polyvinyl alcohol (PVA) (BDH, mol. wt. ca. 22 000) was added in such a way that the resulting solution contained 8.0–10.0 wt. % equivalent SnO_2. The mixed solution was stirred and finally aged to obtain the precursor sol.

Film deposition. Soda lime silica glass substrates (25 mm in diameter and 2–3 mm thick for spinning; 75 mm long, 22 mm wide, and 1–2 mm thick for dipping) were first treated with 1–2% Extran pure (E. Merck India Ltd.) solution in deionised water for 10–15 min and subsequently ultrasonicated in the same medium for 30 min. The substrates were then washed thoroughly with distilled water, followed by treatment with GR grade acetone (E. Merck India Ltd.). Finally, they were dried in an air oven at 100 ^oC for 10 min. The substrates were then preserved in a dry desiccator after cooling them to ambient temperature.

The barrier layer, ca. 0.2 μm thick, was deposited on soda lime silica glass (SLS) substrates by dipping (withdrawal speed 15–17 cm/min), utilizing the precursor (7 wt. % equivalent SiO_2). The gel film initially formed was cured at ca. 450 °C for 30 min in air. The FTO coatings were deposited on the above substrates already coated with a barrier layer by following the same dipping and the spinning methods and conditions used for the SiO_2 film. The lifting speed for the dipping and the RPM for the spinning were optimised to 5 cm/min and 3000, respectively. After each operation, curing was done at the same temperature under similar conditions. The dip coated samples were designated as Fd-1–Fd-6 (Table 1), according to the number of operations. Similarly, the spin-coated samples were designated as Fs-1–Fs-5.

The electrical conductivity of the films was tested by measuring sheet resistance using a two-probe system (Philips multimeter, model PM 2525). The thickness and refractive index of the films were measured at 632.8 nm with an Rudolph Auto EL II ellipsometer. An optically determined physical thickness of a higher order was considered and verified in some cases by measuring thickness with the Stylus method (Sloan Dektak FLM, USA), which measures the step-height of a film mechanically.

The vertical resolution of the equipment was ±2.5 nm. The spectral reflection and transmission of the samples in the UV–visible region were recorded using a Shimadzu UV-VIS-NIR spectrophotometer, model UV 3101 PC. Phase identification for the films was made with a Philips Expert pro X-ray diffractometer with CuK_α radiation. The microstructure of the films was studied utilizing a LEO S 430 I scanning electron microscope.

3. Results and discussion

In our earlier work [14], we have observed that F-doped SnO_2 (FTO) films prepared from the precursors Sn:F ranging from 97:3 to 99:1 were typically etched out by fluoride ions, resulting in relatively high sheet resistance even for large thickness (eg., 550 nm). In this case, we did not use any organic binder. To overcome the above difficulty, we deposited FTO from a precursor based on an organic binder. Polyvinyl alcohol (PVA) was used as the organic binder, as it may deactivate fluoride ion etching. In addition, the added HF has a tendency to evaporate during curing.

Table 1. Sample designation, refractive index, physical thickness and sheet resistance of the F-doped SnO_2 films

Sample designation	Physical thickness (nm)		Refractive index[1] (±0.003)[2] (at 632.8 nm)	Sheet resistance kΩ/□
	Ellipsometric method (±0.5)	Stylus method (±5)		
Fd-1	195.5–216.0	240	1.650–1.707	2500
Fd-2	230.5–254.0		1.663–1.726	40.0
Fd-3	412.0–449.5		1.672–1.733	20.0
Fd-4	454.0–479.5		1.660–1.752	3.4
Fd-5	575.0–610.0		1.657–1.803	2.7
Fd-6	631.0–652.5	580	1.680–1.781	1.4
Fs-1	74.5–85.5	105	1.670–1.789	1300
Fs-2	190.5–201.5		1.675–1.799	62.0
Fs-3	223.5–259.5		1.687–1.807	10.9
Fs-4	234.0–260.0		1.701–1.820	9.0
Fs-5	441.0–452.0	370	1.710–1.823	3.3

[1]The apparent inconsistency of the refractive index is due to the inhomogeneous density of the films. For each film, the R. I. range was obtained from measurements at different points (about 10) of the films deposited on glasses with dimensions of 25 mm x 25 mm for rectangular shape and 25 mm in diameter for circular shape.

[2]The instrumental accuracy of the R. I. measured at a single point.

Hence, in the presence of the binder we made an attempt to incorporate a relatively high content of fluoride ions (Sn:F = 90:10). In the case of dipping, severe inhomogeneity with staining below 1.0 mm was observed at the bottom edge of the substrate – excess sol, adhered to the gel layer during the withdrawal of the substrate from the sol bath, drifted down due to gravitation and rested in lower part of the sub-

strate. On the other hand, in the case of spinning, staining below 0.5 mm was generated at the periphery of the substrate, because excess sol was allowed to stay at the periphery after spinning off due to centrifugal force.

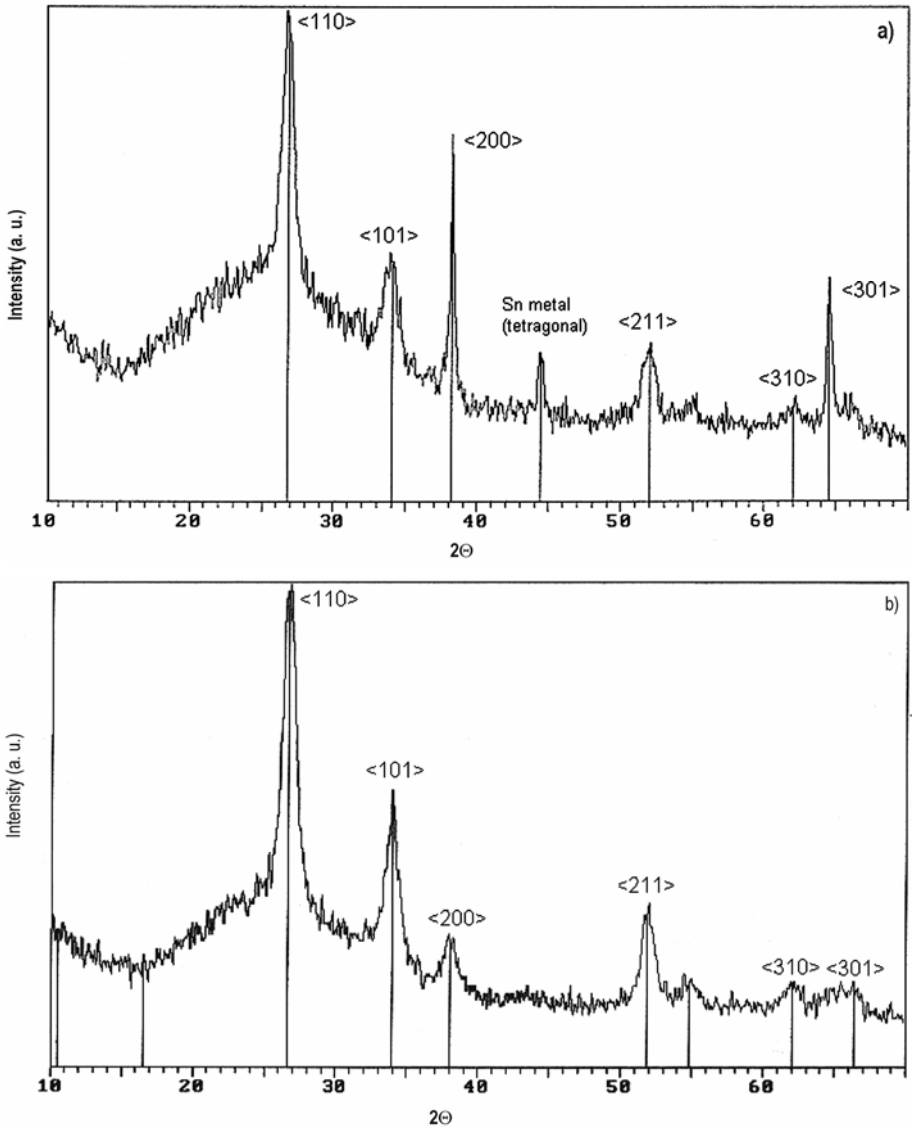

Fig. 1. XRD pattern of spin-coated Fs-5 (a) and dip coated, Fd-6 (b) F-doped SnO_2 samples

In Table 1, the sheet resistances of developed films with various thicknesses are given. The sheet resistance decreased considerably with increasing thickness. We were successful in depositing layer with the thickness above 600 nm by six-fold dipping, while we could not proceed beyond ca. 440 nm (five dipping operations) in the

case of spinning. Any attempt for additional operation beyond the above would result in the peeling of coated layers. Multiple coating operations were carried out in order to increase the physical thickness of the films. Surprisingly, multiple coating operations do not increase the physical thickness of films in a cumulative manner, especially after the 2nd and 4th operations for dip coated films and after 3rd and 4th operations for spin-coated films (Table 1). In the case of dipping, thickness seemed to increase effectively after each alternate coating operation. Since each coating operation was followed by a curing treatment, it can be concluded that curing a particular layer two times is more suitable for the effective addition of a subsequent layer. Spin-coated samples, however, do not show such regularity regarding the increment of physical thickness, but the effectiveness of multiple curing treatments instead of multiple layer depositions cannot be ruled out.

Films with relatively low thickness (> 240 nm) prepared under two different techniques did not show any characteristic peaks in their X-ray diffractograms (not shown here), since the diffractometer could not record very weak reflections of the film material. Figure 1 shows X-ray diffractograms of FTO films (Fd-6 and Fs-5, Table 1) of relatively high thickness (in the range 440–600 nm). The tetragonal cassiterite phase was more prominent in this case. It is interesting to note that the tetragonal phase of Sn-metal was mixed with the cassiterite phase of SnO_2 for coating with the spinning method. This metallic phase was not observed for the dip coated FTO. The formation of the Sn metal depends on the deposition technique.

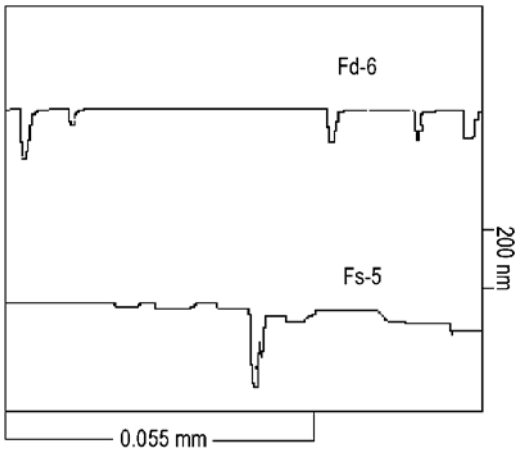

Fig. 2. Surface profiles of samples deposited with different sol-gel deposition methods: dipping, Fd-6 and spinning, Fs-5

It has been reported [1] that tin dioxide coatings behave as transparent films with little surface roughness. We have observed [14] etching of film surfaces due to doping with F^-, resulting in surface roughness. In the present report, we conclude that surface roughness decreases after adding an organic binder to the precursor, as evident from the surface profiles (Fig. 2) of the coated samples. The spin-coated surface is smoother than the dip coated surface, because there are fewer pores in the case of spin-coated system. There is a lowering trend for thickness at the edge of the substrate

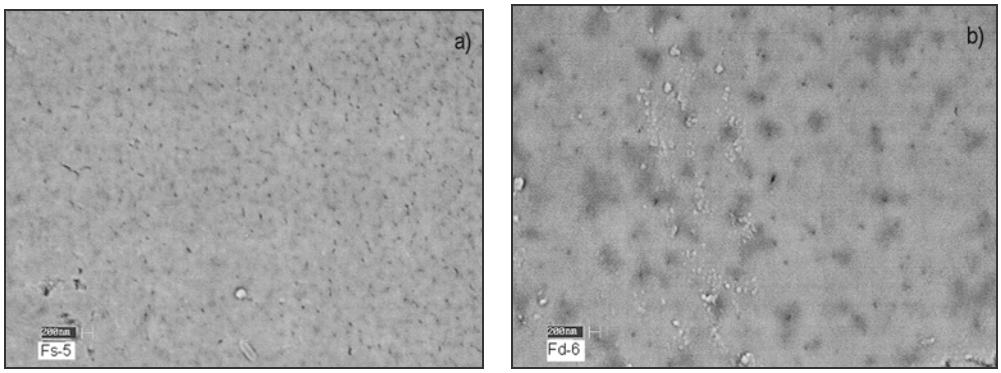

Fig. 3. SEM pictures of spin-coated Fs-5 (a) and dip coated Fd-6 (b) samples

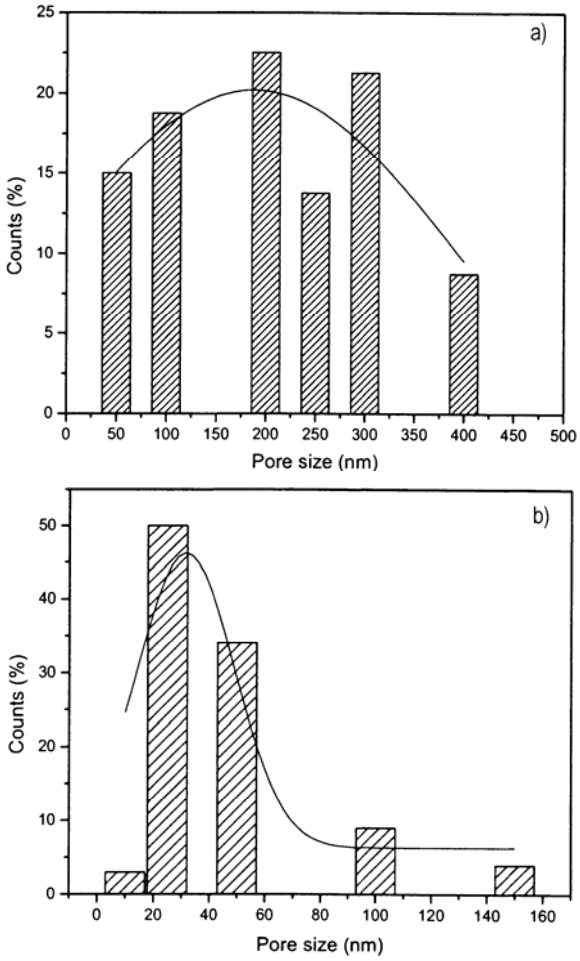

Fig. 4. Pore size distributions of the dip coated Fd-6 (a) and spin-coated Fs-5 (b) samples

due to spinning. As a result, the stylus moves downwards in the radial direction. The surface features revealed by SEM (Fig. 3) also confirm the surface smoothness of the spin-coated sample – the average pore size distributions (Fig. 4) of the spin-coated films were smaller (32 nm) than those of dip coated films (190 nm). Physical thicknesses of the films were measured ellipsometrically, and verified in a few cases by the stylus method. They did not increase linearly with the number of coating operations. The successive deposition of an FTO based on an organic binder would possibly require surface treatment, which would increase the adherence of the layers. This feature requires detailed work, which is under progress.

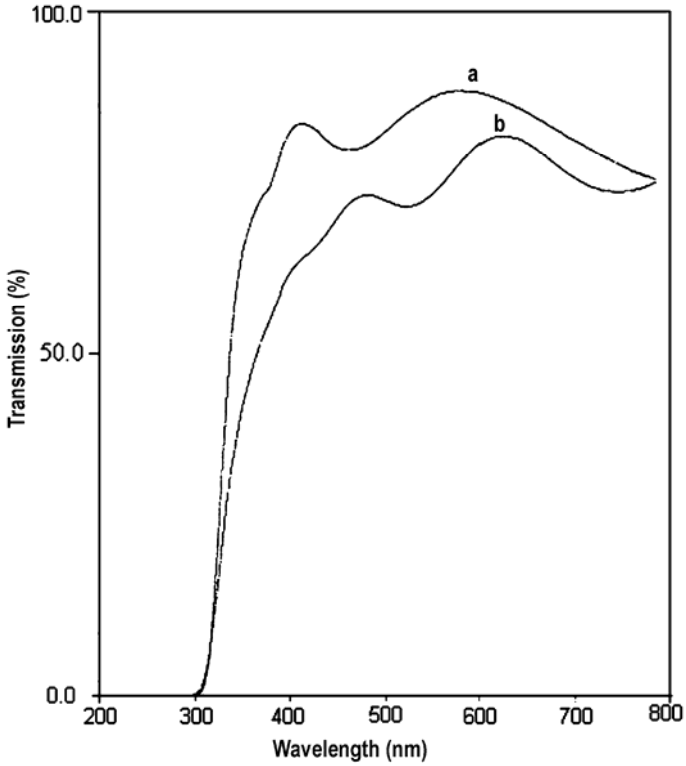

Fig. 5. Transmission spectra of spin-coated Fs-5 (a)
and dip coated Fs-6 samples (b)

The refractive index of the films increased with increasing thickness from 1.650 to 1.823. The transmission of the dip/spin-coated samples decreased with increasing physical thickness (not shown here). Typical examples of the transmission spectra of dip and spin-coated samples with maximum physical thickness are shown in Fig 5. The lowering of transmission for the dip coated sample may be caused by scattering by the pores observed in the surface profiles (Fig. 2) and SEM images (Fig. 3). When the sheet resistance for films with almost the same thickness and prepared by the two techniques is compared, it can be seen that the dip coated films exhibit relatively high

sheet resistance (20 kΩ/□ for the thickness of 412–450 nm) with respect to the spin-coated films (3.3 kΩ/□ for the thickness of 441–452 nm). This may be due to the presence of porous microstructures.

4. Conclusions

Fluorine-doped tin oxide thin films with high contents of fluorine (Sn:F = 90:10) were prepared by simple sol-gel dipping and spinning techniques. The surface roughness due to etching by fluoride ions was minimized by adding an organic binder, polyvinyl alcohol (PVA), to the precursor. This approach helped to develop crystallized FTO in a simpler way. Consequently, the electrical conductivity increased. The surface profiles as determined by SEM and the stylus method also reveal rather smooth surfaces. The spin coating technique yielded coatings of better performance.

Acknowledgments

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