Bulletin of Electrochemistry 1 (5) Sep.-Oct. 1985, pp. 499-501

SURFACE TREATMENTS OF FLUORINE DOPED TIN OXIDE FILMS

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ABSTRACT

Fluorine-doped tin oxide films prepared by spray pyrolysis were subjected to chemical etching using hydrazine hydrate, mechanical polishing and electrochemical etching (cathodic), and the consequent changes in the sheet resistance and optical transmission of the films are reported. Scanning electron microscopic examination revealed a change in the surface morphology of the films.

Key words: Fluorine doped tin oxide, spray pyrolysis, surface treatment

INTRODUCTION

Tin oxide (SnO_2) and indium-tin oxide (ITO) semiconductor films are useful as highly electrically conducting and transparent substrates for photovoltaic films in solar cells. They are also used as antireflection coatings. These films can be fabricated even over large areas by simple and inexpensive processes like spray pyrolysis. This paper deals with the studies on the effect of surface chemical treatments, mechanical polishing and electrochemical etching (cathodic) on fluorine-doped SnO_2 films prepared [1] on glass substrates for photoanodic layers of cadmium chalcogenides and related compounds. The optical transmission and electrical conductivity of these layers are also discussed in this paper.

EXPERIMENTAL

Chemical etching

Hydrazine hydrate treatment of SnO_2 films from the point of view of chemical etching appears not to have been studied so far. SnO_2 films were treated with pure hydrazine hydrate and hydrazine-water mixtures (50-50 by volume) for different durations by dipping the samples in these solutions: the high resistance (2.5-3.0 k ohm/square) SnO_2 films being treated for longer duration and the low resistance (~ 80-100 ohm/square) SnO_2 films for shorter duration. After the treatment, the plates were cleaned using teepol and distilled water and thoroughly dried before measurements.

Mechanical polishing

Mechanical polishing was found to introduce an anomalous visible photoresponse extending to 600 nm in the case of strontium titanate photoanodes [2, 3]. Hence thin films of SnO_2 were subjected to mechanical polishing with luster Ronuk compound 'Tripol A'. These were then degreased, washed in dilute HCl, cleaned with distilled water and dried.

Electrochemical etching

Electrochemical etching of SnO_2 has been studied earlier [4]. The material being an oxide, the electrochemical etching has to be carried out only cathodically, since this involves a reduction reaction influencing the oxide layer. It has been reported that the etch rate is independent of dilution between HCl and water in the ratios of 1:3 and 1:10 [4]. Higher concentrations of acid resulted in lower etch rates. In the present study, etching has been done in dil. HCl (1:10) at room temperature for five minutes. The SnO_2 film acted as cathode while a platinum foil was used as anode. A d.c. power supply was employed and experiments were carried out at different current densities and for different durations.

The sheet resistance of the films were measured by a two probe d.c. method and the optical absorption measurements were made using a Beckmann DU Spectrophotometer.

RESULTS AND DISCUSSION

Chemical etching

Table I shows the decrease in the surface resistance values with duration of chemical etching treatment for the high resistance films in pure hydrazine hydrate as well as in 50-50 mixture of hydrazine hydrate and water; the decrease being more rapid in pure hydrazine hydrate.

Table I: Effect of concentration of chemical etchant on the sheet resistance of SnO_2 films

Initial resistance k ohm/sq	Resistance (k ohm/sq) after treatment for different durations (hr)							
	3	5	40	75	100	120	125	145
(A) Pure hydrazine hydrate								
2.95	–	0.92	–	0.79	0.68	–	0.69	–
(B) Hydrazine hydrate-water mixture (50-50)								
2.48	2.24	–	2.28	–	–	1.78	–	1.79

Figure 1 depicts the lowering of surface resistance values for two low resistance film samples A and B, in pure hydrazine hydrate for different durations. The optical transmission of the film A is shown in figure 2. It can be seen that the optical transmission increases from 58 % to 79 % for 700 nm (peak values). Thus, it has been found that treating in pure hydrazine hydrate not only decreases the surface resistance but also improves the optical transmission. These properties were monitored over a period of time (about one month) and found to remain constant.

The films are generally known to be sensitive to changes of surface resistance due to adsorption. The influence of hydrazine hydrate on any adsorbed species during the preparation of the layers might in consequence influence the resistivity. Further studies may be necessary to understand the behaviour [5].

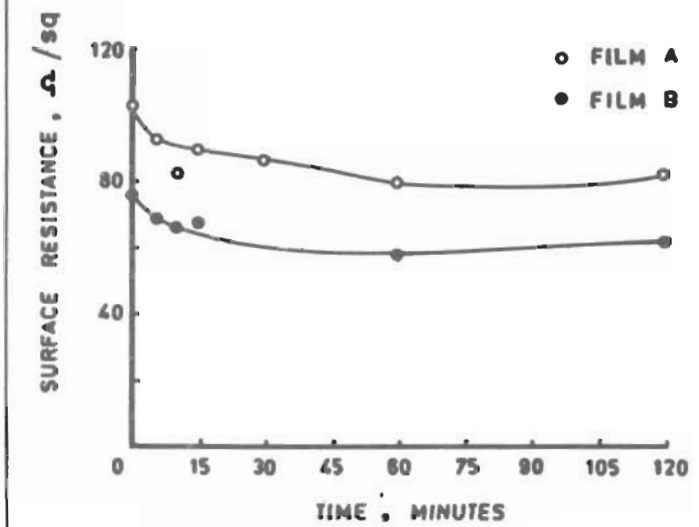

Fig. 1: Variation of surface resistance with duration of treatment with pure hydrazine hydrate for low resistance (~80-120 ohm/square) films.

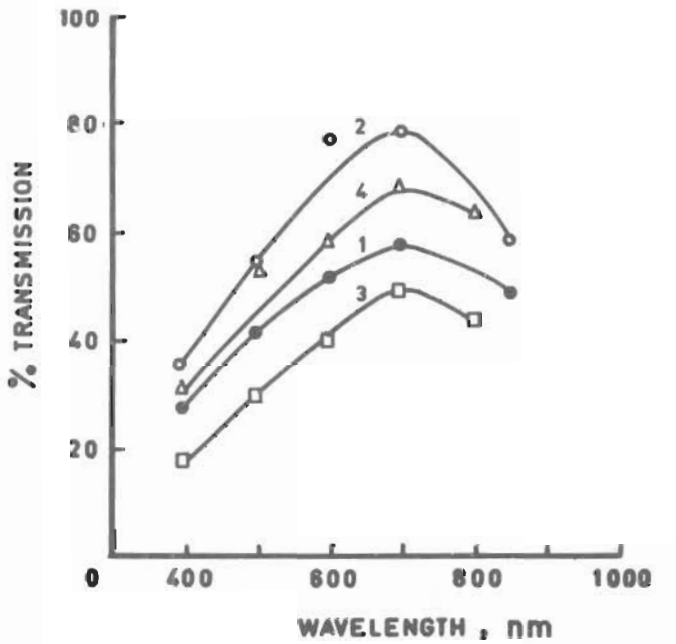

Fig. 2: Transmission spectrum of the film with chemical etching (1 & 2) and mechanical polishing (3 & 4) 1 & 3 = before treatment; 2 & 4 = after treatment

Surface morphology of the SnO_2 films before and after hydrazine hydrate treatment is shown in figure 3 (a) and (b) respectively. It can be seen that bigger crystals are discernible after the treatment.

Mechanical polishing

The surface resistance of SnO_2 films before and after mechanical polishing is shown in Table II. The optical transmission of the SnO_2 film before and after treatment is given in figure 2.

As a result of the polishing process, the undisturbed polycrystalline surface becomes more and more disturbed and fragmented. The high local temperatures generated by the mechanical polishing may result in a partially amorphous surface in the case of materials not having high melting points. Such a condition may be responsible for the increase in resistance of SnO_2 films after mechanical polishing [6].

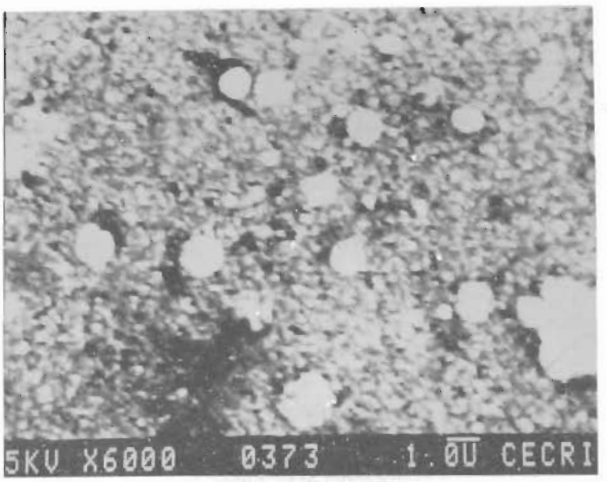

Fig. 3 (a): SEM picture of the SnO_2 film in the as prepared condition

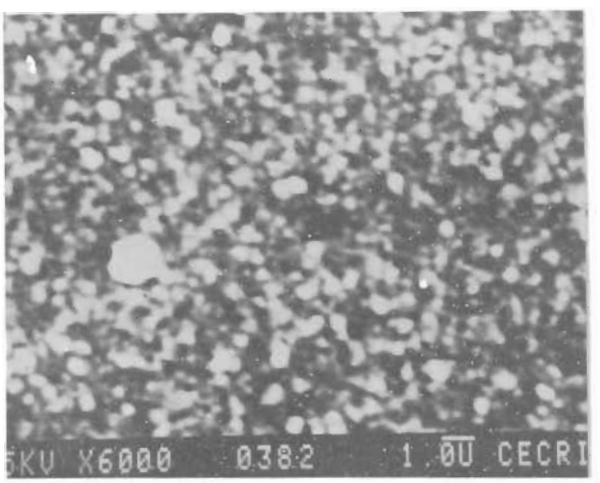

Fig. 3 (b): SEM picture of the SnO_2 film after hydrazine treatment

Table II: Surface resistance of SnO_2 films before and after mechanical polishing.

Before polishing (ohm/square)	12.5	82.9	99	33
After polishing (ohm/square)	31.2	210	130.9	102

Surface morphology of the SnO_2 film after mechanical polishing is shown in figure 4. Though there is an increase in surface resistance, optical transmission improves considerably.

Electrochemical etching

It has been suggested [4] that during electrochemical etching, SnO_2 is reduced to metallic tin by the nascent hydrogen produced at the cathode by the passage of current and with the metallic tin dissolving in the electrolyte. In the present study, a grey layer has been observed to form which soon dissolves in the electrolyte.

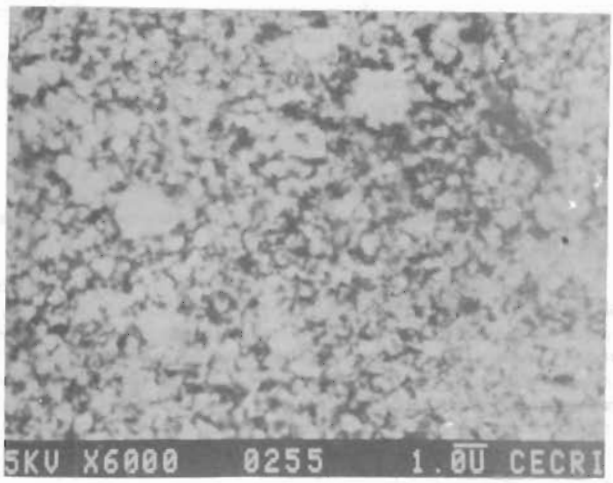

Fig. 4: SEM picture of the SnO_2 film subjected to mechanical polishing

Tables III and IV show the changes in the surface resistance and optical transmission of SnO_2 films before and after electrochemical treatment.

Table III: Variation of surface resistance with current density on electrochemical etching in dilute HCl (1 : 10) Duration = 5 mts

Current density mA.cm^{-2}	Sheet resistance (ohm/square) Before etching	After etching
10	180	77.5
20	700	144.4
40	86.6	80.9

Table IV: Variation in transmission spectrum of tin oxide films subjected to electrochemical etching in dilute HCl (1 : 10) Duration = 5 mts

Wavelength nm	Current density of 20 mA.cm^{-2}		Current density of 40 mA.cm^{-2}	
	Before etching (%)	After etching (%)	Before etching (%)	After etching (%)
500	51	49	42.5	46.5
600	54	55	52.5	60
700	66	66	66.5	69
850	39	47	43	44

Reduction in surface resistance is greatest at a current density of 20 mA.cm^{-2}. But the optical transmission improves in direct proportion to the current density (Table IV).

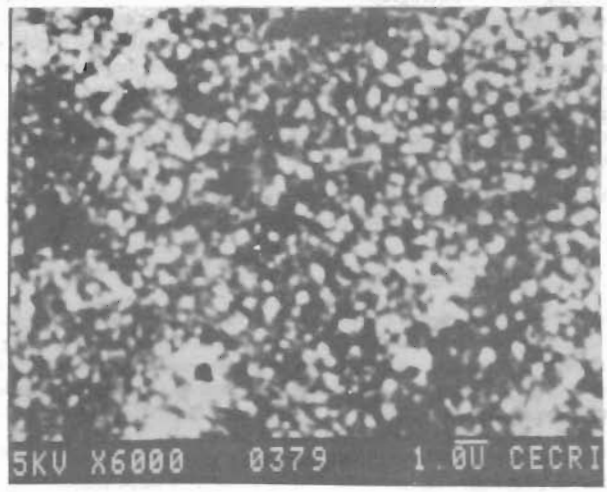

Fig. 5: SEM picture of the SnO_2 film after electrochemical etching (cathodic)

Surface morphology of the film after electrochemical etching is shown in figure 5 where bigger crystallites are seen.

CONCLUSIONS

Treatment with hydrazine at room temperature for five minutes improves both the electrical conductivity and optical transmission of the SnO_2 films.

Mechanical polishing improves the optical transmission but results in an increase in the surface resistance.

Electrochemical etching at a current density of 40 mA.cm^{-2} improves the optical transmission. There is no marked change in the surface resistance. But at a current density of 20 mA.cm^{-2} the surface resistance decreases enormously while there is no change in the optical transmission.

Acknowledgements: The authors thank Dr V K Venkatesan, Head of the Division of Electrochemical Materials science and Electrophysics for his keen interest and encouragement and Mr Y Mahadeva Iyer and Mr K R Ramakrishnan for providing the SEM pictures of the samples.

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