

The Diffusion of Sodium Ions into Tin Oxide Thin Films from Glass Substrates

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SYNOPSIS

Electrical resistance and X-ray photoelectron depth profile analysis are studied for antimony doped tin oxide films developed on silica, alkali-free and soda-lime slide glass substrates. The sodium ions diffused from the substrates to the films prevented the crystal growth of rutile type tin oxide in the film, resulting in the high electrical resistance. A diffusion layer has been detected for each film with diffuse profiles of multi valent cations (Sn, Si or Ca) at the interface of the tin oxide film and substrate. A greater amount of sodium atoms have been detected in the film developed on the soda-lime glass while almost no sodium atoms have been found in those on the other substrates. This can be explained by the diffusion of the sodium ions in the substrate due to a drastic hydronium-sodium exchange mechanism under highly acidic conditions during the dipping and drying processes.

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1. INTRODUCTION

Tin oxide thin films on glass substrate are very important materials for application to highly electroconductive and transparent electrodes, antireflection coatings on solar cells or heat reflecting windows¹⁾. They have been prepared through several techniques such as spray pyrolysis^{2,3)}, chemical vapor deposition^{4,5)} and dip coating^{6,7)}. The dip coating technique is more advantageous than the other techniques for its applicability on wider area. The properties, however, of the films depend on not only the compound, solvents, developing and pyrolysis temperatures but also the substrates used. When a soda-lime glass substrate is used, sodium chloride crystallites are deposited in the films developed by the spray pyrolysis of tin tetrachloride solutions where the sodium ions may come from the substrate. The sodium diffusion from the substrate has also been seen in the tin oxide films due to the dip coating of antimony doped organo-tin compound solutions⁷⁾. The behavior of cations in the glass substrate has not understood yet very well at the dip coating procedure. The present work is carried out as a part of preparation and analysis of transition metal oxide thin films developed through the dip coating technique by the use of organometallic compounds. The diffusion behavior of the cations in the glass substrates such as soda-lime slide glass and alkali-free slide glass (Corning #7059^R) was examined by the X-ray photoelectron spectroscopy (XPS), and was correlated with the crystal size and electric resistance.

2. EXPERIMENTAL PROCEDURE

The tin containing raw material doped with antimony in the atomic ratio Sb/Sn=0.1 was kindly provided by the Nippon Ekusuran Kogyo (Japan Exran Co. Ltd., Osaka, Japan). The stable aqueous solution of tin oxalate was named SN-2⁸⁾ and used for dip coating after diluting the received solution with an equal amount of distilled water. The pH value of the dipping solution was about unity. The substrate glasses were silica glass, alkali free glass (Corning #7059^R) and soda-lime glass (Micro Slide Glass, Iwaki Glass Co. Ltd., Tokyo) of 26x76mm in size. The substrate glasses were soaked in an ultrasonic water bath and rinsed with ethanol before they were dipped in the developing solution and pulled at a rate of 5.85cm/min. The developed solution

films were dried at 100°C in air for 1h, and pyrolysed at 600°C for the films on the soda-lime and alkali free glass substrates and at 1000°C for those on the silica glass substrate. After the four iterations of dipping-drying and heating processes, the tin oxide film was subjected to characterization by means of XPS and near-IR spectroscopy and X-ray diffraction (XRD). XPS spectra were measured with Shimadzu ESCA-750 Electron Spectrometer with Mg Ka radiation. Electric resistance (S/cm^2) was also measured through the four-electrode method after evaporating aluminum electrodes on the films. The films intentionally doped with sodium oxalate in the atomic ratio Na/Sn=2, 10 and 20 were also prepared and characterized in the same way.

3. RESULTS AND DISCUSSION

3.1 Electrical resistance

The XRD measurements indicated that all the films prepared in the present experiments consisted of rutile type tin oxide crystallites though their crystallinity depended on the treatments. Table 1 lists the measured electrical resistance (S/cm^2) for the films ($SnO_2/0.1Sb$) heat treated at 600°C, indicating very high resistance of that developed on the slide glass. This experimental result suggests the effect of mobile cations diffused from the substrate to the film. This will be confirmed in the next section 3.2 by means of XPS technique.

Table 1. Electric resistance (S/cm^2) of the $SnO_2/0.1Sb$ films developed on the glass substrates due to the dip coating technique.

Substrate	Resistance (S/cm^2)
Soda-lime glass	6.7×10^5
Alkali-free (Corning #7059 ^R)	170
Silica glass	90

4-fold dipping-drying-600°C pyrolysis.

Fig. 1 shows the variation of resistance of the sodium doped tin oxide films on the alkali free glass substrate as a function of the atomic ratio Na/Sn (%). Also plotted here was the tin oxide

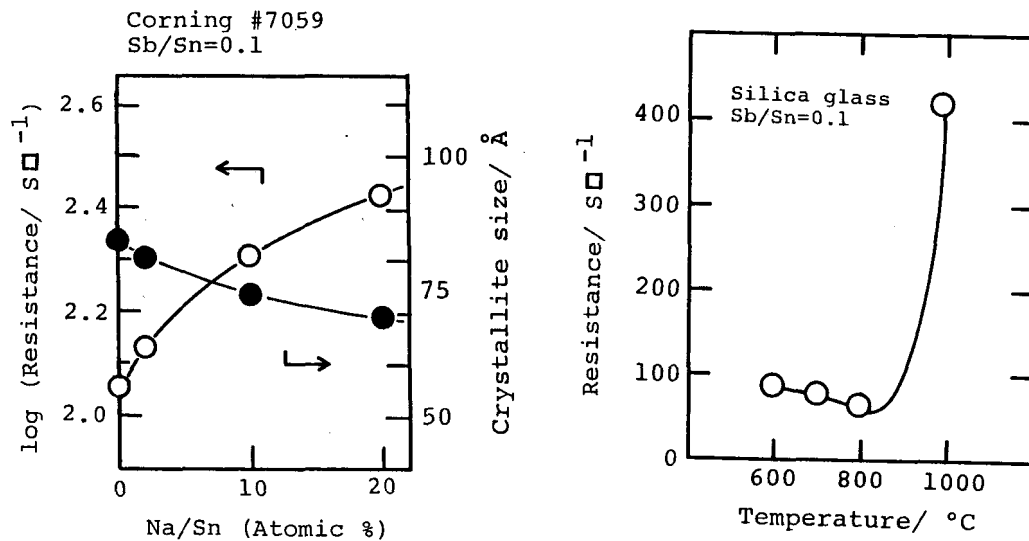


Fig. 1(left). Electric resistance and crystallite size (rutile) for the Na doped SnO₂ films (600°C, the alkali-free glass substrate.)

Fig. 2(right). Effect of pyrolysis temperature on the resistance of the tin oxide films on the silica glass substrate.

crystallite size evaluated by the Scherrer equation⁹⁾ with the (110) reflection of rutile type SnO₂. The crystal size generally increases with the heating temperature, accompanied with the decrease in the resistance. Fig. 2 indicates the effect of the heating temperature on the resistance for the tin oxide films developed on the silica glass substrate. A sudden increase in the resistance for the sample heated at 1000°C is due to the sublimation of the antimony atoms. On these basis, it is concluded that the presence of the sodium ions in the films increases the sheet resistance and prevents the crystal growth. Another effect of the sodium ions is illustrated by Fig. 3 which shows the near-IR spectra of the sodium doped tin oxide films. The optical absorption in this region is due to the oxygen vacancies of the films¹⁰⁾. The lesser absorption for the samples with a greater amount of the dopant in Fig. 3 indicates the neutralization of the oxygen vacancies produced by the presence of antimony ions in the tin oxide films. It is thus likely that if the sodium free films are of metallic type conduction the sodium doped films are of semiconductor type conduction due to annihilation of the oxygen vacancies.

Fig. 4 shows the resistance vs. reciprocal of absolute temperature relation for the SnO₂/0.1Sb films doped with sodium ions. The films of lesser amount of sodium shows no temperature dependence, while

those with 10 and 20% sodium/tin doping indicate fairly larger temperature dependence and the values of apparent activation energy are approximately 0.44 and 0.81kJ/mol, respectively. It is therefore indicated that some activation process is involved in the conduction of the sodium doped films. Since the resistance is measured in open air, the possibility cannot be ruled out that the humidity of the air results in such dependence on the degree of doping and temperature. It can be said, however, that the contribution of the sodium ions to the conduction of the films is very low taking their very small activation energy values into account.

3.2 Diffusion of glass component cations into tin oxide films

XPS depth profiles were obtained for tin oxide films doped with antimony (Sb/Sn=0.1). Fig. 5 shows the depth profiles of Si and Sn for the tin oxide films developed on the silica glass substrate. The depth of about 0.2 μ m can be reached by Ar ion etching for 10 min. The signals down to 2min etching come from the tin oxide film and those from 5 min

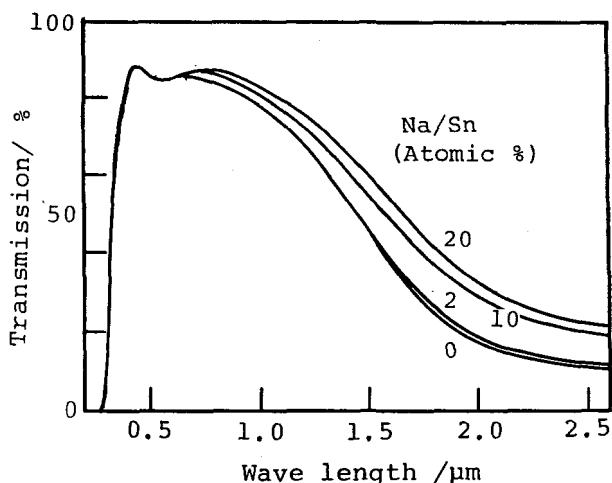


Fig. 3. Near-IR spectra of the Na doped SnO_2 films (the alkali-free glass, 600°C).

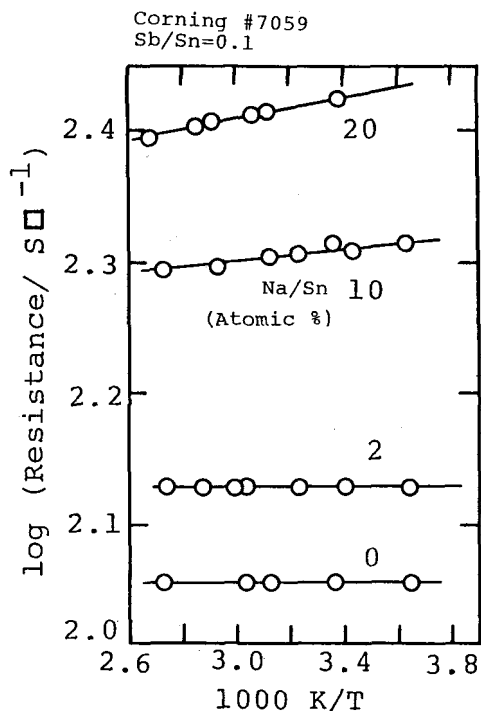


Fig. 4. The resistance vs. $1/T$ plots for the Na doped SnO_2 (the alkali-free glass substrate).

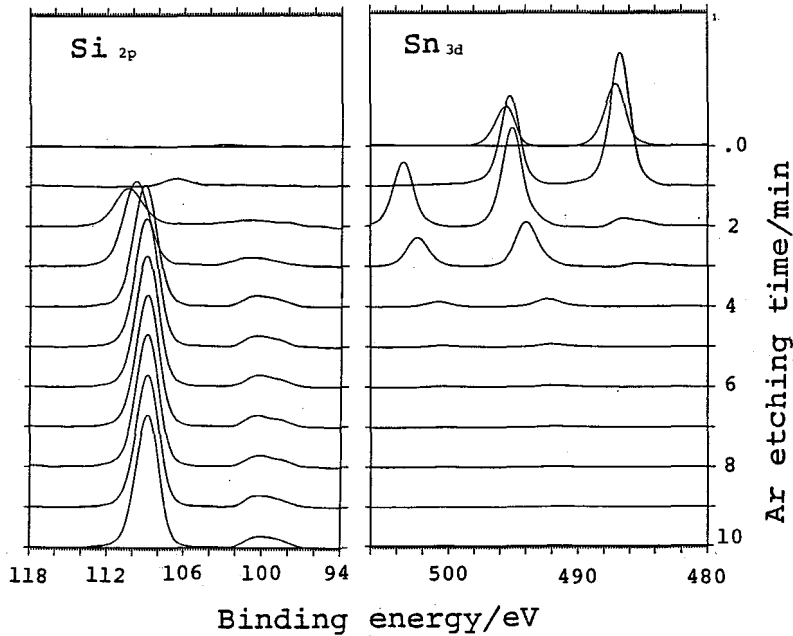


Fig. 5. The Si and Sn XPS spectra for the $\text{SnO}_2/0.1\text{Sb}$ films (1000°C , the silica glass substrate).

or deeper are from the substrate silica glass. The layers appearing after 2 to 4 min etching are the diffusion layers where the Sn peaks are located at positions different in the binding energy from those for the film. The different peak position for Sn indicates that the Sn atoms in the diffusion layer differ in the chemical states, e.g., the oxygen coordination or valence states, from those in the film. The fraction of the peak area for the cations and oxygen was plotted in

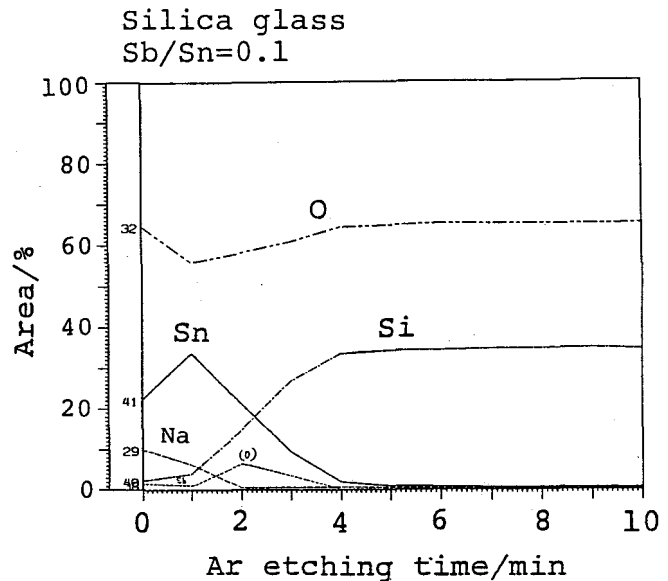


Fig. 6. The XPS depth profiles for the SnO_2 films (silica glass substrate).

Fig. 6 for the films developed on the silica glass. The diffusion layers can be seen at 2 to 4 min etching. It seems strange that the sodium ions are detected near the surface. If the substrate itself is contaminated with sodium ions the distribution of the sodium atom must be much uniform as shown later. The sodium ions detected here have presumably come by chance into the film as an impurity at the end of the heat treatment process. The decrease in the Sn area at the surface is due partly to the presence of the sodium ions and is due partly to the annihilation of the oxygen vacancies which is indicated by the sudden increase in the O area at the surface.

Similar sudden changes of the Sn and O area are illustrated in the depth profiles, Fig. 7, for the films developed on the alkali free glass substrate. The tin oxide film corresponds to the depth down to 4 min etching, thicker than that on the silica glass (0-1 min etching). The diffusion layer corresponds to the layers of 4 to 6 min Ar etching in this film.

Trace but a detectable amount of the sodium ions are present in the film. They have probably come

into the film as the contamination of the substrate surface because the distribution of Na in Fig. 7 is uniform and independent of the depth.

Fig. 8 illustrates the depth profiles for the tin oxide film developed on the soda-lime slide glass substrate. The film layer down to the depth of 6 min etching is thicker than any other films on the silica and alkali-free glass substrates. The changes in the peak area for the oxygen and tin atoms are similar to those previously found in the other films on silica and alkali-free glass substrates. The diffusion layer is seen at the depth from 4 to 8 min etching. The silicon atoms have a diffuser profile with a longer tail than in any

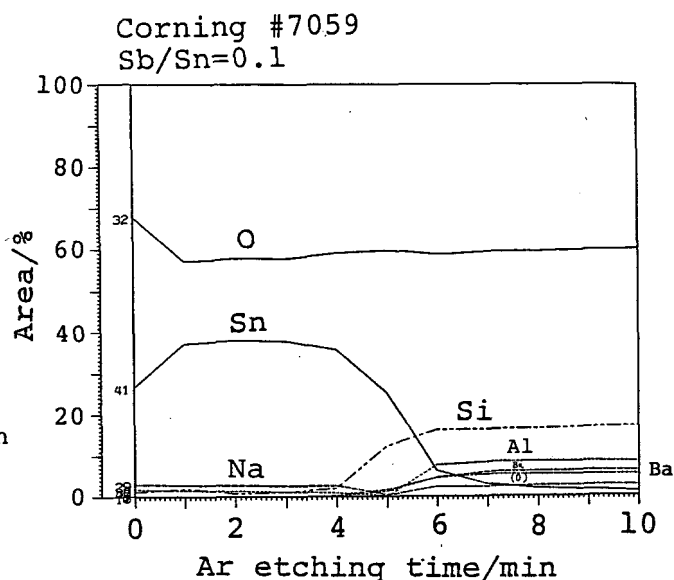


Fig. 7. The XPS depth profiles for the SnO_2 films (alkali-free glass substrate, 600°C).

other films developed on the silica or alkali-free glass substrates. Potassium atoms are diffused into the film-substrate interface, and calcium atoms are present in a detectable amount everywhere in the film and substrate. A prominent difference from the other is the very high amount of sodium atoms distributed throughout the film and diffusion layer. What is more interesting, the peak area of the sodium ions is larger in the film than in the substrate. It should be remembered that the

present tin oxalate solution for the dipping has a pH value as low as 1. Therefore, hydration of the glass surface takes place during the dipping process, and it is enhanced even more at the drying process at 100°C. Doremus suggested¹¹⁾ that the hydration of soda glass involves ionic interdiffusion. Lanford et al. reported¹²⁾ that the exchange took place between H_3O^+ and Na^+ with the atomic ratio $H/Na=3/1$, while Tsong¹³⁾ reported that sodium ions were diffused into a leaching layer in a hydronium-sodium ion exchange mechanism though the ratio varied from 2 to 3 depending on the glass composition. Since the presence of the sodium ions at the surface of the film has been found in Fig. 6 for the silica glass substrate the possibility cannot be ruled out that the sodium ions in the film has been brought in the form of a surface contamination impurity at any preparation processes. However, the higher amount of Na in the film can be explained by a drastic exchange between the hydronium and sodium ions under a very acidic conditions because the longer diffusion profile of Si is a result of a reaction of water and Si-O-Si bonds. In order to improve the film conductivity the cleanliness of the substrate and the undercoat of Na ion absorbing layer will be necessary.

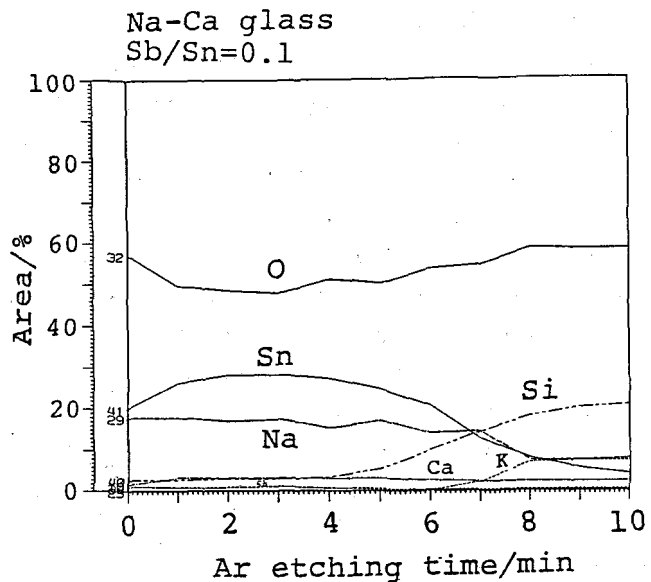


Fig. 8. The XPS depth profiles for the SnO_2 films (600°C, the soda-lime glass substrate).

4. CONCLUSION

Tin oxide thin films doped with antimony have been prepared on the substrates such as silica glass, alkali-free glass and soda-lime glass by the use of a tin oxalate solution due to the dipping and pyrolysis technique. Characterization of the films is carried out by the measurement of electrical resistance (S/cm^2), near-IR spectra and X-ray photoelectron depth profiles of the component atoms. The presence of the sodium ions in the films prevented the crystal growth of rutile type tin oxide and decreased the oxygen vacancies which otherwise are introduced by the antimony ion doping, resulting in the increase in the resistance. The diffusion of the sodium ions from the substrate to the film has been detected by the X-ray photoelectron depth profile analysis for the soda-lime glass substrate. A greater amount of Na in the film has been correlated to a hydronium-sodium ion exchange under very acidic conditions at the dipping and drying processes.

Acknowledgment

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