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CONDUCTIVE SnO_2 THIN FILM FABRICATION BY SOL-GEL METHOD

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Abstract

Transparent conducting tin(IV) oxide thin films have been studies and developed for the electrode materials of solar cell substrate. Fabrication of tin oxide thin films by sol-gel method is process development of lower cost photovoltaic solar cell system. The research is focused on the establishment of process condition and development of precursor. The precursor solution was made of tin isopropoxide dissolved in isopropyl alcohol. The hydrolysis rate was controlled by addition of triethanolamine. Dip and spin coating technique were applied to coat tin oxide on borosilicate glass. The resistivity of the thin film was lower than 0.1Ω-cm and the transmittance is higher than 90% in a visible range.

Keywords : *Tin(IV) oxide, Tin isopropoxide, Triethanolamine, Sol-Gel, Solar cell*

1. INTRODUCTION

Transparent conducting tin(IV) oxide coated glass are currently receiving attention and being developed for solar cell substrate and LCD display due to its high transmittance and low resistivity. The high transmittace in visible light is due to high band gap (over 3eV) and high conductivity is due to free electrons in oxygen vacancy holes[1)-3)] The similar properties were found in Cd, In, Zn oxides[4)]. These properties were utilized for sensor, thermal protective film, low reflectivity glass and etc.[5),6)] Tin(IV) oxide were usually prepared by CVD, PVD or spray pyrolysis method[7)]. However, these methods needs high manufacturing cost and are not appropriate for large size substrate. In this study sol-gel method was applied to fabricate conductive tin(IV) oxide thin film. The advantages of sol-gel method are low cost in manufacturing, uniform thickness of coating and low temperature in processing[8)]. To form thin film in sol-gel method, three types of coating technique were usually applied; spin coating, dip coating and spray coating[9)]. In this study, spin coating and dip coating were applied. Alkoxide was used to prepare precursor solution since it is less corrosive and less influenced by impurities[10)-12)].

2. EXPERIMENTAL PROCEDURES

2. 1 Preparation of Precursor Solution and Substrate

Tin(IV) precursor solution was prepared from tin(IV) isopropoxide dissolved in isopropyl alcohol. To prevent rapid hydrolysis, triethanolamine (TEA) was added. Tin(IV) isopropoxide was dissolved and stirred for 2hrs in excess amount of isopropyl alcohol, and then TEA diluted with isopropyl alcohol was added to the solution. The required amounts of water was added to the solution. Water was also diluted with isopropyl alcohol to prevent local precipitation. Silicon wafer, Corning 2948, Corning 7059 glass were used as substrates. Prior to the coating, all substrates were cleaned with aceton to remove organics on the surface and washed with distilled water. And then substrates were soaked with TEA diluted isopropyl alcohol to prevent local hydrolysis. Fig. 1 shows the flow sheet of precursor solution preparation.

2. 2 Coating and Characterization

Spin and dip coating technique were applied. Rotational speed in spin coating were varied from 1500RPM to 3000RPM. Lifting speed in dip coating were varied from 3 to 12cm/min. Precursor solution coated glass were cured for 1hr at 100℃ and then were preheat treated for 10min at 500℃ for repeated coating. The final heat treatment was conducted at 600℃ for 1hr in air. The coating thickness was measured from SEM image of cross sectional view. The transmittace were measured with UV-VIS spectrophotometer. The electrical conductivity and sheet resistance were measured and calculated with 4 point probe and Hall measurement equipment. X-ray diffractometer was used to analyze the surface crystalline.

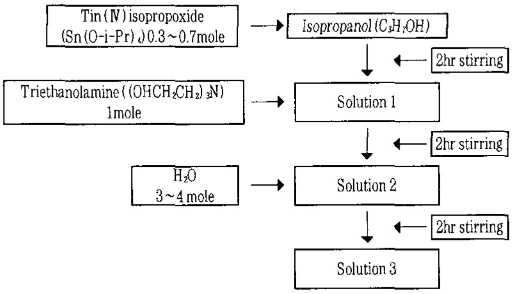


Fig. 1 Flow sheet of precursor solution preparation

3. RESULTS AND DISCUSSION

3. 1 Stability of Precursor Solution

TEA was added to the precursor solution to control the rate of hydrolysis. When the molar ratio of TEA to tin(IV) isopropoxide is less than 1, the precursor solution was gelatinized. And then to prevent rapid hydrolysis of precursor solution, the ratio should be maintained at least 1. However, when the molar ratio is too high, the stains observed on the film surface. It is due to the late vaporization of TEA during the heat treatment. Table 1 is the effect of TEA to tin(IV) isopropoxide molar ratio on precursor solution.

Table 1. Status of precursor solution with TEA concentraiton.

	TEA : Tin(IV) Propoxide	Precursor Solution
1	0.5	Gel
2	0.75	Gel
3	0.8	Gel
4	1	Sol
5	1.2	Sol
6	1.25	Sol

3. 2 Comparison of Film Thickness

The optimum thickness and conductivity of film was hardly obtained at once in sol-gel method. And then multiple coating was required to obtain the desired film thickness. Fig. 2 shows the thickness of film with the application number. Every single application of 0.5M solution gives 50 and 100nm film thickness in spin and dip coating respectively. The film thickness and application number has a linear relationship. Fig. 3 shows the results of XRD analysis with application number. The SnO_2 characteristic peaks were appeared and grown with increasing film thickness. Fig. 4 shows the change of sheet resistance with heat treatment duration. The best conductivity was obtained at 1hr heat treatment and after 1hr the conductivity was decreased. It is due to the concentration of holes were decreased with increasing time.

3. 3 Comparison of Coating Technique

Two types of coating technique were compared in Fig. 5. The surface morphology in spin

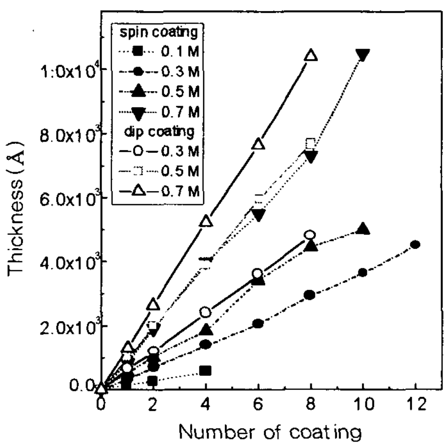


Fig. 2 The thickness of SnO_2 film versus coating application number. TEA ratio=1, Water ratio=4.

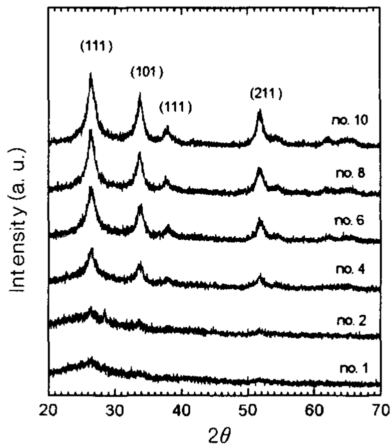


Fig. 3 XRD patterns with application number. Heat treatment duration: 1hr at 600℃.

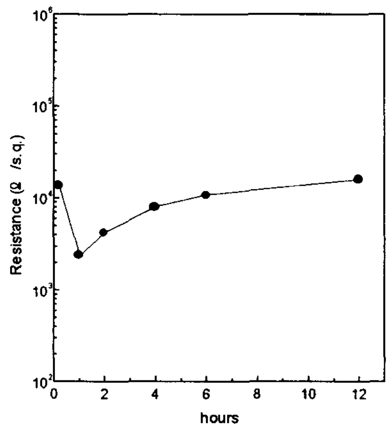
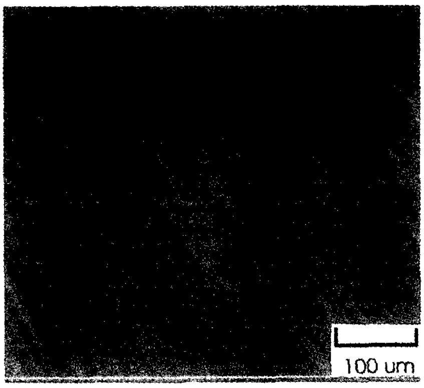
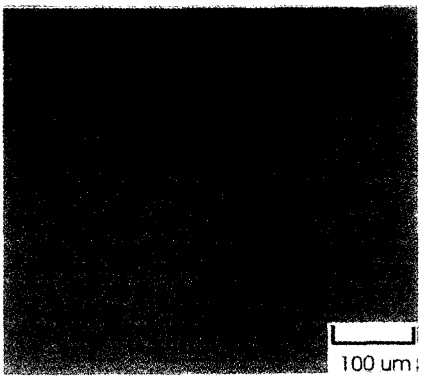


Fig. 4 Sheet resistance versus heat treatment duration.

coating was less uniform compared with that in dip coating. The uniform surface gives higher conductivity and transmittance of film. The less uniform surface morphology in spin coating is considered that the high rotational speed and repeated heat treatment had bad influence on flow patterns during spin coating. The rotational speed and concentration of precursor solution had been changed, however, the similar results were obtained.



(a) spin coating



(b) dip coating.

Fig. 5 Optical microscopic images of film surface

3. 4 Effects of Application Number on Transmittance

The transmittance of film was measured with application number. Fig. 6 shows the results of film transmittance between 250 and 800nm in wavelength. The average transmittance of $1\mu m$ thick film at 500nm in wavelength is over 90% for all films regardless of film thickness. Generally, the required transmittance of transparent conductive thin film for solar cell substrate is over 85% and then the results is encouraging. However, the transmittance and conductivity of

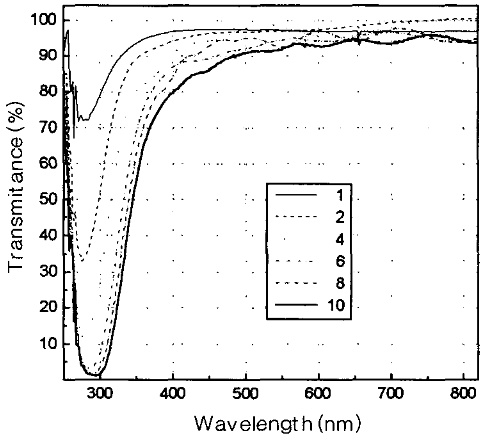


Fig. 6 Transmittacne in visible light wavelength for different film thickness.

film has the reverse relationship. As the concentration of holes was increased, conductivity was increased, however, transmittace was decreased due to the light dispersion effect of holes. And then to obtain the optimum condition of conductive film, the relationships between transmittance and conductivity should be investigated.

4. CONCLUSION

1) The stable sol precursor solution was obtained from tin(IV) isopropoxide. To control and inhibit the hydration rate, the ratio of triethanolamine to tin(IV) isopropoxide should be at least 1.

2) The thickness of coating were 50nm and 100nm for each application of spin and dip coating respectively. The thicker coating can be obtained as the results of repeated coating.

3) The surface from dip coating was more uniform than that from spin coating. It is due to that the application number of spin coating is

twice of that of dip coating.

4) The transmittance of thin film, over 1㎛ in thickness, is higher than 90% in visible range of light. And the resistivity of film is less than 0.1 Ω-cm.

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