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Fabrication of Tin(IV) Oxide Film by Sol-gel Method

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Abstract

Transparent conducting tin (IV) oxide thin films have been studied 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 conditions 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 0.01-cm and the transmittance is higher than 90% in a visible range.

초 록 : 태양전지의 전극 기판으로 사용되는 전도성 투명 산화주석 박막의 제조 방법에 대하여 연구하였다. 졸-겔법을 이용하여 산화 주석 박막을 제조하는 경우에 저가의 공정으로 대면적의 박막을 얻을 수 있는 장점이 있다. 본 연구에서는 공정 조건의 확립과 전구체의 설정에 중점을 두었다. 전구체 용액을 isopropyl 알코올에 tin isopropoxide를 용해한 용액을 사용하였으며 수화 반응을 억제하기 위하여 triethanolamine(TEA)을 첨가하였다. Corning 유리 위에 spinning과 dipping 방법을 이용하여 코팅을 하였으며 이후 열처리하여 최종 산화주석 박막을 제조하였다. 이렇게 제조된 박막은 가시광선 영역에서 90% 이상의 투과도를 보였으며 0.01 Ω·cm 이하의 비저항을 나타냈다.

Key words: SnO_2, Sol-gel, Tin Isopropoxide, Resistivity, Conductivity

1. Introduction

Transparent conducting tin(IV) oxide coated glass is currently receiving attention and being developed for solar cell substrate and LCD (Liquid Crystal Display) due to its high transmittance and low resistivity. The high transmittance in visible light is due to high band gap (over 3 eV) and high conductivity is due to free electrons in oxygen vacancy holes.[1-3] The similar properties were found in Cd, In or 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 (Chemical Vapor Deposition), PVD (Physical Vapor Deposition) or spray pyrolysis method.[7] However, these methods need 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.[10,11]

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 and Corning 7059 glass were used as substrates. Prior to the coating, all substrates were cleaned with acetone 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. GR grade high purity chemicals were used as reagents. Fig. 1 shows the flow sheet of precursor solution preparation.

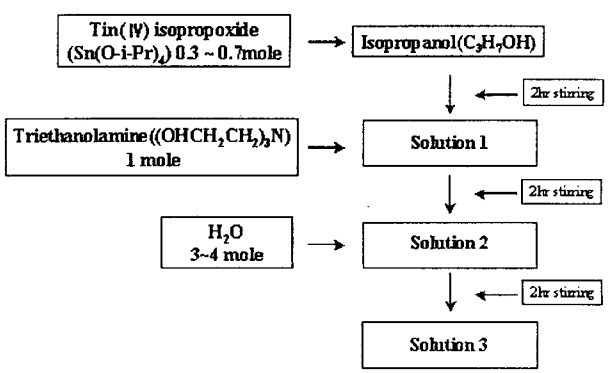

Fig. 1. Flow sheet of precursor solution preparation.

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2.2. Coating and Heat Treatment

Spin and dip coating technique were applied. In spin coating, spin coating machine can control the rotational speed and time. In dip coating, dip coating machine can control the lifting speed with step motor. Rotational speed in spin coating was varied from 1500 RPM to 3000 RPM. Lifting speed in dip coating was varied from 3 to 12 cm/min. Precursor solution coated glass was cured for 1hr at 100°C and then was preheat treated for 10 min at 500°C for repeated coating. The final heat treatment was conducted at 600°C for 1 hr in air.

2.3. Characterization of Film

The thickness was measured from SEM image of cross sectional view. The transmittance in visible wavelength range were measured with UV-VIS spectrophotometer. The electrical conductivity and sheet resistance were measured and calculated with 4 point probe and hole measurement equipment. X-ray diffractometer was used to analyze the surface crystalline. To analyze the temperature effects on crystalline, TG-DTA was used.

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 are observed on the film surface. It is due to the late vaporization of TEA during the heat treatment. Table 1 lists the effect of TEA to tin(IV) isopropoxide molar ratio on precursor solution.

3.2. Analysis of TG-DTA

To examine the heat treatment characterization, TG-DTA analysis was conducted on the powder obtained from drying of precursor solution. Even the characteristics of powder and film were not exactly the same, the heat treatment temperature can be obtained from the TG-DTA analysis. Fig. 2 is the results of TG-DTA for the different concentration of TEA. The crystallization peak was appeared at 426°C and the mass was being reduced continuously until over 500°C from the Fig. 2a). And then to complete the crystallization of SnO_2 and evaporation organic solvent, the heat treatment should be conducted over 500°C. When excess TEA was added, the crystallization peak was increased up to 500°C. It is due to excess TEA formed strong bonded with tin atom and then it causes the delay of crystallization from amorphous.

Table 1. Status of precursor solution with TEA concentraion

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

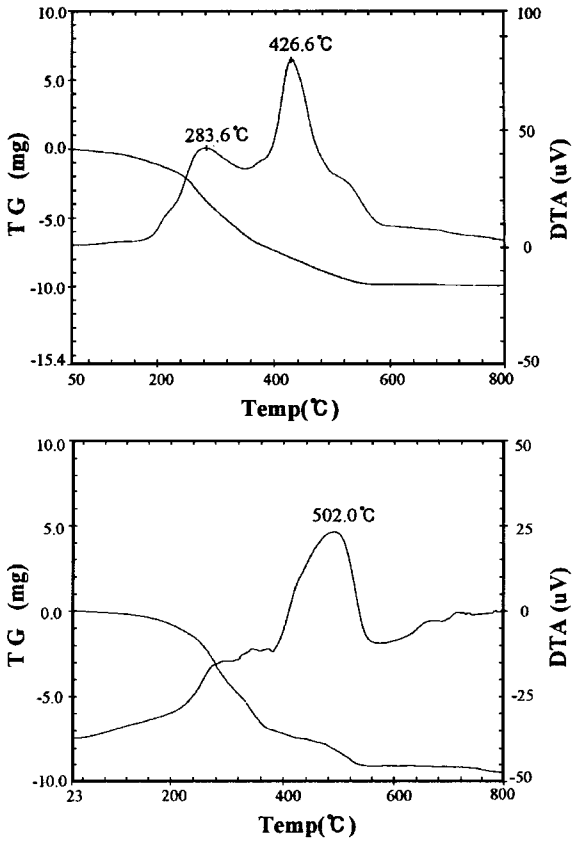

Fig. 2. TG-DTA results of SnO_2 powder a) TEA=1 b) TEA>1 in molar ratio.

3.3. Comparison of Film Thickness

The optimum thickness and conductivity of film was hardly obtained at once in sol-gel method. And then multiple coat-

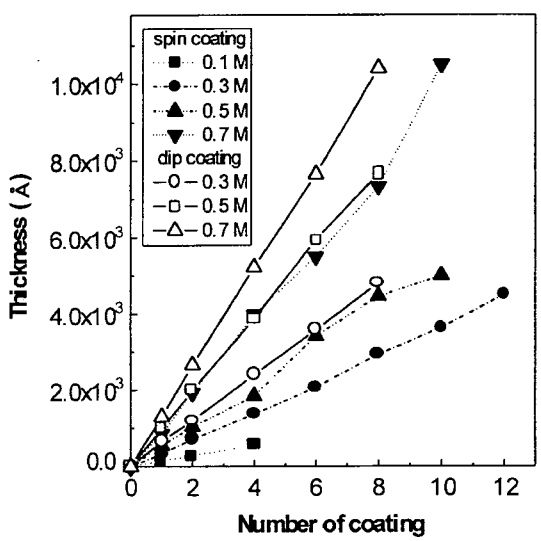

Fig. 3. The thickness of SnO_2 film versus coating application number. TEA ratio=1, Water ratio=4.

ing was required to obtain the desired film thickness. Fig. 3 shows the thickness of film with the application number. Every single application of 0.5 M solution gives 50 and 100 nm film thickness in spin and dip coating respectively. The film thickness and application number has a linear relationship. Fig. 4 shows the results of XRD analysis with application number. The SnO_2 characteristic peaks were hardly appeared once or twice application. However, the characteristic peaks were appeared and grown with increasing film thickness. Fig. 5 shows the change of sheet resistance with heat treatment duration. The best conductivity was obtained at 1hr heat treatment and after 1 hr the conductivity was decreased. It is due to the concentration of holes were decreased with increasing time.

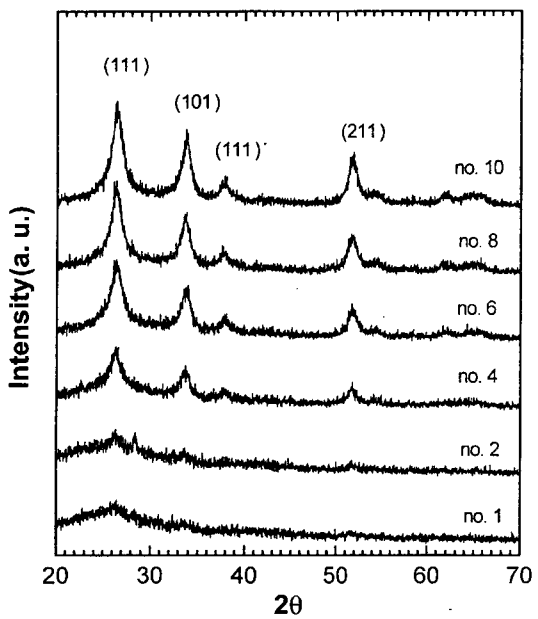

Fig. 4. XRD patterns with application number. Heat treatment duration: 1 hr at 600°C.

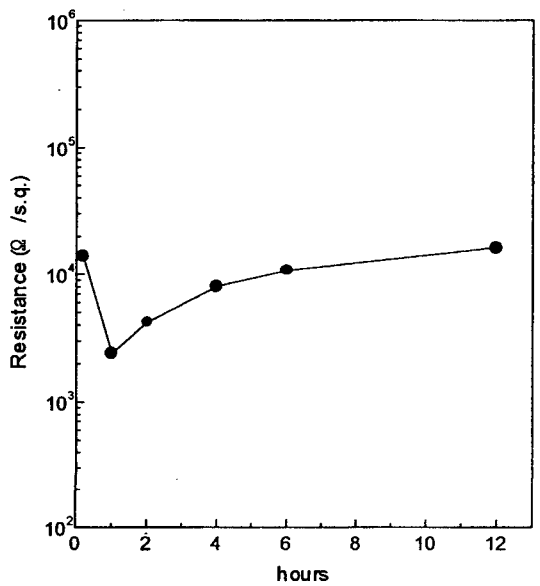

Fig. 5. Sheet resistance versus heat treatment duration.

3.4. Comparison of Coating Technique

Two types of coating technique were compared in Fig. 6. The surface morphology in spin coating was less uniform compared to 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. Even if the rotational speed and concentration of precursor solution had been changed, the similar results were obtained.

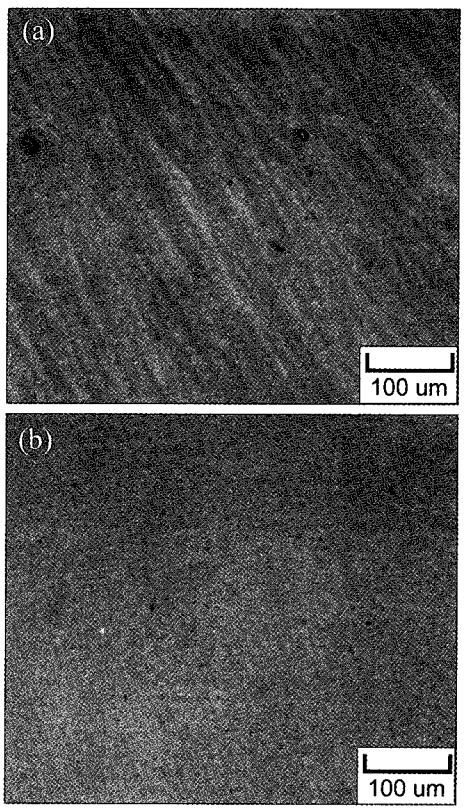

Fig. 6. Optical microscopic images of film surface a) spin coating b) dip coating.

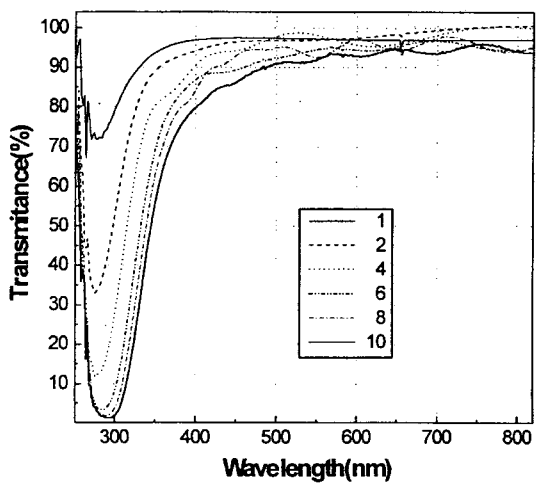

Fig. 7. Transmittance in visible light wavelength for different film thickness.

3.5. Effects of Application Number on Transmittance

The transmittance of film was measured with application number. Fig. 7 shows the results of film transmittance between 250 and 800 nm in wavelength. The average transmittance of 1mm thick film at 500 nm 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 film has the reverse relationship. As conductivity was increased, 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

The important conclusions derived from the research conducted are enumerated below.

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.

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

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.

The transmittance of thin film, with 1mm thickness, is higher than 90% in visible range of light. And the resistivity of film is less than 0.01-cm.

Acknowledgement

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References

1. J. P. Chatelon et al., *Thin Solid Films*, **247**, 162 (1994).
2. C. Terrier et al, *Thin Solid Films*, **295**, 95 (1997).
3. S. Park, H. Zheng, and J. D. Mackenzie, *Materials Letters*, **22**, 175 (1995).
4. T. M. Racheva and G. W. Critchlow, *Thin Solid Films*, **292**, 299 (1997).
5. A. Maddalen, et al., *J. Non-Crystalline Solids*, **121**, 365 (1990).
6. J. Touskova et al., *Thin Solid Films*, **293**, 272 (1993).
7. S. G. Ansar et al., *Thin Solid Films*, **295**, 271 (1997).
8. S. S. Park, J. D. Mackenzie, *Thin Solid Films*, **258**, 268 (1995).
9. C. J. Brinker and G. W. Scherer, Sol-Gel Science, Ch. 13, Academic Press (1990).
10. M. J. Hampden-Smith, T. A. Wark, and C. J. Brinker, *Coordination Chemistry Review*, **112**, 81 (1992).
11. Y. Takahashi et al., *J. Electrochemical Soc.*, **137**, 267 (1990).