Effect of Temperature and Time on Etching Rate of Tin Oxide Thin Films

Chokchai Kahattha[1] and Wisanu Pecharapa[2]

[1]Department of Applied Physics, Faculty of Science, King Mongkut Institute of Technology Ladkrabang, Bangkok 20520, Thailand

[2]KMITL Nanotechnology Research Center, King Mongkut Institute of Technology Ladkrabang, Bangkok 20520, Thailand

**Corresponding author. E-mail: kpewisan@kmitl.ac.th*

ABSTRACT

Etching processes and characterization of transparent conducting Tin Oxide thin film grown by sputtering on glass substrate was conducted. The samples were cleaned before etching process. 0.35 M-Oxalic acid were selected as etching solvent. Temperature and etching time are two crucial parameter affecting etching rate and etching quality. Etching Thickness and etching rate were determined by optical technique. The results revealed that Oxalic acid showed the capability of etching solvent for tin oxide thin film. The increasing in etching temperature from 25°C to 45°C caused in significantly increasing rate from 0.6 nm/min to 2 nm/min. With etching time longer than 30 mins., the constant etching rate of 1 nm/min is obtained.

Key words: Tin oxide, Etching rate

INTRODUCTION

Tin oxide thin films are among the most useful transparent conductive metal oxides due to their high optical transmittance in visible range and excellent electrical conductivity. It have gained great attention due to its suitable properties for wide range of applications including solar cells, heating devices(Takeuchi et al., 2003), electrodes of rechargeable batteries (Khonsari et al., 2003), as well as gas sensors.(Chung and Lim, 2003). Tin oxide thin films can be prepared by various techniques such as spray pyrolysis, sputtering, electron beam evaporator, and chemical vapor deposition (Takeuchi et al., 2003). Additionally, due to requirements for fabrication of optical device application, transparent electrode must be etchable for device patterning. Typically, wet and dry etching techniques are employed and wet method is simpler and gives higher throughput than wet method. Recently, many related research works were devoted on indium tin oxide (ITO) thin films with both wet etching (Tsai and Wu, 2006; Huang et al., 2004) and dry etching (Lee et al., 2001; Park et al., 2000). However, few literatures on etching process of tin oxide thin films were reported (Chung and Lim, 2003). In this paper, an attempt has been made to etch tin oxide thin film by chemical solution. The effect of temperature and etching time on etching rate determined by optical method is also investigated.

MATERIALS AND METHODS

Commercial tin oxide thin films used in this study were deposited on glass substrate by conventional sputtering method at Bangkok Solar Cell Co., Ltd. Prior to etching process, the samples were cleaned in ultrasonic bath successively using deionized water for 15 mins., acetone for 15 mins., isopropanol for 15 mins. and methanol for 15 mins. and dried by nitrogen gas. The etchant used in this study is mainly from Oxalic and its temperature was monitored and controlled by heating bath. During etching process, the etching cell was rotated and vibrated using magnetic stirrer and ultrasonic bath. The concentration of etchants, etching duration and temperature was varied so that the effect of them on etching rate is understood. The surface morphologies of the etched films were carried out by Atomic Force Microscopy (AFM). The etching rate determined by the thickness of the thin films was obtained from transmission spectra using UV-VIS spectrophotometer

RESULTS AND DISCUSSION

Figure 1 is SEM image showing the cross section of the sample before etching. From this image the average thickness of tin oxide thin film of 900 nm is obtained. The surface morphologies of the films before etching and after etching by 0.35M-Oxalic acid at 30°C for 60 mins. is illustrated in Figure 2(a) and (b), respectively. From AFM image, it is clearly seen that surface grain size of tin oxide film after being etched by Oxalic acid are bigger and rougher than grain size of the film before etching suggesting that tin oxide film can be etched by this process.

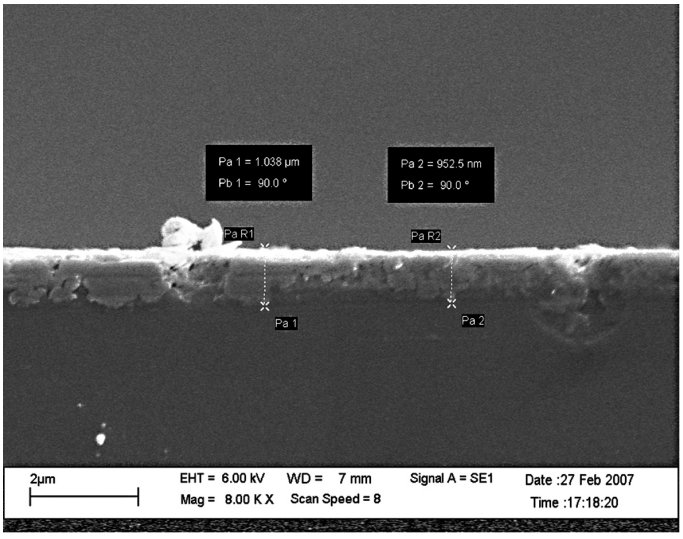
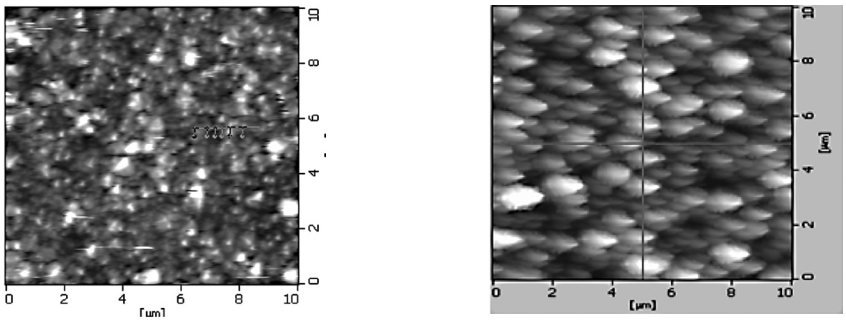


Figure 1. SEM cross-section image of tin oxide film. The inset word boxes showed thickness of 1.038 µm and 952.5 nm at different positions on the film.



(a) (b)

Figure 2. The surface morphology of tin oxide film (a) before etching (b) after etching by 0.35M-Oxalic acid at 30°C for 60 mins.

After etching with designated condition, the etched films were put in UV-VIS spectrophotometer to measure its optical transmission property. Figure 3 shows the transmission spectra in range of 370-380 nm. The transmission spectra of the etched films in visible range are however not chosen for etching rate determination due to effect of optical interference. The etching time is kept constant at 60 mins. As temperature increases, the higher transmission percentage is obtained reflecting that the thickness of the film decreases. Therefore, it could be deduced that temperature during etching process affects on the etching rate of tin oxide film. In order to determine the etching rate of the film as function of temperature, the simple calculation is introduced using Beer-Lambert Law,

$$I_T = I_0 \, exp(-\alpha d) \tag{1}$$

Where, I_T and I_0 is the intensity of the incident light and after passing through the film, respectively. α and d is the absorption coefficient and thickness of the film, respectively. Taking d_1 as the thickness of the films before etching, I_1 and I_2 as the transmitted light intensity from the film before and after etching, respectively, the etched thickness (Δd) which leads to the determination of etching rate can be easily obtained by the following expression,

$$\Delta d \left[\frac{In\ I_1 - In\ I_2}{In\ I_1 - In\ I_0} \right] d_1 \tag{2}$$

The etching rate of tin oxide film by Oxalic acid as function of temperature is calculated using equation (2) and shown in Figure 3. All experimental data used in calculation was the values at 370-380 nm range. The etching rate increases from 0.6 nm/min to about 2.0 nm/min as temperature increases from 25°C to 45°C. As temperature increases, more heat energies are supplied to the system, resulting in the acceleration of the reaction between the etching solvent and tin oxide (Huang et al., 2004).

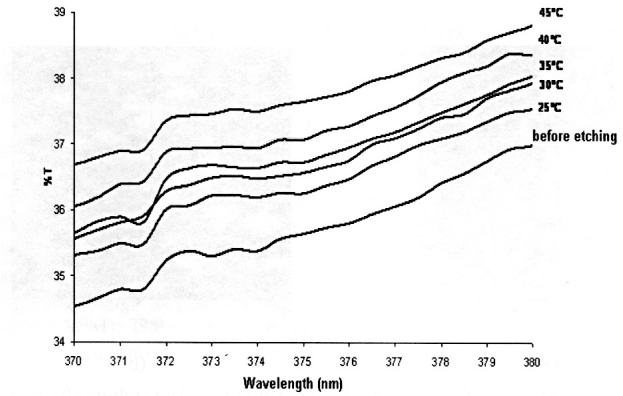


Figure 3. Transmission spectra of etched tin oxide films at different temperature. The etching duration of all samples is kept at 60 mins.

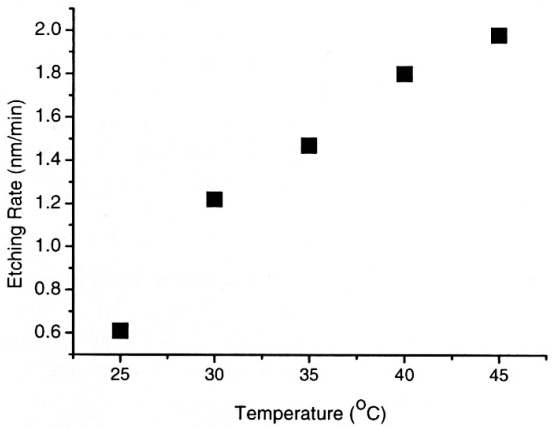


Figure 4. Etching rate as function of temperature at 60 mins.- etching duration.

The effect of etching time on etching rate was also investigated. The etching time was varied from 30 mins. to 150 mins. at 40°C. The transmission spectra of etched samples were collected and demonstrated in Figure 5. The corresponding etching rate is calculated and depicted in Figure 6. As etching duration is less than 30 mins., the etching rate is about 2 nm/min. After etching time is longer, the etching rate tends to decrease and then almost constant at about 1 nm/min. This behavior may be due to the accumulation of reaction residues which can retard the reaction between etchant and tin oxide.

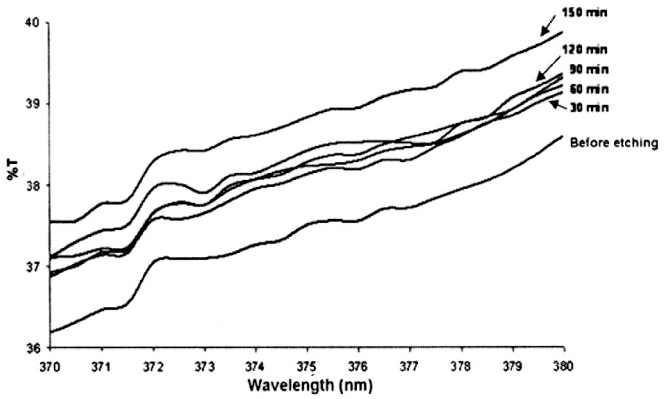


Figure 5. Transmission spectra of etched tin oxide films at different etching time. The etching temperature of all samples is kept at 40°C .

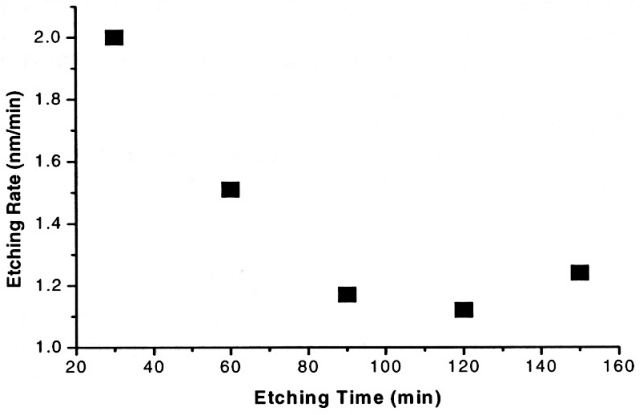


Figure 6. Etching rate as function of etching time at 40°C.

CONCLUSION

Effect of temperature and etching time on etching rate of tin oxide wet etching using Oxalic acid was investigated. AFM image reveals that Oxalic acid can be used as potential etching solvent of tin oxide thin films. Optical method by mean of transmission measurement was introduced to determine the etching rate of the films. The etching rate increases significantly from 0.6 nm/min to 2.0 nm/min as temperature increases from 25°C to 45°C due to assistance of heat energy on etching reaction. However, increasing etching time may cause the additional residue in the solvent reflecting the decrease of etching rate with increasing time.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Department of Applied Physics, King Mongkut Institute of Technology Ladkrabang of the research facilities. This work is supported by National Nanotechnology Center.

REFERENCES

Chung, W. Y., and J. W. Lim. 2003. Patterning of thin tin oxide film with nano-size particle for two-dimensional micro-gas sensor array. Curr. Appl. Phys. 3: 413-416.

Huang, C. J., Y. K. Su, and S. L. Wu. 2004. The effect of solvent on the etching of ITO electrode. Mater. Chem. Phys. 84: 146-150.

Khonsari, F. A., N. Bauduin, F. Donsanti, and J. Amouroux. 2003. Deposition of transparent conductive tin oxide thin films doped with fluoride by PACVD. Thin Solid Films 427: 208-214.

Lee, Y. J., J. W. Bae, H. R. Han, J. S. Kim, and G. Y. Yeom. 2001. Dry etching characteristics of ITO thin films deposited on plastic substrates. Thin Solid Films 383: 281-283.

Park, J. Y., H. S. Kim, D. H. Lee, K. H. Kwon, and G. Y. Yeom. 2000. A study on the etch characteristics of ITO thin film using inductively coupled plasmas. Surf. Coat. Tech. 131: 247-251.

Takeuchi, T., K. Shoji, T. Tadano, I. Doteshita, and S. Onodera. 2003. Preparation of sub-nanometer thickness-controlled tin dioxide films by pulsed atomic-layer CVD. Thin Solid Films 442: 98-201.

Tsai, T. H., and Y. F. Wu. 2006. Wet etching mechanisms of ITO films in oxalic acid. Microelectron Eng. 83: 536-541.