ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 12, No. 4. 2006

Kinetics of Residual Stresses in Electrochemically Doped ITO Thin Films

Arnoldas UŽUPIS[1*], Bonifacas VENGALIS[2], Vaclovas LISAUSKAS[2], Sigitas TAMULEVIČIUS[3], Liudvikas AUGULIS[4]

[1]*Lithuanian University of Agriculture, Faculty of Water and Land Management, Department of Physics Universiteto 10, Akademija, LT-53361 Kaunas, Lithuania*
[2]*Semiconductor Physics Institute, Goštauto 11, LT-01108 Vilnius, Lithuania.*
[3]*Institute of Physical Electronics of Kaunas University of Technology, Savanorių 271, LT-50131 Kaunas, Lithuania*
[4]*Institute of Materials Science, Kaunas University of Technology, Studentų 50, LT-51368 Kaunas, Lithuania*

Received 30 August 2006; accepted 24 October 2006

Indium-Tin-Oxide (ITO) thin films were deposited by a reactive DC magnetron sputtering at $T = (100 \div 700)$ °C on amorphous quartz substrates. Oxygen content of the as grown films was varied by electrochemical doping using 20 % water solution of acetic acid (CH_3COOH). The dependence of residual stress of the system ITO – quartz substrate was studied in a course of the electrochemical doping. We have found that residual stress of the ITO thin films decreased with doping by additional oxygen ions into the films from the solution.
Keywords: indium tin oxide, residual stress, electrochemical doping, magnetron sputtering.

INTRODUCTION

Many kinds of transparent conducting oxide (TCO) films such as impurity-doped indium oxide, tin oxide, and zinc oxide systems have been widely used as transparent conductors for numerous opto-electronic applications [1 – 3].

Indium tin oxide (ITO) is one of the most widely investigated and used transparent conducting oxides, because of it's relatively low resistivity and high optical transmittance in a visible spectra region compared to other transparent conducting oxide films such as SnO_2, ZrO_2 or ZnO [4 – 6].

ITO film properties depend on their structural characteristics, crystallinity, presence of impurities (or doping), defect characteristics, uniformity, stoichiometry. Hence, thin ITO films deposited by different techniques, show a considerable variation in properties. Careful optimization of technological parameters is essential to obtain a good reproducibility of film properties.

As the need for more efficient performance and precise, high-quality thin films has arisen, together with the advancement of multilayer coatings, the development of existing alternative techniques has been sought. One of such techniques is magnetron sputtering [3, 7], the deposition tool used in this work. Magnetron sputtering is a low-pressure process that has gained increasing popularity in the last two decades. It permits large-scale deposition of high-quality films (e.g. homogeneous thickness, high density and superior adhesion to substrate) at relatively high rates. Another advantage is that material can be deposited on substrate at room temperature. The structure of ITO thin films depends on deposition conditions, which have a strong influence on the mechanical properties and the development of stress [8, 9].

Residual stress in thin films can cause several problems for applications. For instance, excessive residual stress can limit the reliability and function of various ITO film-based structures due to peeling, cracking and curling. So, the control of the residual stress is very crucial in almost all coatings.

Both electrical and optical properties of ITO thin films may be tuned in wide ranges by varying oxygen content in the films during post deposition annealing at various oxygen pressure conditions. However, there is also a promising possibility to control oxygen content into the films by electrochemical doping. Low temperature of the process is an advantage, as far as annealing of the films at high temperatures may introduce significant residual stress resulting cracking or peeling the films and bending of the substrate. Precise control of oxygen amount in thin ITO film during different technological steps is an important factor for providing a reliable thin film device structures.

EXPERIMENTAL

A DC magnetron reactive sputtering system was used to deposit the ITO films. Further details about the experimental set up have been reported elsewhere [9]. Pure In target containing 9 wt.% of Sn was disk-shaped with a diameter of 100 mm.

The films were deposited on quartz substrates (for optical measurements) and crystalline silicon substrates (for the stress measurement), which were placed 40 mm apart and parallel to the target surface. The target was pre-sputtered for 10 min. The thickness of the films ranged from 1 μm to 1.2 μm. The substrate temperature measured by a thermocouple was set in the range of 100 ºC to 700 ºC. The film thickness (d) was determined by profilometer. Typical deposition rate of the films was 0.2 nm/s. The films were deposited onto 0.27 mm thick quartz substrates. After deposition, the films were doped additionally by oxygen at room temperature electrochemically. The water solution used for the electrochemical

*Corresponding author. Tel.: +370-37-752363; fax.: +370-37-752392.
E-mail address: *arnoldas.uzupis@lzuu.lt* (A. Užupis)

doping contained about 20 % of acetic acid (CH_3COOH). The density of current during doping was kept fixed (15 μA/cm^2). The temperature of the solution during experiment was 20 °C. The influence of oxygen content on resistivity of thin films was controlled *in situ*. The schematic illustration of the oxygen doping and resistivity measurement technique is shown in Fig. 1. (Direction of the current ("+" or "–" through the sample) was changed by the buttons P1).

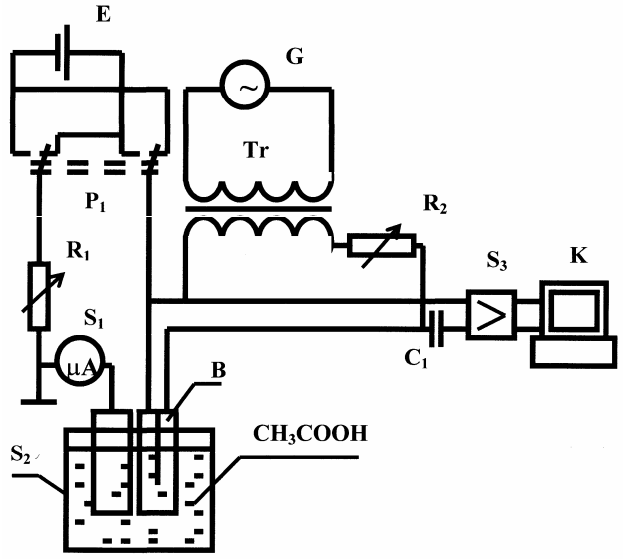

Fig. 1. Schematic illustration of the technique used both for electrochemical doping of ITO films by oxygen and *in-situ* electrical resistivity measurement: B – sample (ITO); E – power supply (0 – 12 V); G – ac current generator (G3-112/1); R1, R2 – resistance; K – computer; Pt – chemically stable platinum electrode; S1 – micro-ampermeter; S2 – test-tube of glass; S3 – amplifier of ac signal (data precision 3500); Tr – transformer; C1 – capacitance, P1 – buttons (for changing direction of the current)

X-ray diffraction (XRD) measurements were carried out in order to examine crystallinity of the films as a function of deposition temperature and doping. Cu K_α radiation source and a conventional $\Theta - 2\Theta$ set-up was used for the investigations.

Optical transmission of the films was measured in the spectra region of wavelengths 300 nm – 800 nm using (UV – Vis) spectrometer.

The residual stress in the plane of thin films perpendicular to the length of cantilever was calculated according to the Stoney's formula [10]:

$$\sigma = \frac{1}{6}\frac{E_s d_s^{\,2}}{(1-\nu_s)d_f}\left(\frac{1}{R_2}-\frac{1}{R_1}\right), \qquad (1)$$

Where E_s is the Young's modulus of the substrate, d_s is the thickness of the substrate, d_f is the thickness of thin film, ν_s is Poisson's ratio of the substrate, R_2 and R_1 are the radii of the substrate after and before thin film deposition respectively. The radii of the substrate were defined using a laser interferometer described in [10].

RESULTS AND DISCUSSIONS

The electrochemical doping was used to change the oxygen content in the surface layer of ITO thin films after the deposition. Depending on the current direction (and time of exposure), the amount of oxygen on surface at ITO thin films can be either increased or decreased. The corresponding resistivity changes of the as deposited films were observed. Resistivity kinetics of the films measured in situ during electrochemical doping are shown in Fig. 2. Resistivity of ITO thin films increased when positive voltage was applied on platinum electrode (first part of the curve in Fig. 1) while a decrease of film resistivity was observed when Pt electrode was negative (second part of the curve in Fig. 1). These reproducible dramatic resistivity changes demonstrate variation of oxygen content in the surface layer of ITO films depending on the direction of current between platinum electrode and ITO film.

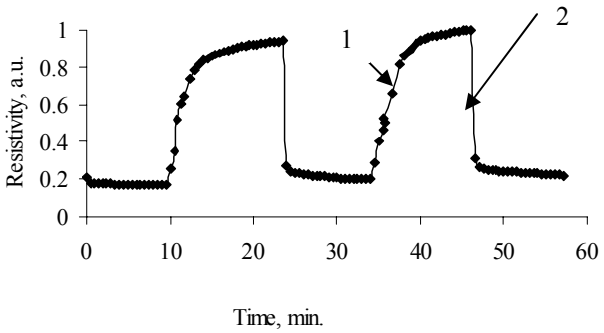

Fig. 2. Kinetics of the resistivity of ITO thin films during their electrochemical doping

According to our previous experimental results, the residual stress of the as prepared thin ITO films depended strongly on deposition temperature [11]. This is good agreement with the results of other researchers [4] that have demonstrated that the intrinsic compressive component of stress always dominates for the conductive ITO films. So, the residual stress changes with deposition temperature can be attributed to a complicated variation of ITO film microstructure during film synthesis [9].

Residual stress in the films can be minimized either by annealing in oxygen ambient or by electrochemical doping. Results of our experiments revealed an increase of tensile stress component for the ITO thin films related to a diffusion of oxygen into the films [9].

This increase is dependent on the structure of ITO thin films (or temperature of deposition) as reported as well in [4, 5, 12]. The electrochemical doping was applied for the ITO thin films with small stoichiometric changes that reflected by their good resistivity (~ 10^{-2} Ωcm – 10^{-3} Ωcm) and optical (transparence about 80 % ÷ 85 %) properties. Residual stress was evaluated as a function of time of electrochemical doping. From Fig. 3 (a and b) one can see, that residual stress in indium tin oxide films deposited at different temperatures can be minimized by electrochemical doping. An increase of resistivity of ITO thin films by about 15 % – 30 % followed by a slight variation in

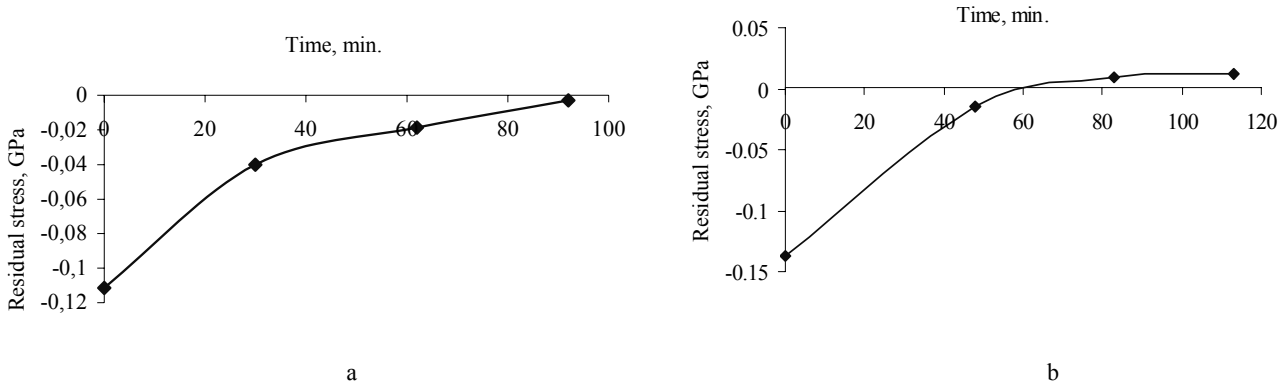

Fig. 3. Kinetics of residual stress of ITO thin films deposited at: a – 150 °C, b – 700 °C, during their electrochemical doping

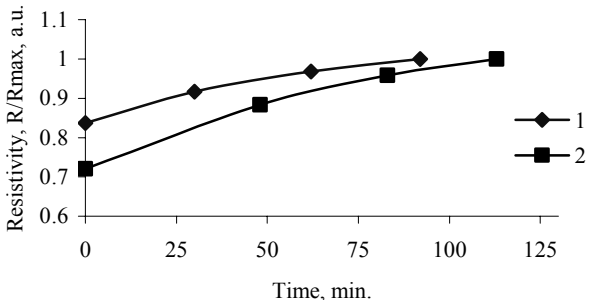

Fig. 4. Kinetics of resistivity of ITO thin films, during at time of electrochemical doping, deposited at: 1 – 150 °C, 2 – 700 °C

optical transmittance were indicated after electrochemical doping (Fig. 4).

CONCLUSIONS

The ITO thin films have been deposited on amorphous quartz substrates by magnetron sputtering. It has been observed experimentally that residual stress in indium tin oxide films deposited at different temperatures can be minimized at room temperature by applying extra electrochemical doping by oxygen. Changes of the residual stress due to electrochemical doping depended on microstructure of the prepared ITO thin films. The minimum residual stress (close to zero) and corresponding increase of resistivity (by 15 % – 20 %) was obtained for ITO thin films deposited at 700 ºC (with the biggest crystallite size).

REFERENCES

1. **Shigesato, Y., Koshi-ishi, R., Kawashima, T., Ohsako, J.** Early Stages of ITO Deposition on Glass or Polymer Substrates *Vacuum* 59 2000: pp. 614 – 621.
2. **Granqvist, C. G., Hultaker, A.** Transparent and Conducting ITO Films: New Developments and Applications *Thin Solid Films* 411 2002: pp. 1 – 5.
3. **Teixeira, V., Cui, H. N., Meng, L. J., Fortunato, E., Martins, R.** Amorphous ITO Thin Films Prepared by DC Sputtering for Electrochromic Applications *Thin Solid Films* 420 – 421 2002: pp. 70 – 75.
4. **Shao, S., Fan, Z., Shao, J., He, H.** Evolutions of Residual Stress and Microstructure in ZrO_2 Thin Films Deposited at Different Temperatures and Rates *Thin Solid Films* 445 2003: pp. 59 – 62.
5. **Kim, Y. S., Park, Y. C., Ansari, S. G., Lee, J. Y., Lee, B. S., Shin, H. S.** Influence of O_2 Admixture and Sputtering Pressure on the Properties of ITO Thin Films Deposited on PET Substrate Using RF Reactive Magnetron Sputtering *Surface and Coatings Technology* 173 2003: pp. 299 – 308.
6. **Salehi, A., Gholizade, M.** Gas-sensing Properties of Indium-doped SnO_2 Thin Films with Variations in Indium Concentration *Sensors and Actuators B: Chemical* 89 (1 – 2) 2003: pp. 173 – 179.
7. **Yeon, S. J., Sung, S. L.** Development of Indium Tin Oxide Film Texture during DC Magnetron Sputtering Deposition *Journal of Crystal Growth* 259 2003: pp. 343 – 351.
8. **Bhagwat, S., Howson, R. P.** Use of the Magnetron-sputtering Technique for the Control of the Properties of Indium Tin Oxide Thin Films *Surface and Coatings Technology* 111 1999: pp. 163 – 171.
9. **Užupis, A., Tamulevičius, S., Augulis, L., Jankauskas, J., Butkutė, R., Vengalis, B.** Thermal and Intrinsic Stress in DC Magnetron Sputtering Deposited Thin ITO Films on Amorphous Silica Substrates *Lithuanian Journal of Physics* (*Lietuvos Fizikos Žurnalas* 42 (4) 2002: pp. 291 – 296.
10. **Tamulevičius, S., Augulis, L., Laukaitis, G., Puodžiukynas, L.** Techniques for Measurements of Strain in Thin Films *Materials Science* (*Medžiagotyra*) 2 (7) 1998: pp. 40 – 50.
11. **Užupis, A., Tamulevičius, S., Butkutė, R., Vengalis, B.** Effect of Substrate Temperature on the Properties of Indium – Tin Oxide Films *Materials Science* (*Medžiagotyra*) 7 (4) 2001: pp. 217 – 220.
12. **Užupis, A., Tamulevičius, S., Butkutė, R., Vengalis, B., Lisauskas, V.** Post – Deposition-annealing Effects in DC Reactive Magnetron *Materials Science* (*Medžiagotyra*) 8 (3) 2002: pp. 240 – 245.

Presented at the National Conference "Materials Engineering'2006" (Kaunas, Lithuania, November 17, 2006)