A Study of ZnO Buffer Layer Effect on Physical Properties of ITO Thin Films Deposited on Different Substrates

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ABSTRACT: *The improvement of the physical properties of Indium Tin Oxide (ITO) layers is quite advantageous in photovoltaic applications. In this study the ITO film is deposited by RF sputtering onto p-type crystalline silicon (c-Si) with (100) orientation, multicrystalline silicon (mc-Si), and glass substrates coated with ZnO and annealed in vacuum furnace at 400°C. Electrical, optical, structural and morphological properties of the ITO films were analyzed by four point probe, UV/VIS/IR spectrophotometer, X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The quality of films deposited on buffer layer is found to be superior to those grown directly on a substrate. The structural, optical and electrical studies reveal that ZnO buffer layers improve the crystalline quality, optical and electrical properties of ITO thin films.*

KEY WORDS: *RF sputtering, Indium tin oxide, Zinc oxide, Transparent conductive oxide films, Buffer layer.*

INTRODUCTION

Transparent Conductive Oxide (TCO) Indium Tin Oxide (ITO) is a highly degenerate n-type wide gap~3.7eV semiconductor and is transparent in the wavelength range of 400-800nm and has high infrared reflectance for 800-1200nm, it has very good electrical conductivity and excellent substrate adherence and hardness [1]. Due to its unique properties, ITO has found extensive application in photovoltaic technology [2], flat panel displays [3], heat reflecting mirrors [4], LEDs [5] and so on. Conduction mechanism of this material is due to oxygen vacancy and tin impurities. Oxygen vacancies dominate the conduction mechanism of ITO by contributing two free electrons to the lattice, while Sn^{+4} ion can provide only one free electron [1,6]. There exist many deposition techniques for obtaining high quality ITO film, such as RF and DC sputtering [7,8], E-beam evaporation [9], Pulsed Laser Deposition (PLD) [10], spray pyrolysis [11]. Among these techniques, sputtering of ITO is quite useful for all

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applications where a low process temperature is desired. Furthermore, the stoichiometry of the films is more controllable than other techniques [1].

Zinc oxide (ZnO) is an n-type semiconductor with both wide band gap (~3.37eV) and a large exciton binding energy of 60meV [12-14] that finds application in ultra-violet/blue emission devices, laser diodes, solar cells and in acoustic devices. ZnO is a prominent excitonic material suitable for light emission applications since its bound electron hole pairs have a high radiative recombination probability. Multilayer thin films show different physical properties other than the conventional monolayer thin films [15]. The quality of films deposited on buffer layer is found to be superior to those grown directly on a substrate [15, 16].

The aim of this paper is to investigate the influence of ZnO as a buffer layer on the properties of ITO film deposited on different substrates.

EXPERIMENTAL SECTION

The substrates used in this study were micro slide glass of thickness ~150 µm, p- type (100) c-Si ~500 µm and mc-Si ~300 µm. All substrates were cleaned by RCA method (DI water, ammonia, hydrogen peroxide 5:1:1). Afterwards the Si wafers were dipped in 10% HF solution to remove any surface oxide, and then rinsed with DI water. The ZnO buffer layer~100 nm was deposited on all substrates by RF sputtering at constant power of 150 W from a ZnO source, with a purity of 99.99%. Subsequently, the ITO layer with a thickness of 300 nm was deposited onto the ZnO film on the corresponding substrates. The distance between the source and the substrates was 60 mm. The vacuum chamber was evacuated down to a base pressure of about 6×10^{-6} Torr prior deposition. The reactive sputtering gas was high purity argon (99.999%). The deposition was carried out at a constant pressure of 20 mTorr. After deposition, samples were annealed at 400°C in vacuum at a pressure, lower than 5×10^{-5} Torr [17]. Annealing in an oxygen-deficient atmosphere not only promotes crystalline growth but also increases the carrier concentration of ITO by creation of oxygen-vacancy [18]. In order to study the physical properties of these layers, the structural, morphological, electrical and optical properties of ITOs are analyzed by X-Ray Diffraction (XRD) (Philips spa), data are collected in the 2θ range of 10-60° at a scan rate of 1°/min, scanning electron microscopy (SEM), four point probe system (Keithley 196 & 224) and UV/VIS/IR spectrophotometer (Varian Cary 500), respectively.

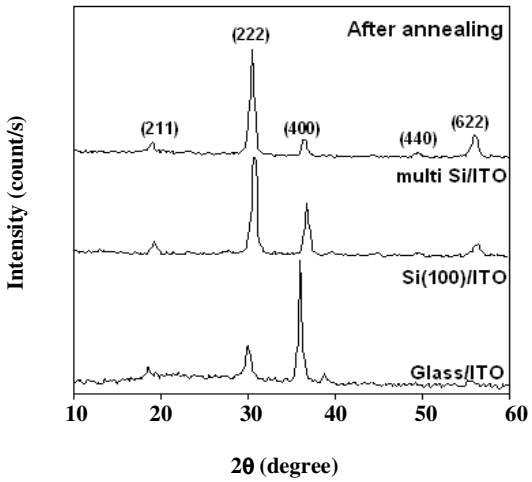

Fig. 1: XRD patterns of ITO films on all substrates [1].

RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectra of ITO thin films on different substrates correspond to a card of cubic In_2O_3 number ASTM 6-0416, with thickness of 300 nm after annealing at 400ºC. Five peaks were observed in the spectra labeled as (211), (222), (400), (440), (622); two of them show strong intensities. As shown in Fig. 1, none of the spectra indicated any characteristic peaks corresponding to Sn, SnO and/or SnO_2, which means that the tin atoms were probably doped substitutionally into the In_2O_3 lattice. In the XRD spectra of ITO on mc-Si substrates, the highest intensity is related to (222) planes correspond to a preferred orientation along {111} direction, while the highest peak is related to (400) matching {100} orientation for layer deposited on glass substrate [1].

It is observed that all deposited and annealed ITO thin films are crystalline and have (222) and (400) preferred orientations. When films are deposited on mono and multicrystalline Si substrates, the islands of material with the surface energy will grow over the critical size and continue so, thus reducing the free energy [19]. We see here (222) orientation for ITO films on c- and mc-Si substrates. Positions of (222) and (400) peaks are

Table 1: Structural properties of ITO thin films on different substrates

Samples	$d_{(222)}$ (Å)	$d_{(400)}$ (Å)	$I_{(222)}/I_{(400)}$	Lattice constant (Aº)	$2\Theta_{(222)}$ (˚)	$2\Theta_{(400)}$ (˚)
Standard	2.921	2.529	3.330	10.118	30.56	35.53
Glass/ITO	2.924	2.536	0.268	10.144	30.54	35.36
mc-Si/ITO	2.924	2.534	6.802	10.129	30.54	35.38
Glass/ZnO/ITO	2.925	2.532	1.10	10.132	30.52	35.40
mc-Si/ZnO/ITO	2.922	2.527	5.45	10.122	30.55	35.47

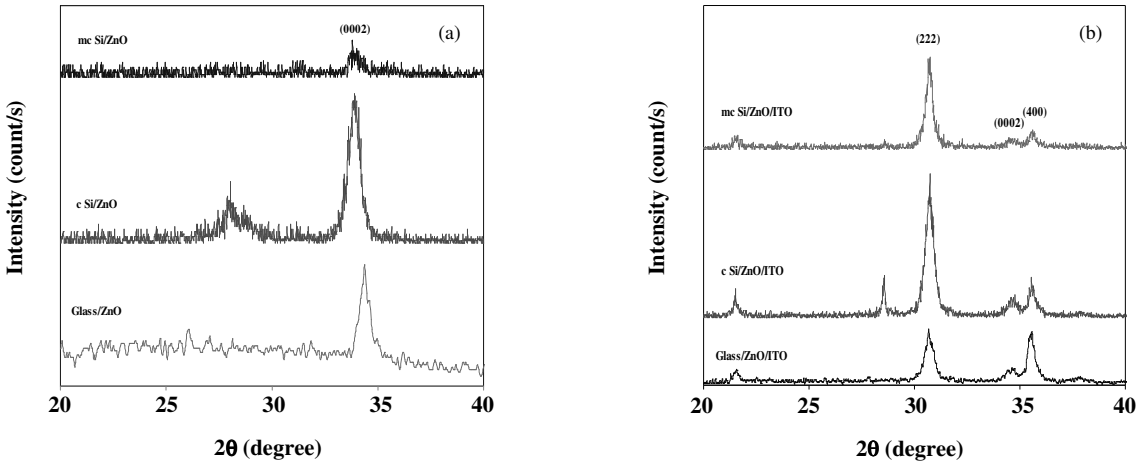

Fig.2: XRD patterns of (a) ZnO and (b) ITO films on all substrates.

different for ITO on different substrates. The different substrates will lead to different crystal lattice mismatch between substrates and ITO films, and the crystal lattice mismatch will cause different strain and stress in the films. Inner pressure stress in ITO films grown on glass and c-Si substrates causes reduction in lattice plane spacing and increase of angle of XRD, while inner tensile stress for the films on mc-Si wafer causes increase of lattice plane spacing and reduction of angle of XRD. For the films on c-Si and glass substrates, the stress in the ITO changes from the pressure stress to tensile stress after annealing at 400ºC. For the films on mc-Si, the stress in ITO film changes from the tensile stress to pressure stress after annealing [1].

The structural properties of ZnO film on different substrates were analyzed by X-Ray Diffraction (XRD). Fig. 2a shows the XRD spectra of ZnO with thickness of ~100 nm on all substrates after annealing at 400˚C. It can be seen from Fig. 2a that all ZnO films deposited, have (0002) preferred orientation and this peak is highest for the ZnO layer deposited on c-Si. To evaluate the grain size (D) of the film from XRD data, the Scherrer formula is adopted:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where λ , β and θ were X-ray wavelength (1.54054 Å), the FWHM of (0002) diffraction line, and Bragg diffraction angle (*Rad*), respectively. The grain size of ZnO on glass, c-Si and mc-Si are 13.9, 21.3 and 32 nm which shows the growth improvement of ZnO on the mc-Si substrate. Fig 2b shows the XRD spectra of ITO film of ~300 nm deposited on all substrates with ZnO buffer layer and annealed at 400˚C. As shown in Fig. 2b, the peaks of (222) and (400) are assigned to the cubic bixebyite structure of In_2O_3 and the (0002) peak is from ZnO, and the highest intensity is related to (222) planes corresponding to {111} plane direction (Table 1).

Table 2: Average reflectance of ITO on mc-Si with and without ZnO buffer layer.

Sample	R_{avg} % (400-800)	R_{avg} % (800-2000)
ITO/ ZnO/mc-Si	2.87	10.06
ITO/ZnO/c-Si	24.24	19.29
ITO/mc-Si	2.88	10.26
ZnO/c-Si	15.49	26.41

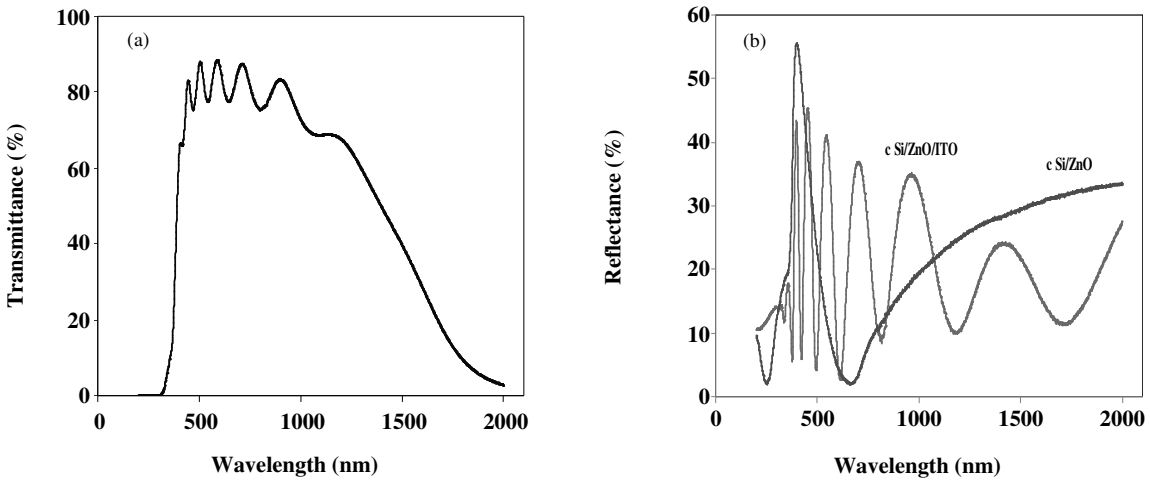

Fig. 3: (a) Transmittance spectra of ITO on glass substrate with ZnO buffer layer, (b) reflectance spectra of ITO films on c-Si /ZnO.

The electrical resistivity of the films was measured by four point probe system. The measured values demonstrate that resistivity of ITO/ Glass and ITO/ mc-Si structures are 1×10^{-4} and $3.6\times10^{-4}\Omega$cm, respectively and they vary by 0.9×10^{-4} and 9×10^{-4} Ωcm by applying ZnO buffer layer for ITO/ZnO/Glass and ITO/ZnO/mc-Si structures. Comparison of the results shows that resistivity of ITO thin film on glass substrate with ZnO buffer layer is the least. This is due to the highest number of vacancies. The highest carrier concentration is described by XRD spectra, where the intensity of the (400) peak is the strongest and is related to the highest number of vacancies or carrier concentration [19].

Fig 3a shows the average transmittance spectra of ITO film on glass, with ZnO buffer layer annealed at 400˚C, is 80.6% in the visible and 45% in the infrared regions.

The low transmittance in the infrared region is due to the high carrier concentration [20], which is due to the (400) peak in the XRD pattern (see Fig. 2(b)).

Fig 3b shows the effect of ZnO buffer layer on the reflectance spectra of ITO from c-Si. The average reflectance of ITO films from c-Si and mc-Si is summarized in Table 2. According to Fig 3b, the highest value of average reflectance is for the c-Si substrate, which is due to high mismatch of the refractive indices, between ITO and c-Si [21].

In order to investigate the morphological properties of ITO on different substrates, the cross-sectional microstructure of ITO films has been imaged by SEM. Fig. 4 shows SEM images of ITO on Si and glass substrates after annealing at 400ºC. The SEM photographs reveal that the growth mechanisms of the ITO films on the substrates are different. The ITO film on Si crystallizes in a three-dimensional manner, and a granular crystalline structure is formed, whereas, the ITO film on glass grows in two dimensions and a domain structure is formed as is shown in Fig. 4. One domain has many micrograins that gathered in the same orientation. SEM cross-section of the layers clearly shows these

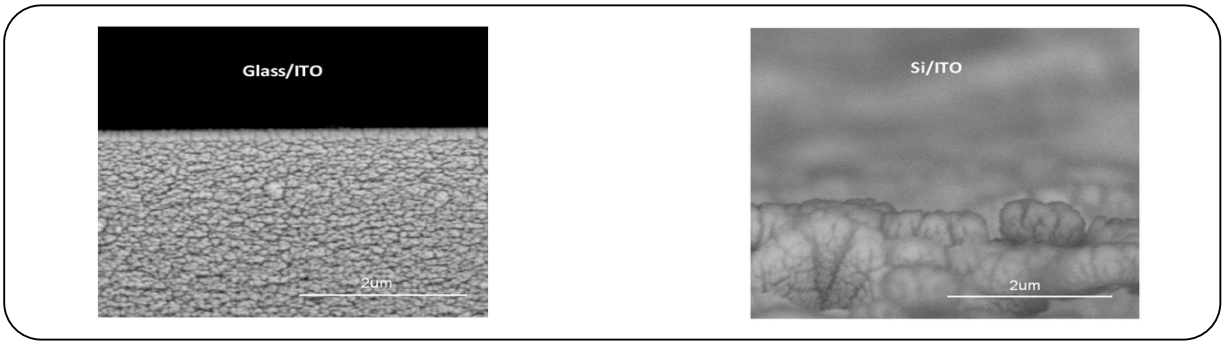

Fig. 4: SEM images of ITO thin films on glass and Si substrates [1].

Fig.5: SEM images of ZnO on all substrates.

situations. The difference of the growth may be explained by surface bonding mechanism between the silicon and glass substrates with ITO [1].

Fig 5 shows the plane view SEM images of ZnO films on different substrates. As shown in Fig 5, the ZnO films on mc-Si have larger grain sizes, than those on glass and c-Si substrates. Fig 6 shows plane view images of ITO films on different substrates using ZnO buffer layer.

Fig 6 reveals that ITO films on ZnO/mc-Si have the largest grain size. The bigger grain size of ITO on mc-Si with ZnO buffer layer is the result of bigger grain size of ZnO/mc-Si substrate which is consistent with XRD results.

CONCLUSIONS

The effect of ZnO buffer layer on the structural, morphological, electrical and optical properties of ITO films on various substrates were analyzed. To show that ZnO buffer layer can improve the physical properties of ITO, some results are presented without the buffer layer. It is shown that the ITO/ZnO/glass structure has the highest conductivity and minimum transmittance in the infrared. This is due to the increase of free electron density which is concluded from the higher (400) peak intensity in the XRD pattern. The highest value of average reflectance is of ITO/ZnO/c-Si which probably is due to the high mismatch between the refractive indecies originating from the high mismatch of the refractive indices of ITO and Si. The SEM images reveal that the flat surface of the ITO film on ZnO/mc-Si structure is a result of matching of mc-Si with ZnO. Results show that the quality of films deposited on buffer layer is found to be superior to those grown directly on a substrate.

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REFERENCES

[1] Manavizadeh N. et al., Influence of Substrates on the Structural and Morphological Properties of RF Sputtered ITO thin Films for Photovoltaic Application, *Thin Solid Films,* **517**, p. 2324 (2009).

[2] Krebs F., Spanggard H., Kjaer T., Biancardo MMM., Alstrup J., Large Area Plastic Solar Cell Modules, *Material Science Engineering: B,* **138**, p. 106 (2007).

[3] Betz U., Kharrazi Olsson M., Marthy J., Escolá M.F., Atamny F., Thin Films Engineering of Indium Tin Oxide: Large Area Flat Panel Displays Application, *Surface and Coatings Technology,* **200**, p. 5751 (2006).

[4] Boiadjiev S.I., Dobrikov G.H., Rassovska M.M.M., Preparation and Properties of RF Sputtered Indium-Tin Oxide Thin Films for Applications as Heat Mirrors in Photothermal Solar Energy Conversion, *Thin Solid Films,* **515**, p. 8465 (2007).

[5] Hung K.-Y., Pei C.-C., Hu C.-J., Yang T.-C., Manipulation Image Processing Algorithmic Technology to Realize 1.8, RGBW Transflective TFT-LCDs with Adjustable Colour Gamut, *Displays*, **29**, p. 526 (2008).

[6] Adurodija F.O., Izumi H., Ishihara T., Yoshioka H., Motoyama M., Effect of Sn Doping on the Electronic Transport Mechanism of Indium-Tin-Oxide Films Grown by Pulsed Laser Deposition Coupled with Substrate Irradiation, *Journal of Applied Physics* **88**, p. 4175 (2000).

[7] Yang C., Lee S., Lin T., Chen S., Electrical and Optical Properties of Indium Tin Oxide Films Prepared on Plastic Substrates by Radio Frequency Magnetron Sputtering, *Thin Solid Films,* **516**, p. 1984 (2008).

[8] Sato Y., Taketomo M., Ito N., Miyamura A., Shigesato Y., Comparative Study on Early Stages of Film Growth for Transparent Conductive Oxide Films Deposited by dc Magnetron Sputtering, *Thin Solid Films*, **516**, p. 4598 (2008).

[9] Fallah H.R., Ghasemi M., Hassanzadeh A., Steki H., The Effect of Annealing on Structural, Electrical and Optical Properties of Nanostructured ITO Films Prepared by e-beam Evaporation, *Materials Research Bulletin*, **42**, p. 487 (2007).

[10] Viespe C., Nicolae I., Sima C., Grigoriu C., Medianu R., ITO Thin Films Deposited by Advanced Pulsed Laser Deposition, *Thin Solid Films,* **515**, p. 8771 (2007).

[11] Rozati S.M., Ganj T., Transparent Conductive Sn-Doped Indium Oxide Thin Films Deposited by Spray Pyrolysis Technique, *Renewable Energy*, **29**, p. 1671 (2004).

[12] Klingshirn C., The Luminescence of ZnO under High One - and Two-Quantum Excitation, *Phys. Status Solidi B*, **71**, p. 547 (1975).

[13] Kassis A., Saad M., Fill Factor Losses in ZnO/CdS/$CuGaSe_2$ Single-Crystal Solar Cells, *Sol. Energy Mater. Sol. Cells*, **80**, p. 491 (2003).

[14] Ozgur U., Ya I., Alivov C., Liu A., Teke M.A., Reshchikov S., Dogan V., Avrutin S.J., Cho H., A Comprehensive Review of ZnO Materials and Devices, *J. Appl. Phys.*, **98**, 041301-103 (2005).

[15] Hong R., Shao J., He H., Fan Z., Enhancement of Near-Band-Edge Photoluminescence of ZnO Thin Films in Sandwich Configuration at Room Temperature, *J. Appl. Phys.*, **99**, 093520-093523 (2006).

[16] Herrero J., Guillen C., Improved ITO Thin Films for Photovoltaic Applications With a Thin ZnO Layer by Sputtering, *Thin Solid Films,* **451–452**, p. 630 (2004).

[17] Manavizadeh N., Khodayari A., Asl-Soleimani E., Bagherzadeh S., Maleki M., Structural Properties of Post Annealed ITO Thin Films at Different Tempratures, *Iran. J. Chem. Chem. Eng.*, **28**(2), p. 57 (2009).

[18] Guillén C., Herrero J., Polycrystalline Growth and Recrystallization Processes in Sputtered ITO Thin Films, *Thin Solid Films*, **510**, p. 260 (2006).

[19] Herrero J., Guillén C., Transparent Films on Polymers for Photovoltaic Applications, *Vacuum,* **67**, 611 (2002).

[20] Meng L.-J., Crossan E., Voronov A., Placido F., Indium-Tin-Oxide Thin Film Prepared by Microwave-Enhanced d.c. Reactive Magnetron Sputtering for Telecommunication Wavelengths, *Thin Solid Films*, **422**, p. 80 (2002).

[21] Gao M., Shi H.-G., Substrate Dependence of Properties of Sputtered ITO Films, *Chin. Phys. Lett.*, **22(5)**, p. 1228 (2005).