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Effect of Annealing on Electrical Properties of Indium Tin Oxide (ITO) Thin Films

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Abstract: The RF-sputtering technique was employed to prepare thin films of Indium Tin Oxide (In_2O_3+SnO_2 or ITO) on glass substrates. Five slides of ITO films were annealed at different temperatures ranging from 100 to 400 °C for a constant time of 15 minutes. The ITO thin films were observed to possess resistivities in the range 5×10^{-4} - $11.5\times10^{-4}\Omega$-cm at different annealing temperatures. The increase in resistivity due to heat treatment was associated with filling up of oxygen vacancies and decrease in resistivity was attributed to rearrangement and removal of defects as well as improvement in the crystallinity. ITO thin films were of comparable quality to those deposited elsewhere for use as window layers in solar cells.

Key Words: Electrical Resistivity, Annealing, Thin Films, Sheet Resistance, Activation Energy, ITO

Introduction

Numerous studies have been carried out over many years to prepare indium oxide (In_2O_3 or IO) and indium tin oxide (In_2O_3 + SnO_2 or ITO) films for the application of their transparent-conductive nature (Feng *et al.*, 1979, Fan, and Bachner, 1975 and Green *et al.*, 1976). Many studies have reported the properties of those films prepared by reactive evaporation (Mizuhashi, 1980, Amanullah *et al.*, 1995), magnetron sputtering (Morgan, *et al.*, 1998; VanDer Meerakker *et al.*, 1993 and Zahirul Alam *et al.*, 1996), chemical vapour deposition (Turner *et al.*, 1981, Srinivasa Murty, 1982), spray pyrolysis (Manifacier, 1982, Kostlin *et.al*, 1975 and Keshmiri *et al.*, 1995), sol-gel dip-coating (Nishio *et al.*, 1996) and pulsed laser deposition (Adurodija *et al.*, 2000). The ITO thin films have found extensive applications in optoelectronics devices and window coatings for many years (Hamberg and Granqvist, 1996). Other applications such as: gas sensor, transparent heating element (on the glass windshield of cars, planes and ships), anti-electrostatic coating, microwave shield coating and surface layer on temperature control coatings on orbiting satellites (Chopra *et al.*, 1983, Dawar and Joshi, 1984, Lampert, 1987) are also of much interest. The attractiveness of ITO is related to its low resistivity (~10^{-4} Ω-cm), high optical transmittance to visible light and high infrared reflectance it displays. However, the attainment of these properties is strongly dependent on the growth conditions such as oxygen pressure and substrate temperature (T_s) (Song *et al.*, 1998; Vink *et al.*, 1995 and Yi *et al.*, 1995). The former determines the oxidation state, while the later controls the activation of cation (Sn) in the film during deposition. The need to develop technologies that can meet low T_s growth of ITO films is on the rise. This is due to the innovative optoelectronic application including liquid crystal displays, which now use heat sensitive substrates such as polymers. Such technologies are expected to meet the low T_s need, while retaining the high electro-optical qualities of the films. Efforts to produce high quality film at low T_s using sputtering and electron beam evaporation have often resulted in amorphous films with poor electrical properties (Shigesato *et al.*, 1992; Oyama *et al.*, 1992; Terzini *et al.*, 1999 and Song *et.al*, 1999). It is well known that high quality ITO films are easily obtained at high T_s (>300 °C) using most of the deposition techniques available (Tahar *et al.*, 1998). Among the techniques available for ITO thin film production, sputtering is the most widely investigated and large-scale deposition setups are also available (Morgan *et al.*, 1998; VanDer Meerakker *et al.*, 1993; Zahirul Alam *et al.*, 1996 and Takaki *et al.*, 1988). In the present study, we have investigated the effect of heat treatment on the electrical properties of ITO thin films prepared by RF-sputtering and deposited on glass substrates.

Experimental Techniques: Indium Tin Oxide (ITO) thin films were deposited by RF-sputtering on cleaned Corning glass substrates at University of Northumberia, UK. Deposition technique has been described elsewhere (Tariq Bhatti, 1992). Five slides of ITO films were annealed at different temperatures ranging from 100-400°C for a constant time of 15min. The electrical resistivity of these samples was then measured by well-known four-point probe technique (Rana *et al.*, 1999). The contact resistance was determined by two-probe method using transmission line model (TLM) (Reeves and Harrison, 1982). For this purpose two springy gold electrodes (diameter 1.5mm) were used. The ITO/Au contacts were made tight to ensure good Ohmic behavior. Temperature dependent resistivity measurements were made by increasing the temperature at a rate of ~ 5K/min at the Department of Physics/Materials Science, Bahauddin Zakariya University, Multan, Pakistan.

Results and Discussion

The electrical transport properties of thin films are strongly dependent on their structure (grain size and shape, structural defects as well as characteristics of the contact between them) and purity (nature and concentration of impurities, absorbed and adsorbed gases etc.). Heat treatment of thin films can modify these structural characteristics and hence the electrical conductivity of such films may change too. Therefore the study of the heat treatment effects on electrical resistivity can provide information on the processes taking place.

Annealing Effect

Sheet Resistance and Contact Resistivity: Plot of Sheet resistance R_s of ITO thin films at ambient temperature (20°C) and as a function of annealing temperature T_A is shqwn Fig. 1

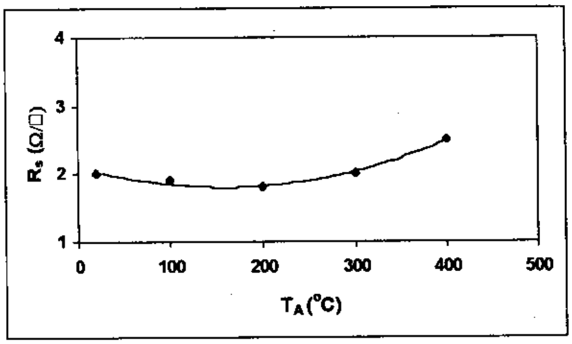

Fig. 1: Plot Of Sheet Resistance "R_s" Vs Annealing Temperature "T_A" for ITO Thin Films.

It is clear that R_S shows only slight variations up to annealing temperature 300 °C and then a rapid rise in R_S is observed. Present results are inconsistent with those of Hai Ning Cui and Shi-Quan Xi. The increase in ITO sheet resistance is attributed to a decrease in current carrier density by filling up a oxygen vacancies due to air annealing (Guillen *et al.*, 1997).

According to TLM, total resistance "R_T" of the film between two electrodes having distance "l" is the sum of contact resistance and sheet resistance as given by

$R_T = 2\,\rho_c + R_s\,l\,/\,w$

Where ρ_c is the contact resistivity and w is the electrode width. Contact resistivity can be determined by a plot of R_T Vs l. Such plots for ambient ITO slide and ITO films annealed at 100-400 °C are shown in Fig. 2.

The values of ρ_c obtained from the intercepts of this graph on the R_T axis (i.e at l = 0) are plotted as a function of annealing temperature in Fig. 3.

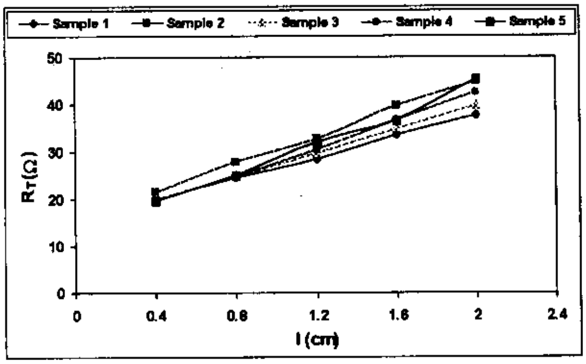

Fig. 2: Plot Of Displacement "L" Vs Total Resistance "R_T" for Sample 1 (Ambient Slide), 2, 3, 4, 5 Annealed in Air at Temperatures 100, 200, 300 and 400 °C Respectively.

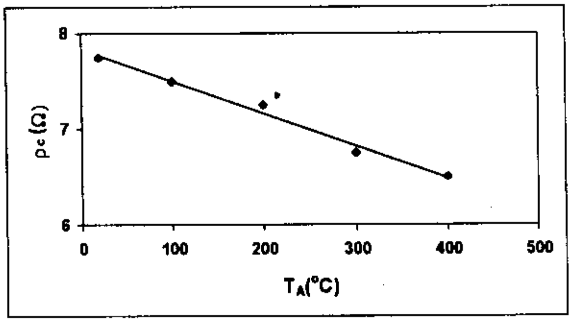

Fig. 3: Plot of Contact Resistivity "ρc" Vs Annealing Temperature "T_A" for ITO Thin Films

This Fig. depicts a decrease in the contact resistivity with rising temperature. This decrease can be associated with the improvement in the grain structure of the film just under the contact and its vicinity (Girtan *et al.*, 2000). The lowest value of specific contact resistance observed in this investigation is ~ 0.144 Ω-cm^2.

Electrical Resistivity: The variation of resistivity for ITO coated glass slide as a function of annealing temperature is drawn in Fig. 4. The minimum value of resistivity (5.4×10^{-4} Ω-cm) is observed for ambient slide and is comparable with already quoted value of 5×10^{-4} Ω-cm (Sze, 1981). The resistivity shows a rise for annealing at 100 °C up to 11.5×10^{-4} Ω-cm and above this temperature it decreases progressively.

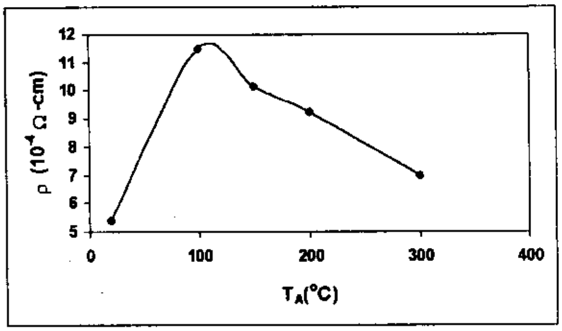

Fig. 4: Plot Of Electrical Resistivity Vs Annealing Temperature For ITO Thin Films

Electrical resistivity of ITO is found to depend on Sn concentration as well as oxygen content. Low resistivity ITO films can be achieved by increasing SnO_2 concentration up to 12mol% and/or by increasing the oxygen vacancies (Nishio *et al.*, 1996, Winchkler, 1992). Therefore rise in resitivity (Fig. 4) on annealing at 100 °C may be due to decresing current carriers by filling up of oxygen vancancies (Guillen *et al.*, 1997). Whereas the fall of resistivity (Fig. 4) may be associated with the rearrangement and removal of point defect clusters and recombination centers, which lead to an increase in carrier density (Girtan *et al.*, 2000).

Temperature Dependence: Electrical resistivity of ITO thin films (ambient slide) as a function of temperature is presented in Fig. 5.

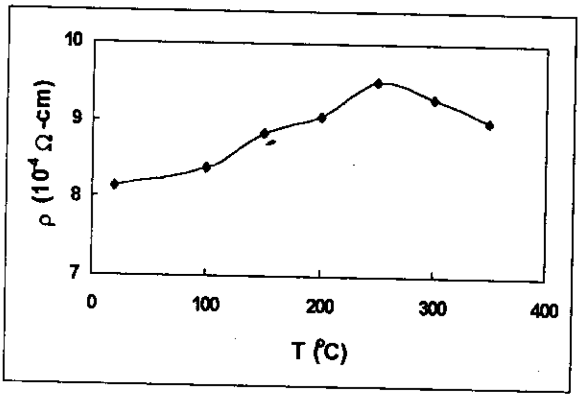

Fig. 5: Plot of Electrical resistivity Vs temperature for ITO thin film (ambient slide).

The resistivity is found to increase with temperature up to 250 °C. After attaining a maximum it starts decreasing for further increase in temperature. This type of behavior is normally observed for disordered materials. Moreover the incorporation of oxygen atoms (due to heating in air) can cause a decrease in current carriers and hence a increase in resistivity. The fall in resistivity can be explained by the improvement in the crystallinity of ITO films with raising temperature. Nishio *et al.* (1996) observed through x-ray diffraction measurements that ITO begins to crystallize close to 400 °C and is fully crystallize at 600 °C.

Considering the well known dependence of electrical resistivity on temperature: $\Delta\rho = A \exp(E / 2 k_B T)$, where E is the thermal activation energy for electrical conduction, A is a constant that depends on the nature of the film and k_B is the Boltzmann constant, $\Delta\rho$ is the difference between resistivities at temperature T and room temperature. The $\ln \Delta\rho = f(1000/T)$ curve for ITO film (ambient slide) is illustrated in Fig. 6.

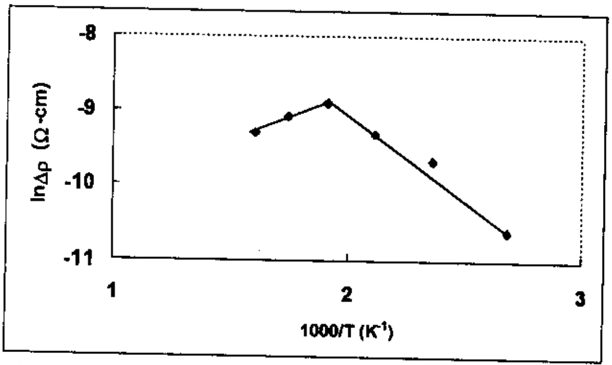

Fig. 6: Arrhenius plot of relative electrical resistivity "lnΔρ" Vs reciprocal of temperature.

The activation energy of 0.42 eV is found for the region where resistivity rises. This value is consistent with that reported by Richard Wing (1992).

The nature and type of the film was determined through thermoelectric measurements by hot probe method. It was concluded that ITO film is n-type and it agrees with the work of (Winchkler, 1992, Fahrenbruch and Richard Bube, 1983).

Conclusion

It was concluded from the present work that:

- Below 400 °C annealing causes no change in sheet resistance but at/above this temperature sheet resistance increases rapidly.
- Contact resistivity shows a decrease with rising annealing temperature.
- Electrical resistivity increases by annealing up to 100 °C but decreases above this temperature. The increase in resistivity is attributed to decrease in carrier density by filling up oxygen vacancies and decrease in resistivity may be associated with the improvement in the grain structure.
- Temperature dependent resistivity shows the behavior similar to that of disorder material and decrease in resistivity is associated with the improved crystallinity of the films.

References

A. H. M. Zahirul Alam, Y. Takashima, K. Sasaki, T. Hata, 1996. Thin Solid Films, 279, 131.

A. L. Dawar and J. C. Joshi, 1984. J. Mat. Sci., 19, 1-23.

A. M. Rana, A. Qadeer and T. Abbas, 1999. Proc. 6th Int. Symp. Adv. Mat., 151.

Alan L. Fahrenbruch, Richard H. Bube, 1983. "Fundamental of Solar Cells", Academic Press.

C. Guillen, M. A. Martinez, M. T. Gutierrez and J. Herrero, 1997. 14th Euro. Photovol. Solar Energy Conf. Barcelon Spain, 1212.

C. H. Yi, Y. Shigesato, I. Yasui, and S. Takaki, 1995. Jpn. J. Appl. Phys., Part 2 34, L244

C. L. Lampert, 1987. Proc. Int. Center for Theo. Phys.

D. V. Morgan, Z. H. Aliyu, R. W. Bunce, A. Salehi, 1998, Thin Solid Films, 312, 268.

E. Terzini, G. Nobile, S. Loreti, C. Minarini, T. Ploichetti, and P. Thilakan, 1999. Jpn. J. Appl. Phys., Part 1 38, 3448.

F. M. Amanullah, K. J. Pratap, V. H. Babu, 1995. Thin Solid Films, 254, 28.

F. O. Adurodija, H. Izumi, T. Ishihara, H. Yoshioka, M. Motoyama and K. Murai, 2000. J. Vac. Sci.Technol., A 18: 814.

G. K. Reeves and H. B. Harrison, 1982. IEEE Conf., USA.

H. Kostlin, R. Jost, W. Lems, 1975. Phys. Stat. Sol., (a) 29, 87.

Hai-Ning Cui and Shi-Quan Xi, 1996. Thin Solid Films, 288, 325.

I. Hamberg and C. G. Granqvist, 1996. J. Appl. Phys., 60, 123.

J. C. C. Fan, F. Y. Bachner, 1975. J. Electrochem. Soc., 122, 1719.

J. C. Manifacier, 1982. Thin Solid Films, 90, 297.

J. E. A. M. Van Der Meerakker, E. A. Meulenkamp, M. Scholten, 1993. J. Appl. Phys., 74: 3282.

Jane Mc Queen Winchkler, 1992. Ph.D. Thesis, Faculty of Engn. Sci. and Tech., New Castle Upon Tyne Polytechnic.

K. L. Chopra, S. Major and D. K. Pandya, 1983. Thin Solid Films, 102, 1-46.

K. Nishio, T. Sei and T. Tsuchiya. 1996, J. Mat. Sci., 31, 1761.

M. Green, W. C. Smith, J. A. Weiner, 1976. Thin Solid Films, 38, 89.

M. Mizuhashi, 1980. Thin Solid Films, 70, 91.

M. Tariq Bhatti, 1992. PhD Thesis, Uni. of Northumberia, UK.

Mihaela Girtan, G. I. Rusu, G. G. Rusu, 2000, Mat. Sci. Engn., B 76, 156.

P. K. Song, Y. Shigesato, M. Kamei, and I. Yasui, 1999. Jpn. J. Appl. Phys., Part 1 38, 2921.

P. K. Song, Y. Shigesato, I. Yasui, C. W. Ow-Yang, and D. C. Paine, 1998, Jpn. J. Appl. Phys., Part 1 37, 1870.

P. Turner, R. P. Howson, C. A. Bishop, 1981. Thin Solid Films, 83, 253.

R. B. H. Tahar, T. Ban, Y. Ohya, and Y. Takahashi, 1998. J. Appl. Phys., 83, 2631.

Richard Wing, 1992. PhD Thesis, Faculty of Engn. Sci. and Tech., New Castle Upon Tyne Polytechnic.

S. H. Keshmiri, M. M. Bagheri-Mohagheghi and S. M. Baizaee, 1995, Proc. 4th Int. Symp. Adv. Mat., 492.

S. M. Sze, 1981, "Physics of Semiconductor devices", 2nd Edn. A Willey-Intersci. Pub.

S. Takaki, K. Matsumoto, and K. Suzuki, 1998. Appl. Surf. Sci., 33/34, 919.

T. Feng, A. K. Gosh, C. Fishmann, 1979, J. Appl. Phys., 50, 4972.

T. J. Vink, W. Walrave, J. L. C. Daams, P. C. Baarslag, and J. E. A. M. Van der Meerakker, 1995. Thin Solid Films, 266, 145.

T. Oyama, N. Hashimoto, J. Shimizu, Y. Akao, H. Kojima, K. Aikawa, and K. Suzuki, 1992. J. Vac. Sci. Tech., A 10, 1682.

Y. Shigesato, S. Takaki and T. Haranoh, 1992, J. Appl. Phys., 71, 3356.