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Compositional and Surface Morphological Analysis on Indium Tin Oxide Thin Films Prepared by Radio Frequency Sputtering†

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In the present work, we report the results of compositional and surface morphological analysis on indium tin oxide thin films prepared by RF magnetron sputtering of a ceramic oxide target with quartz substrate under Ar gas atmosphere. Radio frequency power and substrate temperature were held at 250 W and 150 ºC respectively. Indium tin oxide films were characterized by EDX, XPS and TEM analysis. TEM images evidence the formation of crystalline indium tin oxide films with nano grained structure. XPS study shows the substitution of In^{3+} sites with Sn^{4+} and EDX result reveals the uniform distribution of In and Sn on the surface supported by the smoother surface with nano grains. These results reveal that a combination of high RF power (250 W) and moderate substrate temperature (150 ºC) is capable of producing thermally stable and device quality indium tin oxide films.

Key Words: Radio frequency sputtering, Indium tin oxide, TEM, EDX, XPS.

INTRODUCTION

Despite long and extensive research effort the interest in transparent and conducting oxide (TCO) layers has not ceased. The reason is the ever increasing economic interest in these materials as many optoelectronic devices rely on high quality TCO layers[1]. Indium tin oxide (ITO) is an important transparent conducting material and finds application in many fields due to its excellent properties[1-3]. The attractiveness of indium tin oxide is related to the low sheet resistance (R_s) and high optical transmittance from visible to near infrared (NIR) region[4,5]. However, the attachements of these properties are strongly dependent on the growth conditions such as oxygen partial pressure, bias voltage and substrate temperature. Indium tin oxide is a highly degenerate *n* type semiconductor with a wide band gap (3.5-4.3 eV), having low enough electrical resistivity of about 10^{-4} Ω cm making it easy to be interfaced with electronic circuits and simultaneously shows high transmission in the visible and near infrared (NIR) regions of the electromagnetic spectrum[6]. Its low electrical resistivity results from either the non stoichiometry produced by oxygen deficiency or by the incorporation of tin as tetravalent dopant or from both[7]. The higher carrier concentration results in widening the band gap due to the Burstin-Moss shift[8] and increase of the free-carrier absorption in the visible and near-infrared regions. Lower resistivity can be obtained by higher carrier concentration or mobility, while the carrier concentration is dominated by the number of oxygen vacancies and substitutional tin[1].

It is well known that high quality indium tin oxide films are easily obtained at high T_s (> 300 ºC) using most of the deposition techniques available[9-11]. Among the technologies available for indium tin oxide thin film production[12,13], sputtering is the most widely investigated and large-scale deposition technique[14]. In previous study[15], role of different substrate temperatures on the structural, optoelectronic and morpholo-gical properties of RF sputtered indium tin oxide thin films during deposition with RF power at 250 W have been extensively studied and reported. XRD results confirm cubic structure with (400) preferential orientation for the indium tin oxide films deposited with substrate at 150 ºC. The lowest resistivity was 2.2×10^{-3} Ω cm with a transmi-ttance of about 85 % in the visible region. The optical and electrical studies confirm the formation of highly crystalline, void free and compact indium tin oxide films at 150 ºC. This is supported by the very low roughness values associated with the

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film surfaces as observed from the atomic force microscope images.

In this manuscript, we present the results of compositional analysis using EDX and XPS studies and the surface morphological analysis using TEM image and SAED pattern on radio frequency sputtered indium tin oxide thin films deposited with radio frequency power at 250 W and substrate at 150 ºC.

EXPERIMENTAL

Indium tin oxide films were deposited on quartz substrates at 250 W using 13.56 MHz radio frequency magnetron sputtering system with 99.99 % pure tin doped indium oxide (indium 90: tin 10 at %) ceramic target. The base pressure of the deposition chamber was maintained at 10^{-6} torr and the working pressure was kept at 5×10^{-3} torr under pure argon ambience. Sputtering was carried out by keeping the target to substrate distance constant at about 8 cm through out the experiment. The substrate temperature was increased from 50 to 250 ºC in steps of 50 ºC and the deposition was carried out for different durations from 5 to 30 min so as to maintain the thickness of the films in the range 400-450 nm. The quartz substrates were first cleaned by a detergent, washed with distilled water, kept in freshly prepared hot chromic acid for 1 h, again thoroughly cleaned with distilled water and finally subjected to ultrasonic cleaning for 1 h.

Film thickness was measured by the Stylus Profilometer (Mitutoyo). The optical transmittance measurements were made in the wavelength range 300-2400 nm using a Hitatchi-330 UV-visible-near infrared spectrophotometer. X-ray diffraction measurements were carried out with X'pert Pro PANalytical-3040 using CuK$_\alpha$ radiation (λ = 1.5406 Å) to study the structural properties of the films. Electrical properties were measured by the four probe method with a Four probe set up model DEP-02 (Scientific Equipment) DC power supply. Hall mobility and carrier concentration were calculated from the hall votage measured by Vander Pauw method with a Ecopia HMS 3000 Hall constant measurement system. The surface morphology was anlayzed using a Nanoscope E-3138j AFM/STM atomic force microscope (AFM). In the present study, X-ray spectrometer attached to the SEM instrument (JSM 35CF JEOL) was used to perform elemental analysis of all elements. Analysis of chemical state of elements was achieved using Multilab 2000 X-ray photoelectron spectroscope (XPS) using MgK$_\alpha$ (BE = 1253.6 eV). TEM image and selected area electron diffraction (SAED) pattern were recorded using a JEOL 2010 TEM Instrument.

RESULTS AND DISCUSSION

The presence of indium, tin and oxygen on radio frequency sputtered indium tin oxide thin films deposited with RF power at 250 W and substrate at 150 ºC is found out using EDX and XPS analysis. Surface morphological analysis is performed by using TEM analysis and the results are reported.

Compositional analysis of indium tin oxide films:

EDX analysis: Compositional analysis of the 10 % Sn doped In_2O_3 films using EDX analysis was carried out for the indium tin oxide film deposited at a temperature of 150 ºC on quartz substrates keeping the radio frequency power constant at 250 W and is shown in Fig. 1. Since uniform distribution of dopants is very essential in nanocrystalline films, the dopants should be exactly incorporated into the matrix to the maximum extent possible. If this is not achieved, segregated doping occurs leading to the presence of separated In_2O_3 and SnO_2 particles which will degrade the optical and electrical properties of indium tin oxide films rendering them not useful in opto-electronic devices[16].

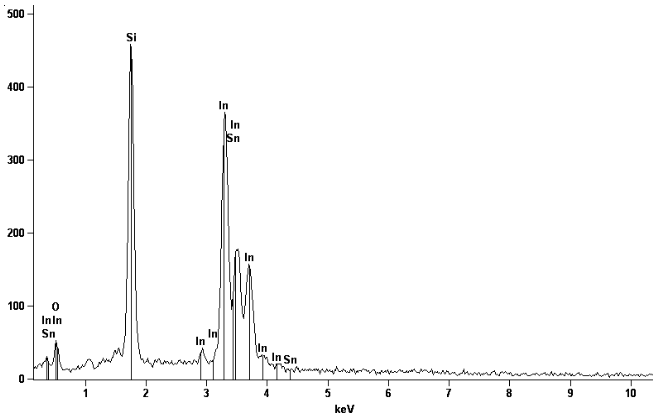

Fig. 1. EDX spectrum of indium tin oxide thin films deposited at 150 ºC and 250 W

The EDX spectrum shows the peaks corresponding to the presence of indium and oxygen elements. The % of tin observed from this analysis is about 9.2 %. Large number of peaks with highest intensity is pertained to indium which confirms its major content in the films. The observed % of tin content reveals that most of the tin content in the sputter target is incorporated into the indium tin oxide film. Indium tin oxide film deposited with 10 % Sn doping concentration at a substrate temperature of 150 ºC with lowest resistivity confirm the usefulness of RF sputtering technique in depositing nearly stoichiometric semi conducting oxide films.

Elemental analysis by XPS: To analyse the chemical states of elements present in the indium tin oxide films deposited by keeping RF power at 250 W and substrate temperature at 150 ºC, the XPS wide scan and narrow scan spectra of In $3d_{5/2}$, Sn $3d_{5/2}$, O 1s and C 1s were recorded in the binding energy range from 0 to 1100 eV. Fig. 2(a) shows the wide scan XPS spectrum of indium tin oxide film deposited at a temperature 150 ºC. Fig. 2 (b,c,d and e) show the narrow scan of XPS spectra of In, Sn, O and C elements. The binding energy of O 1s peak is at about 529.28 eV which can be assigned to the lattice oxygen in In_2O_3. The In $3d_{5/2}$ peak at 444.07 eV expresses the In^{3+} bonding state from In_2O_3. The peak at 486.37 eV is assigned to the binding energy of Sn $3d_{5/2}$ that corresponds to the Sn^{4+} bonding state in the indium tin oxide lattice. The XPS peaks are sharp without peak splitting thus confirming the absence of SnO phase with lower valence Sn^{2+} bonding state. The C 1s peak at 284.98 eV is related to the surface pollution from the adsorbed carbon atoms from the chamber. These observations show the formation of highly conducting indium tin oxide film with oxygen bonded to indium and further the presence of Indium and tin in the In^{3+} and Sn^{4+} bonding states.

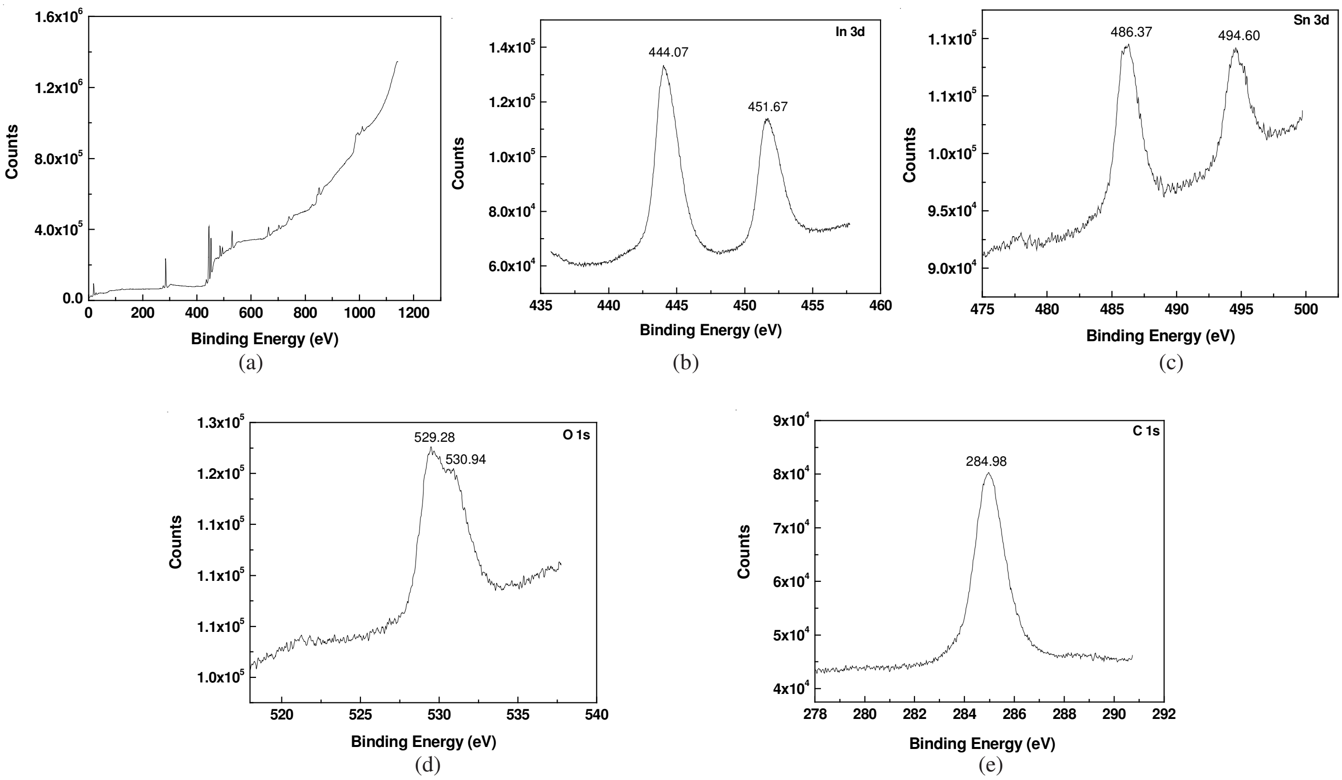

Fig. 2. Wide scan (a) and Narrow scan (b) In $3d_{5/2}$, (c) Sn $3d_{5/2}$, (d) O 1s and (e) C 1s of XPS spectra for the indium tin oxide films deposited at 150 ºC and 250 W

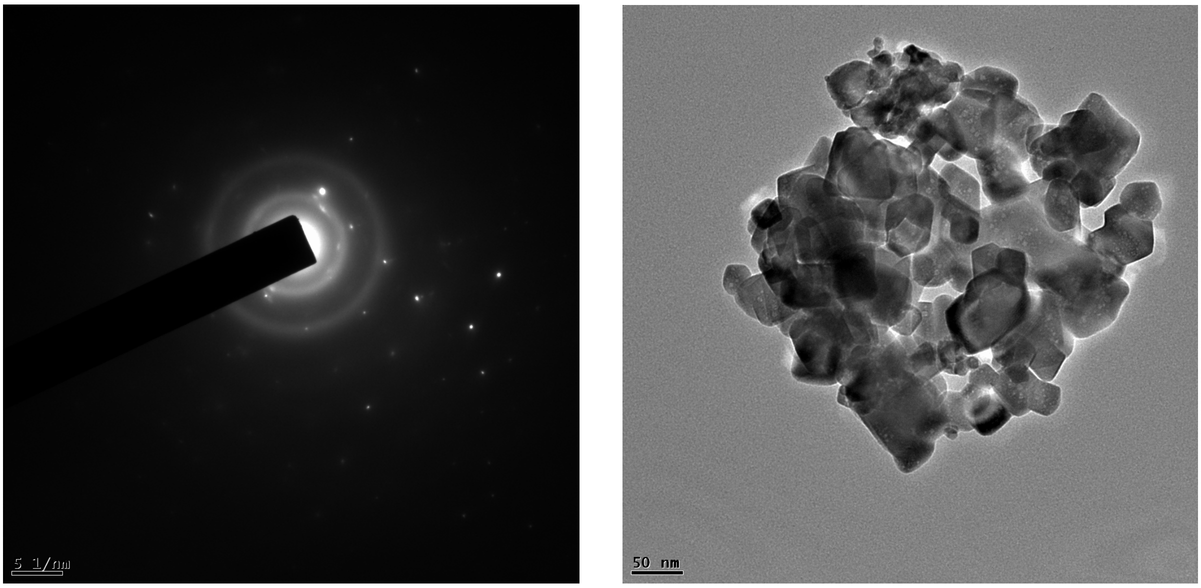

Fig. 3 (a) SAED pattern and (b) TEM image of indium tin oxide films deposited at 150 ºC and 250 W

Surface morphological analysis of indium tin oxide thin films

TEM studies: Surface morphological and the crystallographic informations were obtained using TEM studies. The size, shape and arrangement of the particles and their degree of order, detection of atomic-scale defects in areas of a few nanometers in diameter can be obtained by analysing the images. The diffraction rings seen in SAED pattern of Fig. 3(a) confirm the formation of crystalline indium tin oxide films at 150 ºC with nano grained structure. Fig. 3(b) shows the TEM picture of the particles present in the indium tin oxide films deposited at 150 ºC. The size of the particles vary from about 6 to 83 nm as can be measured using the graduation given in the picture itself. Some grains are observed to be big due to overlapping of the particles.

Conclusion

The RF magnetron sputtering technique has been used to deposit indium tin oxide thin films on quartz substrate at 250 W with different substrate temperatures in argon ambient without oxygen. TEM images at 150 ºC and 250 W evidence the formation of poly crystalline indium tin oxide films in the present study with nano grained structure. XPS study shows the substitution of In^{3+} sites with Sn^{4+} and EDX result reveals the uniform distribution of In and Sn on the film surface. These results reveal that a combination of high RF power (250 W) and moderate substrate temperature (150 ºC) is capable of producing thermally stable and device quality indium tin oxide films with preferential orientation, lower resistivity and high transmittance.

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