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COMPARISION OF THERMAL EVAPORATION AND PLASMA ASSISTED THERMAL EVAPORATION PROCESSES FOR DEPOSITION OF TIN OXIDE THIN FILMS

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Tin oxide (SnO_2) thin films are of great interest in optoelectronics industries due to their promising properties such as conductivity and optical transparency in visible-infrared (VIS-IR) region. Improvement in these two key properties of SnO_2 is of technological importance. In order to find ways for these improvements in the present study, SnO_2 thin films have been prepared by Thermal Evaporation (TE) in oxygen (O_2) partial pressure and Plasma Assisted Thermal Evaporation (PATE) using RF (13.56 MHz) O_2 plasma. Optical, structural, compositional and electrical properties of the deposited films have been investigated by varying substrate temperature in range of 250-350 °C keeping other process parameters constant. The optical transmission spectra measured in VIS-IR region of films deposited by PATE have higher transparency (~80-90 %) in comparison to the films grown by TE (~60-70 %). X-ray Diffraction (XRD) study reveal SnO & SnO_2 phases present in the film. Also X-ray Photoelectron Spectrosocpy (XPS) analysis showed SnO_{2-x} as the only content, which is in agreement to XRD results. Surface morphology study by Scanning Electron Microscopy (SEM) shows more needle shape grains in case of films deposited by TE as compared to PATE grown films. Both types of the films were subjected to Four-probe method for the measurement of resistivity, which is in the order of 10^{-4} Ω-cm and 10^{-3} Ω-cm for PATE and TE grown respectively.

Keywords: *TRANSPARENT CONDUCTING OXIDE, TIN OXIDE THIN FILMS, PLASMA ASSISTED THERMAL EVAPORATION, OPTICAL PROPERTIES, X-RAY DIFFRACTION, X-RAY PHOTOELECTRON SPECTROSCOPY, SCANNING ELECTRON MICROSCOPY.*

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1. INTRODUCTION

Tin oxide (SnO_2) thin films are n-type semiconductor with a rutile tetragonal structure and has wide band gap of 3.6 eV. SnO_2 is the first transparent conductor to receive significant commercialization due to its high transparency and very good electrical conductivity. Owing to its low resistivity and high transmittance properties, SnO_2 is the most attractive and preferred Transparent Conducting Oxide (TCO) for the application of window layer in

solar cells, heat reflectors, liquid crystal displays, various gas sensors, photo-detectors, and protective coatings [1-5]. Recently, various nano-structured metal oxides as anode material for Li-ion batteries have been extensively studied due to their excellent electrochemical properties and high recycling rates. Among them, tin oxides such as SnO, SnO_x ($1 < x < 2$) and SnO_2 have been identified as most promising anode material due to much higher reversible charging capacities than graphite and have better stability [6]. SnO_2 films have been fabricated on several different substrates by numerous techniques such as Physical Vapour Deposition (PVD) including thermal evaporation [7], DC and RF magnetron sputtering [8,9], Chemical Vapor Deposition (CVD) [10], sol-gel dip coating [11], spray pyrolysis [12] and plasma based evaporations [13].

In the present work, we aim a detailed comparative study of SnO_2 thin films grown by two techniques such as TE in O_2 partial pressure and PATE using RF (13.56 MHz) O_2 plasma. The detail optical, structural, compositional and electrical analysis of the deposited films have been performed using optical transmission spectroscopy, XRD, XPS, SEM and Four-probe setup respectively.

2. EXPERIMENTAL

SnO_2 films are deposited by evaporating the metallic tin (99.99%) on glass, polished SS samples and silicon wafers substrates at 250 & 350 °C substrate temperatures using TE and PATE (fig. 1) in the presence of O_2 partial pressure and O_2 plasma using RF source respectively. The vacuum chamber is evacuated to base pressure of 2×10^{-6} mbar prior to each depositions. In order to enhance the reaction of evaporated Sn atoms and O_2, the O_2 plasma is generated between the resistively-heated Molybdenum boat and substrate holder, kept 10 cm away for PATE process. A triode based RF power source developed in house is used and RF power was coupled to the plasma through impedance matching network. Following are the process parameters: O_2 partial pressure = 4-4.5 $\times 10^{-4}$ mbar, deposition rate = 2 to 3 nm/sec for TE and 1 to 1.5 nm/sec with RF-power = 25 W for PATE. The transmission of

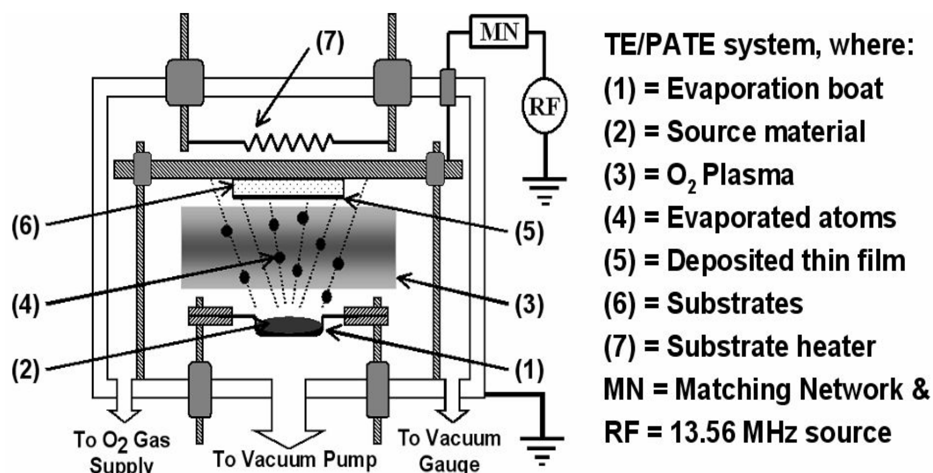

***Fig. 1** – A schematic diagram of Thermal Evaporation/Plasma Assisted Thermal Evaporation for Tin Oxide thin film depositions*

the deposited films in the VIS-IR region is measured using the spectrometer consisting of a 1/8m monochromator, a silicon-photo detector and a dual phase lock-in amplifier. The crystallinity of the film is investigated by XRD using CuK_α radiation (Rich Seifert & Co., Germany), whereas XPS measurement are carried out on film deposited on SS samples in a Multitechnique Surface Analytical System (5702) supplied by Physical Electronics USA. The measurements are performed using monochromatic AlK_α source with resolution of 0.5 eV FWHM of the Ag $3d_{5/2}$ peak, which is also used to calibrate the binding energy scale. SEM (LEO, UK) used to study surface morphology and thickness of films by cross-sectional measurement. The resistivity of the films is obtained at room temperature by the Four-probe method using a Keithley source meter (2400-C).

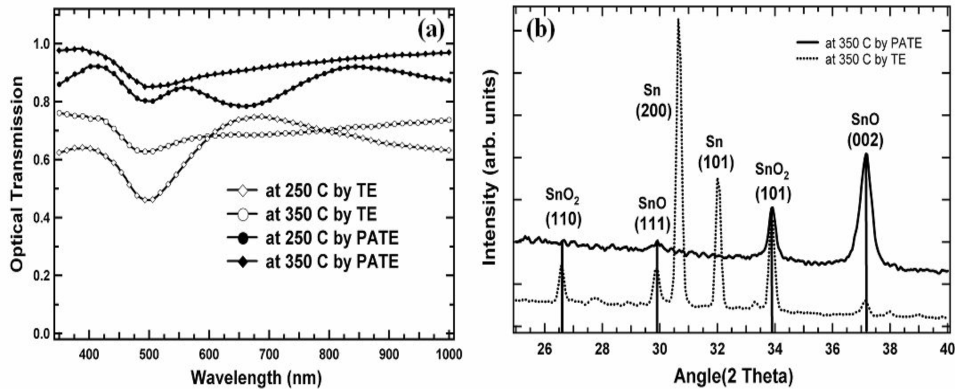

***Fig. 2** – Optical transmission spectra of SnO_2 films deposited on glass substrates by TE and PATE at temperature 250 °C and 350 °C (a). XRD patterns of SnO_2 films deposited on glass substrates by TE and PATE at temperature 350 °C (b)*

3. RESULTS AND DISCUSSION

Figure 2a shows the optical transmission spectra in the range of 350 to 1000 nm of SnO_2 thin film deposited by both techniques. It is observed that the optical transmission of SnO_2 films deposited by PATE having an average transmittance (~ 80-90 %) is higher than TE deposited films (~ 60-70 %). Further, films grown by both methods at substrate temperature 350 °C have higher transmission than the films deposited at 250 °C identified the role of substrate heating during deposition. XRD patterns of SnO_2 thin films deposited at 350 °C are shown in Figure 2 b. Films deposited at 250 °C are nearly amorphous for both deposition techniques whereas the increase of substrate temperature to 350 °C caused the crystallization of the films as it is noticed by other researchers also [14]. The films deposited by PATE at 350 °C show only three peaks namely SnO (002), SnO_2 (101) and SnO (111) whereas the films deposited by TE show as many as six peaks corresponding to Sn (200), Sn (101), SnO (111), SnO (002), SnO_2 (101) and SnO_2 (110). Hence, it is evident from XRD that the films grown by TE contains SnO, SnO_2 and also un-reacted Sn phase which may be causing the reduction in transmittance, as reflected in transmission spectra for TE films. Whereas

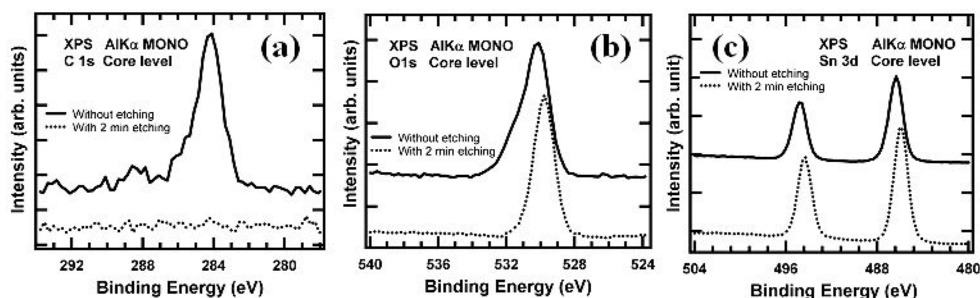

Fig. 3 *– XPS analysis for SnO_2 thin film deposited by PATE process on SS sample at 350 °C without and with 2 min etching for C 1s (a) O 1s (b) Sn 3d (c) core levels*

the films prepared by PATE have only SnO and SnO_2 phases, confirming the enhancement of reactions for Sn-evaporated atoms with ionized O_2.

Fig. 3a-c shows XPS spectra of C 1s, O 1s and Sn 3d core levels of the deposited films obtained without and with surface cleaning. While a small amount of adsorbed carbon (BE = 284 eV) is presented on the as-obtained thin film surface, which is absent in the bulk of the deposited films as seen after 2 min surface etching (Fig. 3a). Similarly the oxygen is presented on the surface as a SnO_2 with BE = 530.1 eV, while in the bulk of the films SnO_{2-x} present with BE = 529.7 eV (Fig. 3b). The clean Sn 3d peaks are obtained for without and with surface cleaning of films (Fig. 3c). On the surface SnO_2 is present with $3d_{5/2}$ at BE = 486.3 eV, whereas after etching $3d_{5/2}$ shifted to BE = 485.6 eV indicating SnO_{2-x} phase present in the bulk of the films.

SEM images (Fig. 4a-b) shows that the films prepared by both techniques are continuous and pinhole free. As seen in SEM monograph, films deposited by both process have characteristic needle shaped grains, also reported for doped SnO_2 thin film [15] and are more in case for TE in comparison to PATE. The electrical resistivity of SnO_2 films is measured at room temperature using Four-probe technique; show the conducting nature of the all deposited films. The electrical resistivity of films deposited by TE and

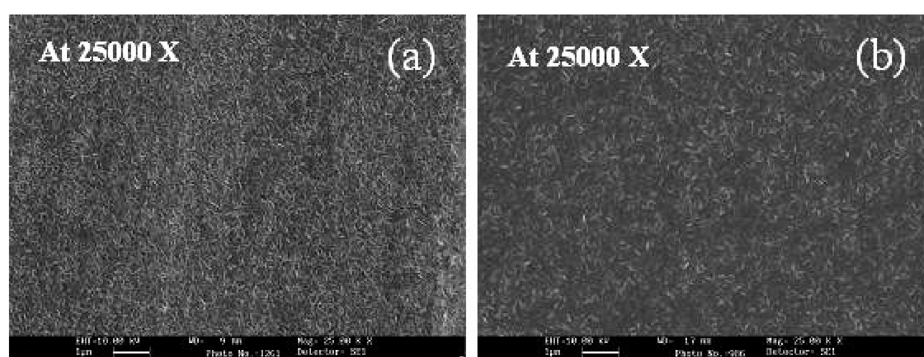

Fig. 4 *– SEM monographs of SnO_2 thin film deposited at a substrate temperature 350 °C by TE (a) and PATE (b) techniques with 25000X magnification*

PATE are in the range of 2-3 × 10^{-3} Ω-cm and 2-6 × 10^{-4} Ω-cm respectively. Hence, the films grown by TE have an order of magnitude higher resistivity, which could be due to higher quantities of needle shaped grain seen by SEM analysis in comparison to the films deposited by PATE, identified the importance of PATE technique.

4. CONCLUSION

We have investigated optical, structural, compositional and electrical properties of SnO_2 films deposited by TE and PATE at substrate temperature in the range of 250-350 °C. An average transmittance of ~ 80-90 % and electrical resistivity 2-6 × 10^{-4} Ω-cm in comparison to ~ 60-70% and 2-3 × 10^{-3} Ω-cm are obtained for films deposited on glass by PATE and TE respectively. XRD patterns confirmed that the films prepared at 350 °C possess crystallinity are absence of un-reacted Sn in the films grown by PATE shows the importance of plasma based process. Chemical composition analysis by XPS proves SnO_{2-x} phase present in the bulk of the films. Surface morphology revealed by SEM shows less needle shaped grains present in the films deposited by PATE compare to TE grown films. This may be playing a role in the variation of conductivities of these films. Hence, higher UV-VIS transmission and lower electric resistivity of SnO_2 films obtained by PATE makes this process useful for application in developing optoelectronics devices.

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