

Nanostructured Al Doped SnO₂ Films Grown onto ITO Substrate via Spray Pyrolysis Route

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We report on nanostructured films of Al doped tin oxide grown by facile spray pyrolysis route, and their physical properties were investigated. The sprayed films were grown onto indium tin oxide (ITO) substrate at 300 °C from the precursor (SnCl₄, 5H₂O). The content of Al is kept at 3 % in the solution. Structural, optical, electrical and surface properties were investigated. X-rays pattern reveals polycrystalline structure and SnO₂ phase occurrence. The visible transmittance exceeds 85 %, the band gap is found to be 3.7 eV. Nanotips were observed by 3D atomic force microscope (AFM) observation. Using the Hall effect measurements system (HMS), the films exhibit very low resistivity found to be 9.85 10⁻⁵ Ω.cm, a high electron concentration is around 10²¹ cm⁻³, and the mobility reaches the value of 20 cm²/Vs.

Keywords: Al doped tin oxide, Sprayed films, ITO substrate, Nanostructured films, Transmittance, Hall measurement.

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1. INTRODUCTION

Tin oxide belongs to a transparent conductive oxide (TCO) family which are the most studied. Tin oxide is wide band gap n type semiconductor (~ 3.6-3.8 eV) [1], which is employed in many applications like sensors, light emitting diodes and solar cells [2]. Many works have been achieved on tin oxide (SnO₂) thin films because of their high electrical conductivity, high transparency in the visible solar range, and high reflectivity in the infrared region [3]. Spray pyrolysis (SPD) is one of the common used deposition techniques to prepare SnO₂ due to its capacity to deposit large uniform area, low fabrication cost, simplicity and low deposition temperature [4-5].

In this work, we report on nanostructures of Al doped tin oxide grown on ITO substrate via facile spray pyrolysis method, and their structural, optical, surface morphology and electrical properties. The outlook is to achieve a device from these films which will be used in solar cell and photovoltaic application.

2. EXPERIMENTAL PROCEDURE

The deposition of the films by homemade system SPD technique was carried out as follows, the set up scheme was described in Figure 1. The sprayed aluminium doped SnO₂ films were deposited onto ITO substrate supplied by Aldrich. The starting material was (SnCl₄.5H₂O) and the doping source was aluminium (Al³⁺) chloride (AlCl₃). Both, precursor and doping compound were dissolved in methanol. The starting material concentration was 0.2 M and the doping ratio Al/Sn was 3 % in the solution. Spray rate and substrate to nozzle distance were maintained respectively at 20 ml/min and 25 cm. The glass substrate was heated at temperature of 300 °C which was controlled by digital thermometer connected to the heater. X-rays diffraction patterns of the TO films were analyzed at room temperature using Bruker AXS D8 Discover diffrac-

tometer with CuK_{α1} radiation ($\lambda = 1.5418 \text{ \AA}$) between $20^\circ \leq 2\theta \leq 80^\circ$. The UV-VIS-NIR transmittance spectra of the Al doped SnO₂ films were recorded via a Shimadzu UV-3600 PC double beam spectrometer. The electrical resistivity of the films was carried out by Hall Effect measurement system (HMS) 3000 ECOPIA at room temperature using S/N magnet having a magnetic field of 0.58 T. AFM analysis of the sample was made by using a Quesant Model 250 system having an (80 × 80) micrometer head, in the wave mode in air. For the (3 × 3) micrometer square images the resolution was (300 × 300) pixels at fixed scan rate of 2 Hz. All analyses were performed with the software from the WSXM system.

3. RESULTS AND DISCUSSIONS

Figure 2 showed X-rays pattern of sprayed aluminium doped tin oxide films. The pattern demonstrated a polycrystalline structure and the main reflections were (110), (211) and (310) located respectively at 21.3°, 51° and 60.5°. Others peaks were shown (101), (200) and (220), which identify the SnO₂ phase with tetragonal structure. Similar trends were revealed by Thanachayanont et al. [3]. ITO peaks, apparent in the

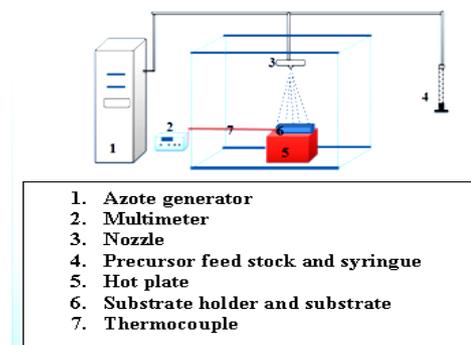


Fig. 1 – Schematic diagram of spray pyrolysis deposition set-up

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X rays spectrum, are signed by star. The grain size was determined using the well known Scherrer formula [6],

$$G = 0.94\lambda/\beta \cos\theta \quad (1)$$

Where θ (rd) is half of Bragg angle λ (Å) is photon wavelength β (rd) is full width at medium height. The grain's size were found to be ~ 13 and 8 nm according respectively to strong (110) and (211) peaks. It was observed that the peaks' base was broadened. It should confirm the nanostructures occurrence of the Al SnO₂ sample, which was in well agreement with the AFM (3D view) observations.

The transmittance of Al doped SnO₂ was depicted in Figure 3. The transmittance increases rapidly in UV range and reaches 86.8 % in visible spectrum, and few oscillations were revealed around 600 and 800 nm. A decay of transmittance was observed in IR range from 1350 nm.

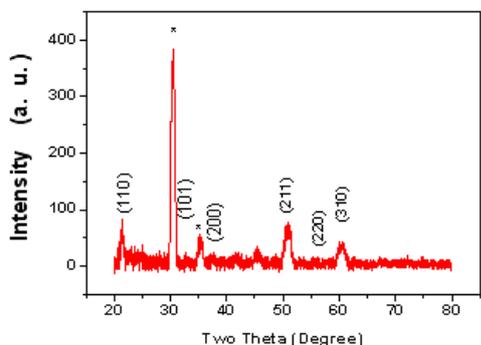


Fig. 2 – X-rays pattern of 3 % Al doped SnO₂ grown onto ITO substrate

The optical band gap E_g was calculated from the allowed direct transition given by [7],

$$\alpha h\nu = (h\nu - E_g)^{0.5} \quad (2)$$

Where α (m⁻¹) is the absorption coefficient h (J.s) is Planck's constant ν (Hz) is the photon frequency, and E_g (eV) –is the band gap energy. The optical band gap is determined by extrapolating of the linear part of the curve $(\alpha h\nu)^2$ which intercepts the energy axis, E_g is found to be 3.7 eV as can be easily seen in Figure 4. A gap of 3.4 eV was obtained by Yakuphanoglu for SnO₂ deposited on ITO substrate [8]. In recent works, E_g , of tin oxide films, varies in the range 3.6-3.8 eV [9].

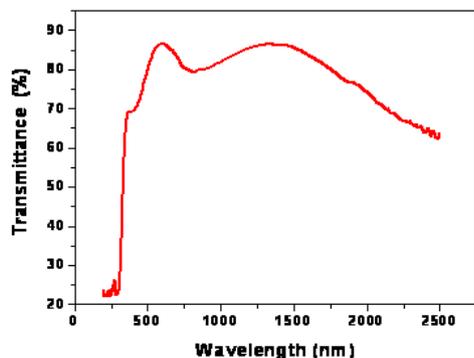


Fig. 3 – Transmittance against photon wavelength of 3% Al doped SnO₂ grown onto ITO substrate

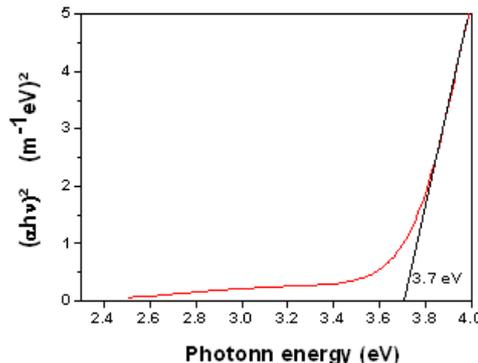


Fig. 4 – Dependence of $(\alpha h\nu)^2$ on photon energy of 3% Al doped SnO₂ grown onto ITO substrate

The Figure 5 exhibits the AFM surface morphology of Al doped SnO₂. Moreover, the films reveal homogenous surface and the grains were elongated from the inner towards the surface. Their shape looks like nanotips (signed by arrow in AFM picture) which were assembled with few voids. The average size was evaluated at 90 nm as described in 2D view (top of Figure 5), and films roughness (RMS) was around 4.49 nm. Grain size was less than 100 nm which confirms the presence of nanostructures. In addition, these nanograins were clearly observed in 3D AFM picture, the grains were concentrated with no well boundaries. Similar nanostructures SnO₂ morphology was found in literature [10-12].

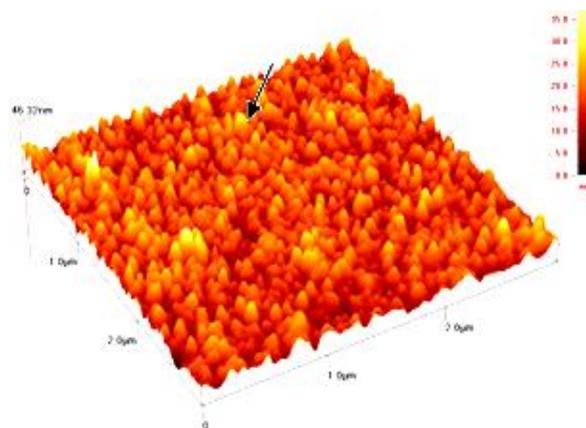
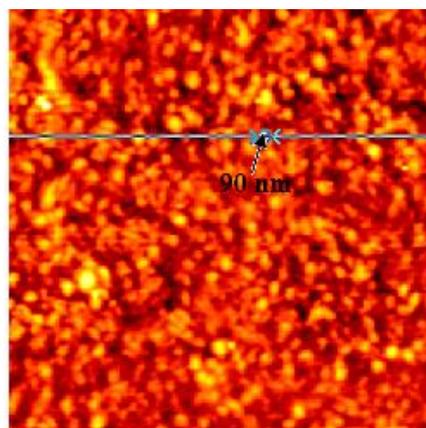


Fig. 5 – AFM 2D view (top) 3D view (bottom) of 3% Al doped SnO₂ grown onto ITO substrate (dimension of picture are 3 $\mu\text{m} \times 3 \mu\text{m}$, the height is 46.32 nm)

Using the HMS set up, the films were maintained by four gold probes as shown in picture (figure 6). The films exhibit very low resistivity found to be $9.85 \cdot 10^{-5} \Omega \cdot \text{cm}$, a high electron concentration around $3 \cdot 10^{21} \text{ cm}^{-3}$, and the mobility attains $20 \text{ cm}^2/\text{Vs}$. The sample owns a magneto-resistance equals to $1.16 \cdot 10^{-2} \Omega$, a high electrical conductivity found to be 10^4 S/cm and an average Hall coefficient around $10^{-3} \text{ cm}^3/\text{C}$. Similar result, high

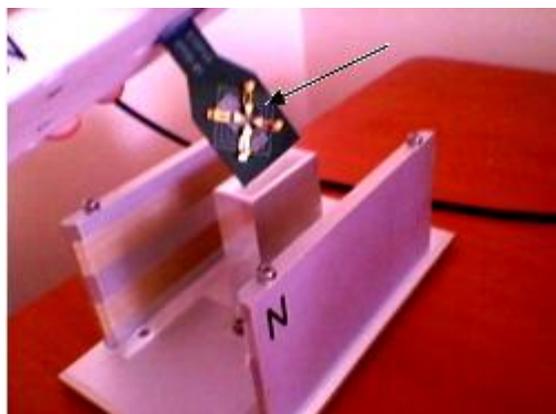


Fig. 6 – Hall measurement apparatus of 3% Al doped SnO_2 grown onto ITO substrate, the films were kept by four Au probes as signed by arrow

carrier concentration and low mobility were found to be respectively 10^{20} cm^{-3} , $7 \text{ cm}^2/\text{Vs}$ for 2 % Sb doped tin oxide [1], for B doped SnO_2 [13-14].

4. CONCLUSIONS

Nanostructures of aluminum doped tin oxide sprayed onto ITO were investigated. The 3 % Al doped tin oxide sprayed films reveal high visible transmittance ($> 85 \%$) and optical band gap found to be 3.7 eV . A very low resistivity ($9.85 \cdot 10^{-5} \Omega \cdot \text{cm}$) and high transmittance in visible spectrum give Al: SnO the characteristics of a best transparent conductive oxide (TCO). High electrical conductivity and high carrier concentration were hopeful parameters which can give the best characteristics of solar and photovoltaic devices.

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