NANOSTRUCTURED Al DOPED SnO$_2$ FILMS GROWN ONTO ITO SUBSTRATE VIA SPRAY PYROLYSIS ROUTE

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ABSTRACT

We report on nanostructured films of Al doped tin oxide grown by facile spray pyrolysis route, and their physical properties are investigated. The sprayed films are grown onto ITO substrate at 300°C from (SnCl$_4$, 5H$_2$O)as precursor. The content of Al is kept at 3 % in the solution. Structural, optical, electrical and surface properties are investigated. X-rays pattern reveals polycrystalline structure and SnO$_2$ phase occurence. The visible transmitance exceeds 85%, the band gap is 3.7 eV.Nanotips are observed by 3D atomic force microscope (AFM) picture. The films exhibits very low resistivity found to be 9.85 10^{-5}Ω.cm, a high electron concentration around 10^{21}cm^{-3}, and low mobility 20 cm^2/Vs.

Key words: Al doped tin oxide, sprayed films, ITO substrate, Nanostructured films, Transmittance, Hall measurement.

INTRODUCTION

Tin oxide is among a transparent conductive oxide (TCO) 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 researchers have been achieved on tin oxide (SnO$_2$) 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 depositionroutes to prepare SnO$_2$ 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 tin oxide doped with Al grown on ITO substrate via facile spray pyrolysis route, and their structural, optical, surface morphology and electrical properties are investigated. Our outlook is to achieve a device from this film which will be used in solar cell and photovoltaic application.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

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

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aluminum doped films are deposited onto ITO substrate supplied by Aldrich methanol. The starting material concentration is 0.2 M and the doping ratio Al/Sn is 3 % in the solution.
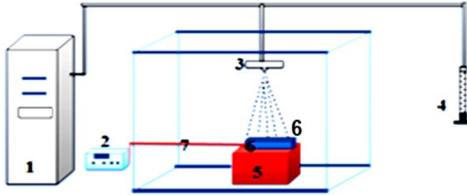
1. Azote generator
2. Multimeter
3. Nozzle
4. Precursor feed stock and syringe
5. Hot plate
6. Substrate holder and substrate
7. Thermocouple

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

Spray rate and substrate to nozzle distance are maintained respectively at 20 ml/minand 25 cm. The glass substrate is heated at temperature of 300 °C which controlled by digital thermometer connected to the heater. X-rays diffraction patterns of the TOfilms are analyzed at room temperature using Bruker AXS D8 Discover diffractometer with $CuK_{\alpha 1}$ radiation ($\lambda = 1.5418$ Å) between $20° \leq 2\theta \leq 80°$.The UV-VIS-NIR transmittance spectra of the Al doped SnO_2 films are recorded via a Shimadzu UV-3600 PC double beam spectrometer. The electrical resistivity of the films is carried out by ECOPIA HMS 3000 Hall Effect measurement system 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 (80x80) micrometer head, in the wave mode in air. For the (3 x 3) micrometer square images the resolution was (300 x 300) pixels at fixed scan rate of 2 Hz. All analyses were performed with the software from the WSXM system.

RESULTS AND DISCUSSION

Figure 2 shows X-rays pattern of sprayed aluminum doped tin oxide film. The pattern demonstrates a polycrystalline structure and the main reflections are (110), (211) and (310) located respectively at 21.3°, 51°, and 60.5°.
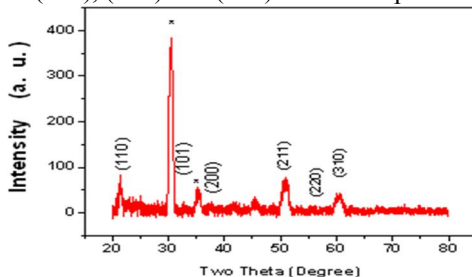

Fig. 2 – X-rays pattern of 3% Al doped SnO_2 grown onto ITO substrate

Others peaks are shown (101), (200) and (220), which identify the SnO_2 phase with tetragonal structure. Similar trends are revealed by Thanachayanont et al.[3]. ITO peaks, apparent in the X rays spectrum, are signed by star. The peak base is broadened and using the expression 1, the grain size G ac-

cording to the preferential (211) direction is around 8 nm. The selected peak (width=1.04° and height=66.72) was fitted by Gaussian profile. It should confirm the nanostructures occurrence of the Al SnO$_2$ sample, which is in well agreement with the AFM (3D view) observations. The gain size is determined using the well known Scherrer formula [6],

$$G = \frac{0.94\lambda}{\beta \cos\theta} \qquad (1)$$

Where θ – is half of Bragg angle λ– is photon wavelength β – is full width at medium height. The grain size determined by Gaussian deconvolution is found to be according to (211) orientation,

Transmittance of Al doped SnO$_2$ is depicted in *figure 3*. The transmittance increases rapidly in UV range and reaches 86.8 % in visible spectrum, and few oscillations are revealed and then it decreases in IR range. 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 SnO$_2$ deposited on ITO substrate [7].
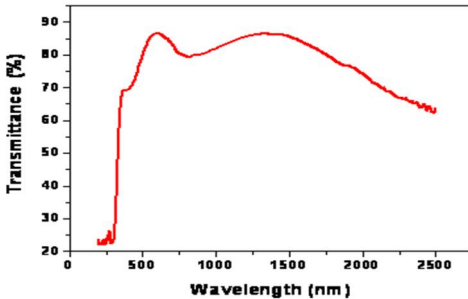

Fig. 3 – Transmittance against photon wavelength of 3% Al doped SnO$_2$ grown onto ITO substrate
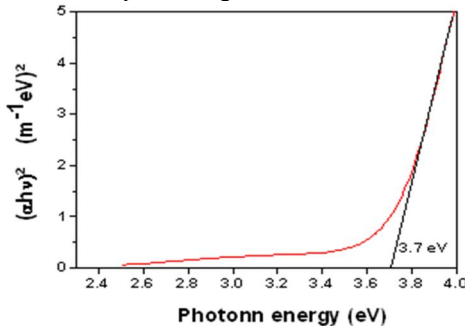

Fig. 4 – Dependence of ($\alpha h\nu$)² on photon energy of 3% Al doped SnO$_2$ grown onto ITO substrate

The optical band gap is calculated from the allowed direct transition given by [8],

$$\alpha h\nu = (h\nu - E_g)^{1/2} \quad (2)$$

Where α–is the absorption coefficient h–is Planck's constant ν–is the photon frequency, and E$_g$–is the band gap energy.

The *figure 5* exhibits the AFM surface morphology of Al doped SnO$_2$. Moreover, the film reveals homogenous surface and the grains are elongated from the inner towards the surface. Their shape looks like nanotips (signed by arrow in AFM picture) which are assembled with few voids. The average size is evaluated at 90 nm as described in 2D view (left of *figure 5*), and film roughness (RMS) is around 4.49 nm.

Grain size is less than 100 nm which confirms the presence of nanostructures. In addition, these nanograins are clearly observed in 3D AFM picture, the grains are concentrated with no well boundaries. Similar nanostructures SnO_2 morphology is found in literature [9-11].
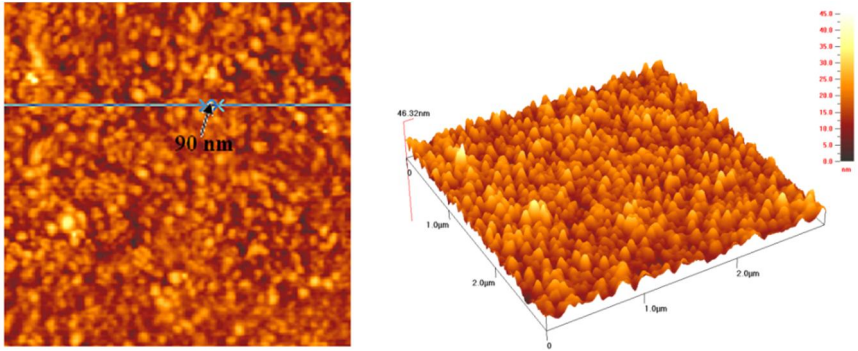

Fig. 5– AFM 2D view (left) 3D view (right) of 3% Al doped SnO_2 grown onto ITO substrate (dimension of picture are 3μm x 3μm, height is 46.32 nm)

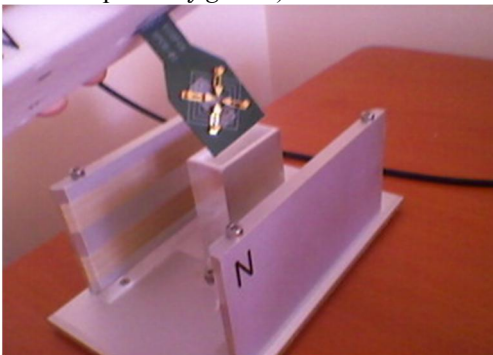Using the HMS set up, the film is maintained by four gold probes as shown in picture (*figure 6*).

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

The film exhibits very low resistivity found to be 9.85 10^{-5} Ω.cm, a high electron concentration around 3 10^{21} cm^{-3}, and low mobility 20 cm^2/Vs. The sample owns a magneto-resistance equals to 1.16 10^{-2} Ω, a high electrical conductivity found to be 10^4 S/cm and an average Hall coefficient around 10^{-3} cm^3/C. Similar result, high career concentration and low mobility were found to be respectively 10^{20} cm^{-3}, 7 cm^2/Vs for 2% Sb doped tin oxide[1], for B doped SnO_2 [12].

CONCLUSIONS

Nanostructures of aluminum doped tin oxide sprayed onto ITO are investigated. The 3% Al doped tin oxide sprayed film reveals high visible transmittance (>85%) and optical band gap found to be 3.7 eV. A very low resistivity

(10^{-5} cm) and high transmittance in visible spectrum give Al:SnOthe characteristics of a best TCO.High electrical conductivity and high career concentration are hopeful parameters which can give the best characteristics of solar and photovoltaic devices.

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