JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 4 No 1, 01011(3pp) (2012)
ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 4 № 1, 01011(3cc) (2012)

Nanostructured Al Doped SnO_2 Films Grown onto ITO Substrate via Spray Pyrolysis Route

M. Benhaliliba[1,*], C.E. Benouis[1], Y.S. Ocak[2], F. Yakuphanoglu[3]

[1] *Physics Department, Sciences Faculty, USTOMB University, BP1505 Oran, Algeria*
[2] *Department of Science, Faculty of Education, University of Dicle, Diyarbakir, Turkey*
[3] *Firat University, Physics Dpt., Faculty of Sciences and Arts, 23119, Elazig, Turkey*

(Received 25 October 2012; revised manuscript received 26 February 2012; published online 14 March 2012)

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 ($SnCl_4$, $5H_2O$). 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 SnO_2 phase occurence. The visible transmitance 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 $9.85\ 10^{-5}\ \Omega$.cm, a high electron concentration is around 10^{21} cm^{-3}, and the mobility reaches the value of 20 cm^2/Vs.

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

PACS numbers: 81.07. – b, 81.15. – z

1. INITRODUCTION

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 (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 deposition techniques to prepare SnO_2 due to its capacity to deposit large uniform area, low fabrication cost, simplicity and low deposition temperature [4-5].

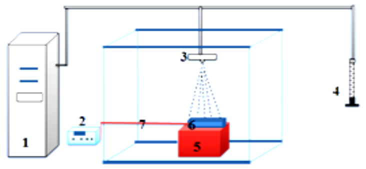
In this work, we report on nanostructures of Al doped tin oxide grown on ITO substrate via facile spray pyrolysis method, and their structural, optical, surface morphology and electrical properties. The outlook is to achieve a device from these films which will be used in solar cell and photovoltaic 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 SnO_2 films were deposited onto ITO substrate supplied by Aldrich. The starting material was ($SnCl_4.5H_2O$) and the doping source was aluminium (Al^{3+}) chloride ($AlCl_3$). 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 diffractometer with $CuK_{\alpha 1}$ radiation ($\lambda = 1.5418$ Å) between $20° \le 2\theta \le 80°$. The UV-VIS-NIR transmittance spectra of the Al doped SnO_2 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 aluminum 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 SnO_2 phase with tetragonal structure. Similar trends were revealed by Thanachayanont et al. [3]. ITO peaks, apparent in the



1. **Azote generator**
2. **Multimeter**
3. **Nozzle**
4. **Precursor feed stock and syringue**
5. **Hot plate**
6. **Substrate holder and substrate**
7. **Thermocouple**

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

---

[*] bmost_31@yahoo.fr

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

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

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 SnO_2 sample, which was in well agreement with the AFM (3D view) observations.

The transmittance of Al doped SnO_2 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.

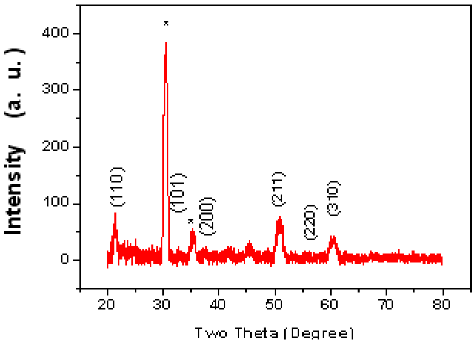


Fig. 2 – X-rays pattern of 3 % Al doped SnO_2 grown onto ITO substrate

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

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

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 SnO_2 deposited on ITO substrate [8]. In recent works, E_g, of tin oxide films, varies in the range 3.6-3.8 eV [9].

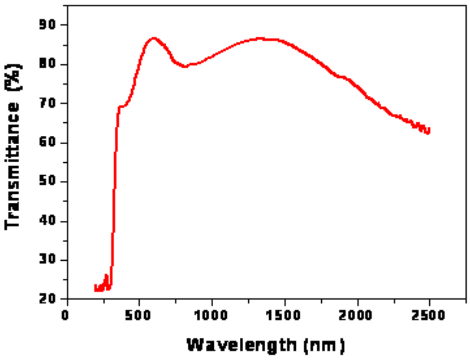


Fig. 3 – Transmittance against photon wavelength of 3% Al doped SnO_2 grown onto ITO substrate

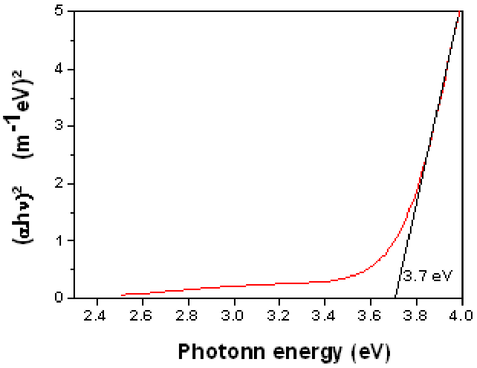


Fig. 4 – Dependence of $(\alpha h\nu)I$ on photon energy of 3% Al doped SnO_2 grown onto ITO substrate

The Figure 5 exhibits the AFM surface morphology of Al doped SnO_2. 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 SnO_2 morphology was found in literature [10-12].

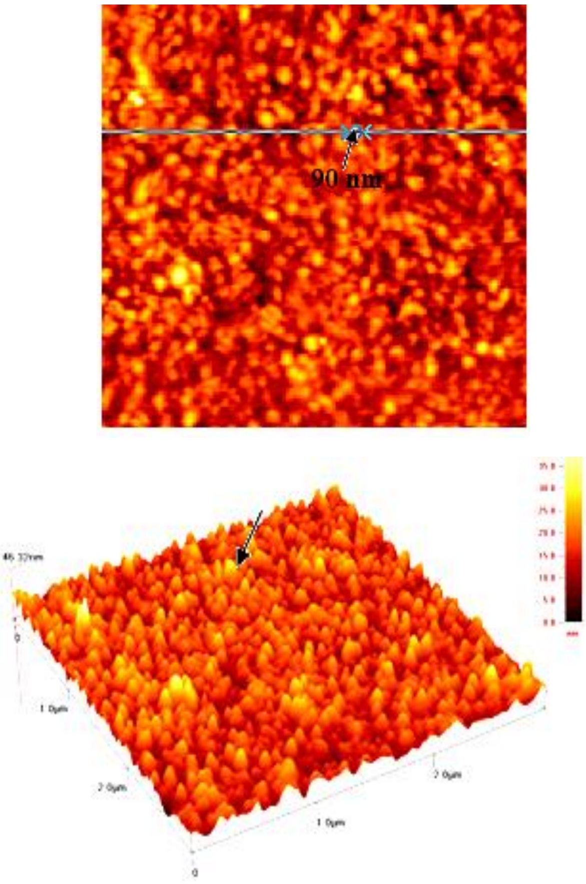


Fig. 5 – AFM 2D view (top) 3D view (bottom) of 3% Al doped SnO_2 grown onto ITO substrate (dimension of picture are 3 µm × 3 µm, the height is 46.32 nm)

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 10^{-5} Ω.cm, a high electron concentration around 3 10^{21} cm^{-3}, and the mobility attains 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 carrier 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 [13-14].

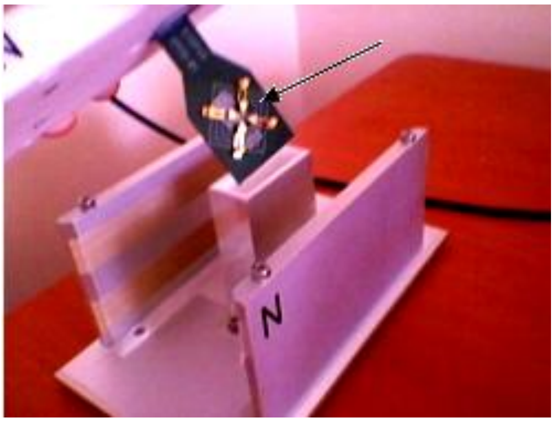


Fig. 6 – Hall measurement apparatus of 3% Al doped SnO_2 grown onto ITO substrate, the films were kept by four Au probes as signed by arrow

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 ($9.85 \cdot 10^{-5}$ Ω.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.

ACKNOWLEDGEMENTS

This work is included in CNEPRU project N° D01920080054 supported by Oran university of sciences and technology. Authours would like to thank the generous assistance of Pr. Hamzaoui head of SEM Microscope Laboratory, USTO Oran-Algeria. The authors also acknowledge the support of BAP project (10-ZEF-165) at Dicle University Diyarbakir – Turkey.

REFERENCES

1. Timonah N. Soitah, Chunhui Yang, Liang Sun, Materials Science in Semiconductor Processing 13 (2010) 125-131.
2. J. Zhao, X.J. Zhao, J.M. Ni, H.Z. Tao, *Acta Mater.* **58**, 6243 (2010).
3. C. Thanachayanont, V. Yordsri, C. Boothroyd, *Mater. Lett.* **65**, 2610 (2011).
4. A.R. Babar, S.S. Shinde, A.V. Moholkar, C.H. Bhosale, J.H. Kim, K.Y. Rajpure, *J. Alloy Compd.* **509**, 3108 (2011).
5. C.E. Benouis, M. Benhaliliba, F. Yakuphanoglu, A. Tiburcio Silver, M.S. Aida, A. Sanchez Juarez, *Synthetic Met.* **161**, 1509 (2011).
6. M. Benhaliliba, C.E. Benouis, M.S. Aida, A. Sanchez Juarez, F. Yakuphanoglu, A. Tiburcio Silver, *J. Alloy Compd.* **506**, 548 (2010).
7. M. Benhaliliba, C.E. Benouis, M.S. Aida, F. Yakuphanoglu, A. Sanchez Juarez, *J. Sol-Gel Sci. Technol.* **55**, 335 (2010).
8. F. Yakuphanoglu, *J. Alloy. Compd.* **470**, 55 (2009).
9. Lin Tan, Lihong Wang, Yude Wang, *J. Nanomater.* **2011**, 529874 (2011).
10. Ashok B. Bhise, Dattatray J. Late, Pravin Walke, Mahendra A. More, Imtiaz S. Mulla Vijayamohanan K. Pillai, Dilip S. Joag, *J. Phys. D: Appl. Phys.* **40** 3644 (2007).
11. Saji Chacko, Ninan Sajeeth Philip, K.G. Gopchandran, Peter Koshy, V.K. Vaidyan *Appl. Surf. Sci.* **254**, 2179 (2008).
12. M. Lei, Q.R. Hu, S.L. Wang, W.H. Tang, *Mater. Lett.* **64**, 19 (2010).
13. B. Zhang, Y. Tian, J.X. Zhang, W. Cai, *Vacuum* **85**, 986 (2011).
14. B. Zhang, Y. Tian, J.X. Zhang, W. Cai, *Mater. Lett.* **65**, 1204 (2011).