Physical Sciences Research International
Vol. 2(4), pp. 62-67, November 2014
Full Length Research Paper

The physical properties of SnO_2 thin films deposited by rheotaxial growth and thermal oxidation method

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Accepted 21 November, 2014

ABSTRACT

This research SnO_2 thin films was prepared by using rheotaxial growth and thermal oxidation (RGTO) method. The pure Sn powder was evaporate by using melbedume bot at vacuum 10^{-6} torr on glass substrate till it reached its evaporate temperature. Thin films at thickness 3000^{o}A were prepared, after that treated with 450°C and to obtain SnO_2 thin films in the presence of O_2. The X-ray Diffraction (XRD) results refer to polycrystalline phase Scanning Electron Microscopy (SEM), which studies the local morphology and the surface of SnO_2 thin films obtained by Rheotaxial Growth and thermal Oxidation (RGTO) method. SEM shows a fractal-like morphology of nanograins (22 nm typical size). The optical properties were studying by using uv-vis spectra and it was found that the transmittance was ~70%. The value of energy gap was 3.85 eV.

Keywords: RGTO thin films, thin dioxide thin film.

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INTRODUCTION

Tin dioxide (SnO_2) serves as an important base material in a variety of resistive-type gas sensors (Katsiev et al., 2008). The widespread applicability of this semiconducting oxide is related both to its range of conductance variability and to the fact that it responds to both oxidizing and reducing gases (Barsan et al., 1999). Till now, commercial gas sensors devices (mainly used for domestic applications in the gas alarm systems) based on SnO_2 have been fabricated with thick (about 1 mm) films, of which a fundamental limitation is large power consumption (Ihokura and Watson, 1994). This limitation does not concern the thin solid film gas sensors (Batzill et al., 2003; Batzill et al., 2004; Batzill et al., 2006; Batzill and Diebold, 2006; Katsiev et al., 2007).

Among various techniques for the preparation of SnO_2 thin films the Rheotaxial Growth and Thermal Oxidation (RGTO) method first proposed by Sberveglieri (Batzill et al., 2004; Batzill et al., 2006) looks like one of the most effective methods in view of gas sensing applications. This technique is based on a two-step process. It consists of: i) deposition of a thin Sn film on a substrate maintained at a temperature slightly exceeding the Sn melting point (231.8°C) (first step); and ii) a subsequent long-term post-deposition oxidation at high temperature up to 700°C (second step). In the first step, a discontinuous Sn film is formed composed of isolated, almost spherical droplets. Due to the absence of percolation in the plane, electrical resistivity of the thin film is infinite. The granular structure is preserved during the final oxidation but the Sn droplets undergo a significant increase in size due to oxygen incorporation. This results in an almost 30% increase of the film thickness. Moreover, the second step, via oxidation, creates connecting “necks” between the formerly isolated Sn droplets, and such necks open a percolation path for the flow of electric current in the RGTO SnO_2 based gas sensing devices (Sberveglieri et al., 1990; Sberveglieri, 1992; Sberveglieri et al., 1992). In present work, we propose a microscopic investigation of such optimized RGTO samples. X-ray Diffraction (XRD) data of SnO_2 sample is presented and discussed in comparison with Scanning Electron Microscopy (SEM) images and the

Table 1. Summary of deposition conditions.

Coating unit	INFICON V90
Materials	Tin powder 99.99%
Substrates	glass slides
Vacuum	~ 6×10^{-6} torr
Substrate to film gap	18 cm

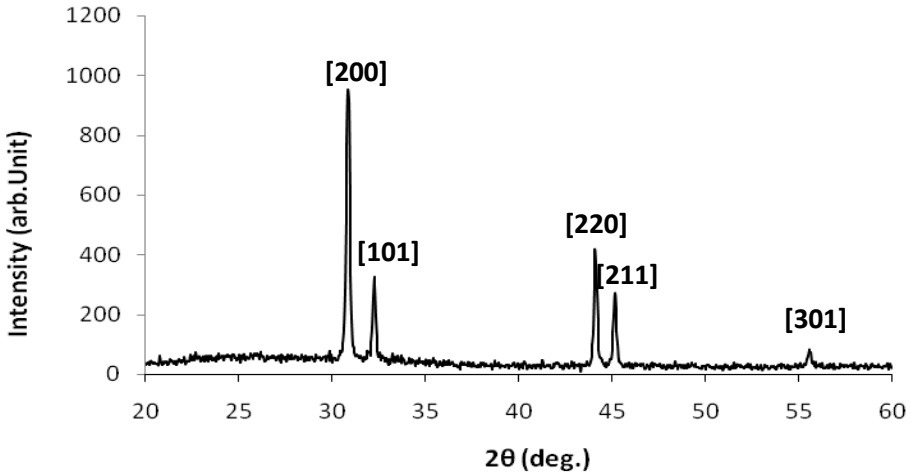


Figure 1. X- ray diffraction of Sn metallic.

optical properties of SnO_2 prepered in RGTO are studied.

EXPERIMENTAL

Tin dioxide (SnO_2) thin films were deposited according to the RGTO method. In the first step, thin metallic tin layers were deposited by classical vacuum thermal evaporation. The evaporation was carried out in a conventional vacuum coating unit (INFICON V90) under a vacuum of order of 6×10^{-6} torr with controlled deposition rate by using pure Sn. A summary of the deposition conditions is shown in Table 1. The second step, involving the thermal oxidation of Sn thin layer, was performed for 4 h at 450°C in dry air atmosphere inside a reaction chamber of a diffusion furnace. The crystallinity and the crystalline phases present in the films were checked by XRD using an X-ray diffractometer with CuKα radiation (model "Shimadzu XRD 6000"). For the different conditions of preparing SnO_2 sample, recorded was for a range of 2θ from 10^o to 60^o at 2^o glancing angle.

The local surface morphology were investigated by scanning electron microscopy (SEM), model (VEGA3 TESCAN). The absorbance and transmittance of the deposited thin film was measured using UV-VIS spectrum (Optima Sp – 300 Plus) in the wavelength region of 200 to 1100 nm.

RESULTS AND DISCUSSION

The RGTO thin film crystalline structure has been investigated with XRD. Figure 1 shows a typical Bragg-Brentano spectrum taken on an identically prepared film grown on glass. Diffraction data show the presence of the [110], [101], [200], [211] and [220] diffraction peaks from crystalline SnO_2 in the cassiterite rutile phase. The diffraction pattern perfectly matches with the SnO_2 reference crystal structure 1997 JCPD file v.1:30. Figure 2 is the main diffraction line from a coexisting SnO phase which should be observed when the heat tratement of Sn is about 250°C as shown in Figures 1 and 2. Thus our results are in line with what already reported in literature (that is, absence of coexisting SnO phase when the heat tratement of Sn is about 450°C for 4 h) and with the expectation of a complete transition to a SnO_2 phase upon annealing in oxygen at temperatures above 450°C as shown in Figure 3 (Dieguez et al., 2000).

The SEM investigation of the RGTO SnO_2 thin film without annealing shows surface morhplogy of fractal like morphology of nanograins (22 nm typical size) with homogenious distributions. The crystallography of fractal looks like a rectangular prism with square base and this is one of the classes of Tetragonal Bravais lattices of SnO_2 as shown in Figure 4.

The optical properties were studied by measuring the

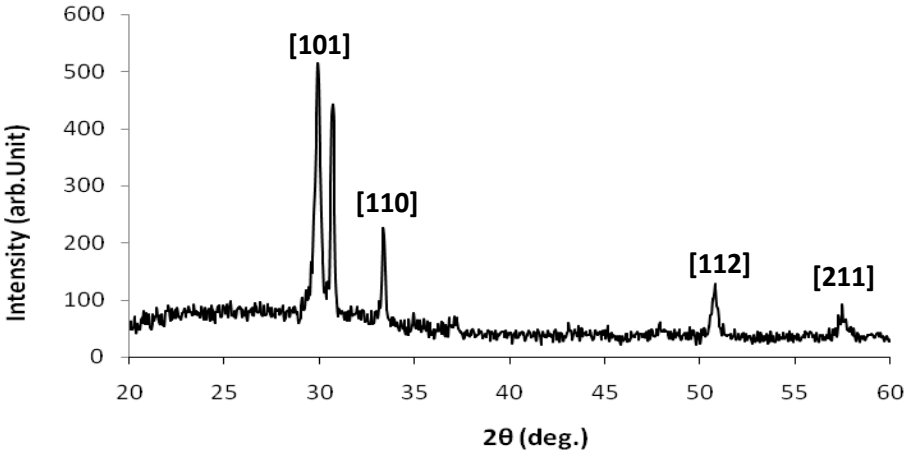


Figure 2. X-ray diffraction of SnO thin films at 250°C oxidation of Sn.

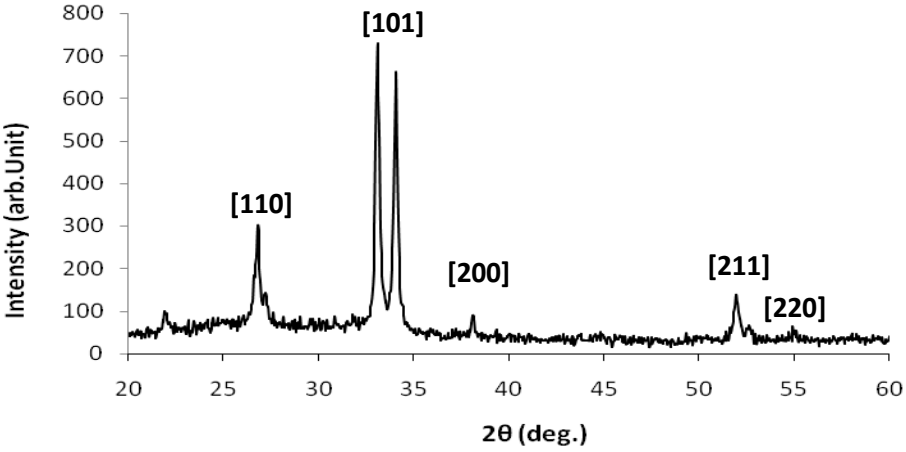
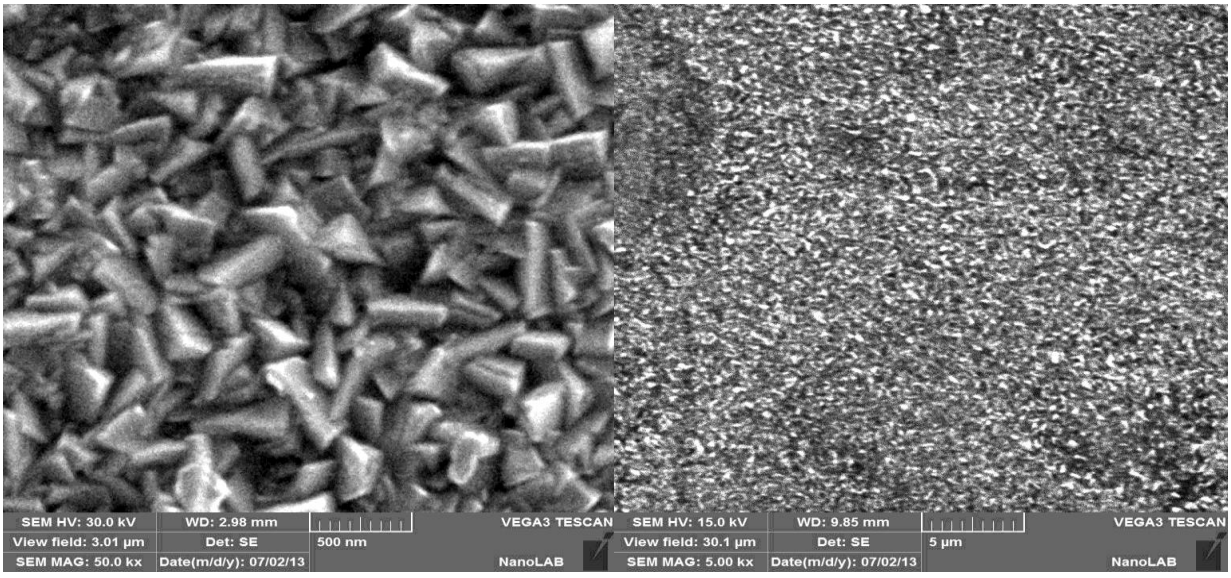


Figure 3. X-ray diffraction of SnO_2 thin films at 450°C oxidation of Sn.



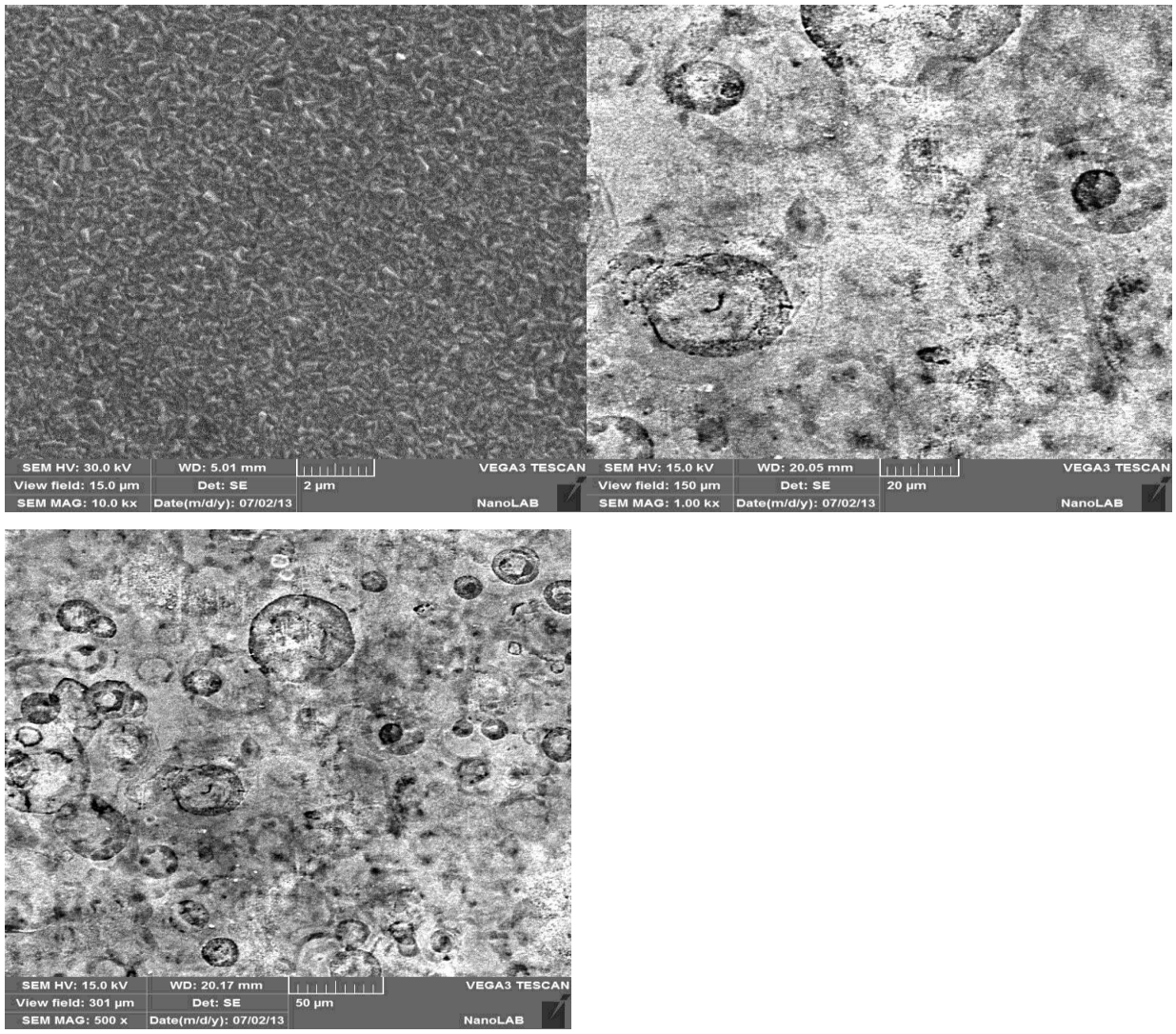
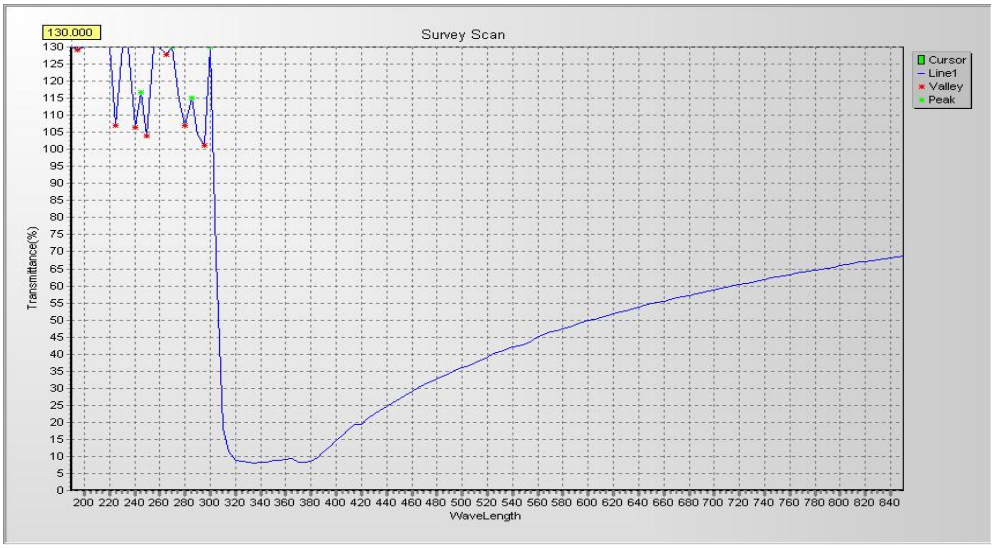


Figure 4. From the top to bottom and left to right SEM images at increasing magnification (500kx, 1.00kx, 5.00kx, 10kx, 50kx) of nanograins of SnO_2.



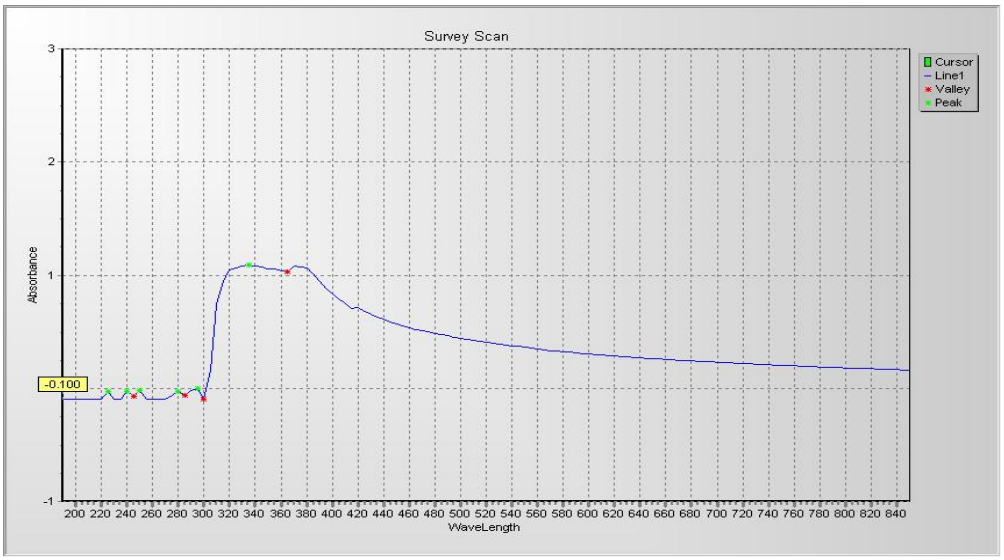


Figure 5. Transmittance and absorbance spectra of SnO_2 films.

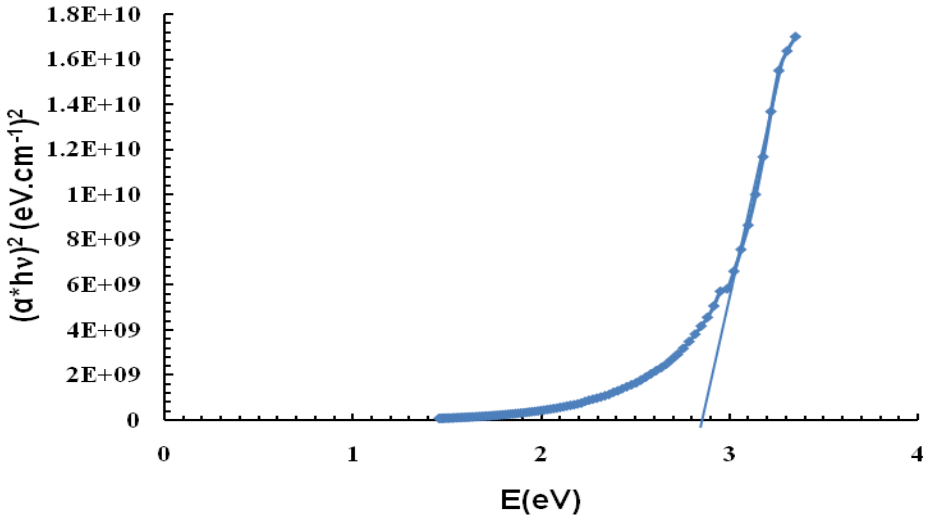


Figure 6. Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ curve of $ZnO:In_2O_3$ thin film.

transmission and absorbance spectra as shown in Figure 5. We found that the film has high transmission at long wave lengths approximately (65 to 70%), and decreasing transmission to 10% at short wavelengths.

The energy gap (Eg) was determined by employing the following relation (Kim et al., 2008):

$$\alpha = A(h\nu - Eg)^n / h\nu \quad (1)$$

Where α is absorption coefficient, A a constant (independent from ν) and n the exponent that depends upon the quantum selection rules for the particular material. The photon energy (hν) for y-axis can be calculated using Equation 2.

$$E = h\nu = hc/\lambda \quad (2)$$

Where h is Plank's constant (6.626×10^{-34}), c is speed of light (3×10^8) and λ is the wavelength. The values of energy gap Eg is 2.85eV as shown in Figure 6.

CONCLUSIONS

In this paper, we present the results of comparative study of surface morphology of RGTO SnO_2 thin films using the XRD, SEM. XRD study of the atomic structure confirms the existence of SnO_2 polycrustalline phase, and it is found that in 450°C for 4 h the existence of SnO_2 are

without any coexisting SnO phase. SEM study of local surface morphology show a fractal like morphology of nanograins (22 nm typical size). The transmittance of the thin films is ~70%; the value of energy gap was 3.85eV.

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Citation: Jami SSB, 2014. The physical properties of SnO_2 thin films deposited by rheotaxial growth and thermal oxidation method. Phys Sci Res Int, 2(4): 62-67.