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Research Article

Crystalline Structure and Surface Morphology of Tin Oxide Films Grown by DC-Reactive Sputtering

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Abstract

Tin oxide thin films were deposited by dc reactive sputtering system at working gas pressures of (0.015-0.15) mbar. The crystalline structure and surface morphology of the prepared SnO_2 films were introduced by X-ray diffraction (XRD) and atomic force microscopy (AFM). These films showed preferred orientation in (110) plane and according to AFM micrographs, the grain sizes increased non-uniformly as working gas pressure increased.

Keywords: *DC Sputtering, Reactive sputtering, Thin films, Tin oxide*

1. Introduction

Tin dioxide (SnO_2) is one of the most widely used materials in thin film devices and applications, such as solar cells, photo catalysts, gas sensors, optical coatings and self-cleaning materials (Garzella, C. et al., 2000; Kurtz, S. R., and Gordon, R.G., 1987; Parkin, I., and Palgrave, R.G., 2005). In general, SnO_2 is very inert, surpassing glass in its resistance to attack of common solvents and acids. It acts as a catalyst for various organic reactions and, as a thin film, it is used as a dielectric for thin film capacitors and as an antireflection coating on silicon. In recent years, it has been investigated as an electrode for photoelectron chemical c ells, and for detectors of oxygen and hydrogen (Bak, T. et al., 2002; Nowotny, J. et al., 2005; Francioso, L. et al., 2007; Shimizu, Y. et al.,).

Reactive sputtering is widely used to prepare SnO_2 thin films. Generally, high flows of the reactive gas such as oxygen is required for formation of Tin compound films during reactive sputtering of tin metal. The deposition rate of the film, however, drops abruptly when compounds are formed on the target surface at high flows of the reactive gases (Kadlec, S., and Musil, J., 1996). The pressure of reactive gases, evaporation rates, and substrate temperatures are main parameters used to influence the packing density of the films, the films crystallinity, and the optical properties (Musil, J. et al., 1996).

In this work, we have studied the structural, electrical and optical properties of SnO_2 thin films prepared by D.C. reactive sputtering technique at different applied pressure to determine optimum conditions for SnO_2 thin films was used as gas sensor.

2. Experimental Work

The plasma sputtering system was made of a stainless steel cylinder (inner diameter 30cm, height 34cm), closed by stainless steel plates and sealed by O-rings. The electrodes and the metallic rods are encapsulated in Teflon shell so that only the electrode surfaces are in contact with the gas and edge effects are avoided. The shells used to cover the electrodes have a circular open area of 78.5 cm^2, which is the effective surface area of the electrode in contact with the gas. The electrodes were made of stainless steel of 15 mm in thickness and100 mm in diameter. Before each experiment the electrodes are mechanically polished and chemically cleaned in dichloromethane. The pressure is controlled by a manual throttle valve mounted between the reactor and the pumping unit. The pumping system is composed of a rotary vane pump and a diffusion pump. The gas through put is set at 150 cm^3/s by a gas flow-controller. Different gases used for the experiment with purity of 99.99 %. Before performing each measurement, the reactor was brought to a base pressure of about $3x10^{-5}$ mbar. A high voltage dc power supply was used to deliver 3kV voltage between the electrodes.

3. Result and Discussion

X-ray diffraction pattern for the deposited SnO_2 thin films was prepared by dc reactive sputtering on glass substrate for different working pressures (0.15 to 0.015 mbar), and, at argon/oxygen mixed flow (1/2), sputtering time is 60 min, distance and biasing voltage between anode and cathode are 5 cm and 4kV, respectively.

Reflections from the tetragonal crystallographic phase (cassiterite) of SnO_2 became more defined and progressively more intense and sharp for films with increase working pressures. In all samples randomly oriented tin oxide crystalline formation starts planes corresponding to (110), (101), (211) and (002) planes of SnO_2 for 2θ values of 26.51, 33.85, 51.69 and 57.93, resp.

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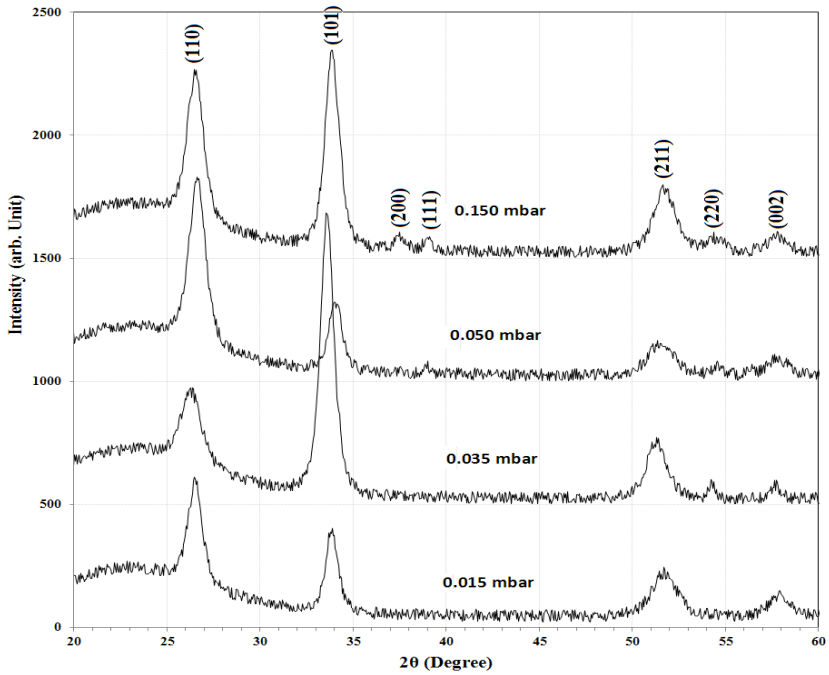

Fig. (1) XRD of sputtered SnO_2 thin films on glass substrate for different working pressure.

Figure (2), indicate that our films are textured and the degree of texturing depends on the value of working pressure, we indicate that the change of predominant orientation of crystallites, forming gas sensitive matrix, and confirms the cassiterite structure of nanocrystalline SnO_2 (Korotcenkov, G. et al., 2001). The (110) is the dominant crystal structure of low-index crystal faces for this material due to its stability. This is the desired structure of SnO_2 for sensing applications since its prevalent (110) growth plane is extremely stable and can reject oxygen with little distortion (Sensato, F. R. et al., 2002). The growth of this plane helps in achieving high oxygen vacancy concentrations at low temperature.

Table (1) The AFM and SEM data images of SnO_2 thin films deposited on glass substrate for different condition.

Biasing voltage (kV)	Applied pressure (mbar)	Argon/Oxygen mixed flow	Average Roughness (nm)	Average Grain Size (nm)
4	0.15	1:2	1.08	138.29
4	0.05	1:2	0.353	98.66
4	0.035	1:2	1.85	78.73
4	0.015	1:2	1.58	97.19

Table (2) Parameter of SnO_2 films prepared at different sputtering working pressure and mixing Ar/O_2 ratio

Ar/O_2	Pressure (mbar)	Thickness (nm)	E_g (eV)
1:2	0.15	317.82	4.0
1:2	0.05	185.33	3.94
1:2	0.035	215.53	3.92
1:2	0.015	209.42	3.96

Two and three-dimensional AFM images of the as-deposited SnO_2 films with different discharge current, working pressure, and Ar/O_2 mixed flow is shown in Fig. (2). The average grain size and root mean square roughness (RMS) of these films are shown in table (1). The AFM images of all samples displayed are granular structure. The granular films show higher surface area, which is conductive for film-gas interaction and results in higher gas sensitivity (Gadkari, S.C. et al., 2013). The gas sensitivity has a proportional relationship with film roughness (Deshpandea, N.G. et al., 2009).

As shown in the table (2). The value of the optical energy gap decreases as working pressure decrease for all samples, vest verse, and increasing as the ratio of argon to oxygen increases as shown in Fig. (2) and table (2). The relatively small value of band gap can be caused by high degree of non-stoichiometric disorders in the film. This indicate that the high conducting electron density is caused by deviations from the ideal single crystal structure, i.e., oxygen vacancies, interstitial atoms and dislocations acting as conducting electron donors (Kotkata, M.F. et al., 2009).

Figure (2) shows the decrease grain size from 138.29nm at pressure 0.15mbar to 78.73nm at pressure

0.035mbar and increase after that, while the roughness increase from 1.08 nm at 0.15mbar to 1.85nm at 0.035mbar and decrease after that. The low dense plasma and have not enough energy to re-nucleation leads increasing average roughness and decrease grain size.

The transmission spectra of SnO_2 thin films as a function of wavelength ranging from (200-1100) nm are show in Fig. (4). The spectral dependence shown in the figure reveals three main zones of interest. The presence of these oscillations in Fig. (2) is indicative of the good optical quality of the films. All the films were transparent, adherent to the substrate uniform, and stable for long period when kept in atmosphere. The average transmission

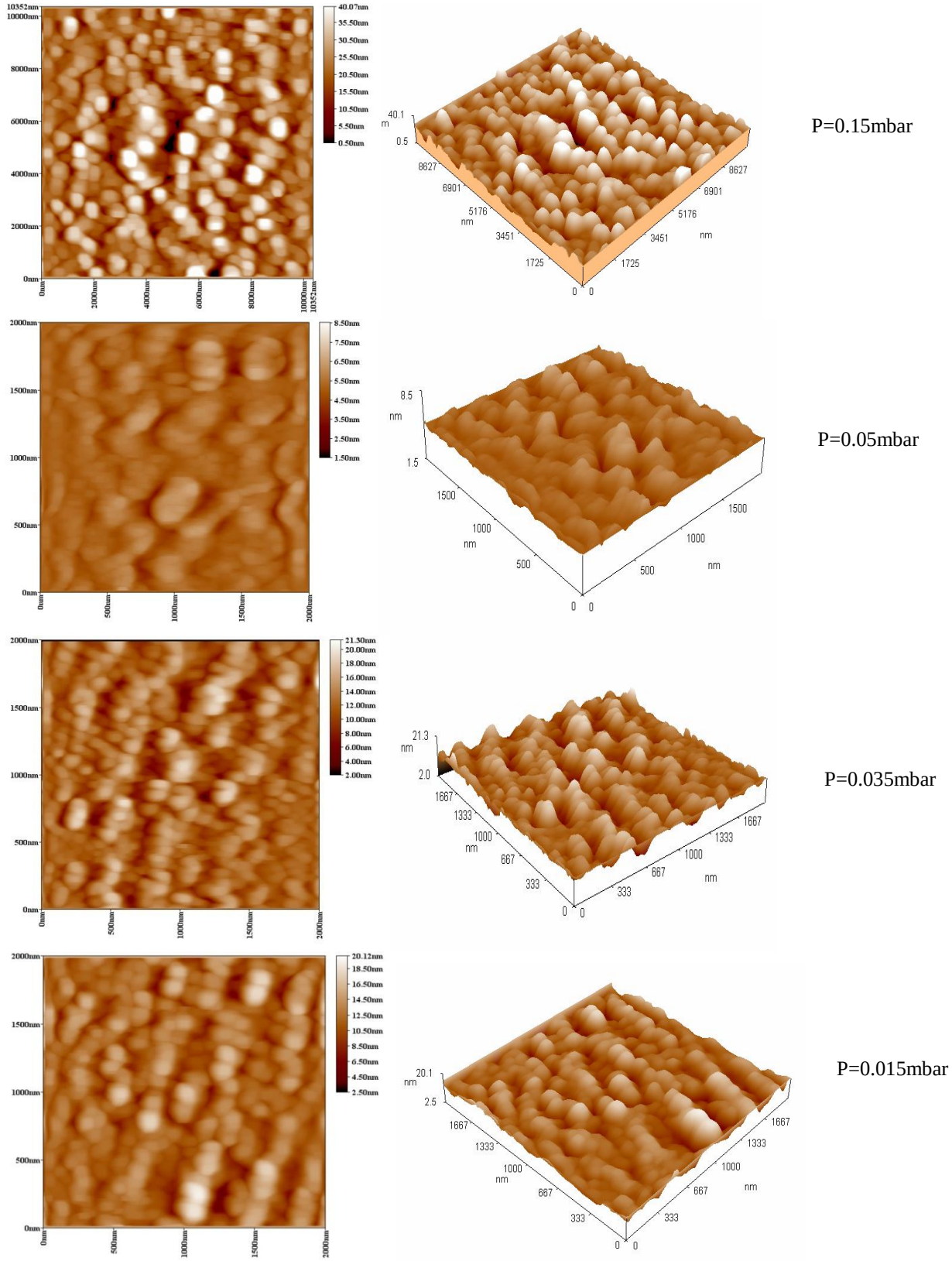

Fig. (2) The AFM images of SnO_2 thin films deposited on glass substrate for different applied pressure.

of the SnO_2 films deposited on glass substrates is more than 80% over the range 400 to 800 nm and is agreement with previous study (Chacko, S. et al., 2007). A sharp fall in transmission at about 310 nm is due to absorption edge of SnO_2 semiconductor films. The transparency of the films decreases in major portions of the visible range with the built-up thickness which is also clear from the fringes in the transmission spectra. The absorption edge also shifted slightly to higher wavelengths with the increase in applied pressure as shown in Fig. (3) and with increased argon to oxygen mixed flow as shown in Fig. (4). The transmittance falls rapidly in the low wavelength region.

With increase in film thickness, the onset of absorption edge becomes less sharp, this may be due to the presence of bigger crystalline sizes and increased scattering due to the surface roughness (Sahay, P. P. et al., 2007; Ray, S., and Gurdeep Singh, P.S., 2010).

The transmission increases but not systemically with the decreasing of applied pressure because of more atoms deposit on the film so more crystallinity and states will be available for the photons to be absorbed as shown in Fig. (3).

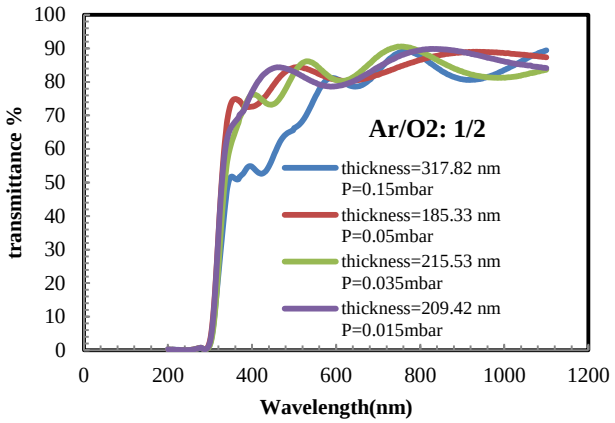

Fig. (3) Transmission spectrum as a function of wavelength for sputtering SnO_2 films at different working pressure.

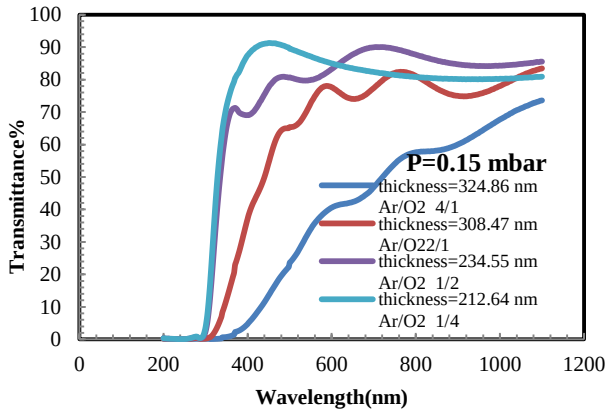

Fig. (4) Transmission spectrum as a function of wavelength for sputtering SnO_2 films at different Argon/Oxygen mixture ratio.

4. Conclusion

Reflections from the tetragonal crystallographic phase (cassiterite) of SnO_2 became more defined and progressively more intense and sharp for films with increase working pressures. In all samples randomly oriented tin oxide crystalline formation starts planes corresponding to (110), (101), (211) and (002) planes of SnO_2 for 2θ values of 26.51, 33.85, 51.69 and 57.93, respectively. The (110) is the dominant crystal structure of low-index crystal faces for this material due to its stability. This is the desired structure of SnO_2 for sensing applications since its prevalent (110) growth plane is extremely stable and can reject oxygen with little distortion. The granular films show higher surface area, which is conductive for film-gas interaction and results in higher gas sensitivity and the gas sensitivity has a proportional relationship with film roughness.

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