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 direct current (DC) reactive sputtering at gas pressures of 0.015 mbar – 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 the (110) plane. Due to AFM micrographs, the grain size increased non-uniformly as the working gas pressure increased.

Keywords: Sputtering, reactive sputtering, thin films, tin oxide

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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 [1–3]. 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 coated on silicon. In recent years, it has been investigated as an electrode for photoelectron chemical cells and for detectors of oxygen and hydrogen [4–8].

Reactive sputtering is widely used to prepare SnO_2 thin films. Generally, high flow 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 [9]. 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 [10].

In this work, the structural and optical properties of SnO_2 thin films prepared by the direct current (DC) reactive sputtering technique were studied at different working pressures in order to determine optimum conditions to use these SnO_2 thin films as gas sensors.

2. Experimental work

The plasma system was made of a stainless steel cylinder (inner diameter: 30cm, height: 34 cm), closed by stainless steel plates and sealed by o-rings. The electrodes and the metallic rods were encapsulated in the teflon shell so that only the

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electrode surfaces were in contact with the gas, and edge effects were avoided. The shells used to cover the electrodes had a circular open area of 78.5 cm^2, which was the effective surface area of the electrode in contact with the gas.

The electrodes were made of stainless steel of 15 mm in thickness and 100 mm in diameter. They included an internal channel to pass the cooling water coming from and going to a digital controlled cooling system. Both electrodes were kept at constant temperature (–150 ℃) to avoid the negative effects of increasing cathode temperature as well as decreasing anode temperature. Before each experiment, the electrodes were mechanically polished and chemically cleaned in dichloromethane. The pressure was controlled by a manual throttle valve mounted between the reactor and the pumping unit. The pumping system was composed of a rotary vane pump and a diffusion pump. The gas throughput was set at 150 cm^3/s by a gas flow-controller. Different gases were used for the experiment with the purity of 99.99%. Before each measurement, the reactor was brought to a base pressure of about 3×10^{-5} mbar. A high voltage DC-power supply was used for delivering 3 kV between two electrodes.

3. Result and discussion

Figure 1 shows the X-ray diffraction pattern for the deposited SnO_2 thin films prepared by DC reactive sputtering on the glass substrate for different working pressures (0.15 mbar to 0.015 mbar), and at argon/oxygen mixed flow (1/2), sputtering time was 60 min, the distance and biasing voltage between the anode and cathode were 5 cm and 4 kV, respectively. In all samples, randomly oriented tin oxide crystalline formation started in 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.

As proved by Fig. 1, the prepared films were textured, and the degree of texturing depends on the working pressure, therefore, the change in predominant orientation of crystallites formed the gas-sensitive matrix and confirmed the cassiterite structure of nanocrystalline SnO_2 [11]. 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 [12]. The growth of this plane helps in achieving high oxygen vacancy concentrations at low temperature.

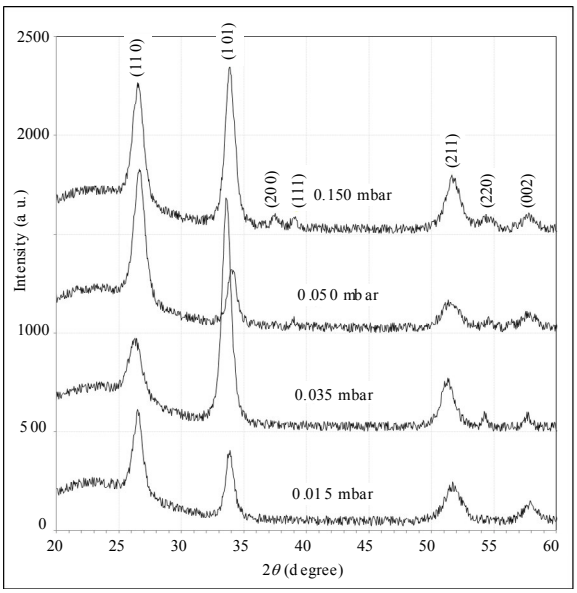

Fig. 1 XRD results of the sputtered SnO_2 thin films on glass substrates at different working pressures.

Two and three-dimensional atomic force microscopy (AFM) images of the as-deposited SnO_2 films at different discharge currents, working pressures, and Ar/O_2 flowing mixtures, are shown in Fig. 2. The average grain size (GS) 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 the higher surface area, which is conductive for film-gas interaction and results in the higher gas sensitivity [13]. The gas sensitivity has a proportional relationship with film roughness [14].

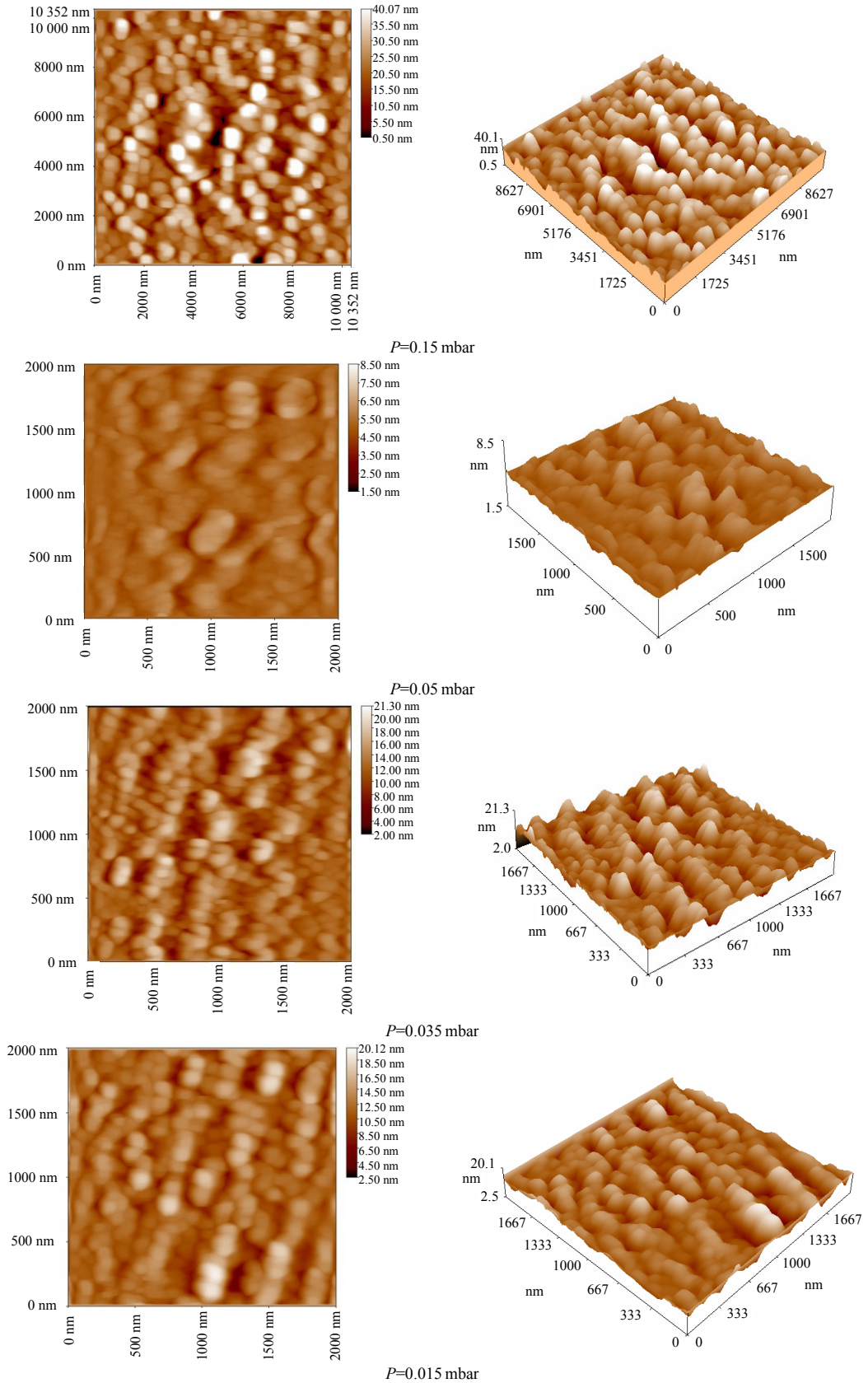

Fig. 2 AFM images of the sputtered SnO_2 thin films on glass substrates at different working pressures.

Table 1 AFM and SEM data images of SnO_2 thin films deposited on the glass substrate for different conditions.

Biasing voltage (kV)	Working pressure (mbar)	Argon/Oxygen mixture 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

Figure 2 shows that the grain size was decreased from 138.29 nm at the pressure of 0.15 mbar to 78.73 nm at the pressure of 0.035 mbar. At pressures lower than 0.035 mbar, the grain size was increased. The roughness was increased from 1.08 nm at 0.15 mbar to 1.85 nm at 0.035 mbar and decreased after that. The low-density plasma did not provide enough energy for the grains for renucleation that led to an increase in the average roughness and a decrease in the grain size.

From the absorption edge shown in Fig. 3, one can determine the optical energy gap, as shown in Table 2. The value of the optical energy gap changed as the working pressure did for all samples and increased as the ratio of argon to oxygen did, as shown in Fig. 3 and Table 2. The relatively small value of the band gap can be attributed to the high degree of non-stoichiometric disorders in the film. This indicates 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 [18].

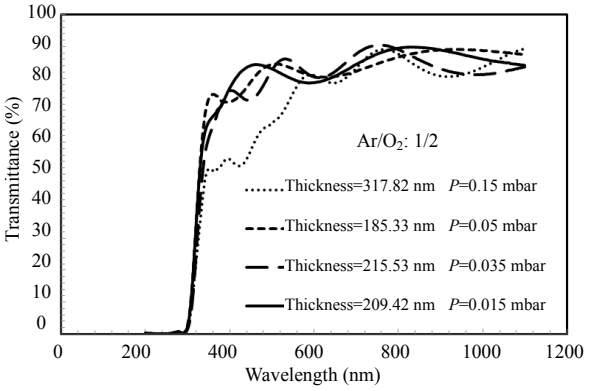

Fig. 3 Transmission spectra of the sputtered SnO_2 films at different working pressures.

Table 2 Parameters of SnO_2 films prepared at different sputtering working pressures and different Ar/O_2 mixing ratios.

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

The transmission spectra of SnO_2 thin films are shown in Fig. 3 as functions of the wavelength ranging in the region of 200 nm – 1100 nm. The presence of oscillations in these spectra was indicative of the good optical quality of the prepared films as they all were transparent, uniform, adherent to the substrate, and stable when kept in atmosphere for a long time. The average transmission of the SnO_2 films deposited on glass substrates was more than 80% over the range 400 nm – 800 nm and was in good agreement with the published studies [15]. A sharp fall in transmission at about 310 nm was due to the absorption edge of SnO_2 semiconducting films. The transparency of these films decreased in major portions of the visible range with the built-up thickness which was also clear from the fringes in the transmission spectra. The absorption edge also was shifted slightly to higher wavelengths with increasing the applied pressure as shown in Fig. 3. The transmittance rapidly fell at the short-wavelength region as the film thickness was increased, and the onset of the absorption edge became less sharp. This might be attributed to the presence of larger crystalline sizes and increased scattering due to surface roughness [16, 17].

The transmission increased in the non-symmetrical way with decreasing the pressure because more atoms deposited on the film, so more crystals and states would be available for the photons to be absorbed, as could be concluded from Fig. 3.

4. Conclusions

Tin oxide films were prepared by the DC reactive sputtering technique. The properties of the

prepared films were highly affected by the working gas pressure. High-quality and uniform nanocrystalline films were obtained at the working gas pressure of 0.035 mbar and the gas mixture (Ar/O_2) of 0.5 mbar. Results showed that the structure of SnO_2 films was polycrystalline with the tetragonal structure (rutile) with the preferential orientation in the (110) direction. As well, the results showed that SnO_2 surfaces were homogenous with columnar structures and the AFM analysis revealed porous morphology of spherical particles. From optical measurements, the transmission of the prepared films increased with a decreasing in the gas pressure, and the optical transition was direct.

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