

THE EFFECTS OF OXIDIZED TEMPERATURES ON MICROSTRUCTURES, ELECTRICAL AND GAS-SENSING PROPERTIES OF TIN OXIDE NANO THIN FILMS

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ABSTRACT

Nano thin films of tin oxide are synthesized by sputtering for gas sensors application. The fabrication includes of deposition tin metal thin films on thermally oxidized SiO₂ followed by thermal oxidation at 300°C, 400°C, 500°C and 600°C in air. The effect of oxidized temperatures on the morphologies; microstructure and gas sensing properties are investigated. Tin oxide tin films showed very high sensitivity to NO_x at ppm level. The nano thin film oxidized at 400 °C showed highest sensitivity compared to others.

I - INTRODUCTION

Tin oxide is a n-type semiconductor with band gap of 3.6 eV and has been used for gas sensors application due to its high sensitivity to oxidizing and reducing gases [1, 2]. The common method to synthesized thin film of tin oxide-based sensors is rheotaxial growth thermal oxidation (RGTO) technique [3]. In which, the synthesis includes of tin metal deposition followed by oxidation processes. The microstructure, atomic composition and electrical properties of tin oxide depend strongly on the oxidized temperature. The microstructure and atomic composition in turn affect on the gas sensing of thin film oxide. Although the thin films of tin oxide have been synthesized for gas sensors application but the relationship between the nanostructure, atomic composition, electrical and gas sensing properties have not been fully yet.

In this work, we study about the relation between oxidized temperature, nanostructure,

electrical conductivity and gas sensing properties of nano thin films tin oxide. The synthesis, characterization and NO_x sensing properties of nano thin film tin oxides are investigated and reported.

II - EXPERIMENT

Thin films of tin metal were deposited on thermally oxidized silicon substrates supported comb-type electrodes by using a dc sputter system. A two inches tin (99.99%) target was used for the deposition. The deposition conditions were: based pressure of 10⁻⁶ Torr, Ar working pressure 2x10⁻³ Torr, and plasma power of 10 watt. The tin thin films with thickness of 100 nm were deposited on the substrate using a shallow mask. The oxidation process was performed in air by using a tube furnace. In detail, the Sn thin films were placed in the center zone of a quart tube and then the temperatures were increased to oxidized temperature T_{ox} (300°C, 400°C, 500°C, and 600 °C) in 30 min, dwelled for 2h at T_{ox} and then

cooled to room temperature. The scanning electron microscopy (SEM), x-ray diffraction (XRD) and Raman spectroscopy were used to characterize the synthesized materials. Electrical and gas sensing properties of tin oxide thin films are measured by using a Keithley model 2400.

III - RESULTS AND DISCUSSION

1. Morphology and formation

The surface SEM image of as-deposited tin thin film is shown in Fig. 1 (a). The tin thin film was not smooth, continuous but porous with a granular size of about 300 nm (Fig. 1(a)). The cross sectional SEM image showed the film

thickness of ~100 nm (Fig. 1(b)). The formation of granular structure of thin film was due to the weak interaction between deposited tin atoms and substrate. The advantage of porous structure of tin oxide thin film is that it enhances the active surface area for sensor application. The surface SEM images of nano film tin oxide after oxidizing at 300°C, 400°C, 500°C, and 600°C are shown in Fig. 1(c-f), respectively. The morphologies of samples changed a little comparing to as-deposited film due to the melting of Sn and the oxidation (Fig. 1(c-f)). During the oxidization process, at the initial states the tin thin films were not oxidized yet, therefore it melted and formed some small nanoparticles attached on the surface of samples.

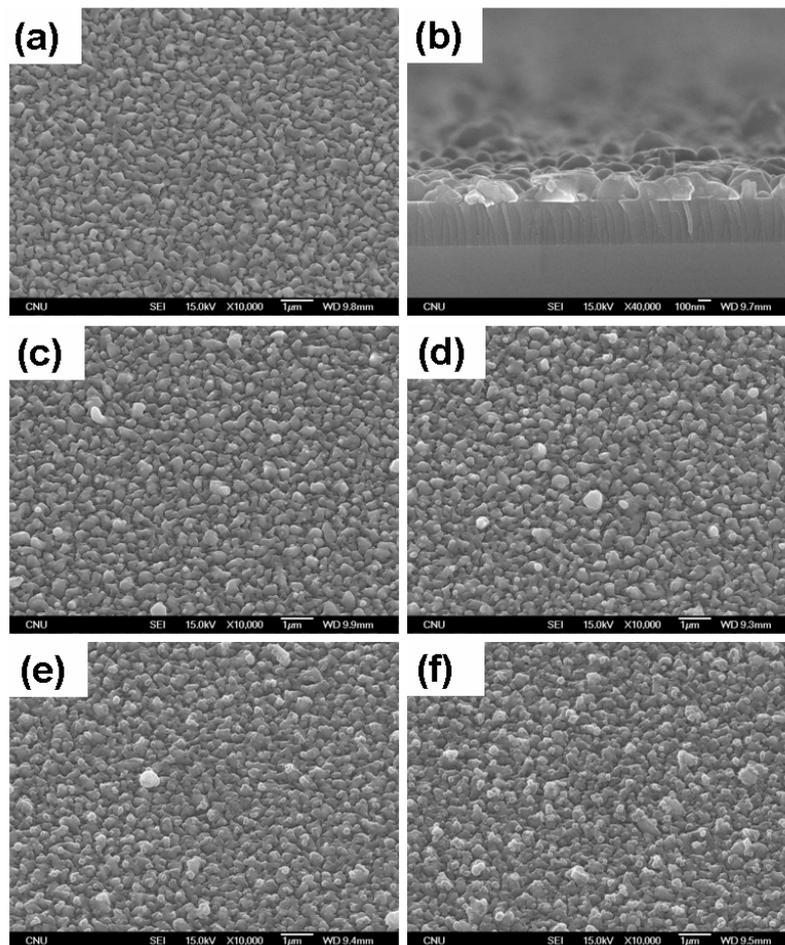


Fig. 1: SEM images of as-deposited tin thin film (a, b), and after oxidized at different temperatures, (c)-300°C, (d)-400°C, (e)-500°C, (f)-600°C

The dynamic oxidation process of tin oxide thin films can be evaluated by Raman spectra with variation of oxidized temperature as shown in Fig. 2. It was known that, after oxidation process, the metallic tin (Sn) thin film can be oxidized in to tin monoxide (SnO) and/or tin dioxide (SnO₂) depending on oxidized temperature. The Raman spectrum of thin film oxidized at 300°C shows two strong Raman modes at 112 and 210 cm⁻¹. Those Raman modes belong to SnO as reported in ref. [4]. If increasing the oxidized temperature to 400°C the intensity of Raman modes at 112 and 210 cm⁻¹ decreased and appeared some new Raman modes at 315, 350 and 370 cm⁻¹ belonging to the acoustic modes of SnO₂ [5]. Raman spectrum of sample oxidized at 500°C showed some more new modes at 140 cm⁻¹ and 170 cm⁻¹ ascribing to non-stoichiometric tin dioxide SnO_{2-δ}. When the oxidation temperature increased to 600°C, the Raman modes in the low

wavelength region decreased and disappeared suggesting a reaction towards SnO₂.

XRD patterns of nano thin films oxidized at different temperatures are shown in Fig. 3. The XRD pattern of thin film oxidized at 300°C showed the diffraction peaks of both tetragonal structure of Sn (JCPDS file No. 86-2265) and SnO (JCPDS file No. 06-0395). The relative intensity ratio of SnO peaks is higher than Sn peaks indicates larger phase percent of SnO comparing to Sn. After oxidized at 400°C, the XRD showed only peaks of tin monoxide. At higher oxidized temperatures of 500, 600°C, the XRD showed the diffraction peaks of orthorhombic structure SnO₂ (JCPDS file No. 78-1063). The XRD data are well agreement with Raman data. The results indicated the tin thin film was first oxidized in to tin monoxide (SnO) and then into tin dioxide (SnO₂) according to the equations: $\text{Sn} + 1/2\text{O}_2 = \text{SnO}$, $\text{SnO} + 1/2\text{O}_2 = \text{SnO}_2$.

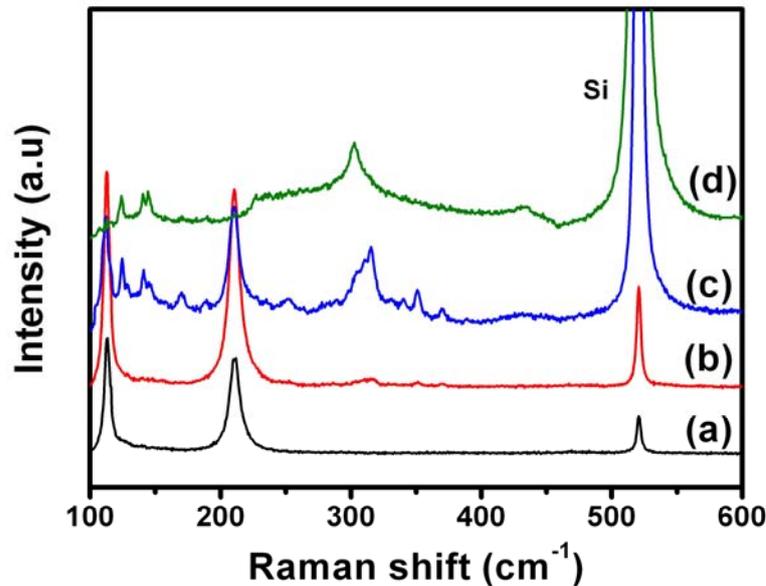


Fig. 2: Raman spectra of tin oxide thin films oxidized at different temperature, (a)-300°C, (b)-400°C, (c)-500°C, (d)-600°C

2. Electrical and gas sensing properties

The sensing properties of tin oxide thin films oxidized at different temperature to 60 ppm NO_x were measured at room temperature;

data were shown in Fig. 4. The initial resistances of sensors were 16400, 1080, 350, 255Ω for thin films oxidized at 300, 400, 500, and 600°C, respectively. The electrical

resistance of sensors increased rapidly when exposures to NO_x . It was interesting that the nano thin films tin oxide could detect the NO_x at room temperature. Tin oxide is known as an n-type semiconductor due to the vacancy of oxygen in crystal structure whereas the NO_x is oxidizing agent. When NO_x molecule adsorbs on the surface of tin oxide it captures electrons from the SnO_2 , decreases the carrier number resulting in increase the electrical resistance of

sensors [6]. The sensor response defined as $S=100(R_g-R_o)/R_o$, where R_g and R_o are resistances of sensor in NO_x and air, respectively. The sensor response was 187%, 449%, 6.7%, 10.7% for sample oxidized at 300°C, 400°C, 500°C and 600°C, respectively. The results showed that, the sensor response was highest for sample oxidized at 400°C and smaller for others oxidized at higher temperatures.

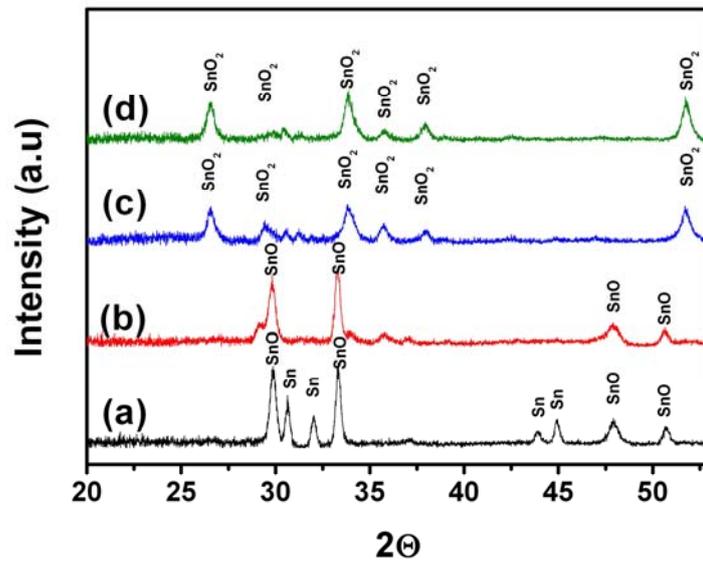


Fig. 3: XRD patterns of tin oxide thin films oxidized at different temperatures, (a)-300°C, (b)-400°C, (c)-500 °C, (d)-600°C

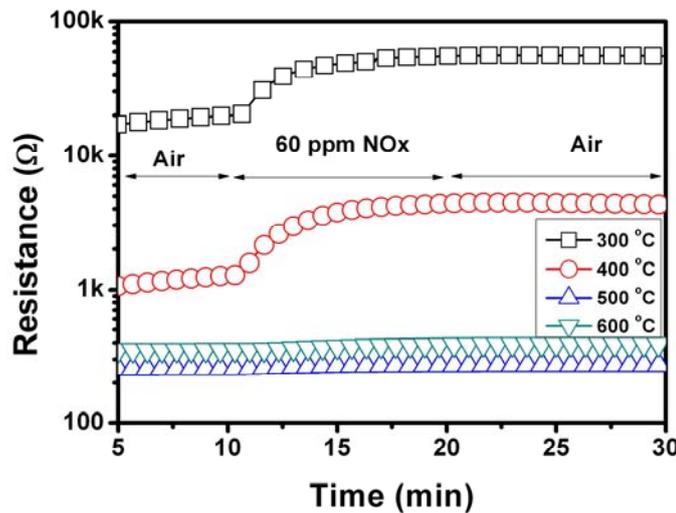


Fig. 4: The changes in electrical resistances of tin oxide thin films oxidized at different temperatures upon exposures to 60 ppm NO_x measured at room temperature

IV - CONCLUSION

In conclusion, the effects of oxidized temperatures on microstructure, electrical and gas sensing properties of tin oxide nano thin film was investigated and reported. The tin metal was oxidized into tin monoxide SnO at temperature of 300°C and then tin dioxide SnO₂ at temperature of 400°C and higher. Nano thin film tin oxide showed increase in electrical resistance upon exposure to NO_x. The thin film oxidized at 400°C showed highest response to NO_x. The results indicated that the gas sensing properties of tin oxide thin films not only depend on the active surface area but also depend on their initial resistances.

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