

Deposition and gas sensing properties of tin oxide thin films by inductively coupled plasma chemical vapor deposition

Y. C. Lee · O. K. Tan · H. Huang · M. S. Tse

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Abstract Tin oxide thin films have been deposited by a custom-designed inductively coupled plasma chemical vapor deposition (ICP-CVD) system in order to explore its application as an alternative approach for thin film gas sensor preparation. The as-deposited SnO₂ films were of polycrystalline structure with nano-size grains of 12 nm. The SnO₂ films exhibited a maximum sensitivity of 43 to 1000 ppm H₂ at an optimum operating temperature of 350°C. The response time of the SnO₂ films was 12 s and full recovery was achievable.

Keywords Tin oxide · Gas sensing · Chemical vapor deposition

1 Introduction

Since the demonstration of tin oxide (SnO₂) as a gas sensor device based on electrical resistance change in different environments by Taguchi [1] in the 1970s, the SnO₂ has attracted increasing attention on gas sensing applications due to its suitable physicochemical properties such as high stability, high reactivity to reducing gases at relatively low operating temperature, and possibility to improve sensitivity through the introduction of different metal dopings [2]. The recent decades has seen the progressive development from the early form of bulk SnO₂ ceramic to thin film type gas sensors owing to the trend of miniaturization in electronic components. The utilization of silicon manufacturing technology in the fabrication of gas sensors is promising to achieve small

size, low cost, low power consumption, high reproducibility and multi-sensor gas detection systems. Recent literatures reported the integrated micro gas sensor arrays with pattern recognition aiming to improve the selectivity of the gas sensors [3], where the realization of a gas sensor array that can detect multiple gases of interest has become a major focus of research. This signifies the increasing importance of thin film type gas sensors in the field of chemical gas sensing.

Various processing techniques have been successfully utilized to prepare SnO₂ thin films, including radio frequency sputtering [4], pulsed laser deposition [5], sol-gel process [6], electron beam evaporation [7], spray pyrolysis [8] and PECVD [9]. In this work, the inductively coupled plasma chemical vapor deposition (ICP-CVD) technique was utilized to prepare SnO₂ thin films. The ICP-CVD technique is suitable for thin films deposition due to its advantages in independent control of ion bombardment energy that can produce different film microstructures on the substrate, high density of ions that translates to the efficient use of feedstock gases for deposition process, and low deposition temperature made possible by the plasma dissociation of reactants. The ICP-CVD technique has been applied in IC manufacturing for high aspect ratio dielectric gap filling of submicron device fabrication [10] but in the field of gas sensors, the gas sensing layers are seldom prepared by the ICP-CVD technique. It was therefore the aim of this study to explore its possibility as an alternative approach in the preparation of thin film type gas sensing materials. In this paper, the preparation of SnO₂ thin films by ICP-CVD, together with their respective gas sensing properties are presented.

2 Experimental

The setup used to deposit SnO₂ thin films is a custom designed cold wall, horizontal ICP-CVD system and the

Y. C. Lee (✉) · O. K. Tan · H. Huang · M. S. Tse
Microelectronics Center, School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
e-mail: eyclee@ntu.edu.sg

Table 1 Typical deposition parameters for SnO₂ thin films

Substrate material	SiO ₂ /Si wafer
Precursor source	(C ₄ H ₉) ₂ Sn(OOCCH ₃) ₂
Precursor source temperature	90°C
Carrier gas (Ar) flow rate	50 sccm
O ₂ flow rate	50 sccm
Substrate temperature	600°C
RF power	1200 W
Deposition pressure	90 mTorr

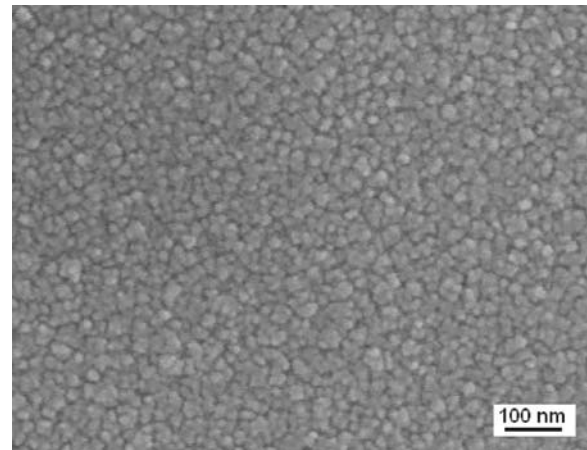
details of the setup have been described elsewhere [11]. The ICP plasma was ignited in a quartz tube wound externally with a copper band powered with a 13.56 MHz, 2 kW rf generator with an automatic matching network. Dibutyltin diacetate, (Fluka, 98% purity), (C₄H₉)₂Sn(OOCCH₃)₂, was used as the precursor source. The precursor source was maintained at 90°C and its vapor was transported into the chamber using Ar as the carrier gas. The precursor vapor was introduced downstream of the plasma while O₂ was admitted into the plasma for pre-activation. The flow rate of both Ar carrier gas and O₂ was controlled by MKS electronic mass flow controllers (MFCs). The chamber pressure was monitored by a MKS Baraton pressure gauge and pressure control was achieved with a MKS throttle valve. The detailed deposition parameters used are summarized in Table 1.

The structural properties of the SnO₂ films were characterized by a Rigaku RINT 2000 X-ray diffractometer (XRD) with Cu K_α radiation. A Leo 1550 field emission scanning electron microscopy (FESEM) was used to observe the microstructure of the films. Interdigitated Au electrodes were deposited on the film surface by electron beam evaporation to make the gas sensing device. The gas sensing properties were characterized using a Keithley 236 source measurement unit connected in a home-designed gas sensing characterization system programmed using the National Instruments Labview. The MKS MFCs were used to control the concentration of the test gas, H₂, and the carrier gas, synthetic air, in the chamber. The heating rate and the operating temperature of the tested sensor devices were controlled by a Linkam TMS 93 temperature controller.

3 Results and discussion

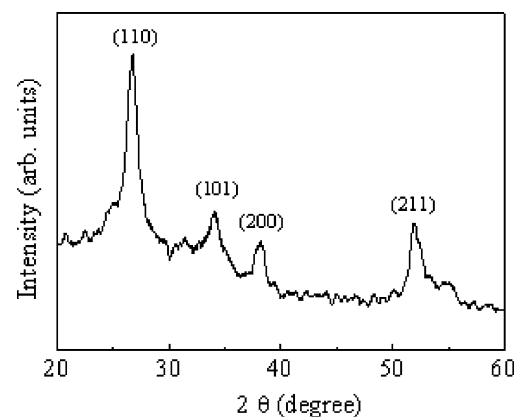
Figure 1 shows SEM micrograph of the SnO₂ thin film deposited at 600°C. The grains were uniformly distributed across the film surface and clearly in the nano-size regime (<100 nm). The nano-size grains have been shown to enhance the gas sensing properties of SnO₂ thin films due to the near fully depleted charge carrier grains that enables the control of surface conduction at grain level [12, 13].

The X-ray diffraction pattern of the as-deposited SnO₂ film is given in Fig. 2. All the major XRD peaks can be

**Fig. 1** SEM micrograph of the SnO₂ thin films prepared at 600°C

indexed by (110), (101) and (211) planes of cassiterite SnO₂ with tetragonal rutile structure. No other phases such as SnO, Sn₂O₃, or Sn₃O₄ were detected in the film indicating a stoichiometric SnO₂ composition was obtained. The as-deposited SnO₂ film showed a (110) preferential orientation, which was different from the (101) preferential orientation reported by us in the SnO₂ thin films prepared by PECVD using the same system [14]. The difference in the preferential orientation was believed to be attributed to the different roles of plasma during deposition. In this work, only O₂ was activated by the plasma with precursor vapor introduced at the downstream of plasma while both reactants were activated by the plasma in PECVD. The average grain size calculated using Scherrer's equation was 12 nm corresponding well with the observed SEM micrograph in Fig. 1.

Figure 3 shows the relative resistance vs. operating temperature of the SnO₂ thin film gas sensor. The testing gas was 1000 ppm H₂ in dry air. The relative resistance is defined as the resistance ratio $R_{\text{air}}/R_{\text{gas}}$ for the gas, where R_{air} and R_{gas} are the electrical resistances of the sensor in air and in gas, respectively. The relative resistance is also referred as

**Fig. 2** XRD patterns of the as-deposited SnO₂ thin film

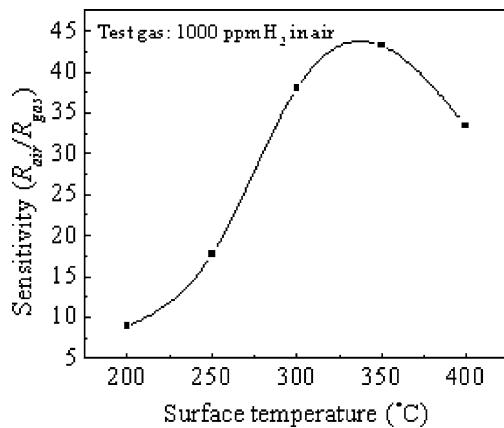


Fig. 3 H₂ sensitivity vs operating temperature of the SnO₂ thin film

the sensitivity of the gas sensor. For the ICP-CVD derived SnO₂ thin film gas sensor, the highest sensitivity, which was 43.3, was found at an operating temperature of 350°C. A further increase in operating temperature showed a decrease in sensitivity. This behavior can be explained in analogy with the mechanisms of gas adsorption and desorption on SnO₂ [15]. An *n*-type metal oxide can absorb oxygen from the atmosphere both in the O₂⁻ and in the O⁻ species. The adsorption of O⁻ is the most interesting process in gas sensors because this oxygen ion is the more reactive and thus makes the material more sensitive to the presence of reducing agents. At relatively low temperature, the surface preferentially adsorbs O₂⁻ and the sensitivity of the material is consequently very small. As the temperature increases, the dominant process becomes the adsorption of O⁻, then the sensitivity of the materials increases too. If the temperature increases too much, progressive desorption of all oxygen ionic species previously adsorbed occurs and the sensitivity decreases [16].

Figure 4 is the response curve of the SnO₂ thin film for three successive cycles of step change in composition from air to 1000 ppm H₂ in air at the optimized operating temperature of 350°C. The response time, i.e., the time needed by the

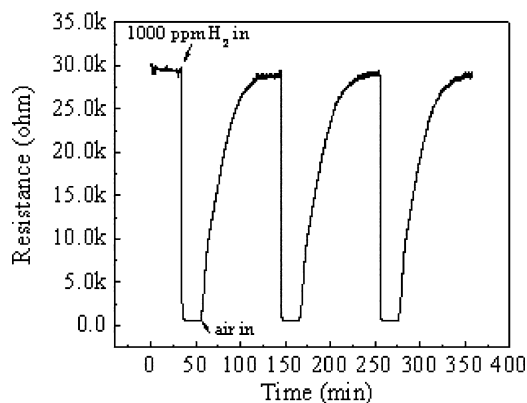


Fig. 4 Response curve of SnO₂ thin film to 1000 ppm H₂ at 350°C

sensor's resistance to undergo a 90% variation with respect to its equilibrium value following a step increase in the test gas concentration, was found to be 12 s. The recovery time, defined as the time taken by the sensor's resistance to return to 10% below its equilibrium value in air following the removal of test gas was 40 min for our prepared SnO₂ thin film. The fast response time is a desirable characteristic demanded in real situations while the recovery of the sensor is important to ensure that the sensor can be restored to the standard conditions and thus make it reusable. The ICP-CVD derived SnO₂ thin films have been shown to fulfill both requirements for gas sensing application.

4 Conclusions

Tin oxide thin films have been successfully prepared using the ICP-CVD technique. The films were comprised of uniform granular grains with an average grain size of 12 nm. The sensitivity of the SnO₂ thin film achieved its maximum of 43 to 1000 ppm H₂ at 350°C. The response time of the thin film was 12 s and could achieve full recovery to its equilibrium resistance value in air upon the removal of test gas.

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