The growth and gas sensing properties of Al-Zn codoped SnO_2 via Solid-State Chemical Vapor Deposition

L.S. Chuah

***Abstract*— Solid state chemical vapor deposition (SSCVD) is a beneficial approach for the synthesis of films, contributing the choice of yielding good quality films, larger area uniformity, and availability of various ambient in situ doping processes. Al-Zn co-doped SnO_2 films have been synthesized on p-type silicon (100) substrates by solid-source chemical vapor deposition using $SnCl_2.2(H_2O)$, $AlCl_3$ and $Zn(O_2CCH_3)_2(H_2O)_2$ as the precursor. To the best of our knowledge, this is the first time that Al-Zn co-doped SnO_2 films grown by SSCVD have been reported. The XRD patterns of nanostructured films reveal the crystalline behavior and are tetragonal structure. Observations of the microstructure of undoped SnO_2 and Al-Zn doped SnO_2 were performed by scanning electron microscopy (SEM). Results reveal that Al-Zn co-doped SnO_2 films have improved gas sensing achievement in distinguishing with undoped SnO_2 materials. The gas sensing mechanism of Al-Zn co-doped SnO_2 films was also studied.**

***Index Terms*— gas sensor; Al-Zn codoped; SnO2; thin film; Si**

I. INTRODUCTION

Tin oxide (SnO_2) is an n-type metal oxide with a wide energy (3.6 eV) bandgap, which has been intensively investigated for the detection various toxic gases for example H_2, CO, CH_4, NO, and ethanol [1-3]. For the purpose of develop the gas sensing properties of the sensors, numerous studies have been concentrated on the apply of the thin catalytic metal layer, generally group VIII transition metals such as for example platinum (Pt), silver (Ag), and palladium (Pd) [4-6].

Hydrogen gas has historically been applied as a reducing agents in metallurgy and as a courier gas in semiconductor producing manner. A hydrogen gas leaks simply from gas lines and systems and is one of the most flammable gases. In consequence, a high safety, for example extended essential, faster response time, durability, small humidity dependence and long term immovability, is essential in discovery of hydrogen. Hydrogen has a high chemical activity and the smallest molecular size among reducing gases, so that struggles were formed to capture the selectivity to hydrogen by applying the molecular sieve effect [7-9]. So to distinguish H_2 at these levels, high accuracy sensors which can identify a leak of 0.5% - 4 % are required. The level of leak tolerability alters with regard to the utilization. Doping is basic to restraint the characteristics of the semiconductors and to get new multifunctional materials. In this paper, we will present the development of the sensor and microstructural characteristics of the undoped and Al-Zn codoped SnO_2 grown onto the Si substrates using solid state chemical vapor deposition (SSCVD) method. The hydrogen gas sensing performance for an operating temperature in 200°C has been studied.

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II. EXPERIMENTAL

Al-Zn co-doped SnO_2 films have been synthesized on p-type silicon (100) substrate by solid-source chemical vapor deposition. $SnCl_2.2(H_2O)$, $AlCl_3$, $Zn(O_2CCH_3)_2(H_2O)_2$ were used as the precursor and air from atmospheric as the oxygen source. The boat were loaded into a furnace (as shown in Fig. 1). The source temperature and substrate temperature fixed at 430°C. The deposition time was 3 min. After the furnace cooled down to room temperature naturally, silicon substrates were removed for inspection.

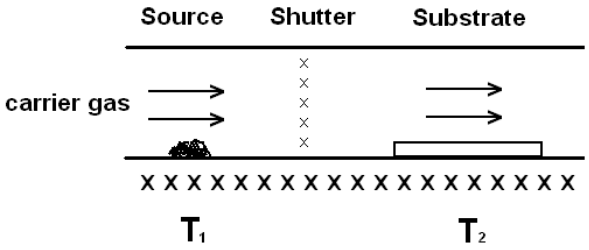

Fig. 1. Schematic diagram of the horizontal furnace.

The surface morphology of samples was studied utilizing a scanning electron microscope operating at low voltage (15kV) to minimize charging effects. SEM digitized micrographs were obtained with a magnification 30,000 X. The structural properties of the as-grown Al-Zn co-doped SnO_2 films were investigated by X-ray diffraction (XRD) with Cu Kα radiation. A platinum (Pt) metal was deposited on the Al-Zn co-doped SnO_2 by sputtering.

The gas sensing properties of the sensors were studied in a test chamber that allows the heating of their substrate (operating temperatures in the 200 °C were studied). Additionally the sensors were evaluated for their response in dry air and humid air (60-70 % humidity). For the measurement of electrical properties, the current-voltage (*I-V*) characteristics were measured by using high-voltage source/measure unit. The applied voltage was varied from 0 to 6 V. The current was measured 2 s after applying the voltage.

III. RESULT

The XRD patterns of the undoped SnO_2 thin films (Figure 2a) reveal reflection from the (110), (101), (200), (211) and (301) planes of SnO_2 for 2θ values of 26.7°, 34.0°, 38.1°, 51.9° and 65.4°, respectively. The Al-Zn co-doped SnO_2 films

displayed polycrystalline tetragonal structure. For the Al-Zn co-doped SnO_2 films, in XRD pattern, insignificant minimization in magnitude of the SnO_2 peaks are perceived.

For estimate the particle size of the deposited films, the Debye-Scherrer formula was used on the XRD pattern of the undoped and doped SnO_2 thin films which is given as $d = (0.9\lambda / \beta \cos \theta)$ where, λ is the wavelength of the X-ray employed which in this case is 0.15418 nm for Cu-kα. β is the FWHM (full width at half maximum) and θ is the usual Bragg's angle (deg). Estimating 'd' from the premium two XRD patterns, it has been detected that the mean particle thickness of the prepared undoped and doped films is about 38.1 nm and 37.9 nm, respectively.

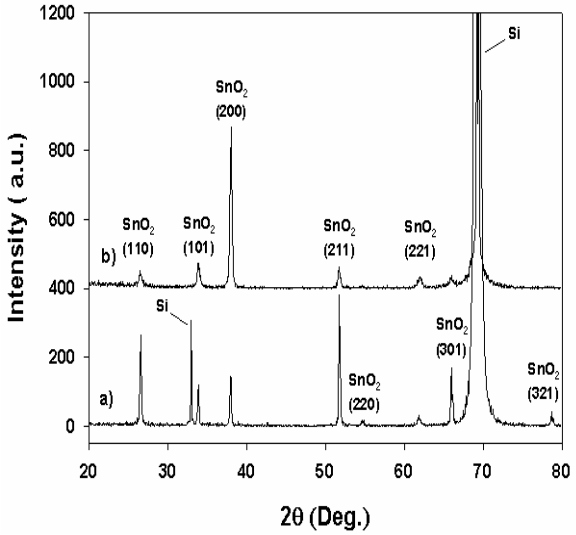

Fig. 2. X-ray diffraction patterns of the SnO_2 films. (a) undoped SnO_2 film. (b) Al-Zn co-doped SnO_2.

Surface morphologies gained throughout Scanning Electron Microscope (SEM) of undoped and Al-Zn co-doped SnO_2 films are revealed in Figure 3. The Figure 3b shows a comparatively smoother film surface for Al-Zn co-doped SnO_2 films. Figure 4 shows the dynamic response of the gas sensor device at 200 °C. The sensor was biased at 1.09 x 10^{-4} A constant current. The initial current was approximately 11.9 x 10^{-5}A. After the purge H_2 was introduced in the chamber at measured amounts. The total flow rate was maintained at 2 L min^{-1}.

The voltage applied here was 0.1 V. H_2 is previous to touch the surface but when its purged it's supposed to remove all the H_2 off the surface, but we noticed that there is some residue left on the surface and that doesn't let the sensor to reach the exactly same response as the before cycle. The change in the signal is not linearly proportional to the amount of H_2. The initial drop in current can only be explained by the possession of contaminants on the surface. As shown by the characteristics of Figure 4, the gas sensor shows a fast response and short recovery time. Spread of hydrogen over the Pt layer is probable not the restrict element in the improving of the device properties, as the device react very quickly when H_2 is introduced into the furnace tube, pointed that diffusion through the Pt layer is immediately.

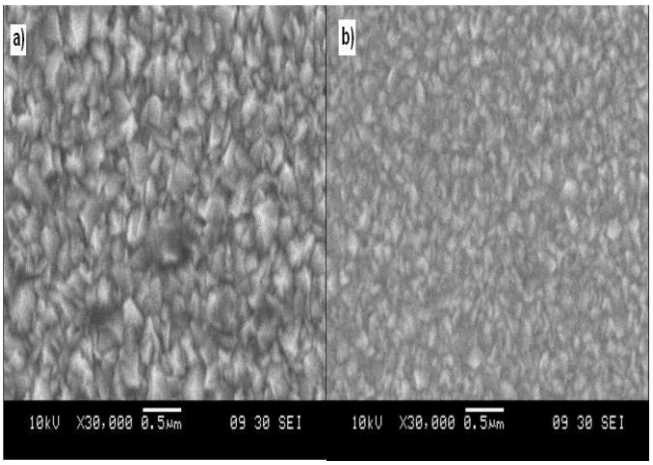

Fig. 3. SEM images of SnO_2 thin films: (a) undoped SnO_2, (b) Al-Zn co-doped SnO_2.

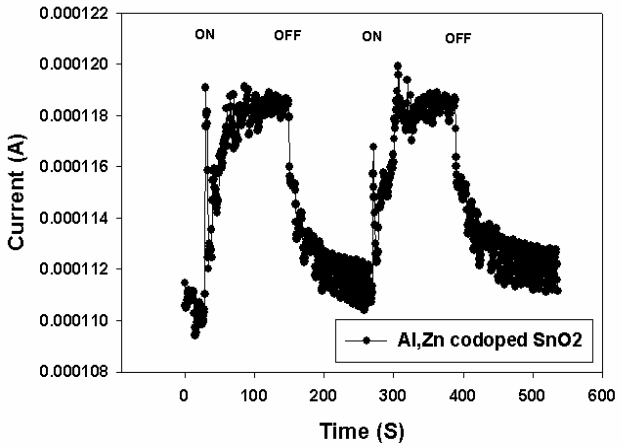

Fig. 4. Response of forward bias voltage for Al-Zn co-doped SnO_2 films to H_2 in 200°C.

Figure 5 exhibits the change in undoped SnO_2 gas sensor at operating temperature of 200 °C as a function of time. The device current changed abruptly when the hydrogen was introduced into the furnace tube. Over the next 20 min, the current decreased, slowly recovering from the H_2 exposure. The removal of hydrogen from the samples could be delayed if hydrogen were incorporated into the SnO_2.

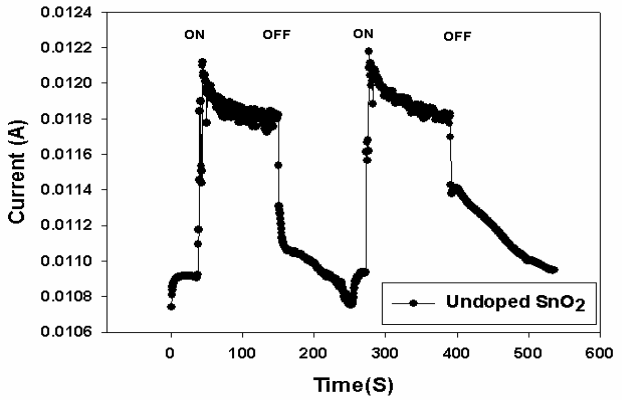

Fig. 5. Response of undoped SnO_2 films to H_2 in 200°C.

IV. Conclusion

In summary, Al-Zn codoped SnO_2 films have been synthesized on silicon substrates by SS-CVD with the substrate temperature of 430°C. It was found that the nanocrystalline SnO_2 grains possesses structure features of the tetragonal rutile structure. Conclusions symbolize that Al-Zn co-doped SnO_2 architectures are highly promising for gas sensor utilizations.

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