Detecting CH_4 and CO Gases Using Micro-Structural Doping Compound Oxide Films on Si-Substrates

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ABSTRACT

The gas-sensing films used in commercial gas sensors are deposited on an insulating Al_2O_3-substrate. In order to improve the gas sensing properties such as the selectivity to CH_4 and CO, long-term thermal stability, low power consumption and consistency, the micro-structural doping compound oxide gas sensing films (Ti/SnO_2) on Si-substrates have been deposited by using the radio frequency magnetron co-sputtering technique with composite target and annealed at high temperature. The gas sensing materials structure, size and image are examined by XRD and SEM, respectively. This paper presents the effect of gas sensing film characteristics on gas sensing properties. A significant effort is devoted to exploring reactive mechanism between Si-based microstructure doping compound oxide gas sensing materials and CH_4/CO based on the study of microstructure, the chemical composition of the gas sensing material ion store layer and the ion conduction layer and interface condition between them.

Keywords: sensor, chemical, gas, film

1 INTRODUCTION

CH_4 is flammable and explosive gas, and is the primary component of firedamp, natural gas and various liquid fuels. The burst lower level of CH_4 is 4.9% in the air. CO is a poisonous gas in small concentration. A concentration of 0.1% in the air is toxic to people. Exposure to CO concentrations higher than 1% is fatal. Therefore detecting CH_4 and CO gases is very important to insuring safety.

Kugishima *et. al* [1] deposited La_2O_3/SnO_2 thick films gas sensor. The results showed that compared with un-doped SnO_2, films resistance and sensitivity increased several magnitudes when La_2O_3 concentration attained to 5%. Akbar *et. al* [2] deposited TiO_2-SnO_2 compound oxide gas-sensing fiber. They found that the gas-sensing material had good gas-sensing properties to H_2. Chakraborty *et. al* [3] prepared SnO_2/Fe_2O_3 gas sensing sensor using PEVCD. The gas sensor can improve selectivity to CH_4 and CO via temperature modulation.

Preparation of doping compound oxide gas-sensing films and selectivity and stability to CH_4/CO has already become an international topic. However, most gas-sensing films have been deposited on an insulating Al_2O_3 –substrate up to now. Our work is to deposit gas-sensing films on Si-substrate, study the gas-sensing properties of the compound oxide system and explore the effect of Si-substrate on gas-sensing reaction. Our focus is to realize a controllable experimental process for depositing microstructure doping compound oxide gas-sensing films on Si-substrates which have low power consumption, high stability and high selectivity to CH_4/CO.

In this paper, Ti/SnO_2 films were prepared on Si substrates by the radio frequency co-reactive magnetron sputtering technique. The effects of doping levels on the crystal structure, surface morphology and gas sensing properties of Ti/SnO_2 films were studied.

2 EXPERIMENTS

Ti-doped SnO_2 (Ti/SnO_2) films were prepared on p-type silicon (100) wafers by using the radio frequency co-reactive magnetron sputtering technique. The Si substrates were ultrasonically cleaned in acetone and rinsed in deionized water. In order to adjust the Ti concentration in the deposited Ti/SnO_2 film, the relative sputtering area of Ti-chips, were attached on an Sn target (99.99% purity, 60 mm in diameter), was varied in the range of 0–5%. The sputtering area of Ti-chips was varied to control the concentrations of Ti impurities in the SnO_2 films. The films prepared without using Ti-chip, and with the Ti-chip covering about 2% and 5% of the effective sputtering area are denoted as sample A, B, and C, respectively. The target-to-substrate distance was 50 mm. High-purity argon and oxygen were used as the sputtering and reactive gas, respectively. The base pressure for the system was 2×10^{-4} Pa and film growth was carried out in the growth ambient with Ar: O_2 is 15:10 sccm at a working pressure of 1.0 Pa. Ti/SnO_2 films were deposited on substrates heated at 300 ℃ with RF power of 100 W used during sputtering for 2 h (The thickness of the films was about 400nm). All the films annealed at an air at temperature of 600 ℃ for 1.5 h in order to produce structurally stable materials ready for gas detection measurements between room temperature and 350 ℃.

The crystal structures were studied by using x-ray diffraction (XRD, D/Max-2400). The films surface

morphology was characterized by scanning electron microscopy (SEM, JSM-6701F).

3 RESULTS

The crystal structure, surface morphology, and experimental condition analysis are presented in this section.

3.1 Crystal Structure & Surface Morphology

Fig. 1 shows the XRD patterns of (a) pure SnO_2, (b) 2% Ti-doped SnO_2 and (c) 5% Ti-doped SnO_2. All patterns exhibit peaks corresponding to the rutile structure of polycrystalline SnO_2 films with the maximum intensity peak from (110) planes. SnO_2 (110) diffraction peak values of the three samples were 26.42°, 26.52° and 26.48° respectively. It also shows that the crystalline structure of SnO_2 is developed with the Ti concentrations increasing (Sample B), and then decreased as the Ti concentration further increased (Sample C). However, no XRD peak for Ti is observed in the XRD patterns, indicating that Ti gets incorporated into the tin oxide lattice.

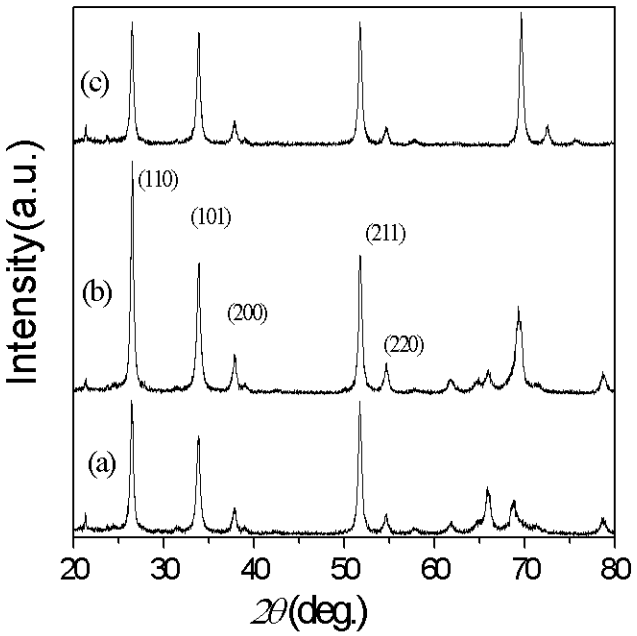

Figure 1: XRD spectra of the samples: (a) pure SnO_2; (b) 2% Ti/SnO_2; (c) 5% Ti/SnO_2.

The average particle size was of the order of around 80 nm, when calculated from the X-ray diffraction patterns using Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where λ, θ and β are the X-ray wavelength (1.5406 Å), diffraction angle and FWHM of the SnO_2 (110) peak.

The lattice constant 'a' of the samples was 0.6722, 0.6727 and 0.6742 nm, respectively, which could be calculated by Bragg formula: $\lambda = 2d\sin\theta$, where 'd' denotes the crystalline plane distance for indices (hkl). The lattice constants 'a' can be calculated by the following formula [8]:

$$d_{hkl}^{\ 2} = \left[\frac{4(h^2+k^2+hk)}{3a^2} + \frac{l^2}{c^2}\right]^{-1} \qquad (2)$$

Where 'a' and 'c' are the lattice constants, and d_{hkl} is the crystalline plane distance for indices (hkl). According to Eq. (2), the lattice constant 'a' is equal to 2d for the (110) diffraction peak.

Fig. 2 shows the scanning electron microscopy images of the samples: (a) pure SnO_2; (b) 2% Ti/SnO_2; (c) 5% Ti/SnO_2.

It is notable that all particles are uniform in shape (hexagonal) and particle size; the average diameter of the particles is about 100 nm estimated from the SEM image, and the rod-like product may be TiO_2 particles. The typical SEM image in Fig. 2 (c) shows that the product consists of a large number of hexagonal-shaped particles and a small number of nanorods. The rod-like products (may be TiO_2) uniformly presented on the Ti/SnO_2 surface. On the other hand, a comparatively smaller crystallite size can be effectively obtained by addition of Ti as crystallite growth inhibitor (Sample B and C). The possible reason is that incorporation of TiO_2 as a secondary component had a dramatic effect on the thermal stability of SnO_2, because the TiO_2 acted as a barrier against the advancement of grain boundaries of SnO_2 and effectively prevented the grain growth.

3.5 Experimental Condition Analysis

The gas-sensing films used in commercial gas sensors are deposited on insulating Al_2O_3-substrates. In order to improve the gas sensing properties such as the selectivity to CH_4 and CO, long-term thermal stability, low power consumption and consistency, our group has deposited gas-sensing films on Si-substrate. At present, a large effort is devoted to explore reactive mechanisms between Si-based microstructure doping compound oxide gas sensing material and CH_4/CO based on the study of microstructure, chemical composition of gas sensing material ion store layer and ion conduction layer and interface condition between them.

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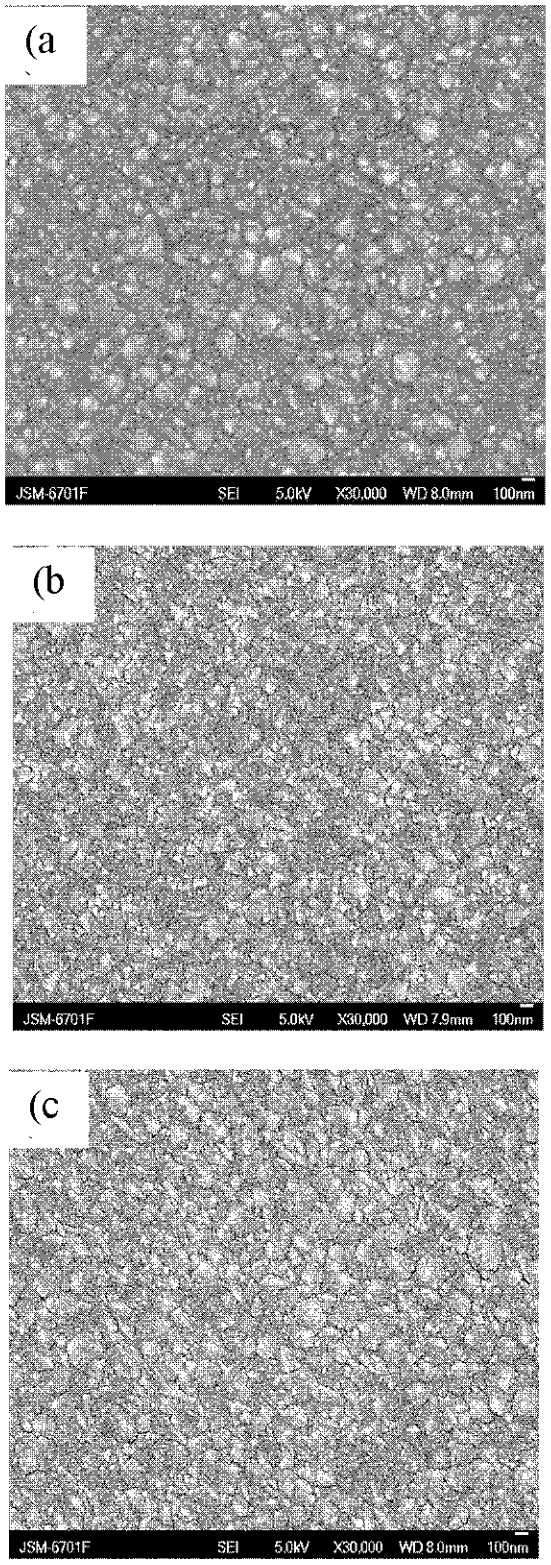

Figure 2: Scanning electron microscopy images of the samples: (a) Pure SnO_2; (b) 2% Ti/SnO_2; (c) 5% Ti/SnO_2.

4 DISCUSSIONS

In this paper, Ti/ SnO_2 thin films were prepared on Si substrates by using radio frequency magnetron sputtering technique. XRD measurements revealed that the crystalline structure of SnO_2 is developed with the Ti concentrations increasing, and then decreased as the Ti concentration further increased. The typical SEM image shows that all particles are uniform in shape and particle size, and a comparatively smaller crystallite size can be effectively obtained by addition of Ti as crystallite growth inhibitor.

Fluctuation-enhanced chemical sensing with commercial gas sensors has already been studied [4-7]. Gas sensors with improved sensitivity can be accomplished by fluctuation-enhanced sensing with measuring fluctuations in the resistance rather than changes in the dc resistance; the former are correlated to low frequency components of the dynamic disorder [8]. This fluctuation spectroscopy provides a new detection principle, as elaborated recently [9-10]. Fluctuation-enhanced chemical sensing can also be used to reduce the number of sensors needed in gas sensing and to realize the automation of gas sensing. The theoretical study shows that the compound oxide gas-sensing films on Si-substrates have high selectivity to CH_4/CO, obvious fingerprint spectrum in fluctuation-enhanced chemical sensing measurement and good stability at high temperature. We will use the films presented in this paper to study the effect of Si-substrates on gas sensing material and to detect CH_4 and CO gases using fluctuation-enhanced chemical sensing.

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