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Spray deposited Mg-doped SnO_2 thin film LPG sensor: XPS and EDX analysis in relation to deposition temperature and doping

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ABSTRACT

Magnesium doped SnO_2 polycrystalline thin films are deposited by Spray pyrolysis by adding small amount of Mg between 0.3 and 1.2 wt%. Mg doping significantly modifies the gas sensing properties of tin oxide thin films by yielding (1 1 0) and (1 0 1) crystallite orientation to accommodate oxygen vacancies which lead to enhanced oxygen adsorption. A correlation is established between the crystallite orientation and the gas sensing magnitude by plotting the texture coefficient. The structure, surface chemical composition, and the optical and electrical properties are studied in relation to the gas sensing magnitude. It is shown that the magnesium doping in SnO_2 maintains tetragonal rutile structure in stable cassiterite phase over low doping concentrations. The grain dimensions are influenced by both doping concentration and substrate temperature. Electronic surface states identified by the XPS are deconvoluted to establish the constituent oxygen states, while the EDX compositional analysis indicates added oxygen adsorption. As the temperature is raised for the response measurement, the adsorbed oxygen may transform to O^- or O^{2-} which is supported by the increase of film resistance. It is shown that the sensor response to LPG is improved significantly (93%) by the addition of minor amounts of Mg to SnO_2 thin film sensors.

1. Introduction

The last decades have witnessed, a great deal of research undertaken to develop semiconductor gas sensing devices for practical applications ranging from toxic gas detection to industrial process monitoring. Continuous research and development activities have been underway to explore a gas sensor for detection of low concentrations of LPG (liquid petroleum gas) in atmosphere at substantially lower temperature, to meet the demand for environmental pollution monitoring, public security, industrial process control and mining applications [1,2]. Since LPG is inflammable and unsafe immediately above LEL (lower explosive limit = 1.8% volume of gas in air) at room temperature, it is essential to develop reliable, yet inexpensive, gas sensors to detect the gas within the preset limit.

Solid state gas sensors using semiconductor metal oxides have been proved to be potential materials for the development of commercial gas sensors due to their accessibility to easy manufacturing methods, their ability to maintain structural integrity in harsh conditions and due to their high sensor response. The functional properties of the metal oxide-based gas sensors can be improved not only by incorporating additive metal catalysts on crystalline oxide matrix but also by tailoring the crystallite phase and orientation, in addition to the size [3,4]. They enjoy additional advantages such as short response time, low cost and reduced size. Even with these qualities they suffer from the lack of selectivity in addition to the high operating temperatures [5].

Tin oxide (SnO_2), an n-type semiconductor material with multivalent anion, widely finds application as sensing element in gas sensors. The most attractive aspect of SnO_2 material, perhaps, is its ability to form in a stable crystal phase with oxygen deficient SnO_{2-x} mode, accomplishing it to change the electrical resistance based on adsorbed surface species [6]. The augmentation in the sensing properties of the materials has been mainly achieved by improving the formation methods of sensors, together with the addition of noble or transition metals into and out of the matrix. The effects of these additives on SnO_2 sensor are often quite remarkable with regard to sensor response. There are numerous examples of the modification of sensor response in tin oxide by additives [7–13]. Apart from this, nanoparticles, plates, and nanowires of SnO_2 have been recently reported to enlarge the LPG sensing advancement [14,15].

The gas sensing process of tin oxides involves a change in the electrical transport by gas interaction or adsorption which depends highly on surface stoichiometry, microstructural features (grain

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size, crystallite orientation, connectivity and geometry of the particles) [16], and adsorption related properties (electrostatic affinity, heat of sorption and diffusion coefficients). This article reports on the composition and gas sensing properties of alkaline earth metal, magnesium (Mg) doped SnO_2 thin films, grown by the spray deposition method. The effects of deposition temperatures (280–420 °C) on crystalline orientation, grain size and the O/Sn ratio of the films for LPG sensing are investigated in addition to sensing temperature. Besides, the responses are compared in the low doping concentration and the cited temperature range to resolve the sensing mechanism.

2. Experimental methodology

2.1. Sample preparation

In the present investigations undoped and Mg doped SnO_2 films are deposited on glass substrate using the spray pyrolysis technique. For undoped SnO_2 films, a solution of stannous chloride with isopropyl alcohol is used and the method is described elsewhere [17]. The filtered solution is sprayed using clean compressed air as the carrier gas. The solution flow rate is 8 mL/min with the spray nozzle to substrate distance, 60 cm. The films are deposited on the glass substrates in the temperature range of 200–420 °C, but comprehensive studies pertaining to gas sensing activity on Mg doping are carried out in the range of 285–355 °C. The variation in the substrate temperature during the spray process is restricted to ±5 °C. To change the doping, the Mg to SnO_2 proportion is varied from 0.3 to 1.2 wt%. After spraying, the substrate is cooled slowly at a rate of 10 °C/min. The average thickness of the formed films is in the range of 250–350 nm, measured using profilometer (Sloan Dektak 6M).

2.2. Characterisation

The analysis of the formed polycrystalline thin films is carried out by X-ray diffraction (XRD – Bruker D-8 advance using Cu Kα line), Scanning electron microscopy (SEM – Hitachi S 2400) and Fourier transform infra-red spectroscopy (FTIR – Bruker – Tensor 27 using ATR mode). Crystallite size is estimated from the average broadening of SnO_2 (1 1 0) and (1 0 1) diffraction peaks [18]. The compositional analysis and electronic behaviour of SnO_2:Mg thin films with different sensing responses (prepared at different conditions) are studied using X-ray photoelectron spectroscopy (XPS – Kratos Analytical – Axis Ultra).

The XPS analyses are carried out using a monochromatic Al Kα source ($h\nu$ = 1486.6 eV, 10 mA, 15 kV). Both the survey and the high-resolution narrow-scan spectra are recorded at pass energies of 50 and 20 eV respectively. Any charging shifts produced by the samples are carefully removed using C 1*s* binding energy (BE) of the adventitious carbon line at 284.8 eV [19,20]. The error in all the measured BE values is within ±0.05 eV. The Au $4f_{7/2}$ energy peak at 84.0 ± 0.1 eV is used to calibrate the BE scale of the spectrometer. Instrument base pressure is 8×10^{-9} Torr. High-resolution spectra obtained are subjected to non-linear least-squares curve fitting by so-called Voigt profile performed with Vision processing® software.

An optical absorption study has been carried out in the wavelength range of 270–900 nm using a double beam spectrophotometer. The electrical properties are studied in an in-house made setup using the Van der Pauw configuration. The films deposited on a glass substrate are heated for sensing measurement to a temperature in the range of 280–350 °C, by enclosing in a quartz tubular furnace (Fig. 1). The steady-state resistance of the sensor element is measured in air.

The target gas along with air flow is then monitored through gas flow meters and introduced into the chamber in the required concentrations. A constant current is applied across the element. The dynamic resistance is then measured by switching on and off the test gas. The LPG sensor response % is measured as the ratio of, change in resistance (ΔR) under air-LPG mixture to that of the initial resistance in air (R_a) entirely multiplied by 100 [10], by

$$S\% = (\Delta R/R_a)100. \quad (1)$$

3. Results and discussion

The obtained Mg doped tin oxide films are clear without any abruptions and reflective in appearance within the deposition temperatures of 280–420 °C. The deposited films have polycrystalline structure and lower degree of crystalline order is present when the deposition temperature falls below 280 °C, which is consistent with an earlier article [21].

3.1. Micro structural studies

3.1.1. XRD

The analysis of X-ray diffraction patterns (Fig. 2) shows that the as deposited, doped tin oxides films, can be indexed to the tetragonal rutile phase of tin oxide (JCPDS card No. 21-1250) with lattice parameters $a = b = 4.738$ Å and $c = 3.188$ Å which belongs to the space group $P4_2/mnm$. No obvious diffraction peaks from impurities or metallic Sn are observable. At lower formation temperature of 285 °C, the peak intensity (Fig. 2) is less, indicating weakened crystallinity due to lesser number of atoms in the diffracting lattice plane. The crystallinity is improved by increasing the temperature to 305 °C. Care has been taken to keep the thickness almost unchanged upon increase in the deposition temperature by adjusting the deposition time. When the deposition temperature is about 325 °C, SnO_2 films with good crystallinity are formed. The variation in intensities of (1 1 0) and (1 0 1) planes in the diffractograms of tin oxide thin films formed at temperature 355 °C can be described as the gradual reduction of tetragonal SnO_2, resulting apparently from the removal of bridging oxygen atoms from the stoichiometric SnO_2 [22]. Fingerprints for the formation of sub-oxides on smaller scale in films deposited above a temperature of 355 °C are observed [23], but these are beyond scope of this report.

A single phase of SnO_2 is detected in the XRD pattern (Fig. 2) of films deposited at 325 ± 5 °C, containing 0.6 wt% Mg, which consists entirely of the specific tetragonal cassiterite tin oxide phase in (1 1 0), (1 0 1), (2 0 0), (1 1 1), (2 1 1), (2 2 0), (3 1 0) and (3 0 1) crystallographic directions. The increase in the characteristic (1 1 0) SnO_2 diffraction peak indicates that the addition of magnesium in small amounts favors privileged growth of the film, at a lower temperature. The theoretical and experimental studies [24,25] suggest that the surface energy sequence of SnO_2 is $\mathcal{E}(1\,1\,0) < \mathcal{E}(1\,0\,0) < \mathcal{E}(1\,0\,1) < \mathcal{E}(0\,0\,1)$. Thus, the SnO_2 (1 1 0) surface which has the lowest surface energy is thermodynamically most stable [26] and the plane (1 1 0) would be expected to feature privileged growth predominantly when in the tetragonal phase. The stimulated growth of (1 1 0) can be described by this approach.

The preferential growth of polycrystalline thin films is studied by calculating the texture coefficient (TC) [27] from the reflection intensities of the XRD lines.

$$TC_{(hkl)} = \left[I_{(hkl)}/I_{0(hkl)}\right] / \left[(1/N)\sum_{N} I_{(hkl)}/I_{0(hkl)}\right], \quad (2)$$

where $I_{(hkl)}$ is the measured intensity of X-ray reflection, $I_{0(hkl)}$ is the corresponding conventional intensity from the JCPDS data card No. 21-1250 and N is the number of diffraction peaks observed in the XRD pattern.

Fig. 3 illustrates that the $TC_{(1\,1\,0)}$ and $TC_{(1\,0\,1)}$ occupy a relatively higher TC value along with a minimal value for the (2 1 1) and (3 0 1) planes for the highest sensor response 0.6 wt% Mg doped SnO_2 films deposited at 325 °C.

The particle dimensions are influenced both by doping concentration as well as by substrate temperature. The crystallite size determined from XRD for the Mg-doped films initially decreases with an increase in dopant contents up to 0.9 wt% by certain inhibit process and showing a fixing up of crystallite orientation in presence of additive, which gets increased by further addition of dopant.

For 0.6 wt% Mg doped SnO_2, crystallite size, 46 nm at 285 °C, decreases to reach a minimum of 36 nm at 325 °C, and thereafter increases to 53 nm at 415 °C. The initial decrease in crystallite size may be due to the break out of oxygen from stoichiometry resulting from the higher kinetic energies of reactants at higher deposition temperature, up to a point where the fusing of the agglomerates takes over.