Original Article

Effect of annealing on humidity sensing properties of Sm-doped SnO₂ thin films

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ABSTRACT

Samarium doped tin oxide (Sm-doped SnO₂) nanoparticles were sputter deposited on a Silicon substrate to investigate the effect of dopant on humidity sensing properties of tin oxide thin films. Post deposition treatment was done to improve the surface roughness for more reaction sites to be formed. The thickness of thin film was 100 nm and the average grain size of doped samples was found to be 24 nm with a low dopant concentration. SEM and AFM characterizations of annealed samples were done and resistance variations with respect to humidity were experimentally recorded for the samples. The resistance of Sm-doped thin film was found to reduce from 1.435MΩ to about 0.4 MΩ for increasing humidity values of 30–90%RH and gave an appreciable current output in the range 4.34–12.5 μA. The Sm-doped sample exhibited improved sensitivity as compared to pure tin oxide and hence can be employed for real-time humidity measurements.

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1. Introduction

Metal oxide semiconductors are a broad class of materials with extensive applications in gas and humidity sensing. Oxides of certain post-transition metals like Al, Bi, Sn and Zn show interesting transition phenomena and exhibit excellent sensing behavior [1,2]. Among these metal oxide semiconductors (MOx), SnO₂ is a promising gas and humidity sensing material owing to its high surface area, excellent conductivity, good reversibility, robust mechanical properties, and low production cost [3]. In order to improve the speed of response and sensitivity further, low concentrations of dopant is added to the MOx layer. In recent years, most of the studies on SnO₂ thin films have been focused on the effects of doping on the optical, magnetic and gas sensing properties of SnO₂ thin films.

The reports about the effects of rare-earth-element (RE)-ion doping on the magnetic properties of SnO₂ thin films are still limited [4]. It was envisaged that the doping of RE-ion in SnO₂ matrix would result in exciting optical and magnetic properties. Considering the fact that addition of dopant improves the overall sensitivity of tin oxide thin films, several rare-earth ions doped transition metal oxides were reviewed [5–7]. The choice of samarium is considered on account of its high dielectric, thermal and magnetic properties.

Since theionic radius of Sm (0.109 nm) is large compared to tin oxide (0.069 nm), it causes structural modifications and superficial stresses in the host. In our previous work, the crystallite size of SnO₂ was found to vary linearly with dopant concentration. Considering the low doping concentration of Sm atoms and high density of oxygen vacancies in Sm-doped SnO₂ film, the chance for Sm atoms being nearest neighbor-
hood is very minimal hence the Sm dopant would be adjacent to oxygen vacancies [8]. The humidity sensing properties of lanthanides doped Ferric oxide have been reported by Hefeng Zhou et al. [9]. They have experimentally demonstrated the variations in repeatability, speed of response and hysteresis of three different lanthanides (Sm, Ln and Nd). Sm-doped Fe2O3 was proved to show excellent sensing properties compared to the other two dopants. The fine grain size of the thin films enhances the adsorption process after dissociation of water molecules at varying humidity conditions.

Sensitivity, linearity, repeatability and response time are important parameters in identifying a sensor for a particular application. In the work of Korotcenkov et al, grain size is an important influencing parameter in humidity sensing MoOx thin films [10]. SnO2 and In2O3 nanomaterials were synthesized by spray pyrolysis and subjected to post-deposition heat treatment like annealing and milling to study the change in crystallite size. They reported that small size, have appreciably stronger improvement in the conductivity of thin film in humid atmosphere. A qualitative analysis was performed between as-deposited and annealed thin films with respect to sensitivity, change in resistance, response and recovery time when subjected to different humidity conditions [11]. Results indicated that annealed thin films (300 °C for 2 h) showed faster response time and recovery time of 58 and 45 s against as-deposited sample response time and recovery time of 75 and 65 s respectively.

T Krishna Kumar et al [12] have experimentally observed the humidity sensing properties of pure tin oxide nanoparticles and achieved better results in terms of sensitivity factor. But the response time and recovery time were high compared to other similar research works. Hence doping of tin oxide with Sm has been projected in this work to achieve quicker response to humidity. Qin Kuang et al have reported the humidity sensing characteristics of a single SnO2 nanowire of 250 nm diameter and observed highly linear variation in resistance when subjected to 30–85%RH and achieved sensitivity up to 55% [13]. Dueborg et al made TiO2 humidity sensitive paste and developed it for the screen printing process on a large scale. They analyzed the resistance variations and sensor repeatability when humidity was changed from 12 to 52% for every 10 min interval. The sensor response was almost identical during the measurements [14].

Hydrothermally synthesized tin oxide/rGO nanocomposite deposited on polymers was developed to study humidity sensing properties of by exposing it to a broad humidity range of 11–97%RH at room temperature [15]. Compared with traditional humidity sensors, the SnO2 modified graphene sensor demonstrated an ultrahigh sensitivity and repeatability.

2. Methods and materials

Commercially available highly pure tin oxide (Sigma-Aldrich) was procured and a small concentrate of Sm (0.5%) was doped for sputter deposition on Si substrate. Stoichiometric quantities were mixed homogeneously using mortar and pestle and calcined at 850 °C in a programmable muffle furnace for 8 h. Upon grinding further, these fine powders were pressed using hydraulic press and sintered at 850 and 1000 °C to achieve 2-inch diameter pellets. Sputter targets were sputtered on silicon substrate using RF magnetron DC sputtering to achieve a uniform thickness of 100 nm. Post deposition, ERTA for 60 s was done in high vacuum of 5 × 10⁻⁶ mbar for all thin film samples, where the substrates are manually upturned and placed over graphite boats and raster-scanned by an electron beam that is accelerated by 4 kV potential.

3. Structural characterization

3.1. Crystallography

The X-ray Diffraction (XRD) studies of pure and Sm-doped SnO2 thin film revealed their crystalline nature. As shown in Fig. 1, the peaks observed at 27.9, 34.3 and 52.4° corresponds to the (110), (101) and (211) planes of polycrystalline rutile/tetragonal structure of tin oxide which coincides with JCPDS21-1250. It is observed that the crystalline nature of SnO2 reduces with the incorporation of Sm. This may be ascribed to the inclusion of large ionic radius (1.08 Å) Sm³⁺ ions into the SnO2 lattice, which intrudes and reduces the crystalline nature of the material.

3.2. Morphology

Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) images of the annealed SnO2 and Sm-doped SnO2 thin films are shown in Figs. 2 and 3 respectively. Fig. 2 shows the SEM images of the annealed tin oxide and doped samples. It gives a clear picture of the fine and uniform distribution of grain size in Sm-doped sample. This may be attributed to the strain effect in the crystal lattice of tin oxide owing to the larger radius of Sm. Fig. 3 shows the AFM images of the undoped and doped samples. The images expose an increased rate of agglomeration and improved surface roughness due to ERTA treatment in Sm-doped SnO2 thin film. Since grain size and surface roughness are two influencing factors
that affect the sensitivity of thin films, a comparative analysis has been done to observe the extent of variation when subjected to humidity changes.

4. Humidity sensing mechanism

Two different humidity sensing mechanisms are prominent in thin films. At lower %RH levels (or at high temperatures) chemisorption mechanism is prominent while at higher %RH (or at low temperatures) physisorption play a key role. Physisorption is more related to physical absorption of water molecules on surface by Van der Waals force whereas chemisorption relates to the chemical reaction between water molecules and the sensing film. Hence, for a wide range of humidity measurements, combined action of both the processes takes place [18]. At lower values of humidity, water vapor molecules dissociate into $\text{H}^+$, $\text{OH}^-$ ions and further dissociate into $\text{O}^-$ ions. These hydroxyl ions have greater affinity towards metal ions present in metal oxides donating free electrons and hence cause movement of free charge carriers at the surface leading to increased electronic mobility and conductivity as well. This may be established by the chemical reaction at the surface of thin film given by Eq. (1) and Fig. 4.

$$2\text{H}_2\text{O} + 4\text{Sn} + \text{O}_2^- \leftrightarrow 4(\text{Sn}–\text{OH}) + 2\text{e}^- \quad (1)$$

5. Humidity measurement

Humidity sensing studies have progressed rapidly and humidity sensors, regardless of fabrication technique, have been widely employed in industrial and household applications as instrumentation equipment or for human comfort issues. In order to perform humidity studies on Sm-doped SnO$_2$ thin films, the conventional two contacts technique was adopted. The distance between the two contacts was maintained at 5 mm. The sensor was carefully placed on a glass slide using a suitable thermal insulation and was kept inside the humidity chamber over a ceramic plate. The chamber was initially pre-
heated to a temperature of 50 °C and the sensor was mounted inside the chamber. The lead wires were taken out of the chamber for the measurement of resistance and were connected to a Keithley LCR meter. The humidity measurement was carried out in the range of 30–90%RH which is the active region of the sensor. The temperature was measured using RTD and was maintained at 40 °C throughout the experiment. The humidity inside the chamber was measured using a standard hygrometer and the values were simultaneously displayed on a digital display outside the chamber. The resistance was measured every time after the stabilization of humidity level for every step change of 5%RH. As indicated in Fig. 5, the resistance was found to decrease with increasing values of humidity and was found to vary between 1.435 kΩ to 401 kΩ for the above-mentioned parameters. A constant bias voltage of 5 V was applied to the sensor. The current was found to vary from 4.34 to 12.5 μA corresponding to 30–90%RH. For the decreasing values of %RH, the hysteresis was minimal. The sensor response was calculated using the following expression:
\[
\text{Sensor response} (S) = \frac{(R_e - R_s)}{R_s}
\]
where \(R_e\), Resistance corresponding to the humidity variation; \(R_s\), Resistance in dry air.

6. Results and discussion

Fig. 5 shows the variation in resistance of the Sm-doped SnO\(_2\) thin films and its sensitivity as a function of %RH. The sensitivity increased linearly from 0.1 to 0.85 to the corresponding change in humidity. The dissociation and subsequent adsorption of water molecules cause a linear change in resistance. Fig. 6 shows the linear increase in output with respect to %RH. Tin oxide, being an n-type semiconducting material, exhibited improved conductance due to variation in electron concentration when exposed to water vapor. Fig. 7 indicates a comparison between the sensitivities of the two samples where the undoped sample showed a maximum sensitivity of 0.7 against the Sm-doped sample maximum sensitivity of 0.85. Sensor response time was found to be 35 s and recovery time was 58 s. This is quite a lower value compared to similar works available in literature. The shorter response time of the sensor may be attributed to the increased reaction sites post-annealing in the Sm-doped sample when it was exposed to changing humidity conditions. The experiment was repeated to affirm the reproducibility of the sensor and the response was found to be good as shown in Fig. 8.

The following table gives an overview of the sensitivity of tin oxide thin films from previous work developed by other methods (Table 1).

7. Conclusion

The characterization and experimental results clearly indicate the effect of annealing and dopant in humidity sensing properties of pure tin oxide thin films. The annealed samples differed
in the distribution of grain size and rate of agglomeration. The sensors were subjected to varying humidity conditions and the change in resistance was noted. A comparative analysis between the sensitivities indicated doped samples show slightly higher sensitivity compared to pure tin oxide. Thus the treated samples exhibited better sensitivity, low hysteresis, an appreciable current output and short response time.

Conflicts of interest

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

The Article we have submitted to the journal for review is original, has been written by the stated authors and has not been published elsewhere.

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The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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