Synthesis, Characterization and H\textsubscript{2}S Gas Sensor Performance of Hydrothermal Prepared SnO\textsubscript{2} Films Nanostructures

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Abstract: In this work, tin oxide thin films were successfully synthesized by hydrothermal method and depositing on silicon substrates by spin coating technique at room temperature with thickness of about 325±5 nm. The structural, surface morphological, optical and gas sensor properties have been investigated. The XRD results showed that SnO\textsubscript{2} films are polycrystalline in nature with tetragonal . The FESEM images of SnO\textsubscript{2} clearly indicate that the oxide possesses has like cauliflower like shapes. The optical properties show that the optical energy gap follows allowed direct electronic transition calculated using Tauc’s equation. The H\textsubscript{2}S toxic gas sensing properties of SnO\textsubscript{2} thin film are examined as a function of time and operating temperature. High sensitivity (197\%) was attained at operating temperature of 200 °C with fast response and recovery times.

Keywords: Tin oxide, hydrothermal method, gas sensor , spin coating technique

1. Introduction

Tin oxide (SnO\textsubscript{2}) is a tetragonal rutile structure with lattice parameters a=b = 4.737 Å and c = 3.826 Å [1]. The unit cell contains two tin and four oxygen atoms. Each tin atom is bounded to six oxygen atoms at the corners of a regular octahedron, and every oxygen atom is surrounded by three tin atoms at the corners of an equilateral triangle [2]. The SnO\textsubscript{2} films are n-type semiconductors with a direct band gap of about (3.6- 4.3) eV. Deposition technique has strong effect on the thin film form and its structure, so it may be formed as polycrystalline or amorphous. SnO\textsubscript{2} semiconducting transparent thin films have various appealing features for technical applications in solar energy conversion, flat panel displays, electrochromic devices, invisible security circuits, LEDs, gas sensing, etc. Hence large area SnO\textsubscript{2} films on cheap and easily available substrates are of considerable interest for the formation of most of the photonic structures [3, 4]. In the current paper, we report the production of SnO\textsubscript{2} used hydrothermal way and the training of structural, morphological of surface, electrical, optical, and H\textsubscript{2}S sensing applications of the SnO\textsubscript{2}films deposited by used spin coating method. The original achievement of the current work
was the little operating temperature for SnO₂ film H₂S gas sensor created by rather small cost method, with great sensitivity, fast response and recovery times.

2. Experimental

2.1. Materials

Tin (II) chloride Stannous chloride dehydrate (99.9%) (SnCl₂·2H₂O) and hexamine (C₆H₁₂N₄), are of analytical grade and using short of further purification. Double-distilled water is using for films preparation and description.

2.2. Preparation of SnO₂ nanostructures

0.1 M Tin(II) chloride (SnCl₂·2H₂O) solution was dissolved in 50 ml distilled water with continuous stirring at R.T. for 15 min. 0.1 M solution of Hexamine (C₆H₁₂N₄) in 50 ml distilled water was prepared with continuous stirring at R.T. at 15 min. Hexamine (C₆H₁₂N₄) solution were adding drop wise on tin (II) chloride solution with continuous stirring at R.T. for 30 min. Final solution is moved into a Teflon-lined stainless steel hydrothermal reactor. The hydrothermal reactor is closed quickly and maintained at 150 °C for 6 h in a digital temperature measured oven. The hydrothermal reactor is cool to room temperature naturally. The precipitate is filtered and wash away with water several times and finally with acetone, until the supernatant fluid is colorless, and then dried at 50 °C in an oven. This precipitate is annealed in air atmosphere at temperature of 400 °C for one hour and left in the furnace to reach room temperature after turning off the furnace to obtain SnO₂. 0.05 g SnO₂ was dissolved in 15 mL of distilled water and 15 mL ethanol and put these solutions in ultrasonic for 3 h to be good dispersed. “Finally, this solution is placed on prepared silicon substrates by using spin coating technique spin coating technique as following. An excess amount of the SnO₂ solution is firstly dropped onto the surface of silicon (111) wafer substrate. The spin coater then rotates the substrate at a speed of around 1600–2100 rpm for 60 s in order to spread the solution by centrifugal force. To get homogeneous films, several different factors are important and have to be considered which are, evaporation rate of the solvent, viscosity of the fluid, concentration of the solution, angular velocity (rotating speed) and spinning” time

3. RESULTS AND DISCUSSION

3.1. Result of XRD

Fig (1) shows the XRD pattern of SnO₂ thin films. It can be noticed that all the patterns exhibit diffraction peaks around (2θ~ 26.67°, 33.3°, 37.8°, 51.69°, 57.38°, 62.6° and 79.009°) referred to (110), (101), (200), (211) (002), (221), and (321) planes respectively, which is in agreement with the (JCPDS) card No 41-1445. The strongest peak happens at 2θ~37.8° which is denoted to (200) plane. The locations of the peaks and the occurrence of further than one spreading peak main to the decision that the samples were polycrystalline in nature with a crystalline tetragonal structure, which in agreement [5, 6], and it can be noticed also that the lattice constants (a and c) for SnO₂ are equal to 4.726 and 3.214 Å respectively which shows that the prepared samples has the nearest (a and c) values to the
standard lattice constants 4.738 and 3.187 Å respectively.

![XRD patterns of SnO2 thin films.](image)

Figure 1: XRD patterns of SnO2 thin films.

The crystallite size (D), is estimated by Scherers method [6]:

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]  

(1)

Where K is a shape factor, \( \lambda \): wave length of X ray radiation, \( \beta \): half maximum of full width of the peak and \( \theta \): angle Bragg diffraction for the XRD peak. The crystallite size is found to be (18.4 nm). The larger crystallite size value indicate better crystallization of the films [7-9].

### 3.2. FESEM analysis

FESEM micrograph of nanocrystalline SnO2 thin film at 100 kx and 200 kx magnifications are shown in Figure (2). From the Figure, a same and unchanging distribution of SnO2 ended the look over area can be detected and cauliflower similar shape are formed with an average grain size 29±2 nm.
Figure 2. FESEM images of SnO$_2$ nanostructures films at (a) 100 kx and (b) 200 kx magnifications.

3.3. Optical analysis

Optical absorption spectrum of SnO$_2$ sample for (200-1100 nm) is recorded by used UV–visible spectrophotometer. Fig (3) illustrates the relative between absorbance ($A$) and wavelength for SnO$_2$ nanostructures. The absorbance increases rapidly at short wavelengths corresponding to the energy gap of SnO$_2$. This evident increase of energy is due to the interaction of the material electrons with the incident photons which require enough energy for the occurrence of transitions of electron.

![Absorbance vs Wavelength](image)

Figure 3. Absorbance ($A$) against wavelength ($\lambda$) for SnO$_2$.

The optical energy gap ($E_g$) is given by Tauc’s relation [6, 10]:

$$\alpha h\nu = B(h\nu - E_g)^r$$

(2)

Where $\alpha$ the coefficient of absorption, $h\nu$ the photon energy, $E_g$ is the optical band gap, $B$ is constant and $r$ be determined by on optical transitions. In this work, direct band gap is resolute by plotting a graph between $(\alpha h\nu)^2$ and $(h\nu)$ in eV, where the straight line of extrapolation for $(\alpha h\nu)^2 = 0$ gives the value of the direct band gap of the material. It can be noticed that the band gap value equal 5.449 eV. This value in the band gap can be related to the structural modification of the sample.
Figure 4. The relation between \((ahv)^2\) and \(hν\) for SnO\(_2\) nanostructures

3.4 Measurement of H\(_2\)S Gas

Thin films specimens are examined for H\(_2\)S gas sensing (H\(_2\)S is an electron donor gas \([104,105]\)) with concentration of 25 ppm at changed operation temperatures starting from (30, 50, 100, 150 and 200) °C. Figure (5) show the sensing properties and the variation for all samples.

Figure 5. The difference of resistance with time for SnO\(_2\) thin film as H\(_2\)S gas sensor

The figure shows lessening in value of resistance when samples are exposed to H\(_2\)S gas, [Gas- ON], at that point the resistance of going up value at the end of the gas [Gas- OFF]. Electron transferring can cause the changes in resistance and work function of the sensing material. The gas sensing things of the sensor is measured by recording a change in resistance over two sensing electrodes under H\(_2\)S gas. The change in the sensor resistance is attributed to ion adsorption of gas molecules, surface reaction of target gas with adsorbed oxygen on the surface of metal oxide.
“Adsorbed ions are responsible for a change in conductivity. The negative charged ions are responsible for absorbing electrons and upward band bending around the edge of the grain. By absorbing oxygen molecules on the surface of metal oxide, they extract electrons from the conduction band $E_c$ and electrons are trapped at the surface in form of ions. This mechanism causes a band bending and the electron depleted region near the surface of each grain [12], as shown Figure (5). During the adsorption process at elevated temperatures, different oxygen species are formed on the surface of SnO$_2$ as $O_2^-$ and $O^-$ [12, 13]. The sensing mechanism of SnO$_2$ gas sensors can be explained by the adsorption of oxygen on the surface of metal oxide grains and its reaction with H$_2$S gas molecules. By introducing H$_2$S gas molecules, the electrical conductivity of film changes due to the surface reactions at the grains. The H$^+$ ions react with adsorbed oxygen ions and form water vapor, and as a result of this reaction, electrons transfer back to the film according to the reaction [14]. Therefore, the transfer of electrons to the conduction band of semiconductor changes the conductivity of the film. For n-type semiconductor material such as SnO$_2$, the resistance decreases with increasing the number of electrons in the film. As described in the previous section, metal oxide gas sensors show a change in a resistance in contact with H$_2$S target gas at different operating temperatures”.

The sensitivity (S%) is calculated using [6,15]:

$$S = \left( \frac{R_a - R_g}{R_a} \right) \times 100\%$$

(3)

where, $R_a$ and $R_g$ the resistance of electrical for the samples in the air and in presence of H$_2$S gas, respectively.

Table 1 shows the sensitivity, response time and recovery time of SnO$_2$, which are deposited on silicon substrate. Results show that the sensitivity of film increases with increasing of the operating temperature, and the Table (1) shows the sensitivity as a function of operating temperature for SnO$_2$ nanostructures. The gas sensitivity tests were performed at (30, 50, 100, 150 and 200) ºC. An increase in the operating temperature leads to an improvement of the films sensitivity which is attributed to increase in the rate of surface reaction of the target gas. Thus, the gas sensitivity at (30 ºC) has low value, the reason for this may be that the surface would be unable to oxidize the gas so intensively thus, the gas sensitivity was decreased. Since the sensor response of materials is strongly dependent on their morphologies and surface area, thus SnO$_2$ are believed to be desirable for the gas sensing applications [16, 17]. The optimal temperature ($T_o$) is seen at temperature of 200 ºC, at this temperature the activation energy may be enough to complete the chemical reaction [14]. The table shows that the samples exhibit a fast response speed and small recovery time less than 1 s where there are square pulses[18]. For all the samples the response and recovery times increase with the increase in operating temperature”[19].

Table 1. Response time, recovery time and sensitivity % of SnO$_2$ at different operating temperatures.

| T       | 30 ºC | 50 ºC | 100 ºC | 150 ºC | 200 ºC |
|---------|-------|-------|--------|--------|--------|
| sensitivity% | 87    | 134   | 139    | 140    | 197    |
| response time | 0.792 | 0.801 | 0.808  | 0.837  | 0.854  |
| recovery time | 0.816 | 0.821 | 0.838  | 0.848  | 0.862  |
3.5 Conclusions

In this work, tin oxide (SnO$_2$) has successfully synthesized by using hydrothermal method and depositing SnO$_2$ on silicon and glass substrates by spin coating technique at room temperature with thickness of about 325 nm. From the results, the crystallite size estimated by Scherrer’s formula. The sensitivity to H$_2$S gas increases with increasing the operating temperature and the maximum sensitivity was observed at the optimal temperature ($T_o=200\, ^{\circ}\mathrm{C}$). The response and recovery times increase with the increase in operating temperature. All gas sensor devices against H$_2$S toxic gas have square pulses, which mean fast response and recovery time.

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