Effect of heat treatment on the characteristics and NH$_3$ Sensing properties of Tin Dioxide SnO$_2$ Thin Film

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Abstract: In this research, Spray pyrolysis technique used to prepared Tin dioxide (SnO$_2$) thin films on glass substrate with thickness about 200± 8 nm by dissolved 2.2563 g of SnCl$_2$.2H$_2$O in 100 ml of ethanol then added 60 drops from concentrated hydrochloric acid (HCl). After that the films were annealed at different temperatures (300, 400 and 400 °C ). X-ray analyses shows that the structure of all SnO$_2$ films is polycrystalline with tetragonal rutile crystalline structure with preferential orientation in the direction (200). The optical measurements show that the optical transition has been direct and the average band gap has been tendency to decreases from 3.98 eV to 3.73 eV with increasing of T$_a$. The extent and nature of transmittance and optimized band gap of the material assure to utilize it for sensor applications.

From sensing measurements for NH$_3$ gas at different operating temperature (100,200,250 and 300)°C and gas concentration (5%, 10%, 15%, 20%, 25%, 30%, and 35% ) can be seen that the sensitivity increases with increasing operating temperature and gas concentration, the response time decreases to smallest value (4s) at operating temperature 200 °C while the recovery time (22 s).

Keywords: Operating temperature; Response time; Recovery time; Sensitivity ; Spray pyrolysis; Tetragonal.

1. Introduction

In the development of the last few decades and until the present day, SnO$_2$, CdO, and ZnO are semi conducting metal oxides with large optical band gaps that are very dynamic materials in study. Because of its greater stability in atmospheric conditions, mechanical hardness, high-temperature resistance, and chemical inertness, SnO2 is the most common material among the accessible TCOs (Transparent conducting oxides). High electrical conductivity tends to be an aspirant for gas sensors, optoelectronic applications such as window layers for solar cells, light-emitting diode (LED), and phototransistors [1-5] because of its distinct physical characteristic features such as high transparency in the visible region of the spectrum and greater reflectivity in the infrared region.

The presence of flammable and harmful gases in the atmosphere can be dangerous to public health and safety [6]. Then there are new applications for gas sensors, such as dangerous and environmental gas detection, wearable electronics, portable gas analyzers, and the Internet of Things (IoT). Fast response/recovery times and low detection limits are anticipated from new sensors lower
power consumption, work at a lower temperature, high sensitivity, good selectivity, and long-term stability[7].

Chemical sensors using semiconducting metal oxides like (SnO$_2$, Zno, WO, and TIO) are one of the most intensively investigated gas-sensing systems [6,8]. The sensors based on these materials change their conductivity in the presence of reducing and oxidizing gases as electron density, this adsorbed oxygen is trapped at the grain boundary trap states or the absorption and desorption of O$^2$, O$_2$, or O$^-$, cause that the surface is modified thereby increasing the grain boundary potential barrier so the Small grain size, which has been shown to increase sensitivity [9]. The sensing mechanism involves a discernible change in the resistance of the metal oxide upon exposure to reduction or oxidation happens with the detected gas [6,8]. The change in conductivity is due to the interaction of the surrounding gas with the sensing layer [10].

This study explains how gas sensors respond, discussing how gases are absorbed on the surface of semiconductor materials and their impact on the properties of semiconductors, also focused on the efficiency of gas sensor made of nanostructures in the form of thin SnO$_2$ film and treated under different annealing temperature to sensing different gas concentration and different operating temperature.

2. Experimental procedure.

Structure at the nanostructures. The SnO$_2$ film was made by spraying a 0.1 M tin salt solution on a glass substrate. The solution was prepared at a temperature of 450°C by solving 2.2563 g of SnCl$_2$.2H$_2$O was dissolved in 100 ml of ethanol then added 60 drope from concentrated hydrochloric acid (HCl) by using drop by drop technique the solution put on magnetic stirrer for 30 minits. The addition of HCl rendered the solution transparent. Microscope glass slides, cleaned with HCL, distilled water solvents, and then put in ultra sonic cleaner for 15 mints. After that put it in ethanol and distilled water solvent and again put in ultrasonic cleaner for 15 mints, finally the substrates put in 100 ml of distilled water and eject it, then wait for it to dry. The solution’s spray rate was set to one sprinkling per minute. The sprinkling time was approximately 10 seconds. The spray nozzle’s normalized distance from the substrate was 30 cm. SnO$_2$ films were thermally treated at various temperatures (300, 400, and 500) °C for two hours in air.

The thickness of the films (t) was determined using the weighing-method as shown in the following equation:

$$t = \frac{\Delta m}{\rho A}$$

where $\Delta m$ represents the mass difference of slide after and before the deposition, $A$ represents the area of the film and $\rho$ is the SnO$_2$ density which is 6.85 g/cm$^3$ at room temperature, the thickness of the films prepared about 200 nm.

The structure of the films was examined using X-Ray Diffraction (XRD) using a Philips X-ray diffractometer system which records the intensity as a function of Bragg’s angle. The source of radiation was Cu (k$\alpha$) with wavelength $\lambda=1.5406$ Å, the current was 30 mA and the voltage was 40 kV. The scanning angle 2$\theta$ was varied in the range of 20°-60°.

The transmittance and absorbance of the films was measured using UV-VIS spectrophotometer Shimadzu UV/Visible recorder spectrometer model 12600 in the spectral range 200-1100 nm.

The intensity of light (I) after crossing thickness of material x in an isotropic medium can be estimated by [11]:

$$I = I_0 \exp (-\alpha x)$$

where $I_0$ is the initial intensity.
The whole sensor test system as figure (1). The voltage of bias is 10 volts, and the chamber pressure in range of \((1 \times 10^{-2} \text{ bar})\). The mixing of the gas with air have been controlled by flow meter. The variation of sensor sensitivity \(S\), as calculated using the equation:[12]

\[
S = \left( \frac{\Delta R}{R_o} \right) \times 100 \% = \left( \frac{R_{\text{gas}} - R_o}{R_o} \right) \times 100 \% = \left( \frac{\sigma_{\text{gas}} - \sigma_o}{\sigma_o} \right) \times 100 \% \quad \ldots (3)
\]

where \(R\) is the electrical resistance and \(\sigma\) is the electrical conductance.

![Gas sensor testing system.](image)

**Figure 1.** Gas sensor testing system.

3. Results and discussion

3.1. Structure Properties

The analyses of XRD for \(\text{SnO}_2\) thin film deposit on glass substrate shown in figure (2), which indicates that, the structure of the films polycrystalline. It is well known that tin dioxide \(\text{SnO}_2\) has a tetragonal rutile crystalline structure [13]. The major diffraction peaks of some lattice planes can be indexed to the tetragonal unit cell structure of \(\text{SnO}_2\) with lattice constants \(a = 4.71 \, \text{Å}\) and \(c = 3.19 \, \text{Å}\), which are consistent with the standard values for bulk \(\text{SnO}_2\) (JCPDS-041-1445, card No. 96-900-9083) [13]. There are six apparent peaks with 20 values of \((26.58^\circ, 33.8^\circ, 37.87^\circ, 51.64^\circ, 61.7^\circ \text{ and } 65.7^\circ)\) corresponding to \(\text{SnO}_2\) crystal planes peaks of \((110), (101), (200), (211), (310), \text{ and } (301)\) respectively.

The crystallite size \(D\) and the \(d\) space which determined from Scherer’s formula equation (4) [14] and Bragg equation equation (5) [15] respectively are listed in table (1).

\[
D = \frac{0.9\lambda}{\beta \cos \theta} \quad \ldots (4)
\]

\[
n\lambda = 2d \sin \theta \quad \ldots (5)
\]
where $\lambda$ is the wavelength of X-ray ($\lambda = 1.5406\text{Å}$), $\theta$ is the angle of diffraction, and $\beta$ is the full-width at half-maximum (FWHM) intensity (in radians).

Figure 2. X-ray diffraction (XRD) pattern of SnO$_2$ thin film at different annealing temperatures.
Table 1. Experimental and stander XRD data for SnO$_2$ films at different annealing temperatures.

| T (°C) | 2θ (Deg.) | FWHM (rad.) | G.S (nm) | d$_{hkl}$ Exp.(Å) | d$_{hkl}$ Std.(Å) | Phase | hkl |
|--------|-----------|-------------|----------|-------------------|-------------------|-------|-----|
| RT     | 26.57     | 0.0047      | 32.1     | 3.3523            | 3.3498            | Tetragonal | (110) |
|        | 33.81     | 0.0044      | 35.5     | 2.6491            | 2.6439            | Tetragonal | (101) |
|        | 37.87     | 0.0047      | 33.6     | 2.3737            | 2.3686            | Tetragonal | (200) |
|        | 51.64     | 0.0051      | 32.1     | 1.7686            | 1.7642            | Tetragonal | (211) |
|        | 61.70     | 0.0046      | 32.5     | 1.5022            | 1.4981            | Tetragonal | (310) |
|        | 65.70     | 0.0065      | 27.3     | 1.4200            | 1.4149            | Tetragonal | (301) |
|        |           |             |          |                   |                   |        |     |
| 300    | 26.55     | 0.0049      | 30.8     | 3.3549            | 3.3498            | Tetragonal | (110) |
|        | 33.83     | 0.0044      | 34.8     | 2.6476            | 2.6439            | Tetragonal | (101) |
|        | 37.92     | 0.0050      | 31.4     | 2.3707            | 2.3686            | Tetragonal | (200) |
|        | 51.69     | 0.0055      | 29.9     | 1.7670            | 1.7642            | Tetragonal | (211) |
|        | 61.78     | 0.0065      | 26.7     | 1.5004            | 1.4981            | Tetragonal | (310) |
|        | 65.79     | 0.0069      | 25.8     | 1.4183            | 1.4149            | Tetragonal | (301) |
|        |           |             |          |                   |                   |        |     |
| 400    | 26.59     | 0.0051      | 29.7     | 3.3498            | 3.3498            | Tetragonal | (110) |
|        | 33.81     | 0.0047      | 33.1     | 2.6491            | 2.6439            | Tetragonal | (101) |
|        | 37.91     | 0.0052      | 30.1     | 2.3713            | 2.3686            | Tetragonal | (200) |
|        | 51.65     | 0.0063      | 26.3     | 1.7683            | 1.7642            | Tetragonal | (211) |
|        | 61.73     | 0.0070      | 24.6     | 1.5015            | 1.4981            | Tetragonal | (310) |
|        | 65.73     | 0.0070      | 25.1     | 1.4194            | 1.4149            | Tetragonal | (301) |
|        |           |             |          |                   |                   |        |     |
| 500    | 26.56     | 0.0065      | 23.6     | 3.3536            | 3.3498            | Tetragonal | (110) |
|        | 33.81     | 0.0048      | 32.6     | 2.6491            | 2.6439            | Tetragonal | (101) |
|        | 37.87     | 0.0053      | 29.6     | 2.3737            | 2.3686            | Tetragonal | (200) |
|        | 51.63     | 0.0063      | 26.1     | 1.7689            | 1.7642            | Tetragonal | (211) |
|        | 61.71     | 0.0084      | 20.7     | 1.5019            | 1.4981            | Tetragonal | (310) |
|        | 65.73     | 0.0077      | 23.1     | 1.4194            | 1.4149            | Tetragonal | (301) |

3.2. Linear Optical Properties

Tauc equation has been used to calculated the optical energy gaps for allowed direct transition: [11]

\[ (\alpha h \nu^r ) = B (h \nu - E_g)^{1/2} \]

which B is Tauc constant and hν is the energy of incant photon, \( \alpha \) is the absorption coefficient and \( r = 1/2 \) for allowed direct transition. Figure (3) shows the energy gap \( E_g \) of the samples which evaluated from the intercept of the linear portion of each curve with the \( h \nu \). The obtained values of energy
gap for different annealing temperatures are shown in table (2), Band gap lies in the range of (3.98-3.72) eV our results are in good agreement with those reported in literature[16]. The values of optical energy gaps as shown decrease with increasing annealing temperatures this may be attributed to the increase in the localizes levels near the band edges.

| T_a (K) | E_g (Ev) |
|---------|----------|
| R.T     | 3.98     |
| 573     | 3.86     |
| 673     | 3.83     |
| 773     | 3.72     |

3.3. gas sensor measurements
Sensing measurements are investigated at different NH_3: air mixing ratio (5%, 10%, 15%, 20%, 25%, 30%, and 35%) and different operating temperature (R.T, 100, 200, 250, and 300 °C) to. Figure (4) shows the variation of the sensitivity with operating temperature which is obvious that the sensitivity increases with increasing operating temperature and the best temperature as clearly shown is about ~200 °C due to increase the rate of surface reaction of target - gas. From the figure the high sensitivity obtained at annealing temperature 300 °C.
The sensitivity measurements of SnO$_2$ film for different ratio of NH$_3$: (5%, 10%, 15%, 20%, 25%, 30%, and 35%) have been done it using equation (3). Figure (5) shows that the sensitivity of the sensor increases linearly in the low gas concentration region less than 30%, which is provide advantage to detect and estimate the low concentrations of combustible gases. While with higher of gas concentration the sensitivity tends to saturate, which is resulted due to saturation of adsorption of NH$_3$ atoms at the Al electrode/SnO$_2$ interface, and lack of adsorbed oxygen ions at the surface [17]. Our result good agreement with L.Kamble et.al [2].

![Figure 4. The variation of the sensitivity with operating temperature at gas concentration 30%.](image)

![Figure 5. The sensitivity dependence of SnO$_2$ sensor on NH$_3$ gas concentration.](image)

The response and recovery times of the sensor at annealing temperature 573 K and gas ratio 30% shown in figure (6). The response time of the sensor decrease with increasing operating temperature at which the lowest response time about 4s and the recovery time about 22 s at operating temperature 200 °C and the highest recovery times about 37 s at R.T.
4. Conclusion.

There are main conclusions that have obtained from this work. From X-ray diffraction results can be concluded that the structure of SnO$_2$ films is ploycrystalline with tetragonal rutile structure with preferential orientation in the (200) direct ion. Annealing process leads to improve in the crystallization. From the optical properties concluded that the optical transitions in SnO$_2$ is direct transition and the optical energy gap decreases with annealing temperature. From the above study for gas sensor properties can be concluded that the SnO$_2$ sensors demonstrated high sensitivity to NH$_3$ gas. Moreover, the annealing temperatures were causing improvement of performance in sensitivity. The response – recovery time of SnO$_2$ sensing element was in range of 4s and 22 s respectively for operating temperature 200 °C and 30% NH$_3$ ratio at annealing temperature 300 °C, which are considered as workable and appropriate to get fast and sensitive gas sensor capable of detecting toxic and flammable gases.

So it can be concluded that the best operating temperature is about 200 °C, the best sensitivity at gas mixing ratio 30 %, and the optimum annealing temperature 300 °C for SnO$_2$ material which benefits an actuator to enabling it to detect different concentrations of combustible gases.

References

[1] S. Palanichamy, J. Raj Mohamed, K. Deva Arun Kumar, P.S. Satheesh Kumara, S. Pandiarajand, L. Amalraj, 2019, [Physical properties of rare earth metal (Gd3+) doped SnO2 thin films prepared by simplified spray pyrolysis technique using nebuliser], Optik, Vol. 194, p. 162887.

[2] Dilip L. Kamblea,b, Namdev S. Haralec, Vithoba L. Patilc, Pramod S. Patilc, Laxman D. Kadama, 2017,[ Characterization and NO2 gas sensing properties of spray pyrolyzed SnO2 thin films], Journal of Analytical and Applied Pyrolysis, Volume 127, P.P. 38-46.

[3] Y. Bouznita,b, A. Hennic, 2019, Characterization of Sb doped SnO2 films prepared by spray technique and their application to photocurrent generation], Materials Chemistry and Physics, Volume 233, P.P. 242-248.

[4] Salam Amir Yousif, Jenan Mohamed Abass, 2013,[ Structural, Morphological and Optical
Characterization of SnO2:F thin films prepared by Chemical spray Pyrolysis], International Letters of Chemistry, Physics and Astronomy, 13, P.P. 90-102.

[5] C. Jariwala1,* M. Dhivya1,2, R. Rane1, N. Chauhan1, P.A. Rayjada1, P.M. Raole1, P.I. John1, 2013., Preparation and Characterization of Antimony Doped Tin Oxide Thin Films Synthesized by Co-Evaporation of Sn and Sb using Plasma Assisted Thermal Evaporation], J. NANO- ELECTRON. PHYS. vol. 5, no 2, P. 02029.

[6] Tang-Yu Laia, Te-Hua Fanga, Yu-Jen Hsiaob, Ching-An Chana, 2019, [Characteristics of Au-doped SnO2–ZnO heteronanostructures for gas sensing applications], Volume 166, P.P. 155–161.

[7] WojciechMaziarz, 2019., [TiO2/SnO2 and TiO2/CuO thin film nano-heterostructures as gas sensors ], Applied Surface Science, Vol. 480, 30, P.P. 361-370.

[8] Alexandra Tischner, Thomas Maier, Christoph Stepper, Anton Köck, 2008, [Ultra-thin SnO2 gas sensors fabricated by spray pyrolysis for the detection of humidity and carbon monoxide], Sensors and Actuators B 134, P.P. 796–802.

[9] M. Boshta, F. A. Mahmoud, , M. H. Sayed, 2010, [Characterization of Sprayed SnO2:Pd Thin Films for Gas Sensing Applications], Journal of Ovonic Research, Vol. 6, No. 2, 2010, P.P. 93 – 98.

[10] Eva Lacknera*, Johanna Krainera, Robert Wimmer-Teubenbacher, Florentyna Sosadaaa, Marco Delucaaa, Christian Gspanba, Karl Rohracherc, Ewald Wachmann, Anton Köcka, 2017, [Carbon monoxide detection with CMOS integrated thin film SnO2 gas sensor ], Materials Today: Proceedings 4, P.P. 7128–7131.

[11] J.Taus, 1974, [Amorphous and Liquid Semiconductor] Plenums Press, New York and London, 271.

[12] L. A. Patil, A. R. Bari, M. D. Shinde, V. V. Deo, and D. P. Amalnerkar, 2011, Synthesis of ZnO nanocrystalline powder from ultrasonic atomization technique, characterization, and its application in gas sensing, IEEE Sensors. journal, Vol. 11, No. 4, P.P. 939 – 946.

[13] JCPDS-International Centre for Diffraction Data. All rights resaved, PCPD Fwin Vol.1.30, card no 96-900-9083, N 1997.

[14] Radhyah Mahdi Shaker Jarrah, 2016, Effect of Substrate Temperature and Zn Additive to CdTe Thin Films on AC Mechanism and Cole-Cole Diagram, International Journal of Science and Research, Volume 5 Issue 5, P.P. 1557-1563.

[15] Rachana Gupta and Mukul Gupta, 2005, Phys. Rev. B, 72, 024202.

[16] A.Mohammed, M. Bagheri, D. Mohagheghi, M. Shokooh, Saremi, 2004, “The influence of Al doping on the electrical, optical and structural properties of SnO2 transparent conducting films deposited by the spray pyrolysis technique”, J. Phys. D. Appl. Phys., Volume 37, P.P. (1248-1253).

[17] R K Mohammad, R A Madloli, N M Umran and F I Sharrad, 2016, [Structure and electronic properties of substitutionally doped cycloheptane molecule using DFT Results], Phys. 6, 1036.