Influence of Heat Treatment on the Characteristic of SnO2 Thin Films for Gas Sensor Application

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Abstract: Nano-crystalline SnO2 films were deposited on glass substrates using dip coating by sol–gel technique for gas sensor applications. These films have been annealed in air at 300, 350, 400, and 450 °C for 60 min, and at 400 °C for 15, 30 min. The films have been analyzed through x-ray diffraction and optical absorption spectroscopy. The deposited films have shown tetragonal rutile structures. The average crystallite size increased as annealing temperature increased. The crystallite sizes of the annealed films were 8 nm at 300 °C, 10 nm at 350 °C, 14 nm at 400 °C, and 22 nm at 450 °C for 60 min. Whereas the crystallite sizes showed 16 and 15 nm at annealing temperature of 400 °C for 15 and 30 min, respectively. The energetic values of optical band gaps of the films showed increment with the elevation in annealing temperatures. The optical band gap energies were 2.86, 2.86, 3.14 and 3.35 eV at annealing temperatures of 300, 350, 400, and 450 °C, for 60 min, respectively, and 3.43 and 3.35 eV at annealing temperature of 400 °C for 15 and 30 min, respectively. Electrical D.C. conductivity were measured at temperatures ranging from 30 ºC to 170 ºC, and these measurements showed an exponential increment as the temperature and time increased. The films were studied in the matter of sensing capabilities for CO gas through evaluation at various times and temperatures. The optimum sensitivity was found at annealing temperature 400 °C. The outcomes revealed a high sensitivity of the deposited films for carbon monoxide at operation temperature of 200 ºC.

Keywords: Nanocrystalline SnO2 films, sol-gel dip method, annealing temperature, optical properties, CO gas sensor.

1. Introduction

Tin dioxide (SnO2) has an importance in resistive gas sensors. The wide applications of oxide semiconductors are attributed to variety in their conductivities and gas responsivity [1][2]. Tin dioxide is a semiconductor of n-type with a tetragonal rutile structure, and a direct optical band gap approximately of 3.6 eV. SnO2 has considerable attention due to very high sensitivity and low cost of production [3][4][5][6]. Sensors for gases that used in homes as gas alarm systems were fabricated mainly using tin dioxide (SnO2) thin films with thickness of 1 mm, for achieving significant power consumption [7]. Gas sensors based on SnO2 thin films showed substantial sensitivity to several poisonous and flammable gases, which attributed to their considerable reaction with reduction in the molecules of gases with chemisorption of oxygen species oxygen (O2 or O) on the surfaces of semiconductor surface, where the oxide particles may suffer a reduction in potential barrier that can be minimized through electron releasement towards the band of conduction of SnO2 [8]. Tin dioxide (SnO2) films have been prepared using several techniques such as DC-magnetron sputtering [9], sputtering by ion beam [10], coating by dipping and coating by spinning of the sol-gel [11], chemical vapor deposition [4], paralysis deposition [5] and chemical bath deposition [6]. In this research, sol-gel dip coating technique was selected for preparation of nanocrystalline SnO2 films due to advantage of low-temperature deposition in aqueous environments and relatively large areas of deposited films. Dip coating is a low-cost deposition technique with possibility of using of high-purity initial materials, with no need for vacuum equipment. Oxidation of SnO2 films can be conducted by annealing in air. At temperatures higher than 500 °C, a considerable nanocrystalline growth occurs. This leads to
formation of normal tetragonal phases and high-pressure orthorhombic phases [9][10][11]. The aim of this work is evaluation of the impact of annealing conditions on the structural, optical, electrical and sensing properties of SnO$_2$ with nanocrystalline structure that deposited using the dipping in sol-gel.

2. Experimental part

Solution-dip coating method was conducted in preparation of tin dioxide SnO$_2$ thin films, through the following steps. First, the dissolution of chloride dehydrates (SnCl$_2$.2H$_2$O; 2g, Fisons, UK) in C$_2$H$_5$OH (15 ml) was conducted. This solution was magnetically stirred for 1hr at 75-80 ºC, and the glycerin (C$_3$H$_8$O$_3$) was added to the solution for achieving a stability dispersion in the sol-gel for coating by dipping. The glass substrates with dimensions of 26 mm×76 mm×1 mm were used. These substrates were cleaned ultrasonically by immersion in a bath for 5 min and then washed with ethanol. Later, these films were produced through dipping the substrates into the sol bath and then pulled out at a relatively slow rate of 80 mm/min from the bath. The films were subjected to drying at temperature of 100 ºC for 30 min. Afterward, these films were heat treated at temperatures of 300, 350, 400 and 450 ºC for 60 min and at 400 ºC for 15 and 30 min. The heat treatment at 400 ºC was chosen as an optimum condition in this research. X-ray diffractometry analysis was used for determination the crystalline phases and average crystal sizes in the achieved films. X-ray diffractometer with CuKa$_1$ radiation at $\lambda$=1.54 Å, 30 kV, and 30 mA (model Shimadzu X-ray diffraction) was used in this procedure. The measurements of optical transmittance and absorbance have conducted for wavelengths extend from 200-1000 nm using a spectrophotometer (Shimadzu UV-1800).

3. Outcomes and Discussion

3.1 Structural properties of films

The XRD results showed the occurrence of crystalline growth of the deposited SnO$_2$ films when annealed at different temperatures and times in the air. These results have exhibited significantly finite diffraction peaks revealing clear crystallinity in the annealed films as indicated in Fig.1. The diffraction peaks were similar with given reference in JCPD database (#41/1445). All heat-treated samples were shown polycrystalline tetragonal crystal structures with crystallographic preferential growth along the plane (110). Additional peaks (101), (200), (211), and (220) were also appeared confirming the polycrystallinity nature of the films under annealing treatment. Higher annealing temperatures and times have improved relatively the crystallographic orientation as indicated in Fig.1. The full width at half maximum of the recorded peaks has decreased with the elevation in the annealing temperature, which is consistence with earlier reports [1][2][3][4][5]. The crystalline size film was obtained from Scherrer Debye relation [6]:

$$D = (0.9 \times \lambda)/(\beta \times cos\theta) \ldots \ldots (1)$$

where $\lambda$ is the wavelength of used x-rays (1.54 Å), $\beta$ is the full width at half maximum, and $\theta$ is the Bragg angle. The crystalline sizes were 8, 10, 14, and 22 nm at 300, 350, 400, and 450 ºC in 60 min, respectively, and 16 and 15 nm at 400 ºC in 15 and 30 min, respectively. When elevation in the annealing temperature reached up to 400 ºC, these peaks (110), (101), (200), and (211) were appeared very clear. This can be attributed to the occurrence of tensile stress due to the presence of oxygen vacancies in the lattices of SnO$_2$ films. The tetragonal phase has been indicated by the peaks (110), (101), (200), and (211), whereas the presence of (220) reflections corresponds with orthorhombic [7][8][9][10].

The following diffraction peaks (110), (101), (200) and (211), were observed at annealing temperature of 450 ºC, which are belonged to the tetragonal crystal structure, as well as one peak at (220) that corresponding the orthorhombic. The relative intensity increments of peaks especially for (110) indicate the improvement in the crystallographic orientation with annealing temperature. This can be attributed to the enhancement in the mobility of defects under such temperatures and hence increasing the atomic rearrangement in the SnO$_2$ films [10][11][12][13]. The following table shows the measured crystalline sizes at different annealing temperature and times.
Figure 1: XRD patterns of SnO$_2$ films at different annealing temperatures for 60 min (top) and at different annealing times at 400 °C (bottom).

3.2 Optical properties of films

The variation in the optical transmittance with wavelength at different annealing temperatures for 60 min is illustrated in Fig.2, as well as at annealing temperature of 400 ºC for different annealing times is shown in Fig.5. Significant transmission was observed in the visible spectrum starting from 400 nm. Gradual evolution in the transmittance continued with the elevation in the temperature of annealing, which imputed to the homogeneity evolution in the deposited films [14][15]. The following equation was used in calculation of the absorption coefficient ($\alpha$) using the values of absorbance ($A$) and thickness ($t$) of the film [16]:

$$\alpha = 2.303 \frac{A}{t} \ldots \ldots (2)$$

The variation in the coefficient of absorption for the doped and pure films with wavelength at various annealing temperatures for 60 min is illustrated in Fig.3, where the absorption coefficient was decreased clearly with the wavelength increment. The absorption coefficient ($\alpha$) also has increased up to $10^5$ cm$^{-1}$ with increasing in annealing temperature, which indicates the effect of direct electronic transitions [17][18][19].

The annealing had a significant effect on the values of optical energy gap as shown in Fig.4 and illustrated in Table 1. The values were increased from 2.86 to 3.35 eV as temperature of annealing raised from 300 to 450 °C for 60 min and this is illustrated in Table 1. This is caused by elimination of the crystal defects during the annealing process. The increment in the crystallite size and hence decrement in the defect density has resulted in improvement of the crystallinity of the films as annealing preceded, which in turns reflected on the values of energy gaps [11][20][21].

Figure 2: Variation of the optical transmittance with wavelength at different annealing temperatures for 60 min.
3.3 Electrical properties of films

The electrical properties of the deposited films were conducted using measurement of D.C. electrical conductivity at testing temperatures varies from 30 to 170 °C. The results showed an increment in the conductivity exponentially as the testing temperature and time increased as illustrated in Fig.7, where the concentration of carriers raised as the testing temperature increased.

Figure 3: Variation of absorption coefficient with wavelength at different annealing temperatures for 60 min.

Figure 4: Effect of annealing temperatures on the resultant values of the energy gaps of annealed films for 60 min.

Figure 5: Variation of the optical transmittance with wavelength at different annealing times at 400 °C.
It has been observed two conductivity mechanisms with energies \((E_{a1})\) and \((E_{a2})\), that appear at high and low temperatures, respectively. The conduction that occurs in the excited states beyond the mobility edge was caused by \(E_{a1}\), whereas the transfer of carriers to locations at the vicinity of valance states and conduction band lead to the conduction assisted by \(E_{a2}\). The increase in the electrical conductivity with the temperature of annealing was due to the elevation in the carrier concentration through generation more oxygen vacancies at higher temperatures \([8][13]\). Moreover, the relative microstructure growth at higher temperatures leads to spreading of grain boundaries and hence an increase in conductivity. The energy activation was calculated by \([13][22]\):

\[
\sigma = \sigma_0 e^{(E_a/kt)} \quad ... (3)
\]

where \(\sigma, \sigma_0, E_a, k, T\) are the conductivity, constant, activation energy, Boltzmann constant and temperature, respectively. The energy of activation refers the number of site \(n\) for levels of trap under the band of conduction. The current results showed an increase in the activation energy as annealing temperature and time increased as illustrated in Table 1.

| Annealing temperature (°C) | Annealing time (min.) | Crystallite size (nm) | Optical energy gap (eV) | \(E_{a1}\) (eV) | \(E_{a2}\) (eV) |
|----------------------------|------------------------|-----------------------|------------------------|----------------|----------------|
| 300                        | 60                     | 8                     | 2.86                   | 0.35           | 0.022          |
| 350                        | 60                     | 10                    | 2.86                   | 0.35           | 0.025          |
| 400                        | 60                     | 14                    | 3.14                   | 0.45           | 0.035          |
| 400                        | 15                     | 15                    | 3.43                   | 0.42           | 0.031          |
| 400                        | 30                     | 16                    | 3.35                   | 0.44           | 0.031          |
| 450                        | 60                     | 22                    | 3.35                   | 0.50           | 0.038          |

Figure 6: Effect of annealing times on the resultant values energy gaps of annealed films at 400 °C.
Figure 7: Variation in the electrical conductivity at different annealing temperatures for 60 min (left) and for different annealing times at 400 °C (right).

3.4 Sensing properties of films
Gas sensing properties are related normally to the surface sensitivity. The presence of nanoparticles associated with a relatively large surface area enhances the probability of gas-sensing reactions and then sensitivity. Exposure of the surface of SnO$_2$ films to the air results in formation of electron depletion layer through the absorption. Low electron density low in this layer leads to formation of high resistance layer, and the species of O and O$_2$ will be existed as adsorbed oxygen. SnO$_2$ thin films exhibited a high resistance in the air. Exposing the surface of SnO$_2$ film to CO gas results in release additional electrons due to the surface reaction. The additional electrons are move back towards the band of conduction leading to an increase in the conductivity of SnO$_2$ films [23]. The sensitivity ($S$) for sensor of a gas is defined as the ratio percentage of the resistance by surface $R_g$ of the sensor’s thin film in air to its counterpart in the environment gas $R_a$ [24]:

$$S = \left| \frac{R_g - R_a}{R_a} \right| \times 100 \ldots \ldots (4)$$

Figure (8) shows the sensitivity of all of the samples regarding CO gas, where a decrease in the sensitivity was obtained with increment in both temperature and time of annealing, and that is caused due to change in particles’ sizes [25]. The times of responsivity and recovery represent elementary factors of any gas sensor. Figure (9) illustrates the sensitivity of the film to monoxide gas relative to temperature at different annealing temperatures and times. The sensitivity was gradually increased with increasing temperature, where it reached to its maximum at 200 °C, and then decreased gradually at 300 °C. The optimum sensitivity was found at temperature 400 °C as shown in Figure 8 and 9. The high value of sensitivity for SnO$_2$ thin films to CO gas can be clarified based on models of the adsorption of gas. The sensitivity relates mainly to the occurrence of oxygen species and CO gas interactions on the surfaces of films [24][26]. The increase of the adsorbed oxygen species due to the temperature increment up to 50 °C was achieved by electrons addition come from the band of conduction. This behaviour is associated by an increment in the electrical resistance. Therefore, the higher values of sensitivity were found at 200 °C are attributed to the chemisorption of the oxygen kinds at high rates and significant oxidation of CO gas. Up to 200 °C, the species of oxygen from the surfaces of sensor were suffered of adsorption and hence densities of these species were reduced, which resulted in decrease in the measured sensitivity [4][24].
Figure 8: Variation in sensitivity with response time for different annealing temperatures for 60 min (left) and for different annealing times at 400 °C (right).

Figure 9: Variation in sensitivity with working temperature for different annealing temperatures for 60 min (top) and for different annealing times at 400 °C (bottom).

4. Conclusions
Improvement in the crystallinity, transmittance, conductivity and energy gaps were obtained with increasing of annealing temperature and times. This was attributed to the microstructural evolution of the deposited films under annealing conditions of temperatures and times. The optimum sensitivity was found at temperature 400 °C. Sensing properties were exhibited gradual increment and decrement with increase the working temperatures due to increase and decrease in adsorption behaviour oxygen species, respectively.

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