INFLUENCE OF BATH TEMPERATURE ON TIN OXIDE LPG SENSOR

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Abstract:
Tin oxide (SnO_2) thin films were synthesized by using CBD method at room temperature (25ºC) and at higher temperature (80ºC). The structural, morphological, optical properties were investigated by using XRD, SEM, and EDAX spectroscopy respectively. The structural studies revealed that synthesized annealed films of SnO_2 showed tetragonal crystal structure. SEM study of the annealed film depicts nano spheres like morphology which grown over complete substrate. The annealed films have been successfully applied for LPG gas sensor at different operating temperatures and at different concentrations. The room temperature synthesized annealed thin film (sample A2) of SnO_2 showed maximum LPG gas response 44.85% at operating temperature 325˚ and 28 ppm gas concentration.
Keywords: SnO_2 thin Films, Chemical bath deposition, X-Ray Diffraction, Gas sensing.

1. Introduction:

In recent years, there has been a consistent awareness about the gas sensors for safety control requirement and for monitoring of toxic and combustible gases. The proper working of ecosystem is necessary to bridge between the human life and natural habitat. Due to enormous growth of industrial sector, the huge discharge of gaseous pollutants such as sulfur oxide, nitrogen oxide is increased to serious extent. And they produce some serious environment issues. The rapid evaporation of toxic gases such as NH_3, H_2S, ethanol, LPG etc. make them dangerous to living entities and more corrosive at its high concentrations in the atmosphere. Hence, currently the environmental safety regulations have been toughened worldwide. These gases can cause several kinds of diseases such as allergies, headache, nausea, asthma and emphysema. Therefore, the development of gas sensors to monitor toxic and combustible gases is essential for environmental pollution and safety requirements for the industries. Generally, sensor provides an interface between the electronic equipment and the physical world typically be converting nonelectrical physical or chemical quantities into electrical signals. A better quality gas sensing system should have high sensitivity, reliability, and stability. Semiconducting metal oxide finds favorable in satisfying above characteristic to the greater extent. The basic principle lying behind metal oxide sensor is the change of conductivity of sensor when they are exposed to certain target gases at optimum temperature. Though the mechanism of gas sensing is complicated, it is believed that the decrease in resistivity in n-type semiconductor gas sensor as exposed to reducing gases results the desorption of oxygen adsorbed on the surface and grain boundaries of metal oxides at high temperature in air. C. Wang *et.al.* [1] Reported that post-transition metal oxides like ZnO, In_2O_3, and SnO_2 are more sensitive to many combustible, oxidizing and reducing gases. Tin oxide is n-type semiconductor [2] and has wide band gap energy (E_g = 3.6-3.8 eV) [3]. Different methods have been employed to synthesize SnO_2 such as thermal, Sol-gel, Spray pyrolysis, Magnetron sputtering and Thermal evaporation [4-7] etc. However, relatively high temperatures during the synthesis are necessary

while synthesis and further thermal annealing is usually necessary to obtain good crystalline samples [9]. Therefore, the development of synthetic routes for the production of SnO_2 nanostructures with controlled size and tunable shapes by wet chemical method remains a challenge [9-10]. Among the facile chemical deposition methods, Chemical bath deposition (CBD) method is suitable for the synthesis of tin oxide due to its easy working, cost effectiveness, and rapid results. Aponsu *et al*. [11] had reported effects of enhanced photovoltaic dye-sensitized solar cell for Tin oxide. J. Kim *et al.* [12] had reported Photo catalytic activity of tin oxide and Gas sensor applications [13-14]. In present work, Tin oxide thin film has been successfully deposited by using chemical bath deposition method at room temperature and at high temperature. The synthesized tin oxide thin film characterized by different physic-chemical methods and applied for LPG gas sensing application.

2. Experimental:

2.1 Chemicals Used

Chromic Acid [Mixture of Concentrated Hydrochloric Acid (HCl) + Potassium Dichromate ($K_2Cr_2O_7$)] Anhydrous Stannic Chloride ($SnCl_4$), Triethanolamine ($C_6H_{15}NO_3$), Sodium Hydroxide (NaOH) Chemicals were purchased by Alfa Acer and used without any further purification.

2.2 Experimental Procedure

Synthesis of SnO_2 thin films was carried out by using CBD which is based on the stirring of alkaline bath of tin salt containing the substrates immersed in it. Initially, the glass micro-slides were cleaned with the soap solution and chromic acid and then subsequently washed with double distilled water followed by ultrasonically cleaning for 15 min. Afterward, 2.60 gm of anhydrous stannic Chloride was dissolved in Double distilled water to prepare 0.1M solution of Stannic Chloride. Then 1 ml Triethanolamine was added drop wise with continuous stirring for complex formation. Again, to this solution 2N Sodium hydroxide (NaOH) was added with constant stirring till the solution reaches to its superstation point. Finally this solution was kept at room temperature along with vertically inserted washed substrates for 48 hours without any disturbance. White colored deposition was obtained on glass substrates. These films were air dried for 2-3 hours and then subjected to annealing at temperature 500˚C for 2 hours. Similarly, another bath was prepared by maintaining same preparative parameters as stated above and this bath was maintained at 80°C. The uniform and homogeneous films were obtained. Synthesized as deposited Tin oxide thin film obtained at room temperature (25˚C) is named as sample (A1) and annealed film named as sample (A2) similarly, film obtained at high temperature (80˚C) is named as sample (C1) annealed film named as sample (C2). To study the structural properties of as-deposited and annealed films, X-ray diffraction patterns were obtained using X-ray diffractometer over 2θ (scanning angle range of 10°–80° with Cu Ka radiation). The surface morphological studies were carried out with scanning electron microscopy. Energy dispersive X-ray analysis (EDAX) was employed for the compositional studies. The gas sensing properties of synthesized films were studied using a "static gas-sensing system." There were electrical feeds through the base plate. The heater was fixed below the base plate to heat the sample under test up to required operating temperatures. Al-Cr thermocouple was used to sense the operating temperature of the sensors. The output of the thermocouple was connected to digital temperature indicators. A gas inlet valve was provided at one port of the base plate. The required gas concentration inside the static system was attained by injecting a known volume of test gas using a gas-injecting syringe. For electrical measurements, silver paste contacts were made on the sample of area 1 cm×1 cm. Initially, the I–V characteristics were studied within ±10V and it was found that in the above voltage range, the silver contacts showed ohmic behavior. The electrical resistance of films in air (Ra) and in the presence of test gas (Rg) was measured to evaluate the gas response, S, defined as follows.

$$S\ (\%) = \frac{Ra - Rg}{Ra} \times 100 \qquad \ldots\ldots\ldots\ldots (1)$$

2.3 Reaction Mechanism

Nanoparticles growth involves two steps. In first step dissociation of Chloride salt of Tin was carried out in distilled water. Solutions of appropriate concentrations had been prepared and dissolved in distilled water with continuous stirring. After 5 min, stirred solutions were converted in to water soluble hydroxides of tin. Afterwards 1 ml Triethanolamine complexing

agent was added with drop wise stirring. This results into the complex formation. Finally 2N NaOH solution was added to it. Initially, on addition of NaOH clear solution becomes converted into white viscous liquid but on addition of excess solution of NaOH solution turns to clear transparent solution. These reactions can be represented stepwise by following reaction mechanism in equation (2) to (5). In second step, Nanoparticles so deposited on glass slide were annelid at 500˚C temperature to remove hydrated water containt. So, the Similar mechanism was observed in sample A1, A2, C1, C2.

The chemical bath deposition is based on the formation of solid phase from a solution, which involves two steps as nucleation and particle growth. In the nucleation, the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film by heterogeneous reactions at the substrate surface [15]

$$SnCl_4 + TEA \longleftrightarrow [Sn(TEA)]^{4+} + 4\,Cl^- \quad \ldots.(2)$$

$$[Sn(TEA)]^{4+} \longleftrightarrow Sn^{4+} + TEA \quad \ldots.(3)$$

$$Sn^{4+} + 4NaOH \longleftrightarrow Sn(OH)_4 + 4\,Na^+ \quad \ldots.(4)$$

$$Sn(OH)_4 \longleftrightarrow SnO_2 + 2\,H_2O \quad \ldots.(5)$$

3. Results and discussion

3.1. X-RD analysis

The structural changes and identification of phases of SnO_2 thin films obtained by CBD are investigated with the help of X-ray diffraction (XRD). Synthesized sample was characterized by Philips automated X-Ray diffractometer (PW-3710) equipped with crystal monochromator employing Cu-Kα radiation of wavelength 1.5406 A°. The diffracting angle (2θ) is varied between 20°- 80° and the recorded XRD patterns for the thin films are shown in **Fig.1.** It is observed that the films deposited at room temperature (25˚C) and at high temperature (80˚C) with and without annealed sample A1, A2, C1, and C2 has tetragonal lattice crystal structure shown in fig 1. The major peaks appear at 2θ = 26.42º, 33.4º, 37.6º and 52.1º which are corresponds to planes of (110), (101), (200) and (211) respectively. Which matches with the standard JCPDS file no.41 -1445[16].

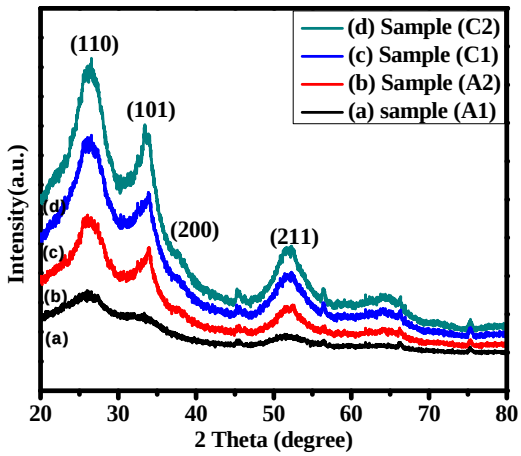

Fig 1: X-Ray diffraction pattern of (a) and (b) SnO_2 prepared at Room temperature with and without Annealing (c) and (d) SnO_2 prepared at high temperature (80˚C) with and without Annealing respectively.

No obvious reflection peaks from impurities such as unreacted Sn or SnO were detected, that there is no any secondary phases are present, thus indicating the high purity of the product with a tetragonal rutile structure. It is further observed that the film deposited at higher bath temperature i.e sample (C2) shows improved crystalline without any remarkable change in the plane orientation. This might be observed due to increase in mobility of high temperature of bath [17]. The average particle sizes were calculated from X-ray line broadening using the Scherer formula (6).

$$D = K\lambda/\beta COS\,\Theta \quad \ldots.(6)$$

Where, K is constant called as the shape factor = 0.94, λ is the Wavelength, β is Full width at half maximum (FWHM) given in radian, Θ = It is the Bragg's angle, D = Nanoparticle size in nanometer. The Average crystallite size of sample A2 is 29.89 nm nm and that of sample C2 has 42.34 nm.

3.2. SEM and EDAX analysis

Fig. 2 shows SEM micrographs of annealed SnO_2 thin films deposited at room temperature and at higher temperature (80˚C). The SEM micrograph films deposited at room temperature (A2) showed well defined nano spherical structure like morphology with interconnected clusters of particles. However, the SEM micrograph of sample (C2) showed agglomerated nano sphere like morphology with interconnected clusters of particles as shown in **Fig 2 (a)** and **(b)** respectively. The increase in particle size at higher bath temperature might be due to the embryos formed initially would re-dissolve at this temperature and thus by reducing the density of nuclei. This causes to increase in particle size as there is more reactant per nucleus as it is observed in **Fig. 2(b)**. Such novel morphologies find applications in gas sensors.

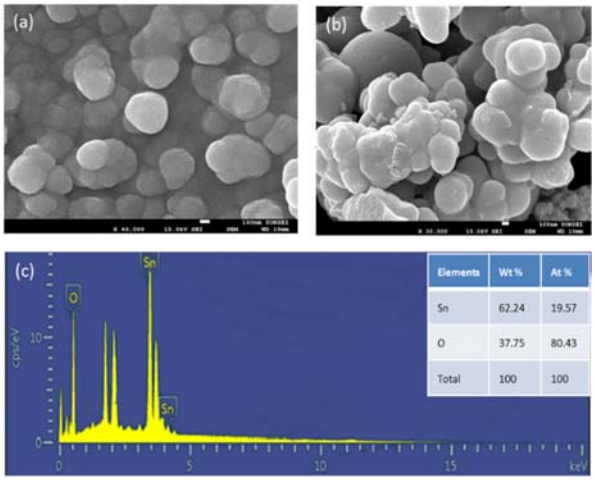

Fig 2 (a) and (b) SEM images of the films deposited at room temperature (25˚C) and at higher temperature (80˚C) sample annealed sample A2 and C2 respectively. c) EDAX spectrum of SnO_2 film, *Inset* shows the elemental composition of the SnO_2 film of sample A2.

The samples were characterized by an energy dispersive X-ray analyzer to find the elemental composition of the films. **Fig. 2(c)** shows the EDAX of sample A2 and *Inset* shows the elemental composition of the SnO_2 films formed by CBD method. It was found that the atomic percentage Sn and O is 19.57 and 80.43 respectively. The result of EDAX highlights presence of high concentration of oxygen.

3.3 Gas sensing properties

3.3.1 Effect of temperature

Before exposing to LPG gas, the SnO_2 films were allowed to be stable for electrical resistance for half an hour and the stabilized resistance was taken as Ra. Initially the gas response was studied as a function of operating temperature for annealed SnO_2 film. The temperature of the sensor surface is one of the most major parameters. The temperature affects the physical properties of the semiconductor such as charge carrier concentration, Debye length, work function etc. The optimum operating temperature for an effective sensor performance corresponds to that value at which material able to catalytically reduce or oxidize the target gas, simultaneously changing the electrical properties of the sensor material. Response of sensor depends on speed of chemical reaction on the surface and the diffusion of gas molecules to that surface. These are activation processes, and the activation energy of chemical reactions is higher. At low temperature, the sensor response is restricted by the speed of chemical reaction while at higher temperature it is restricted by the speed of the diffusion of gas molecules to the surface. At some intermediate temperature, the speeds of two processes become equal, and at that point the sensor response reaches to its maximum [18]. According to this mechanism, for every gas, there is a certain temperature at which the sensor

response reaches at its peak value. Above this maximum temperature, the gas response decreases due to desorption of the oxygen which are adsorbed on the surface of the sensor [19]. Another reason for the decrease in the gas response could be the increase in the carrier concentration due to intrinsic thermal excitation which decreases the Debye length [20]. This length describes the size of the space-charge region next to the surface where the free carrier concentration may be affected by the surface species.

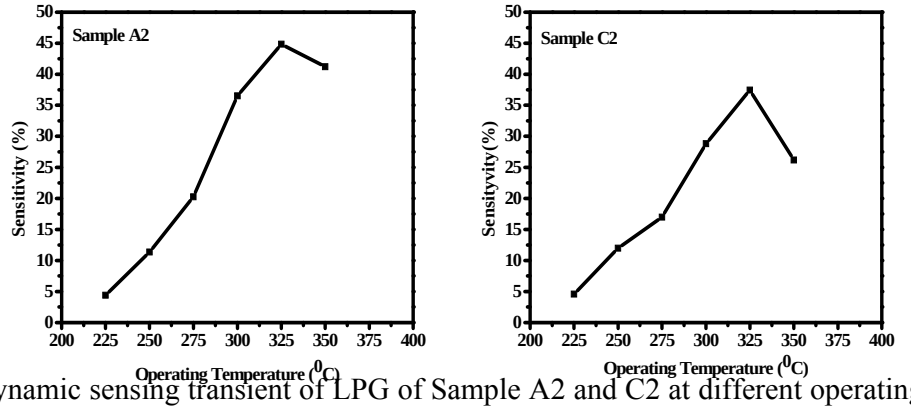

Fig. 3. Dynamic sensing transient of LPG of Sample A2 and C2 at different operating temperatures with 28 ppm gas for sample A2 and sample C2.

In the present case we found that the sensor response reaches maximum at 325˚C. The gas response is 44.85% for sample A2 and 37.45% for sample C2 and then decreases at 350˚C upon exposure of 28 ppm of LPG gas as shown in **Fig. 3.** Therefore, the temperature 325˚C was taken as an optimum operating temperature for further studies. Once the operating temperature was fixed the sensor response was studied at different gas concentrations. Similarly, dynamic response transient of Sample A2 and C2 at 325^{0}C temperature for 28 ppm LPG gas concentration was shown in **Fig. 4.**

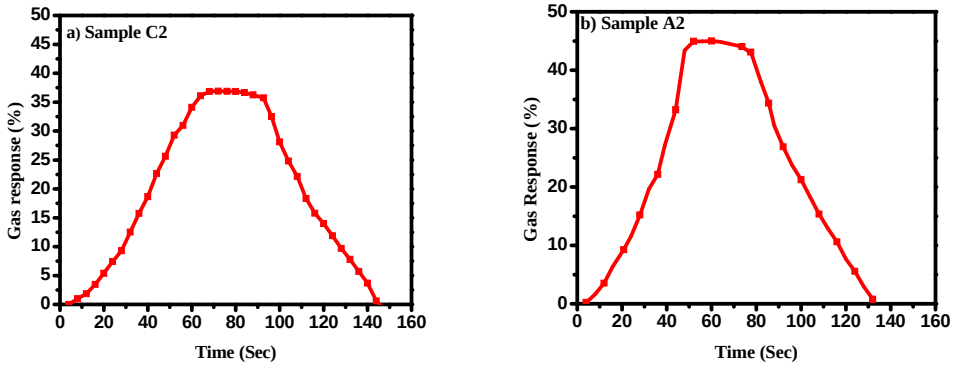

Fig. 4. Dynamic response transient of Sample A2 and C2 at 325^{0}C temperature for 28 ppm LPG gas concentration.

3.3.2 Effect of LPG gas concentration

The **Fig. 5** reveals that at the constant operating temperature 325˚C, response increased from 15.89 to 44.85% for the sample A2 while from 13.80 to 37.45 % for the sample C2 with respect to LPG gas concentration increased from 16 to 28 ppm. As the gas concentration increased from 16 to 28 ppm of LPG the response increased rapidly with concentration. However, at higher concentrations the increase in gas response value was steady and saturated. The response of a sensor mostly depends on the removal of adsorbed oxygen molecules by reaction with a target gas and generation of electrons. For a small concentration of gas, when gas exposed on a fixed surface area of a sample there is a lower coverage of gas molecules on the surface hence, minor surface reaction takes place. Increases in surface reaction observed with increase in gas concentration due to a larger surface coverage. A further increase in surface

reaction will be gradual when the saturation point of the coverage of molecules is reached.

3.3.3 Sensing mechanism

LPG gas sensing mechanism of n-type semiconducting metal oxide is based on the electron transport between the sensor surface and chemisorbed species that modify the surface conductivity of the sensor [21]. When the sensor is exposed to air, the atmospheric oxygen molecules are adsorbed on the surface of sensor, and then capture electrons from the conduction band to form the chemisorbed oxygen species (O_2^-, O^-, O^{2-})

O_2 (ads) + e− → O_2^- (ads) (between 25^{0}C and 150^{0}C) ….(7)

O_2^- (ads) + e− → 2 O^- (ads) (above 150^{0}C) ….(8)

O^- (ads) + e− → O^{2-} (ads) ….(9)

Therefore, the adsorbed oxygen molecules acting as acceptors and thus by deplete the surface electron states and reduce the free carrier density, consequently resulting in the electron depletion region generated at the surface of the sensor.

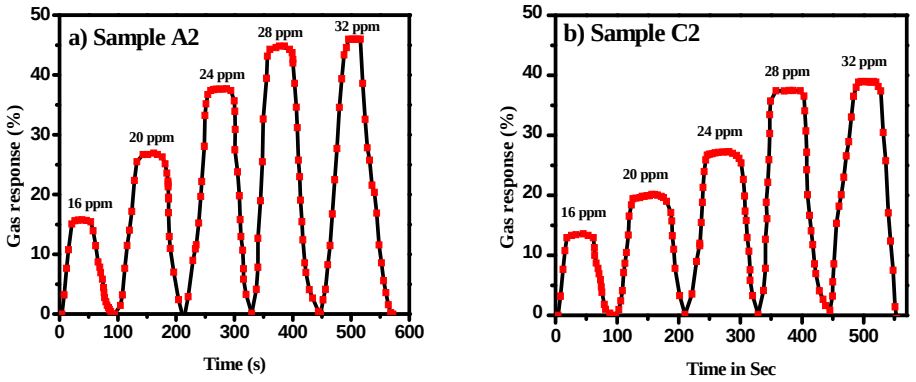

Fig. 5. Response under different gas concentration of LPG at operating temperature 325˚C..

When the sensor is exposed to target gas LPG, It reacts with chemisorbed oxygen molecules. On interaction with hydrocarbons (C_nH_{2n+2}) of LPG the adsorbed oxygen is removed, forming gases species and water vapor. Consequently the resistance changes which is due to the change in depletion layer. And the overall reaction of LPG with the chemisorbed oxygen may takes place as shown below. It releases electrons back to the conduction band of materials. These electrons recombine with holes, which increases the electrical conductivity of the semiconductor. These processes can be described by the following reactions,

$$2C_nH_{2n+2} + 2O_2^- \longrightarrow 2C_nH_{2n}O + 2H_2O + 2e- \quad \ldots(10)$$

When the LPG reacts with the surface oxygen ions then the combustion products such as water and carbon dioxide departs after oxidation and a potential barrier to change transport would be developed i.e., this mechanism involves displacement of adsorbed oxygen species by formation of water and carbon dioxide as shown in **Fig. 6 (a and b).** The formation of barrier is due to reduction in the concentration of conduction carrier and thereby, results in an increase in resistant of the sensing element with time. As the pressure of the gas inside the chamber increases, the rate of the formation of such product increases and potential barrier to change transport becomes strong which has stopped the further formation constituting the resistance constant.

The sample A2 showed a better response than sample C2 due to homogeneity of the deposited film (as seen in SEM) which offered more surface area for interaction and increases electron channels between the adjacent nano spheres, make the SnO_2 agglomerated nano sphere-built network film a better framework for gas sensor.

Above stated results and the present work propose that SnO_2 are good candidates for gas sensors with high sensitivity and low operating temperature.

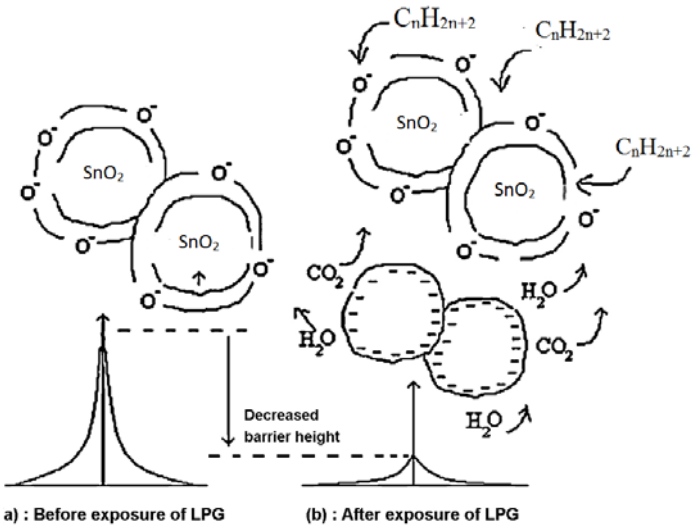

Fig 6 a) LPG sensing mechanism of SnO_2 thin film before exposure of LPG and b) After exposure of LPG C_nH_{2n+2}

4. Conclusion

The SnO_2 thin film was synthesized by using chemical bath deposition method at room temperature as well as at 80°C. It is concluded that the bath temperature is found to be strongly influence on the structural, morphological, compositional properties of SnO_2 thin films Synthesized at room temperature and at high temperature. Synthesized as-deposited and annealed films at room temperature and at high temperature samples were showed tetragonal phases of SnO_2. SEM investigations was revealed well defined spherical structure and agglomerated nano spheres like morphologies for sample A2 and sample C2 respectively. The EDAX analysis of sample A2 showed the presence of high concentration oxygen. The gas response for film synthesized at room temperature (sample A2) showed 44.85% response upon exposure of 28 ppm of LPG gas at 325˚C temperature while the gas response for SnO_2 thin film synthesized at high temperature (80°C) bath temperature is 37.45% for 28 ppm of LPG gas concentration at 325˚C operating temperature.

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