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Thermally Evaporated Tin Oxide Thin Film for Gas Sensing Applications

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In this study tin oxide thin film is deposited on glass substrate by Thermal Evaporation technique for gas sensing applications. While deposition the distance between source and the substrate is maintained at 8cm, the pressure of the chamber is kept at 2.5×10^{-5} torr and rate of deposition is about 6-10 Å/sec at substrate temperature 35-40 °C. Structural, micro structural, optical and gas sensing properties are studied. Here thickness of the film is maintained in between 400-450 nm. The film is annealed at 500 °C for one and half hours. Surface morphology is examined from SEM micrographs by using Scanning Electron Microscope Model – Philips XL 30. From this study the grain size is found to be around 40-45 nm. The structural study of the films was carried out by XRD measurement using SIEMENS diffractometer (Model) D 5000. From the observation it is confirmed tetragonal rutile structure of tin oxide. Optical characteristics are studied by UV/VIS Spectrophotometer Model ELICO-SL-159 in the wavelength range 300-1000 nm and refractive index, thickness of the thin film and band gap are calculated. From this study of optical properties it is observed that the maximum transmittance is about 80 %. The measured refractive index is 2.17 which nearly the same with the theoretical result. The film is investigated for sensing of carbon monoxide gas. Sensitivity test is carried out by a hand make sensitivity tester. Sensitivity of the film to CO gas is measured at different temperatures and was found to be highly sensitive at 220 °C.

Keywords: Thermal Evaporation, Tin Oxide, Spectrophotometer, XRD.

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1. INTRODUCTION

From the recent past environmental pollution rapidly growing due to industrialization, air pollution and became a major threate to globe. To prevent the hostile air pollution, it is essential to control and safety monitoring of the hazardous gases. In the process of air pollution management hazardous gas detection becomes very essential. There are different methods for gas detection like gas chromatography, IR spectroscopy, solid state gas sensing and many others. Among them solid state semiconducting gas sensors are having more advantages due to many factors. Fabrication of semiconducting gas sensors is very easy, less costly and can be designed to operate at different temperatures. Different semiconducting metal oxides have been used as gas sensing material. Among themSnO_2 is a reliable material.

Tin Oxide (SnO_2) is a most important material used in gas sensing applications in domestic, commercial and industrial sectors. Tin Oxide is also known as Stannic Oxide which is an inorganic substance and generally an n-type semiconductor. It has energy band gap of 3.6 eV which is generally high. Tin Oxide crystallizes tetragonal rutile structure with unit cell parameters a, $b = 4.737$ Å and $c = 3.186$ Å. Tin oxide thin films have beneficial properties, such as transparency for visible light (In visible spectrum the film is more transparent due to high band gap), reflectivity for infrared light, low electrical sheet resistance, etc., make them suitable for a wide variety of applications such as intransistors [1], gas sensors [2-4], Photochemical and photoconductive devices in liquid crystal display [5], photo voltaic cells, Protective and wear-resistant coating on glass containers, transparent conductive electrode for solar cells [6], etc. The properties of SnO_2 that influence its potential applications depend on the different phases of its fabrication history. Tin oxide thin films can be synthesized by various methods, such as Spray Pyrolysis [7], ultrasonic spray pyrolysis, Thermal Evaporation [8-9], Laser Pulse Evaporation [10], R.F. Magnetron Co- sputtering [11], Chemical Vapor Deposition [12-13], Sol-Gel [14], Vapor deposition technique [15], etc. Thermal evaporation has advantages for synthesis of non-doped thin films as concern for uniform deposition, easy control over thickness and overall it is cost effective. Tin Oxide thin films are one of the right choices due to their high electron mobility, low operating temperature, high sensitivities, high chemical stability, mechanical simplicity of sensor design, and low manufacturing cost. Un-doped/doped SnO_2 thin films have been using for the detection of gases like NO_2 [2], CO [4, 16-17], H_2S [3, 18], NH_3 [19], etc. We studied tin oxide thin film gas sensing properties for CO gas at low temperatures about 220 °C and at optimal concentration of the gas as 50PPM.

2. EXPERIMENTAL PROCEDURE

In this present paperwork, we prepared tin oxide thin films on coring 7059 glass substrates by thermal evaporation process (Thermal Evaporation unit model - 12A 4D) and studied the Structural, micro structural, optical and gas sensing properties for CO gas. The structural study of the films was carried out by XRD measurement using SIEMENS diffractometer (Model D 5000). Morphological study was carried out from SEM micrographs by using Scanning Electron Microscope Model – Philips XL 30. Optical characteristics were studied by UV/VIS Spectrophotometer Model ELICO-

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SL-159 in the wavelength range 300-1100 nm and refractive index, absorption coefficient, thickness of the thin film and band gap were calculated. Gas sensitivity test was carried out by a homemade sensitivity testing device. Sensitivity of the film to CO gas was measured at different temperatures.

2.1 Fabrication of Thin Film

Tin oxide thin films were prepared by thermal evaporation unit model – 12A 4D on glass substrates (corning 7059, 7.6 cm/2.6 cm/0.1 cm). Before deposition, glass plates were cleaned thoroughly with cleaning liquid soap and then with acetone using ultrasonic cleaner which can remove organic particles on the surface of the glass plate. Finally washed with distilled water and dried. The cleaned substrates were placed inside the vacuum chamber of Thermal Evaporation unit (model 12A 4D). Pure tin oxide (SnO_2) in powder form taken into a toungsten boat and connected between the electrodes, The pressure of the chamber was maintained at 2.5×10^{-5} torr and rate of deposition fixed at 6-10 Å/sec at substrate temperature 35-40 °C. During the process the target and source was maintained at 8 cm apart.

2.2 Annealing

After successful deposition, the substrates were taken out from vacuum chamber and placed in a furnace (Indfurr muffle furnace). Here the samples were annealed at 500 °C temperature for one and half hour.

3. RESULT AND DISSCUSSION

3.1 Optical Characterization

Optical properties of tin oxide thin films were analyzed from the transmission % vs. wavelength graph which was plotted from the data carried out by the equipment ELICO UV/VIS spectrophotometer (model SL-159) in the range from 300 nm to 1100 nm. Refractive index, thickness of the film, absorption coefficient and band gap energy were calculated.

Refractive index is given by,

$$n = \left\{ N + \left(N^2 - \mu^2 \right)^{\frac{1}{2}} \right\}^{\frac{1}{2}} \quad (1)$$

Where

$$N = 2\mu \frac{T_u - T_l}{T_u T_l} + \frac{\mu^2 + 1}{2} \quad (2)$$

And n is the refractive index of thin film μ the refractive index of the substrate, T_u and T_l the transmission maximum at upper envelop and transmission minimum at lower envelop for a particular wavelength λ.

From Fig. 1, for maxima:

$\lambda_1 = 730.208$ nm, $T_u = 0.7963$, $T_l = 0.6105$ and $\mu = 1.5$

by subsituting in (2) we get $N_1 = 2.7716$

from this by equation (1) $n_1 = 2.2588$

for minima:

$\lambda_2 = 828.565$ nm, $T_u = 0.7943$, $T_l = 0.6532$ and $\mu = 1.5$

by subsituting in (2) we get $N_2 = 2.4408$

from this by equation (1) $n_2 = 2.0895$

Thickness of the film is calculated from transmission spectra data.

Thickness of the film d [20] is given by,

$$d = \left| \frac{\lambda_1 \lambda_2}{4\left(n_1 \lambda_2 - n_2 \lambda_1\right)} \right| \quad (3)$$

Where n_1 and n_2 be the refractive index of thin film at maxima (for wavelength λ_1) and corresponding minima (for wavelength λ_2)

Using the values of n_1 and n_2 we calculated thickness of the film as 437 nm.

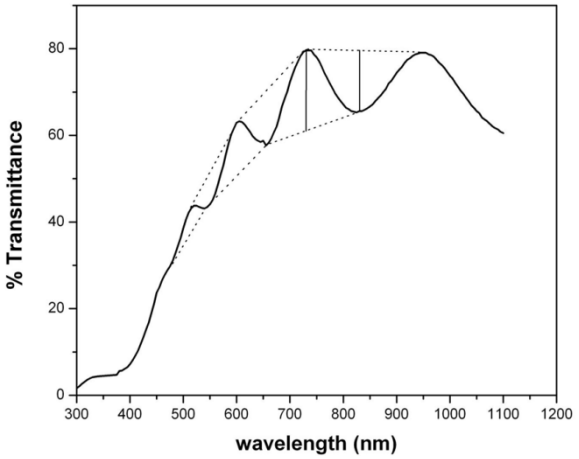

Fig. 1 – Transmittance % vs.wavelength graph

The band gap energy of tin oxide thin film was calculated from the graph $(\alpha h\nu)^2$ vs. $(h\nu)$. When the linear portion of the graph is extended back it intersect eV axis and this intercept is the energy band which is measured as 3.67 eV.

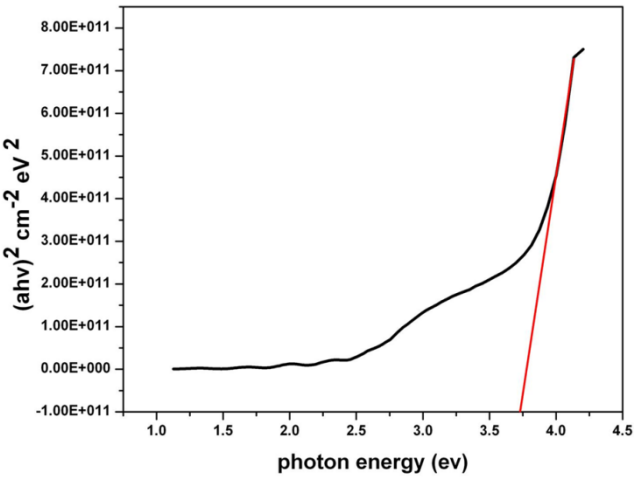

Fig. 2 – $(\alpha h\nu)^2$ vs Photon energy $(h\nu)$

Absorption coefficient α_a is given by the formula,

$$\alpha_a = \frac{1}{d} \ln\left(\frac{1}{T}\right) \quad (4)$$

Here d – thickness of the film, T – optical transmission.

By substituting the value of thickness of the film and optical transmission in equation (4), absorption coefficient was calculated. It was about 10^4 cm^{-1}.

3.2 Structural Analysis

The structural study of the films was carried out by SIEMENS diffractometer (Model) D 5000 using Cu Kα having wavelength $\lambda = 1.540$ Å radiation with a diffraction angle 10° to 70°. From the fig. 3 it was observed that well defined sharp diffraction peaks were formed nearly at the same angle 2θ of tetragonal rutile structure of SnO_2 (JCPDS card no. 88-0287). These well defined diffraction peaks match with the standard interplanar spacing as given in JCPDS card no.88-0287. Since XRD peaks are very narrow and sharp, it indicates higher crystalline quality of SnO_2 thin film. Since the intensity of (101) plane is more, it may be believed that the preferential growth along (101) direction of Sn forms an interstial bond with oxygen and exists as rutile SnO_2. Lattice constants from standard tetragonal rutile structure of SnO_2 $a = b = 4.7373$ Å and $c = 3.1864$ Å, from XRD data we found $a = b = 4.8041$ Å and $c = 3.2585$ Å.

Table 1 – *hkl* value of SnO_2 – XRD

2θ (XRD data of SnO_2 thin film) in degree	*h k l* plane
28.60	110
36.00	200
39.98	111
53.92	220
56.78	002
63.87	221

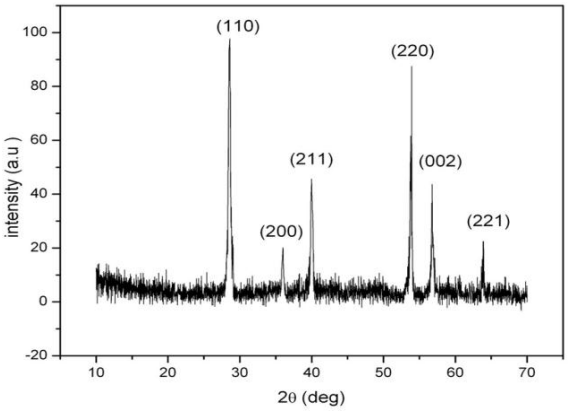

Fig. 3 – XRD paterns of Tin oxide thin film ($h\nu$)

Mean grain size (D):

By using Debye – Scherer formula [21]

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where D is mean grain size, λ the wavelength of X – ray used (1.540 Å), θ is the angle of diffraction and β – FWHM (Full Width Half Maximum) of observed peaks. By using this formula we calculate average grain size as 44.38 nm.

SEM measurement was carried out by Scanning Electron Microscope Model- Philips XL 30. SEM micrograph are shown in the figure4 which shows agglomeration of the grain particles. The average grain size calculated is about 44 nm.

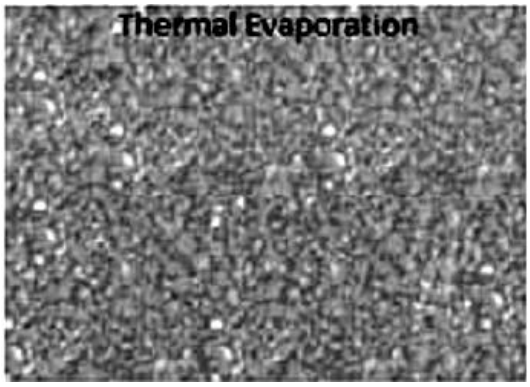

Fig. 4 – SEM images of SnO_2 film

SEM micrograph of thin film contains domes like structure which may be believed as the top surfaces of the grains of the film. Analyzing the data of XRD and SEM measurement for grain size we observed there is no marked difference in grain size calculated by XRD and SEM methods. The grain size calculated by XRD method was nearly same as that estimated by using SEM images.

3.3 Gas Sensitivity Analysis

When thin film of SnO_2 was exposed to air, oxygen from the air is adsorbed onto the surface of the SnO_2 thin film. Electrons from the surface region of the SnO_2 are transferred to the adsorbed oxygen, leading to the formation of an electron-depleted region near the surface of the SnO_2 film. The electron depleted region, where electron density is less, is an area of high resistance and the core region of the film, where electron densities are high, is an area of relatively low resistance. Now the adsorbed oxygen becomes O^- and O_2^- species. When the thin film of SnO_2 is exposed to a reducing gas like CO, surface reactions such as CO+ $O_{ads}^- \rightarrow CO_2 + e^-$ and $2CO + O_{2,ads}^- \rightarrow 2CO_2 + 2e^-$ took

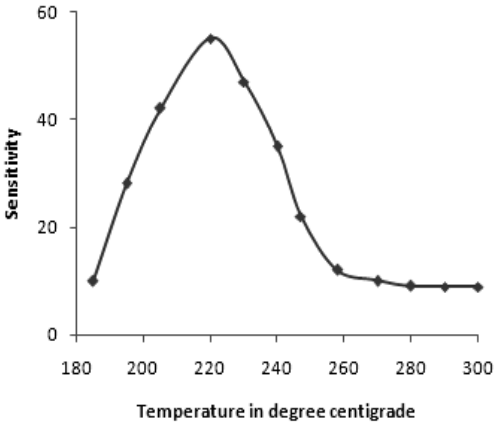

Fig. 5 – Sensitivity vs. Temperature in °C

place. Due to which electrons releases and the electrons released from surface reaction transfer back into the conduction band leading to a decrease in the resistance or increase in conductance of the SnO_2 thin film.

The sensitivity of the SnO_2 thin film for carbon monoxide gas has been studied at concentration 50 ppm. The variation of the sensitivity with temperature is shown in the Fig. 5.

Fig. 5 depicts that maximum sensitivity occur at temperature at 220 °C. At low temperatures there is less oxygen coverage, when the sensor is exposed to air and therefore when the target gases are introduced there is negligible change in sensitivity. As the operating temperature increases, number of adsorbed oxygen species would have reacted more and more number of electrons which are released due to this reaction sent back to conduction band i,e desorption rate of adsorbed gases also increases with increasing temperatures.

4. CONCLUSION

Tin oxide thin films were synthesized by thermal evaporation method. From optical measurement the band gap was measured as 3.67 eV. XRD and SEM study revealed the grain size 44.38 nm and 44 nm respectively. The film was studied for carbon monoxide gas sensing. It was observed that the sensitivity of the film for CO gas at 50 ppm was more at 220 °C due to available of more surface area to expose.

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