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ETHANOL GAS SENSING MEASUREMENT USING SPIN COATED NANOCRYSTALLINE TIN OXIDE (SnO2) THIN FILM

Electronics

Amrut S. Lanje* Professor and Head Department of Electronics, Dr. Ambedkar College, Chandrapur (M. S.) – 442 410, India. *Corresponding Author

Gopesh Kumar Singh Department of Electronics, Anand Niketan College, Warora (M. S.) – 442 410, India.

ABSTRACT

Metal oxides semiconductors like Tin Oxide (SnO2) gas sensors are widely used for the detection of toxic and hazardous gases such as CO, NH3, CH3OH, H2S and LPG etc. In the present work, SnO2 nanoparticles thin films on glass substrate were prepared using sol-gel synthesis method. The crystallographic, morphological and gas sensing properties of SnO2 nanoparticles are studied.

SnO2 nanoparticles are prepared by sol-gel route at 500 ºC using stannous chloride as a precursor, ammonia solution as a precipitating agent. X-ray diffraction (XRD) study reveals tetragonal rutile structure of SnO2 nanoparticles without any secondary phase. Scanning electron microscopy (SEM) image shows the spherical grain morphology of SnO2 nanopaticles. The average crystallite size of SnO2 nanoparticles is found to be 11.26 nm using Scherrer formula. This particle size is same as the average particle size from TEM image. Ethanol gas sensing measurement of prepared spin coated thin film (at 30 sec., 4000 rpm and 5 layers) are carried out using gas sensing chamber. It shows that the sensor with high response/selectivity and low response/recovery times based on SnO2 thin film can stand as good sensor for detection of ethanol gas.

KEYWORDS

Nanoparticles; Sensor; SnO2 Ethanol; Thin film.

INTRODUCTION

Tin oxide is one of the important and widely used transparent conductors with high conductivity, optical transparency in the visible region, high reflectivity in the IR region and high gas sensitivity, which makes it technologically prospective material. Tin oxide with low electrical resistance [1] and presence of oxygen vacancies, makes it a promising material for electrical applications [2-4]. Electrical conductivity in transparent materials occurs in just a few systems like 4d metal oxides SnO_2 and In_2O_3. Kilik *et al.* investigated the transparent conductivity related to the existence of shallow donor levels near conduction band formed by large concentration of oxygen vacancies [5].

Synthesis processes of nanoparticles have been to affect crystallinity, microstructure and defect structure of the nanoparticles. Several methods including sol-gel [6], hydrothermal [7], electrospinning [8] have been utilized to synthesize SnO_2. Among these methods, the sol-gel method seems to be the most suitable due to its simplicity, easy of adding dopants, promise for mass production and low cost. The properties of SnO_2 are found to be dependent on the processing conditions and nature of the precursors used. The precursors play an important role in growth, the structure and the morphology as well as optical and electrical characteristics of the doped material. Optical devices like solar cells, panel displays are mainly affected by signal loss and delay. Hence, we have to improve the conductivity without affecting the transmission. Similarly, Tin oxide play an important role for applications in solar photo-thermal conversion [9, 10]. Due to the limitation of solubility, these ions act as grain growth inhibitors and remain aggregates at the grain boundaries. Metal oxide gas sensors are widely used for the detection of toxic and hazardous gases such as CO, NH_3, CH_3OH, H_2S and LPG etc.

In the present work, sol-gel synthesis is used to obtain SnO_2 nanoparticles thin films on glass substrate. The crystallographic, morphological and gas sensing properties of SnO_2 nanoparticles are studied.

Synthesis And Characterization Of SnO_2 Nanoparticles

Experimental

Synthesis

Nanocrystalline SnO_2 samples are prepared by a sol-gel route using Sn precursors taken in the form of chlorides. In a typical synthesis process of SnO_2, dissolve 8g of $SnCl_4$. $2H_2O$ from Merck India, in 100 ml ethanol solution (Ethanol+ Water 1:1) and Stirred about 20 min until a transparent sol is produced. Add aqueous Ammonia solution (25% Merck, India) drop wise to the solution under constant stirring and pH of solution is adjusted to a value up to 8. After 24 Hr of aging in the air resulting opal gel are centrifuged and washed with ethanol at least 5 times to remove ammonia and chloride impurity. The collected gel is dried in furnace over 80 ^{0}C/4h in the air to remove moisture and then the sample is crushed and sintered at 500 ^{0}C/4 Hr. Finally, an ash colored nanoparticles are formed [11-12].

The chemical reaction for the reduction of SnO_2 is as follows:

$$SnCl_2.2H_2O + 2NH_3 \rightarrow SnO_2 + 2NH_4Cl(aq) + H_2 \quad ---(1)$$

Material Characterization

Synthesized nanoparticles are characterized using X-ray diffraction (XRD) measurements using a Bruker D8 Advance diffractometer with monochromatic CuK_γ radiation (λ=1.5406 A^0) by recording θ in the range of 20-70^0 in a step of 0.02^0. To study the surface morphology & grain sizes, Scanning Electron Microscope (SEM), JEOL JSM 5600 with Resolution: 3.5 nm, Magnification: x18 to 300,000, Accelerating Voltage : 0.5 to 30 kV and Transmission Electron Microscope (TEM) model JEOL/JEM 2100 was employed with acceleration voltage 200kV and 2000X – 1500000X magnification. ImageJ computer program was used to investigate the particle size distributions. Fourier Transform Infra-red (FT-IR) spectra of the powder was recorded using a Bruker, Germany, Model vertex 70 using the KBr pellet technique in the range 400 to 4000 cm^{-1} with a resolution of 0.5 cm^{-1}.

Finally, ethanol gas sensing measurement of prepared spin coated thin film (at 30 sec., 4000 rpm and 5 layers) are carried out using gas sensing chamber. The ethanol sensing measurements is carried out by placing the sensor in a chamber, as ethanol gas is exposed to the sample surface by Hamilton syringe. The resistance of the sample was measured by two-point probe method using USB NI 6210 on PC. The measurement setup is interfaced with computer and automated with the help of LabVIEW program. The data is continuously measured with time, to be used for the calculation of gas sensitivity, response time, recovery time, reproducibility and stability.

Table 1: Grain size, Volume, Microstrain (ξ), dislocation density (δ) and Intensity at (110) of SnO_2 nanoparticles

	D (nm)	a (Å)	c (Å)	V (Å^3)	strain ξ X 10^{-4})	δ x10^{14} line/m^2)	Intensity (110)	δ x10^{14} line/m^2)
SnO_2	12	4.740	3.184	71.555	19.45	59.17	717	59.17

RESULTS AND DISCUSSION

Structural and Morphological analysis

To study the crystallite size, structure and lattice parameters of SnO_2, XRD data is used. The X-ray diffraction patterns of SnO_2 nanoparticles sintered at 500 ^{0}C shown in Fig. 1 XRD peaks are indexed using Powder X software and matched with the tetragonal rutile structure of SnO_2 and are observed to be in consistent with those in the standard card (JCPDS 77-0452), with a maximum intensity corresponding to (110) plane [13]. Further, it has been observed that lattice parameters a,

c and cell volume are calculated using unit cell software program as shown in Table 1. All calculated values are in good agreement with those reported in JCPDS 77-0452.

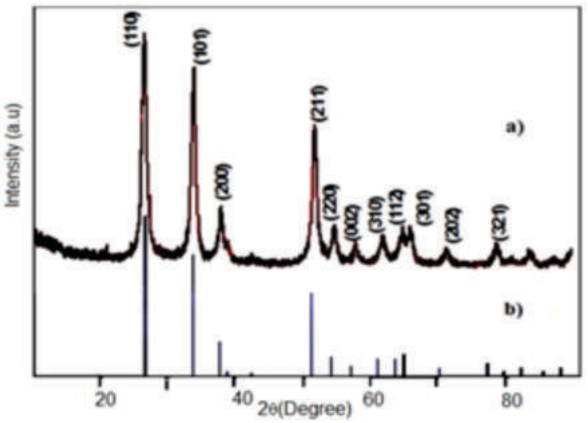

Fig. 1: (a) Plot of XRD pattern of SnO_2 nanoparticle sintered at 500 ^{0}C (b) JCPDS file No. 77-0452

Moreover, the texture coefficient (TC) gives information regarding the maximum preferred orientation along with the diffraction plane. It means the increase in the preferred orientation is related with the increase of the number of grains along that plane. $TC_{(hkl)}$ values are calculated from XRD data [14]:

$$TC_{(hkl)} = \frac{I(hkl)/\ I_0(hkl)}{N^{-1}\Sigma I(hkl)/\ I_0(hkl)} \quad \text{----(2)}$$

Where, I(hkl) is the measured intensity of X-ray data, I_0(hkl) is the corresponding intensity obtained from the JCPDS 77-0452 card and N is the number of diffraction peaks observed in the XRD pattern. TC is one of the important structural parameter to secure the implementation of the prepared materials. Agashe et al. [15] reported (200) preferred orientation of SnO_2 thin films, is suitable for many optoelectronic and gas sensing applications. Elongovan et al. [16] reported that SnO_2 surface having a very high reactivity for the oxidation reactions due several chemisorbed oxygen species.

The average size of the crystalline grains of the sample was calculated using at full width half-maximum (FWHM) and Debye-Scherrer's formula [17] given by:

D_{hkl}=0.9l/bcosq ----------(3)

Here, D_{hkl} is the crystalline size, l is the X-ray wave length, b is the (110) full width at half maximum (FWHM) and q is the angle of diffraction. The estimated sizes at the most intense crystallographic plane (110) are given in Table 1. The crystallite size of the pure SnO_2 nanoparticles are observed to be 12nm. The ratio of the lattice parameters a and c is a measure of lattice distortion, calculated from XRD data (Table 1). From the above discussion, it can be concluded that the narrowing or broadening of the XRD peaks of SnO_2 occurred due to atomic diffusion and lattice strains and not by lattice distortions. The particle size calculated by Scherer formula for SnO_2 have been further validated by Transmission Electron Microscopy (TEM) observations. Increase in unit cell volume shows expansive strain in the particles and decrease in unit cell volume shows compressive strain in the particles.

On the other hand, geometric mismatch between crystalline lattices of thin films and substrate may develop stresses [18], and these stresses can cause microstrains (z) in the films. The microstrain values are calculated by following relation [19]:
z = (1/sinq) [(l/D) - (bcosq)] ----------(4)

Where, b is FWHM of (110) peak and D is the average grain size.

Dislocation is one of the important factors to investigate growth mechanism. It plays an important role in the variation of electrical resistance due to increase in the dislocation density then gives rise to disorders, crystal defects in lattice and decrease in the crystallinity. Dislocation density (d) gives information on length of dislocation lines per unit volume (lines/m^2). It can be estimated by following relations [19].

$d = 1/D^2$ ----------(5)All calculated values of z and d are given in Table 1.

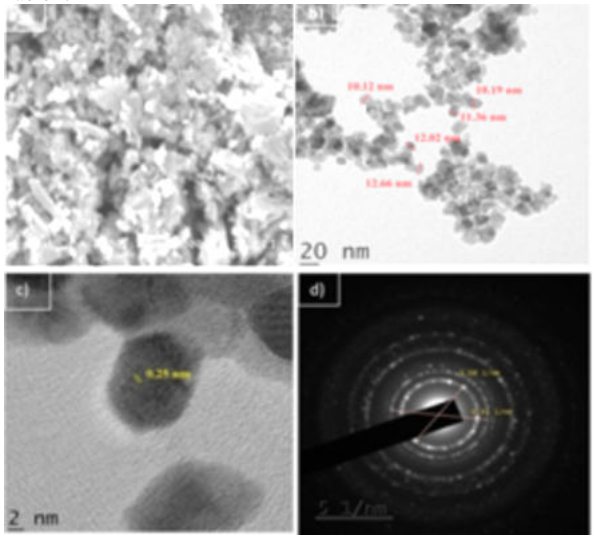

Figure 2: (a) SEM and (b), (c) and (d) TEM images of SnO_2 nanopartilces

Fig. 2 (a) shows the typical morphology of SnO_2 nanoparticles. Powder samples were used for SEM analysis. Powder was placed on the sample holder using double sided tape and gold coated with sputter coater. It is seen that SEM image of SnO_2 microstructure of these powder samples shows the presence of large spherical aggregates of smaller individual nanoparticles with variations in particles size. Due to the large surface and high surface energy of primary nanoparticles, tin oxide tiny particles are prone to be aggregated. The randomly grown grains give rise to scattering effect, which reduces the transmittance [20]. The surface state of such oxide nanoparticles influence optical and electrical properties.

Fig. 2 (b), (c) and (d) shows TEM image of prepared SnO_2 nanoparticles with an average diameter of about 11.26 nm. The powder samples were dispersed in ethanol and sonicated in an ultrasonic bath. The particle size obtained from TEM analysis closely match with the crystalline size calculated from XRD data.

Effect Of Temperature And Concentration On Gas Response:

The gas sensitivity of tin oxide as a function of operating temperature range, 150 to 350 ^{0}C and ethanol gas concentration (100 -1500 ppm) is displayed in Fig 3.

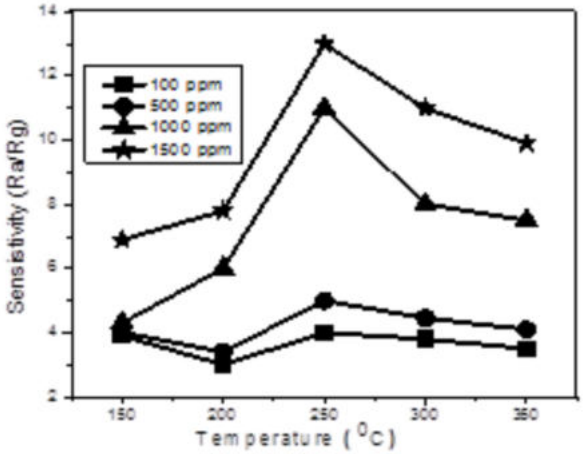

Figure 3: Plot Of Variation Of Sensitivity Of SnO_2 Thin Film For Ethanol Gas

It shows variation of sensitivities tin oxide gas sensor from 150 to 350 ^{0}C for 100-1500 ppm concentration of ethanol gas. It is observed that

highest sensitivity is achieved under exposure to concentration of 1500 ppm of ethanol gas at 250 ^{0}C. However, further increasing the temperature sensitivity decreases. At the optimum sensitivity, gas sensor is able to overcome the activation energy barrier, while reduction in gas sensitivity is due to the difficulty in adsorption of the gas [21].

Response And Recovery Time:

The response time is the time taken by the sensor element to achieve 90% of stable output when the gas is introduced. The recovery time is the time taken by the sensor element to reach 90% of its original value. Fig. 4 shows the response and recovery time of SnO_2 sensor at 250^{0}C and 100-1500 ppm ethanol gas.

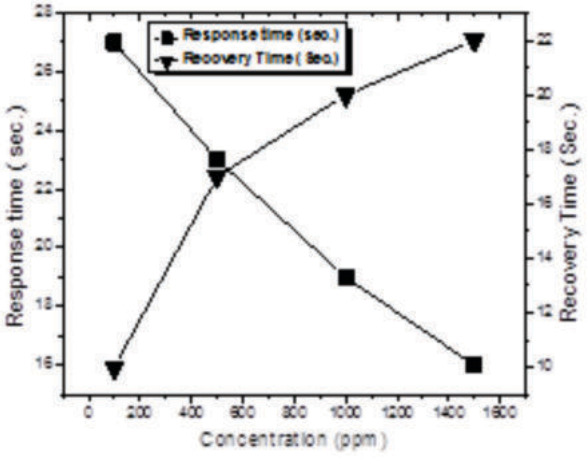

Figure 4: Variation Of Response And Recovery Time Of SnO_2 Sensor With Ethanol Concentration

It is observed that when the target gas is inserted in the gas sensing chamber, the resistance of the sensor decreases drastically. However, when air is introduced in the chamber, the resistance regains its original value. Fig. 5 shows the variation of response time and recovery time with concentration of ethanol gas in the chamber.

Reproducibility and stability study of SnO_2 sensor:

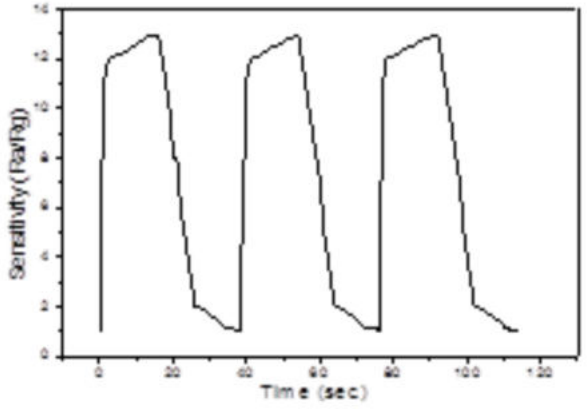

Figure 5: Plot Of Reproducibility Of SnO_2 Thin Film Sensor At 1500 Ppm Of Ethanol Gas

In order to study the reproducibility of SnO_2 thin film gas sensor, the sensing test was repeated three times at 1500 ppm gas concentration and at 250 °C, shown in Fig. 5. It is observed that the response of the SnO_2 sensor towards ethanol is nearly constant confirming the reproducibility of the sensor.

In order to investigate the stability of the SnO_2 sensor at 1500 ppm of ethanol gas and at operating temperature of 250 °C, the response of the film was measured for 60 days at an interval of 15 days and the result is shown in Fig. 6.

It is observed that the response time dropped initially and after 30 days nearly constant with 57% stability. This decrease in the gas sensing response with the number of days can be attributed to the formation of layer of oxides/moisture [22]. Thus, it can be concluded that the sensor with high response/selectivity and low response/recovery times based on SnO_2 thin film can stand as good sensor for detection of ethanol gas.

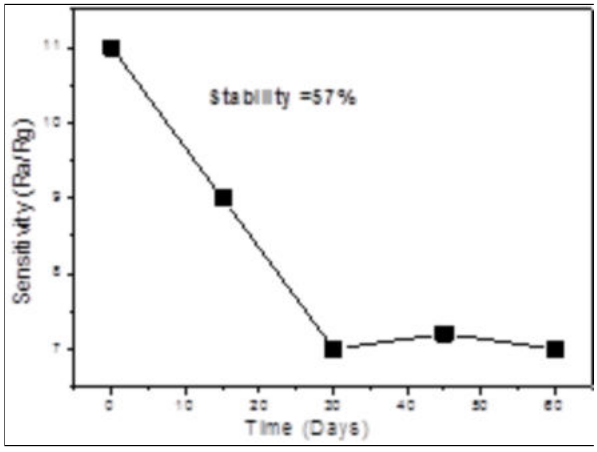

Figure 6: Variation stability study of SnO_2 sensor

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