

## Influence of the Substrates Nature on Optical and Structural Characteristics of SnO<sub>2</sub> Thin Film Prepared by Sol-Gel Technique

Sumanta Kumar Tripathy<sup>1,\*</sup>, Bhabani Prasad Hota<sup>2</sup>

<sup>1</sup> GVP College of Engineering (Autonomous), Madhurawada, Visakhapatnam, A.P., India

<sup>2</sup> Godavaris Mahavidyalaya, Banpur, Khurda, Odisha, India

(Received 06 February 2013; revised manuscript received 02 July 2013; published online 12 July 2013)

In this presentation we synthesized SnO<sub>2</sub> thin film by sol-gel process. Starting from Tin(II) chloride as precursor and methanol as solvent the film was deposited on glass and quartz substrate by novel dip coating method. Structural and morphological analysis was carried out by X-Ray diffraction (XRD) measurement and Scanning electron microscopy (SEM). Optical characteristics were analyzed from the study of transmission spectrum data obtained by UV / VIS Spectrophotometer. It is observed that the transmission and grain size were more in case of quartz than glass substrate whereas the band gap was more in glass than quartz substrate. From XRD measurement it was confirmed the tetragonal structure of SnO<sub>2</sub>. EDS analysis depicts the weight percentage of Sn and O as 78.71 % and 21.29 % respectively and also confirms the purity of the film. From the study we concluded that the structural configuration changed a little with change in substrates at same conditions and quartz is the preferable substrate than glass.

**Keywords:** Rutile structure, SEM, Sol-Gel Method, Transmittance and XRD.

PACS numbers: 68.37 Hk, 68.55. – a, 78.40. – q

### 1. INTRODUCTION

Since last two decades nanotechnology has been chosen as top priority among science and technology due to its adherence with almost all the branches of science. These days the study and applications of thin film technology is concurred entirely the research community. The current paper which describes the synthesis and study of characteristics of Tin Oxide (SnO<sub>2</sub>) is really more interesting for researchers due to its vast applications. Due to the properties like reflectivity, transparency, low electrical sheet resistance etc., tin oxide thin films has immense applications such as gas sensing material for gas sensors devices [1-3], in transistors [4], photovoltaic cell [5], transparent conductive electrode for solar cells[6-7], photochemical and photoconductive devices in liquid crystal display [8] etc. Till today so many methods were adopted to synthesize doped or un-doped tin oxide films such as Thermal Evaporation [9-10], Chemical Vapor Deposition [11-12], R.F. Magnetron Co-sputtering [13], Laser Pulse Evaporation [14-15], Spray Pyrolysis [16-18], ultrasonic spray pyrolysis [19] and sol-gel [20-22]. Above all Sol-gel method gives more attention due to many advantages like less processing cost, simple experimental arrangement, easy control on film thickness, greater homogeneity and more purity etc. In addition to above advantages Sol-gel technique controls the film morphology and particle size which is more useful for sensors.

The rehabilitated curiosity of researchers in SnO<sub>2</sub> is due to its properties like reflectivity, transparency, low electrical sheet resistance, hardness and chemically stability. Tin Oxide crystallizes tetragonal rutile structure with unit cell parameters  $a = b = 4.737 \text{ \AA}$  and  $c = 3.186 \text{ \AA}$ . It is a *n*-type semiconductor having high band gap energy ( $\approx 3.6 \text{ eV}$ ) [23] and is more transparent in the region of visible spectrum due to high band gap, having high electrical conductivity due to free electrons in oxygen vacancy holes.

In this study we visualized dip coating method. Starting from Tin (II) Chloride, methanol as solvent and glacial acetic acid as chelating agent a transparent solution was prepared and SnO<sub>2</sub> thin film was synthesized on a glass and quartz substrate by sol-gel dip coating technique. Our main objective in this work was to prepare SnO<sub>2</sub> thin films by the sol-gel method on glass and quartz substrate and to investigate the influence of the nature of the substrate on the optical and morphological properties.

Transmission spectrum was studied with the help of ELICO UV / VIS spectrophotometer (Model – SL-159) in the wavelength range 300 nm to 1000 nm. From the transmission graph optical properties were analyzed and it was concluded that for nearly same thickness and at same conditions transmission was more in case of quartz than glass substrate and also band gap was less in case of quartz substrate. Structural analysis of the films was carried out by XRD measurement using SIEMENS Diffractometer (Model D5000). The study confirms tetragonal rutile structure of SnO<sub>2</sub>. Surface morphology was examined from SEM micrographs by using Scanning Electron microscope (Model- Philips XL 30). From both XRD and SEM it was observed that the grain size and strain of SnO<sub>2</sub> thin film was more in the case of quartz substrate than glass substrate. EDS analysis substantiated the purity of the SnO<sub>2</sub> thin film.

### 2. EXPERIMENTAL PROCEDURE

A clear and homogeneous solution was prepared by dissolving 1 gm of anhydrous Tin (II) chloride (SnCl<sub>2</sub>) in 50 ml of methanol (CH<sub>3</sub>OH) with 1 gm glacial acetic acid (CH<sub>3</sub>COOH) and stirred by a stirrer for 45 minutes at NTP. Before coating on the substrates both the glass and quartz substrates were thoroughly cleaned with cleaning liquid soap and then with acetone to remove organic particles on the surface and

\* sktripathy2009@gmail.com

then washed with distilled water. To prevent local hydrolysis the substrates were then soaked with TEA diluted isopropyle alcohol for 10 minutes and then dried. Then the substrates were dipped in the prepared solution by hand and withdrawn [24]. The coated glass substrates were dried at 150 °C in a muffle furnace for 1 hr and then heat treated at 300 °C for about 15 minutes. The above procedure was repeated for a number of times to get the desired thickness. In this investigation we repeated the procedure for six times to get a thickness of 645-650 nm. After getting the required thickness finally heat treatment was carried out on each substrate at 500 °C for one and half hour in a muffle furnace in air.

Optical characterization was studied from transmission % vs. wavelength curve which was plotted from the data obtained from transmission spectrum analysis of the film by ELICO UV / VIS spectrophotometer Model – SL-159 in the wavelength range 300 nm to 1000 nm. The refractive index and the thickness of the film were calculated using the formula [25]

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

where,

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

and

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

Where  $n$  and  $d$  are the refractive index and thickness of the thin film  $\mu$  refractive index of the substrate,  $T_u$  and  $T_l$  be the transmission maximum at upper envelop and transmission minimum at lower envelop for a particular wavelength  $\lambda$ ,  $n_1$  and  $n_2$  be the refractive index of the thin film at maxima (for wave length  $\lambda_1$ ) and corresponding minima (for wave length  $\lambda_2$ ) where phase difference is  $\pi$ . The optical band gap was obtained from the plot of  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  in SnO<sub>2</sub> thin film deposited on quartz and glass substrate. It has been observed the band gap were 3.7 eV and 3.62 eV in case SnO<sub>2</sub> thin film deposited on glass substrate and quartz substrate, respectively. XRD measurement was carried out by using SIEMENS Diffractometer and study of morphology was done by Scanning Electron microscope.

### 3. RESULTS AND DISCUSSION

#### 3.1 Optical Measurement

Optical characteristics of SnO<sub>2</sub> thin films on glass and quartz substrates were studied from transmission % vs. wavelength curve in the wavelength range 300 nm to 1000 nm. From Fig. 1 it was clear that the surface quality and homogeneity of the thin film were brilliant and this substantiates that SnO<sub>2</sub> thin film reveals semiconducting properties as it was established by Nowak that the pure semiconducting compounds

have a sharp absorption edge [26]. In the visible region of the spectra, the transmission of SnO<sub>2</sub> thin film was very high, due to the fact that the reflectivity is low and there is less absorption due to excitation of electrons from the valence band to conduction band [27].

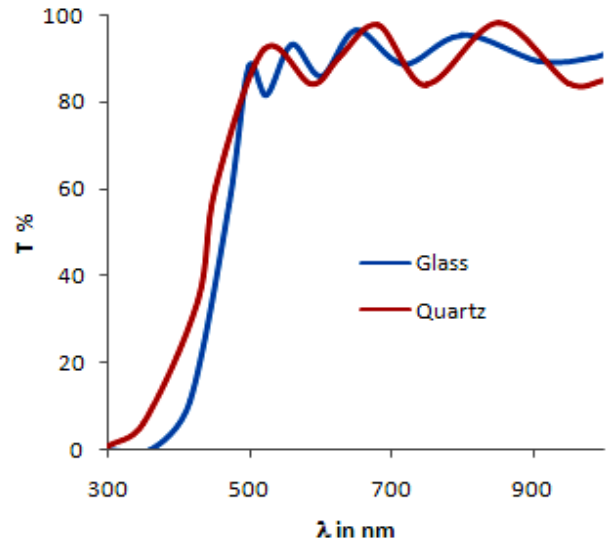


Fig. 1 –  $T\%$  vs.  $\lambda$  in mm in the wavelength range 300 nm-1000 nm.

From Fig. 1 it was noticeable that transmittance was more in case of quartz substrate than glass substrate. It may be due to high porosity and larger grain size and less absorption in the film deposited on quartz substrate. It was also obvious that transmission values were more than 0.80 at wave length greater than 450 nm in both the cases.

From the Transmission vs. wavelength graph average refractive index and thickness were calculated and the values were mentioned in Table 1.

Table 1 – Film thickness and refractive index of the film

Substrate	Film thickness (nm)	Avg. Refractive Index (n)
Glass	645.98	2.07
Quartz	649.31	2.13

Looking at the data presented in Table 1, one can wind up that the refractive index of SnO<sub>2</sub> thin film deposited on quartz substrate was more than the refractive index of SnO<sub>2</sub> thin film deposited on glass substrate at same conditions which may be due to little porosity in the film grown on quartz substrate.

The values of the refractive index  $n$  for SnO<sub>2</sub>, thin films as calculated were plotted against the wavelength in Fig. 2. It was observed from this figure that the refractive index  $n$  decreases with the increase in the wavelength  $\lambda$  and refractive index of SnO<sub>2</sub> thin film was more in case of quartz substrate than glass substrate. The higher value of refractive index may probably due to the increase of inhomogeneity and surface roughness of the films due to larger grain size in case of quartz substrate.

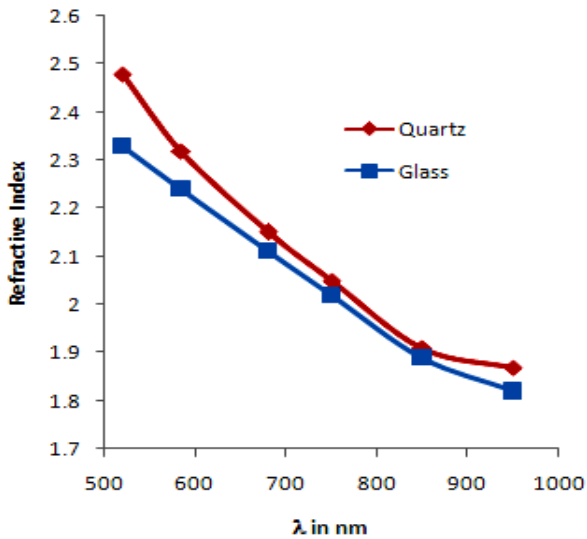


Fig. 2 – Refractive Index (*n*) vs. Wavelength (*λ*) in nm

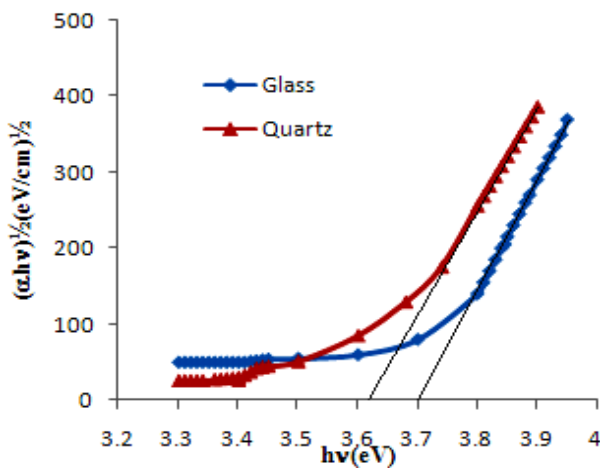


Fig. 3 –  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  for SnO<sub>2</sub> films deposited on different substrate

The absorption coefficient ( $\alpha$ ) was calculated from the expression [28].

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right)$$

where  $d$  thickness of the film and  $T$  optical transmission. The calculated absorption co-efficient was about  $10^4 \text{ cm}^{-1}$  for both the cases. The calculated absorption coefficient data was fitted to the relation given by Davis and Mott [29] as

$$\alpha h\nu = A(E - E_g)^2$$

where  $A$  a constant which was almost independent of the chemical composition of the semiconductor,  $E = h\nu$  the photon energy  $E_g$  the optical band gap. The Fig. 3 shows the plot of  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  in SnO<sub>2</sub> thin film deposited on quartz and glass substrate. It has been observed that the graph was linear over a wide range of photon energies which was due to direct type of transition. When the linear portion was extrapolated to the  $h\nu$  axis the intercept gives the band gap which was 3.7 eV and 3.62 eV in case SnO<sub>2</sub> thin film deposited on

glass substrate and quartz substrate respectively. The reported band gap values for SnO<sub>2</sub> thin film were between 3.3 and 4.0 eV and for single crystal 3.6 eV [30]. The band gap of SnO<sub>2</sub> thin film deposited on quartz substrate was less than the band gap of SnO<sub>2</sub> thin film deposited on glass substrate due to growth of grain and improvement of the degree of crystallization.

### 3.2 Structural Analysis

Fig. 4 shows the XRD pattern of SnO<sub>2</sub> thin film deposited on quartz and glass substrates. XRD measurement was carried out by Siemens Diffractometer Model D-5000 using CuK $\alpha$  having wavelength  $\lambda = 1.540 \text{ \AA}$  radiation with a diffraction angle  $10^\circ$  to  $70^\circ$ .

XRD pattern indicates that in both the cases well defined sharp diffraction peaks were seen nearly at same angle of  $2\theta$  which may be considered to be the crystalline tetragonal rutile structure of SnO<sub>2</sub> (JCPDS Card No. 88-0287). XRD peaks were very narrow and sharp which shows higher crystalline quality of the SnO<sub>2</sub> film. The (101) peak has the largest intensity in both the cases, so it may be believed the preferential growth along direction (101) hence Sn forms an interstitial bond with oxygen and exist as rutile SnO<sub>2</sub>. The figure depicts a significant increase in the intensity of the X-ray diffraction peaks in case of quartz substrate this may be due to additional nucleation centers for the SnO<sub>2</sub> growth due to which grain size also increased.

The well-defined peaks which match the standard interplanar spacing were shown in the Table 2.

Table 2 – hkl value of XRD

$2\theta$ in degree	hkl (Plane)
26.6	110
33.9	101
38	200
39	111
51.8	211
54.8	220
61.9	310

XRD spectrum was analyzed with Gaussian function where FWHM was determined. By using Debye-Scherrer formula

$$D = 0.94\lambda / \beta \cos\theta,$$

where  $D$  mean grain size,  $\beta$  – FWHM (Full width and half maxima) of the observed peak,  $\lambda$  – wavelength of X-Ray used for diffraction,  $\theta$  – angle of diffraction. Using the above formula the average grain size of the deposited film was calculated as 48.54 and 51.27 nm for the film grown on glass and quartz substrate. This difference may be probably due to the presence of strains distributed unevenly in the film.

Strain of SnO<sub>2</sub> thin films on glass and quartz substrates, was calculated by a formula [31]. From calculation it was found that the value of strain of SnO<sub>2</sub> film deposited on glass and quartz substrate were 0.0097 and 0.0114, respectively. Thus strain on quartz was more due to larger grain size and from the morphology study it is believed that mechanical strains are unevenly distributed over the film thickness.

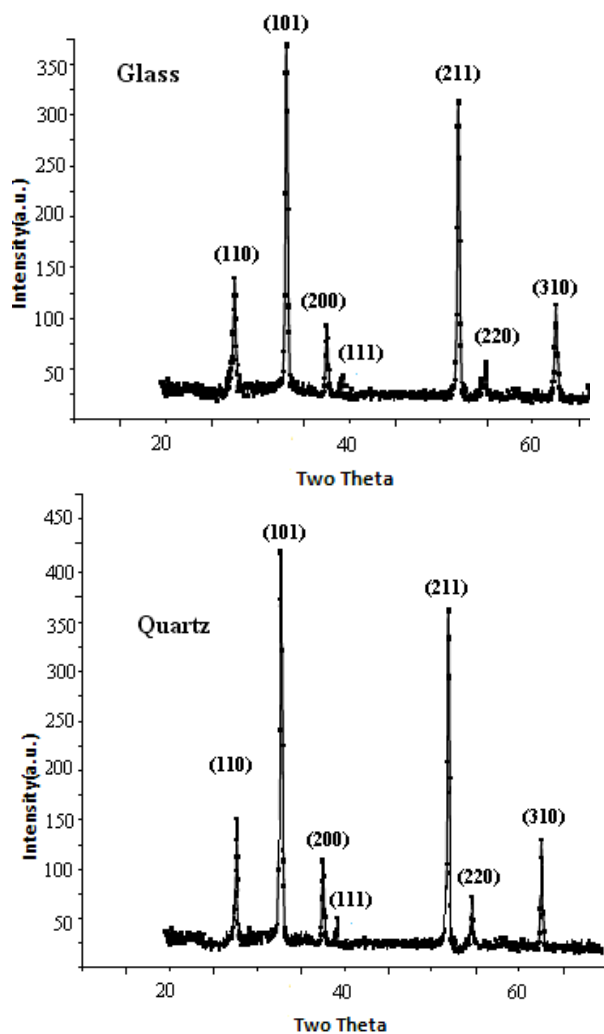


Fig. 4 – XRD Pattern of SnO<sub>2</sub> thin film deposited on glass and quartz substrate

### 3.3 Morphological Analysis

SEM images of SnO<sub>2</sub> thin film deposited on glass and quartz substrates were shown in Fig. 5. SEM measurement was carried out by Scanning Electron Microscope Model- Philips XL-30. SEM micrograph shows agglomeration of the grain particles in both the cases with larger grain size in case of quartz substrate. From the SEM images it was clear that micro-structural properties as well as grain size changes when substrates were different at same conditions. SEM micrograph of thin film contains dome like structure and the size of the domes was more in case of quartz crystal. This dome like structures may be believed as the top surfaces of the grains of the film. In case of quartz more agglomeration of grains observed. Since the size of domes was more in case of quartz substrate so it may be concluded that the grain size of the film deposited on quartz was bigger than the grain size of the film deposited on glass substrate.

From the data of XRD and SEM measurement for grain size we experienced a significant discrepancy in grain size calculated by XRD and SEM methods. The grain size calculated by XRD method was smaller than that estimated by using SEM images. It was

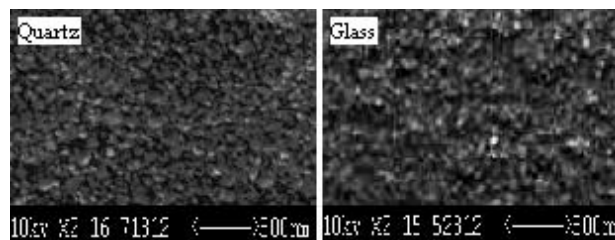


Fig. 5 – SEM images of SnO<sub>2</sub> film for quartz and glass substrate

observed that for glass substrate the grain size 50.12nm in SEM measurement and 47.34nm in case of XRD measurement where as for quartz substrate the grain size is 52.45 nm in SEM measurement and 51.27 nm in XRD measurement.

### 3.4 Energy Dispersive Spectroscopy Analysis

The quantitative analysis of the films was carried out by Energy Dispersive Spectroscopy and the spectrum obtained shown in the Fig. 6. From the spectrum it is clear that only Sn and O are present in the film which confirms the purity of SnO<sub>2</sub> thin film.

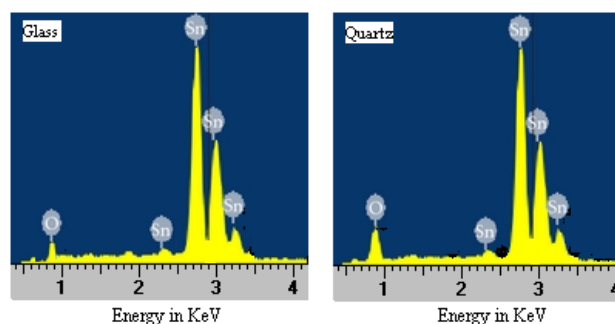


Fig. 6 – EDS spectrum of SnO<sub>2</sub> thin film

Stoichiometrically the weight percentage of Sn and O should be 78.77 % and 21.23 %, respectively. But we observed percentage of Sn and O in the film grown on quartz substrate as 78.49 % and 21.51 % respectively and for glass substrate it is 78.71 % and 21.29 %, respectively.

## 4. CONCLUSION

By sol-gel (dip coating) method SnO<sub>2</sub> thin films were synthesized on glass and quartz substrate. Comparing the results obtained we brought to a close that nature of substrate influences on film morphology as well as grain size. From XRD study it was concluded that the structural configuration changes with change in substrates. XRD study wraps up that grain size of the SnO<sub>2</sub> thin film deposited on quartz substrate was more than deposited on glass substrate. Optical characteristics of the thin film were determined from the transmittance spectra in the UV-VIS region using the envelop method. It was observed that transmittance was more in case of quartz substrate and band gap was more in case of glass substrate and transmission value were more than 0.80 at wave length greater than 450 nm in both the cases. XRD result confirms that the

product was tetragonal rutile structure. From SEM images it was concluded that the surface roughness of the film in case of quartz substrate was more. EDS result confirms the purity of the SnO<sub>2</sub> thin film. As sensing of gas by thin film will be more in case of more surface roughness, the obtained experimental results can be suitably used for gas sensors.

## REFERENCES

1. A. Sutti, C. Baratto, G. Calestani, C. Dionigi, M. Ferroni, G. Faglia, G. Sberveglieri, *Sensor. Actuat. B: Chem.* **130**, 567 (2008).
2. L.A. Patil, D.R. Patil, *Sensor. Actuat. B* **120**, 316 (2006).
3. H.J. Lim, D.Y. Lee, Y.J. Oh, *Sensor. Actuat. A* **125**, 405 (2006).
4. M.S. Arnold, P. Avouris, Z.W. Pan, Z.L. Wang, *J. Phys. Chem. B* **107**, 659 (2003).
5. H. Cachet, J. Bruneaux, G. Folcher, C. Levy-Clement, C. Vard, M. Neumann-Spallart, *Sol. Energ. Mat. Sol. C.* **46**, 101 (1997).
6. A. Aoki, H. Sasakura, *Jpn. J. Appl. Phys.* **9**, 582 (1970).
7. A. Mohammadi-Gheidari, E. Soleimani Asl, M. Mansorhoseini, S. Mohajerzadeh, N. Madani, W. Shams-Kolahi, *Mater. Res. Bull.* **40**, 1303 (2005).
8. U. Betz, Kharrazi, M. Olsson, J. Marthy, M.F. Escola, F. Atamny, *Surf. Coat. Technol.* **200**, 5751 (2006).
9. E. Comini, G. Faglia, G. Sberveglieri, Z. Pon, Z.L. Wang, *Appl. Phys. Lett.* **81**, 1869 (2002).
10. V.S. Vaishnav, P.D. Patel, N.G. Patel, *Thin Solid Films* **490**, 94 (2005).
11. P.M. Gorley, V.V. Khomyak, S.V. Bilichuk, I.G. Orletsky, P.P. Hovly, V.O. Grechko, *Mater. Sci. Eng. B* **118**, 160 (2005).
12. R.Jr. Mamazza, D.L. Morel, C.S. Ferekider, *Thin Solid Films* **484**, 26 (2005).
13. K.S. Yoo, S.H. Park, J.H. Karg, *Sensor. Actuat. B* **108**, 159 (2005).
14. H.T. Yang, Y.T. Cheung, *J. Cryst. Growth* **56**, 429 (1982).
15. F. Hui, T.M. Miller, R.M. Magruder, R.A. Weller, *J. Appl. Phys.* **91**, 6194 (2002).
16. A.A. Yadav, E.U. Masumdar, A.V. Moholkar, K.Y. Rajpure, C.H. Bhosale, *Sensors Transd. J.* **92**, No 5, 55 (2008).
17. D.W. Lane, J.A. Coath, K.D. Rogers, B.J. Hunnikin, H.S. Beldon, *Thin Solid Films* **221**, 262 (1992).
18. F. Paraguay, D.W. Estrada, L.D.R. Acosta, N.E. Andradeb, M. Miki-Yoshida, *Thin Solid Films* **350**, 192 (1999).
19. G. Blandenet, M. Court, Y. Lagarde, *Thin Solid Films* **77**, 81 (1981).
20. O. Culha, M.F. Ebeoglugil, I. Birlik, E. Celik, M. Toparli, *J. Sol-Gel Sci. Technol.* **51**, 32 (2009).
21. J.P. Chatelon, C. Tenier, E. Bemstein, R. Berjoan, J.A. Roger, *Thin Solid Films* **247**, 162 (1994).
22. B. Oreal, U. Lavrencic-Stangar, Cmjak-Olel, P. Bukovea, M. Kosec, *J. Non-Cryst. Solids* **167**, 272 (1994).
23. C. Kilic, A. Zunger, *Phys. Rev. Lett.* **88**, 095501 (2002).
24. S.K. Tripathy, P.V. Rajeswari, B.P. Hota, *Bull. Mater. Sci.* **36** (2013) (in Press).
25. J.C. Manificier, J. Gasiot, J.P. Fillard, *J. Physics E: Sci. Instrum.* **9**, 1002 (1976).
26. M. Nowak, *Thin Solid Films* **266**, 258 (1995).
27. K.Y. Rajpure, M.N. Kusumade, M.N. Neumann-Spallart, C.H. Bhosale, *J. Mater. Chem. Phys.* **64**, 184 (2000).
28. R.D. Tarey, T.A. Raju, *Thin Solid Films* **128**, 181 (1985).
29. E.A. Davis, N.F. Mott, *Philos. Mag.* **22**, 903 (1970).
30. J.E. Dominquez, X.Q. Pan, L. Fu, P.A. Vanrompay, Z. Zhang, J.A. Nees, P.P. Pronko, *J. Appl. Phys.* **91**, 1060 (2002).
31. N.G. Semaltianos, G. Karczewski, B. Hu, T. Wojtowicz, J.K. Furdyna, *Phys. Rev. B* **51**, 17499 (1995).

## ACKNOWLEDGEMENT

Authors are thankful to the Prof. T.S.N. Somayaji, Director, Centre for Nano Science and Technology, GVP College of Engineering (Autonomous) for utilizing the laboratory and continuous inspiration to carry out the research.