ELECTRICAL AND GAS SENSING PROPERTIES OF Cd-DOPED SnO_2 THIN FILMS USING PVD TECHNIQUE

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Abstract: Tin oxide has been a very promising material due to its properties like mechanical hardness, stability to heat treatment etc. Addition of impurities (dopants) improves the film quality as well as their chemical properties. In this paper, the preparation of cadmium doped tin oxide, their properties like electrical and gas sensing are explained. The cadmium doped tin oxide thin film samples have been prepared by the Physical Vapour Deposition technique and annealed at 300ºC, 400ºC and 500ºC. Those annealed at 400ºC were considered for all further characterizations, since they showed better results compared to those annealed at other temperatures. The so prepared film samples were then characterized for structural, morphological and electrical characterization for gas sensing. Locally fabricated Static Gas Sensing system was employed to study the electrical as well as gas sensing properties of the film samples. The film samples showed better responses for ethanol vapours over target gases like carbon dioxide, ammonia, chlorine, acetone vapours etc.

Key words: Cd-doped tin oxide, doping, PVD technique, gas sensing, Tin oxide.

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1. Introduction

Tin oxide is one of the versatile materials for toxic gas sensors [1, 2]. The sensitivity and selectivity of these sensors have been improved by the usage of dopants that spontaneously segregate onto the surface of SnO_2 nano particles and nano films during the synthesis process [3–5]. One of the advantages of these dopants is that one may activate and control the sensing properties without needing an additional preparation step for a surface coverage, to do so, reducing time and cost of a large-scale sensor production [6]. Doping also improves the quality of film as well as the physical and chemical properties of thin films, in addition to change the charge carrier's concentration of the metal oxide matrix, catalytic activity, the surface potential, the phase composition, the size of crystallites, and so on [7]. Moreover, some studies have already been carried out on the potential sensing activities of Cd-doped SnO_2 [8-10]. It is established fact that reduction in grain size of a material increases sensitivity [11, 12]. Yamazoe et al. [13] studied effects of additives in semiconductor gas sensors. Tianshu et. al. [14] investigated Cd-doped SnO_2-based sensor for the detection of ethanol and hydrogen.

2. Deposition of Thin Film Samples:

The film samples were prepared by evaporating tin wire and a lump of cadmium in vacuum chamber at pressure of about 10^{-5} Torr on thoroughly clean glass substrates at room temperature**.** Vacuum system VS150D was used for the purpose. Pure tin wire and a lump of cadmium were vaporized in tungsten spiral filament by passing an appropriate amount of current through it with the help of a dimmerstat. The so prepared film samples were then annealed at 300°C, 400°C and 500°C. The annealing is usually performed to reduce the intrinsic strain, to improve the lattice mismatch and create longer mean paths for the free electrons in getting better electrical conductivity [15, 16]. Those samples annealed at 400°C are considered for all investigations since they showed better results over those annealed at other temperatures.

3. Results and Discussion

Locally fabricated Static Gas Sensing system (Fig. 4) was employed to study the electrical as well as gas sensing properties of the film samples. Although the film samples were rigorously analyzed, only gas sensing with electrical characterizations are considered.

3.1 Electrical Properties

Electrical characterizations were carried out in two parts- first by I-V characteristics (Fig.1) and second by variation in sample resistance as a function of temperature (Fig.2 and 3).

3.1.1 I-V Characteristics

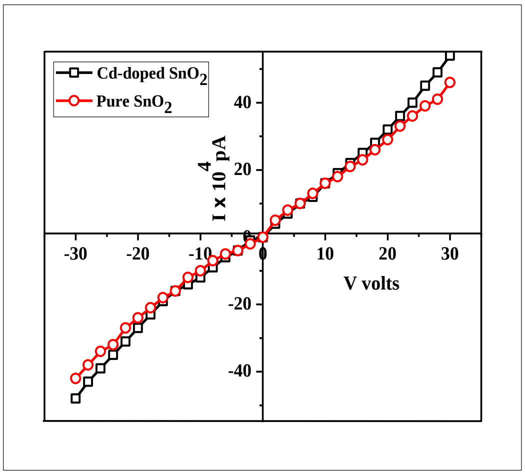
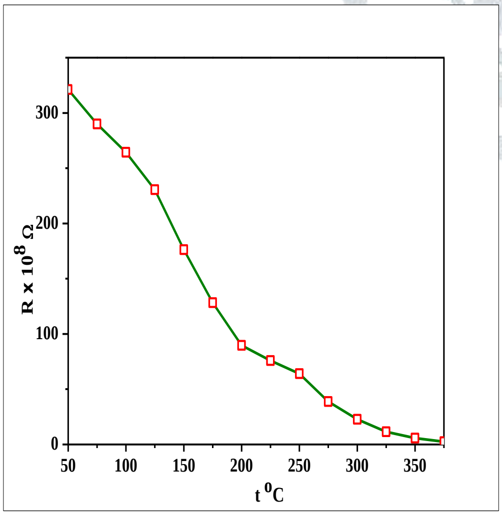


Fig. 1 I-V Characteristics of film samples

I-V characteristics were studied by using simple electric circuitry consisting of a regulated voltage source with variable output in series with sample and a picoammeter. Sample resistance and its linearity were estimated from I-V characteristics.

3.1.2 Resistance Measurement

Sample resistance was measured by using voltage divider consisting of a standard resistor of a few tens of megaohm in series with the sample and a regulated voltage source. The resistance was measured as a function of sample temperature (Fig.2). Negative resistance confirms the semiconducting nature of the material. TCR and activation energy were calculated from resistance versus temperature and logR versus 1000/T (Fig.3) graphs (Arrhenius Plot) respectively. Resistance variation with sample temperature was studied by using the static gas system. The curve shows the transition near 225 ^{o}C. Activation energy was estimated for low and high temperature regions. It was low in the low-temperature region (0.025 eV) since at lower temperatures supplied thermal energy was not enough to overcome the potential barrier. As the temperature increased, supplied energy also increased therefore in high-temperature region activation energy got altered (0.14 eV). The corresponding activation energy values for the undoped film samples are 0.082 eV and 0.17 eV. So, we were expecting that the optimum temperature for gas sensitivity might be somewhere near 225 ^{o}C. Thus, electrical properties of undoped tin oxide surely got modified due to addition of cadmium oxide.



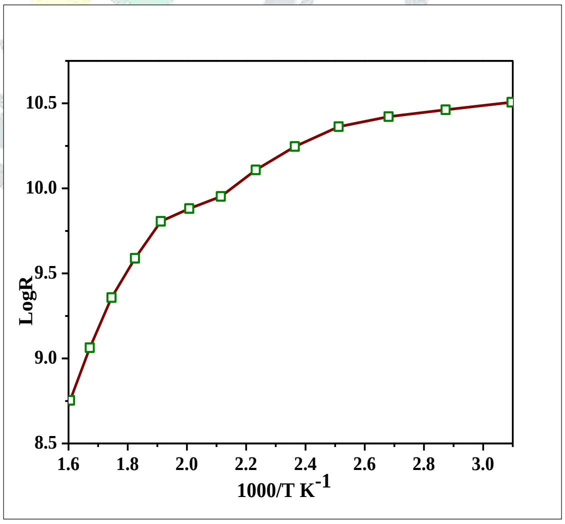


Fig. 2 Resistance Temperature graph Fig. 3 Arrhenius plot

3.2 Gas Sensing Properties

Fig. 5 shows the gas response of different gases for 1000 ppm concentration at operating temperatures ranging from 50-375^{o}C. Ethanol vapours showed higher response of 5.15 at an operating temperature of 225^{o}C. This is as predicted from the resistance temperature variation and Arrhenius plot. Most of the target gases showed maximum gas response near this temperature.

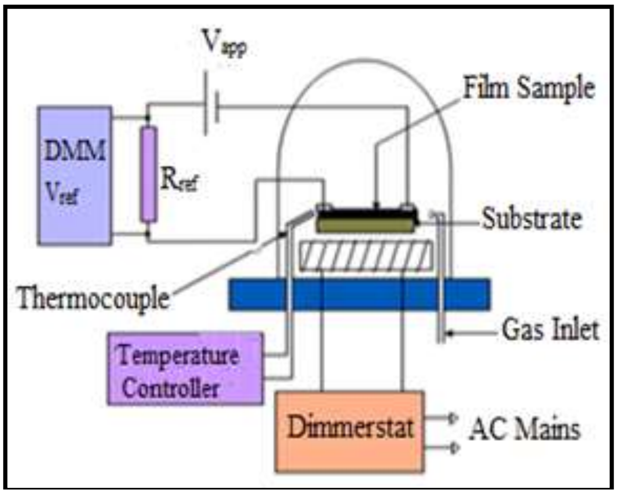


Fig. 4 Static Gas Sensing System

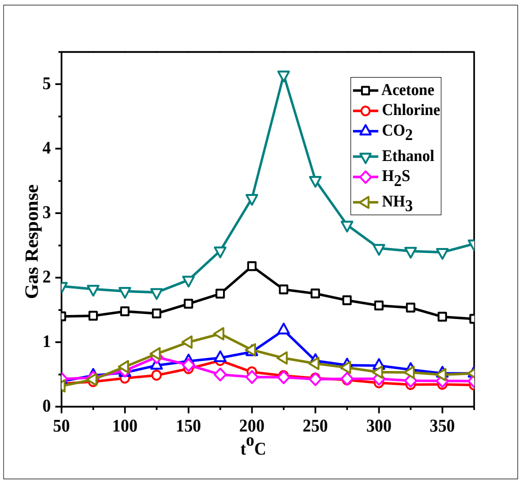


Fig. 5 Gas Responses as function of operating temperature

The n-type semiconductor materials (e.g., SnO_2) have a very few oxygen adsorption sites on the particle surface because of the development of potential barriers [17]. Additionally, a fraction of the surface sites occupied of those available on SnO_2 surface is also very low [18]. Therefore, introducing species with a relatively higher number of adsorption sites with high fractional occupancy in this material plays a significant role on the performance of the sensor [19]. The variations in lattice parameters due to concentration of dopants are considerably small, and since dealing with nanoparticles, these changes can be attributed to micro-strains inducing lattice compression [20, 21].

Selectivity profile of ethanol is shown in Fig. 6. The sensitivity or gas response of the samples was measured over the temperature 50-375°C and gas concentration 1-15 cc. Cd-doped SnO_2 sample is selective to ethanol at 225°C. Ethanol vapour response was higher for all concentrations but the highest for 1000 ppm concentration (Fig. 7) at 225°C.

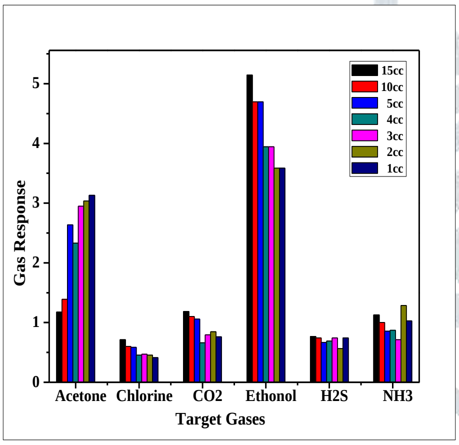


Fig. 6 Selectivity Profile

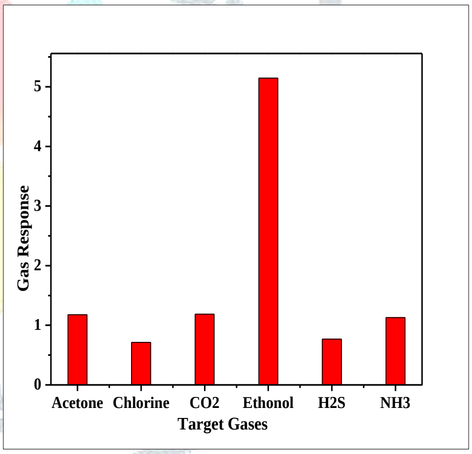


Fig. 7 Selectivity Profile for 1000 ppm concentration

3.3 Gas Sensing Mechanism

The conductivity of the sensor depends upon the oxygen adsorbed on the surface of the material and type of material itself. Thus, there is an increase or decrease in electrical conductivity when oxidizing or reducing gases react with the p-type material surfaces. Exactly opposite happens in case of n-type materials [22, 23]. Also, smaller the grain size, the larger the specific surface area and greater is the oxygen adsorption on the film material. This results into the enhancement of sensitivity [24]. The adsorption and desorption mechanism is shown in Fig.8.

The REDOX mechanism process increases the electron concentration in metal oxide surface by desorption of oxygen from the surface. However, the in-situ gas chromatography study of ethanol reaction with metal oxide material revealed desorption of carbon dioxide from the surface [25]. The film resistance in presence of ethanol vapours was found to be decreased with increase in its temperature. This is because of presence of chemisorbed negative oxygen ions on the film surface which could react with the β-H of C_2H_5OH. When the SnO_2 film is exposed back to air, oxygen ions are adsorbed onto the film surface and O_2^- and O^- ion species are formed by attracting electrons from the conduction band of the SnO_2 thin film. Thus, film resistance increases in the presence of air.

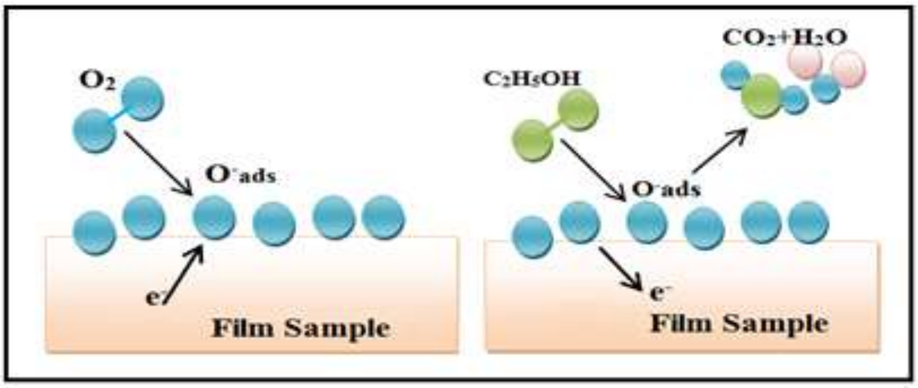


Fig.8 Adsorption-Desorption Mechanism

In case of SnO_2, the carriers are believed to be due to excess ions at the interstitial position due to oxygen vacancies, which act as electron donors. Reducing gas like C_2H_5OH reacts with adsorbed oxygen ions, surface adsorbed oxygen interacts with C_2H_5OH and release electron back to conduction band. These reaction-produced electrons may decrease the resistance which in turn results in increase in output voltage in the presence of gas [25-28]. This represents n-type conduction mechanism that explains how the generated electrons contribute to sudden increase in conductance (i. e. decrease in resistance) of the film.

4. Conclusions

We could successfully prepare Cd-doped SnO_2 thin film samples by Physical Vapour Deposition (PVD) technique. I-V characteristics confirmed ohmic nature and Resistance versus temperature characteristics proved the semiconducting behavior of the samples and an operating temperature could be predicted. The samples were tested for various target gases with varying concentrations over the range of temperature. Samples showed higher response to Ethanol for 1000 ppm concentration and at an operating temperature of 225°C.

5. References

[1] C.O. Park and S.A. Akbar, 2003. Ceramics for chemical sensing, J. Mater. Sci., (38): 4611–4637

[2] S. Nakata, T. Nakamura, K. Kato, Y. Kato and K. Yoshikawa, 2000. Analyst, (125): 517–522

[3] R.H.R. Castro, P. Hidalgo, R. Muccillo and D. Gouvea 2003. Appl. Surf. Sci., (214): 172–177

[4] P. Hidalgo, R.H.R. Castro, A.C.V. Coelho and D. Gouvea 2005. Chem. Mater., (17): 4149–4153

[5] R.H.R. Castro, P. Hidalgo, J.A.H. Coaquira, J. Bettini, D. Zanchet and D. Gouvea 2005. Eur. J. Inorg. Chem., (11): 2134–2138

[6] Ricardo H.R. Castro, Pilar Hidalgo, Henrique E.M. Perez, F.J. Ramirez-Fernandez and Douglas Gouvea 2008. Sensors and Actuators, (B133): 263–269

[7] Seigel R W, Hu E H and Roco M. C. 1997. Nano structured Material, Nano devices Workshop

[8] K. Napo, F.K. Allah, J.C. Bernede, N. Barreau and A. Khelil 2003. Thin Solid Films, (427):386–390

[9] T.S. Zhang, P. Hing, Y. Li and J.C. Zhang 1999. Sens. Actuators, B, Chem. (60): 208–215

[10] G. Sberveglieri, S. Groppelli and P. Nelli 1991. Sens. Actu., B Chem., (4): 457–461

[11] G. Sberveglieri and L.E. Depero 1996. J. Adv. Mater., 8 (4): 334–337

[12] N. Yamazoe and N. Miura 1992. Some basic aspects of semiconductor gas sensor, in: S. Yamauchi (Ed.), Chemical Sensor Technology, vol. 4, Elsevier, Amsterdam

[13] N. Yamazoe, Y. Kurokuwa and T. Seiyama 1983. Effects of additives on semiconductor gas sensors, Sens. Actuators, (B4): 283

[14] Z. Tianshu, P. Hing, Y. Li and Z. Jiancheng 1999. Sens. Actu., (B60): 208–215

[15] Abdul Faheem Khan, M. Mehmood, A.M. Rana and M.T. Bhatti 2009. Applied Surface Science. 255 (255): 8562–8565

[16] Saturi Baco, Abdullah Chik and Fouziah Md. Yassin, Journal of Science and Technology, 61-72

[17] S. R. Morrison 1987. Sens. Actuators, (12): 425

[18] C. O. Park and S. A. Akbar 2003. J. Mater. Sci., (38): 4611

[19] T. A. Miller et. al., Functional Nano Materials-Ed. Kurt E. Geckeler and Edward Rosenberg, 1-24

[20] Y.M. Chiang, D. Birnie and W.D. Kingery, Physical Ceramics 1997 – Principles for Ceramic Science and Engineering, John Wiley & Sibs Inc., New York

[21] E.R. Leite, I.T. Weber, E. Longo and J.A. Varela 2000. Adv. Mater., (12): 965–968

[22] K. Arshak and I. Gaidan 2005. Materials Science and Engineering, (B118): 44-49

[23] G. Martinelli, M. C. Carotta, M. Ferroni, Y. Sadoaka and E. Traversa 1999. Sens. Actuators, B: Chem., (55): 99-110

[24] J. Xu, Q. Pan, Y. Shun and Z. Tian 2000. Sens. Actuators, B: Chem., (66): 277-279

[25] H. Zhao, Y. Li, L. Yang and X. Wu. 2008. Mater. Chem. Phys. (112): 244-248
[26] L. Nanis and G. Advani 1982. Int. J. Electron., (52): 345-349
[27] T. S. Rantala, V. Lantto and T. T. Rantala1993. Sens. Actu., (B 13-14): 234-237
[28] S. B. Deshmukh, R. H. Bari, G. E. Patil, D. D. Kajale, G. H. Jain and L. A. Patil 2012. International Journal on Smart Sensing and Intelligent System, 5 (3): 540-557

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