17. Electrical, Structural and Optical Properties of Vacuum Evaporated ZnO-SnO_2 Thin Films

S. S. Mandawade
Department of Physics, M S G College Malegaon Camp Dist. Nasik, Savitribai Phule University Pune, Maharashtra.
M. B. Deore
Department of Physics, M S G College Malegaon Camp Dist. Nasik, Savitribai Phule University Pune, Maharashtra.
D. B. Sonawane
Department of Physics, M S G College Malegaon Camp Dist. Nasik, Savitribai Phule University Pune, Maharashtra.
A. S. Garde
Department of Physics, M S G College Malegaon Camp Dist. Nasik, Savitribai Phule University Pune, Maharashtra.

Abstract

The IV–V semiconductors are of great importance due to their applications in various electro-optic devices. Thin films of zinc oxide doped Tin oxide (ZnO-SnO_2) were prepared by physical vapour deposition method. The ZnO–SnO_2 thin film was deposited on glass substrate at a pressure of 10^{-5} torr. This paper is aimed at studying the behavior of zinc oxide doped tin oxide on the thin films which were fired at 450^0C temperature for 30 minutes in air atmosphere. The ZnO-SnO_2 thin films were characterized by scanning electron microscopy (Morphological). The UV-VIS absorption spectrum shows an absorption band at 385 nm due to ZnO-SnO_2 thin film annealed at 450^0C.The energy band gap of ZnO-SnO_2 thin film calculated by Tauc relation. The D.C resistance of the films was measured by half bridge method in air atmosphere at different temperatures. The films showed decrease in resistance with increase in temperature indicating semiconductor behaviour. The TCR, activation energy and specific resistance of films were evaluated at 450^0C temperatures.

Keywords: ZnO-SnO_2 thin films, UV-visible Spectroscopy, TCR, resistivity, activation energy.

1. Introduction

The last several decades, All transition metal oxides have been exploited in many challenging fields of Solar cells, Energy, nanomaterials, Computer science, defense, Opto-electronics devices. Among transition metal and metal oxides, the IV–V semiconductors are of great importance due to their applications in various electro-optical devices [1]. The semiconductor metal oxide gas sensors like SnO_2, ZnO, WO_3 etc. have been studied due to their range of conducting variability and their strong response to reducing as well as oxidizing gases [2-3]. The Zinc oxide (wurtzite) and Tin oxide (Tetragonal) is an n-type semiconductor with band gap energy about 3.37 Ev and 3.6 eV at room temperature respectively while the optical band gap of Zno-SnO_2 thin films were in the range 3.5–3.62 eV, depending on the deposition conditions.[1].It is cheap, nontoxic and has strong oxidizing power, high photochemical corrosive resistance, good electrical, optical and piezoelectric behavior. The methods for preparation of thin film have been used by the researchers to synthesize metal oxide thin films in various structured forms. Some of the methods are chemical vapour deposition [4], spray pyrolysis techniques [5], sputtering [6], activated reactive evaporation [7] etc. Physical Vapour Deposition (PVD) method is straight forward and simple one. It has several advantages of this method [8] such as (a) Minimum impurity concentration in the film, (b) sublimation of materials at lower temperature under vacuum, (c) considerably large mean free path of the vapour atoms at lower pressure and hence a sharp pattern of the film is obtained, (d) wide substrate selection. Another advantage of this method is that evaporation yields a large number of films of uniform thickness. The deposition of thin film takes place in four stages [9, 10].Moreover, the post treatments like annealing, etc. are important, too in obtaining the desired phases and the stoichiometry. Annealing of films is a necessary step to control grain growth, altering the stoichiometry of the film, introducing dopants and oxidizing the film, inducing compressive stresses in the film are some of the reasons for post-film deposition processing [11]. Therefore, in this paper, we prepared ZnO doped SnO_2 thin films on the thoroughly cleaned glass substrates and were sintered in muffle furnace for 60 minutes to allow sufficient oxidation. These samples were further annealed at 450°C. The Electrical and optical properties of the samples were studied and discussed.

2. Experimental Work

$ZnO\text{-}SnO_2$ thin films were prepared by thermal evaporation method using a vacuum coating unit at 10^{-5} torr pressure. Initially Glass substrates were thoroughly cleaned by hot chromic acid to remove contamination. They were then rinsed with distilled water followed by acetone. Finally the substrates were dried under IR lamp at 80-100^{0}C. The high purity Zinc (99.99%, 100 g) thin foils and pure Tin metal granular (99.99% Pure, 100 mg) obtained from the Loba Chemicals Ltd., were placed in single boat in the Hind High Vacuum coating unit at a pressure of 10^{-5} torr.

The clean glass substrates were placed in the substrate holder nearly 12 cm above the tungsten boat carrying materials. In this method, Tin was first evaporated by appropriate current passing through tungsten basket using dimmerstat and later zinc to get bilayer of Zn-Sn thin films. The deposited film samples were annealed at 450^{0}C for 30 minutes to inter-diffuse Zn and Sn elements for constant temperature [12].

2.1 Material Characterization

The optical UV- Visible spectrophotometer model UV-1900 was used to record absorbance spectra of Zn–Sn thin films at room temperature. The thickness of the $ZnO\text{-}SnO_2$ thin films were measured by gravimetric method. The film thickness (d) of $ZnO\text{-}SnO_2$ thin films was measured by gravimetric methods (±100Å) using the relation [13]

$$d = \frac{M}{\rho \times A} \qquad \ldots\ldots(1)$$

Where

A - Surface area of the film, M - Mass of the film material, ρ - Density of the film material. The above techniques of thickness measurements agreed within ±10% for very thin films.

The electrical measurements were carried out by using the half bridge method. The electrical resistance of the $ZnO\text{-}SnO_2$ thin film samples was calculated by the relation [14]. Sheet resistivity (ρ_s) of each thin film samples was calculated from the dimension of the film samples. Sheet resistivity $(\rho_s) = \rho/t$, where ρ = resistivity of $ZnO\text{-}SnO_2$ thin film resistors, t = thickness of the thin film samples. The effect of temperature on the resistance was studied to determine the TCR and calculated as

$$TCR=\frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right)/^{O}C \qquad \text{..... (2)}$$

where ΔR = change in resistance between temperature T_1 and T_2, ΔT = temperature difference between T_1 and T_2, R_o = Initial resistance of the film sample. Using Arrhenius relation, the activation energy of thin film samples were evaluated

$$R=R_o e^{-\Delta E/KT} \qquad \text{..... (3)}$$

Where R_o is constant, ΔE is the activation energy of the electron transport in the conduction band, K is Boltzmann constant and T is Absolute temperature.

3. Result and Discussion

3.1. UV-Visible Spectrophotometer Analysis

The UV-visible optical absorption spectra were measured from a double beam spectrophotometer in the range 200–800 nm. A record spectrophotometer (BSR UV-VIS-NIR Model No.UV-1900) was used for these optical measurements of ZnO-SnO_2thin film samples deposited on glass substrate fired at different temperature.

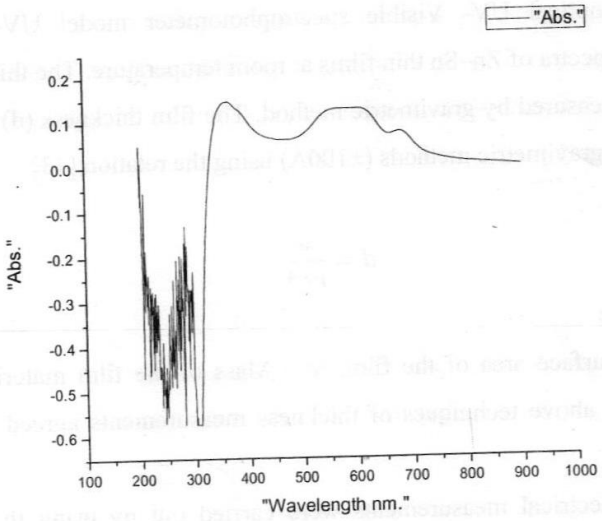

Fig:1. Absorbance spectra of ZnO-SnO_2 thin film samples fired at 450^{0}C.

Figure 1, It is seen that the absorption spectrum of ZnO doped SnO_2 thin films deposited on glass substrate fired at 450^{0}C exhibits a shoulder at 360 nm along with an ill-defined band at 385 nm. The variation of optical density with wavelength was analyzed to find out the nature of transition involved and the optical band gap. The wavelength at which 'α' rises suddenly

corresponds to the band gap energy estimated [15]. The absorption coefficient is found to be 0.15 supporting the presence of direct band gap. The energy band gap found to be 3.22 eV.

3.2. Scanning electron micrographs of ZnO-SnO_2 thin film.

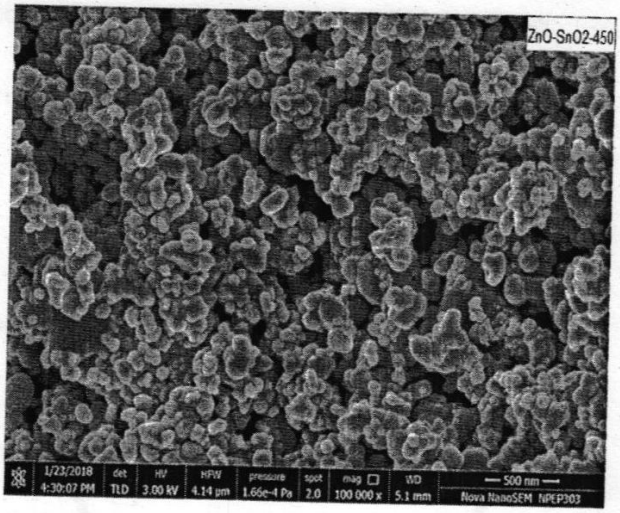

Fig.2. Scanning electron micrographs of ZnO-SnO_2 thin film deposited on glass substrate fired at 450^{0}C.

Figure 2 shows the typical SEM micrographs of ZnO doped SnO_2thin film deposited on glass substrate fired at 450^{0}C for studying the surface morphology. The SEM micrographs of ZnO doped SnO_2 thin films fired at 450^{0}C shows polycrystalline structure with number of pores distributed on the surface of the film, basically due to evaporation of organic solvent during the firing of the films. The average particle size being 157nm at 450^{0}C was observed for the ZnO doped SnO_2 thin films deposited on glass substrate.

3.3 Electrical Analysis

The DC resistance of the ZnO doped SnO_2 thin films fired at 450^{0}C, was measured using half bridge method as a function temperature. The resistance of thin films decreases with increase in temperature showing semiconducting behavior. **Figure 3(a)** shows the resistance variation of ZnO doped SnO_2 thin films fired at 450^{0}C temperatures in air. ZnO doped SnO_2thin film samples exhibited three regions of resistance similar to semiconducting materials prepared screen printed thin film resistors. The plot shows different conduction region such continuous fall of resistance, an exponential fall region and finally saturation region. Any increase in temperature of thin film causes the electrons to acquire enough energy and cross the barrier at

grain boundaries. There is a decrease in resistance with increase in temperature indicating semiconducting behavior [16], obeying $R=RO\ e^{-\Delta E/KT}$ in the temperature range of 50 to 400^0C.

The initial value of resistances at room temperature of the ZnO-SnO_2 thin films fired at 450^0C are evaluated. The resistance of the ZnO-SnO_2 thin film at room temperature is 428560 Mohm.

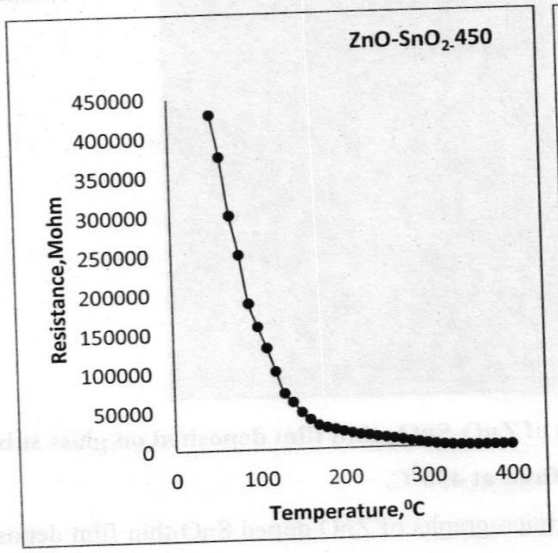

Fig.3 (a) Variation of resistances with temperature of ZnO-SnO_2 thin film samples fired at 450^0C.

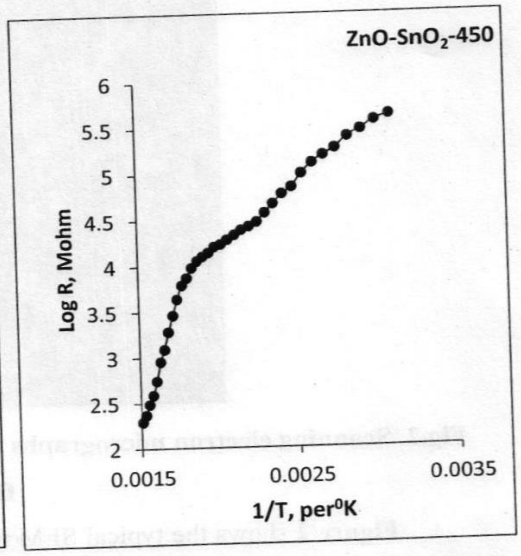

Fig.3(b) Variation of Log R with reciprocal of temperature of ZnO-SnO_2 thin films fired at 450^0C.

Figure 3(b) shows Variation of Log R with reciprocal of temperature of ZnO-SnO_2 thin films fired at 450^0C.This variation is reversible in both heating and cooling cycles obeying the Arrhenius equation $R=Roe^{-\Delta E/KT}$. It is seen that the curve has two distinct regions of temperature namely low temperature region (323 to 433^0K at 450^0C) and high temperature region (553 to 663^0K at 450^0C). The activation energy in the lower temperature region is always less than the energy in the higher temperature region because material passes from one conduction mechanism to another. From lower to higher temperature region, activation energy decreases, because a small thermal energy is quite sufficient for the activation of the charge carriers to take part in conduction process. In other words, the vacancies/defects weakly attached in lattice can easily migrate. Hence increase in the conductivity in the lower temperature region can be attributed to the increase in charge mobility.

The value of Sheet resistivity, TCR and activation energy of the ZnO doped SnO_2 thin films fired at temperatures of 450^0C is summarized in Table 1.

Table:1. TCR, Sheet Resistivity and Activation Energy of ZnO doped SnO_2 thin films fired at 450^0C [Thickness of film samples: 8μm]

Firing Temp (^{0}C)	TCR, x 10^{-3} (/0C)	Sheet Resistivity ρs x$10^{11}\Omega/\square$	Activation Energy, eV	
			Low Temperature Region	High temperature Region
450	6.209	0.26785	0.26697	0.83348

Conclusion

Zinc oxide doped Tin oxide based thin films deposited on glass substrate using Physical vapour deposition technique. The SEM micrographs of ZnO doped SnO_2 thin films fired at 450^0C shows polycrystalline structure with number of pores distributed on the surface of the film. The average particle size being 157nm at 450^0C was observed for the ZnO doped SnO_2 thin films deposited on glass substrate. The Pure and ZnO doped SnO_2 thin film resistors was observed to be semiconducting behaviour and showed a negative TCR. From optical studies, the maximum absorption of spectra of ZnO doped SnO_2 was found to be 0.15 at 450^0C. The energy band gap found to be 3.22 eV. The DC resistance of thin films was measured by using half bridge method as a function of temperature. The resistance of doped Tin Oxide thin films decreases with increase in temperature indicating semiconductor behaviour. It also shows porous between the particles basically due to evaporation of the organic solvent during the firing of the films.

References

1. Eda Goldenberg, S Goldsmith, Raymond Leon Boxman, Optical properties of transparent ZnO–SnO_2 thin films deposited by filtered vacuum arc Journal of Physics D Applied Physics 39(9)(2006)1878.
2. Y. Shimizu, E. D. Bartolomeo, E. Traversa, G. Gusmano, T. Hyodo, K. Wada, M. Egashira-Effect of surface modification on NO2 sensing properties of SnO_2 varistor-type sensors, Sensors and actuators B, vol. 60 (1999)118-124.
3. M. Stankova, X. Vilanova, J. Calderer, I. Gracia, C. Cane, X. Correig- Nanograin WO_3 thin films as active layer for resistive type gas sensors, Journal of Optoelectronics and Advanced Materials, Vol. 7, No.3, (2005)1237-1242.

4. R. H. Bari, R. S. Khadayate, S. B. Patil, A. R. Bari, G. H. Jain, L. A. Patil, and B. B. Kale ,Preparation, Characterization, and H_2S Sensing Performance of Sprayed Nanostructured SnO_2 Thin Films ISRN Nanotechnology Vol. 2012, (ID 734325) 5.
5. Supriyonoa, Hedi Surahmana,Yuni Krisyuningsih Krisnandia , and Jarnuzi Gunlazuardia , Preparation and characterization of transparent conductive SnO_2-F thin film deposited by spray pyrolysis: relationship between loading level and some physical properties, Procedia Environmental Sciences 28 (2015) 242 – 251.
6. T. Gui, L. Hao, J. Wang, L. Yuan, W. Jai, X. Dong-Structure and Features of SnO2 Thin Films prepared by RF Reactive Sputtering, Chinese Optic Letters, vol.8, (2010)10134-03
7. H. S. Randhawa, M. D. Matthews and R. F. Bunshah, SnO2 films by activated reactive evaporation, Thin Solid Films, vol. 83 (1981)267-271.
8. Punit Patel ,Ayyan Karmakar, Chetan Jariwala, Jayesh P.Ruparelia, Preparation and Characterization of SnO_2 Thin Film Coating using RF-Plasma Enhanced Reactive Thermal Evaporation, Procedia Engineering Vol. 51(2013) 473-479.
9. K. L. Chopra, Thin Film Phenomena, McGraw-Hills, New York (1969).
10. K S Thakare et.al, Gas Sensing Studies of Tin Oxide Thin Films Annealed at Different Temperatures, Institute of Research Advance, 9(2) (2017)10-15.
11. R.F.Bunshah , Handbook of Deposition Technologies for Films and Coatings, 2nd ed., Noyes Publications, NJ (Ed.) (1994).
12. Chun-Min Wang ,Chun-Chieh Huang, Jui-Chao Kuo , Dipti Ranjan Sahu and Jow-Lay Huang, Effect of Annealing Temperature and Oxygen Flow in the Properties of Ion Beam Sputtered SnO_2-x Thin Films, Materials, 8(2015) 5289-5297.
13. K. S. Thakare, S. J. Patil, R. Y. Borse and R. R. Ahire -Influence of annealing Temperature on Structural and Electrical Characteristics of Pure SnO_2 Thin Films Deposited by Physical Vapour Deposition Technique, Research Journey' International Multidisciplinary E- Research Journal online (2016)15-22.
14. U. P. Shinde, A.V. Patil , C. G. Dighavkar, S.J. Patil, K.H. Kapadnis, R.Y. Borse and P.S. Nikam , "Photoconductivity study as a function of thickness and composition of Zn-Te thin films for different illuminated conditions at room temperature" Optoelec. and Adv. Mate-Rapid Comm., 4(2010) 291.

15. A. S. Garde, Electrical and Structural Properties of WO_3-SnO_2 Thick-Film resistors Prepared by Screen Printing Technique, Research Journal of Recent Sciences, Vol. 4(1) (2015) 55-61.
16. Karzan Abdul Kareem Omar, Bashdar Ismael Meena, Srwa Ali Muhammed, Study on the activity of ZnO-SnO_2 nanocomposite against bacteria and fungi, Physicochem. Probl. Miner. Process, 52(2) (2016) 754−766.
17. R. Y. Borse and A. S. Garde, Electrical and Gas Sensing Properties of SnO2 Thick Film Resistors Prepared by Screen-printing Method, Sensors & Transducers Journal, Vol. 97(10) (2008) 64-73.