



Thermodynamic and Gas Sensing Properties of Cu²⁺ Doped SnO₂ Thin Films

M.C. Rao^{1*}, K. Ravindranadh¹, T. Srikumar¹, G.V. Ramana², K.L. Sirisha², T. Rosemary³, M. David Raju⁴, M. Manoranjani⁴ and G. Nagarjuna⁵

¹Department of Physics, Andhra Loyola College, Vijayawada - 520008, India

²Department of Chemistry, Andhra Loyola College, Vijayawada - 520008, India

³Department of Botany, Andhra Loyola College, Vijayawada - 520008, India

⁴PG Department of Chemistry, P.B. Siddhartha College of Arts & Science, Vijayawada - 520010, India

⁵Department of Chemistry, S. R. R. & C. V. R. Govt. College, Vijayawada-520 005, India

Abstract: SnO₂ is a special oxide material because it has a low electrical resistance with high optical transparency in the visible range. SnO₂ sensor is invariably anion deficient and oxygen vacancies are mainly responsible for making available free electrons for the conduction process. Cu²⁺ doped SnO₂ thin films were prepared by using chemical spray pyrolysis method. The prepared thin films were characterized by FTIR, electrical, gas sensing and thermo emf. The bands at the low wave numbers 500-1000 cm⁻¹ could be attributed to SnO₂. The peaks at 677, 786 and 965 cm⁻¹ were assigned to O-Sn-O, Sn-O-Sn stretching vibrations and lattice vibrations, while the peaks at 569 and 864 cm⁻¹ were due to Sn-OH bonds of the SnO₂ crystalline phase. The thermo emf of Cu²⁺ doped SnO₂ thin films increased with the increasing of temperature. At low temperatures the Seebeck coefficient is observed to be high and the Seebeck coefficient decreases with increasing of temperature. The large values of thermoelectric power of Cu²⁺ doped SnO₂ thin films are typical of semiconductor behavior.

Keywords: SnO₂, Thin films, Spray pyrolysis, FTIR, Thermo emf, Gas Sensing and Electrical.

Introduction:

Since the last decade there has been a great deal of interest in the preparation of inexpensive thin films of SnO₂. This is because tin dioxide based thin films with large band gap ($E_g > 3$ eV) n-type semiconductors are attractive from the scientific and technological point of view. Several potential applications have been reported previously, such as a transparent conductive electrode for solar cells [1, 2] a gas sensing material for gas sensors devices transparent conducting electrodes, photochemical and photoconductive devices in liquid crystal display [3] gas discharge display, lithium-ion batteries, etc. SnO₂ is a special oxide material because it has a low electrical resistance with high optical transparency in the visible range. Due to these properties, apart from gas sensors, SnO₂ is being used in many other applications, such as electrode materials in solar cells, light-emitting diodes, flat-panel displays and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area and in transparent electronics, such as transparent field effect transistors [4, 5]. SnO₂ owing to a wide bandgap is an insulator in its stoichiometric form. However, due to the high intrinsic defects, that are oxygen deficiencies, tin oxide possesses a high conductivity. It has been shown that the formation energy of oxygen vacancies and tin interstitials in SnO₂ is very low. Therefore, these defects form readily, which explains the high conductivity of pure, but nonstoichiometric, tin oxide.

The undoped SnO₂ [6] has low electrical resistance and high optical transparency in the visible range of the electromagnetic spectrum. These properties make tin oxide suitable for many applications, particularly as an electrode material in solar cell, light emitting diodes, transparent electromagnetic shielding materials, etc. Numerous works have been reported concerning doped and undoped tin oxide thin films using various preparation techniques such as chemical vapor deposition [7], thermal beam evaporation [8], and spray pyrolysis [9], and sputtering techniques [10]. Among these techniques, spray pyrolysis has proved to be simple, reproducible and inexpensive, as well as suitable for large area applications. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coatings make them useful for industrial as well as solar cell applications. In addition, spray pyrolysis opens up the possibility to control the film morphology and particle size in the nm range. As demonstrated [11], spray pyrolysis is a versatile technique for deposition of metal oxides.

Up to now, many researchers have prepared SnO₂ using chemical spray pyrolysis. For example, it has grown tin dioxide thin films [12] by spray pyrolysis on Si substrates and reported evolution of the crystallographic orientation of the films with variation of the pyrolysis temperature. It is reported that the crystallite sizes in the films could be controlled over a nm range by varying the film thickness, deposition method and post-deposition annealing temperature. Also some recent studies on the sensing properties of pure nanocrystalline SnO₂ thin films toward H₂S and H₂ [13] seemed to contradict the general trend that higher sensitivity is to be expected for smaller crystals, and it was, therefore, concluded that small size of crystals was an essential but not sufficient condition for the achievement of maximum gas sensitivity and fast response. The deposition process needs fine droplets to react on the heated substrate, owing to the pyrolytic decomposition of the solution. The hot substrate provides the thermal energy for the thermal decomposition and subsequent recombination of the constituent species. In many cases large droplets of the solution do not vaporize before reacting to deposit on the substrate. They hit the surface and form a powdery deposit. If it strikes at a high enough velocity, the droplet will splatter and form a dispersed powdery layer. As mentioned above, the droplet cannot be completely vaporized before it hits the surface and for this reason, film growth cannot occur. In the present work, Cu²⁺ doped (0.01 mol %) SnO₂ thin films were prepared by using chemical spray pyrolysis method. The prepared thin films were characterized by FTIR, electrical, gas sensing and thermo emf.

Experimental:

All the chemicals used in the work were of analytical grade. Cu²⁺ doped SnO₂ thin films were prepared by chemical spray pyrolysis. Spray solution was prepared by mixing 0.1 M aqueous solutions of SnO₂ and CuO (0.01 mol %) using a magnetic stirrer. The automated spray solution was then transferred to the hot substrate kept at the normalized deposition temperature of 673 K using filtered air as carrier gas at a flow rate normalized to approximately (1.8) ml/min. To prevent the substrate from excessively cooling, the prepared solution was sprayed on the substrate for 10 s with 15 s intervals. The films deposited onto micro-glass slides were first cleaned with detergent water and then dipped in acetone. The thermo emf of the prepared samples was studied between the temperature ranges from 275 to 325 K by using thermal probe method. The gas sensing chamber had been employed for testing of the films to gases. The dc electrical conductivity measurements were made on the experimental films by employing the standard van der Pauw method.

Results and Discussion:

Cu²⁺ doped (0.01 mol %) SnO₂ thin films were prepared by using chemical spray pyrolysis method. The FTIR, electrical, gas sensing and thermo emf were carried out on to the prepared films. The analysis of X-ray diffraction pattern revealed that the prepared tin oxides films are pure crystalline in nature.

FT-IR Studies

FT-IR spectrometry was used for the determination of existing surface species. The FT-IR spectrum of Cu²⁺ doped SnO₂ thin films was illustrated in Fig. 1. The bands at the low wave numbers (500-1000 cm⁻¹) could be attributed to SnO₂. The peaks at 677, 786 and 965 cm⁻¹ were assigned to O-Sn-O, Sn-O-Sn stretching vibrations and lattice vibrations, while the peaks at 569 and 864 cm⁻¹ were due to Sn-OH bonds of the SnO₂ crystalline phase [14]. The bands observed in the region 2500-1640 cm⁻¹ are due to symmetric and asymmetric vibrations of hydroxyl ions situated at different sites in the lattice.

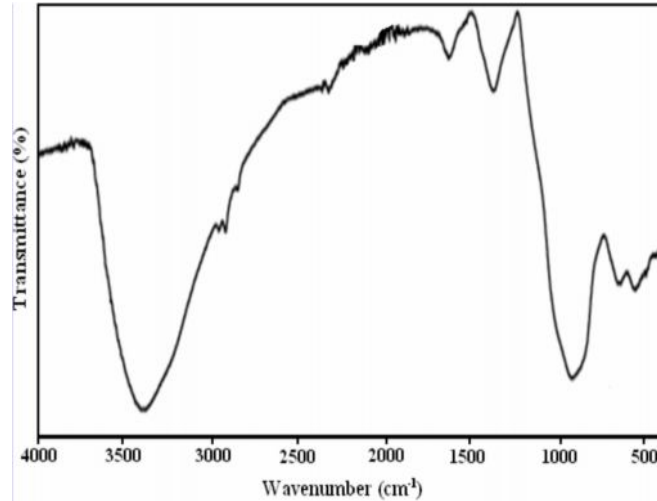


Fig. 1 FT-IR spectrum of Cu^{2+} doped SnO_2 thin films

Thermo emf: The thermo power or Seebeck coefficient, of a material measures the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material and the entropy per charge carrier in the material. The sign of the thermo power determines which charged carriers dominate the electric transport. The temperature difference ΔT between the two ends of a material is small and then the thermo power of a material is defined approximately as:

$$S = - \Delta V / \Delta T$$

and a thermoelectric voltage of ΔV is seen at the terminals.

The thermo emf of Cu^{2+} doped SnO_2 thin films was studied in the temperature range from 275 K - 325 K by using thermal probe method. The thermo emf was measured and the Seebeck coefficient of the material was also calculated. The plot of thermo emf versus temperature difference between the two junctions is found to be linear (Fig.2) indicating that the temperature dependence of thermo emf is the characteristic conduction of Cu^{2+} doped SnO_2 thin films. The thermo emf of Cu^{2+} doped SnO_2 thin films increased with the increasing of temperature. At low temperatures the Seebeck coefficient is observed to be high and the Seebeck coefficient decreases with increasing of temperature. The large values of thermoelectric power of Cu^{2+} doped SnO_2 thin films are typical of semiconductor behavior.

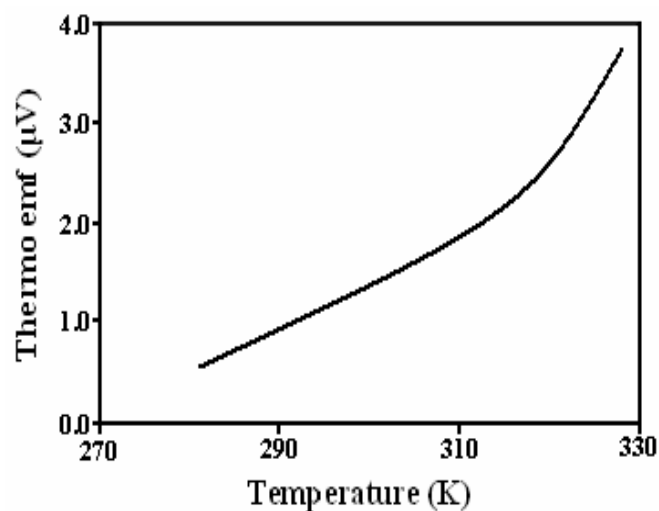


Fig. 2 Temperature dependence of the thermo emf of Cu^{2+} doped SnO_2 thin films

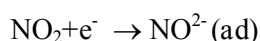
Gas Sensing Properties: The basic gas sensing characteristics of the SnO₂ thin films were investigated as a function of operating temperature and test gas concentration. In the present studies the films were characterized by various parameters such as sensitivity, selectivity and response and recovery time. The sensitivity (S) is defined as $S = (R_a - R_g)/R_g$, where R_g is the resistance in presence of test gas and R_a the film resistance in dry air, measured at respective temperatures. A positive value of S implies film resistance decreases on gas exposure and vice versa. The selectivity or specificity of a sensor towards an analyzing gas is expressed in terms of dimension that compares the concentration of the corresponding interfering gas that produces the same sensor signal. This factor is obtained by

Selectivity = (sensitivity of sensor for interfering gas) / (sensitivity towards desired gas).

The response time is the time interval over which resistance attains a fixed percentage (usually 90%) of final value when the sensor is exposed to full scale concentration of the gas. A small value of response time is indicative of a good sensor. The recovery time is the time interval over which resistance reduces to 10% of the saturation value when the sensor is exposed to full scale concentration of the gas and then placed in clean air.

Cu²⁺ doped SnO₂ conductometric sensors were mounted on an electric heater. Gas response measurements of the devices were performed in a stainless steel test chamber made from Teflon, which was sealed in a quartz lid. The heater was controlled by a regulated DC power supply providing different operating temperatures. The total flow rate was kept constant at 50 sccm and dry synthetic air was used as the reference gas. Subsequently, the device was exposed to sequences of different concentrations of NO₂ for several hours. In the Cu²⁺ doped SnO₂ sensor, change in the oxygen balance of the oxide layer leads to a variation in its conductance. In the case of an oxidizing gas (NO₂), reactions directly take place on the oxide surface. During the interaction process, molecules consume conduction electrons and subsequently increase the depletion region at the surface and the resistivity of the sensor increases as presented below.

Cu²⁺ doped SnO₂ films were exposed to different concentrations of NO₂ gas at various temperatures. The sensor was placed in a stainless steel test chamber. A continuous flow of gas passes through the chamber, which makes the pressure in the test chamber to be nearly atmospheric. The desired gas concentration is obtained by mixing the appropriate flows of gases by means of mass flow controllers. The films are generally heat treated before exposure to different gasses because it produces contacts between grains, many of which are between grains having different crystal structures. When both the films are exposed to NO₂ gas, the dc electrical resistance of the film dramatically increased. Since Cu²⁺ doped SnO₂ is an n type semiconductor, its electrical behavior upon exposure of NO₂ oxidizing gas can be explained by a decrease of conduction carrier density. The amount of oxygen ions available on the Cu²⁺ doped SnO₂ surface increases at the operating temperature. The adsorbing NO₂ molecules interact directly with the adsorption sites at the oxide surface. Therefore the interaction between the film and NO₂ is as follows;



The interaction with NO₂ results in a decrease in the free electron concentration. The decrease in free carrier concentration causes a rise in the film resistance.

The sensitivity of the prepared Cu²⁺ doped SnO₂ thin films for various gas concentrations can be calculated from the equation defined as follows:

$$S = R_a/R_g$$

where S is the sensitivity, R_a is the resistance of a sensor in air medium and R_g is the resistance of a sensor in a test gas medium. The calculations were made by taking the resistance values at the time after which there was no significant decrease in the resistance. The results of the sensing experiments were graphically presented in Fig. 3. When the reducing gas is exposed to the sensing element, it reduces the resistance of the material, which confirms the typical characteristic of a n-type material. It is clearly observed that, as the test gas concentration was increased the resistance decreased drastically.

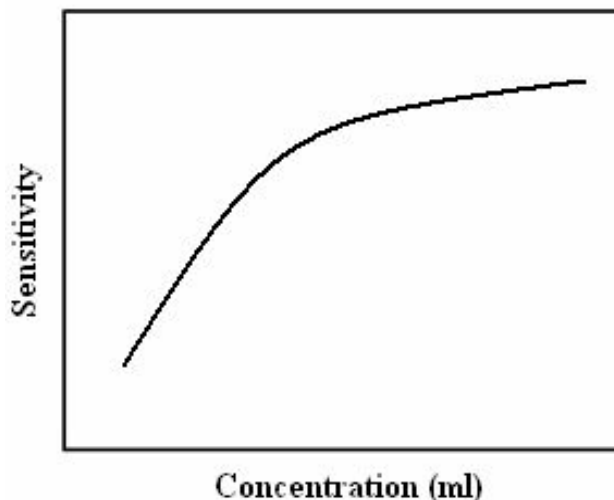


Fig. 3 NO₂ concentration as a function of sensitivity of Cu²⁺ doped SnO₂ thin films

Electrical Properties: The electrical resistance of Cu²⁺ doped SnO₂ thin films was measured by the four - point probe method. The plot of log R as a function of reciprocal absolute temperature (1000/T) is found to consist of two linear parts shown in Fig.4. The dc dielectric resistance is found to vary as

$$R=R_0 \exp (\Delta E / K T)$$

The presence of distinct values of ΔE in different temperature ranges may be attributed to two activation processes namely (1) it is intrinsic conduction at band gap in high temperature region and (2) in low temperature region, conduction is due to hopping of charge carriers in the localized states at Fermi level. The electrons may be promoted into these defects by giving electrical or optical energy thereby increasing the conductivity of the films [15-19].

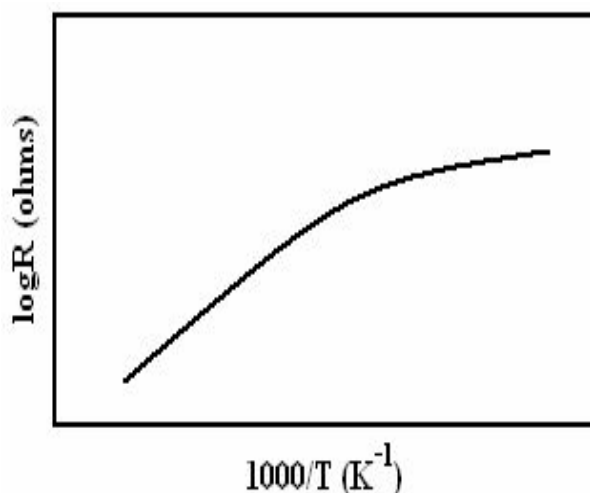


Fig. 4 Plot of Log R versus 1000/T of Cu²⁺ doped SnO₂ thin films

Conclusions:

SnO₂ films have a wide range of applications because of their excellent performance along with high mechanical, chemical and environmental stability and low cost material. Thin films of Cu²⁺ doped SnO₂ were prepared by spray pyrolysis method. The FTIR, electrical, gas sensing and thermo emf of the prepared samples were studied. The bands at the low wave numbers 500-1000 cm⁻¹ could be attributed to SnO₂. The peaks at 677, 786 and 965 cm⁻¹ were assigned to O-Sn-O, Sn-O-Sn stretching vibrations and lattice vibrations, while the peaks at 569 and 864 cm⁻¹ were due to Sn-OH bonds of the SnO₂ crystalline phase. The plot of thermo emf

versus temperature difference between the two junctions is found to be linear indicating that the temperature dependence of thermo emf is the characteristic conduction of the films. Cu²⁺ doped SnO₂ thin films were exposed to different concentrations of NO₂ gas at various temperatures and the sensitivities of the films were recorded at various temperatures.

References:

1. Aoki A. and Sasakura H., J. Appl. Phys., 1970, 9, 582
2. Chopra K.L., Major S. and Pandya D.K., Thin Solid Films, 1983, 102, 1-7.
3. Betz U, Kharrazi, Olsson M, Marthy J, Escola M. F. and Atamny F., Surf. Coat. Technol., 2006, 200, 5751.
4. Luck L. D., J. Electrochem. Soc., 1963, 110, 1081.
5. Manificier J. C., Murcia M. D., Fillard J. P. and Vicario E., Thin Solid Films, 1977, 41, 127.
6. Manificier J. C., Szepessy L., Bresse J. F., Perotin M. and Stuck R., Mater. Res. Bull., 1979, 109, 163.
7. Kohnke E. E., J. Phy. Chem. Solids, 1962, 23, 1557.
8. Geetha S., Rup R. and Mansingh A., J. of Phy. Review B, 1991, 44, 5672.
9. Das D. and Banerjee R., Thin Solid Films, 1987, 149, 291.
10. Shamala K.S., Murthy L.C.S. and Rao K. N., Bull. Mater. Sci., 2004, 27, 295.
11. Patil P. S., Mater. Chem. Phys., 1999, 59, 185.
12. Korotcenkov G., Cornet A., Rossinyol E., Arbiol J., Brinzar V. and Blinov V., Thin Solid Films, 2005, 471, 310.
13. Korotcenkov G., Macsanov V., Tolstoy V., Brinzari V., Schwank J. and Faglia G., Sensor Actuat.-B: Chem., 2003, 96, 602.
14. Khan A.F., Mehmood M., Aslam M., Ashraf M., Appl. Surf. Sci., 2010, 256, 2252.
15. Agarwal T. N. and Saxena R. N., Ind. J. Pure and Appl. Phys., 1981, 19, 1057.
16. Agarwal T. N. and Saxena R. N., Ind. J. Pure and Appl. Phys., 1982, 20, 780.
17. Patel A. R. and Mysorewala D. V., Mater. Res. Bull., 1970, 5, 1031.
18. Neugebauer C. A., and Webb M. B., J. Appl. Phys., 1962, 33, 74.
19. Neugebauer C. A., Phy. of Thin Films, 1964, 2, 25.
