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Electrical and Gas Sensing Properties of Fe^{3+} Doped Tin Oxide Thin Films

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Abstract: Semiconducting tin oxide thin films with suitable catalysts in the form of nanoparticles, overlayers and clusters are known to exhibit enhanced sensitivity, better selectivity and fast response speeds to various reducing gases. SnO_2 sensor is invariably anion deficient and oxygen vacancies are mainly responsible for making available free electrons for the conduction process. Fe^{3+} doped tin oxide thin films were prepared by chemical spray pyrolysis. The prepared thin films were characterized by electrical, gas sensing and thermo emf. The thermo emf of Fe^{3+} 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 Fe^{3+} doped SnO_2 thin films are typical of semiconductor behavior.
Keywords: SnO_2, Thin films, Spray pyrolysis, Electrical, Gas Sensing and Thermo emf.

Introduction:

The presence of small particles and nano-sized elements leads to changes in material properties such as electrical conductivity, refractive index, band gap, magnetic properties, strength and others. One of the most promising materials in this regard is tin dioxide (SnO_2). Semiconducting tin oxide thin films with suitable catalysts in the form of nanoparticles, overlayers, clusters etc. are known to exhibit enhanced sensitivity, better selectivity and fast response speeds to various reducing gases. SnO_2 sensor is invariably anion deficient and oxygen vacancies are mainly responsible for making available free electrons for the conduction process. In addition, the surface morphology of the sensing layer is also important for realization of sensor with enhanced response characteristics, which in turn depend on the growth kinetics. SnO_2 films have a wide range of applications because of their excellent performance along with high mechanical, chemical and environmental stability and low cost material [1-4]. The crystallinity, transmittance and conductivity of the films were observed with annealing in either air or vacuum and with change in thickness. The earlier studies of SnO_2 films were mainly on the film structure, resistivity, Hall effect and Optical properties reported by [5, 6]. The specimens from crystals of natural Bolivian cassiterite studied the electrical conductance of these samples in the temperature range 100 ^{0}C to 500 ^{0}C and found the activation energy of 0.72 eV [7]. Polycrystalline bars of stannic oxide, undoped and doped with antimony in the temperature range 100 ^{0}C to 900 ^{0}C were prepared by [8].

The undoped SnO_2 [9] 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 [10], thermal beam evaporation [11], and spray pyrolysis [12], and sputtering techniques [13]. In the present work, Fe^{3+} doped (0.01 mol %) SnO_2 thin films were prepared by using chemical spray pyrolysis method. The prepared thin films were characterized by electrical, gas sensing and thermo emf.

Experimental:

All the chemicals used in the work were of analytical grade. Fe^{3+} doped SnO_2 thin films were prepared by chemical spray pyrolysis. Spray solution was prepared by mixing 0.1 M aqueous solutions of SnO_2 and Fe_2O_3 (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 dc electrical conductivity measurements were made on the experimental films by employing the standard van der Pauw method. The gas sensing chamber had been employed for testing of the films to gases. The thermo emf of the prepared samples was studied between the temperature ranges from 275 to 325 K by using thermal probe method

Results and Discussion:

Fe^{3+} doped (0.01 mol %) SnO_2 thin films were prepared by using chemical spray pyrolysis method. The electrical, gas sensing and thermo emf were carried out on to the prepared films.

Electrical Properties:

The electrical resistance of Fe^{3+} doped SnO_2 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.1. The dc dielectric resistance is found to vary as

$R=R_0 \exp(\Delta E / KT)$

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 [14-18].

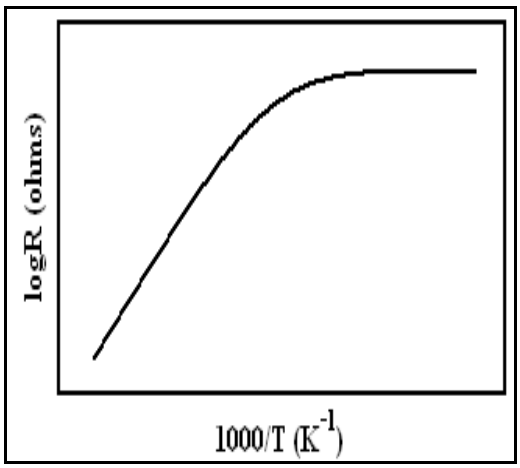

Fig. 1 Plot of Log R versus 1000/T of Fe^{3+} doped SnO_2 thin films

Gas Sensing Properties:

The deposition parameters such as substrate temperature, deposition rate, film – substrate combination, vacuum during the film deposition etc. greatly influence the physical and chemical properties of the oxide thin films. The electrical conductance of a semiconducting oxide-based gas sensor depends on the chemisorbed oxygen ions, oxygen vacancies and the interstitial ions. The target gases change the oxygen balance of the oxide sensor, leading to a variation in its conductance. It is believed that in most of semiconducting oxide-based devices, the electrical conductance of a semiconducting oxide-based gas sensor depends on the chemisorbed oxygen ions, oxygen vacancies and the interstitial ions. The target gases change the oxygen balance of the oxide sensor, leading to a variation in its conductance.

The conductance of the sensor in dry air was measured by means of conventional circuitary by applying constant voltage and measuring the current by picoammeter. The conductance was measured both in the presence and absence of test gas. The gas response (s) is defined as the ratio of change in conductance in gas to air to the original conductance in air

$$S = (G_g - G_a) / G_a$$

Fe^{3+} doped SnO_2 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 NO_2 for several hours. In the Fe^{3+} doped SnO_2 sensor, change in the oxygen balance of the oxide layer leads to a variation in its conductance. In the case of an oxidizing gas (NO_2), 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.

Fe^{3+} doped SnO_2 films were exposed to different concentrations of NO_2 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 NO_2 gas, the dc electrical resistance of the film dramatically increased. Since Fe^{3+} doped SnO_2 is an n type semiconductor, its electrical behavior upon exposure of NO_2 oxidizing gas can be explained by a decrease of conduction carrier density. The amount of oxygen ions available on the Fe^{3+} doped SnO_2 surface increases at the operating temperature. The adsorbing NO_2 molecules interact directly with the adsorption sites at the oxide surface. Therefore the interaction between the film and NO_2 is as follows;

$$NO_2 + e^- \rightarrow NO^{2-}(ad)$$

The interaction with NO_2 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 Fe^{3+} doped SnO_2 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. 2. 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.

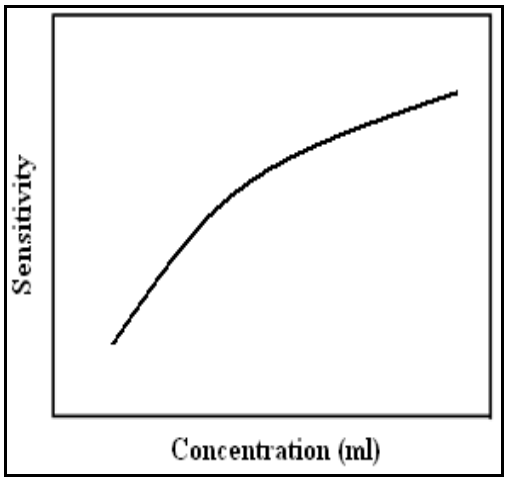

Fig. 2 NO_2 concentration as a function of sensitivity of Fe^{3+} doped SnO_2 thin films

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 [13]. The term "thermo power" is a misnomer since it does not measure power, but measures the voltage induced in response to a temperature difference. An applied temperature difference causes charged carriers in the material to diffuse from the hot side to the cold side. Mobile charged carriers migrating to the cold side leave behind their oppositely charged nuclei at the hot side thus giving rise to a thermoelectric voltage. The material's temperature and crystal structure influence S; typically metals have small thermo powers because of half-filled bands caused by equal negative and positive charges cancelling each other's contribution to the induced thermoelectric voltage. In contrast, semiconductors can be doped with excess electrons or electron holes, causing the magnitude of S to be large. 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 Fe^{3+} 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.3) indicating that the temperature dependence of thermo emf is the characteristic conduction of Fe^{3+} doped SnO_2 thin films. The thermo emf of Fe^{3+} 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 Fe^{3+} doped SnO_2 thin films are typical of semiconductor behavior.

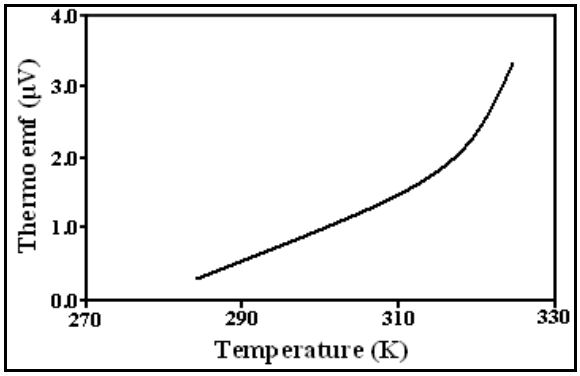

Fig. 3 Temperature dependence of the thermo emf of Fe^{3+} doped SnO_2 thin films

Conclusions:

SnO_2 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 Fe^{3+} doped SnO_2 were prepared by spray pyrolysis method. The electrical, gas sensing and thermo emf of the prepared samples were studied. Fe^{3+} doped SnO_2 thin films were exposed to different concentrations of NO_2 gas at various temperatures and the sensitivities of the films were recorded at various temperatures. 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.

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