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H_2S SENSING PROPERTIES OF METAL OXIDE (SNO_2-CUO-TIO_2) THIN FILMS AT ROOM TEMPERATURE

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Abstract

In this present study we have developed the H_2S gas sensors of metal oxide thin films such as SN3-(70SnO_2-15CuO-15TiO_2), SN4-(80SnO_2-10CuO-10TiO_2) and SN5-(90SnO_2-5CuO-5TiO_2) prepared by screen-printing technique. Variation of sensitivity with concentration of H_2S (ppm) gas at room temperature (303 K) shows that SN4-(80SnO_2-10CuO-10TiO_2) sensor has the maximum sensitivity and found to be fast rise in sensitivity from 20 to 100 ppm concentration of H_2S gas but after that it is independent of concentration of H_2S gas.

The sensing mechanism described as p-n junction like structure is formed due to this result in decrease of electrical resistance, with increase in H_2S gas concentration. Hence the samples resistance of the thin films decreases in presence of H_2S gas.

Keywords: Metal oxide thin films, SnO_2-CuO-TiO_2, H_2S gas sensor.

I. Introduction

H_2S gas is toxic in nature it may paralyze the lungs. Therefore it is necessary to monitored and controlled in the laboratories, industrial area. The Tin oxide based gas sensors are widely used for the detection of various H_2S, No_x, LPG, C_2H_5OH, H_2, CO_2, CH_4 etc [1]. The pure Tin oxide and three kinds of *p*-type metal oxide (CuO, NiO and Bi_2O_3) doped thin films shows a very high sensitivity for H_2S gas detection at low temperature [2]. The microstructure of thin films plays an important role for H_2S gas sensing mechanism, if the SnO_2 is prepared as controlled size 0.7 nm (monolayer) the mechanism of gas sensing will be enhanced [3]. Ishibashi et al [4] shows improvement in of H_2S sensing properties of In_2O_3-based sensors attempted by optimizing their microstructure and compositions. ZnO, TiO_2, SnO_2 are n-type semiconductor materials, which are most promising candidates for gas sensor [5]. In this present work we have prepared the solid solutions of TiO_2, SnO_2 and CuO as a H_2S gas sensor. The sensitivity and resistance measured at room temperature. The aim of the study is to develop a sensor which exhibit better sensor characteristics towards the H_2S detection i.e higher sensitivity and shorter response time at the room temperature.

II. Experimental

In the present work we have selected a metal oxide semiconductor material TiO_2, SnO_2 and CuO (AR grade). The chemicals are taken in powder form and where mixed in different stechiometery in mol% as a sample SN3-(70SnO_2-15CuO-15TiO_2), SN4-(80SnO_2-10CuO-10TiO_2) and SN5-(90SnO_2-5CuO-5TiO_2). The materials used for gas sensors are generally prepared in the form of bulk, pellet or a film (thin or thick). The films were deposited on glass and alumina substrates. In this present study, the sensors are prepared in the form of thin films and deposited on glass substrates. Initially the single/multi-component chemicals were calcinated at 900^{O}C for 4–5 hrs in air atmosphere in furnace (Tempo make ,India). After calcinations the fine powder was formed. These calcinated chemicals (AR grade) are weighted on monopan balance (K-Roy, India) with proper mole percent of TiO_2, SnO_2 and CuO. The two components are mixed together in an acetone to form medium homogeneous mixture. The mixture is then placed in a porcelain crucible and subjected to heating at 700 ^{O}C for one hour duration.

After the calcinations, the fine powder was formed by using Agate and Morter. This calcinated chemicals of (AR grade) are than weighted on monopan balance (K-Roy India) with proper proportation of mole % of TiO_2, SnO_2 and CuO. These three calcinated fine powder components are mixed with the nitrocellulose and n-anylacetate for the screen printing. This paste was screen printed on the glass substrate in the form of thin film having the surface of the film (19×10^{-4} m^2). All this film was sintered at 50^{0}C for half an hours. The sintered thin film where polished and the electrodes form by printing the conductive sliver paint on the adjacent sides of the film.

The electrical resistance of the thin films was measured by voltage drop method which was adopted by Yawale et al [6]. Here we select air tight glass jar having 1935 cc volumes as a H_2S gas sensor chamber. Where, H_2S gas inlet and outlet provided on the top glass jar. The H_2S gas was produced with the help of Kipp's apparatus. For the constant flow of H_2S gas a gas flow meter (FLOWTRAN make, India) was used. The sensitivity the device characteristics of percepting a variation in electrical properties of the sensing material under gas exposure and it can be define as in the equation (1)

$$\text{Sensitivity (S)} = (R_g - R_a)/R_a \qquad \text{If } R_g > R_a \qquad (1)$$

$$\text{Sensitivity (S)} = (R_a - R_g)/R_a \qquad \text{If } R_a > R_g \qquad (2)$$

where, R_g is the change in resistance of the sensor in presence of gas /vapors and R_a is the original resistance of sensor in presence of air.

III. Result & Discussions:

The variation of sensitivity with concentration of H_2S gas at room temperature (303K) for sensor SN3-(70SnO_2-15CuO-15TiO_2), SN4-(80SnO_2-10CuO-10TiO_2) and SN5-(90SnO_2-5CuO-5TiO_2) shown by fig.(1). From the fig. it is found that the sample SN4-(80SnO_2-10CuO-10TiO_2) has highest sensitivity maximum sensitivity and fast rise in sensitivity from 20 to 100 ppm concentration of H_2S gas but after that it is nearly constant for 100 to 400 ppm concentration of H_2S gas. While for sample SN3 and SN5 the change in sensitivity is linear up to 200 ppm concentration of H_2S gas but after that it is independent of concentration of H_2S gas. That means sample may go in to saturation state after 200ppm of H_2S gas hence we have observed the sensitivity of sensors becomes constant.

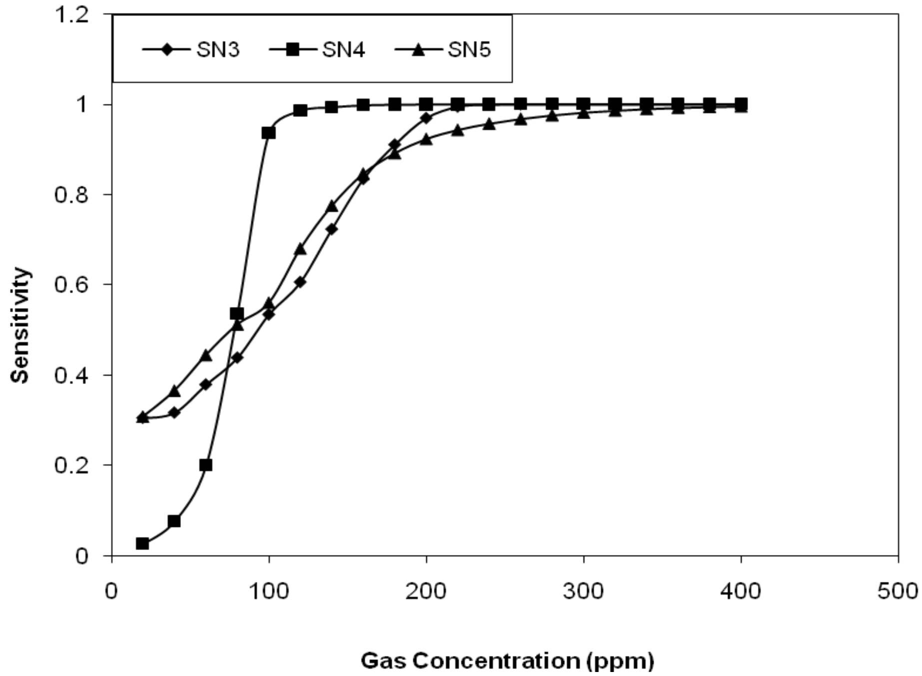

Figure.(1)**:** Variation of sensitivity with concentration of H_2S gas at room temperature (303K) for sensor SN3, SN4 and SN5

Fig. (2). shows the variation of log of Conductivity with Concentration of H_2S Gas at Constant Temperature (303K) for Sensor SN3-(70SnO_2-15CuO-15TiO_2), SN4-(80SnO_2-10CuO-10TiO_2) and SN5-(90SnO_2-5CuO-5TiO_2), it is observed that conductivity of the sensors increases linearly with change in concentration of H_2S gas and found to be SN4 has maximum sensitivity.

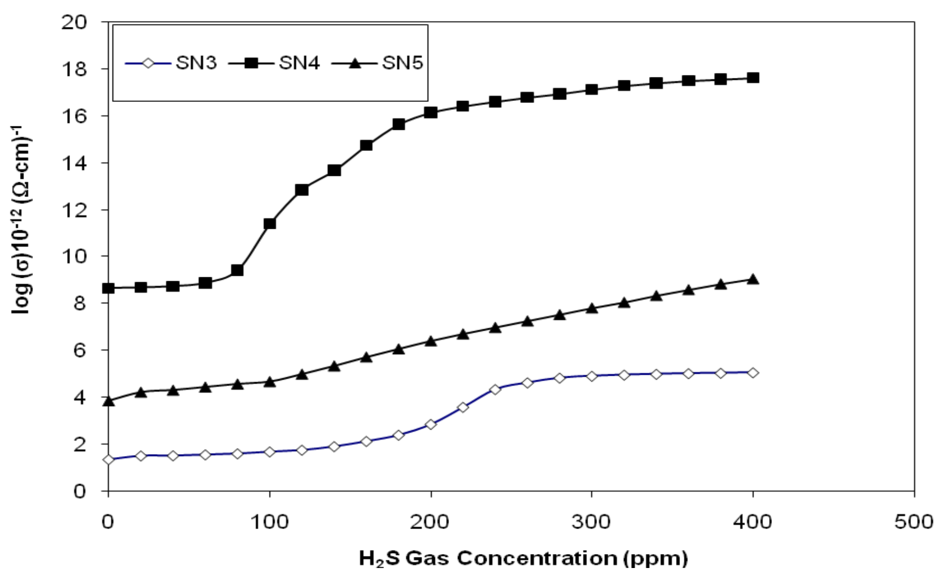

Figure (2): Variation of log of Conductivity with Concentration of H_2S Gas at Constant Temperature (303K) for Sensor SN3, SN4 and SN5

IV. Conclusions:

In this present study TiO_2 is specially added for the temperature improvement characteristics. The mechanism of SnO_2: CuO thin films explain in the many literature and shows that there is decrease in the resistance of the thin films in presence of H_2S gas. CuO and SnO_2 which are p and n type semiconductor, respectively have a strong electronic interaction due to which the CuO: SnO_2 surface consist of numerous p-n junctions causing a very high resistance of the film in the air nearly equal to $70x10^9\Omega$.When we exposed the sample in the presence of H_2S gas the highest sensors resistance is found to be $50x10^9$ Ω for SN4 at 5 ppm concentration of the H_2S gas. CuS is metallic in nature and its formation will destroys the p-n junction existing on the surface which causes the large decreases in electrical resistance. The surface oxygen atoms are desorbed when sensor is exposed to H_2S gas. A p-n junction like structure is formed where at equilibrium a flow of electrons from lower work species to the higher work species starts. This flow of electrons is very easy because of no barrier exist between them. As the flow of electron is more, this result in decrease of electrical resistance [7]. Hence the conductivity of sample increases with increasing concentration of H_2S gas [8].

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