Hydrogen Sulphide gas sensing characteristics of mixed metal oxide thin films grown by spray Pyrolysis technique

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Abstract: Gas sensing behavior of NiO and SnO_2 thin films, synthesized by conventional spray pyrolysis technique have been investigated for H_2S gas. X-ray diffraction (XRD) pattern revealed the polycrystalline nature of the film with a mixed phase comprising of NiO and SnO_2. The surface morphology studied by scanning electron microscopy (SEM), the granular, tubular, uniformly covering entire substrate surface observed in synthesized thin films. The gas sensing studies performed in dry air at constant temperature 100^oC indicated better sensing characteristic for H_2S gas. And also influence of variation of Ni and Sn concentrations on the sensor performance have been investigated for the same gas. H_2S gas exhibits reducing behavior for n-type semiconductor and oxidizing behavior for p-type semiconductor.

Key words: NiO, SnO_2, Spray pyrolysis, gas sensing, XRD and SEM.

1. INTRODUCTION

Over a period of four decades mixed metal oxide semiconductor based sensors have been under extensive investigations, due to their applications in industries and domestic sectors [1-3]. Amongst the large number of metal oxides, SnO_2, ZnO, TiO_2, NiO, CuO and WO_3 have been the materials of particular choice in most of these investigations. It has been widely accepted that, the gas sensing mechanism consists of "receptor" and "transducer" functions. The receptor function deals with the surface chemical/catalytic property, whereas the transducer function is due to surface semiconducting property and grain size of the base oxide used. The receptor function can be tailored by dispersing foreign species on the metal oxide grains. H_2S is one of the most toxic gas, present in the emissions of a number of industrial enterprises in various industries. The sensor based on thick and thin films of metal oxide semiconductors with the addition of number of catalysts including Pt, Pd, Au, and Ag are used [4-7].

Applications of nano-crystalline mixed metal oxide, in gas sensors, have attracted much attention due to their high sensitivity, fast response and low operating temperature [8, 9]. The working principle of mixed metal oxide gas sensors is associated with the change of electrical conductivity due to its adsorption/desorption of target gas in a given ambience. NiO is an interesting p-type semiconductor; SnO_2 is a most promising n-type semiconductor. Mixed metal oxides have a wide range of applications, such as super capacitor, chemical gas sensors, fuel cell electrodes etc. It is known that the gas sensing behaviour of mixed metal oxide gas sensors (MMOGS) is related to the microstructure of thin films. Several approaches have been studied to improve the "sensitivity" and "selectivity" of different mixed metal oxides. It is known that MMOGS are mostly non-selective for different gases. Various techniques have been used to improve the sensitivity and selectivity of sensor device, such as using filters and catalysts [10]. Moreover in real applications, humidity has an adverse effect on the gas sensing property of the device. Though numerous investigations have been carried out, there is only limited information is given about the sensitivity, selectivity and reliability issues of the gas sensors. The samples were characterised for structural, electrical and optical properties, moreover the effects of operating temperature, humidity, thickness, grain size and porosity. In the H_2S gas the sensor characteristics which include the above said characteristics along with response time and recovery time are largely determined by two factors, the reactivity of the active centres of the sensors and the diffusion of the gas to these centres.

In this study mixed metal oxide thin films (NiO-SnO_2) were fabricated using low cost chemical spray pyrolysis technique. These films were uniform and grain size was in the range of µm-nm on the glass substrate. In order to enhance the sensing characteristics of these mixed metal oxide thin films, the doping concentration is increased with constant temperature.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

All the chemicals used for the synthesis of NiO and SnO_2 thin films were of high puriy. Stannous Chloride ($SnCl_4.5H_2O$) which was used as precursor was obtained from Thomas Baker, India. Ethanol used as the solvent, for synthesis of all thin films, was obtained from SD-fine Chem., India.

The NiO thin film is prepared by using nickel chloride ($NiCl_2.6H_2O$) dissolved in Ethanol solution with fixed concentration of 0.06 M. The SnO_2 thin film is prepared by using Stannous Chloride dissolved in Ethanol of fixed concentration of 0.2 M.

The spraying system consists of spray nozzle, air compressor and mechanical arrangement for one dimensional motion. Heating unit consists of a hot plate, thermocouple, temperature indicator and variac. The spray nozzle and hot plate with glass substrate are housed in a metallic box and the outlet of the box is fitted with an exhaust fan to remove the toxic gases produced

during the decomposition of spray solution. Typical NiO and SnO_2 thin films were synthesised with fixed concentrations dissolved in Ethanol and stirred well for long duration and filtered using a filter paper to get clear solutions. The glass slides were washed with deionised water, rinsed in Ethanol and dried and placed in a laboratory oven at temperature approximately 40°C. 20 ml solution of NiO and SnO_2 were sprayed on a glass substrate. The temperature of the substrate was maintained at a constant temperature 400°C by using variac and digital temperature controller. The nozzle to substrate distance kept constant at 40 cm. The entire solution was sprayed continuously in about 8-12 minutes. For the uniform deposition of the solution the substrate is kept stationary while the nozzle is made to move to and fro on a line with a programmed stepper motor using a microcontroller.

The films of NiO and SnO_2 were characterized by XRD and SEM techniques. In order to use these films and mixed metal oxides thin films were cut into small pieces having width of 5 mm and 7 mm in length. 30 ml solution of SnO_2 is mixed with NiO of different concentration like 0.5 M, 1 M, 1.5 M, 2 M. Similarly 12 ml of SnO_2 mixed with 8 ml of NiO and vice versa. And also 15 ml of SnO_2 mixed with 5 ml of NiO and vice versa. To test the workability of the sensing element H_2S gas was used. It was generated using FeS crystals and dilute HCl in a sealed container. The chemical reaction is given below.

$$FeS\downarrow + 2HCl\downarrow \rightarrow FeCl_2\downarrow + H_2S\uparrow$$

3. RESULTS AND DISCUSSION

The XRD analysis was carried out by using X-ray powder diffractometer with Nickel filtered CuK_α (λ=1.5406 Å) radiation for a range of 10°-90° at 2θ angles. The XRD pattern of the synthesized NiO thin film shown in fig 1., the peaks are observed at 26.51° and 38.22° the corresponding indices of crystal planes (111) respectively, which belongs NiO cubic structure.
The average particle size is calculated using Debye's Scherrer formula and is found to be 6.5 nm.

$$D = \frac{0.91\lambda}{\beta \cos\theta}$$

Where, λ-wavelength of X-ray, β-FWHM, θ-Bragg's diffraction angle.

The surface morphology, homogeneity and grain size of the deposited NiO thin films were studied by SEM technique. The grain size is found to be in the range 1µm to 500 nm. The microstructure of prepared NiO thin film is shown in fig 2. The SEM image revealed that the films are formed in rod like structure and sticky.

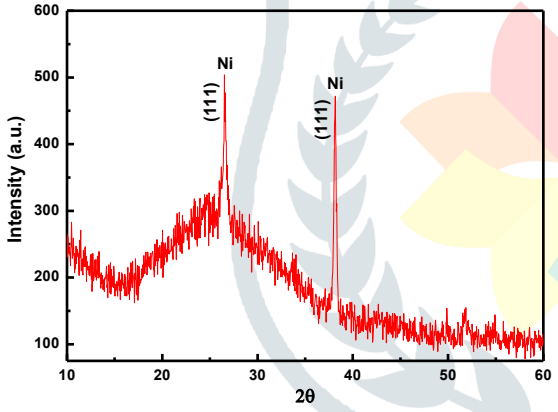

Figure 1. XRD pattern of NiO

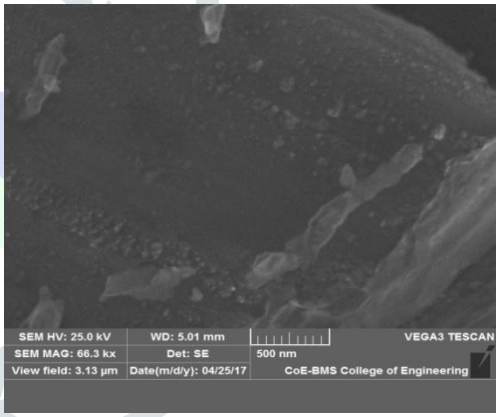

Figure 2. SEM image of NiO

The gas sensing characteristics of thin films of NiO, SnO_2 and their composites were investigated. Sensitivity S is defined as the ratio of effective change in resistance for the test gas to the original value of the resistance in air. It is given by the formula $S = (R_a - R_g)/R_a X100.$. Where R_g is the sensor resistance in the presence of the test gas and R_a is the sensor resistance in dry air. For the sensitivity measurements, first we set the temperature of the oven at 110°C and the resistance of the sensor in air is recorded. A known amount of H_2S gas is injected into the bottle and the cap is locked tightly. The fall in resistance of the sensor with respect to time is recorded. Once the minimum constant resistance value is reached, cap is opened and the sensor is exposed to the atmosphere, now the increase in the resistance value with respect to time is recorded. Similar procedure is repeated for all the synthesized thin films and the data obtained is represented in figures 3-12. Here we observe that, the response time is less and the recovery time is slightly more. The reproducibility is very good.

The composition of NiO+SnO_2 (10 ml each) thin film shows the better response of sensitivity with respect to time, the value of sensitivity is 58.72 as shown in fig. 5. In the remaining composite thin films with different concentrations, shows less sensitivity as compared to NiO+SnO_2 (10 ml each) thin film.

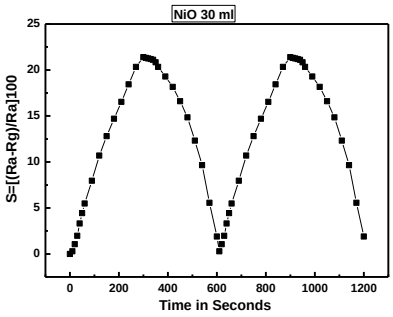

Figure 3. Variation of gas sensitivity with time of NiO thin film

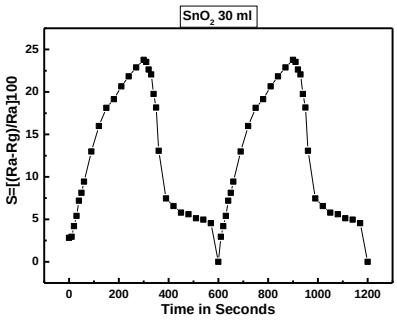

Figure 4. Variation of gas sensitivity with time of SnO_2 thin film

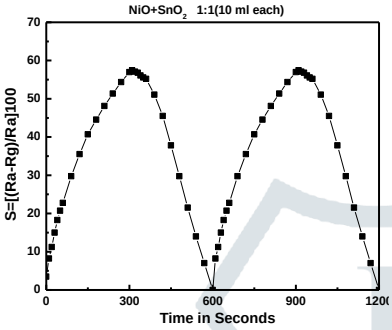

Figure 5. Variation of gas sensitivity with time of $NiO+SnO_2$ (1:1) thin film

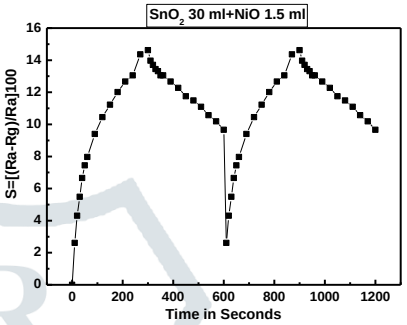

Figure 6. Variation of gas sensitivity with time of SnO_2+NiO (30 ml + 1.5 ml) thin film

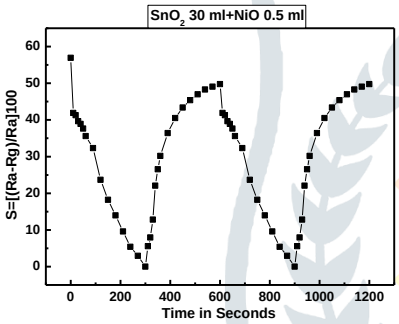

Figure 7. Variation of gas sensitivity with time of SnO_2+NiO (30 ml + 0.5 ml) thin film

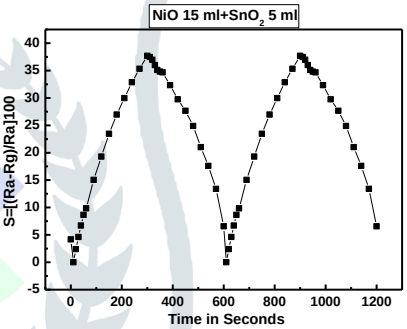

Figure 8. Variation of gas sensitivity with time of $NiO+SnO_2$ (15 ml+5 ml) thin film

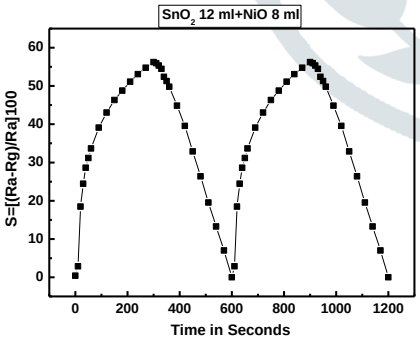

Figure 9. Variation of gas sensitivity with time of SnO_2+NiO (12 ml + 8 ml) thin film

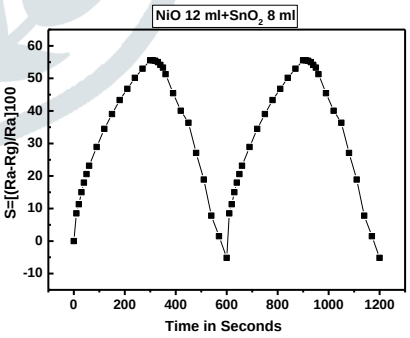

Figure 10. Variation of gas sensitivity with time of $NiO+SnO_2$ (12 ml+8 ml) thin film

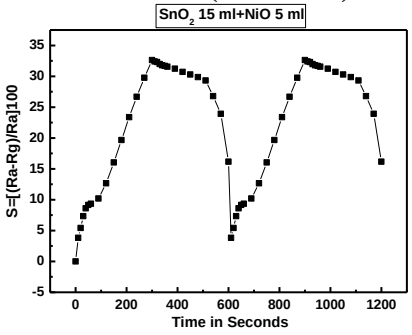

Figure 11. Variation of gas sensitivity with time of SnO_2+NiO (15 ml + 5 ml) thin film

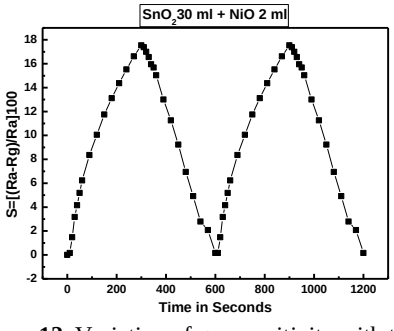

Figure 12. Variation of gas sensitivity with time of SnO_2+NiO (30 ml + 2 ml) thin film

4. CONCLUSION

The NiO, SnO_2 and their composite thin films were synthesized by using Spray Pyrolysis Technique. Structural and surface morphology of the prepared thin films were studied. XRD pattern reveals that the thin films prepared are crystalline in nature. The SEM image shows that the films are formed in rod like structure and sticky. The average grain size is found to be in the range 1µm to 500 nm. The setup has been proposed to measure the H_2S gas response in terms of variation in electrical resistance of sensing element. It is quite simple, portable, cost effective, reliable and sensitive to detect H_2S gas; it is able to measure the sensing property of the mixed metal oxide samples with different concentrations. It can be easily extended to the other sensing materials and also other gases of interest.

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