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AMMONIA GAS(NH_3) SENSING OF SnO_2-CuO MIXED OXIDE THICK FILM AT OPERATING TEMPERATURE

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ABSTRACT

Objective To develop ammonia gas sensor by SnO_2-CuO Mixed oxide thick film which is highly sensitive at particular optimum temperature.

Materials and Methods:The SnO_2 and CuO powder mixed with different ratio and heated at 800^{0}C and then this powder is used to prepared thick films by a screen – printing technique on glass substrate.

Results:The NH_3 gas sensing properties, preferably the rate of response of CuO-SnO_2 sensors are influenced by the CuO doping and operating temperature. XRD analysis showed that crystallite size is small (97.3nm) for 50SnO_2-50CuO composition. Thermal analysis (TG/DTA) is the calculate of change in weight and energy in the form of heat as the material is being cooled or heated at a constant rate. The resistance change per ppm is found to be 82 MΩ for SA5 sample.

Conclusion : 50SnO_2-50CuO composition sample is optimize for better sensing material as regards to other.

Keywords: Ammonia gas; SnO_2-CuO; Sensors; operating temperature,X-Ray Diffraction,TG/DTA.

INTRODUCTION

Gas sensors using transparent SnO_2 semiconductors to detect different gases at relatively low operating temperature have been reported [1–3].

Although from its natural origin, there are so many sources of ammonia, like the chemical industry. The different application areas for ammonia sensors or measurement systems and different techniques available for manufacture selective ammonia sensing devices. As one of the common pollutants and toxic gases, ammonia (NH_3) can cause different effects on the human body like irritation of the eyes, skin, throat, and respiratory system. According to the US Occupational Safety and Health Administration (OSHA), the exposure of under 35 ppm of ammonia by volume in environmental air for 15 min or under 25 ppm of volume for 8 h get harms people's health [1-3]. However, it is difficult for humans to detect ammonia below 50 ppm, which reflects the advantage of ammonia sensing. Hence, a more sensitive and selective room temperature NH_3 gas sensor is highly desirable in todays world.The sensor showed good sensitivity to NH_3 gas and therefore it can be applied for monitoring NH_3 gas in air with relatively low power consumption and also optimizing low operating temperature.

MATERIALS AND METHODS

Construction of sensor

SnO_2 and CuO is mixed (Sample code SA_2: 20:80, SA_5 :50:50, SA_8:80:20) thoroughly in an acetone medium by using a mortal and pestle and then heated at 800^{0}C in a furnace. The paste used in Screen-printing was prepared by maintaining inorganic to organic material ratio at 70:30.The paste was screen printed on an glass substrate [4], of size was 75mm X 25 mm .The films were dried at 150 ^{0}C for about 20 min to remove the organic material. The film was aged for 4 weeks in open air [5] for drying. For the electrical characterization purpose form the electrode on two side of thin film by using silver paste.

Measurement of gas sensing characteristics

The gas sensing properties of these samples (thick film) were studied in a home –built static gas characterization system. The system consist of a base plate with gas inlet, insulator base, glass plate, heater (one nicrome, 1.5kW, R=120Ω), DC power supply, resistor (Rs), DC Millivoltmeter (Systronics type, Model No.412, ±1μV), Digital thermometer (SE-221 P-K, Sonit) ,dimmerstat (0-250V) and chamber(Volume :24 lit). The base plate, insulator plate, heater plate and glass plate are placed one above the other. This whole assembly is kept inside the chamber. The temperature of the sensor material was increased from 27-100 ^{0}C by put it on the heater .The temperature of the heater was controlled through dimmerstat. The temperature of the sensor sample was measured by digital thermometer. Using silver paste deposited between two sides of thick films forms the electrodes. The DC power supply (V) in series with resister (Rs=1MΩ) is connected to sensor. The voltage drop (Vs) across the Rs is measured by the microvoltmeter. The required gas concentration inside the system is achieved by passing gas through flow meter with flow rate 200 ml/min in the airtight chamber at ambient condition. The samples were tested for a wide range of concentration of NH_3. The sensitivity is calculated by using the formula

$$S = \frac{R_g - R_a}{R_a}$$

Where R_a & R_g are the electrical resistance of the sensor in presence air and gas+air respectively.

The structure was of sensor material was examined by X-ray diffractometer (PANalytical PW: 3040/60 made in Netherland) using CuKα radiation (1.5418 Å) in the 2θ range of 5 -100^o. The 2θ step and step acquisition time were 0.0170^o and 7.7523 s respectively. Thermal analysis of sample is studied using Differential Thermal Analysis (DTA)/ Thermogravimetry (TG) (Perkin Elmer instruments Model No.:PYRIS Dimond M-code:k-A101005820)

RESULTS

The thrust for the present work was to study the gas sensing characteristics of SnO_2: CuO thick films. The results obtained are

analysed, discussed and presented in the following part of this section.

Characterization of film by XRD

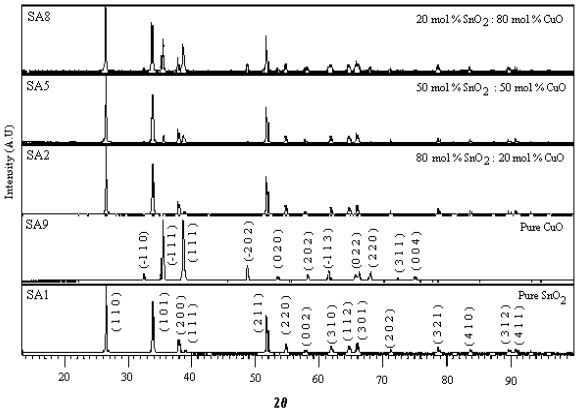

Fig. 1: XRD patterns of SnO_2:CuO {SA2(80:20), SA5(50:50), SA8(20:80) powder

In Fig. 1, shows XRD spectrum of pure SnO_2, pure CuO and composite of SnO_2 and CuO. The crystallite size for all the samples is calculated by using the Scherrer equation [6]

$D=0.9\lambda/\beta\cos\theta$

where *D* is the crystallite size, *k* is the constant (= 0.9 assuming that the particles are spherical in size), λ is the wavelength of X-ray radiation, β is the line width (obtained after correction for the instrumental broadening) and θ is the angle of diffraction. The average crystallite size of the different sample for SnO_2:CuO system for different composition i.e.80:20,50:50,20:80 is found to be 108.5, 97.37 and 122.1 nm respectively.

Thermal analysis (TG/DTA)

Thermal analysis of SnO_2: CuO compound was conducted on Perkin Elmer TG/DTA instrument in Ar gas (20^0C) from room temperature to 950^0C with a heating rate of 10^0C /min. Fig 2(a),(b) and (c) shows TG/DTA curve for SA_2,SA_5 and SA_8 sample respectively. In all TG/DTA curve, in the range 20-750^0C,the DTA curve does not shows endothermic peaks. TG curves show rapid weight losses i.e ~0.7 to 3.6 % in range room temperature to 150^0C except SA_8 sample due to water content. In the temperature range 150 to 700^0C TG curve shows weight loss in the range ~0.84 to 4.16%. Onwards 700^0C, a sudden weight loss in the range of ~4.44 to 15 % is observed which is due to transformation of SnO→SnO_3O_4[7] and CuO →Cu_2O [10].

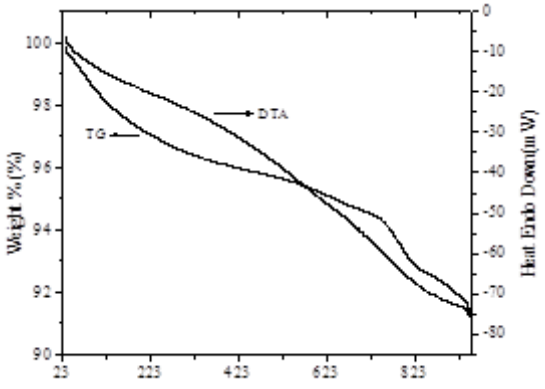

Fig. 2(a): TG/DTA Curve of SnO_2:CuO(80:20) Powder

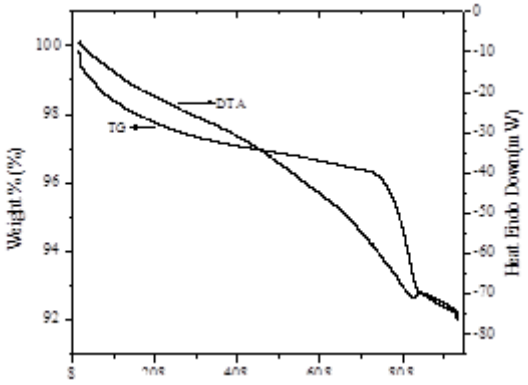

Fig. 2(b): TG/DTA Curve of SnO_2:CuO(50:50) Powder

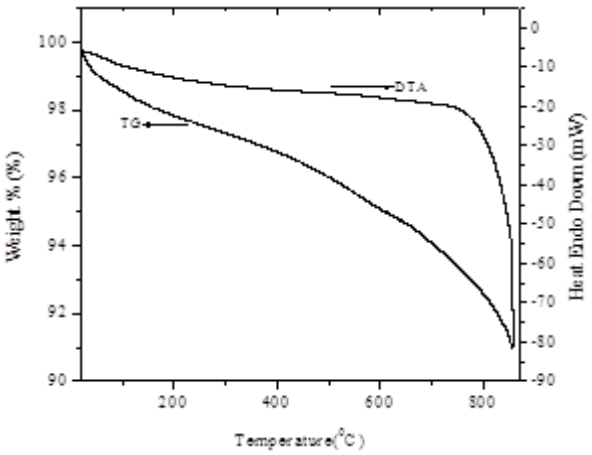

Fig. 2(c): TG/DTA Curve of SnO_2:CuO(20:80) Powder

Effect of operating temperature

Fig 3 shows the variation of sensitivity with temperature for NH3 gas 200 ppm. From fig 3 it is clear that the sensitivity for SA_5 sample decreases with increasing operating temperature, reaches minimum value of sensitivity at the certain temperature and increases with further increase in temperature. The sensitivity is found to be best for SA_5 sample at room temperature (33^0C). The maximum value of sensitivity equal to 0.85 (T_{opr} 33^0C) and 0.75 (T_{opr} 50^0C) are obtained for the NH3 gas for SA_5 sample. Another observation is that SA_2 and SA_8 samples, the curves shows one more maxima at the higher temperature.

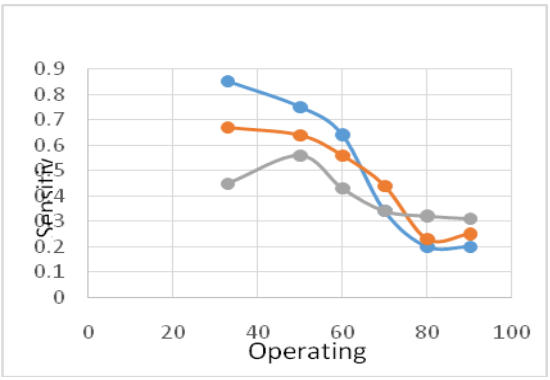

Fig. 3: Variation of sensitivity with temperature for different samples at 200ppm of NH_3 gas

Temperature has pronounced effects on the sensitivity of SnO_2 gas sensors, as it influences the physical properties of semiconductors (change of the free carrier concentration, Debye length,etc), but also because every reaction taking place at the surface of the semiconductor, as well as the most probable species adsorbed and, hence, the reaction sites, are temperature dependent. So, temperature specially affects those properties related to the processes occurring at the surface of the sensor.

Static response of sensor

Fig. 4 shows the static response of the SnO_2-CuO sensors for a NH3 gas exposure at 80 ppm at room temperature. It is seen that from static response the 80 SnO_2 – 20 CuO and 20 SnO_2 – 80 CuO sensor takes about response time 80 s & 110 s respectively, whereas the other compositions are relatively slower. The recovery time is reported in table 1.1 .The observed response time of the SnO_2 – CuO sensor is found to be quite fast as compared to the reported sensors in literature [8, 9].

Table 1: Response and Recovery time of SnO_2- CuO sensor in static condition

Sr.no	Composition of sample SnO_2 - CuO	Response time (s)	Recovery time (s)
1	80 -20	80	280
2	50 - 50	140	160
3	20 - 80	110	170

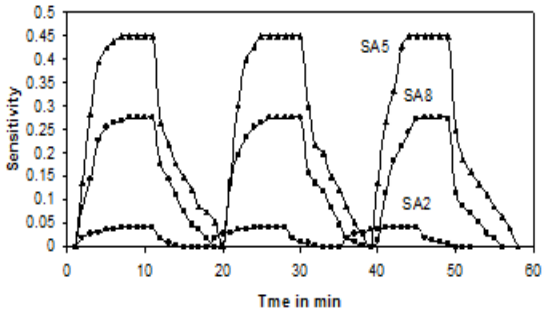

Fig. 4: Static response of SnO2-CuO Sensor

Effect of crystallite size

If the crystallite size is small so that the space-charge region extends through a large fraction of the grain or if the whole grain is included completely in this region, the gas sensor sensitivity could be high [4]. From calculated value seen that the crystallite size is small for 50SnO_2-50CuO sample in a SnO_2-CuO system and hence it gives higher sensitivity than the other sample.

Sensing mechanism

The lone pair of electrons of NH_3 gives strong electron acceptor behaviour. But it acts as an electron donor to the metal oxide, when reach with the adsorbed oxygen ions on the surface by reverting the trapped electrons. Nguyen *et al.* [11] proposed the mechanism that generates free electrons accomplished by the number of oxygen ions reacted with NH3 molecules, given in the Eqs. has been adopted by most of the authors.

$$\left.\begin{array}{l} 2NH_3 + 3O^-_{(adsorbed)} \rightarrow N_2 + 3H_2O + 3e^- \\ \quad\quad or \\ 4NH_3 + 3O^-_{2\,(adsorbed)} \rightarrow 2N_2 + 6H_2O + 6e^- \end{array}\right\}$$

$$2NH_3 + 4O^-_{(adsorbed)} \rightarrow N_2O + 3H_2O + 4e^-$$

$$2NH_3 + 5O^-_{(adsorbed)} \rightarrow 2NO + 3H_2O + 5e^-$$

In humid atmosphere, the kind of reactions that takes place on the surface, which would modify its resistance are yet to be investigated. However up to 60 and 72% of RH did not affect the sensing performance of the sensor [12,13].

CONCLUSION

The screen –printed thick films of SnO_2:CuO gas sensor system revealed that:

The optimum gas sensing temperatures for NH_3 for SA_2,SA_5,SA_8 sample are 50^0C , 33^0C & 50^0C respectively, from the above results it clearly indicates that the SA_5 sample is highly sensitive at 33^0C operating temperature. The thickness and crystallite size of the 50SnO_2: 50CuO sensor is 18.5 μm and 97.37 nm respectively. The CuO (50 mol %):SnO_2(50 mol %) sensor is extremely sensitive to NH_3 gas at minimum operating temperature . For other composition sensitivity decreases because the high coverage of CuO compound on the surface of SnO_2 restrained from NH_3 sensing reaction to occur at the interface between SnO_2 and catalyst.

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