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CO_2 Gas Sensing Properties of ZnO-Fe_2O_3 Composites

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ABSTRACT

ZnO-Fe_2O_3 composites of 0–100 mol% composition range were fabricated in the form of thin films by sintering powders at 800°C and their electrical conductivity and CO_2 gas sensitivity were measured between 30 and 80°C. SnO_2-rich composites showed higher sensitivity values than pure ZnO. Fe_2O_3-rich composites have more porous microstructure and thus are more sensitive to CO_2 gas at all temperatures than pure Fe_2O_3. The effects of microstructure and composition on the gas sensitivity were discussed.ZnO– Fe_2O_3 grain boundary was also proposed to be responsible for the gas sensitivity.

Keywords: ZnO nanoparticles; Fe_2O_3; Gas sensor; CO_2

I. INTRODUCTION

Semiconductor-type gas sensor for sensing CO_2 has been fabricated with base materials like SnO_2 and In_2O_3. To improve the sensing properties, transition metal oxides, such as La_2O_3, Nd_2O_3, were added as a cytalist on it.[1-4]. Among these sensors, La_2O_3-added SnO_2 sensor showed the most superior sensitivity to CO_2 gas. The La_2O_3 -added SnO_2 sensor was investigated using various methods such as powder mixing, soaking, impregnating, coating, etc. [3,4] .

Seiyama et al have proposed the gas sensors based on ZnO thin films[5]. ZnO is sensitive to many gases of interest, H_2 [6] oxygen [7-12], H_2O [10-11], ethanol [12] and NH_3 [13], etc. It also has a rapid response with a possibility of miniaturization. However, it has some drawbacks, such as high working temperature, normally between 400 and 500 °C, poor gas selectivity and relatively low gas sensitivity [14].

To overcome these disadvantages, considerable research and development are underway. There are various techniques to modify the sensing properties of the gas sensors. One critical approach is to modify the metal oxide surface by using noble metals (Au, Pt or Pd) [15, 16] or rare earth metals (La, Y and Ce) [17,18]. ZnO(n)/CuO(p) heterocontact configuration also showed some possibility of improving the selectivity [19]. Nanto et al have reported that a sensor based on a ZnO thin film doped with Al, In or Ga could detect the ammonia gas whose concentration was as low as 1 ppm [9]. But the working temperature was as high as 350 °C. Recently, Ivanovskaya et al suggested that a sensor based on Fe_2O_3/In_2O_3 nanocomposites exhibited high sensitivity to NO_2 [20].

The present work was undertaken to investigate the gas sensing behavior of ZnO nanoparticle thin films doped with Fe_2O_3 nanoparticles prepared by a screen printing method. Morphological, structural and sensing

properties at room temperature were studied. The ultimate objective of this study is to improve the gas selectivity and sensitivity of the nano-sized ZnO-based sensors at room temperature.

II. EXPERIMENTAL

Appropriate amount of tin oxide (Sd fine, 99.9%) and ferric oxide (Sd fine, 99.9%) powders were calcinated at 800°C for 4 h in the furnace. Initially the single chemicals were calcinated at 800^{0}C for five hours. After calcinations the fine powder was formed in agate and mortar. The paste was prepared by mixing calcinated fine powder with Ethylcellulose and Butylcarbitol for screen printing. The paste was screen printed on glass substrate in the form of thin film. The films were subjected to heating at 150^{0}C for 30 min. For surface conductance measurement the electrodes of silver paint were formed on adjacent sides. Again the films were subjected to heating at 150^{0}C for 30 min for drying the silver paint. Phase and microstructure were characterized by the X-ray diffractometry (XRD) and scanning electron microscopy (SEM), respectively.
The electrical conductivity was measured after it was cooled to the measurement temperature.
All samples showed almost linear Sensitivity–Concentration of CO_2 gas. Resistance values in air and in 500 ppm CO_2 were measured. The specimen was kept in dry air for 30 min before changing the measurement temperature. The gas flow rate was 2ml min^{-1}. Gas sensitivity was defined as R_g-R_a/R_a, where R_a and R_g are the electrical resistance values in dry air and in sample gas, respectively

III. RESULTS AND DISCUSSION

3.1 Phase and microstructure observation

The X-ray powder diffraction patterns of ZnO, Fe_2O_3 and their compositions calcinated at 800ºC for 4-5 h were recorded in terms of 2θ in the range 10-100º and are shown in figs.1 (a) to (c). It is observed that XRD pattern of ZnO and Fe_2O_3 contains 8-10 peaks. The prominent peaks observed in XRD spectra are due to ZnO and Fe_2O_3. The intensity of the peaks varies with ZnO and Fe_2O_3 concentration. The (h k l) values are calculated for various peaks from XRD spectra, ZnO as hexagonal and Fe_2O_3 hematite in structure [23-26].
The lattice parameter values obtained for ZnO are a = b = 3.249 Aº and c = 5.201 Aº with c/a ratio of 1.6, respectively [27]. These values are in good agreement with the values reported in references [28-30]. Intensity of ZnO decreases with increasing composition of Fe_2O_3.The crystallite size (D) calculated from Scherrer formula [21, 22] using the FWHM is listed in (table 1) for each material that used for sensors preparation. The SEM study indicates that the crystallite sizes are different and therefore small intergranular pores and voids are formed and these are responsible for gas sensing.

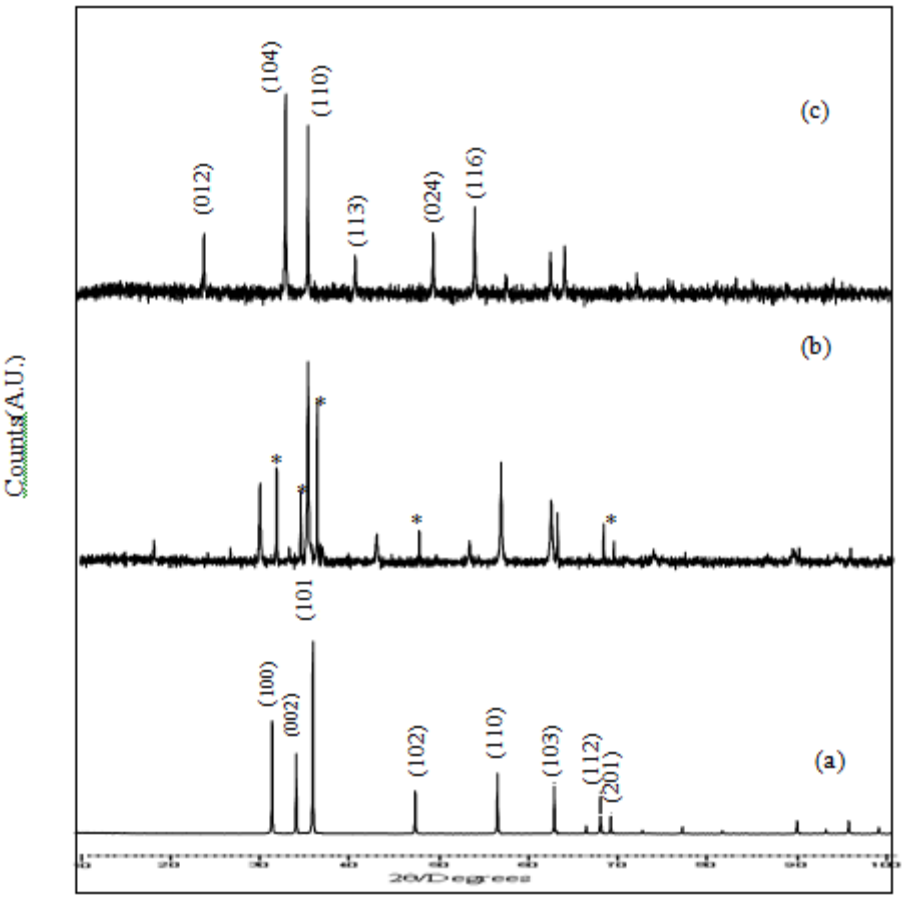


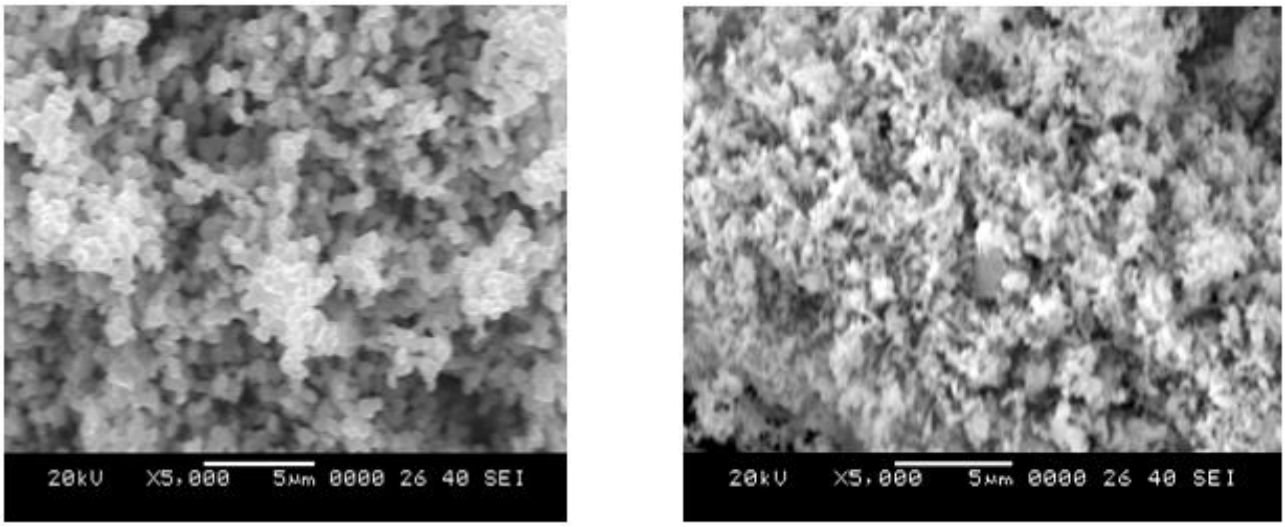
Fig.1: XRD of (a) ZnO (b) 40 Fe_2O_3:60 ZnO, (c) Fe_2O_3 ; * indicates peaks of ZnO (100,101,102,112) planes.

Table(1): Shows the (2θ) position and average crystallite size (D) of ZnO, Fe_2O_3, and their composites.

Chemical composition ZnO - Fe_2O_3 (mol%)	FWHM (2θ) Degree	Average crystallite size (D) (nm)
100 - 0	0.1338	105.38
60 - 40	0.0816	162.80
0 - 100	0.0816	194.45

3.2 SEM of ZnO - Fe2O3:

Fig. 2, shows the SEM photographs of 60ZnO-40Fe_2O_3 sensors for X5000 magnifications. Fig.2, shows the randomly distributed ZnO-Fe_2O_3 grains of larger size and shape distribution. The large number of grains which are leading to high porosity and large effective surface area are available for adsorption of gas species. The non-uniform voids, bigger and flat patches also seen in the ZnO- Fe_2O_3 micrograph. The size of voids varies from ~20 nm to 400 μm and pore size varies from ~50 nm to 10 μm. The average grain size seen from micrograph varies from ~100 to 200 nm.



(a) (b)

Fig.2: SEM picture of (a) Fe_2O_3 and (b) $60ZnO\text{-}40Fe_2O_3$

3.3 Sensitivity of ZnO- Fe2O3 to CO2 gas :

Fig.3 shows the sensitivity variation with concentration of CO_2 gas for SC_1, SC_2 ,SC_3, SC_4, SC_5 and SC_6 sensors at temperatures 303K. The sensitivity increases with increasing concentration of CO_2 gas.

The curves are linear in certain range of CO_2 gas concentration. At higher concentration the curves shows saturation effect. Very small change in resistance is observed at high ppm level. Similar type of behavior is observed at all temperatures. At temperature 303K sensor SC_2 shows higher sensitivity than other sensors. This may be due to small grain size formed in sample SC_2 than other samples. More number of grains formed larger surface exposed to gas.

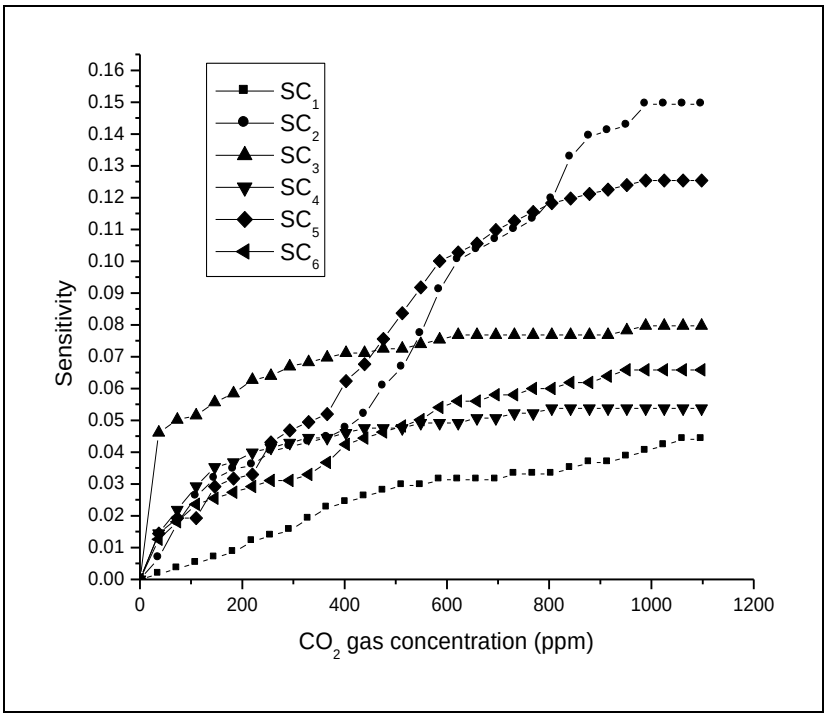


Fig.3: Variation of sensitivity with ppm of Fe_2O_3-ZnO composition at temperature 303K

IV. CONCLUSION

Gas sensors based on Fe_2O_3–ZnO nanocomposites have been prepared with different compositions of Fe:Zn. The sensor with $40Fe_2O_3$-60ZnO (SC2) exhibited good sensitivity and selectivity to CO_2 at room temperature. The response and recovery time of the sensor were about 10 min. The reproducibility of the ZnO gas sensor with $40Fe_2O_3$ -60ZnO was good. The increased sensitivity and selectivity to CO_2 may largely be attributed to the addition of Fe_2O_3 nanoparticles, which can promote the adsorption of CO_2 molecules on the oxide surface and accelerate the oxidizing process.

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