GAS SENSING PROPERTIES OF CUO MODIFIED ZINC STANNATE NANOMATERIAL PREPARED BY SOL – GEL METHOD

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Abstract : Semiconducting Zinc stannate, Zn_2SnO_4, is an important n-type semiconductor with a large band gap of 3.6 eV [1], which is often called zinc tin oxide (ZTO) having face – centred cubic spinel structure. The compound has been successfully prepared by simple method called sol gel citrate method followed by calcinations. The nanocomposite was characterized by means of x-ray powder diffraction. Additionally, sensor performance of undoped and surface modified by 5 wt % copper oxide over ZTO were studied under different operating temperature and different reducing gases such as ethanol, H_2S, CO and LPG. The result reveals that material exhibit excellent sensitivity and selectivity toward carbon monoxide gas at 180^{0}C proving their applicability in gas sensors.

Index Terms - Spinel, Nanocrystalline, XRD, Sensitivity, CO.

1. INTRODUCTION

As there is an increasing demand for various gases in industry and the home, it has become a major task to develop semiconductor gas sensors that enable us to detect the leakage of these gases. Thus, efforts have been concentrated on developing gas sensors with a high sensitivity and selectivity to gases [2]. The monitoring of carbon monoxide (CO) gas is essential since CO is not only a very toxic gas, but also a common gas produced by the incomplete combustion from factories, vehicles, and household appliances. In this paper, Zinc stannate (Zn_2SnO_4) was studied as a sensing material for monitoring CO gas.

Zinc stannate (Zn_2SnO_4) is a typical n-type ternary semiconductor, and has been employed as important multifunctional material in the fields of photocatalytic activity [3], solar cells [4], lithium ion batteries [5], and so forth. Especially, owing to the excellent gas-sensing performance of ZnO and SnO_2 [6 - 8], the application of Zn_2SnO_4 in the field of gas sensors has attracted extensive attention [9 - 11]. Therefore, it would be a meaningful work to prepare Zn_2SnO_4 with novel morphology to lowering the optimum operating temperature and improve the sensitivity, selectivity. It 1s well known that the sensitivity or selectivity to a specific gas can be enhanced by applying some appropriately selected additive to the base materials. CuO was coated on the surface Zn_2SnO_4 in order to modify the gas-sensing properties of Zn_2SnO_4. CuO was known to lower the sensing temperature of SnO_2 and ZnO based gas sensors. Thus it is expected that CuO - coated Zn_2SnO_4 may have an added advantage in the selective detection of CO gas.

2. EXPERIMENTAL DETAILS

2.1 Material Synthesis

All the chemicals and reagents used in the experiment were analytically pure and were used as received without further purification. Nanocomposite Zn_2SnO_4 was synthesized by sol–gel citrate method. For the preparation, zinc nitrate, tin nitrate and ethylene glycol was used as a starting material. Zinc nitrate, tin nitrate was taken in stoichiometric ratio and dissolved in de-ionized water at 80^{0}C for 2 h. Then ethylene glycol was added under constant stirring to obtain a homogeneous and stable sol. The solution was further heated in pressure vessel at about 130^{0}C for 12 h. During this reaction transparent solution was transform into a gel state with very high viscosity. The material was then heated in a furnace at 350^{0}C for 3 h and a violent combustion was occurs which spontaneously propagates until all the gel was burnt out to form a loose powder. The powder was then calcined at 650^{0}C for 6 h in order to improve the crystallinity of materials.

CuO - coated sample was also made by immersing the sintered sample into 5 wt% CuO solution for 1 h. The CuO - impregnated sample was then heated to 350^{0}C for 2 h followed by firing at 650^{0}C for 3 h.

2.2. Characterization techniques

The synthesized sample was characterized for their structure and morphology by X -ray powder diffraction (XRD; Siemens D5000). The X-ray diffraction data were recorded by using CuK_{α} radiation (1.5406 A^0).

2.3. Measurement of sensing properties

The gas-sensing properties of prepared ZTO powder was studied for different reducing gases such as hydrogen sulphide (H_2S), ethanol (C_2H_5OH), liquefied petroleum gas (LPG) and carbon monoxide (CO) whose concentration were fixed at 600 ppm in air. The gas sensitivity (S) was defined as: $S = (R\text{a} - R\text{g})/R\text{a} = \Delta R/R\text{a}$; where, Ra and Rg are the resistance of sensor in air and the test gas, respectively. The gas-sensing properties were measured in a temperature range of 50 – 350^{0}C.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

The crystallinity of the synthesized samples was examined by XRD analysis. XRD pattern of CuO coated ZTO nanoparticle calcined at 650^{0}C was shown in Figure 1. All of the peaks can be readily assigned to a pure phase of Zn_2SnO_4. No extra peak is observed for CuO, which indicated the formation of a homogeneous compound with face-centered cubic structure. The presence of sharp and strong X-ray diffraction peaks suggests that the Zn_2SnO_4 nanowires have good crystallinity. Their average crystallite size of the samples was estimated with the help of Debye-Scherrer formula and it was found to be 35 nm.

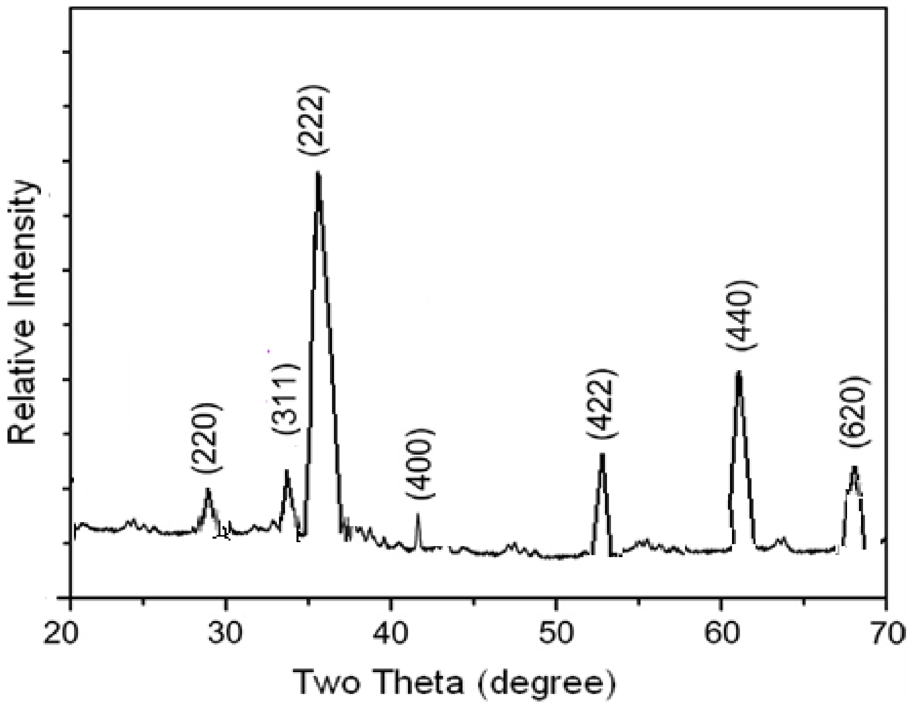

Fig. 1: X-ray diffraction pattern of CuO coated Zn_2SnO_4, calcined at 650^{0}C for 6 h

3.2. Gas sensing characteristics

Since the response of gas sensors is greatly influenced by operating temperature, we have investigated the temperature-dependence behavior of the sensors made of ZTO, calcined at 650^{0}C, to various gases including LPG, H_2S, CO and ethanol at 50–350^{o}C, as shown in Figure 2. It is clear from the figure that the response goes on increasing with increase in operating temperature, attains its maximum and then decreases with further increases in operating temperature. The optimum operating temperature is found to be 220^{o}C.

In order to modify and/or control the surface properties of the ZTO sensor and enhance to sensitivity, surface modified by 5 wt % copper oxide over ZTO is performed. The most important effects of surface modification are to increase of the maximum sensitivity and the rate of response, as well as the lowering of the temperature of maximum sensitivity. The effect of CuO modified ZnO on the sensitivity of CO sensor at an operating temperature of 180^{0}C is shown in Figure 3.

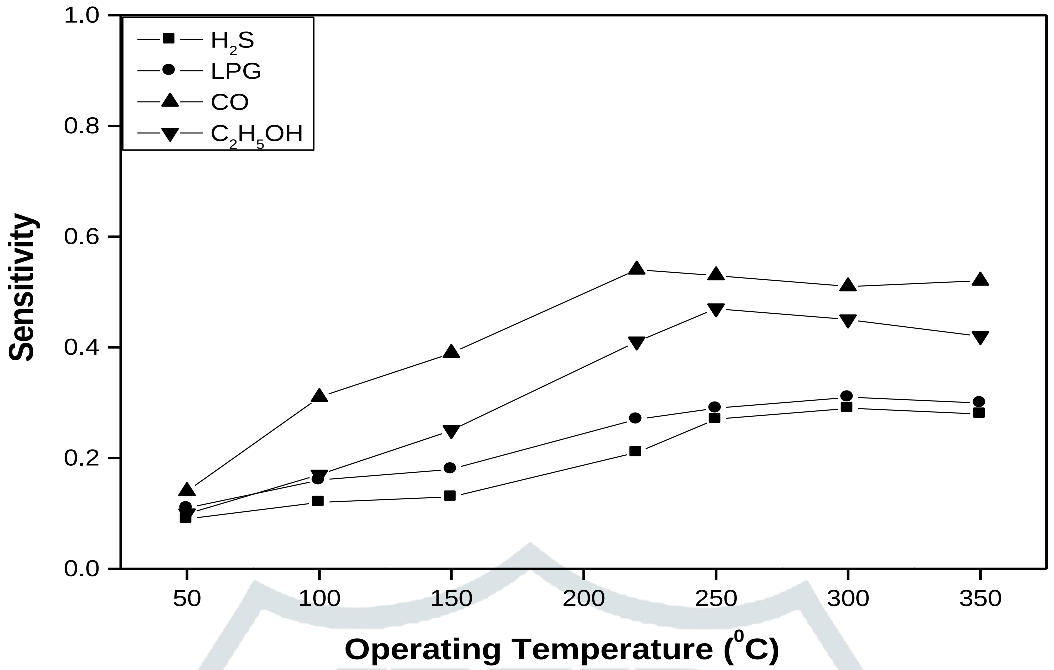

Fig. 2: Sensitivity as a function of operating temperature for ZTO for H_2S, LPG, CO and ethanol.

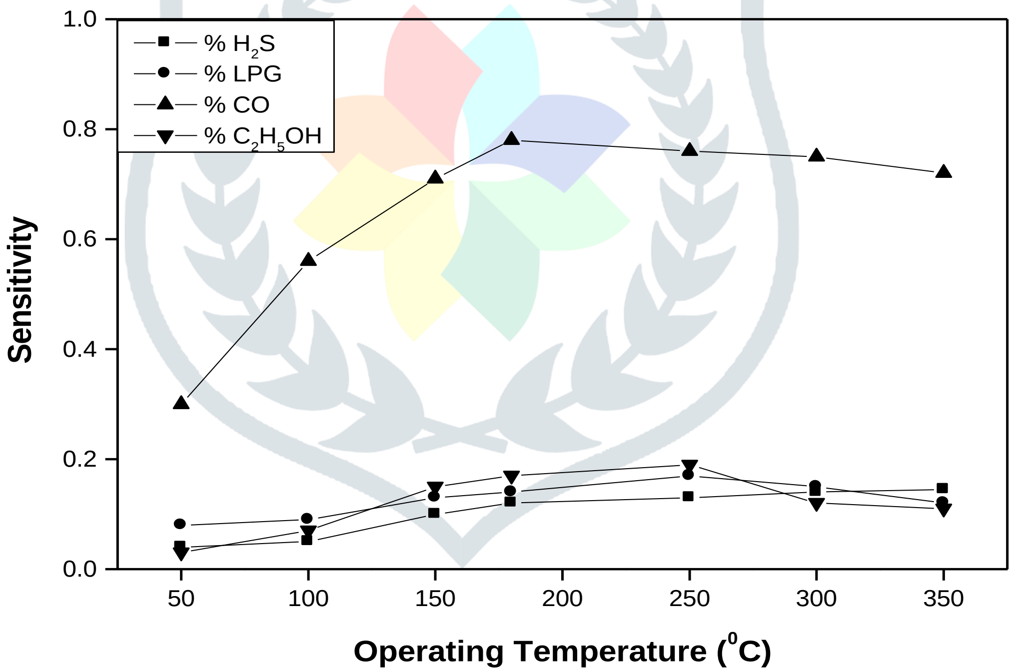

Fig. 3: Sensitivity as a function of operating temperature for 5 wt.% CuO modified ZTO sensor

It is evident from the figure that the 5 wt. % of CuO modified ZTO sensor was highly selectivity to CO gas against ethanol, LPG and H_2S gases. As expected, the sensitivity increased with an increase in the operating temperature. For CO gas, the sensitivity increased and reached saturation values around 180^0C and sensitivity for other gases decreases.

Figure 4 shows the dependence of the sensitivity of 5 wt% CuO modified ZTO sensor on the concentration of CO gas. This sensor exhibits a good dependence on CO concentrations. An increase in the gas concentration raises the surface coverage eventually leading to a saturation level. It was found that the sensitivity for CO gas starts detecting at 200 ppm and further reaches to saturation level at around 600 ppm.

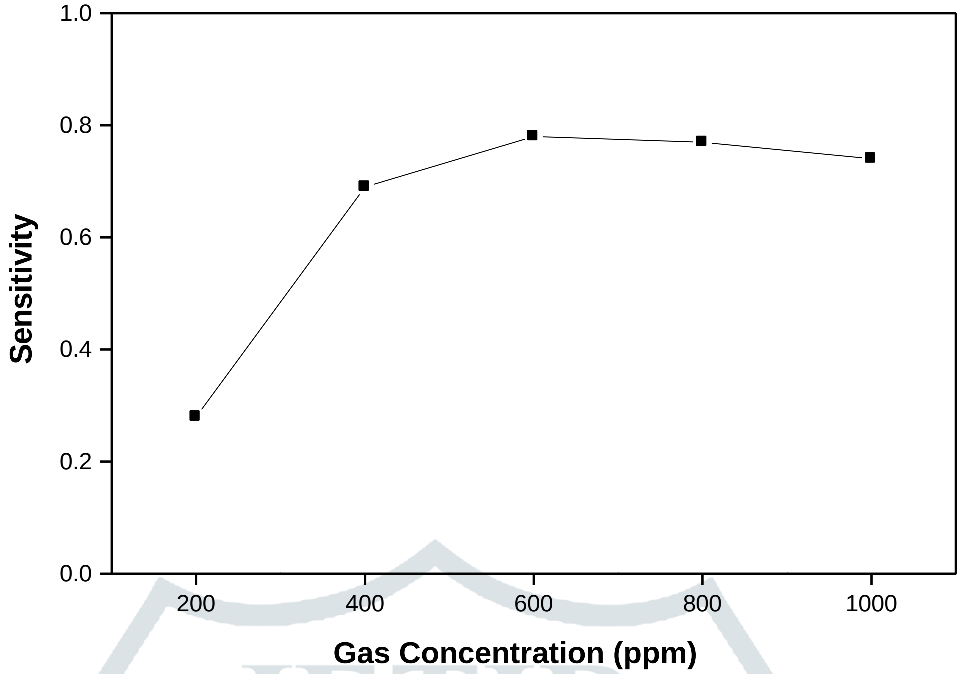

Fig. 4: Variation in response for 5 wt% CuO modified ZTO gas sensor as a function of gas concentration for CO in ppm.

4. CONCLUSION

In summary, (1) we synthesized nanocrystalline 5 wt % Cuo modified ZTO by a using sol-gel citrate method. (2) XRD pattern shows nanocrystalline with average particles size 35 nm. (3) The material was found to be good sensitive towards CO in comparison to other reducing gases.

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