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ELECTRICAL AND HYDROGEN GAS SENSING PROPERTIES OF ZnO-CuO COMPOSITES

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ABSTRACT

Composites of xZnO:CuO with $1 \leq x \leq 3$ composition ratio were fabricated in the form of pellets by sintering at 800°C. Their electrical conductivity and hydrogen gas sensitivity were examined between 100 and 500°C. Sample consisting of 1.5ZnO:CuO was found to have the highest sensitivity to both 5%H_2 and 200 ppm H_2. The sensitivity of the samples was found to decrease for the values of x greater than 2. The samples also shows higher sensitivity to 5%H_2 than 200 ppm H_2 above 250°C. The electrical conductivity of the composites varies with temperature and has a minimum values when the ZnO content is about 60-67 mole% for temperature above 350°C.

INTRODUCTION

Ceramic semiconductors have been used as gas sensors of flammable or toxic gases, such as H_2, CO and CH_4 [1]. Usually, single oxide-type semiconductors such as ZnO, CuO and SnO_2 have been widely used for detection of such gases in which their conductivities are known to varies with gas composition in the air atmosphere [2].

Gas sensor based on interface or p-n hetero-junction have also been reported to have good sensing properties, particularly in terms of selectivity property of those gases [3]. However, such interface has poor reliability due to its mechanical contact, because of the different of its surface structure. The gas sensing system uses mixtures of two or more oxide ceramic semiconductors also has been found to show good gas sensing properties [4]. Such composites may also be used to overcome the problem of mechanical contact of the hetero-junction based sensors. This paper reports a study on the electrical conductivity and the sensitivity of ZnO-CuO composites to 5%H_2:N_2 and 200 ppm H_2 from 100°C to 500°C.

EXPERIMENTAL PROCEDURE

Samples consisting of a mixture of ZnO (Aldrich, 99.99%) and CuO (Aldrich, 99.99%) powders, were prepared with the composition ratio of ZnO to CuO of 1, 1.5, 2, 2.45 and 3. Samples in the form of pellet were prepared by mechanical pressing and sintered at 800°C for 3h in air. The density of the sample was determined by Archimedes principles. The porosity of the sample was determined by the following equation,

$$\eta = [(\rho_t - \rho)/\rho_t] \times 100 \quad (1)$$

where ρ_t and ρ are the theoretical density and sintered density of the sample, respectively. The theoretical density of the sample was determined by,

$$\rho_t = (JMR) \times n)/(V_u \times N_A) \quad (2)$$

with *JMR* is the relative mass molecule, *n* is the atomic number per unit cell, V_u is the unit cell volume and N_A is the Avogadro number.

The structure of the sample was characterized by X-ray diffraction (XRD) (D8 Advance). For measurement of electrical properties, the surface of the sample was painted with Ag paste as the electrode and then sintered at 600°C for 30 minutes. The sample was then placed in a quartz tube (Thermolyne 21100) to measure the electrical conductivity and hydrogen gas sensing properties between 100 and 500°C. The values of resistance in air and in gas were measured using high-voltage sources and picoammeter (Keithley 2000). Gas sensitivity was determined by R_a/R_g, where R_a and R_g are the electrical resistance values in dry air and in sample gas, respectively.

RESULTS AND DISCUSSION

Fig 1. shows the powder X-ray diffraction patterns of the samples. All samples consist only a mixture of ZnO and CuO, there was no intermediate compound in the samples, although they were sintered at 800°C.

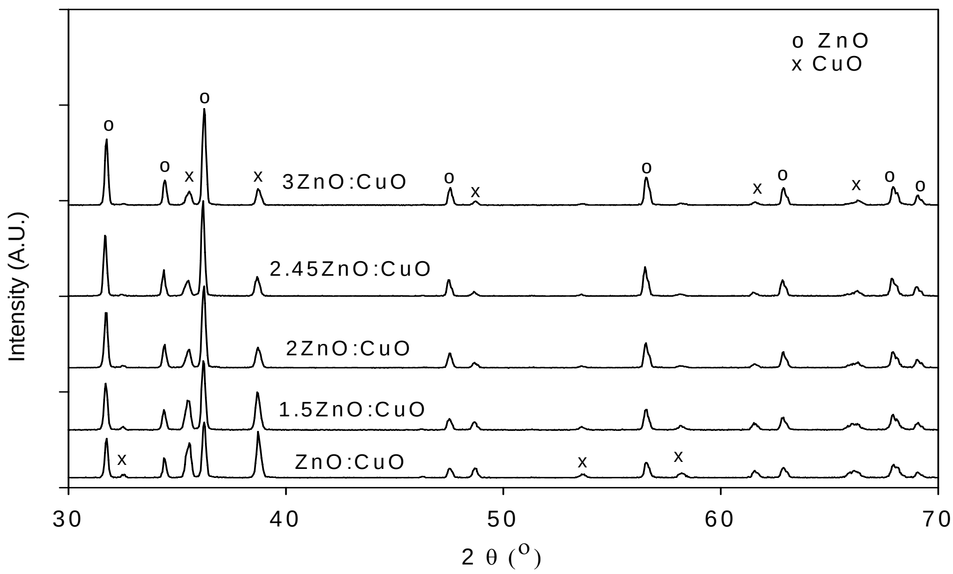

Fig.1. XRD patterns of ZnO-CuO composites sintered at 800°C for 3 h.

Table 1: The composition, sintered density (ρ), porosity (η) and surface area (A) of ZnO-CuO composites.

Samples	Composition		ρ (g cm^{-3})	η (%)	A (cm^2)
	ZnO (mole%)	CuO (mole%)			
ZnO:CuO	50	50	4.7476	22.70	1.0764
1.5ZnO:CuO	60	40	4.6295	23.46	1.1550
2ZnO:CuO	67	33	5.2533	12.25	1.0256
2.45ZnO:CuO	71	29	5.2138	12.31	1.0238
3ZnO:CuO	75	25	5.3873	8.82	1.0219

The density, porosity and sufface area of this samples are shown in Table 1. Sample consisting of 60 mole% ZnO has the lowest sintered density, highest porosity and high surface area. The porosity of the sample become smaller when the content of ZnO in the sample is more than 67 mole%.

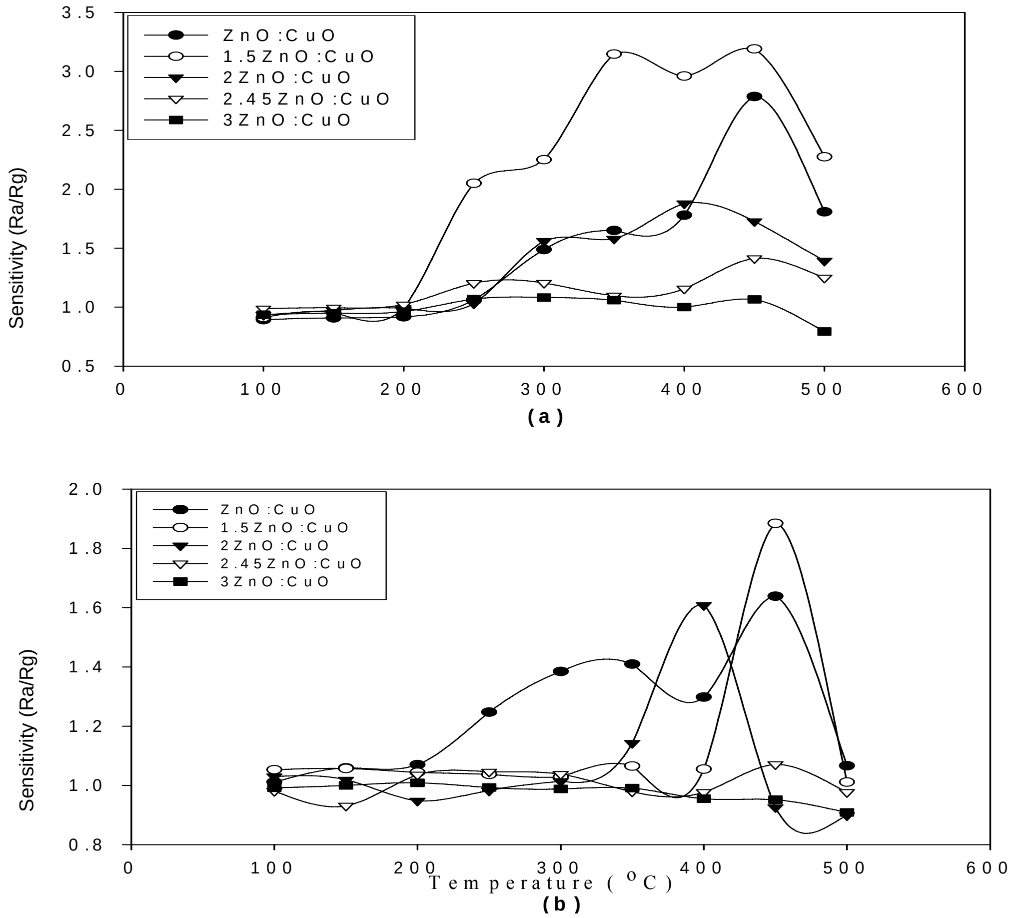

Fig.2. Temperature dependence of sensitivity of ZnO-CuO composites to: (a) 5%H_2:N_2 and (b) 200 ppm H_2.

Fig.2 shows the sensitivity of the samples to hydrogen gas (5%H_2:N_2 and 200 ppm H_2) as a function of temperature. All samples show non-linear sensitivity to temperature. Sample consisting of 1.5ZnO:CuO was found to have the highest sensitivity to 5%H_2:N_2 and 200 ppm H_2. This may be related to the feature that the sample has more porous microstructure than the other samples. For such a sample, gas is easier to diffuse in the sample causing the reaction of the gas and the surface of sample more efficient. It is believed that high sensitivity of the sample was also affected by the hetero-contact between ZnO and CuO as was reported in [5].

Fig.3 shows the comparison of sensitivity between ZnO:CuO and 1.5ZnO:CuO to hydrogen gas with different concentrations as a function of temperature. Both samples were found to have higher sensitivity to 5%H_2:N_2 compared with that of 200 ppm H_2. Higher gas concentration will result in increase of the sample sensitivity [7], thus the concentrations of 5%H_2:N_2 which is higher than 200 ppm H_2 gave higher sensitivity of the sample. This is believed to be related by the chemisorption process, upon increasing H_2 concentrations will lead to a charge carriers (e^-) released to the conduction band, and the resistance decreases.

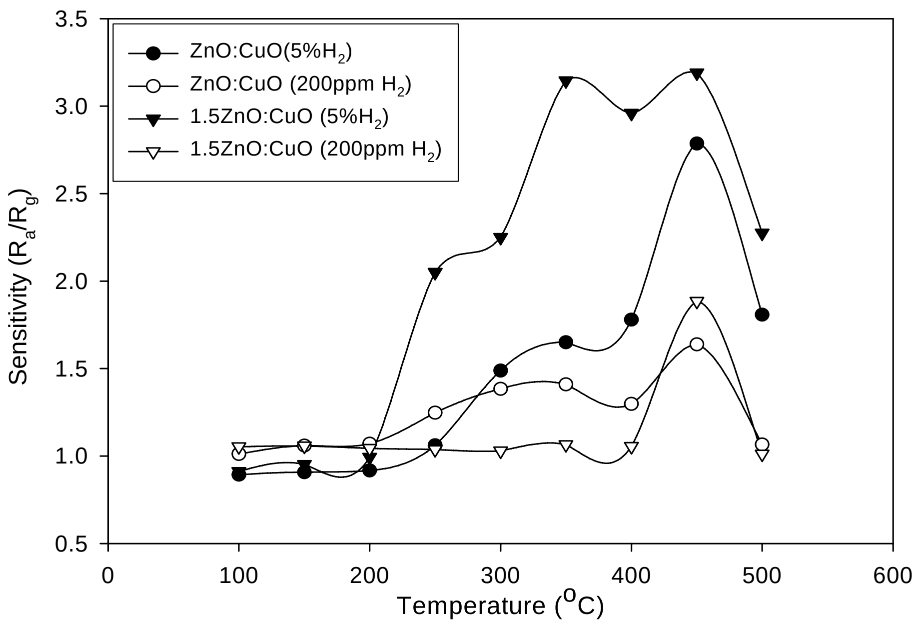

Fig.3. Comparison of sensitivity of ZnO:CuO and 1.5ZnO:CuO to 5%H_2:N_2 and 200 ppm H_2 as a function of temperature.

Fig.4 shows the electrical conductivity of the composite ZnO:CuO measured in air at 250, 350 and 450^{o}C as a function of ZnO content. The conductivity of the composite decreases with an increase addition of ZnO for temperature below 300^{o}C. The electrical conductivity continues to decrease for temperature above 300^{o}C with addition of ZnO up to about 67 mole%, but then increases when ZnO content is more than about 67 mole%. Changes in electrical conductivity might be caused by the reaction of the adsorbed oxygen ion on the sample surface, and also subsequent change in the charge carrier concentration near the surface as was reported in [7]. The valence state of the adsorbed oxygen ion is known to change with temperature.

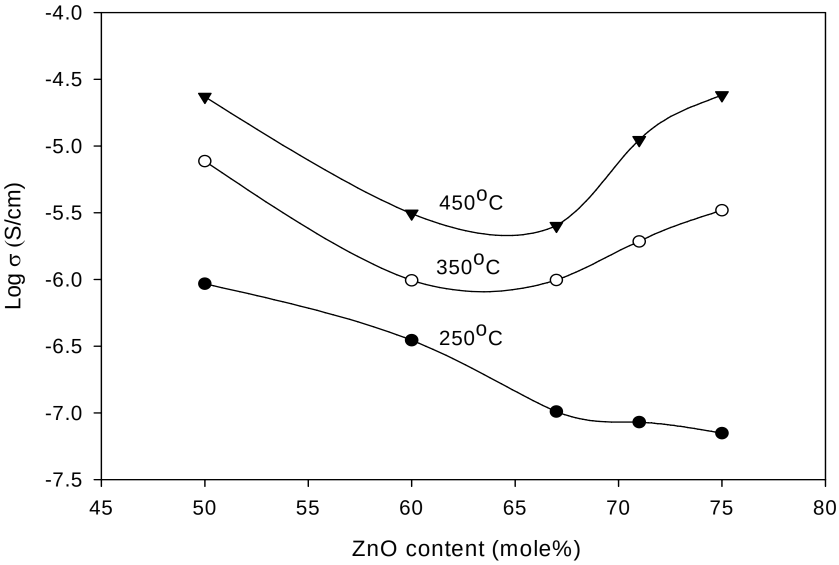

Fig.4. Electrical conductivity of ZnO-CuO composites in air as a function of ZnO content, measure at different temperatures.

It was also reported in [8] that the stable oxygen ion of O_2^- in air exist when temperatures is below 100°C, O^- is between 100 and 300°C and O^{-2} is above 300°C. A part from that, the increase and decrease of the electrical conductivity of ZnO-CuO may also be explained by the substitutional of Cu^+ in ZnO matrix. In general, sample consisting of 50 mole% ZnO exhibits the highest electrical conductivity at all temperatures studied.

CONCLUSIONS

The hydrogen gas sensing properties and electrical conductivity of xZnO:CuO composites with $1 \leq x \leq 3$ were investigated. All of ZnO-CuO composites studied show non-linear characteristics of sensitivity to H_2 gas between 100 and 500°C. The H_2 gas sensitivity of the composites depends on the amount of ZnO content in the samples. Sample consisting of 1.5ZnO:CuO was found to have the highest sensitivity to H_2 gas. The sensitivity of the samples was found to decreased when the composite has ZnO more than 60 mole%. The electrical conductivities of the composites increase with temperature, but decrease with increasing content of ZnO up to about 67 mole%.

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