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CO GAS SENSING PROPERTIES OF HETERO-JUNCTION CuO(*M*)/ZnO (*M*=Al, Pd) SENSOR

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ABSTRACT

Hetero-junction of *p*-type CuO and *n*-type ZnO semiconductors have been prepared by mechanically pressing pellets of the two oxides. The pellets were successfully fabricated by sintering at 800°C for 3 h in air. We have studied the effect of Al_2O_3 and $PdCl_2$ doping in CuO on the sensitivity of the CuO(*M*)/ZnO (*M*=Al, Pd) towards CO gas. The *I-V* characteristic and sensing properties are investigated for samples in 200-ppm CO, 200-ppm H_2 and air. The sample of containing 1-mol% $PdCl_2$ doped with CuO shows the highest sensitivity to the gas.

INTRODUCTION

Ceramics are favored for many sensors application because of their wide availability, low cost, and ease fabrication [1]. Some interesting about a gas sensor that is can demonstrate very high sensitivity, selectivity, response time, reproducibility and stability [2, 3]. The electrical properties of ceramics depend on composition, temperature, atmosphere, and microstructure [4, 5].

In recent years, many studies have been done to improve selectivity. Selection of sensor element can be improved using composites and doped catalysts. The semiconductor gas sensors based on CuO [6], ZnO [7, 8] have been reported to have good sensing properties of CO gas. However, the electrical characteristics of the composite are influenced by many factors, such as the volume fraction, grain size, and the geometric arrangement of each phase [9].

Some advantageous of hetero-contact have been produced, with high stability and increased sensitivity. Semiconductor gas sensors based on CuO/ZnO showed the selective detection of CO gas [10, 11]. In this work, the effects of Al and Pd doping in CuO on the sensitivity of the CuO(*M*)/ZnO (*M*=Al, Pd) towards CO gas are studied.

EXPERIMENTAL PROCEDURE

The sensing materials were prepared from pure CuO (Aldrich, 99.99%), ZnO (Aldrich, 99.99%), Al_2O_3 (Aldrich, 99.99%) and $PdCl_2$ (Aldrich, 99.99%) powder. The CuO powder was doped with 3-mol% Al_2O_3 and 1-mol% $PdCl_2$. The powders were then dry mixed by ball milling in ethanol for 12 h. The powders were calcined at a heating rate of $3^{o}C\ min^{-1}$ up to 800°C, where temperature was held constant for 3 h in air. Then the samples were cooled to room temperature.

The powders were pressed into pellets of about 13 mm in diameter and 5 mm in

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thickness by using hydraulic press at a pressure of 2 metric tons. The pellets were sintered at 800^{o}C for 3 h in air. The phase and microstructure were characterized by X-ray difractometry (Siemens, D500) and scanning electron microscopy (SEM, Philips XL 30), respectively.

For the measurement of *I-V* characteristic, both surfaces of the pellets were painted with platinum paste (Engelhard model #A4338). The samples were fired at 800^{o}C for 30 min. During I-V measurement, the temperature was kept between 100 to 400^{o}C with 50^{o}C step, constantly for 30 min. The H_2 and CO with a concentration of 200-ppm balance nitrogen in air was used as a test gas.

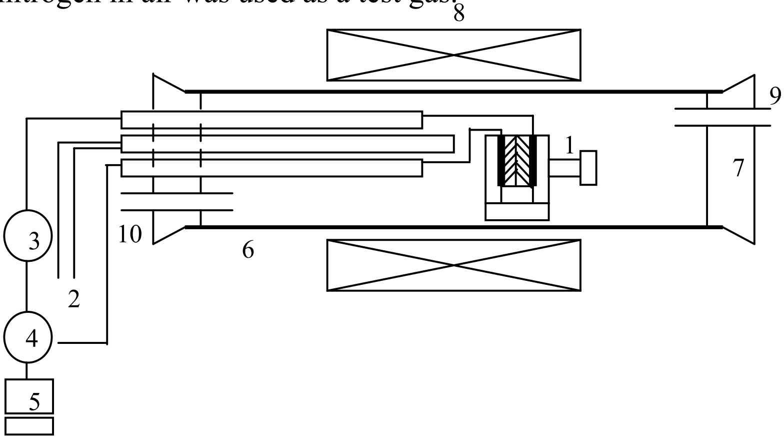

Figure 1: Schematic diagram of: the system for gas sensitivity measurements with the *p-n* hetero-junction gas sensor. 1 sample, 2 thermocouple, 3 DC generator, 4 voltmeter, 5 personal computer, 6 quartz tube, 7 rubber plug, 8 furnace, 9 inlet gas, and 10 outlet gas.

Figure 1 shows the apparatus used in this experiment [10]. Alumina blocks were positioned between specimens to insulate the specimens. The sample was placed in a tube furnace located inside of quartz tube. During constant direct current, the potential drop between two platinum wire and sample temperature was measured with thermocouple. A constant forward d. c. voltage (Good Will GPC 3030D) was applied to the sample. The current after being exposed to the test gas mixture was measured using a digital multi-meter (Good Will GDM 8055). Output of multi-meter related to personal computer to record data. The ratio between the current exposed toward CO gas with the current exposed in air was considered as the sensitivity.

RESULTS AND DISCUSSION

Microstructure

Figure 2 shows powder X-ray diffraction (XRD) patterns of ZnO, CuO, $97CuO\text{-}3Al_2O_3$ and $99CuO\text{-}1PdCl_2$ samples, calcined at 800^{o}C for 3 h. Powder X-ray analysis of the sample showed single phase. The addition of Al_2O_3 and $PdCl_2$ into CuO by XRD experiment shows only CuO peaks. The absence of Al_2O_3 peaks in $97CuO\text{-}3Al_2O_3$ and

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$PdCl_2$ in 99CuO-1$PdCl_2$ samples may be due to the smaller X-ray scattering power of Al_2O_3, $PdCl_2$ than CuO [12]. As seen from Figure 2, there is no significant difference between these patterns except that the intensity of CuO as compared to 97CuO-3Al_2O_3 has a relatively low crystallinity [13].

The sample of 97CuO-3Al_2O_3 (Figure. 3) shows appreciable difference in microstructure from pure CuO. The grain sizes of the CuO and ZnO part of the hetero-contact specimen are ~1µm for CuO and ~0.5 µm for ZnO, respectively. The sample 97CuO-3Al_2O_3 side shows agglomerated particle. The addition of Al_2O_3 to pure CuO shows trend of more porous microstructure than pure CuO. The interface distance of sample are ~2 µm for 97CuO-3Al_2O_3 /ZnO and ~1□µm for CuO/ZnO, respectively. However, gas molecules can be easily transferred to the contact interface between 97CuO-3Al_2O_3 /ZnO than CuO/ZnO [14].

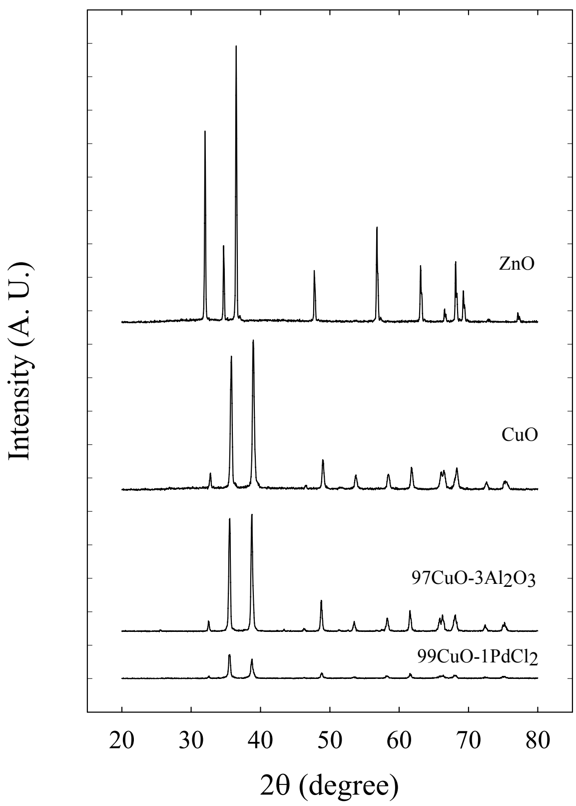

Figure 2: Powders XRD patterns of ZnO, CuO, 97CuO-3Al_2O_3 and 99CuO-1$PdCl_2$ samples calcined at 800^{o}C for 3 h.

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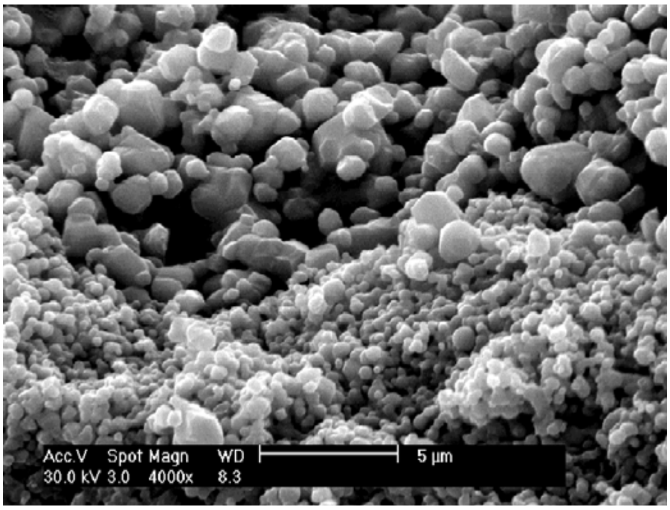
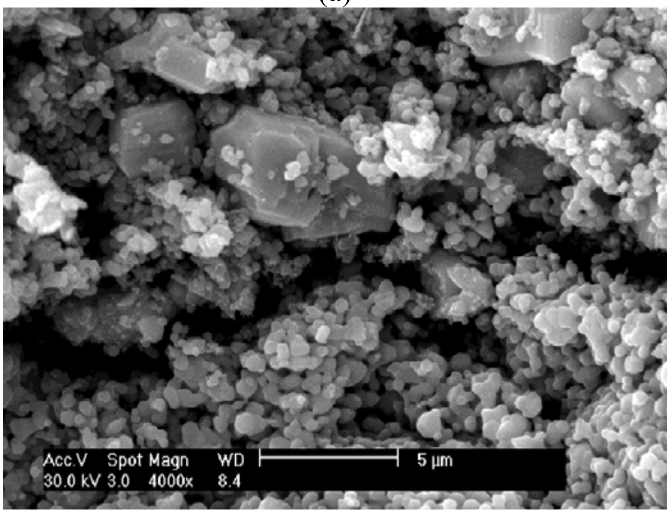


(a)



(b)

Figure 3: SEM micrographs of fractured surface (a) CuO/ZnO, and (b) 97CuO-$3Al_2O_3$/ZnO samples.

I-V Characteristic

I-V curves of all samples were linear in the temperature range of 100°C to 400°C. Current was measured while the bias voltage increased from -10 to 10V. Figure. 4(a) shows current curves of CuO/ZnO nearly overlapped both in CO and H_2 gas, however, current curve difference in air [15]. This indicates sensitivity in CO and H_2 but is not of selectivity in CO, H_2 and air. Figure. 4(b) and 4(c) shows current curves of 97CuO-$3Al_2O_3$/ZnO, 99CuO-$1PdCl_2$ respectively at -10 to 10 volt in CO, H_2 and air. This indicated 97CuO-$3Al_2O_3$/ZnO and 99CuO-$1PdCl_2$ 97C3A samples sensitivity in CO and H_2 gas as well as selective in CO, H_2 and air. This phenomenon was a defect reaction of CuO doped with 3-mol% Al_2O_3, 1-mol% $PdCl_2$ by the following equation respectively

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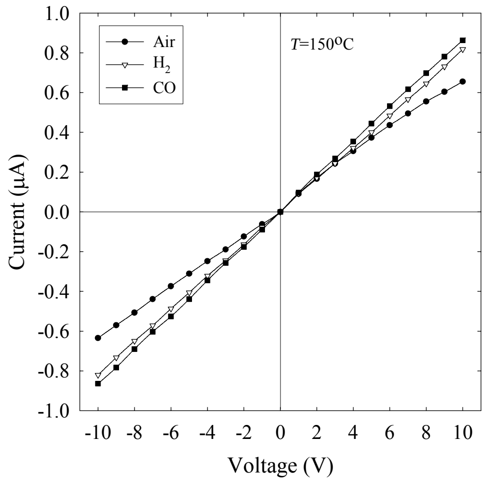
$$Al_2O_3 \rightarrow 2Al^{\cdot}_{Cu} + 2O_o + 1/2O_2 + 2e'$$

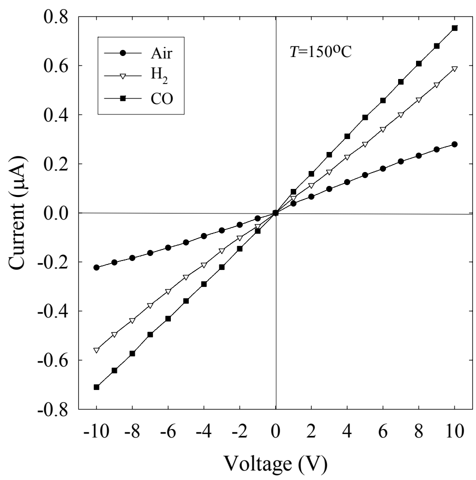
$$2PdCl_2 + \frac{3}{2}O_2 \rightarrow Pd_2O_3 + 2Cl_2$$

$$Pd_2O_3 \rightarrow 2Pd^{\bullet}{}_{Cu} + 2O_{\circ} + \frac{1}{2}O + 2e^{\bullet}$$

3-mol% Al_2O_3 and $PdCl_2$ in CuO will increase the electron concentration of CuO [16].



(a)



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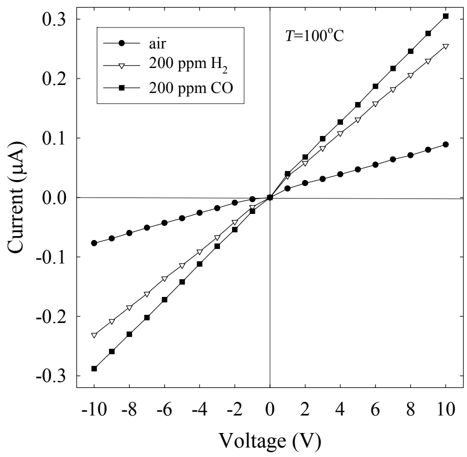

(c)

Figure 4: Atmosphere dependence of *I-V* characteristic for (a) CuO/ZnO, (b) 97CuO-3Al_2O_3/ZnO and (c) 99CuO-1$PdCl_2$ samples.

Sensitivity and response time

Figure 6 shows the selectivity to CO gas defined as the ratio of the CO gas sensitivity with the H_2 gas sensitivity. The CO selectivity exhibited the highest for sample 97CuO-3Al_2O_3/ZnO at about 150°C. Carrier density is influenced by temperature and atmosphere in a number of different defect regimes [16].

Figure 7 shows the effect of Al_2O_3 and $PdCl_2$ doping CuO on the response time of CuO(*M*)/ZnO (*M*=Al, Pd) towards CO gas. The addition of Al, Pd to CuO leads to an increase in response time on exposure to a reducing CO. Addition 3-mol% Al_2O_3 and 1mol% $PdCl_2$ in CuO is more effective to increase the electron concentration of CuO.

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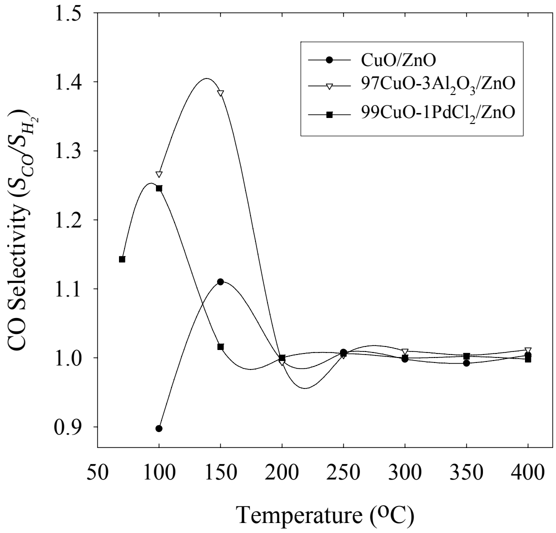
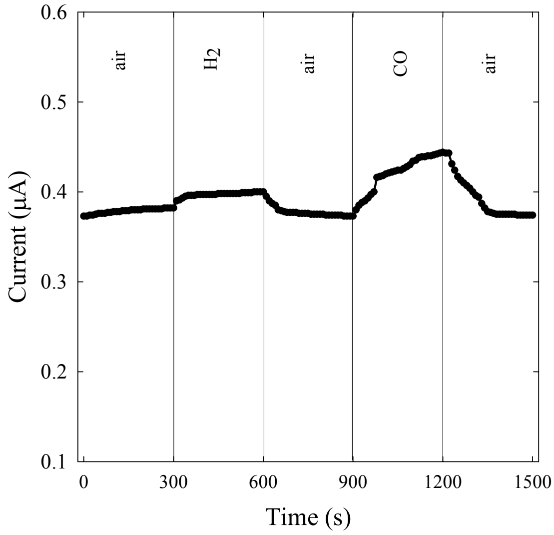


(a)



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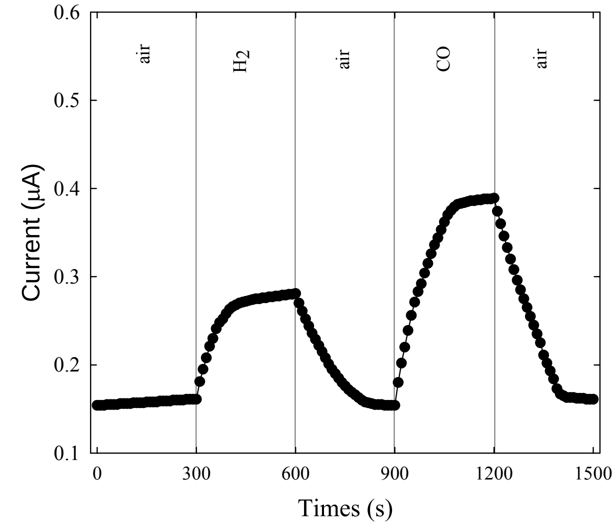

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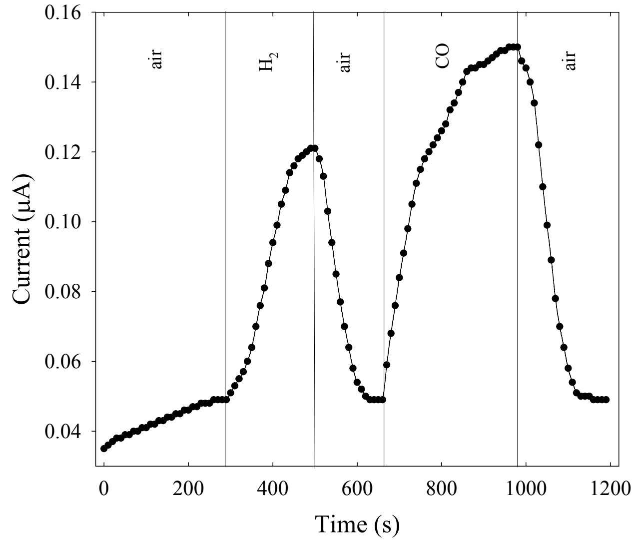

(d)

Figure 6: (a). The temperature dependence of the selectivity to 200-ppm CO gases, (b) response time on CO, H_2 and air exposure of CuO/ZnO (c) 97CuO-$3Al_2O_3$/ZnO (d) 99CuO-$1PdCl_2$ hetero-junction.

CONCLUSIONS

XRD results showed that adding 1-mol% $PdCl_2$ into CuO did not changethe peaks of pure CuO. Doping of Al_2O_3 to pure CuO shows more porous microstructure than that of pure CuO. Addition of Al_2O_3 in CuO is more effective to increase the change current of CuO.

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The sensitivity of hetero-junction sample of 99CuO-1$PdCl_2$ is higher than pure CuO/ZnO. Sensitivity and selectivity were influenced by doping. Sample 97CuO-3Al_2O_3/ZnO showed the best selectivity for CO, H_2, and air. The hetero-junction samples CuO(*M*)/ZnO (*M*=Al, Pd) enabled selective detection of CO gas for CuO/ZnO based on sensor.

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