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# Nano-crystalline Cu-doped ZnO thin film gas sensor for CO

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**Abstract**

A Cu-doped ZnO (CZO) film was prepared on a glass substrate by co-sputtering using ZnO and Cu targets. The CZO film possessed a columnar structure consisting of small crystals with an average grain size of around 5 nm. The CO-sensing properties of the CZO film were tested at operating temperatures of 150, 300, 350 and 400 °C. It was found that CZO-based sensor exhibited the highest sensitivity to CO at 350 °C. An obvious change in resistance of the CZO film was also observed when the sensor was exposed to 6 ppm CO at 150 °C. The sensing mechanism of the nano-structured CZO sensor is discussed.


*Keywords:* Nano-crystalline Cu-doped ZnO; Gas sensor; CO

## 1. Introduction

Several semiconducting oxides such as $SnO_2$, ZnO, $In_2O_3$ and indium tin oxide (ITO) are employed as gas sensors, by utilizing the changes of the electrical conductivity of these materials upon exposing to target gases [1–5]. The utilization of ZnO in gas sensor applications has a long history. Systems composed mainly of ZnO were studied as chemoresistive materials to detect gases like $H_2$ [6], $NH_3$ [7], $CH_4$ [8], $O_2$ [9], seafood smell (TMA or trimethylamine) [10], ethanol [11] and CO [12]. It has been suggested that thin film ZnO gas sensors exhibit higher sensitivities compared to other forms of ZnO sensors [13].

Carbon monoxide (CO) is one of the most dangerous gases in air pollution and human life. CO is produced by incomplete combustion of fuels and commonly found in the emission of automobile exhausts, the burning of domestic fuels, etc. It is highly toxic and extremely dangerous because it is colorless and odorless. CO sensors are, therefore, required in various situations including the detection of smoldering fires. Nano-structured zinc oxide with diverse morphology of nano-wires, nano-rods and nano-belts has been extensively studied due to its unique physical properties such as wide band gap and large excitonic binding energy and electric conducting properties for applications in short-wavelength optoelectronic devices, solar cells, and sensors [13,14]. The recent demonstration of gas sensors based on nano-ZnO has further stimulated substantial efforts to explore ZnO nano-structures for high gas sensitivity. However, a nano-ZnO sensor prepared by an arc plasma method did not show an expected high sensitivity even when exposed to CO at a concentration as high as 5000 ppm [14]. Nakamura et al. [15] and Choi and Choi [12] reported a sensitivity towards a few hundreds ppm CO by utilizing CuO–ZnO hetero-contacts, but the grains were not nano-sized.

Among the various techniques, direct current and radio frequency (RF) magnetron techniques are widely used for preparing ZnO and other metal oxides. The sputtering techniques enable the fabrication of uniform ZnO films on various substrates for device applications. In this work, we use co-sputtering of Cu and ZnO to produce a Cu-doped ZnO (CZO) film and assess its potential for a highly sensitive CO gas sensor.

## 2. Experimental

The CZO thin film was deposited on a glass substrate with a dimension of 10 mm × 20 mm × 1.5 mm. A ZnO target (99.999% pure) and a Cu target (99.99% pure) were used for fabricating CZO thin films. The electric powers used were 5.0 W $cm^{-2}$ for ZnO and 1.5 W $cm^{-2}$ for Cu targets. Argon was employed as the operating gas, and a constant partial pressure

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of $5 \times 10^{-2}$ mbar was maintained during the film deposition. The CZO film was deposited at a constant substrate temperature of 150 °C. The film thickness was controlled by the deposition time (1 h in this work). X-ray diffraction (XRD), atomic resolution transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used to reveal the microstructure and surface morphology of the film. Energy dispersive spectroscopy (EDS) was used to measure the atomic ratio of Cu/Zn in the film. The film thickness was determined by stylus profiling. Then, two electrical contacts (gold) were deposited on the thin film by sputter coating for gas sensing test.

The gas-sensing test was performed in a static system, which was linked to a mechanical rotary pump capable of evacuating the test chamber down to $5 \times 10^{-2}$ mbar. Before the sample annealing and each sensing test, the chamber was evacuated and followed by Ar flushing for three times, and then filled with Ar to the atmosphere pressure. Prior to the sensing test, the sample was annealed sequentially at three temperatures of 150, 300 and 400 °C for 1 h in the test chamber. Several cycles of gas-sensing test were performed, with each cycle consisting of (1) injecting CO; (2) retaining CO gas pressure within the chamber; and (3) purging the chamber with Ar. The amount of $O_2$ in the test chamber was estimated to be up to 500 ppm, by taking into account the stabilized chamber pressure (1 mbar) after closing all the valves, and the $O_2$ concentration (20%) in atmosphere. Commercially diluted CO (5000 ppm in Ar) was injected into the test chamber with a syringe. A heating stage was situated at the center of the chamber and a K-type thermocouple was mounted near the sample to monitor the temperature. Fluctuation of the sample temperature was minimized by an ÜGU AI-700 temperature controller, and the temperature could be controlled with an error less than ±2 °C.

The gas response $S$ of the sample was defined by

$$S = \frac{R_v}{R_g}, \quad (1)$$

where $R_g$ and $R_v$ were the film resistance in the presence and the absence of the testing gas, respectively. Prior to the gas-sensing test, the sample resistance was stabilized at each operating temperature for about 30 min. The data acquisition was achieved by a personal computer (PC) system, which was connected to the multimeter. The home-developed software provided easy data acquisition and storage of the experimental results and testing parameters.

## 3. Results and discussion

The film thickness obtained in this work was about 260 nm. The atomic ratio of Cu/Zn was 0.38. XRD revealed a dominant (0 0 2) peak and weaker (1 0 0), (1 0 1), (1 1 0), (1 0 3) and (0 0 4) peaks of ZnO (see Fig. 1), suggesting that the crystalline particles were basically ZnO. There are no clear peaks of Cu, $Cu_2O$ and CuO in the XRD pattern, but the Cu (1 1 1) and $Cu_2O$ (1 1 1) humps can be identified, indicating the existence a small amount of Cu and $Cu_2O$ in the film. A SEM micrograph of the cross-section revealed that the film had a columnar structure. The width of a column was about 50 nm as shown in Fig. 2. The columnar structure consisted of small crystals. From the TEM image (Fig. 3), the crystalline grains of around 5 nm as well as nano-sized amorphous regions were observed, demonstrating that the film was nano-structured. An AFM image (Fig. 4) further shows the film topography, revealing a surface roughness of less than 5 nm.

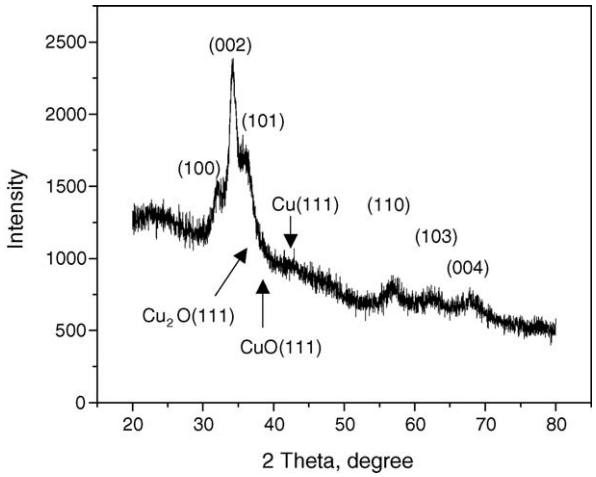


Fig. 1. XRD pattern of the annealed CZO film. All the peaks can be assigned to ZnO. The peaks of Cu, $Cu_2O$ and CuO are also indicated for reference.

Electrical resistance was tested at different CO concentrations and found to be obviously changed upon exposure to CO of as low as 6 ppm at a low operating temperature of 150 °C, as shown in Fig. 5. At a higher operating temperature in the range of 300–400 °C, the gas response much increased. Fig. 6 shows an example of the response transient of the film at 350 °C. It was found that the injection of 40 ppm CO induced a remarkable decrease in electrical resistance of the film, leading to response magnitude of 3. It is also noted from this figure that the signal could return to its initial value after several cycles. This indicates that the adsorption of CO on the film surface was reversible. The CO adsorbed on the surface was surely desorbed when CO gas was pumped out. The sensing properties of the

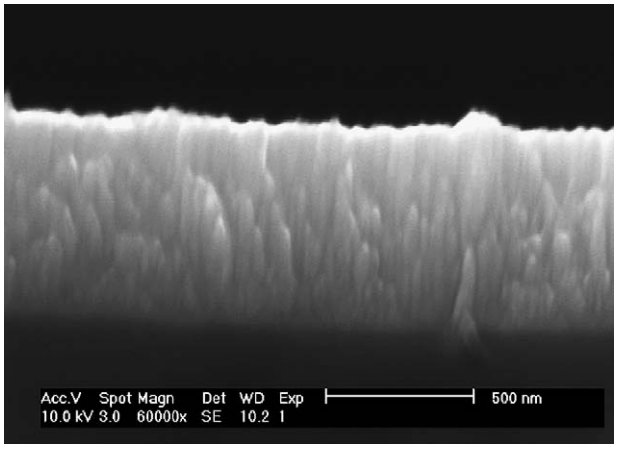


Fig. 2. A cross-sectional SEM micrograph of the annealed CZO film on a glass substrate.