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CuO-plate decorated ZnO nanostructures and their sensing performances

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***Abstract* — In this paper, we report on the gas sensing properties of mixed oxide Zn-Cu nanostructures obtained by self-organized chemical deposition are presented. The nanosensors are made from individual ZnO whiskers and are coated with CuO/Cu_2O. They exhibit selectivity towards H_2 and NH_3 over other tested gases. Measurements were made in the temperature range between 20 - 175 °C. In order to determine the crystalline phases of the studied nanostructures, XRD diffractogram was measured, and SEM images were obtained for the morphological analysis.**

Keywords* — *gas sensor, mixed oxides, nanostructures.

I. Introduction

In recent years, the concerns about environmental pollution, medical applications as well as the need for industrial safety have increased and made it necessary to continuously monitor the level of air pollution. The use of vapor or gas sensors for detection of small quantities of hazardous substances becomes important for various aspects of modern daily life. The main task of the gas sensors is to quickly and stably indicate the presence of harmful or explosive gases to create a warning that could save lives and ensure safety.

With the intensive development of nanotechnologies, the metal-oxide semiconductor sensor becomes a very versatile and easy to manufacturing study object of research. Especially, copper oxides and zinc oxides have been abundantly studied due to their applications in catalysis, gas sensors, biosensors, batteries, solar energy conversion, temperature superconductors, etc. [1], [2]. Ammonia (NH_3) gas detection by such nanomaterials is in researchers attention, since NH_3 is a common reagent produced and used in various domains. [4]. Recently, around 20% of NH_3 has been produced for pharmaceuticals, cleaning products, explosives, and refrigeration by the Haber-Bosch process which employs the reaction between H_2 and N_2 with an Fe-based catalyst under temperatures of ~500°C [5] That's why it is important to develop sensors based on metal oxides to detect both gases, like H_2 and NH_3.

In this work we report on Zn-Cu nanostructures for integration in nanosensors for H_2 and NH_3.

II. Experimental

Synthesis of ZnO, CuO, CuO/Cu_2O and Characterization

Zinc oxide whiskers were produces as tetrapodal particles first via the flame transport synthesis. The ZnO powder was treated for one hour in a 0.1 mM solution of $CuSO_4$. Platelets of copper oxide grew in a self-organized manner with shorter reaction time leading to smaller plates. Scanning electron microscopy (SEM) was performed before and after a heat treatment of the samples at 650 °C.

III. Results

Morphological characterization

Figure 1 and 2 show the SEM images of the CuO-platelet-coated ZnO, before (Fig. 1) and after (Fig. 2) the heat treatment. The coated nanowire was contacted to two gold plates serving as conductors. The connection between the nanowire and the conductor plates was done with platinum in a focus ion beam (FIB) SEM dual set-up as reported before by Lupan et al. [6].

The inside of the quasy-1D heterostructure is made of single crystalline ZnO and it is coated with nanoplates of CuO and Cu_2O, thus increasing the surface of the wire which leads to increased sensitivity. Below we can see Figure 1, which represents the SEM image of the nanowire before thermal treatment [7].

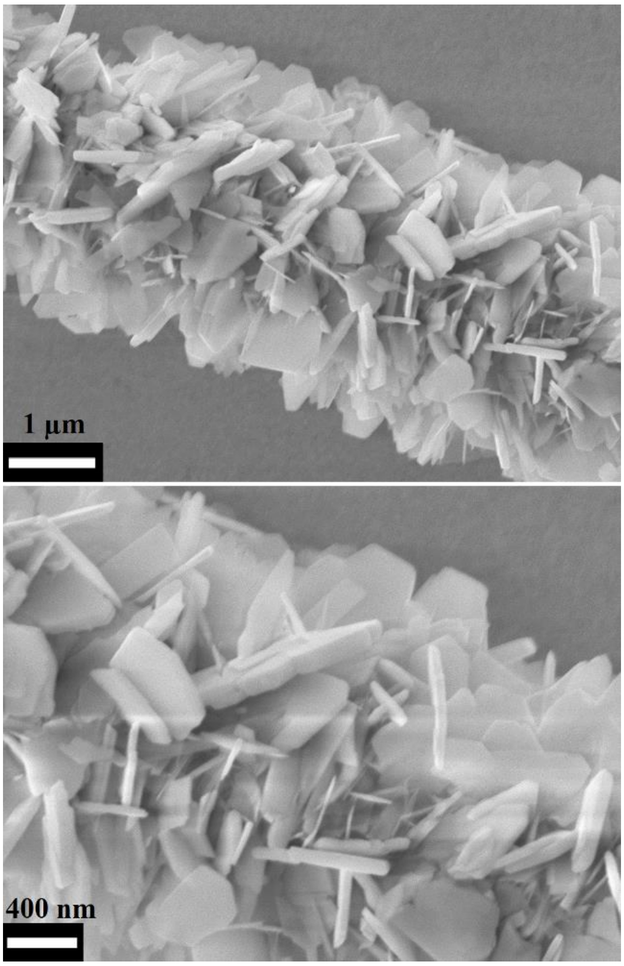

Figure 1. SEM image of ZnO, CuO and Cu_2O/CuO nanowire at the scale of (a) 1 µm and (b) 400 nm before heat treatment.

In order to determine the geometric configuration and the level of influence after the heat treatment on the nanowire, SEM images were taken (fig.2), from which the length of the nanowire was determined, being around 25 µm, the length between the Au contacts is around 14.5 µm. The diameter of the nanowire is around 1.8 µm. From Figure 2d, CuO/Cu_2O nanostructures with a granular surface can be observed, this is due to the heat treatment, thus increasing the porosity in turn and the surface/volume ratio [8]. Such a morphology is beneficial for sensor devices. Since XRD has been performed after the heat treatment, it is likely that the platelets themselves consisted of CuOH and the heat treatment led to an oxidation and additional shrinkage of the material. Thus, it became porous.

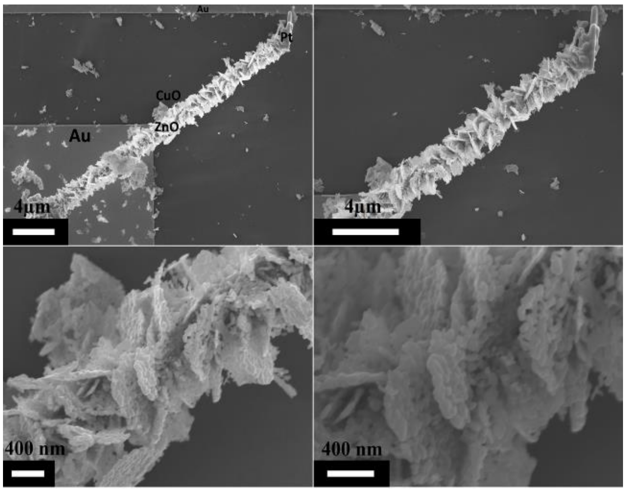

Figure 2. SEM image of ZnO, CuO and Cu_2O/CuO nanowire at the scale of (a, b) 4µm and (c, d) 400 nm after heat treatment at 650 °C.

The samples were studied in the measurement range of 2θ values 10-130°, with the scan step 0.01°. Figure 3 shows the XRD diffractogram for the ZC sample (ZnO mixed with CuO) in the range 30-80°, where the XRD peaks for ZnO, CuO and Cu_2O are observed. The peaks of zinc oxide are of higher intensity than those of copper oxide. The maximum intensity was observed at the (101) peak of zinc oxide, for CuO at the (111) peak, and for Cu_2O at (220).

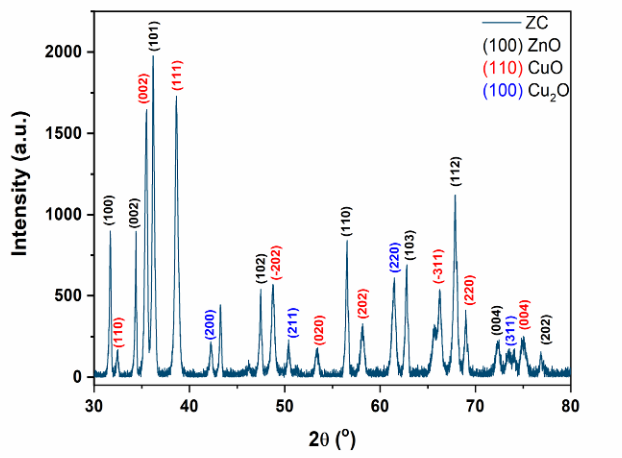

Figure 3. XRD diffractogram in the range 30-80°.

Sensing properties

Gas response is the rate at which the sensor's resistance changes when gas is applied [9]. This is a very important factor, the high sensitivity value for a particular gas indicates that this sensor is quite good for detecting that gas. It is determined by the formula:

$$S = \frac{I_{air}}{I_{gas}} \tag{1}$$

Where S is the response, I_{air} the value of the current when exposed to air and I_{gas} the value of the current when exposed to gas [10].

Figure 4 shows the dynamic response of mixed nanostructures of Zn and Cu to H_2 with a concentration of 100 ppm at an operating temperature of 125 °C and 150 °C, thus the maximum response value S = 4 was obtained at pulse 1 for 125°C. The response time i.e. the time interval in which the increase of the value from 10% to 90% takes place is approximately 0.88 s, and the recovery time i.e. the time interval in which the decrease of the value occurs from 90% to 10% is approximately 19.67 s. A voltage of 200 mV was applied for 20 seconds after which the gas is applied for the next 30 seconds during this time the increase in current can be observed. When the gas is disconnected, the current gradually returns to the initial value. To obtain more pulses the procedure was repeated.

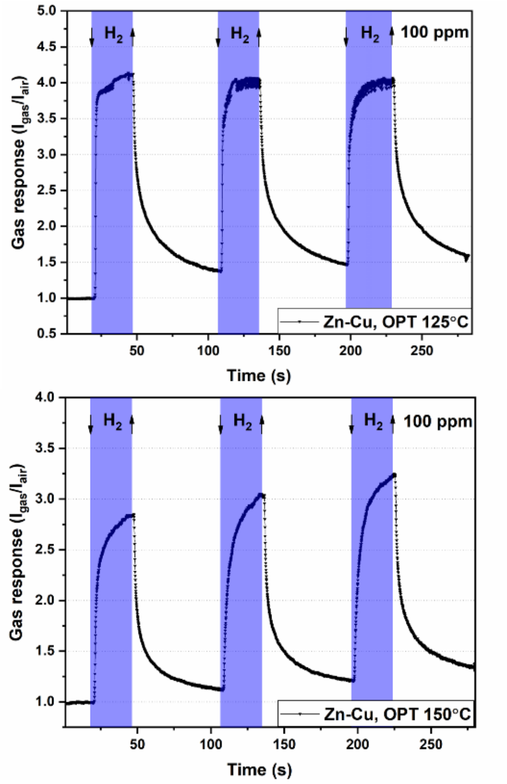

Figure 4. Dynamic response to 100 ppm H_2 at 125 °C and 150 °C working temperature of Zn-Cu nanostructures.

Figure 5 shows the dynamic response of the studied nanostructures to NH_3 with a concentration of 100 ppm at an operating temperature of 175 °C and the maximum response value S = 1.6 was obtained at pulse 2. The response time means the time interval in which it occurs the increase of the value from 10% to 90% is about 12.38 sec, and the recovery time, i.e. the time interval in which the decrease of the value from 90% to 10% takes place, is about 57.64 sec. A voltage of 50mV was applied for 20 seconds after which the gas is applied for the next 30 seconds during this time interval, as in the previous case the increase in current can be observed. When the gas is disconnected, the current gradually returns to the initial value. To obtain more pulses the procedure was repeated.

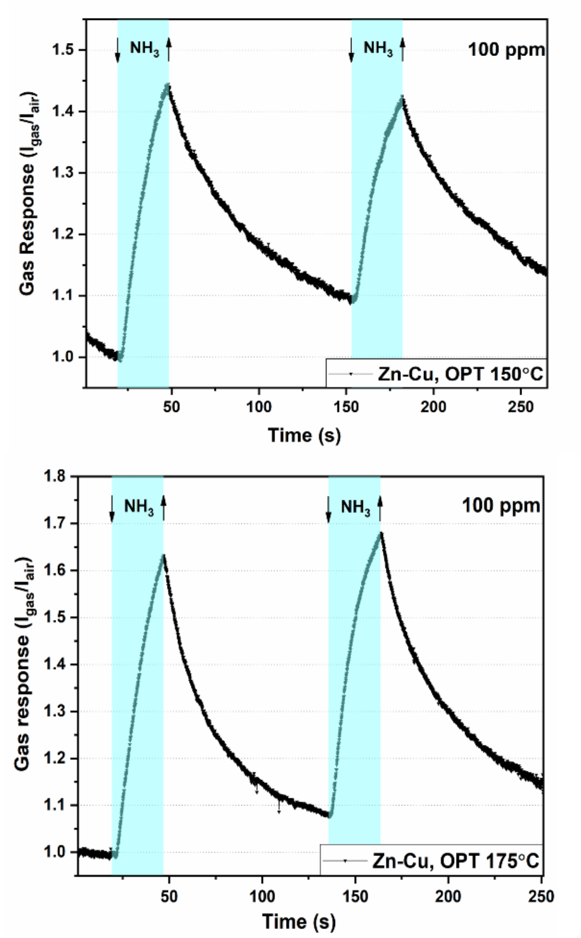

Figure 5. Dynamic response to 100 ppm NH_3 at 150 °C and 175 °C working temperature of Zn-Cu nanostructures.

Figure 6 represents the response to the investigated gases (Hydrogen, Ethanol, Methane, n-Butanol, 2-Propanol, Acetone and Ammonia) with a concentration of 100 ppm depending on the operating temperature where it is observed that the maximum response is S = 6, at operating temperature 100°C for hydrogen, which demonstrates high selectivity.

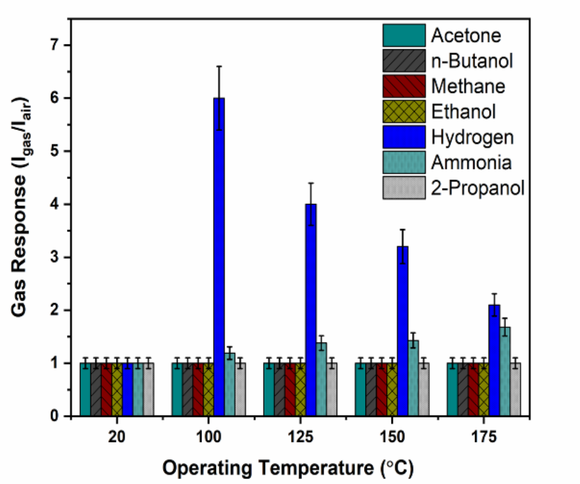

Figure 6. The response to the investigated gases (Hydrogen, Ethanol, Methane, n-Butanol, 2-Propanol, Acetone and Ammonia) at the operating temperatures of 20 °C, 100 °C, 125 °C, 150 °C and 175 °C for the investigated Zn-Cu nanostructures.

IV. Conclusions

This paper presents the data obtained experimentally following the research of the morphological, structural, sensory properties of mixed Zn-Cu oxides [11]. A hydrogen and ammonia response value of 100 ppm concentration was observed, having an operating temperature between 100°C - 175°C and a high selectivity generating response to H_2 and NH_3. Another property of the sensor investigated was the response and recovery times, a more impressive result was obtained for hydrogen gas. In some areas gas detection time plays a significant role, especially for highly flammable gases such as hydrogen [12]. From the X-ray diffractograms, XRD peaks were observed in the range 30-80° for ZnO, CuO and Cu_2O, with the maximum intensity at the (101) peak of zinc oxide, for CuO at the (111) peak, and for Cu_2O at (220).

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