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Al_2O_3/CuO non-planar heterostructures for VOCs vapors detection

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***Abstract*—In this work, the gas sensing properties of the non-planar heterostructures based on CuO thin films, grown by the direct ink writing and covered with an ultra-thin Al_2O_3 layer, are presented as a function of the operating temperature. The obtained results demonstrates the excellent selectivity to volatile organic compounds (VOCs) vapors, namely n-butanol and 2-propanol in a operating temperature range of 200 – 350 ºC. The relatively low gas response was observed at room temperature, which is very important for low-power operation. The dynamic gas response showed an ultra-fast response time of 2 – 3 s. The obtained results demonstrates the excellent potential of non-planar heterostructures based on metal oxides for use in high-performance environmental monitoring applications.**

Keywords*—heterostructures; gas sensor; volatile organic compounds; metal oxide

I. Introduction

The gas sensors based on metal oxides can become the key elements in real-time and wireless monitoring of gases and VOCs levels in environment [1,2]. Metal oxide nano- and microstructures demonstrated a high sensitivity and selectivity to a wide range of reducing and oxidizing gases [1,3]. The combination of different *n*-type and *p*-type metal oxides in form of non-planar heterostructures opened new possibilities to design high-performance gas sensors due to the induced new synergic effects [4,5,6]. Another interesting effect that can be induced is the immunity of the parameters to the water vapors, which is critical for practical outdoor applications of real-time monitoring [7]. However, because there is a possibility to combine the metal oxides in different ways and by different principles, as example by type of conductivity (*n-n*, *n-p* and *p-p*), a lot of investigation in this domain still need to be performed.

In this context, the non-planar heterostructures of metal oxides presents the high interest due to the high-surface area and unique interface properties that can be activated [3,8]. However, in this case there are some critical parameters, that can change radically the gas sensing properties. Recent investigations showed the importance of the top layer thickness in order to involve the heterostructure interface in gas sensing mechanism and in this way to achieve the higher performances [9,10]. In the case of interesting non-planar CuO:Zn/Cu_2O:Zn heterojunctions, where the top CuO:Zn layer was grown by rapid thermal annealing with different thicknesses (~ 24 and ~ 410 nm), it was demonstrated that the thickness of top layer comparable with the hall accumulation layer (HAL) is more preferable for gas sensing due to the involved interface which can enrich and enlarge the HAL [9]. As result, the modulation of HAL under adsorption/desorption of gas molecules is more efficient and the gas response is higher [11,12]. The same effect was also observed in the case of core-shell structures of ZnO-SnO_2 nanowires, where the optimal thickness of top layer was found to be about 40 nm in order to efficiently detect the reducing gases [13].

Using this strategy, the high gas sensitivity to reducing or oxidizing gases can be tuned by modulation of HAL in core material by formation of heterostructures using metal oxides with lower or higher work function [14]. As core material, the p-type CuO is very attractive sensing material with high oxygen adsorption and high reactivity to reducing gases due to the low stability associated with redox reactions promoted by variable oxidation states [15]. On the other hand, the *p*-type materials are less studied as gas sensing materials, compared to *n*-type materials, despite the fact that chemical or electronic sensitization can be performed in the same way [15]. For example, Lupan *et al.* reported on highly sensitive and selective hydrogen gas sensors based on CuO and CuO/Cu_2O columnar films electronically sensitized by

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controlled doping with Zn in the same process of growth [9].

In this work, the CuO thin films were grown using three-dimensional (3-D) printing by direct ink writing metal microparticle stripes of commercially available pure copper particles and further thermal annealing. The top ultra-thin layer of Al_2O_3 was deposited using atomic layer deposition (ALD). The obtained results show the high efficiency of heterostructures formation to obtain high-performance gas sensors to VOCs vapors (n-butanol and 2-propanol), even at room temperature. The further optimization of technological parameters can be performed to extend the domain of applications.

II. Experimental Part

Copper oxide films were prepared using direct ink writing with copper microparticles (diameter of 15 – 25 µm), purchased from Sigma Aldrich [3]. The ink composition is formed from copper microparticles, ethanol (96%) and polyvinylbutyral (PVB) in a mixing ratio of 1:3:1 by weight, respectively. More details on printing with such type of ink are presented in previous work [3]. The printed material was annealed at 425 ºC in air for 30 min with a a heating rate of 40 ºC s^{-1}, which can result in growth of nanowire and nanospikes on the surface of oxidized microparticles, which forms the highly porous networks [3]. This can lead to large surface-to-volume ration and a fast diffusion of gaseous species and therefore to a fast response and recovery of the signal, demonstrated in this work.

The Al_2O_3 ultra-thin layer was deposited using thermal ALD method using Picosun's R200 with the deposition temperature during the process adjusted to 75 ºC [7]. More details are presented in previous work [7]. The thickness of Al_2O_3 layer in this study is about 6 nm.

The gas sensing properties were evaluated according to procedure described previously [7]. As carrier gas the ambient air with relative humidity of 30 – 40% was used, which was introduced in sealed chamber with a flow of 500 sccm. The concentration of VOCs was calculated using the following relation [7]:

$$V_x = (Vol \cdot C \cdot M)/(22.4 \cdot d \cdot p) \cdot [(273 + T_r)/(273 + T_C)] \cdot 10^{-9} \quad (1)$$

where V_x is the volume of the injected volatile organic compound liquid; *Vol* is the chamber volume, where the gas sensor structures are measured; *C* is the required VOC concentration in ppm; *M* is the molar mass of the VOC; *d* is the density of VOC (g/cm^3); *p* the purity; T_r is the room temperature; and T_c is the chamber temperature. The gas response was calculated the following equation [7]:

$$S = \left[(R_{gas} - R_{air})/R_{air}\right] \cdot 100\% \quad (2)$$

where R_{air} and R_{gas} is the electrical resistances of the gas sensor structure under atmosphere tested gas, respectively. The operating temperature in test chamber was controlled using an standard industrial PID controller, connected to the resistive heater, while temperature was measured using a K-type thermocouple. The response and recovery times were calculated from dynamic response as the interval between 10% and 90% of the full response characteristic.

The gas sensing devices were fabricated by deposition of Au/Cr contacts on the surface of the sensing material, using a special designed mask. The resulted distance between contacts is 1 mm. As tested gases, the 2-propanol, n-butanol and ammonia with a concentration of 100 ppm were used.

III. Results and Discussions

Figure 1(a) shows the SEM image of copper oxide nanostructured film covered with ultra-thin Al_2O_3 films with thickness of ~ 6 nm. The grown films are composed of nanometric interconnected spherical grains forming a microporous structure and resulting in high surface-to-volume ratio. This allow a easy diffusion of gas molecules even to inner layers of sensing material and theoretically can results in higher gas response due to higher coverage with oxygen species [3]. The top Al_2O_3 layer is hard to observe with SEM due to ultra-thin thickness of ~ 6 nm, measured in previous work [7].

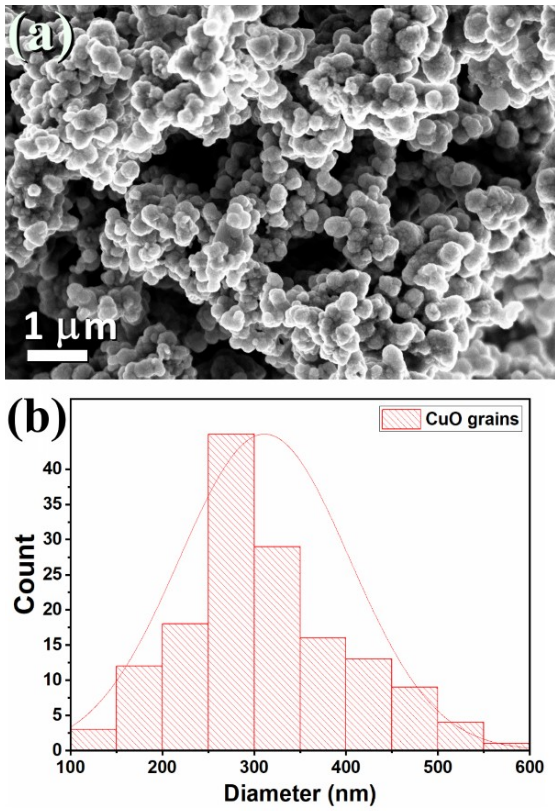

Figure 1. (a) SEM image of copper oxide nanostructured film covered with ultra-thin Al_2O_3 films. (b) The grain diameter distribution for CuO film.

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The distribution of grains diameter for copper oxide nanostructured film, measured directly from Figure 1(a), is presented in Figure 1(b), being an important parameter for gas sensors based on thin films. Theoretically and experimentally, it was demonstrated that smaller grain size can result in higher gas response due to increased surface activity and formation of more potential barriers [5]. In our case, the grain diameter of CuO nanostructured film varies mainly from 200 nm to 400 nm.

Figure 2(a) shows the measured and calculated gas response of Al_2O_3/CuO-3D non-planar heterostructure in a wide range of operating temperature, namely from room temperature (25 ºC) to 350 ºC. From 200 ºC to 350 ºC the temperature was increased with a step ot 50 ºC. It can be observed that in all cases the highest response was detected for VOCs vapors, namely n-butanol and 2-propanol. In order to check the repeatability of the sensor, several measurements were performed under the same condition. The error bars indicate on the deviation of the obtained results. The optimal operating temperature is 250 – 300 ºC, where the gas response to n-butanol and 2-propanol is ~ 60% and ~ 62%, respectively. The gas response at room temperature to 100 ppm of 2-propanol is ~ 4%. All tested sensor structures showed good repeatability and reproducibility. The measurements to hydrogen and methane gas showed no noticeable response, therefore were not included in this work and graph from Figure 2(a).

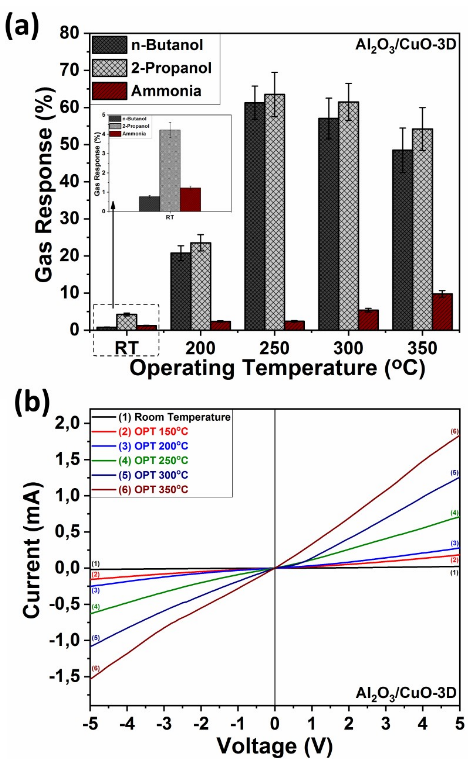

Figure 2. (a) Gas response of Al_2O_3/CuO-3D non-planar heterostructures to 100 ppm of ammonia, 2-propanol and n-butanol. (b) *I-V* characteristic of heterostructures at different oeprating temperatures.

Figure 2(b) shows the current – voltage (*I-V*) dependence of Al_2O_3/CuO-3D non-planar heterostructures at different operating temperatures (from room temperature to 350 ºC). At all tested temperatures, all gas sensor structures showed formation of quasi-ohmic contacts. Therefore, we can conclude that gas sensing properties originate mainly from the sensing layer, while the interface at the contacts have minimum influence. Also, the increase in temperature gives the rise in current, typically for metal oxides.

Figure 3(a) shows the dynamic response of gas sensor structure based on Al_2O_3/CuO-3D non-planar heterostructures to 100 ppm of 2-propanol vapors at room temperature. The gas response of ~ 4% is quickly increased in 5 s with no evident saturation. The recovery of signal after evacuation of vapors from test chamber is much slower and takes about 20 – 25 s. The possibility to detect VOCs at room temperature is very important for practical applications because will exclude the necessity to use the microheaters.

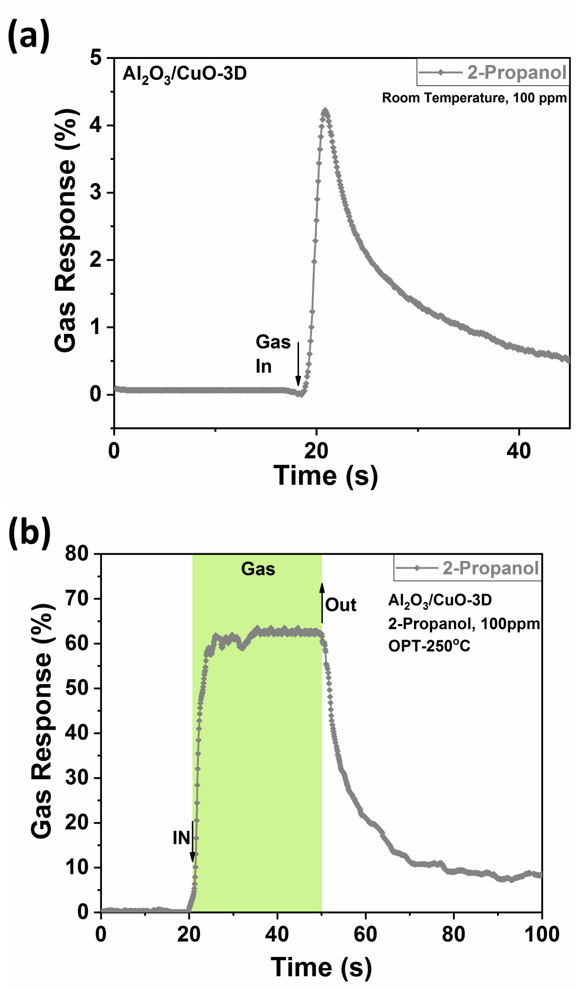

Figure 3. Dynamic gas response of Al_2O_3/CuO-3D non-planar heterostructures to 100 ppm of 2-propanol at: (a) room temperature; (b) 250 ºC.

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Figure 3(b) shows the dynamic response of the same gas sensor structure at operating temperature of 250 ºC, showing the fast saturation of signal after 3 – 5 s. The recovery of signal in this case takes about 30 s. The similar values were obtained for response to 100 ppm of n-butanol. Such fast response is critical in the case of fast leakage detections. However, in the case of outdoor or indoor VOCs level monitoring this is not the most important parameter.

The higher selectivity of CuO nanostructured films to VOCs vapors compared to other gases can be explained based on many other reported results, which frequently demonstrates selective detection of VOCs, especially ethanol vapors [15]. CuO is oxide of transition metal and exhibit various oxidation states because of the electrons in the d shell of the metal atom [15]. Such type of sensing material posses distinctive catalytic activities that promote the oxidation of VOCs, such as 2-propanol and n-butanol [15]. Moreover, previous gas sensing investigations of undoped CuO films grown using chemical solutions based approach at a relatively low temperature < 95 ºC and using the same 3-D printing based method showed the higher gas response to VOCs compared to such gases as H_2, CH_4 and CO [3,9,12]. Therefore, it can be concluded that Al_2O_3 ultra-thin layer have no important impact on selectivity ot the films

IV. Conclusions

In this work, the gas sensing properties of Al_2O_3/CuO-3D non-planar heterostructures to 100 ppm of 2-propanol, n-butanol and ammonia were investigated. The experimental results clearly demonstrate the advantage of the heterostructure formation on the surface of sensing materials in order to obtain high-performance gas sensors with very fast response (3 – 5 s), high gas response and possibility to detect at room temperature. The obtained parameters will allow in future to integrate such sensors in portable devices for VOCs environmental monitoring.

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