



# Al<sub>2</sub>O<sub>3</sub>/CuO non-planar heterostructures for VOCs vapors detection

Magariu Nicolae<sup>1</sup>, Ababii Nicolai<sup>1</sup>, Postica Vasile<sup>1</sup>, Mani Teja Bodduluri<sup>2</sup>, Lupan Oleg<sup>1,3</sup>, Rainer Adelung<sup>3</sup>, Sandra Hansen<sup>3</sup>

<sup>1</sup> Center for Nanotechnology and Nanosensors, Department of Microelectronics and Biomedical Engineering, Technical University of Moldova, 168 Stefan cel Mare str., MD-2004, Chisinau, Republic of Moldova, [oleg.lupan@mib.utm.md](mailto:oleg.lupan@mib.utm.md)

<sup>2</sup> Fraunhofer Institute for Silicon Technology (ISIT), Itzehoe, Germany, [mani.teja.bodduluri@isit.fraunhofer.de](mailto:mani.teja.bodduluri@isit.fraunhofer.de)

<sup>3</sup> Institute for Materials Science, Chair for Functional Nanomaterials, Faculty of Engineering, Kiel, Kaiserstraße 2, D-24143, Kiel, Germany, [ra@tf.uni-kiel.de](mailto:ra@tf.uni-kiel.de)

**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 ultrathin Al<sub>2</sub>O<sub>3</sub> 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 °C. 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<sub>2</sub>O: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<sub>2</sub> 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<sub>2</sub>O columnar films electronically sensitized by

<https://doi.org/10.52326/ic-ecco.2021/EL.03>



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<sub>2</sub>O<sub>3</sub> 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 °C in air for 30 min with a heating rate of 40 °C s<sup>-1</sup>, 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<sub>2</sub>O<sub>3</sub> ultra-thin layer was deposited using thermal ALD method using Picosun's R200 with the deposition temperature during the process adjusted to 75 °C [7]. More details are presented in previous work [7]. The thickness of Al<sub>2</sub>O<sub>3</sub> 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<sup>3</sup>);  $p$  the purity;  $T_r$  is the room temperature; and  $T_c$  is the chamber temperature. The gas response was calculated the following equation [7]:

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

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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> layer is hard to observe with SEM due to ultra-thin thickness of ~ 6 nm, measured in previous work [7].

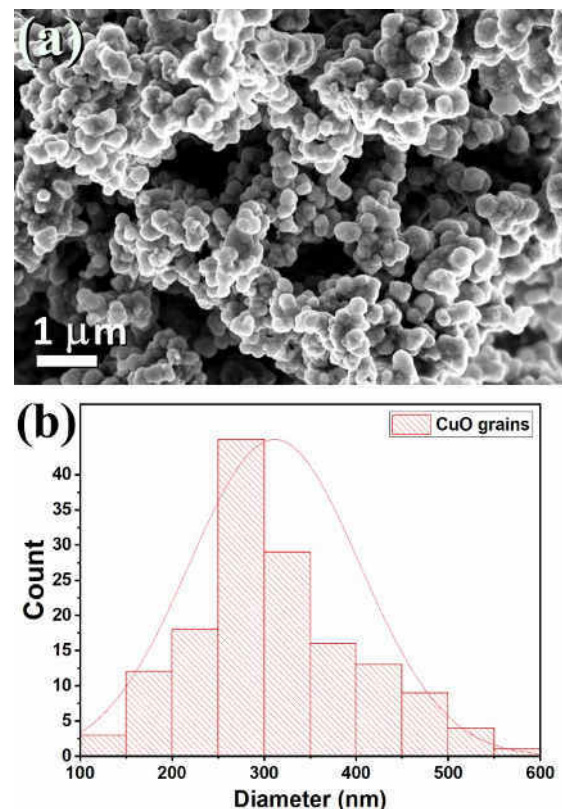


Figure 1. (a) SEM image of copper oxide nanostructured film covered with ultra-thin Al<sub>2</sub>O<sub>3</sub> films. (b) The grain diameter distribution for CuO film.

<https://doi.org/10.52326/ic-ecco.2021/EL.03>



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<sub>2</sub>O<sub>3</sub>/CuO-3D non-planar heterostructure in a wide range of operating temperature, namely from room temperature (25 °C) to 350 °C. From 200 °C to 350 °C the temperature was increased with a step of 50 °C. 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 °C, 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).

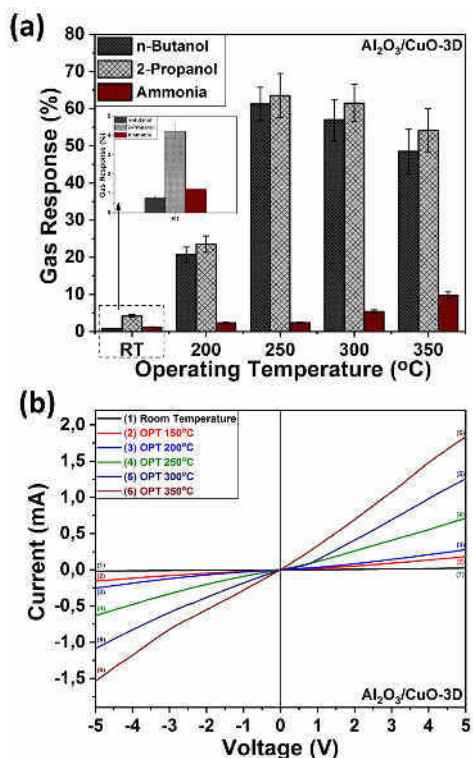


Figure 2. (a) Gas response of Al<sub>2</sub>O<sub>3</sub>/CuO-3D non-planar heterostructures to 100 ppm of ammonia, 2-propanol and n-butanol. (b) *I-V* characteristic of heterostructures at different operating

temperatures.

Figure 2(b) shows the current – voltage (*I-V*) dependence of Al<sub>2</sub>O<sub>3</sub>/CuO-3D non-planar heterostructures at different operating temperatures (from room temperature to 350 °C). 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<sub>2</sub>O<sub>3</sub>/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.

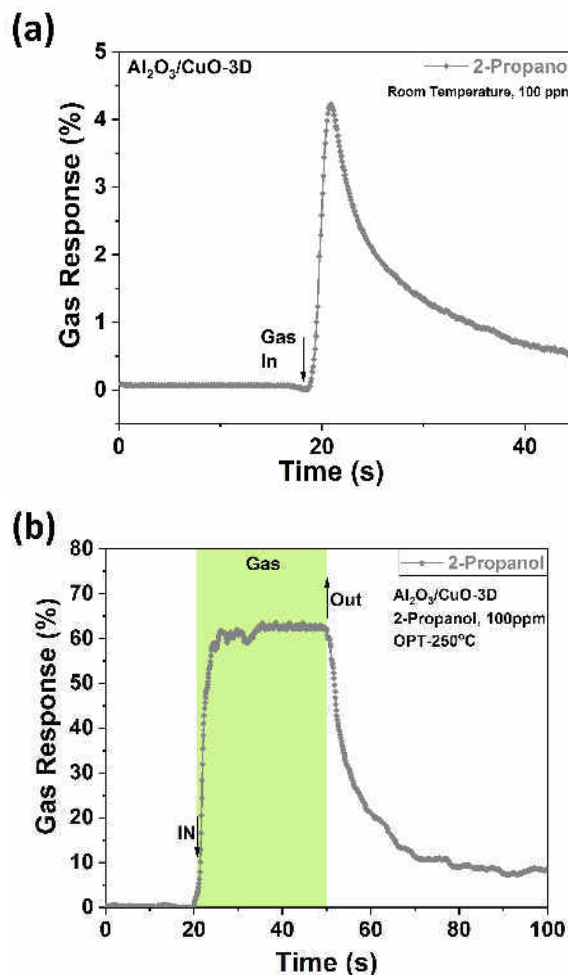


Figure 3. Dynamic gas response of Al<sub>2</sub>O<sub>3</sub>/CuO-3D non-planar heterostructures to 100 ppm of 2-propanol at: (a) room temperature; (b) 250 °C.

<https://doi.org/10.52326/ic-ecco.2021/EL.03>

Figure 3(b) shows the dynamic response of the same gas sensor structure at operating temperature of 250 °C, 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 °C and using the same 3-D printing based method showed the higher gas response to VOCs compared to such gases as H<sub>2</sub>, CH<sub>4</sub> and CO [3,9,12]. Therefore, it can be concluded that Al<sub>2</sub>O<sub>3</sub> ultra-thin layer have no important impact on selectivity of the films

#### IV. CONCLUSIONS

In this work, the gas sensing properties of Al<sub>2</sub>O<sub>3</sub>/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.

#### ACKNOWLEDGMENT

Federal Ministry of Education and Research by the project “PorSSi” (03XP0126 B) and the EKSH for supporting this research by “3D strukturierte Kohlenstoff-Schwefel Gerüstmaterialien als neuartiges und nachhaltiges Kathodenmaterial für Hochenergie Lithium-Ionen Akkus”. This research was partly supported by the Technical University of Moldova. Dr. Oleg Lupan acknowledges the Alexander von Humboldt Foundation for the research fellowship for experienced researchers (3-3MOL/1148833 STP) at the Institute for Materials Science, Kiel University, Germany. This research was sponsored in part by the NATO Science for Peace and Security Programme (SPS) under grant G5634, “Advanced Electro-Optical Chemical Sensors” AMOXES.

#### REFERENCES

- [1] G. F. Fine, L. M. Cavanagh, A. Afonjaand R. Binions. "Metal Oxide Semi-Conductor Gas Sensors in Environmental Monitoring," *Sensors*, vol 10, pp. 2010.
- [2] L. Spinelle, M. Gerboles, G. Kok, S. Persijnand T. Sauerwald. "Review of Portable and Low-Cost Sensors for the Ambient Air Monitoring of Benzene and Other Volatile Organic Compounds," *Sensors*, vol 17, pp. 2017.
- [3] L. Siebert, N. Wolff, N. Ababii, M.-I. Terasa, O. Lupan, A. Vahl, V. Duppel, H. Qiu, M. Tienken, M. Mirabelli, V. Sontea, F. Faupel, L. Kienleand R. Adelung. "Facile fabrication of semiconducting oxide nanostructures by direct ink writing of readily available metal microparticles and their application as low power acetone gas sensors," *Nano Energy*, vol 70, pp. 104420, 2020.
- [4] N. Ababii, M. Hoppe, S. Shree, A. Vahl, M. Ulfa, T. Pauporté, B. Viana, V. Cretu, N. Magariu, V. Postica, V. Sontea, M.-I. Terasa, O. Polonskyi, F. Faupel, R. Adelungand O. Lupan. "Effect of noble metal functionalization and film thickness on sensing properties of sprayed TiO<sub>2</sub> ultra-thin films," *Sens. Actuators A*, vol 293, pp. 242-258, 2019.
- [5] N. Barsan, D. Koziejand U. Weimar. "Metal oxide-based gas sensor research: How to?," *Sens. Actuators B*, vol 121, pp. 18-35, 2007.
- [6] O. Lupan, V. Postica, V. Cretu, N. Wolff, V. Duppel, L. Kienleand R. Adelung. "Single and networked CuO nanowires for highly sensitive p-type semiconductor gas sensor applications," *Phys. Status Solidi RRL*, vol 10, pp. 260-266, 2016.
- [7] O. Lupan, N. Ababii, A. K. Mishra, M. T. Bodduluri, N. Magariu, A. Vahl, H. Krüger, B. Wagner, F. Faupel, R. Adelung, N. H. de Leeuwand S. Hansen. "Heterostructure-based devices with enhanced humidity stability for H<sub>2</sub> gas sensing applications in breath tests and portable batteries," *Sens. Actuators A*, vol 329, pp. 112804, 2021.
- [8] D. R. Miller, S. A. Akbarand P. A. Morris. "Nanoscale metal oxide-based heterojunctions for gas sensing: A review," *Sens. Actuators B*, vol 204, pp. 250-272, 2014.
- [9] O. Lupan, V. Cretu, V. Postica, O. Polonskyi, N. Ababii, F. Schütt, V. Kaidas, F. Faupeland R. Adelung. "Non-planar nanoscale p-p heterojunctions formation in Zn<sub>x</sub>Cu<sub>1-x</sub>O<sub>y</sub> nanocrystals by mixed phases for enhanced sensors," *Sens. Actuators B*, vol 230, pp. 832-843, 2016.
- [10] V. Postica, O. Lupan, A. Gapeeva, L. Hansen, R. Khaledialidusti, A. K. Mishra, J. Drewes, H. Kersten, F. Faupel, R. Adelungand S. Hansen. "Improved Long-Term Stability and Reduced Humidity Effect in Gas Sensing: SiO<sub>2</sub> Ultra-Thin Layered ZnO Columnar Films," *Adv. Mater. Tech.*, vol 6, pp. 2001137, 2021.
- [11] V. Cretu, V. Postica, A. K. Mishra, M. Hoppe, I. Tiginyanu, Y. K. Mishra, L. Chow, N. H. de Leeuw, R. Adelungand O. Lupan. "Synthesis, characterization and DFT studies of zinc-doped copper oxide nanocrystals for gas sensing applications," *J. Mater. Chem. A*, vol 4, pp. 6527-6539, 2016.
- [12] O. Lupan, V. Cretu, V. Postica, N. Ababii, O. Polonskyi, V. Kaidas, F. Schütt, Y. K. Mishra, E. Monaico, I. Tiginyanu, V. Sontea, T. Strunskus, F. Faupeland R. Adelung. "Enhanced ethanol vapour sensing performances of copper oxide nanocrystals with mixed phases," *Sens. Actuators B*, vol 224, pp. 434-448, 2016.
- [13] J.-H. Kim, A. Mirzaei, H. W. Kimand S. S. Kim. "Variation of shell thickness in ZnO-SnO<sub>2</sub> core-shell nanowires for optimizing sensing behaviors to CO, C<sub>6</sub>H<sub>6</sub>, and C<sub>7</sub>H<sub>8</sub> gases," *Sens. Actuators B*, vol 302, pp. 127150, 2020.
- [14] S.-W. Choi, A. Katoch, J.-H. Kimand S. S. Kim. "Remarkable Improvement of Gas-Sensing Abilities in p-type Oxide Nanowires by Local Modification of the Hole-Accumulation Layer," *ACS Appl. Mater. Interfaces*, vol 7, pp. 647-652, 2015.
- [15] H.-J. Kimand J.-H. Lee. "Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview," *Sens. Actuators B*, vol 192, pp. 607-627, 2014.