SENSING STUDIES OF COPPER OXIDE-ZINC OXIDE HETEROJUNCTIONS TO VOLATILE ORGANIC COMPOUNDS

Tudor ZADOROJNEAC [1*],
Nicolai ABABII [1],
Nicolae MAGARIU [1]

[1] *Technical University of Moldova, Faculty of Computers, Informatics and Microelectronics, Department of Microelectronics and Biomedical Engineering, Center for Nanotechnology and Nanosensors, PhD School Computer Science, Electronics and Energy, Chisinau, Republic of Moldova*

* Corresponding author: Zadorojneac, Tudor, e-mail: zadorojneactudor@gmail.com

Abstract. *Detection and differentiation of volatile organic compounds (VOCs) is extremely important since presence of these gaseous pollutants in ambient air is harmful and poses a serious threat to human health even at small concentrations.*
In this paper, a simple and cost-effective method for synthesis of a nanostructured multilayer film of (CuO/Cu_2O)/ZnO:Fe is presented, which allows to form non-planar heterojunctions for efficient vapor detection of volatile organic compounds.

Keywords: *heterostructures, morphology, sensor, selectivity, sensitivity, VOCs*

Introduction

At the moment, there is a great interest for the research of volatile organic compounds sensors based on semiconductor oxides with improved and unique properties. In this context, the combination of two different materials, especially *n*- and *p*-types can cause electrical and chemical behavior specific to the goals, being very interesting and useful for applications in different fields, such as gas sensors with improved selectivity due to use of such heterostructures [1]. One of the most efficient combinations of metal oxides has been demonstrated for *n-p* heterostructures [2]. The most commonly used materials such as *n* and *p* type oxides are ZnO and CuO, respectively [3]. CuO/ZnO heterostructures are known as sensor structures, since they demonstrated a high selectivity to gases such as ethanol [4].

Other studies have shown that in the case of heterostructured nuclei, when the material interface participates in the detection mechanism, a higher gas response can be obtained due to the improved modulation of the electron depletion region [2]. Thus, the thickness of the upper layer of the structures must be comparable to the Debye length of the material [2]. The working function of the materials is another important parameter that must be considered, especially for the functionalized surface structures. As an example, Choi *et al*. have shown that local suppression/extension of the CuO nanowire hole accumulation layer can improve the gas detection properties, respectively the oxidation/reduction of the gases [5]. In this work, multilayered film of (CuO/Cu_2O)/ZnO:Fe that forms non-planar heterojunctions is studied for vapor detection of several volatile organic compounds.

Experimental

In this work, we report on the synthesis of Cu_xO/ZnO:Fe heterostructures produced by the SCS cost-effective chemical solution method [6]. Structural and morphological properties were investigated in detail. Gas detection studies have shown that heterostructures thermally annealed (TA) at 450 °C for 30 min have excellent selectivity to ethanol gas. This can be attributed to a decrease in the diameter of the nanocrystallites after thermal annealing, which leads to the formation of several potential barriers that affect the value of the response to the gas species, as well as from the oxidation of the Cu_2O phase to the crystalline CuO phase.

SEM analysis

Figure 1 shows the scanning electron microscopy (SEM) image of ZnO:Fe films with TA at 450°C for 30 min. The nanostructured film thickness is ~ 1.5 nm (measured in SEM section).

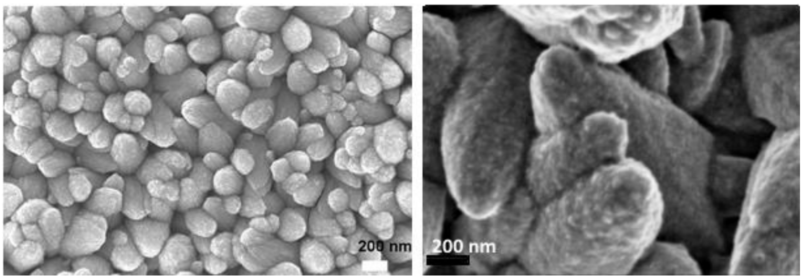

Figure 1. SEM image of CuO/Cu$_2$O/ZnO heterojunctions doped with 0.1 at% of Fe after thermal annealing at 450 ºC for 30 min

The sample consists of column-type granules, densely packed with ZnO:Fe, which completely cover the glass substrate. No large clusters were observed, even on a large scale (see fig. 1). The diameter of the granules for the films of ZnO:Fe with about 0.1 at% of Fe varies in a wide range from 70 nm to 300 nm (see fig. 1).

In general, the sample is composed of granules with a rough surface which is very important for increasing the surface-volume ratio of the nanostructured films (see fig. 1). This is very attractive for detection applications due to its small size but with a larger contact surface [7]. Partial granular interconnectivity is another factor that enhances the detection properties of nanostructured films due to the specific mechanism described in a previous work for Fe doped ZnO [8].

XRD analysis

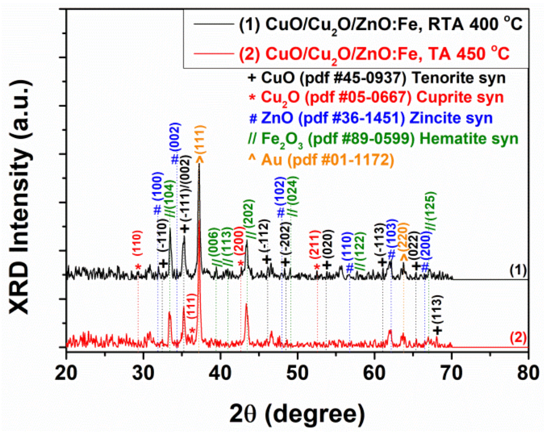

Figure 2. XRD patterns of CuO/Cu$_2$O/ZnO:Fe heterojunctions rapid thermal annealing (curve 1) and thermal annealing (curve 2)

The heterojunctions formation is demonstrated by the coexistence of the CuO, Cu$_2$O and ZnO phases shown in figure 2, such that at the values 2θ of 32.45°, 35.3°, 46.15°, 48.3°, 53.8°, 61.1°, 65.4° and 68.05° reflections (*hkl*) for CuO (Tenorite) copper oxide were obtained with Miller planes (-110) (-111)/(002), (-112), (-202), (020), (-113), (-220) and (113), respectively. The crystalline structure of Tenorite CuO is in monoclinic symmetry with space group *C2/c* [9] with constants *a*=4.685 Å, *b*=3.425 Å, *c*=5.13 Å, and *β*=99.549° [9-10].

Reflections at 2θ of 29.35°, 36.3°, 42.7° and 52.5° with Miller planes (110), (111), (200) and (211), respectively, it is assigned to the phase of Cu$_2$O (Cuprite) which has a cubic structure, of type, of the space group $T_h^2 - Pn3[65W]$ or $O_h^4 - Pn3[72P]$ [11]. Reflections at 2θ of 31.95°, 34.35°, 34.35°, 47.95°, 56.75°, 62.2° and 66.45° with Miller planes (100), (002), (102), (110), (103) and (200), respectively, it is attributed to the zinc oxide ZnO, according to the card (pdf # 36-1451) Zincite syn, which has a hexagonal structure [12].

In addition, reflections of Fe_2O_3 iron oxide are observed demonstrating the doping of zinc oxide with iron impurities and after thermal annealing Fe_2O_3 is obtained according to the card (pdf # 89-0599) Hematite syn with Miller plans (104), (006), (113), (202), (024), (122) and (125) at the 2θ of 33.45°, 39.45°, 40.95°, 43.45°, 49.05°, 57.75° and 67.1°, respectively. The reflections at 37.25° and 63.75° are attributed to metallic Au, which is due to the sprayed contacts.

Gas sensing studies

Figure 3 shows the gas response depending on the operating temperature (OPT) of the $CuO/Cu_2O/ZnO$:Fe sensor structures with different thermal annealing methods that form bi-layer structures, at different gases (acetone, *n*-butanol, ethanol, 2-propanol) with a 100 ppm concentration.

Operating Temperature °C Operating Temperature °C

Figure 3. Response of $CuO/Cu_2O/ZnO$:Fe heterojunctions rapid thermal annealing 400 °C for 60 s (a); and thermal annealing 450 °C for 30 min (b)

All samples demonstrate the response to gases of *p*-type behavior and the increase of the resistance value under the exposure to the reducing gases. Figure 3(a) shows the response of CuO/ZnO:Fe using rapid thermal annealing (RTA) 400 °C heterostructures for 60 s, indicating a high response to butanol and ethanol. The highest gas response was obtained at OPT at 350°C with a gas response of approximately 140%, 175%, 180% and 140% for acetone, *n*-butanol, ethanol and 2-propanol, respectively. In the case of $CuO/Cu_2O/ZnO$:Fe structures using TA 450 °C for 30 minutes, an improved selectivity towards ethanol can be observed with a response of about 40% higher compared to the other gases tested (fig. 3(b)). The optimum OPT (operating temperature) was found to be at 300°C with a gas response of approximately 80%, 80%, 120% and 80% for acetone, *n*-butanol, ethanol and 2-propanol, respectively. An additional increase in gas response was observed for these structures OPT-350°C and gas response is approximately 100%, 110%, 120% and 100% for acetone, *n*-butanol, ethanol and 2-propanol, respectively. It should be noted, the CuO/ZnO:Fe heterostructures depend on the heat treatment methods used and can present both, high responses and high selectivity, which allows us to implement these types of sensors in various fields of the chemical industry, enhancing security and broadening the application range, from the medicine to industry.

Conclusions

In this work, we have reported on the morphological, structural and sensory properties of $CuO/Cu_2O/ZnO$:Fe heterojunctions thermally annealed by different methods, synthesized by a SCS approach. Analyzing the SEM image, one can see a well-formed crystalline structure, the sample is composed of granules with a rough surface that allows to increase the surface-volume ratio of the nanostructured films fully covered with CuO/Cu_2O. The diameter of the granules for the films of ZnO:Fe with ~0.1 at% of Fe varies in a wide range from 70 nm to 300 nm, which allows to fill all the empty spaces between nanocrystallites.

After analyzing all the data obtained experimentally, we identified that the structures formed by $CuO/Cu_2O/ZnO$:Fe using RTA 400 °C for 60 s have a response of about 180% which is the best one from this research, obtained at OPT-350 °C for ethanol. These data are almost identical to the reaction to butanol. For the structures obtained from CuO/ZnO:Fe using TA 450°C for 30 min we obtain a maximum response of 120% to ethanol, which is highlighted by outstanding selectivity, this is a 40% difference from the response to the other gases tested, the result for these gases (acetone, butanol, propanol) is equivalent and makes about 80%. The working temperature for collecting sensor data was determined to be 300 °C.

Finally, we can conclude that the experimental data presented above can be applied in the fields of the chemical industry, the biomedical field, life safety and many other areas that require high precision and small size sensors.

Acknowledgements

Zadorojneac Tudor gratefully thanks to the Microelectronics and Biomedical Engineering Department, especially Univ.Prof. Dr.Habil. Oleg LUPAN, for research support, analysis of the data obtained and the fruitful discussions during MSc studies. 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. LUPAN, O., CRETU,V., POSTICA, V., ABABII, N., POLONSKYI,O., KAIDAS, V., SCHÜTT, F., MISHRA, Y.K., MONAICO, E., TIGINYANU, I., SONTEA, V., STRUNSKUS, T., FAUPEL, F., ADELUNG, R., *Enhanced Ethanol Vapour Sensing Performances of Copper Oxide Nanocrystals with Mixed Phases*. Sensors and Actuators B: Chemical 224**,** 2016, pp.434-448
2. LUPAN, O., S. KOUSSI-DAOUD, B. VIANA, T. PAUPORTE, *Oxide planar p–n heterojunction prepared by low temperature solution growth for UV-photodetector applications* RSC Advances ***6*,** 68254-68260 (2016).
3. LUPAN, O., POSTICA, V., ABABII, N., HOPPE, M., CRETU, V., TIGINYANU, I., SONTEA, V., PAUPORTÉ, T., VIANA, B., ADELUNG, R., *Influence of CuO Nanostructures Morphology on Hydrogen Gas Sensing Performances. Microelectronic Engineering,* 164, pp. 63-70 (2016).
4. ZADOROJNEAC, T. Teza de masterat. *Cercetarea senzorilor de compuși volatili în baza heterojoncțiunilor cu pelicule columnare din oxid de zinc.* UTM, DMIB Chișinău 2020.
5. CHOI, S., KATOCH, A., KIM, J., KIM, S. *Remarkable Improvement of Gas-Sensing Abilities in P-Type Oxide Nanowires by Local Modification of the Hole-Accumulation Layer.* ACS Applied Materials & Interfaces, 7, pp. 647-652 (2015).
6. LUPAN, O., CHOW, L., SHISHIYANU, S., MONAICO, E., SHISHIYANU, T., ŞONTEA, V., CUENYA, B.R., NAITABDI, A., PARK, S., SCHULTE, A. *Nanostructured zinc oxide films synthesized by successive chemical solution deposition for gas sensor applications*, Mater. Res. Bull. 44, 2009 pp.63-69.
7. HOPPE, M.; ABABII, N.; POSTICA, V.; LUPAN, O.; POLONSKYI, O.; SCHÜTT, F.; KAPS, S.; SUKHODUB, L. F.; SONTEA, V.; STRUNSKUS, T.; FAUPEL, F.; ADELUNG, R. *CuO-Cu_2O)/ZnO:Al Heterojunctions for Volatile Organic Compound Detection. Sens.* Actuators, B 2018, 255, 1362−1375.
8. POSTICA, V., HÖLKEN, I., SCHNEIDER, V., KAIDAS, V., POLONSKYI, O., CRETU, V., TIGINYANU, I., FAUPEL, F., ADELUNG,R., LUPAN, O. *Multifunctional device based on ZnO:Fe nanostructured films with enhanced UV and ultra-fast ethanol vapour sensing*, Materials Science in Semiconductor Processing, 49, pp.20-33, 2016
9. ÅSBRINK, S., NORRBY, L. J. *A refinement of the Crystal Structure of Copper(II) Oxide with a Discussion of Some Exceptional e.s.d.'s. Acta Crystallogr.,* Sect. B: Struct. Crystallogr. Cryst. Chem. 1970, 26, 8−15
10. TIGINYANU, I., LUPAN, O.; URSAKI, V., CHOW, L.; ENACHI, M. *Nanostructures of Metal Oxides. In Comprehensive Semiconductor Science and Technology; Bhattacharya, P., Fornari, R., Kamimura, H., Eds.*; Elsevier: Amsterdam, 2011; Vol. 1−6, pp 396−479.
11. MADELUNG, O., RÖSSLER, U., SCHULZ, M., Cuprous Oxide (Cu_2O) *Crystal Structure, Lattice Parameters. In Non-Tetrahedrally Bonded Elements and Binary Compounds* I Eds.; Springer-Verlag: Berlin/ Heidelberg, 1998; pp 1−3.)