Influence of TiO_2 Ultra-Thin Films on Gas Sensing Properties of CuO:Zn

Nicolai ABABII,[†] Tim REIMER,[ǂ] Vasile POSTICA,[†] Mathias HOPPE,[1] Steffen CHEMNITZ,[ǂ] Victor SONTEA,[†] Wolfgang BENECKE,[ǂ] Rainer ADELUNG,[1] Oleg LUPAN[†]
[†]*Technical University of Moldova*; [ǂ]*Fraunhofer Institute for Si Technologies*, [1]*CAU, Germany*
oleg.lupan@mib.utm.md

***Abstract* — Copper oxide is a p-type metal oxide with remarkable optical, electrical, thermal and sensing properties. The oxidation of Cu_2O to CuO can be performed by thermal annealing at relatively low temperatures. The present study reports on the gas sensing properties of the CuO:Zn nano-crystalline films synthesized via a simple synthesis from chemical solutions (SCS) covered with a ultra-thin layer of TiO_2. The TiO_2 ultra-thin films were deposited via the atomic layer deposition (ALD). The gas sensing properties (selectivity, response and recovery times and gas response) were investigated in dependence of the operating temperature.**

***Index Terms* — CuO, TiO_2, gas sensor, films, hydrogen, ALD.**

I. INTRODUCTION

Nowadays, the major issue of humankind is the global pollution of the atmosphere due to the emission of gases (CO_2, CH_4, O_3, etc.) leading to the commonly known greenhouse effect. Therefore, the necessity of ecological and renewable energy sources such as H_2 and ethanol is increasing. However, most of them are harmful, easily flammable and even explosive. For safety reasons, there is a strict necessity for monitoring gas leakages. This is a great challenge for researchers to develop extremely sensitive and selective gas sensors for these purposes. In this context, metal oxide micro- and nanostructures (CuO , ZnO, SnO_2, In_2O_3, WO_3, etc.) are known to be excellent candidates and therefore have been explored for many years as gas sensitive materials [1]. The main advantages of metal oxides are the easy fabrication, high sensitivity, and the capability of miniaturization in order to create portable gas sensors with wireless data transmission. However, up to now the main disadvantage is the low selectivity, i.e. cross-sensitivity [1].

It has been demonstrated that CuO nano-crystalline nanostructured films are highly selective to ethanol vapor, and by doping with Zn impurities the selectivity is changed to H_2 gas [2]. In another work it was demonstrated that by means of doping we can lead the selectivity of CuO films from one gas to another [3].

In this work we covered CuO: Zn nano-crystalline films with ultra-thin TiO_2 layer which have a protective role, because these films have the self-cleaning properties but they are also superhydrophiles [4] which is very important for long-term operation of sensors.

II. EXPERIMENTAL PART

The CuO: Zn nano-crystalline films were grown on a glass substrate (dimensions of 76 mm × 26 mm × 1 mm) using synthesis from chemical solution (SCS) described in our previous work [5]. After growth, the samples were subjected to thermal annealing in the furnace. The sensor structures were fabricated by gold contacts deposition on the surface of nano-crystalline films shaded by a mask with meander configuration. The width between contacts is 1 mm. The gas sensing measurements were performed as was described previously [2]. The TiO_2 ultra-thin films were deposited directly on the surface of the fabricated device using ALD method, where $TiCl_4$ and H_2O were used as the precursors in a Picosun R-200 ALD reactor. ALD deposition was performed at 300°C under vacuum. $TiCl_4$ and H_2O were pulsed 0.2 s each, followed by a N_2 purge of 5 s and 7 s, respectively; a total of 350 such cycles were deposited per sample, yielding an expected thickness of ~14 nm TiO_2.

III. RESULTS AND DISCUSSIONS

The study of sensing properties (gas response and selectivity) of TiO_2/CuO:Zn samples was performed by exposing them to 100 ppm of ethanol vapor and H_2 gas. The gas response was calculated according to the equation (1) derived from [6]:

$$S = ((R_{air} - R_{gas}) / R_{air})\cdot 100\% \quad (1)$$

where R_{air} is the resistance under exposure in air, and R_{gas} is resistance of the device under exposure to the reducing gas.

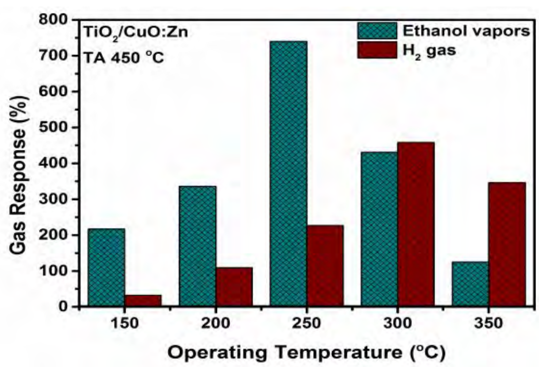

Figure 1. The calculated gas response to ethanol vapor and H_2 gas versus operating temperature of TiO_2/CuO:Zn samples thermally annealed at 450 °C.

Figure 1 shows the gas response to ethanol vapor and H_2 gas versus operating temperature of TiO_2/CuO:Zn samples thermally annealed at 450 °C for 30 min. We note that at operating temperatures of 150 °C, 200 °C and 250 °C the samples are selective for ethanol vapors with a response of 210%, 350% and 740%, respectively, and starting from an operating temperature of 300 °C the selectivity starts to change from ethanol vapor to H_2 gas with a response of 460% and 350%, respectively. Taking into consideration that CuO:Zn is selective to H_2 gas [2], here we can observe that covering the surface of nano-crystalline films with a TiO_2 ultra-thin film can suppress the gas response to H_2 gas, while the gas response to ethanol vapor at relatively low operating temperatures of 150 °C, 200 °C and 250 °C is increasing.

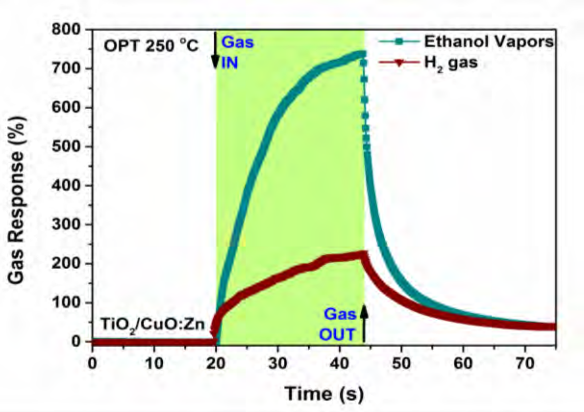

Figure 2. Dynamic response to ethanol vapor and H_2 gas of the TiO_2/CuO:Zn samples thermally annealed at 450 °C at an operating temperature of 250 °C.

Figure 2 shows the dynamic response to ethanol vapor and H_2 gas of a TiO_2/CuO:Zn sample thermally annealed at 450 °C at an operating temperature of 250 °C. From this figure one can observe that the ethanol vapor response is 740% with the response/recovery time of τ_r = 13 s and τ_d = 14 s, respectively, whereas the H_2 gas response is 220% with a response/recovery time of τ_r = 16 s and τ_d = 15 s, respectively. It is worth mentioning that at the operating temperature of 250 °C the response is very high to ethanol vapor, besides the response/recovery times are relatively fast.

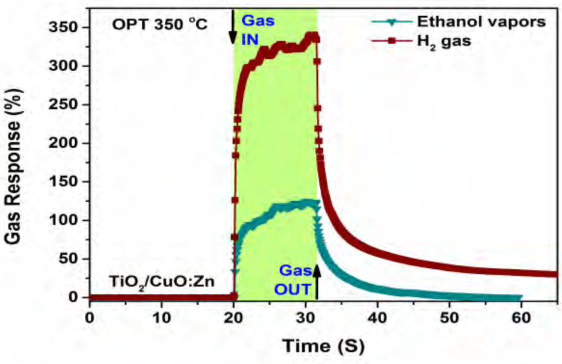

Figure 3. Dynamic response to ethanol vapor and H_2 gas of the TiO_2/CuO:Zn samples thermally annealed at 450 °C at an operating temperature of 350 °C.

Figure 3 shows the dynamic response to ethanol vapor and H_2 gas of the TiO_2/CuO:Zn samples thermally annealed at 450 ºC at an operating temperature of 350 ºC. From this figure one can see that the ethanol vapor response is 125% with response/recovery time of τ_r = 3.5 s and τ_d = 8 s, respectively, while H_2 gas response is 340% with response/recovery time of τ_r = 2,4 s and τ_d = 7 s, respectively.

We note that at an operating temperature of 350 °C the samples are several times faster compared to the operating temperature of 250 °C due to the increased thermal energy which is necessary to activate the surface reactions, but the gas response is lower.

IV. CONCLUSION

In conclusion, we report that by TiO_2 coating of the CuO:Zn nano-crystalline films it is possible to change the sensing properties, i.e. the selectivity to H_2 gas in the operating range of 150 – 250 ºC was considerably reduced, while at high operating temperatures, it was not changed. Also the gas response at these high operating temperatures was reduced. These results are very important to demonstrate that even the covering with ultra-thin layers of TiO_2 for protection and self-cleaning purposes one can induce essential changes in the gas sensing properties.

ACKNOWLEDGMENTS

The authors are particularly grateful for the STCU support under Project 6229.

REFERENCES

[1] N. E. Barbri et al, "Building of a metal oxide gas sensor-based electronic nose to assess the freshness of sardines under cold storage", Sens. and Actuat. B vol. 128, pp.235-244, 2007.

[2] O. Lupan et al, " Non-planar nanoscale p–p heterojunctions formation in $Zn_xCu_{1-x}O_y$ nanocrystals by mixed phases for enhanced sensors", Sens. and Actuat. B vol. 230, pp. 832-843, Jul. 2016.

[3] N. Ababii et al, " Schimbarea selectivității peliculelor nanostructurate de CuO datorită dopării", Conferinţa Tehnico-Ştiinţifică a Colaboratorilor, Doctoranzilor şi Studenţilor, vol. I, pp. 131-134, Nov. 2015.

[4] X.-T. Zhang et al, " Self-Cleaning Particle Coating with Antireflection Properties", Chem. Mater. Vol. 17, pp. 696-700, 2005.

[5] V. Creţu, V. Postica, N. Ababii, V. Trofim, V. Sontea, O. Lupan. "VIII International Conference on Microelectronics and Computer Science" pp. 106-110, Oct. 2014.

[6] V. Postica, N. Ababii, V. Creţu "Synthesis of Aldoped ZnO nanostructured films by SCS method", Conferinţa Ştiinţifică a Colaboratorilor, Doctoranzilor şi Studenţilor UTM ediţia 2013.