Nanocomposite Zn_2SnO_4/SnO_2 Thick films as a Humidity Sensing Material

Maria Vesna Nikolic[1], Milena Dojcinovic[1], Zorka Z. Vasiljevic[2], Miloljub D. Lukovic[1], Nebojsa J. Labus[2]
[1]Institute for Multidisciplinary Research, University of Belgrade, Belgrade, Serbia;
[2]Institute of Technical Sciences of SASA, Belgrade, Serbia

I. Summary And Motivation

Nanocomposite Zn_2SnO_4/SnO_2 powder was obtained by solid state synthesis from homogenized starting nanopowders of ZnO and SnO_2 mixed in the 1:1 molar ratio, structurally and morphologically characterized using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Thick film paste was made by adding organic vehicles to the obtained powder. Three to five layers (layer thickness approx. 12 μm) were screen printed on alumina substrate with small test PdAg electrodes and fired at 600°C for 30 minutes. SEM analysis confirmed formation of a porous structure suitable for humidity sensing. Impedance response was studied at the working temperatures of 25 and 50°C in a humidity chamber where the relative humidity (RH) was 30-90% and measured frequency 42 Hz – 1 MHz. With increase in film thickness the overall sensor impedance increased. It reduced at 100 Hz from 36 to 0.25 MΩ (60 μm), from 23.4 to 0.25 MΩ (48 μm) and from 6.8 to 0.02 MΩ (36 μm) at 25°C, while at 50°C the overall measured impedance was lower, and reduced from 14 MΩ to 0.72 MΩ (48 μm) for RH 30 and 90%, respectively. The response (8 s) and recovery (10 s) was fast, showing that this nanocomposite has potential for application in humidity sensing.

Metal oxide materials have been widely investigated as gas sensing materials, as they are robust, highly sensitive, exhibit a fast response time and are inexpensive [1]. Humidity monitoring and humidity sensors are essential components of future sensor nodes that are part of the first tier in future Internet of Things (IoT) networking platforms [2]. One path for improvement of gas sensing materials is to combine metal oxides together in order to achieve improved properties [3]. Solid state synthesis is a simple and industrially applicable technique for obtaining powders [4], while commercial metal oxide sensors are commonly obtained by screen-printing paste on a sensor substrate with electrodes.

II. Advances over Previous Works

Tin-based functional semiconductors such as SnO_2 and Zn_2SnO_4 have been the subject of much research due to promising application in solar cells, photocatalysis, gas sensors and lithium ion batteries [3, 5]. Zinc oxide (ZnO) and tin oxide (SnO_2) have been extensively investigated as gas sensors [6]. One of the main drawbacks of SnO_2 humidity sensors are long response, slow recovery times and low hysteresis, but good sensitivity [7, 8]. Improved hysteresis and faster response/recovery times have been obtained using composite ZnO-SnO_2 sensors [8]. Much work has focused on SnO_2/Zn_2SnO_4 composites for application in gas sensing. Thus, recently Sun et al [3] achieved improved formaldehyde sensing performance of this composite by synthesizing hollow microspheres. Moon et al [9] determined that adding small amounts of spinel Zn_2SnO_4 to SnO_2 improved sensitivity to CO gas in the temperature range 150-300°C, while Yu and Choi [10] investigated variations of $ZnO/SnO_2/Zn_2SnO_4$ layered sensors. Investigation of the sensitivity of porous Zn_2SnO_4/SnO_2 hierarchical spheres to triethylamine [11] and Zn_2SnO_4-doped SnO2 hollow spheres to phenylamine [12] confirmed that composites of these two metal oxides result in improved gas sensing properties. We have investigated possible application of nanocomposite Zn_2SnO_4/SnO_2 thick films in humidity sensing.

III. Results and Methodology

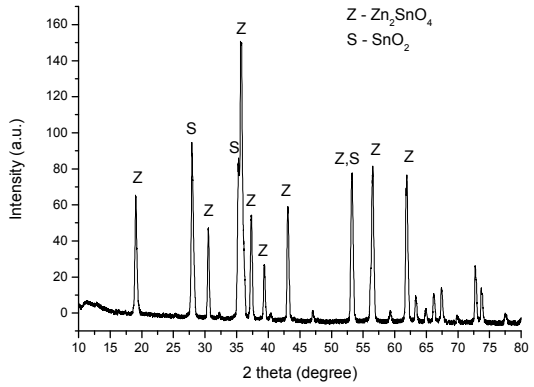

Fig. 1: XRD pattern of Zn_2SnO_4/SnO_2 nanocomposite powder

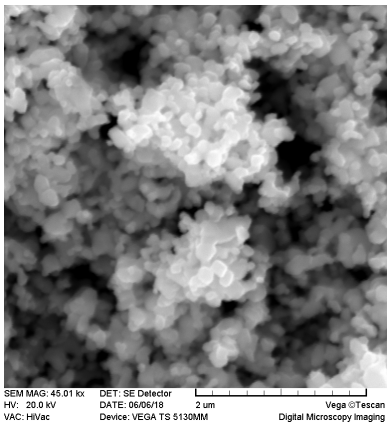

Fig. 2: SEM micrograph of Zn_2SnO_4/SnO_2 nanocomposite powder

Fig. 1 shows the XRD pattern obtained for the Zn_2SnO_4/SnO_2 nanocomposite powder obtained by mixing starting ZnO and SnO_2 nanopowders (grain size <100 nm) in the 1:1 molar ratio, followed by calcination at 1050°C for 2 h, confirming the formation of a spinel Zn_2SnO_4/SnO_2 nanocomposite, with average particle size below 300 nm, as shown in the SEM micrograph in Fig. 2. Thick film paste was made by mixing the obtained powder with organic vehicles using the procedure of Ito et al [13], we have previously applied [14]. It was screen printed on test PdAg electrodes on alumina substrate in 3-5 layers (the average layer thickness was 12 µm) and samples were fired at 600°C for 30 minutes. An image of the obtained porous thick film surface is shown in Fig. 3, while a view of a thick film sample is shown in Fig. 4.

Change in complex impedance of Zn_2SnO_4/SnO_2 thick film samples in the frequency range 42 Hz to 1 MHz with relative humidity (RH) in the range 30-90% was monitored in a JEIO TECH TH-KE 025 temperature and humidity climatic chamber at working temperatures of 25 and 50°C. As shown in Fig. 5 the modulus of complex impedance decreased with frequency and also with increase in relative humidity in the climatic chamber for all analysed samples, most expressed at lower frequencies, as shown in Fig. 6 at 100 Hz for two different sample thicknesses.

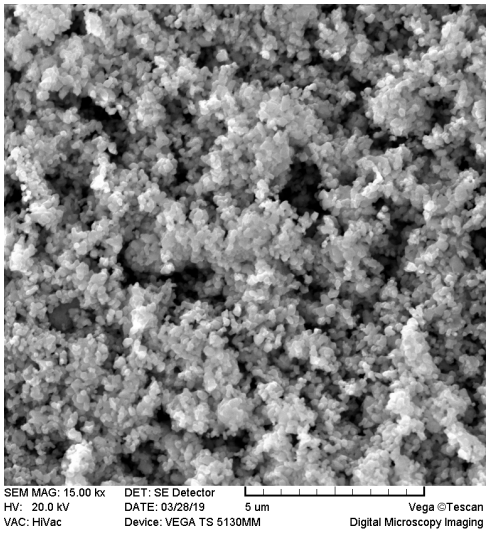

Fig. 3: SEM micrograph of Zn_2SnO_4/SnO_2 nanocomposite thick film sample surface

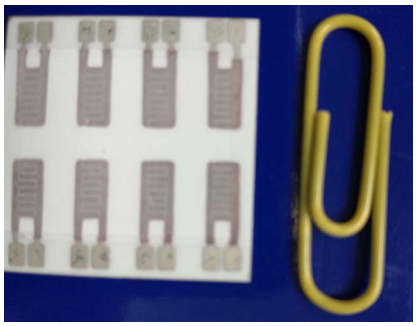

Fig. 4: Zn_2SnO_4/SnO_2 nanocomposite thick film samples printed on alumina substrate with test PdAg electrodes

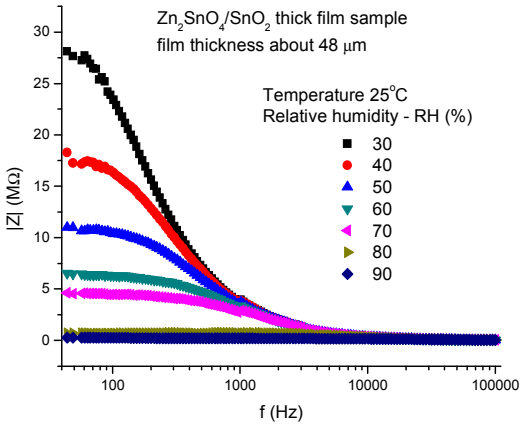

Fig. 5: Change of impedance of Zn_2SnO_4/SnO_2 nanocomposite thick film sample with frequency in the RH range 30-90%

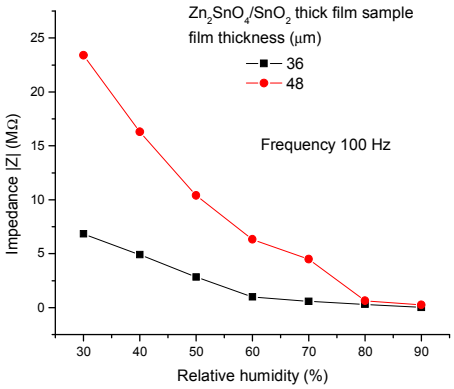

Fig. 6: Change of impedance of Zn_2SnO_4/SnO_2 nanocomposite thick film sample with RH at 100 Hz for different film thicknesses

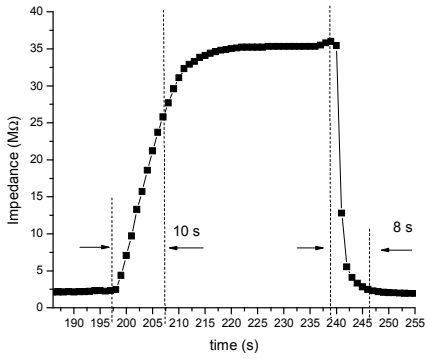

Fig. 7: Response and recovery times for a Zn_2SnO_4/SnO_2 nanocomposite thick film sample with RH at 100 Hz

An example of the response (time needed to reach 90% of the total response to a certain RH value from the baseline value) and recovery time (the time the sensor needs to return to 90% of the starting baseline signal) measured at 100 Hz for a Zn_2SnO_4/SnO_2 thick film 60 µm thick film sample is shown in Fig. 7. The time for the response was slightly faster (about 8 s) than the recovery (about 10 seconds), but both were relatively fast.

These results obtained for Zn_2SnO_4/SnO_2 thick film samples indicate that this nanocomposite material has potential for application in humidity sensing.

REFERENCES

[1] G. F. Fine, L. M. Cavanagh, A. Afonja, R. Binions, "Metall oxide semi-conductor gas sensors in environmental monitoring" Sensors, vol. 10, pp. 5469-5502, 2010

[2] M. S. Khan, M. S. Islam, H. Deng, "Design of a reconfigurable RFID sensing tag as a generic sensing platform toward the future Internet of Things", IEEE Internet of Things Journal, vol. 1, no. 4, pp. 300-310, 2014.

[3] G. Sun, G. Ma, Y. Li, Z. Zhang, Z. Chen, Y. Wang, J. Cao, H. Bala, "Improved formaldehyde-sensing performance of SnO_2/Zn_2SnO_4 nanocomposites by structural evolution" Materials Letters, vol. 191, pp. 145-149, 2017

[4] A. Stein, S. W. Keller, T. E. Mallouk, Turning down the heat: design and mechanism in solid-state synthesis", Science, vol. 259, pp. 1558-1564, 1993

[5] D. An, N. Mao, G. Deng, Y. Zou, Y. Li, T. Wei, X. Lian, "Ethanol gas-sensing of the Zn_2SnO_4 nanospheres", Ceram. Int. vol. 42, pp. 3535-3541, 2016

[6] N. D. Md Sin, S. Ahmad, M. F. Malek, M. H. Mamat, M. Rusop, "Improvement sensitivity humidity sensor based on ZnO/SnO_2 cubic structure, IOP Conf. Ser.:Mater. Sci. Eng. vol. 46, 012005, 2013

[7] Q. Kuang, C.Lao, L. W. Zhong, Z. Xie, L. Zheng, "High sensitivity humidity sensor based on a single SnO_2 nanowire", J. Am. Chem.Soc., vol. 129, pp. 6070-6071, 2007

[8] M. Velumani, S. R. Meher, Z. C. Alex, "Impedometric humidity sensing characteristics of SnO_2 thin films and SnO_2-ZnO composite thin films grown by magnetron sputtering", J. Mater. Sci.: Mater. Electron., vol. 29, pp. 3999-4010, 2018

[9] W. J.Moon, J. H. Yu, G. M. Choi, "Selective CO gas detection of SnO_2-Zn_2SnO_4 composite gas sensor", Sens. Actuators B, vol. 80, pp. 21-27, 2001

[10] J. H. Yu, G. M. Choi, "Current-voltage characteristics and selective CO detection of Zn_2SnO_4 and ZnO/Zn_2SnO_4, SnO_2/Zn_2SnO_4 layered-type sensors", Sens. Actuators B, vol. 72, pp. 141-148, 2001

[11] S. Zhang, G. Sun, Y. Li, B. Zhang, Y. Wang, Z. Zhang, Enhanced triethylamine gas sensing performance of the porous Zn_2SnO_4/SnO_2 hiererachical microspheres, J. Alloys Comp. vol. 785, pp. 382-390, 2019

[12] J. Yang, S. Wang, L. Zhang, R. Dong, Z. Zhu, X. Gao, "Zn_2SnO_4-doped SnO_2 hollow spheres for phenylamine gas sensor application, Sens. Actuators B Chem. vol. 239, pp. 857-864, 2017

[13] S. Ito, P. Chen, P. Comte, M. K. Nazeruddin, P. Liska, P. Pechy, M. Graetzel, "Fabrication of screen-printing pastes from TiO_2 powders for dye-sensitized solar cells", Prog. Photovolt. Res. Appl. vol. 15, pp. 603-612, 2007

[14] M. V. Nikolic, Z. Z. Vasiljevic, M. D. Lukovic, V. P. Pavlovic, J. Vujancevic, M. Radovanovic, J. B. Krstic, B. Vlahovic, V. B. Pavlovic, "Humidity sensing properties of nanocrystalline pseudobrookite (Fe_2TiO_5) based thick films, Sens. Actuators B. Chem. vol. 277, pp. 654-664, 2018