DOI 10.5162/SMSI2025/C5.1

Programable Printing Technology Based on Spark Ablation for the Development of Gas Sensors

Leandro Nicolás Sacco[1], Larissa Egger[2], Maxim Popov[2], Christoph Dösinger[3], Nigel Rising[1], Lorenz Romaner[3], Niels Schouten[1], and Anton Köck[2]

[1] VSParticle, Oostsingel 209, 2612 HL, Delft, The Netherlands,
[2] Materials Center Leoben Forschung GmbH, Roseggerstrasse 12, 8700, Leoben, Austria
[3]Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria

Summary:
Herein, a manufacturing method is presented capable to screen multiple materials on a platform chip hosting 16 devices. This methodology relies on a dry printing process based on spark ablation that enable the deposition of nanoporous layers (NPLs). Different metal oxides semiconductors (MOS) compositions in form of NPLs were printed and tested as a gas sensors upon formaldehyde exposure. The focus of this work is not only on the sensing performance but also in the methods to accelerate the sensing layer production of single sensing units or an array of chemical sensors.

Keywords: Spark ablation, material screening, gas sensing, nanoporous layers, dry printing

Introduction

Gas sensing technology based on metal oxide semiconductors (MOS) needs to improve aspects related to the device selectivity [1], baseline signal drift over time [2], and power consumption [3]. Nanoengineering the sensing layers aroused as suitable approach to outperform the current device MOS device performance [4]. Then, a dry printing technology using a nanoparticle generator based on spark ablation is an attractive solution to produce nanopourous layers (NPLs) for gas sensor detection. Herein, 16 NPLs with different material compositions were printed on a platform chip [5] that were exposed towards formaldehyde gas molecules. The NPLs were based on mixtures of MOS (SnO_2, NiO, and ZnO) and metal catalysts (Ag and Au). Formaldehyde molecules at the 0.1 ppm level were detected with multiple NPLs. As a result, the presented methodology evidence the versatility and simplicity to produce: 1- gas sensing layers, 2- the screening possibility of multiple material composition in the same platform chip, 3- Fast production of an array of sensor or electronic nose.

Experimental section

Spark ablation working principle relies on generating high-energy electrical sparks between two bulk electrodes (metals or properly doped semiconductors) in a leak-tight chamber at atmospheric pressure where a high pure gas is flown. In short, the spark ionizes the gas and ablates the material from the electrodes, creating a vaporized material that rapidly cool down due to temperature difference between the spark zone and the surrounding environment [6]. If inert gas is used as a carrier, the formed NPs preserve the electrode (bulk) composition. Herein, up to three spark ablation generator VSP-G1 (VSParticle B.V.) were used to generate aerosols containing the ablated material in form of NPs [7]. Sn, Ni, Zn Au, and Ag (99.99 % purity) were used as electrodes. Argon was used as a carrier gas with a 1 liter/min flow. The spark power for each element was varied to achieve different material compositions (1.4 W- 13 W), for the catalyst content relatively low power conditions were considered to obtain a low catalyst contain in the aerosol mix (5 mol%<). Typically, Au ablation yield (even at relatively low power spark conditions) is higher than other base material [8]. Then, part of generated aerosol coming from the Au generator was removed (before the mixing aerosol zone) connecting a mass flow controller and an external pump. The generators were connected to a programmable fully dry printing system, named VSP-P1 (VSParticle B.V). NPLs were printed on a multi-sensor platform [5] hosting 16 sensors structures with a 4-probe configuration. The multi-platform chip was loaded into a chamber where the pressure is set at 0.15 mbar at room temperature. A nozzle with a 100 µm diameter orifice size was used and a throughput of 0.08 l/min. The substrate-nozzle distance was fixed at

300 µm. A 500 µm long line was printed on the sensing structure. The printing speed was set at 100 µm/s and the number of passes were varied to target a (5 ± 1) µm NPL thickness. To stabilize and fully oxide the NPLs, an annealing step was performed 400°C flowing in synthetic in a tubular furnace. For the gas sensing measurements, formaldehyde (ready-to-use mixture diluted in N_2) was introduced with stepwise concentrations of 0.1 ppm, 1 ppm and 10 ppm. Humidity level was set to 50% at 20°C, and the sensors operating temperature was 300°C. Sensor response was defined as in previous work [9].

Results and Discussions

Fig. 1 summarizes the resistance variation of 8 NPLs based on different compositions upon formaldehyde exposure steps.

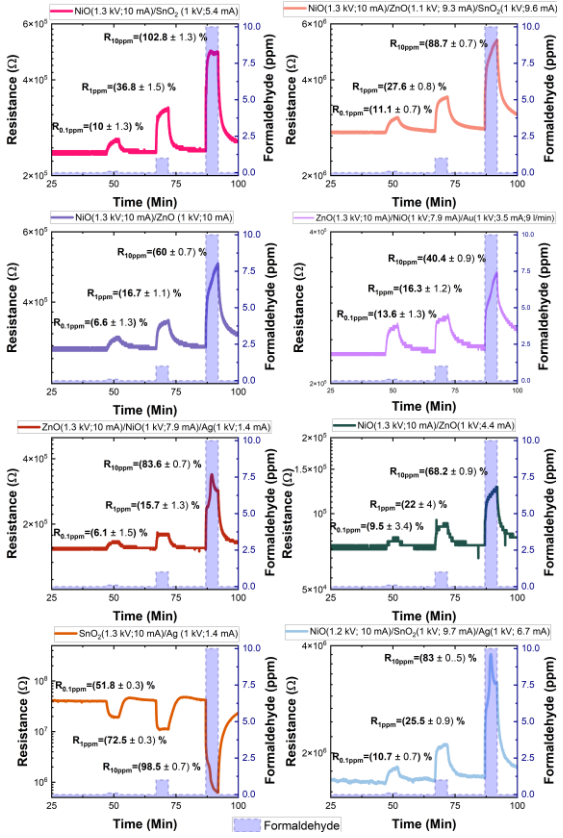

Fig. 1. Dynamic sensing response of NPLs with different material compositions upon exposure to formaldehyde gas in the concetration range from 0.1-10 ppm (Response value at each exposure are indicated).

The remaining 8 different NPLs compositions are not displayed because the device resistances were too high to measure with the used equipment. The resistance increase/decrease for each NPL under the same target gas is attributed to the p-type, n-type, p–n heterojunctions and the relative material compositions of the junctions. Remarkably, all the NPLs compositions are sensitive to 0.1 ppm formaldehyde gas molecules with relative high responses ranging from 6.1 % up to 51.8 % depending on NPL composition. Furthermore, the sensor response increases as the formaldehyde concentration continuously is increased from 0.1 ppm up to 10 ppm (no device saturation was detected).

Conclusions

Collectively, these results aim to dynamize the community work on the gas sensing sector. Firstly, showing that spark ablation coupled with programmable dry printed method can be used to produce high sensitive layers. Secondly, this methodology can substantially accelerate the material discovery to unlock new sensing layers were the current MOS based gas sensor are not capable to properly perform.

References

[1] N. Goel, K. Kunal, A. Kushwaha und M. Kumar, "Metal oxide semiconductors for gas sensing," *Engineering Reports,* 5,12604 (2023); doi: 10.1002/eng2.12604

[2] N. Dennler, S. Rastogi, J. Fonollosa, A. v. Schaik und M. Schmuker, "Drift in a popular metal oxide sensor dataset reveals limitations for gas classification benchmarks," *Sensors and Actuators B: Chemical,* 361, 131668 (2022); doi: 10.1016/j.snb.2022.131668 .

[3] A. Singh, S. Sikarwar, A. Verma und B. C. Yadav, "The recent development of metal oxide heterostructures based gas sensor, their future opportunities and challenges: A review," *Sensors and Actuators A: Physical,* 332,113127 (2021); doi: 10.1016/j.sna.2021.113127.

[4] L. Liu, Y. Wang, Y. Liu, S. Wang, T. Li, S. Feng, S. Qin und T. Zhang, "Heteronanostructural metal oxide-based gas microsensors" *Microsystems & Nanoengineering,* 8, (2022);doi: 10.1038/s41378-022-00410-1 .

[5] L. Egger, L. Reiner, F. Sosada-Ludwikowska, A. Köck, H. Schlicke, S. Becker, Ö. Tokmak, J. S. Niehaus, A. Blümel, K. Popovic und M. Tscherner, "Development of a Screening Platform for Optimizing Chemical Nanosensor Materials," *Sensors,* 24, 5565 (2024); doi: 10.3390/s24175565.

[6] R. Raymond und M. Akram, "Temporal investigation of a fast spark discharge in chemically inert gases," *Journal of Physics D: Applied Physics,* 30, 1125 (1997); doi: 10.1088/0022-3727/30/7/010.

[7] T. Pfeiffer, J. Feng und A. Schmidt-Ott,"New developments in spark production of nanoparticles," *Advanced Powder Technology,* 25, 56-70, 2014; doi: 10.1016/j.apt.2013.12.005.

[8] L. N. Sacco, L. Egger, M. Popov, C. Dösinger, N. Schouten, L. Romaner und A. Köck, "Printing Nanoporous Layers (NPL) Generated by Spark Ablation for Gas Sensing Applications," in *EUROSENSORS XXXVI*, Debrecen (2024); doi: 10.5162/EUROSENSORSXXXVI/OT5.252.