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Printing Nanoporous Layers (NPL) Generated by Spark Ablation for Gas Sensing Applications

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Summary:
Metal-oxides semiconductors (MOS) based nanoporous layers (NPL) were generated by spark ablation and printed by impaction. The printed layers were used as sensing layers to detect a hydrocarbon gas mixture named HCmix, including, acetylene, ethane, ethene, and propene. The impact of the printed layer thickness on the sensing response was assessed. The presented results show that spark ablation is an excellent scalable aerosol route for production of nanoporous layers, suitable for gas sensing applications, where the nanoporous layer can be modulated adjusting the sparkling and printing conditions.

Keywords: gas sensors, spark ablation, nanoporous layers, impaction printing, metal oxides.

1. Introduction

Chemiresistive sensors based on metal-oxide semiconductors (MOS) dominate the gas sensing technologies owning to the relative high sensitivity, easy miniaturization and integration for micro-electromechanical system (MEMS)-based sensors [1]. Nevertheless, the poor selectivity severely limits the implementation of gas sensors in a large number of applications [2]. Several approaches have been developed to overcome the difficulties induced by the cross-selectivity, including chemical functionalization, defect engineering, crystallographic design, and coating with catalytic overlayer [3]. From a material perspective, a sensing layer with a large surface-to-volume ratio that can be easily nano-engineered results in an attractive platform to solve selectivity sensing issues [3].

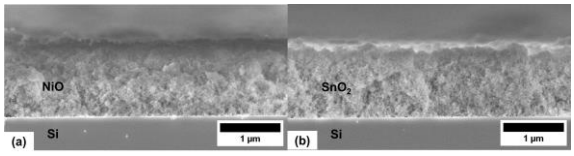

Fig. 1. SEM-cross section images of (a) NiO and (b) SnO_2 NPL used as sensing units for chemiresistive devices.

Herein, we present a process to produce nanoporous layers used as sensing units to detect target gas molecules. The sensing layers are produced by spark ablation, an aerosol nanoparticle (NP) generation route, and deposited by a impaction deposition tool. Spark ablation is a fully dry method, highly reproducible and with a pure material output. It is considered as a versatile NP generator since any solid (semi)-conductor (pure metals, alloys or semiconductors properly doped) can be used and mixed. This a highly desirable property to tackle problems of gas selectivity because it allows to synthesize numerous material compositions in nanostructured form. The NP generator was connected to impaction deposition tool, coupled to a XYZ stage to create deposition patterns, as implemented in the VSParticle nanoprinter (VSP-P1). In short, the impaction deposition relies on accelerating an aerosol through a nozzle towards a surface at sufficiently high velocities to impact on the substrate. In particular, SnO_X and NiO_X layers were printed on a 4-electrodes platform chip. Fig.1. shows a SEM cross-section micrograph of both MOS-based printed nanoporous layers. The NPL thicknesses were varied to assess the impact of the layer morphology on the gas sensing performance in detecting a

hydrocarbon gas mixture. Besides the discussion on the gas sensing performance of devices based on spark ablation, the present work aims to set the basis for the production of chemiresistive devices based on spark ablation/impaction techniques.

2. Materials and Methods

NPL were printed on a 2 cm x 2 cm Si chip with 16 sensor structures with 4-Pt/Ti- electrodes.

Spark ablation generator VSP-G1 (VSParticle B.V.) was used to produce the NP aerosol. For the deposition of NiO_x and SnO_x two pairs of 6 mm Ni and Sn (99.99 % purity) electrodes were used. Argon was used as a carrier gas with a 1 l/min flow, and in both cases the sparking potential and current were set at 1 kV and 10 mA, respectively. The generator was connected to an impaction printer VSP-P1 (VSParticle B.V.) that operated at 0.15 mbar and room temperature. The nozzle diameter was 100 µm. The substrate was placed in a holder that can be moved in the XYZ directions allowing prints without the requirement of lithography steps. A 500 µm long line was printed between the electrodes. The substrate-nozzle distance was fixed at 300 µm. The printing speed (100-1000 µm/s) and the number of passes (2-18) were varied to adjust the NPL thickness. To stabilize and oxidize the NPL, the chips were annealed at 400 °C flowing synthetic air for 10 minutes.

For the gas sensing measurements, synthetic air with controlled humidity was used as a background gas. The humidity level was set to 50% at 20°C. Specific mixture of hydrocarbon gases (HC_{mix}), including acetylene, ethane, ethene, and propene, was used as target gas. The sensors operated at a temperature of 300 °C. The sensor response, denoted as *S*, reflects the relative resistance change in percent due to the interaction with the test gas. It is calculated as follows:

$$S(\%) = 100\% * |R_{air} - R_{Gas}| / R_{air} \quad (1)$$

Where R_{Gas} is the sensor resistance in the presence of the test gas and R_{air} is the sensor resistance in pure synthetic air.

3. Results and discussion

Both types of MOS-NPL, with different thicknesses were sensitive towards the HC_{mix}, as shown Fig.2. The resistance increase/decrease for each NPL under the same target gas is attributed to the *p*-type and *n*-type MOS of NiO and SnO_2, respectively. The thicker layers, generally, lead to higher responses. A sensing saturation response was detected at exposures of 20 ppm of the HC_{mix}. At similar NPL thicknesses (1.2-1.3 µm), the SnO_2-based devices have a stronger response as compared to NiO ones (80 % vs 25% at 10 ppm). The recovery time of SnO_2 devices was longer than the time between the exposure steps, whereas NiO-based devices recovered in 2 minutes. In conclusion, the presented results provide evidence on the capability for producing gas sensing layers adopting a fully dry approach. Our method features a high control of the NPL without need of pattering and can be extended to a myriad of material compositions. Collectively, these properties are highly attractive to pave the way for the next generation of chemiresistive-gas sensors.

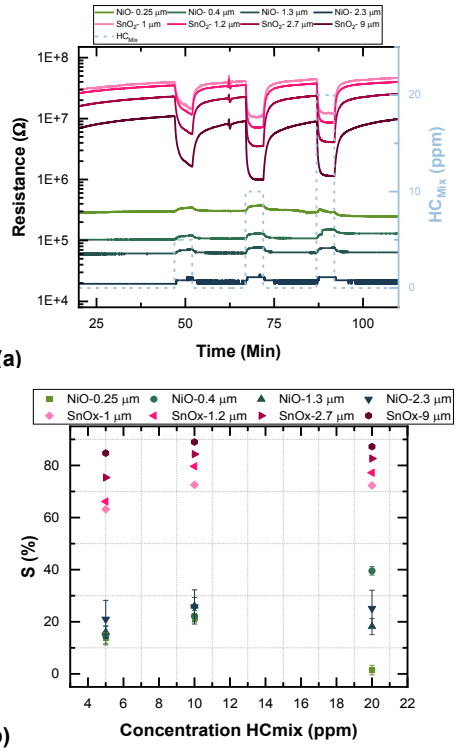

Fig. 2. (a) Dynamic sensing response of NiO and SnO_2 sensors upon exposure to HCmix. (b) Response as function of the HC_{mix} concentration.

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