DOI 10.5162/EUROSENSORS2025/MP48

Morphology Dependent Response of SnO_2 Gas Sensors from Spark Ablation, Spray Pyrolysis, and Sputter Coating Techniques

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Summary: In this work, the response of SnO_2 gas sensing layers manufactured via spark-ablated nanoparticle impaction printing, spray pyrolysis, and sputter coating is tested for acetone, NH_3, and CO_2. The spark-ablation-based layers show a higher response to all test gases. This is due to the high surface-area-to-volume ratio of nanoporous layers, a morphology inherent to spark ablation-made layers. Dry-printing layers via spark ablation is an attractive technique for responsive SnO_2 gas sensors, fabricated in one step without the need for solvents or complicated post-processing. These benefits can help drive innovation in gas sensing layers.

Keywords: MO_x gas sensors, spark ablation, nanoporous layers, sputter coating, spray pyrolysis

Introduction

CO_2, NH_3, and acetone are all pollutants that can harm the environment in small concentrations, and an increasing demand in environmental monitoring, especially in the EU, requires innovation in cheap and mass-producible gas sensors [1][2]. Metal oxide semiconductors (MO_x) gas sensing devices fit this requirement; however tend to suffer from low selectivity, short lifetimes, and high power consumption [3].

In order to alleviate these negatives, the layers need to be engineered on the nanoscale to increase the gas-sensing surface area, and decrease the particle size [4]. Often, fabricating MO_x layers that fulfill these requirements takes multiple, complicated steps both before and after deposition [5].

While still requiring multiple steps, sputter coating and spray pyrolysis are simple techniques that can be used to deposit MO_x layers. Spark ablation is also a simple method, but only requires one step for layer deposition. This work seeks to investigate the effect that these different deposition methods have on the gas sensing response towards NH_3, acetone, and CO_2.

Experimental

Device Fabrication

In this work, SiN-based micro-hotplate chips with integrated heating structure (up to 500 °C) and Pt electrodes were used as substrates to deposit SnO_2 layers using different techniques [6].

Spray Pyrolysis The precursor solution was a tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) in ethyl acetate. The solution was sprayed with an N_2 carrier gas on the chips, which were kept at 400 °C during the spraying process. The sensing film was structured by a photolithography process and dry Ar ion etching.

Sputter Coating: An oxygen partial pressure ratio of 40 % at a working pressure of 1 Pa was used. The Sn target was pre-sputtered for 5 min to remove surface contaminants. During thin film deposition, the Sn target was operated at an average power of 50 W, and the deposition time was adjusted to achieve a film thickness of 50 nm. Neither external heating nor bias voltage was applied to the substrate during the deposition process. The sensing film was structured by a lift- off process.

Spark Ablation: SnO_2 spark ablation devices were deposited using the VSP-P1 nanoprinter. Nanoparticles are first generated via spark ablation in the VSP-G1 creating an aerosol in argon (Ar), and then accelerated due to the pressure difference in the generator (ambient) and the print chamber (0.2 mbar). This creates a network of sintered nanoparticles forming a highly porous thin film. 6 mm diameter Sn (99.99%) electrodes were used with spark current of 10 mA and potential of 1.3 kV. The nanoparticles were transported using 1 l/m 99.999% Ar gas to the 0.1 mm nozzle which is fixed 300 μm from the substrate. A snaked-rectangle pattern was used with a stitch size of 75 μm and a print speed of 100 μm/s.

To stabilize and oxidize the films, the chips were annealed at 400 °C in flowing synthetic air for 10 minutes. The micro- hotplates were mounted on a Kyocera socket and wire bonded.

Device Characterization

All sensors have been measured simultaneously in an automated gas measurement setup. As background gas synthetic air with tunable humidity level was chosen. In this work the humidity was set at 50 %. The operation of the temperature is kept constant during a measurement (25 °C, 150 °C and 300 °C). The target gases are

subsequently introduced into the setup for 5 min with flow meters.

The relative resistance changes due to the interaction with the test gas, i.e. the sensor response *S*, has been calculated according to:

$$S(\%) = \frac{R_{gas} - R_{air}}{R_{air}} * 100\%$$

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.

The average response of the last 30 seconds of the gas pulse was used for R_{gas} and a 30 second average around 500 seconds after the end of the gas pulse was used for R_{air}.

Results and Discussion

Sensors fabricated with spark ablation show a greater response to NH_3, CO_2, and acetone. Sensors manufactured with spray pyrolysis and sputter coating show no response to NH_3 or acetone at all, while spark ablation devices show a 12.3 % response and a 7.6 % response toward 0.5 ppm of the gases respectively. Figure 1 shows the response of all the sensors to each test gas.

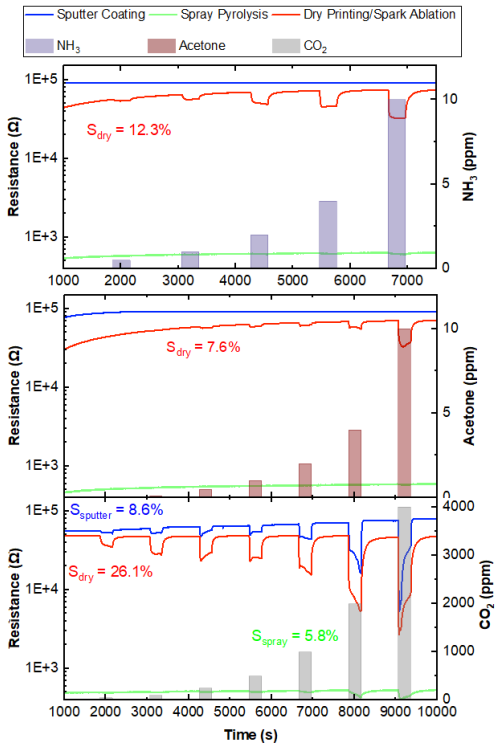

Fig. 1: Gas sensing response of SnO_2 based devices fabricated via sputter coating (blue), spray pyrolysis (green), and spark ablation(red) towards CO_2 (grey bars), NH_3 (purple bars), and Acetone (burgundy bars). Text inset gives the response to the lowest concentration that shows one.

Of the three techniques investigated in this work, sensors fabricated with spark ablation show a superior response for all target gasses. The layers produced through spark ablation are highly porous, and consist of agglomerates of nanocrystals which creates a much larger sensing surface area than the other techniques. This explains the response at much lower concentrations of test gas. Furthermore, the high surface free energy of SnO_2 nanocrystals allows spark ablation based sensors to detect gasses that other fabrication techniques cannot [7].

In addition to the superior performance, spark ablation is also a fully dry, one-step technique for layer deposition, reducing the number of steps and therefore time required for gas sensor production. By reducing the number of steps involved in the deposition, there is less room for defects or other faults that can occur during fabrication and handling [3].

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