

Direct Deposition of CMOS-compatible Sensor Films by Flame Spray Pyrolysis

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ABSTRACT

A rapid, wafer-level, dry process for in-situ synthesis, deposition of stable nanostructured, porous metal-oxide films for gas sensors is presented. Lace-like, nanostructured films of pure SnO₂ featuring high porosity (98%) are self-assembled on a target substrate by flame spray pyrolysis (FSP). The nanoparticles are mainly polyhedral and monocrystalline with a grain size of 8.7 nm and crystal size of 11.8 nm. The sensor performance has been assessed for CO so short response and recovery time were achieved.

Keywords: nanostructured film, tin dioxide, gas sensor, annealing, direct deposition

1 INTRODUCTION

High-temperature metal-oxide-based gas sensors are an attractive class of sensors that can be enhanced with noble metals facilitating sensing reactions as in heterogeneous catalysis. The main advantages include their sensitivity to a large spectrum of analytes, the simple measurement method (chemoresistor) and the relatively low production costs. They usually consist of an isolating substrate (Al₂O₃, SiN, SiO₂), a set of electrodes (Au, Pt), a resistive heater and a sensitive metal-oxide film (SnO₂, ZnO, TiO₂, WO₃) [1].

Design of metal-oxide gas sensors with a low limit of detection in the low and sub ppm range, by sufficient selectivity, sensitivity and long term stability has become increasingly challenging, requiring accurate control of sensing material properties. High sensitivity at low analyte concentration has been achieved mainly by doping and miniaturization of the sensitive metal-oxide down to the nanoscale. State-of-the-art semiconductor gas sensors usually include a nanostructured, thin or thick, sensitive metal-oxide film [1].

In "classical" methods the nanomaterial and the sensitive film are produced in different process steps requiring time-demanding and rather expensive processes. Typically, in a first phase, a sol is produced from the precursor and it is either deposited on the substrate, e.g. by spin coating and drop coating, or dried and calcined leading to nanoparticle synthesis. In the former, the metal-oxide film is obtained by calcination of the deposited material. In the later, the sol-gel-made nanoparticles are mixed with organic binders and solvent to produce a paste, which is deposited on the substrate by doctor blading, screen printing or drop coating, and annealed. These classic wet-

chemistry methods usually suffer of not optimal film reproducibility, due to formation of irreproducible surface irregularities (cracks) during evaporation of liquid components. In addition, to obtain high performance films the paste composition requires to be optimized as a function of particle and film parameters requiring further efforts.

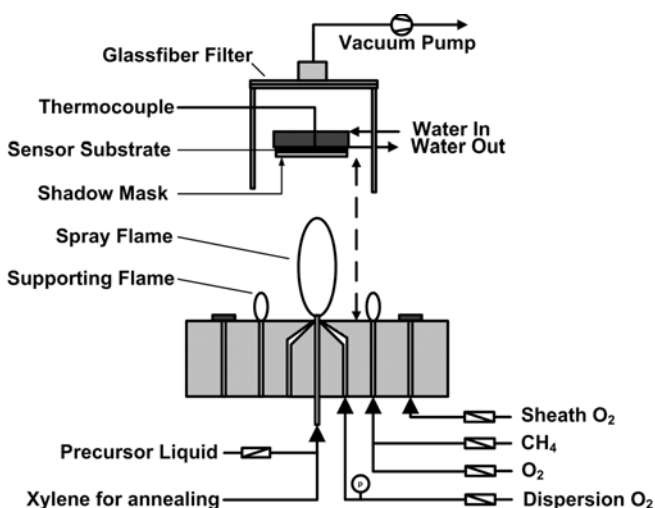


Figure 1: Schematic of the setup for direct sensor synthesis.

The liquid precursor is dispersed and evaporated by the supporting methane flame which leads to nucleation and deposition of the SnO₂ nanostructures on the substrate.

Dry aerosol-based techniques can also be used to produce nanomaterials and offer several advantages in comparison to wet techniques. Aerosol methods are scalable and they are reasonably well understood so that an efficient production of nanoparticles with good control of their characteristics is possible. Most importantly, direct deposition methods can result in crack-free films as solvent evaporation is not taking place. To date, there is an increasing number of promising aerosol-based methods to produce and *directly* deposit thick nanostructured sensing films. These methods include sputtering, spray pyrolysis, cluster beam deposition, spray pulverization, combustion chemical vapor deposition [2] and, recently, flame spray pyrolysis [3]. Cluster beam [4] deposition is a recently developed, aerosol method able of well defined micropatterns deposition and simple synthesis of metal-oxide sensitive film by thermal treatment after deposition. First results on TiO₂ sensors [4] indicate good sensitivity to methanol and several opportunities of optimizing performance.

A direct deposition method (Figure 1) such as by flame spray pyrolysis offers several advantages over “classical”, multi-step, wet-route methods, such as one-step nanoparticle synthesis and film deposition, flexible and simple precursor preparation, high material purity, large number of synthesizable oxide/metal, doping with noble metal and co-synthesis of sensor with other oxides. In fact, the latter self-assembled by thermophoretic forces resulting in a highly porous ($\approx 98\%$), nanostructured morphology. The process has high deposition rate ($\approx 9 \mu\text{m}\cdot\text{min}^{-1}$), small process time ($\approx 1 - 6$ min), while film thickness and composition can be easily controlled [3].

First results on the performance of Pt-doped SnO_2 sensitive films deposited by FSP have shown a low limit of detection of 1 ppm for CO, high sensor signal ($\approx 1 - 4$) and reproducibility [3]. In contrast to films made by wet-route methods, FSP-made films are smooth and highly reproducible reducing costs related to sensor calibration. Despite these promising results, FSP-made films suffer of low mechanical stability limiting their immediate commercial application. Here we focus on developing nanostructured sensing films of high stability

2 EXPERIMENTAL

A flame spray pyrolysis (FSP) burner (Fig. 1) as described in detail elsewhere [3] was used for synthesis and deposition of sensing nanoparticles. The later were prepared as follows: First, tin (II) - ethylhexanoate (Aldrich, purity $> 98\%$) was diluted in xylene (Fluka, purity $> 98.5\%$) with a metal-atom concentration of 0.5 mol/l. This solution was supplied at a rate of 5 ml/min through a nozzle and dispersed to a fine spray with 5 l/min oxygen (pressure drop 1.5 bar). That spray was ignited by an annular-shaped premixed methane/oxygen flame ($\text{CH}_4 = 1.5$ l/min, $\text{O}_2 = 3.2$ l/min) and an additional 5 l/min sheath oxygen flow was supplied from an annulus surrounding that flame to assure overstoichiometric combustion conditions.

The sensor substrate holder (Fig. 1) consists of a circular steal plate (3 mm thick) with one face in contact with a heat exchanger and the other holding the substrate. The temperature of the substrate during deposition was maintained between 140 - 160 °C by water cooling on its backside (Fig. 1) in order to ensure a maximum deposition rate and to avoid water condensation that may alter the film properties. The temperature on the back side of the substrate was measured by an n-type thermocouple. The nozzle-substrate (NS) distance during deposition was 20 cm.

The hot flame gas jet, carrying the freshly formed nanoparticles, impinged on the water-cooled substrate (Fig. 1). The temperature gradient between the impinging gas and the substrate surface generates a thermophoretic flux directed to the substrate surface with subsequent particle deposition and film growth. The films were insitu-annealed ($T = 500^\circ\text{C}$) for 30 s.

3 RESULTS AND DISCUSSION

3.1 Nanoparticles Synthesis and Deposition

Figure 2 show TEM images of SnO_2 powder collected on the filter downstream of the sensor deposition area. Mostly monocrystalline, polyhedral particles with a visible average diameter of 10 - 15 nm are obtained. The XRD analysis (Fig. 3) reveals homogeneous pure cassiterite crystals with an average size of 11.8 nm. The cassiterite lattice (Fig. 1a) is regularly extending through the whole crystal. The BET analysis reveals a specific surface area (SSA) of $100 \text{ m}^2/\text{g}$ ($d_{\text{BET}} = 8.7 \text{ nm}$) indicating formation of monocrystalline nanoparticles.

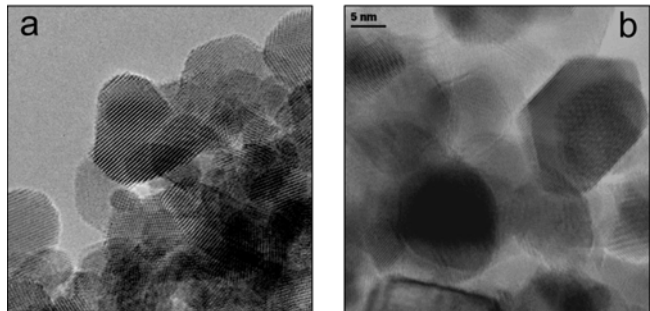


Figure 2: TEM images of SnO_2 particles collected on the filter downstream of the deposition area.

The XRD spectra of the as-prepared film revealed the same composition and crystal size of the powder collected downstream to the deposition area. In fact, at the low deposition temperature (150 °C) the deposition time (180 – 240 s) is not sufficient for crystal growth resulting in ultrafine nanostructures (11.8 nm) with high sensitivity to the EtOH and CO [3] but low mechanical stability. Handling of the films required further mechanical stabilization to avoid dispersion of the deposited material in the surrounding.

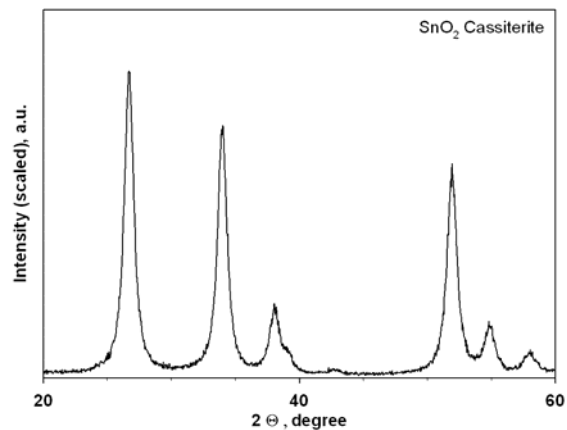


Figure 3: XRD-spectra of the SnO_2 powder collected downstream of the sensor deposition area.

3.2 Sensing Performance

The film sensing performance was investigated for CO. The sensors are tested in a temperature controlled chamber placed inside a circular furnace [5]. Figure 4 shows the response of a SnO₂ sensor to 100 ppm CO in synthetic air. During exposure to 100 ppm CO the film resistance drops steeply from 1.4 to 0.2 MOhm. After switching-off the CO the sensor baseline is readily recovered. The response and recovery times (time to reach respectively 90% of the resistance-change or baseline-recovery) are 1 and 3 minutes respectively, and the film's baseline has excellent stability under exposure to multiple cycles of air/CO.

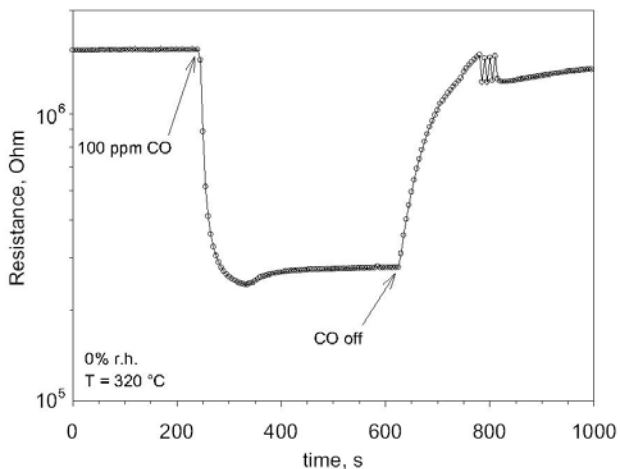


Figure 4: Response of a sensor featuring a SnO₂ film after one deposition/stabilization cycle, to 100 ppm CO at 320 °C and 0% r.h. The sensor baseline is readily recovered after switching off the CO flow.

4 CONCLUSIONS

A rapid (180 s), flame spray (FSP) method for large-scale synthesis of thick, porous, polycrystalline SnO₂ films with high sensitivity has been presented. Uniform, regular, macroporous SnO₂ films have been deposited on a circular area of 6 cm in diameter from the impinging point on the substrate. These films are remarkably stable and sensitive. Gas sensors prepared by this procedure showed fast response and recovery times for CO.

REFERENCES

- [1] G. Eranna, B.C. Joshi, D.P. Runthala, R.P. Gupta, *Crit. Rev. Solid State Mat. Sci.*, 29, 111-188, 2004.
- [2] Y. Liu, E. Koep, M.L. Liu, *Chem. Mat.*, 17, 3997-4000, 2005.
- [3] L. Madler, A. Roessler, S.E. Pratsinis, T. Sahm, A. Gurlo, N. Barsan, U. Weimar, *Sens. Actuators, B*, 114, 283-295, 2006.
- [4] T. Mazza, E. Barborini, I.N. Kholmanov, P. Piseri, G. Bongiorno, S. Vinati, P. Milani, C.

- Ducati, D. Cattaneo, A. Li Bassi, C.E. Bottani, A.M. Taurino, P. Siciliano, Libraries of cluster-assembled titania films for chemical sensing, *Appl. Phys. Lett.*, 84, 103-108, 2005.
- [5] A. Teleki, S.E. Pratsinis, K. Kalyanasundaram, P.I. Gouma, *Sens. Actuators, B*, 119, 683-690, 2006.