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Ultra-sensitive SnO₂ gas sensors based on hierarchical octahedra *

Justyna Jońca¹, Andrey Ryzhikov¹, Audrey Chapelle³, Philippe Menini³, Katia Fajerwerg^{1,2}, Myrtil L. Kahn¹, Pierre Fau^{1,2}

Abstract: The controlled hydrolysis of tin amidure precursor ([Sn(NMe)₂]₂) yields micrometric Sn₃O₂(OH)₂ octahedra, formed by a self-assembly process. The water content and alkylamine surfactants are major parameters for the growth process. These structures have been employed to prepare highly sensitive gas sensors, which present 7% variation of their resistance at only 0.25 ppm CO.

I. INTRODUCTION

SnO₂ nanostructures including nanoparticles [1], nanowires [2], nanobelts [3], and nanotubes [4, 5], have been widely used in many fields, such as gas sensors, solar cells and lithium batteries. Recently, hierarchical and/or hollow SnO₂ micro- and nanostructures have attracted much interest because of their widespread potential applications such as gas sensors [6]. We present here the formation of self-assembled tin oxohydroxide (Sn₃O₂(OH)₂) octahedral supercrystals obtained by an organometallic synthesis. These supercrystals have been characterized by transmission electron microscopy, and field-emission scanning electron microscopy. These octahedra have been used as gas sensitive layers deposited on silicon devices. After an *in-situ* annealing to 500°C, Sn₃O₂(OH)₂ oxidizes into SnO₂ while retaining the initial morphology. The response of the sensors to CO gas has been measured under a relative humidity (RH) of 50%. The sensors present an outstanding dynamic response to very low CO concentrations (0.25 to 20 ppm).

II. EXPERIMENTAL SECTION

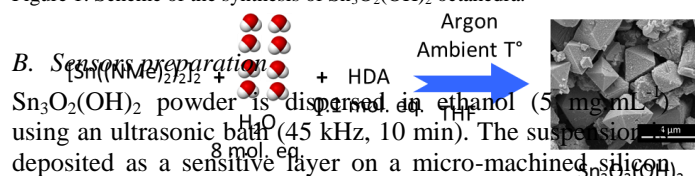
A. Synthesis of Sn₃O₂(OH)₂

The synthesis of tin hydroxide is performed at room temperature and under argon atmosphere in standard Schlenk tubes. In a typical experiment, 2 mL of THF (Braun MB-SPS-800) containing degassed distilled water (72 µL, 8 eq.) is slowly added to a THF (4 mL) solution of [(Sn(NMe)₂]₂ (NanoMePS, 206.9 mg) with hexadecylamine (HDA, 12 mg, 0.1 eq.). After 16 h, the supernatant is removed by centrifugation (1000 rpm, 5 min, and 20°C) and the precipitated powder is washed 3 times with 5 mL of acetone. The resulting product is dried under low vacuum in a

desiccator overnight. A white powder composed of Sn₃O₂(OH)₂ is obtained (Fig. 1).

Figure 1. Scheme of the synthesis of Sn₃O₂(OH)₂ octahedra.

B. Sensors preparation



Sn₃O₂(OH)₂ powder is dispersed in ethanol (5 mg mL⁻¹) using an ultrasonic bath (45 kHz, 10 min). The suspension is deposited as a sensitive layer on a micro-machined silicon substrate using a drop deposition system. The silicon platform is prepared in the MICA group of Laboratoire d'Analyse et d'Architecture des Systèmes (LAAS-CNRS). The sensor die (2×2 mm) comprises a 1.4 µm thick dielectric membrane (SiN_x/SiO₂), a spiral shaped platinum heater, and interdigitated electrodes which contact the sensitive layer. Tests under gas have been performed in a bench equipped with a humidity sensor. The gas sensors are conditioned by an *in-situ* heating the sensitive layer up to 500°C in ambient air. During this anneal, Sn₃O₂(OH)₂ transforms into SnO₂ while keeping the octahedra shape. Then, the sensitive layer resistance is stabilized during few hours at 500°C in synthetic air flow (1 L.min⁻¹, RH 50 %). The sensor performance is measured under to various ppm levels of CO. The normalized response of the sensors is defined as Rn(%) = (R_{air} - R_{gas})/R_{air}*100, where R_{air} corresponds to the sensor resistance in synthetic air and R_{gas} corresponds to the sensor resistance under CO exposure.

III. RESULTS

A SnO₂ octahedra characterization

The growing process of the octahedra in solution has been followed by TEM investigations. After 30 minutes, self-assembled triangular foils are present in solution (Fig. 2a, left). After 7 hours, the sample only displays octahedral structures (Fig. 2a, center). HRTEM imaging has revealed the hierarchical structuration of the octahedra's walls. Self-assembled triangular sheets and octahedral particles are built by the self-assembly of nanoparticles with a diameter of 3.9 ± 0.9 nm (Fig. 2a, right). This suggests that the octahedra

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building process starts by the formation of $\text{Sn}_3\text{O}_2(\text{OH})_2$ nanoparticles stabilized by HDA, which self-assemble by an oriented attachment process into triangular polycrystalline foils in solution. The subsequent assembly of the triangular sheets leads to the tridimensional construction of octahedra by an oriented attachment process (Fig. 2b).

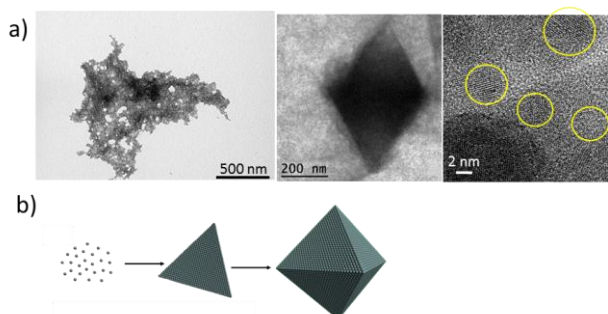


Figure 2. (a) TEM image of the particles obtained in solution after, left: self-assembled triangles shapes obtained after 30 minutes, center: octahedra obtained after 7 hours, left: HRTEM image of the nanoparticles (yellow circles) inside the octahedra walls, (b) scheme of the hierarchical self-assembly process of the octahedra in solution.

B Gas sensing properties of SnO_2 microstructures (octahedra and thin film)

The sensing properties of the above described SnO_2 octahedra sensors have been compared with a standard SnO_2 made of sputtered thin films (grain diameter *ca.* 500 nm, thickness *ca.* 250 nm, commercial source) (Fig. 3).

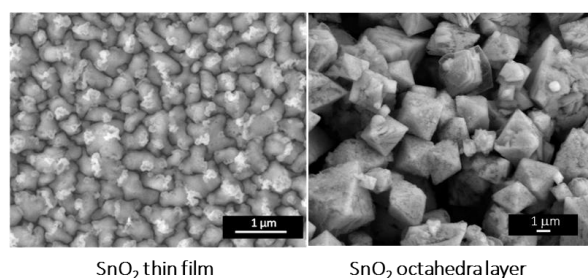


Figure 3: SEM image of SnO_2 sputtered thin film (left), and octahedra (right).

For all sensors, the maximum sensitivity to CO is obtained at an operating temperature of 500°C. The sensors have been exposed to increasing CO concentrations between 0.25 and 20 ppm. Normalized responses for all sensors are presented in table 1.

TABLE I. Comparison of sensor's responses to increasing CO amounts

	CO content (at 500°C)			
	0.25 ppm	1 ppm	10 ppm	20 ppm
Response Rn (%) SnO_2 octahedra	7	20	55	67
Response Rn (%) SnO_2 thin film	0	2.9	10	25

The thin film SnO_2 sensors show no response at all at 0.25ppm CO, whereas the SnO_2 octahedra response Rn is 7%. Thin film sensors give very weak responses to CO in the concentration range of 1-10 ppm with resistance variations of *ca.* 3%-10%, respectively. In the same conditions, normalized responses of the SnO_2 octahedra gas sensors increase from 20% to 55%. Moreover, they exhibit an almost saturated gas response at 20 ppm CO only. These sensors present an unprecedented dynamic of their response in the low CO concentration range (0.25 to 20 ppm) (Fig. 4).

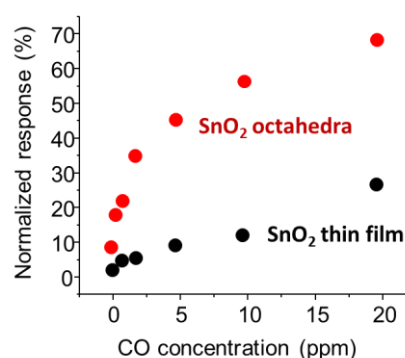


Figure 4. Response of the sensors at CO levels between 0.25 and 20 ppm.

In air at 500°C, the adsorption and dissociation of oxygen species on SnO_2 grains, and grain boundaries, generates an electron depletion layer which extends to few nanometres depth (L). CO molecules directly react with these adsorbed oxygen species during the sensing operation of the device. For nanosized SnO_2 grains, the depletion layer can extend to the whole grain volume oxide and therefore enhance the CO response. With SnO_2 thin films, a material with wide and densely packed grains, the gas sensing properties are mostly controlled by the grain boundary barriers. In the case of octahedral sensitive layers, the combination of a porous microstructure and of nanosized building blocks provides a high response to low CO contents. In addition, according to N. Barsan *et al.*[7], the gas sensor response also strongly depends on the effective contact area between neighboring grains in the sensitive layer. Their model suggest that the sensor signal can be improved by changing the shape or dimensions of grains of the sensitive layers, and the best responses are obtained by the reduction of the effective contact area parameter. Therefore, the superior performance of SnO_2 octahedra layers may also be the consequence of the reduced contact area between the large octahedra grains.

IV. CONCLUSION

In summary, the SnO₂ octahedra sensitive layers present a remarkable response to low CO amounts, and a very dynamic response between 1 and 20 ppm where the saturation threshold is almost reached. The very open structure of SnO₂ octahedra provides a large porosity for an effective gas diffusion, and small contact area between the grains are favorable to a high gas sensitivity. Such hierarchically assembled sensitive layer may be used for applications where ultra-sensitive CO gas sensors are required.

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