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Fabrication of SnO_2 Flexible Sensor by Inkjet Printing Technology †

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Abstract: In this work, a flexible tin oxide (SnO_2) gas sensor was successfully fabricated by inkjet printing technology. This thin film deposition technique requires the formulation of stable suspensions with specific fluidic properties. Aqueous Sol-gel method was applied to synthesize a stable sol based on tin oxide, then transformed into ink with the appropriate viscosity and surface tension to be printed using a drop-on-demand piezoelectric inkjet printer. Thermal analyses of synthetized sol show that a crystallized structure of SnO_2 could be obtained at 350 °C, which is lower than crystallization temperatures of SnO_2 previously reported in the literature, and entirely consistent with our plastic substrate. The printed thin-film was then sintered at 350 °C on polyimide foil (Upilex-50S) and characterized as sensor.

Keywords: flexible gas sensor; SnO_2 ink preparation; sol-gel process; inkjet printing

1. Introduction

In recent years, a significant advance in the development and implementation of flexible sensors has demonstrated the increasing utility of these special types of sensing platforms [1]. In particular, flexible gas sensors based on metal oxide belong to this category, and have an important role in environmental applications. Tin oxide is considered to be one of the most useful materials in gas sensing applications [2] because of its remarkable sensing properties, high chemical stability, and ease of integration during sensor design. The manufacture of flexible gas sensors based on tin oxide thin film is subject to restrictions as it requires a high operating temperature which is not compatible with all plastic foils. In our present work, inkjet printing was adopted as the deposition technique in order to print flexible tin oxide gas sensing films in additive way. A stable sol was synthetized by sol-gel method, and used as a precursor ink with appropriate rheological properties. The electrical response of the sensor to CO gas was characterized.

2. Materials and Methods

2.1. Sol Preparation

SnO_2 precursor solution was prepared using aqueous sol-gel route as described in the literature for the preparation of SnO_2 nanopowders [3]. Tin chloride ($SnCl_2$, Sigma-Aldrich, St. Quentin Fallavier—France) was dissolved in deionized water, then, a 25% ammonia solution (NH_3, Sigma-Aldrich, St. Quentin Fallavier—France) was added dropwise in order to remove the chloride ions. The solid tin hydroxide (Sn(OH)n, $n = 2$ or 4) was recovered by Büchner filtration (0.7 μm filter paper) and washed several times with diluted NH_3 solution. The precipitate was dissolved in glacial acetic acid (Sigma-Aldrich, St. Quentin Fallavier - France) and ethylene glycol (Sigma-Aldrich, St.

Quentin Fallavier—France) was added in order to form a tin complex. The mixture was heated at 90 °C for 1 h to form a stable and yellow solution containing a complex of tin cation.

2.2. Ink Preparation

Once the sol was synthesized, it was transformed into ink with an appropriate rheology to satisfy the printability criteria of the Dimatix printer. Viscosity and surface tension were tuned by adding certain amounts of Ethylene Glycol, Ethanol, Glycerin and 2-isopropoxyethanol. SnO_2 ink was printed onto a polyimide foil named Upilex using commercial Dimatix printer (DMP-2800 Fujifilm USA) with 16 nozzles cartridges of 10 picoliter drop volume (DMC-11610).

2.3. Contact Electrodes on Foil

In order to perform electrical measurements, gold electrodes have to be deposited. A 100 nm thick gold layer was e-beam evaporated onto polyimide, preceded by 3 nm thick chromium layer to act as an adhesion layer. A 1064 nm wavelength, pico-second pulsed laser source (Protolaser R, LPKF) was used to pattern gold onto foil. Electrodes have width of 1 mm and interspace of either 500 μm or 200 μm.

2.4. Characterization

Simultaneous thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) of the SnO_2 xerogel (dried sol) were carried out in a Mettler-Toledo TGA/DSC STARe System under 5 L/h air flow at 10 °C/min. Prior to characterization, the sol was heated at 80 °C for few hours in standard oven to obtain a xerogel, and then it was placed in open alumina pan crucible.

The viscosity and the surface tension were measured using Brookfield LVDV viscometer and goniometer (Apollo Instrument OCA200), respectively. The adjustment of ink rheology can be characterized by dimensionless Z number, which is the inverse of the Ohnesorge (Oh) number defined as in [4]:

$$Oh = \frac{\eta}{\sqrt{\gamma . \rho . a}}$$

where ρ, η, and γ are respectively the density, dynamic viscosity, and surface tension of the fluid and "a" is a characteristic length (diameter of nozzles 21.6 μm). Z must be between 1 and 10 for stable drop formation.

Finally, electrical characterization of the printed sensor containing three SnO_2 layers, with electrodes spacing of 200 μm and 500 μm, was performed using different CO concentrations, at 300 °C in dry air.

3. Results

Figure 1 shows weight loss and heat flow of the sol as a function of temperature as obtained from TGA/DSC. A weight loss is observed between 100 and 210 °C which can be most likely linked to the evaporation of water molecules, acetic acid (Tb 118 °C) and ethylene glycol (Tb 197 °C). This weight loss coincides with two endothermic peaks detected in the DSC curve. The first peak from 90 °C corresponds to the evaporation of water molecules and bounded acetate groups, and the second one at 200 °C corresponds to the evaporation of ethoxy group that are chemically linked to tin metal [3]. Finally, an exothermic peak at 320 °C observed on DSC curve is associated with the formation of stable SnO_2 [5].

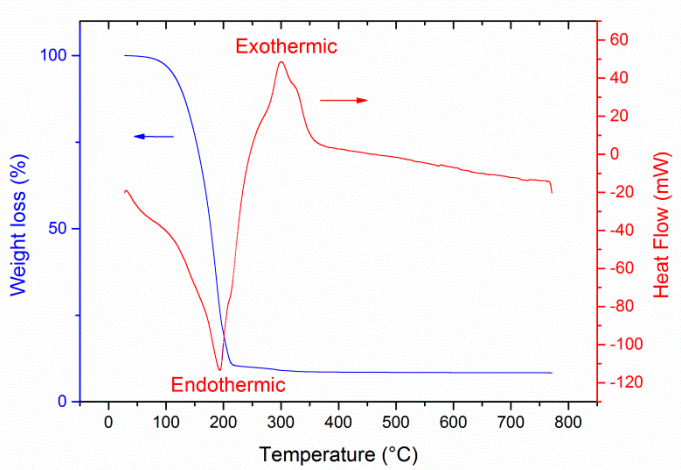

Figure 1. TGA/DSC thermograms of SnO_2.

For printing, a liquid ink from the sol was prepared by adjusting the rheology. A combination of four solvents as ethanol, ethylene glycol, glycerin and 2-isopropoxyethanol was used to adjust the viscosity to 10 cP and the surface tension to 32 mN/m. Z value was 2.7 indicating the good printability of the Ink.

A 5 × 5 mm^2 square shape of SnO_2 was printed onto Upilex and over gold electrodes 3 times, by introducing an annealing step at 350 °C between every single print to avoid cracks formation. The printed film was sintered at 350 °C for 1h with heating ramp of 5°/min. The sensor layout is presented in Figure 2.

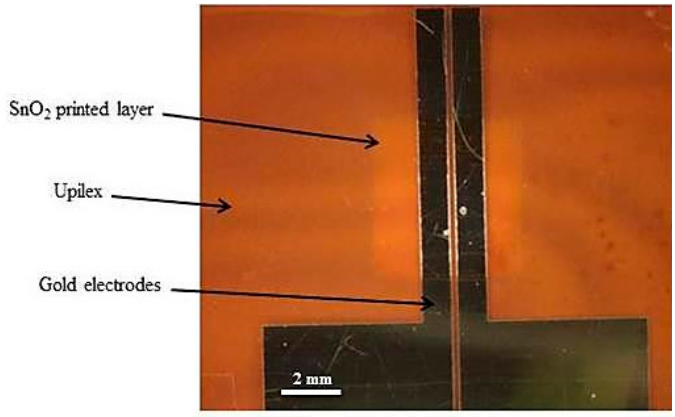

Figure 2. Sensor layout observed by binocular microscope.

Figure 3 shows the response of SnO_2 flexible sensors with electrodes spacing of 200 µm and 500 µm, at 300 °C. The conductance increases upon exposure to different concentration of CO gas (20–100 ppm) (Figure 3a), and it drops and returns to its original state in a few minute when the injection of CO gas is stopped in the testing atmosphere, indicating that the gas sensor has a significant and reversible response for different CO concentrations. Test bench configuration did not allow estimating any response time due to significant dead volume. The relative response defined as $(G-G_0)/G_0$ where G_0 corresponds to conductance value of SnO_2 under air just before the CO injection, and G corresponds to the electrical sensor conductance when exposed to CO gas (Figure 3b) shows that the sensors are quite sensitive in the range 0–60 ppm, but rapid signal saturation occurs for higher CO concentrations. Finally, comparing electrode spacing, either 200 or 500 µm, it can be observed that the response to CO increases by decreasing the electrodes spacing. This correlation, between the electrodes geometry and the gas sensor performance, is compatible with the results discussed in the literature. Indeed, the sensor response increase when the spacing between the electrodes is decreased [6].

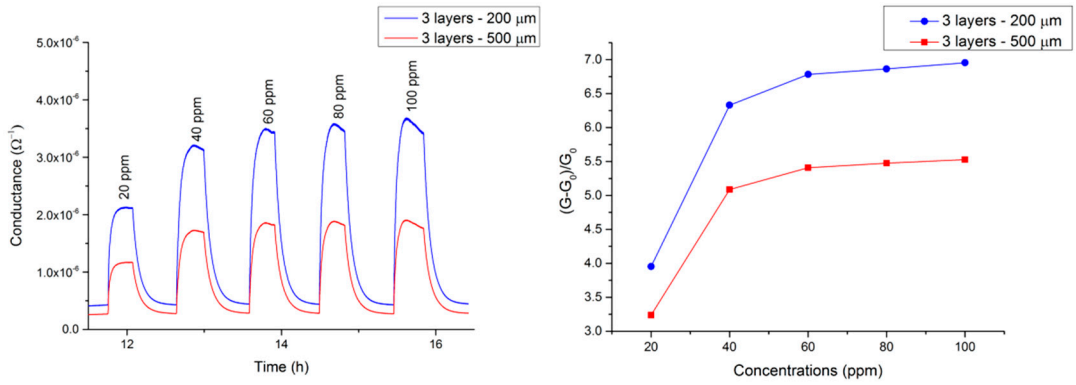

Figure 3. Response of SnO_2 thin film (three layers), with electrodes spacing of 200 µm and 500 µm, upon exposure to different concentrations of CO gas at 300 °C; (**a**) Conductance versus time; (**b**) relative response versus CO concentration.

4. Conclusions

Flexible SnO_2 gas sensors were successfully prepared by inkjet printing technology. SnO_2 precursor solution was synthetized using aqueous sol-gel method. Thermal analysis by TGA/DSC of synthetized sol show that a crystallized structure of SnO_2 could be obtained at 350 °C, which is entirely consistent with our flexible substrate. Preliminary electrical characterizations have demonstrated that the deposited layer by inkjet has adequate properties for gas sensing. We are working now on printing gold electrodes and metallic heater to manufacture a fully inkjet flexible gas sensor.

Conflicts of Interest: The authors declare no conflict of interest.

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