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Synthesis and Inkjet Printing of SnO_2 Ink on a Flexible Substrate for Gas Sensor Application †

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Abstract: Sol based SnO_2 precursor was synthetized by aqueous sol-gel route, then transformed into a stable ink with appropriate viscosity and surface tension to be inkjet printed and sintered at relatively moderate temperature. Plastic foil with thickness of 50 µm was selected as substrate for its high thermal resistance and stability (Upilex-50S). Prepared sol and formulated ink were both characterized by analytical techniques; electrical measurements were performed on the printed sensing film to characterize the response to CO gas in different concentrations, at working temperature of 300 °C.

Keywords: SnO_2; inkjet printing; printed electronics; flexible substrate; gas sensor

1. Introduction

Flexible electronics command a prominent position and are expected to meet emerging technological demands compared to rigid electronics [1]. Particularly, the manufacture of flexible gas sensors based on metal oxide thin film seems to be special and presents an interesting perspective for the progress in many fields especially the smart food packaging [2,3]. However, it is subject to restrictions as it requires high operating temperature which is not compatible with plastic foils. Tin dioxide (SnO_2) is a wide gap semiconductor (3.6 eV) widely used as gas sensor [4] because of its high chemical stability, low cost, rapid response and ease of integration during sensor design. In comparison with other thin film coating technologies used for manufacturing of gas sensor [1], inkjet printing technology is attracting a special attention for the manufacture of electronic components [5] because it has the advantage of being fast, accurate and inexpensive, with low materiel wastage. In the present work, inkjet was adopted as a deposition technique in order to print a flexible tin oxide gas sensing films. A stable sol was synthetized by sol-gel process, and used as precursor ink with appropriate viscosity and surface tension. Thermal and microstructural analyses of elaborate sol were studied.

2. Materiel and Methods

2.1. Sol Preparation

SnO_2 precursor solution was prepared using aqueous sol-gel route [6]. Tin chloride was dissolved in deionized water, then certain amounts of NH_3 (25%) solution were added dropwise in order to remove the chloride ions. The solid tin hydroxide was recovered by Büchner filtration (0.7 µm filter paper) and washed several times with diluted NH_3 solution. Then the filtered precipitate

was peptized by acetic acid solution and 40 mL of ethylene glycol were added. After that, 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 is 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 and Glycerin. SnO_2 ink was printed onto a polyimide foil named Upilex using commercial Dimatix printer (DMP-2800 Fujifilm) with 16 nozzles cartridges of 10 picoliter drop volume (DMC-11610).

2.3. Substrate Preparation

Gold electrodes with thickness of 80 nm were sputtered directly onto Upilex through a mask. Prior to printing, the polyimide was cleaned by acetone, ethanol and water and dried in an oven at 120 °C for few minutes. Finally, the surface of the substrate was treated by UV-O_3 (Nanonex Ultra-100) in order to adjust its surface energy.

2.4. Characterization

Thermal analyses of the obtained sol were carried out by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC), from 25 °C to 800 °C (Mettler Toledo). Microstructural characterization of the SnO_2 thin film was performed using X-ray diffractometry (Siemens D5000). The viscosity and the surface tension were measured using Brookfield LVDV viscometer and goniometer (Apollo Instrument OCA200), respectively.

The behavior of liquid drop can be characterized by the Ohnesorge (Oh) number defined as in [7]:

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

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). A dimensionless constant Z is defined as the Multiplicative inverse of Oh number. Z must be between 1 and 10 for stable drop formation.

Finally, electrical characterization of the printed sensor was performed using 50 ppm and 100 ppm of CO gas, at 300 °C in dry air.

3. Results

Figure 1 shows weight loss and heat flow of the sol as function of temperature as obtained from TGA/DSC. A weight loss between 100 and 210 °C is clearly observed which is related to the removal of acetic acid and ethylene glycol. These two evaporation phases are associated with two endothermic peaks as observed in the DSC curve. The first peak at 90 °C corresponds to the removal of the weakly bound acetate groups and the second one at 200 °C corresponds to the removal of the ethoxy bounds that are linked chemically to the tin metal. Finally, an exothermic peak at 320 °C observed on DSC curve is associated with the formation of stable SnO_2 [8].

X-ray diffraction analysis confirms the rutile structure of crystallized SnO_2 annealed at 350 °C. The grain size of SnO_2 film after annealing was estimated to be approximately 4.5 nm ± 0.1 nm using Scherrer formula. It increases to be 4.8 nm ± 0.1 and 8 nm ± 0.1 at 400 °C and 500 °C respectively. Figure 2 shows that the diffraction intensity of SnO_2 increases when annealing temperature is increased.

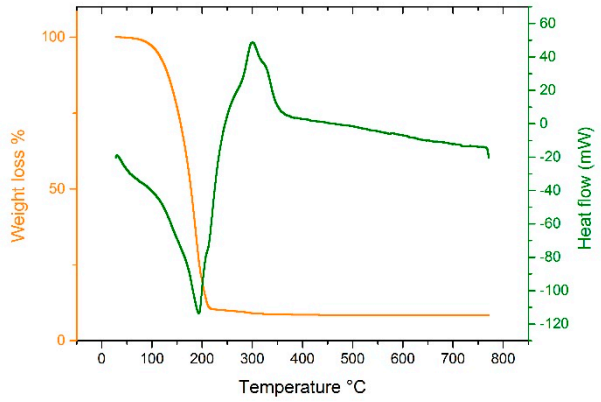

Figure 1. Thermal analysis by TGA/DSC of the sol based SnO_2.

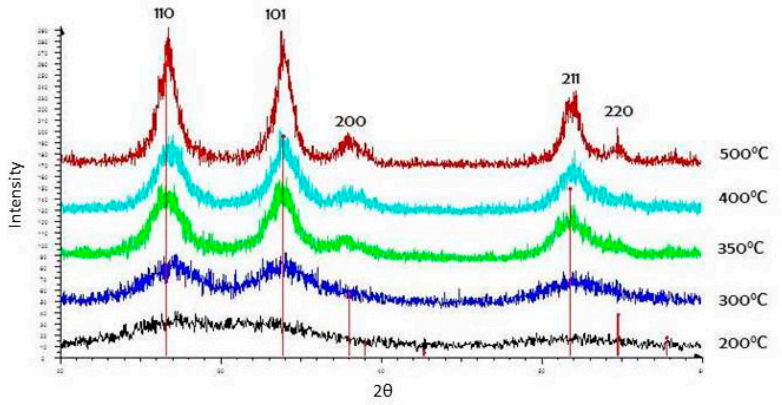

Figure 2. XRD patterns of SnO_2 at different temperatures.

For printing, a liquid ink from the sol was prepared by adjusting the rheology. A combination of three solvents as ethanol, ethylene glycol and glycerin 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.

The SnO_2 ink was then printed onto plastic foil that contain 80 nm thick gold electrodes and heated at 400 °C for 1 h.

Figure 3 reports the conductance variation of printed SnO_2 sensor when two concentration pulses of CO gas (100 ppm and 50 ppm) were fed into the test chamber at a working temperature of 300 °C. This result demonstrates that the deposited layer by inkjet has adequate propreties for gas sensing.

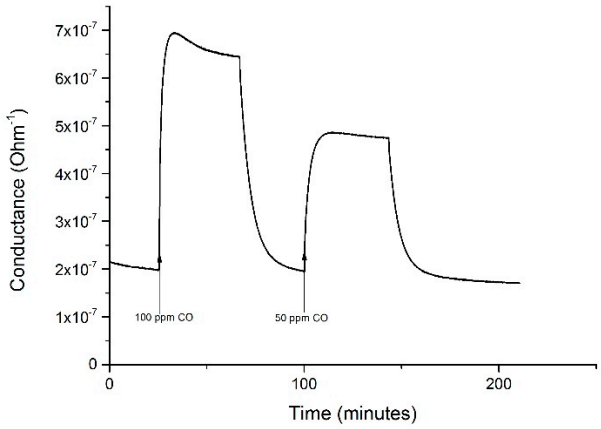

Figure 3. Response of SnO_2 thin film on flexible substrate to CO gas at working temperature of 300 °C.

4. Conclusions

Flexible SnO_2 gas sensors were successfully prepared by inkjet printing. SnO_2 precursor solution was synthetized using aqueous sol-gel method. Thermal analysis by TGA/DSC and microstructural analysis by XRD of synthetized sol show that a crystallized structure of SnO_2 could be obtained at 350 °C, which is entirely consistent with our plastic substrate. We are now working on the optimization of the SnO_2 printed layers and on printing a metallic heater to manufacture an entire flexible gas sensor.

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