

Fabrication of flexible gas sensor based on tin oxide by inkjet printing technology

O.KASSEM^{1,2*}, M.SAADAOUJ², M.Rieu¹, J.P.Viricelle¹

¹ *École Nationale Supérieure des Mines, SPIN-EMSE, CNRS:UMR5307, LGF, F-42023 Saint-Étienne, France*

² *Ecole Nationale Supérieure des Mines de Saint Etienne, CMP-EMSE, F-13048 Gardanne, France*

*Correspondence: omar.kassem@emse.fr; Tel.: +33 4 42 61 67 66

Abstract

In this work, a flexible tin oxide (SnO₂) gas sensor was successfully fabricated by inkjet printing technology. This thin film deposition technique requires the formulation of stable suspensions with specific fluidic properties. Sol-gel method was applied to synthesize a stable sol based on tin oxide, then transformed into ink with the appropriate rheological properties to be printed using a drop-on-demand piezoelectric inkjet printer. Thermal analysis by TGA/DSC and microstructural analysis by XRD of synthesized sol show that a crystallized structure of SnO₂ could be obtained at 350°C, which is lower than crystallization temperatures of SnO₂ previously reported in the literature, and entirely consistent with our plastic substrate. The printed thin-film was then sintered at 350°C on a flexible plastic (Upilex-50S).

Key words: Flexible gas sensor, SnO₂ ink preparation, Inkjet Printing

Introduction

In recent years, a significant advance in the development and implementation of flexible sensors has demonstrated the increasing utility of these special type 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 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 synthesized 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.

Experimental part

The first step consists in synthesizing a stable sol from a precursor based on a tin salt by aqueous sol-gel route using acetic acid and ethylene glycol as complexing ligands. 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 in order to investigate the evaporation of solvents and crystallization of SnO₂.

Once the sol is synthesized, it is transformed into ink with an appropriate rheology to satisfy the printability criteria of the Dimatix printer (DMP-2800 Fujifilm). Viscosity and surface tension were tuned by adding certain proportions of solvents and additives. To prepare sensor electrodes, gold was deposited on Upilex by evaporation under vacuum, and then a 1064 nm Laser beam was used to pattern gold electrodes onto foil with an interspace of 200µm. SnO₂ ink was printed onto these electrodes using commercial Dimatix printer (DMP-2800 Fujifilm), and heated at 350°C for 1 hour in oven. Electrical characterization of the fabricated sensor was

performed using different concentrations of CO gas, at 300°C in dry air.

Results and Discussion

Figure 1 shows weight loss and heat flow of the sol as a 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 evaporation of the weakly bounded acetate groups and the second one at 200°C corresponds to the evaporation of ethoxy bounds [2]. Finally, an exothermic peak at 350°C observed on DSC curve is associated with the formation of stable SnO₂. This crystallization temperature is well suited for plastic foil.

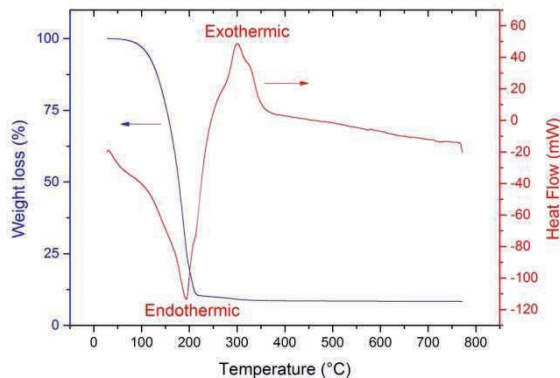


Figure 1: TGA/DSC thermograms of the SnO₂ sol

Once the sol is synthesized, it is transformed into ink with an appropriate pH, viscosity and surface tension. A combination of three solvents as ethanol, ethylene glycol and glycerin was used to adjust the viscosity to 10cP and the surface tension to 32mN/m. The adjustment of ink rheology in regards to solvent can be characterized by dimensionless Z number, which is the inverse of the Ohnesorge (*Oh*) number defined as:

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

where ρ , η , and γ are respectively the density, dynamic viscosity, and surface tension of the fluid and “a” is a characteristic length of the cartridge nozzle [3]. Z must be between 1 and 10 for stable drop formation

A SnO₂ ink with a Z number of (2.7) was successfully printed onto Upilex between two gold electrodes and sintered at 350°C for 1h.

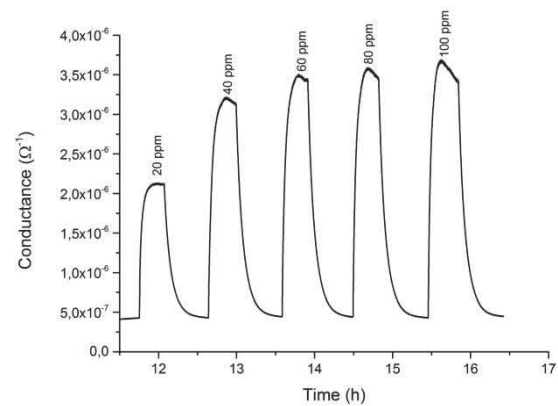


Figure 2: The change of conductance of SnO₂ thin film, upon exposure to different concentrations of CO gas in dry air at 300°C.

Figure 2 shows the response of SnO₂ flexible sensor at 300°C. The conductance increases upon exposure to different concentration of CO gas (20-100ppm), and it drops rapidly and returned to its original state when the injection of CO gas is stopped in the testing atmosphere in each cycle, indicating that the gas sensor has a fast and reversible response for different CO concentrations.

Conclusion

A flexible SnO₂ gas sensor was successfully prepared by inkjet printing. SnO₂ precursor solution was synthesized using aqueous sol-gel method. Thermal analysis by TGA/DSC has shown that a crystallized structure of SnO₂ could be obtained at 350°C, which is entirely consistent with our plastic substrate. Electrical characterizations have demonstrated that the deposited layer by inkjet has adequate properties for gas sensing. We are working now on printing a metallic heater and electrodes to manufacture a fully inkjet flexible gas sensor.

References

- [1] Kenry, J. C. Yeo, and C. T. Lim, “Emerging flexible and wearable physical sensing platforms for healthcare and biomedical applications,” *Microsyst. Nanoeng.*, vol. 2, no. 1, Dec. 2016.
- [2] H. Köse, Ş. Karaal, A. O. Aydın, and H. Akbulut, “Structural properties of size-controlled SnO₂ nanopowders produced by sol-gel method,” *Mater. Sci. Semicond. Process.*, vol. 38, pp. 404–412, Oct. 2015.
- [3] B. Derby, “Inkjet Printing of Functional and Structural Materials: Fluid Property Requirements, Feature Stability, and Resolution,” *Annu. Rev. Mater. Res.*, vol. 40, no. 1, pp. 395–414, Jun. 2010.