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Development of Metallic inks for the Fabrication of a Flexible Metal Oxide Gas Sensors by Inkjet Printing Process

Le Porcher Bastien[1], Rieu Mathilde[1], Viricelle Jean-Paul[1]
[1] Mines Saint-Etienne, Univ Lyon, CNRS, UMR 5307 LGF, Centre SPIN, F-42023 Saint-Etienne, France

Corresponding Author: rieu@emse.fr

Summary:

This study focuses on developing a fully inkjet-printed gas sensor on a flexible substrate. The primary challenge lies in formulating metallic inks with long term stability, high concentration, and inkjet compatible properties. Two distinct methodologies were explored: one centered around nanoparticle-based synthesis, while the other one was particle-free. To achieve an operational sensor, numerous layers were deposited, ranging from gold electrodes to platinum resistance and a SnO_2 sensing layer. Every stage of the manufacturing process has been optimized , allowing to obtain a functional device.

Keywords: Nanoparticles synthesis, Metallic inks, Inkjet printing, Flexible electronic, SnO_2 sensing layer

Introduction

The context of this study is the preparation of a flexible gas sensor onto a plastic substrate, by inkjet printing. In order to get a full sensor, as shown in Fig. 1. semi-conductive metal oxide gas sensors are composed by a sensing material, here, tin dioxide. This layer allows the detection of different type of gas by measuring the resistance change of the semiconductor layer. This semiconductor layer is bridging two gold electrodes that are needed to acquire all the electrical measurement. Electrode are typically made of conductive material such as metals. Gold is frequently used in sensor fabrication field due to is low reactivity with gases. A heater is also printed on the back side of the heater. In this case, this heater is made of platinum layers connected to gold tracks and it is heating the sensor by using Joule effect.

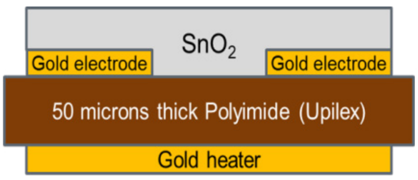

Fig. 1. Scheme of metal oxide gas sensor compositive layers [1]

SnO_2 inks and layers have been developed in previous works [1, 2]. Homemade metallic inks have now to be developed. The advantages of homemade inks comparing to commercial one's is that the compositions are controlled and no additives or pollutants are added.

All the intermediate steps of the metallic ink development involving particles synthesis, ink formulation, printing process, deposition, thermal treatment and coating characterization, will be discussed. At the end of the day, a fully inkjet printed sensor will be characterized.

Materials & methods

Gold nanoparticles (AuNPs) solutions have been made by an optimized Turkevich method [3] using Tanique Acid (TA) and Sodium Citrate (SC) in aqueous medium allowing to obtain 3.9mM solutions.

Platinum nanoparticles (PtNPs) solutions have been synthesized by reduction of a platinum salt by polyols reaction triggered by the presence of a 150°C ethylene glycol (EG) solution.

Both of these nanoparticles solutions have been formulated depending on their own properties (surface tension and viscosity) in order to obtain suitable ink for inkjet process. This was done by adding mixture of solvents to modify these initial values.

Particles free inks have also been developed based on metallic salt solvation in solvents mix, resulting in obtaining a concentrated gold ink and a concentrated platinum ink.

Finally, SnO_2 ink have been developed by a sol-gel process in presence of ethylene glycol that is allowing to obtain a ready to print tin dioxide ink [2].

All these steps were merged together to obtain a complete and functional gas sensor.

Results

The gold nanoparticles solution is composed by a 5 to 15nm gold particles as shown by the particle distribution. Addition of glycerol and isopropanol to the AuNPs solution led to decrease the surface tension from 73mN/m to 31.7 mN/m and to increase the viscosity from 1mPa.s to 14mPa.s. This ink was correctly printed after optimizing the waveform, the tension applied, the nozzle and platen temperature and the wettability of the substrate. A total number of layers of 100 was printed on PI foil and then dried at 110°C and then thermally treated at 350°C for 2 hours. Finally, coating was not continuous as shown by SEM image presented in Fig. 2.

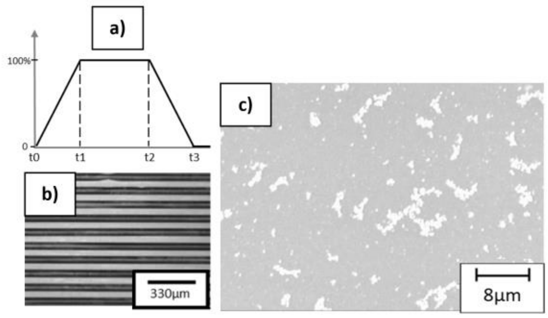

Fig. 2. a) waveform used for inkjet printing of AuNPs ink b) 1D lines obtained after deposition optimization and c) SEM image of 100 layers deposited AuNPs coating

Particle free ink is composed by $HAuCl_4$ directly dissolved in a mixture water, ethylene glycol and isopropanol. The viscosity and surface tension of this ink were measured and are 32 mN/m and 14 mPa.s. All the printing parameters were also optimized and then 60 layers were deposited. Coatings obtained after thermal treatment at 350°C, shown on the Fig. 3., are conductive. The measured resistivity is about $1.0\text{x}10^{-7}$ Ω.m.

Fig. 3. Deposit of 60 layers of particle free gold ink after thermal treatment at 350°C for 2 hours

Combination of AuNPs made ink and precursor made ink make possible to deposit homogeneous, high resolution, and conductive gold electrodes onto polyimide foils.

Polyvinylpyrrolidone (PVP) stabilized platinum nanoparticles has been synthesized by reduction of H_2PtCl_6 salt in near boiling point ethylene glycol solution [4]. Optimized synthesis led to obtaining concentrated EG-PtNPs solutions. This platinum nanoparticles solution was mixed isopropanol and different solvents in order to reach a suitable surface tension and viscosity for the inkjet printing process. This formulation led to deposition of homogeneous and conductive platinum coating by inkjet printing.

Tin dioxide ink is made of $SnCl_2$ which is made to react with NH_4OH and CH_3COOH in order to substitute Cl atom by OH ligand and then CH_3COOH. In presence of ethylene glycol, an oligomeric net named tin glycolate is formed allowing particles to be stable in solution [2].

All these layers were cured at a maximum temperature of 350°C in order to not degrade the PI substrate. This complete device was characterized under reducing and oxidizing gases. Discussion on the benefits of homemade inks will conclude this work

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