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

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Summary:
This study focuses on developing homemade inks in order to prepare 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 can be made of platinum layers connected to gold tracks and it is heating the sensor by using Joule effect.

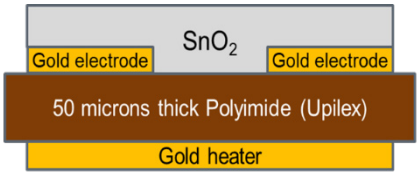

Fig. 1. Scheme of metal oxide gas sensor compositive layers [1]

In this work, homemade metallic inks have been 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 [1] 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 and deposition 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 was 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 73 mN/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 temperatures 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. [3]

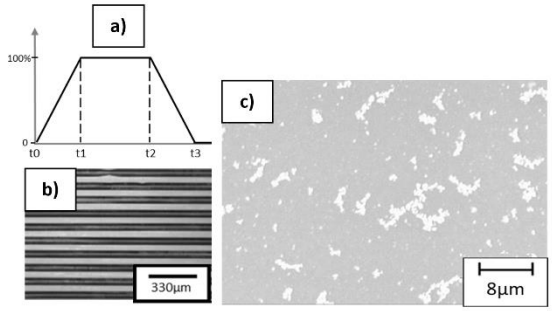

Fig. 2. a) waveform used for inkjet printing of AuNPs ink b) 1D lines obtained after deposition optimization and c) SEM image of 100 layers deposited AuNPs coating

A second goal ink was studied. Particle free ink was 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. Coating obtained after thermal treatment at 350°C, shown on the Fig. 3., is conductive. The measured resistivity is about $1.0x10^{-7}$ Ω.m.

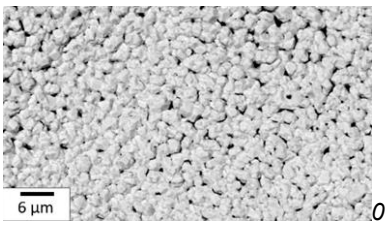

Fig. 3. SEM image of the deposit of 60 layers of particle free gold ink after thermal treatment at 350°C for 2 hours

Combination of AuNPs made ink and precursor made ink make possible to deposit homogeneous, high resolution, and conductive gold electrodes onto polyimide foils [3].

On the other side, platinum ink is developed. 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.

The SnO_2 material was prepared using sol-gel process, the $SnCl_2$ was dissolved in pure ethanol and the mixture was stirred and kept at 80 ◦C for 5 h in a closed vessel to form a transparent tin ethoxide solution ($Sn(OEt)_2$) [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.

Before evaluation of the responses under gases, the sensor was heated up at 350°C for 3 hours which was the working temperature. It was then exposed to reductive gas (CO) and oxidizing gas (NO_2), for 20 minutes and then a stabilizing time of 30 minutes between each gas injection. Gas concentrations were varied from 100 to 300 ppm. Absolute humidity, oxygen percentage and total gas flow were fixed at 1%, 20% and 30L/h respectively. After a short stabilization time, the sensor shows a rapid response to 100 ppm injection of CO. The same behavior is observed for 200 and 300 ppm of CO which mean the sensor is suitable for CO detection. For the NO_2, the response was observable for 200 and 300 ppm injection of NO_2.

Discussion on these homemade sensors will conclude this work.

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