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PHEMA functionalization of gold nanoparticles for vapor sensing: Chemi-resistance, chemi-capacitance and chemi-impedance

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ABSTRACT

A chemical sensor fabricated from gold nanoparticles and poly(2-hydroxyethyl methacrylate) (PHEMA) is presented and its chemi-resistive, chemi-capacitive and chemi-impedance performance is investigated. Detection of humidity and ethanol in the range of 2000–20,000 ppm has been made possible in all the above cases. The sensor was fabricated following a two step process utilizing ink-jet printing to deliver both nanoparticles and PHEMA on oxidized silicon substrates: first a layer of nanoparticles has been delivered on top of gold interdigitated electrodes followed by the successive deposition of PHEMA polymer. By controlling several key design parameters such as nanoparticle size, number of ink-jet printed gold nanoparticles and electrode spacing, the fabrication of chemical sensors with different sensing response and linearity is possible.

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1. Introduction

The application of nanomaterials in the field of bio-chemical sensing has become a hot research topic for the past years. Metallic nanoparticles [1], carbon nanotubes [2], polymers [3], metal oxide semiconductor [4], or hybrid materials composed of different nanomaterials [5] have already been widely investigated. Different sensing mechanisms like chemi-capacitance, chemi-resistance, and chemi-impedance have been studied, exhibiting good performance in sensitivity, selectivity or response speed [1–7].

Thin gold nanoparticle films of varying particle size, incorporating different capping ligands, have been applied to fabricate chemi-resistors for vapor sensing [1,8–10]. Also polymers like PHEMA, PMMA (poly(methyl-methacrylate)), PDMS (polydimethylsiloxane) and EPR (epoxydised novolac with UVI6974 photoacid generator from Shell) are known to have good chemi-capacitive response when exposed to different vapors [11,12].

On the other hand, ink-jet printing is a popular method in the conventional industry due to its fine and arbitrary pattern generation, non-contact injection, solution saving effects, and high repeatability and scalability. In recent years ink-jet printing has also been applied for the delivery/fabrication of nanomaterials [13–15].

In this paper, we present a hybrid material chemical sensor fabricated using gold nanoparticles and PHEMA polymer and investigate its chemi-resistive, chemi-capacitive and chemi-impedance response. Ink-jet printing was adopted for both nanoparticle and PHEMA delivery. A layer of nanoparticles was first deposited on top of gold interdigitated electrodes. A subsequent layer of PHEMA polymer was then printed on top of the nanoparticle film. PHEMA being in liquid phase flows inside the porous nanoparticle film forming a gold nanoparticle/polymer hybrid material. By controlling the size and the quantity of the gold nanoparticles, sensors of different sensitivity and linearity have been fabricated.

2. Experimental

All the experiments were performed under room temperature. Silicon wafers with 1 μm thermal SiO_2 were used as substrates. Gold electrodes of 50 nm in thickness were fabricated by e-gun evaporation using 7 nm of titanium as an adhesion layer. Using optical lithography and the lift-off process, interdigitated gold electrode patterns were fabricated using two different electrode gaps: 5 μm and 30 μm.

Gold nanoparticles stabilized in water and capped with citrate acid (having a negative surface charge) were purchased from British Bio Cell International and were used at the as-purchased concentration. During the experiment, nanoparticles having diameters of

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5 nm and 100 nm have been used. PHEMA polymer was bought from Sigma–Aldrich and prior to its printing it has been diluted in etlyl-lactate with a concentration of 0.5%.

The delivery of both gold colloid and PHEMA was performed by a Microdrop dispenser system (Microdrop Gmbh) [16]. The substrates were first functionalized with a solution of 3-[2-(2-aminoethylamino) ethyl amino] pro-pyltrimethoxysilane (AEEPTMS) [17]. It has been reported that this process leaves the surface hydrophilic with free amino groups (positively charged) directed away from the surface. As a consequence when printing the gold colloid onto this substrate the negatively charged citrate shell nanoparticles bond to the amino groups. Following this surface modification a layer of gold nanoparticles was deposited. By controlling the ink-jet printing frequency (a printing frequency of 5 Hz has been selected) and printing time, nanoparticle films of varying density can be achieved. Following the ink-jet printing of the gold colloid and the evaporation of its solvent (water), a second layer of PHEMA polymer was also delivered by ink-jet printing, on top of the gold nanoparticle film. Using a CCD camera built in the printing system, good alignment of the nanoparticle and PHEMA film is possible.

The hybrid gold nanoparticle and PHEMA film patterns were characterized by optical measurements and Field Emission Scanning Transmission Microscopy (FESEM). Electrical characterization measurements were performed using HP4140B picoampere meter, HP 4284A capacitance meter and HP 4192 ALF Impedance Analyzer. The evaluation of the sensor's response was performed in a small volume (4 mm^3) chamber where relative humidity and temperature are controlled to within 0.1% and 0.1 °C, respectively [11].

3. Results and discussion

3.1. Film formation and characterization

It has been observed that after the ink-jet printing of the nanoparticle solution and the evaporation of the solvent, the particles are self-assembled to the drop edges forming a ring like pattern, as it is shown in Fig. 1. The mechanism governing this "ring" pattern formation can be attributed to a capillary flow mechanism [18,19]. When the gold colloid is ink-jet printed on the SiO_2 surface, water starts to evaporate from the edge of the drop while the drop remains virtually "fixed" to its original shape. This pinning of the drop's contact line causes a flow, driving any solid material dispersed within the drop towards the edge.

The diameter of this nanoparticle ring can be tens of micrometer or millimeter and is dependent on the total number of ink-jet printed drops and on the delivery frequency. As we can see in Fig. 1(b), the printing of 1000 drops of gold colloid on SiO_2, using a deposition frequency of 5 Hz, forms a circle having a diameter of about 420 μm. When gold colloid was printed on SiO_2 previously patterned with gold interdigitated electrodes, the resulting drops become elliptical in shape due to the electrode patterns, as shown in Fig. 1(c).

During the experiments, it was found that by printing on substrates functionalized with AEEPTMS, the produced gold nanoparticle films have a much improved reproducibility and stability. We believe that this is due to the attraction of the negatively charged gold nanoparticles to the positively charged amino groups on the AEEPTMS monolayer. Also the contact angle between printed drops and the substrate will change due to the AEEPTMS functionalization, which can also account for the change in shape of the printed gold colloid drops.

A layer of PHEMA polymer was printed after the gold nanoparticle deposition. As it is shown in Fig. 2(a), hybrid structures consisting of gold nanoparticle matrices embedded in PHEMA films were formed. Gold nanoparticles of different size and printed films of different density were deposited during this experiment. By changing the total number of printed colloid drops, we can get different densities of gold nanoparticles. In Fig. 2(b) and (c), the contrast between two devices fabricated using different printing drop numbers is evident. By using 1000 drops, the nanoparticle film formed on the drop edge is discrete, but for 3000 drops the nanoparticle density on the edge becomes dense, forming a continuous nanoparticle micro/nano wire.

3.2. Sensor characterization

The response of these hybrid nanoparticle/polymer electrochemical sensors in the presence of chemical analytes is strongly

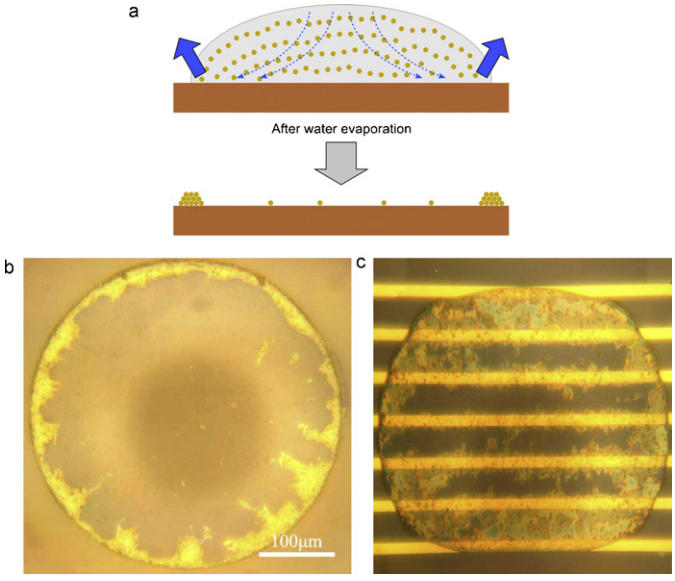

Fig. 1. Optical images of printed nanoparticle films: (a) schematic view of the self assembly of gold nanoparticles after water evaporation; (b) 1000 drops of 100 nm gold nanoparticles deposited on oxidized silicon substrate; (c) 1000 drops of 100 nm gold nanoparticles deposited on gold electrodes fabricated on top of oxidized silicon substrate.

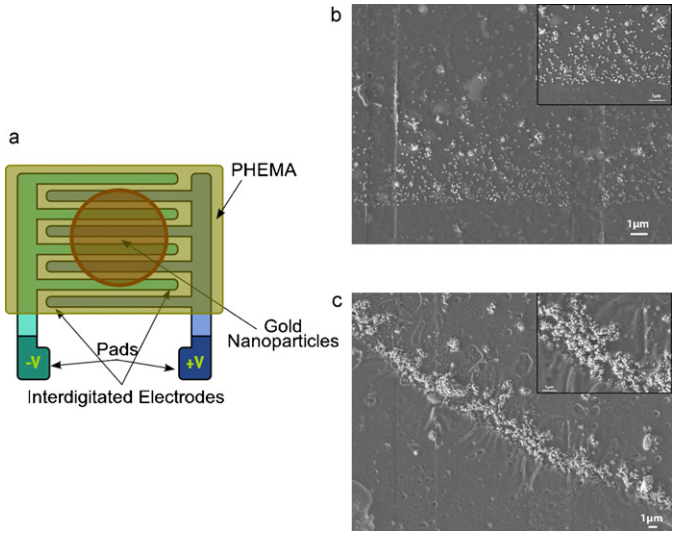

Fig. 2. FESEM images of gold nanoparticles/PHEMA hybrid material: (a) schematic of the nanoparticle and PHEMA hybrid material deposited on gold electrodes; (b) 1000 drops of 100 nm gold nanoparticle colloid and 1000 drops of PHEMA; (c) 3000 drops of 100 nm gold nanoparticle colloid and 1000 drops of PHEMA.

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