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Direct laser printing of graphene oxide for resistive chemosensors

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ABSTRACT

This work presents the pulsed laser printing of graphene oxide, and a subsequent thermal reduction step, aiming towards the fabrication of a chemical sensor device that operates at room temperature. Laser printing was performed using the Laser Induced Forward Transfer technique, which enables for the rapid and highly resolved deposition of liquid and solid phase materials, while printing conditions were also studied, in terms of optimum laser fluence regime and donor-receiver substrates distance, so as to avoid undesirable satellite debris, which has detrimental effects on the sensor performance such as adjacent sensor cross-talk, etc. The evaluation of the reduction efficiency was made by Fourier Transform Reflectance spectroscopy and electrical characterization of the thermally reduced devices. Finally, the response of the sensor upon exposure to water vapors is evaluated, and sensitivities down to 0.22%/%RH were recorded.

1. Introduction

In recent years great interest has arisen towards applying graphene, graphene oxide (GO) and reduced graphene oxide (rGO) in sensing devices. Single layer graphene is however an expensive, difficult to produce in large quantities, material. On the other hand, GO is low cost and may easily be produced using chemical exfoliation of graphite through oxidation, followed by dispersion in a solvent or water [1]. GO is an insulating material, owing to the presence of hydroxyl and epoxy functional groups on its basal plane and carboxyl groups at the edges, formed during the oxidation of graphite to graphite oxide, which may, however, be reduced to graphene by removing the oxygen-containing groups with the recovery of a conjugated structure. This may be achieved with a variety of methods including chemical reduction (e.g. using hydrazine [2,3]), thermal treatment [4–6], flash reduction [7], and more recently laser reduction [8,9]. Alternatively, graphene based materials have been also fabricated and/or microstructured by employing direct laser writing approaches, since lasers are versatile and offer the advantage of selectively patterning an active area, therefore combining GO and rGO features in highly integrated platforms that consist of conductive and non-conductive areas [10–13]. Sensors based on graphene have been reported, showing high sensitivity [14] and able to detect CO_2 [15], NO_2 and NH_3 [16]. Moreover, rGO sensors have been developed for the detection of explosive and chemical-warfare agent stimulants [17], low-concentration NO_2 and NH_3 [4,18], NO_2 and Cl_2 vapors [19] and highly sensitive humidity sensors [20], while they also have found their way even in wireless sensing in [21].

Laser Induced Forward Transfer (LIFT), is a versatile and non-destructive material deposition technique, belonging to the group of direct laser printing methods and has been employed for the deposition of both liquid and solid phase materials for a wide variety of electronic applications [22–25]. In the LIFT technique, usually a donor and a receiver substrate are used in contact or in close proximity to each other, to enable the transfer of the material under investigation. Chemical sensors and biosensors have been fabricated using LIFT, for the detection of octenol vapors [26], ethanol, acetone and methane [27] as well as methanol, water and ethanol vapors [28]. Furthermore, LIFT can be used not only as a stand-alone deposition technique but also as complementary to other laser processes, including laser ablation and laser sintering [29,30] presenting as unique advantages, high spatial resolution and high selectivity, regarding the printed or sintered features/parts, which is important in modern integrated circuit processing.

In this work a chemical sensor based on reduced graphene oxide is presented. The sensor is prepared by laser printing GO, using the LIFT technique, onto gold electrodes. A subsequent thermal reduction step is then performed so as to restore the conjugated sp^2 graphitic network. Fourier Transform Reflectance spectroscopy (FT-IR), and electrical characterization after the thermal treatment confirms the reduction of GO whilst sensor response is evaluated by exposing the sensor to controlled

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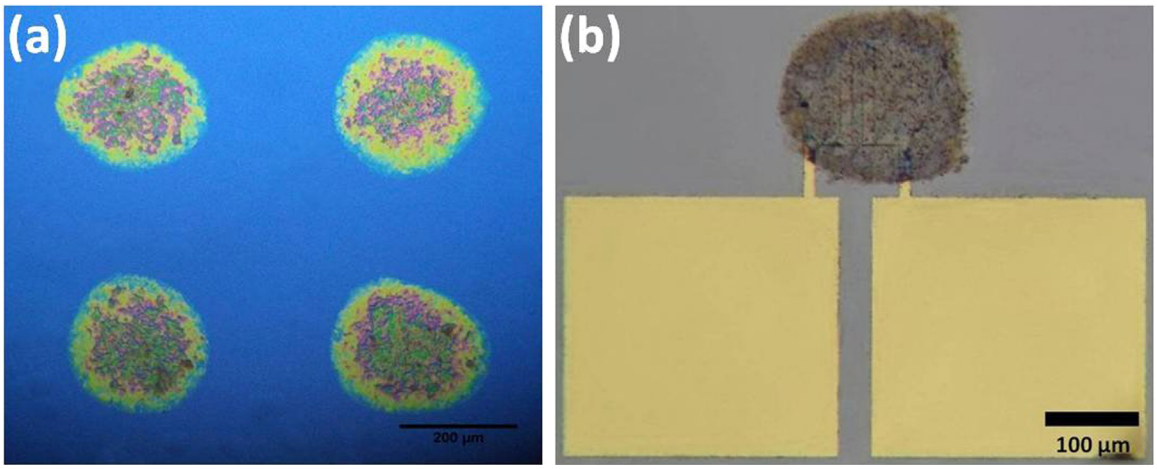

Fig. 1. (a) Array of GO droplets laser printed on a Si/SiO_2 substrate, (b) laser printed and thermally reduced GO droplet on Au contacts.

concentrations of ethanol, xylene and water vapors. We thus focus on the optimization of the laser printing process of GO on Si/SiO_2 rigid substrates using LIFT, which is a novel approach for the deposition of this carbon nanomaterial and on the demonstration of its applicability in resistive chemical sensors.

2. Materials and methods

For the laser printing experiments, a donor quartz substrate, with a thin Ti film as sacrificial layer, was coated with a small amount (~10 μl) of GO solution (Graphenea, 4 mg/ml in water) with a doctor blade. The experimental setup for LIFT can be found in detail in previous work [31]. Briefly, the laser beam was first expanded using a telescopic setup, while a circular mask of variable aperture has been used to select a homogenous part of the beam. Guided through a configuration of mirrors, the Gaussian beam was finally projected, using an objective lens (50 mm), on the donor substrate surface. For the sensors fabrication, gold electrodes were formed using an n-type (1–10 Ω cm) 100 mm Si wafer. The wafer first went through a thermal dry oxidation which resulted in the formation of a 20 nm thick silicon dioxide (SiO_2) layer. The electrodes were then formed on the SiO_2 surface using optical lithography with a mask containing electrode patterns of various electrode lengths (100, 800, 1600 μm) and spacing (5, 10, 20, 40 μm). A 60 nm thick layer of gold (Au) was then sputtered and lifted-off in order to form the electrodes. The wafer was finally cut in $5.6 \times 4.4\ mm^2$ dies that accommodated several pairs of electrodes. The sensors were packaged in Dual in Line (DIL) packages which were placed on a printed circuit board (PCB), that provided the necessary electrical connections to the outside world and was attached to a small volume chamber (7 mm^3). The relative humidity and temperature were controlled to within 0.1% and 0.1 °C respectively. In the gas-delivering unit, initially a dry nitrogen flux was split into a carrier and a diluting part with the help of two mass flow controllers. The carrier part was then bubbled through the analyte of interest and subsequently mixed with the diluting part to achieve the desired concentration level in the chamber. The sensor resistance was monitored using a HP 34401A digital multi-meter. The whole system was controlled via a PC using Labview. The FT-IR measurements were carried out using a Bruker IFS 66 v/S spectrometer and measured at the frequency range of 400–4400 cm^{-1} (mid-IR) at room temperature with a spectral resolution of 2 cm^{-1}. Electrical measurements of the laser printed graphene oxide samples were carried out in ambient conditions by the two-probe method, using an HP 4140B picoamperometer and a wafer probe station with a dark box to provide shielding from ambient light. The morphology of the laser printed features has been investigated through Atomic Force Microscopy (AFM) measurements (Veeco diInnova) and Scanning Electron Microscopy (SEM, FESEM Nova NanoSEM 230). Optical microscopy images were taken using an Optika B-353 MET Microscope, equipped with a CCD camera.

3. Results and discussion

3.1. Pulsed laser printing and thermal reduction of graphene oxide

GO was laser printed using single pulses produced by the 4th harmonic (266 nm) of a pulsed Nd:YAG laser ($\tau = 4$ ns, 2 Hz), at a range of different laser fluences (100–500 mJ/cm^2) first on bare Si/SiO_2, aiming towards the optimization of the laser printing parameters. The fluence study, showed that between 150 and 400 mJ/cm^2, well defined GO droplets can be deposited, while below 120 mJ/cm^2 no deposition was observed indicating the fluence threshold and above 500 mJ/cm^2 laser printing results in irregularly-shaped deposits. The distance between the donor and the receiver substrates was kept at 150 μm for all experiments, while Fig. 1(a) shows an optical image of GO laser printed on Si/SiO_2 at 250 mJ/cm^2. The image is taken after heating the sample at 100 °C for 10 min to remove residual solvent. It can be observed that relatively reproducible droplets can be printed using this laser fluence, resulting in well-shaped circular spots with a mean diameter of 200 μm (Fig. 2(a)) and average thickness of ~70 nm, as calculated using AFM measurements.

Following the laser printing on the bare Si/SiO_2, printing on the actual sensors was performed, followed by the thermal reduction process to reduce GO. This involved heating of the laser printed GO at 300 °C for 1 h. Thermal reduction introduces a significant number of vacancies and/or defects on the GO surface, which is mainly covered by hydroxyl and epoxy groups on its basal plane as well as carbonyl and carboxyl groups at the edges of the flakes [32,33]. These vacancies act as binding sites for the gaseous molecules [17,34] thus enabling the use of rGO in chemical sensors. In addition, the functional groups found on the basal plane are responsible for the disruption of the sp^2 hybridized carbon network directly affecting the electrical properties of GO [4]. After the thermal reduction step, employed in this study, it was observed -as expected- that contrary to the droplet coloration observed in Fig.1(a), the color of the laser printed droplets has turned into a brown-black shade owing to the thermal reduction process (Fig. 1