

Multipurpose Sensing Platform Based on Laser-Reduced Graphene Oxide for Flexible and Ubiquitous Electronics

F. Romero¹, A. Rivadeneyra², E. Castillo¹,
M. Becherer², D.P. Morales¹ and N. Rodriguez¹

¹University of Granada, Campus Fuentenueva s/n, Granada (Spain). E-mails: franromero@correo.ugr.es, encas@ugr.es, diegopm@ugr.es, noel@ugr.es

²Technical University of Munich, Theresienstr. 90, Munich (Germany). Emails: almudena.rivadeneyra@tum.de, markus.becherer@tum.de

Abstract

We present a versatile sensing platform, intended for ubiquitous and flexible electronics sensing applications based on the controlled reduction of Graphene Oxide by a laser diode. This technique allows the fast and ecological production of reduced Graphene Oxide without the need of expensive lithography masks. We will show results of the conductivity calibration by the photothermal reduction power, as well as the electrical characterization of the bare samples. Finally, a simple demonstrator of the platform based on an ultra-low power System on Chip (SoC) is introduced.

1 Introduction

After the award of the Nobel Prize to Geim and Novoselov for the isolation of single Graphene flakes in 2010, this material has stirred the world of research due to its unique spectrum of physical, chemical and electrical properties [1]. However, the huge expectations deposited have not been yet unfolded into real-world applications, due, in part, to the lack of a production technique for large crystalline sheets. The momentum created by Graphene research has driven the interest on other two-dimensional materials such as the one targeted in this work: the Graphene Oxide (GO) which, although can be considered a highly defective form of Graphene, preserves some of its unique properties: structural flexibility, transparency, and high conductivity when it is reduced. Several works have demonstrated the potential application of reduced-GO to implement selective sensors for different gas species [2,3]. Furthermore, the potential application of the GO can be expanded beyond the chemical sensors: reduced-GO presents a perfectly linear resistivity-temperature dependence or strain-capacitance dependence [4]. This versatility paves a new way for the integration of GO/reduced-GO conformal sensors in a broad scope of realistic applications. In this perspective, we present a multipurpose sensing platform based on a Programmable System on Chip (PSoC) which, thanks to its reconfigurable features, facilitates the integration of graphene-based analog sensors, bringing them closer to the end-user applications.

After this introduction the manuscript is divided as follows: Section 2 introduces the fabrication process of rGO-based flexible sensors, with the main focus on temperature transducers. Section 3 presents a prototype of a portable monitoring

system which integrates a rGO thermal transducer. Finally, the main conclusions are drawn in Section V.

2 Flexible thermal transducer based on graphene oxide reduced by laser

GO is basically a strongly oxygenated form of graphene flakes, intrinsically functionalized with hydroxyl (-OH) and epoxy (C-O-C) groups in the basal plane of the atoms [5], which can be synthesized from graphite powder by different approaches of Hummer's method [6]. For our experiments, the GO was diluted at a concentration of 4 mg mL^{-1} and subsequently sonic exfoliated for 30 minutes to obtain, primarily, single-layer GO. Then, the resulted aqueous solution was deposited with a concentration of $70 \text{ }\mu\text{L cm}^{-2}$ on a thin flexible polyethylene terephthalate (PET) substrate. Once the deposition is dried, it is turned into rGO through a reduction process, which is carried out by an *ad hoc* laser photothermal process. This method allows the simultaneous reduction and patterning of the raw material, with a resolution of $\sim 20 \text{ }\mu\text{m}$ at a wavelength of 550 nm in our experimental setup shown in Figure 1a.

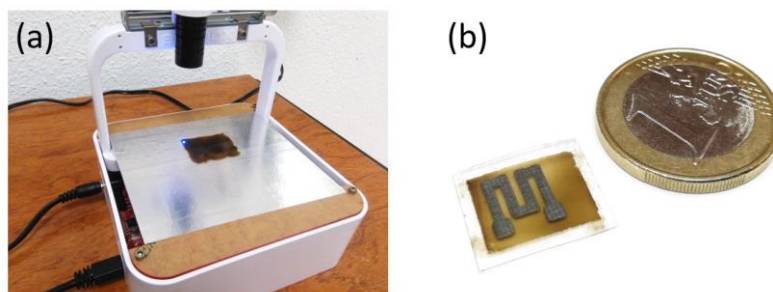


Figure 1. (a) Laser scribing (photothermal reduction) of Graphene Oxide. The laser output power as well as its movement are controlled by a computer software. (b) Final view of the rGO pattern onto the flexible substrate.

As seen in Figure 1b, the rGO sensitive layer can be clearly distinguished due to the change in the GO colour from a brownish tone to black, as a consequence of the reduction process. It is interesting to study how the GO, which is an insulator, turns into conductive rGO, as a result of annealing process of the sp^2 structure [7]. And moreover, the correlation of this process with the laser power; with the aim of achieving an effective GO reduction. Figure 2a shows the laser power dependence of the sheet resistance. When GO is reduced, its sheet resistance decreases exponentially from $>10\text{M}\Omega$ to $<1\text{k}\Omega$ in the range of [65, 105] mW. Therefore, the optimum values of laser power for the photothermal reduction are those in the range [90, 105] mW, where the sheet resistance tends to stabilise at a minimum value without overheating the container substrate.

On the other hand, it is well-know that the sheet resistance of the rGO also presents a strong temperature dependence [8]. This dependence is the basis of the thermal transducers developed in this work. The total resistance (R_T) of a rGO layer is given by:

$$R_T = R_s(T) \cdot (L / W) \quad (1)$$

where T is the temperature, L the transducer length and W its width. Figure 2b shows the resistance of two sensors with different physical dimensions ($W_1 = W_2$, $L_2 > L_1$); as seen, the R - T dependence of rGO is nearly linear and does not present hysteresis, which simplifies the definition of a calibration curve.

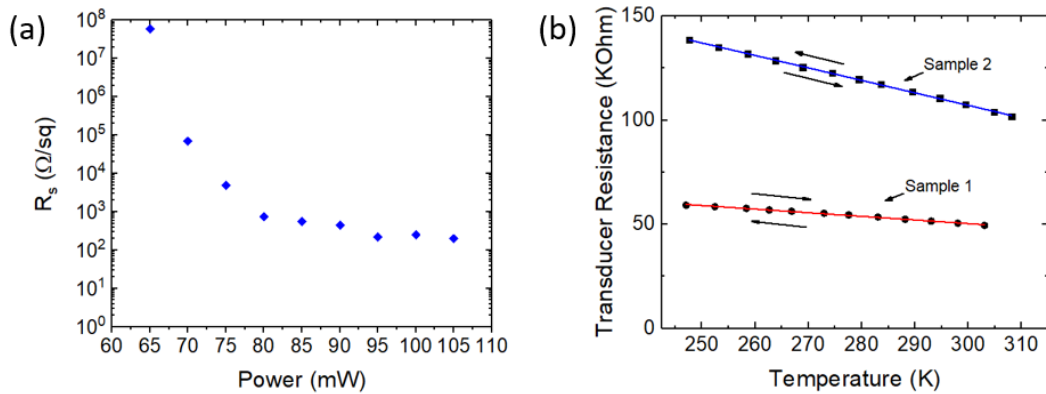


Figure 2. (a) Sheet resistance extracted using a point-contact method of the reduced GO as a function of the laser power ($\lambda = 550 \text{ nm}$). (b) R - T characteristic of two rGO temperature sensors ($W_1 = W_2$, $L_2 > L_1$).

3 Simple demonstrator: Ultralow power conformal thermistor

As a demonstrator of the potential of this technology, we present a complete room temperature monitoring solution based on a reduced Graphene Oxide thermistor, which transducer is fabricated according to the laser scribing technique previously described. The signal conditioning electronics is based on a low-power PSoC architecture [9], which combines programmable and reconfigurable analog and digital domains. Therefore, although for this particular example a temperature sensor is used, it could integrate a wide range of analog sensors by simple modifications of the device firmware.

The block diagram of the system architecture is detailed in Figure 3a. A simple way to measure the thermistor resistance is by means of a ratiometric resistor voltage divider, implemented by the sensor itself and a resistor of reference as represented in Figure 3. The voltage on the transducer is then monitored and amplified using Programmable-Gain Amplifiers (PGA) before its analog-to-digital conversion. The digital filter stage is the last step of the signal conditioning: it is convenient to remove the noise and the high frequency components of the voltage signal, thus getting the desired DC value from which R_T can be calculated.

The integration of the rGO thermistor and the sensing platform is shown in Figure 3b. As seen, the sensitive layer has been sealed using another PET film to avoid non-desired functionalization effects due to the contact with the measurement atmosphere; besides, two Cu contacts have been added to make easier the electrical access to the transducer. The platform also has wireless data transmission capability through a Bluetooth Low Energy (BLE, or Bluetooth 4.0) link, implemented by an external BLE module based on the BLEcore CC2540 [10].

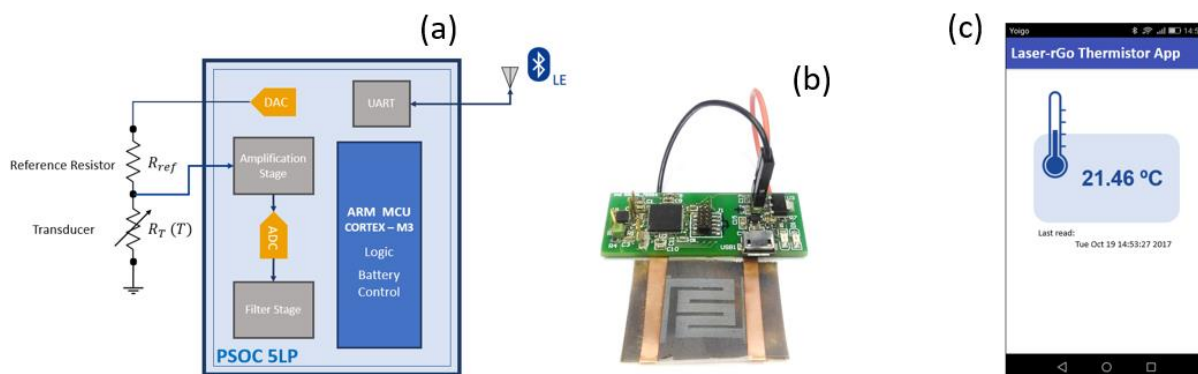


Figure 3. (a) Block diagram of the multi-purpose sensing platform based on the PSoC 5LP. (b) Portable platform for measuring temperature as a surface conformal patch. PCB size: 48 x 19 mm. (c) Android App screenshot.

For the BLE communication schema, the device is a peripheral which implements a thermometer GATT service, therefore the measured temperature can be monitored in real-time using a BLE central device. For this example of application an Android app (Figure 3.c) has been developed to establish the connection (bonding) and data visualization.

4 Conclusion

Laser-scribed reduced graphene oxide has been suited as a promising platform for the development of sensing applications. An actual application example has been demonstrated by implementing a low power temperature monitoring system which uses a flexible rGO transducer.

Acknowledgment

This work has been supported by the Spanish Ministry of Education, Culture and Sport (MECD) through the pre-doctoral grant FPU16/01451, the University of Granada through the scholarship “Initiation to Research”, the National Excellence Research Project TEC2017-89955-P and the European Union by the fellowship H2020-MSCA-IF-2017 794885-SELFSENS.

References

- [1] A. K. Geim, K.S. Novoselov: The rise of graphene, *Nature Materials* 2007, 6, 183-191. [2] Y. Wang, L. Zhang et al.: Ammonia gas sensors based on chemically reduced graphene oxide sheets self-assembled on Au electrodes, *Nanoscale Research Letters*, 2014, 9, 251. [3] D. Acharyya, P. Bhattacharyya: Highly efficient room-temperature gas sensors based on TiO₂ Nanotube-reduced graphene-oxide hybrid device, *IEEE Electron Dev. Lett*, 2016, 37, 656-659. [4] C. Marquez, N. Rodriguez, R. Ruiz, F. Gamiz: Electrical characterization and conductivity optimization of laser reduced graphene oxide on insulator using point-contact methods, *RSC Advances*, 2016, 6, 46231-46237. [5] D.R. Dreyer, S. Park et al.: The chemistry of graphene oxide, *Adv. Mater*, 2010, 22, 4467-4472. [6] W.S. Hummers, R. E. Offeman: Preparation of Graphitic Oxide, *J. Am Chem. Soc.*, 1958, 80, 1339-1339. [7] V. Strong, S. Dubin et al.: Patterning and Electronic Tuning of Laser Scribed Graphene for Flexible All-Carbon Devices, *ACS Nano*, 2012, 6, 1395-1403. [8] P.G. Ren, D.X. Yan, X. Ji, T. Chen, Z.M. Li, Temperature dependence of graphene oxide reduced by hydrazine hydrate, *Nanotechnology*, 2010, 22, 055705. [9] Cypress Semiconductor, PSoC® 5LP: CY8C58LP Family Datasheet, 2017. [Accessed on: 17/10/2017]. [10] Texas Instrument, 2.4-GHz Bluetooth® low energy System-on-Chip: CC2540F128, CC2540F256, 2013. [Accessed on: 17/10/2017].