ELECTRICAL RESPONSE OF THERMALLY REDUCED rGO GAS SENSORS EXPOSED TO AIR/NO_2 MIXTURES WITH DIFFERENT CONCENTRATIONS AND DIFFERENT WORKING TEMPERATURES

D. Bonanni[a], **L. Giancaterini**[b] , **C. Cantalini**[b], **E. Treossi**[c], **V. Palermo**[c], **F. Perrozzi**[a], **S. Santucci**[a] and **L. Ottaviano**[a*]

[a]Dipartimento di Fisica - University of LAquila, LAquila, Italy
[b]Dipartimento di Chimica e Ingegneria Chimica - University of LAquila, LAquila, Italy
[c]CNR ISOF, Bologna, Italy
*Corresponding author: *luca.ottaviano@aquila.infn.it*

Carbon-based materials like multi-walled carbon nanotubes (CNTs) [1] and, more recently, graphene [2] have shown high sensitivity to the detection of NO_2, NH_3, H_2O gases in concentrations below 5 ppm. In this paper we discuss preliminary electrical response of thermally reduced graphene oxide (rGO) gas sensor to NO_2 gas. GO sheets were deposited by drop-casting a solution containing a suspension of GO flakes followed by evaporation at 50°C of the drop on inter-digitated Pt electrodes previously patterned on Si_3N_4, with a sheet density high enough to create several inter-electrode bridging sites. Deposition was then followed by thermal partial reduction of the GO films at 200°C for 2 hours in N_2 gas atmosphere, thus enabling both the creation of percolation paths and lowering the high-energy charge binding sites density. Figure 1 shows a scanning electron microscopy (SEM) picture of the rGO film on the Si_3N_4 substrate. Almost 50% of the full available area is covered after deposition, while bridging of adjacent Pt electrodes (visible as light-gray stripes in the picture) by rGO petals (dark flakes over the substrate) is easily achieved throughout the whole substrate.
Electrical tests were carried out by exposing the rGO films to diluted Air/NO_2 mixtures (from 1 to 6 ppm NO_2) at different operating temperatures (from 25°C to 200°C). Figure 3 shows the resistance variation of a rGO film when exposed to 5 ppm NO_2 in dry air and temperatures ranging from 25°C to 200°C. Each temperature step in the picture last 180 minutes comprising 60' exposure to dry air, 60' exposure to 5 ppm NO_2 and 60' exposure to dry air.
The resistance in dry air (i.e. the base line resistance R_A) is represented at 25°C by the dotted line in the figure. When exposing the film to 5 ppm NO_2 the resistance decreases while degassing in dry air and 25°C, the film does not recover the base line resistance (R_A) as highlighted by the $\Delta 1$ gap in the picture.
The rGO electrical response to NO_2 gas causes a resistance decrease throughout the investigated operating temperatures, in agreement with the expectation of hole injection into a p-type semiconductor [3]. Namely, residual epoxide and carboxylic groups in graphene oxide are electron-withdrawing and promote holes into the conduction band, while additional p-type dopants, such as NO_2 molecules, enhance hole conduction and generate a significant resistance decrease.

With Increasing the temperature the desorption time of NO2 molecules decreases, this improves the base line recovery. Optimal degassing and recovery of the base line are obtained in the range 150-200°C. The sensor practical sensitivity S = (R_A-R_G)/R_A x 100, (R_G gas resistance at saturation, 5 ppm NO_2), is larger but with a slower response times at 25°C, whereas it is smaller but with faster response times at higher temperature. In particular S=28% (18%) at 200°C (RT). These results are in line with what previously reports on CNT based gas sensors [1] and chemically converted graphene using spin-coating of hydrazine dispersions on inter-digitated planar electrode arrays [4]. We stress that to operate a carbon based sensor a trade off between high sensitivity and fast, reversible response has to be achieved. It turns out that both CNTs and rGO films should be operated at temperature between 150° and 200°C with reasonable sensitivity and fast and reversible response. Fig. 2 shows the change of the electrical resistance of rGO film at 150°C and 200° when the NO_2 gas concentration is increased from 1 to 6 ppm in dry air. rGO film results to be sensitive down to 1 ppm NO_2. At 200°C the base line resistance is almost recovered after each exposure, though the sensitivity is decreased as respect at 150°C.
In conclusion, we have confirmed that thermally reduced GO films show *p-type* response when exposed to NO_2 gas in dry air. The time response is relatively slow at room temperature but can be accelerated at elevated temperatures at the expense of sensitivity. There are still open questions about the thermal stability of the film, which eventually can be improved by optimizing the thermally induced reduction procedure of GO films.

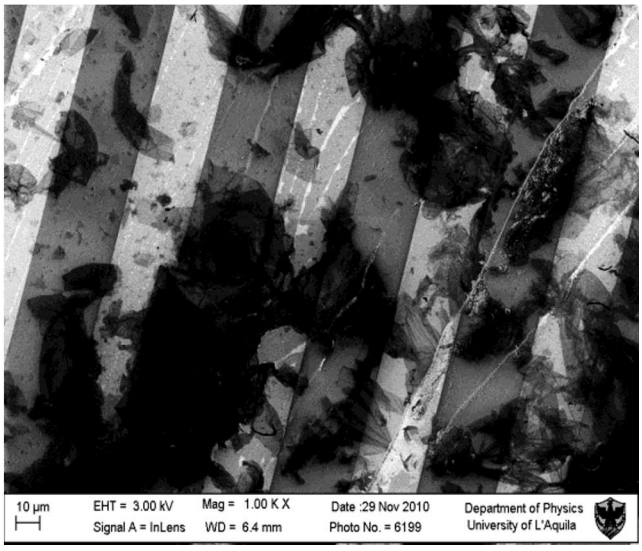

Figure 1: (SEM) picture of dark rGO flakes deposited on Si_3N_4 substrates with Pt Interdigital electrodes.

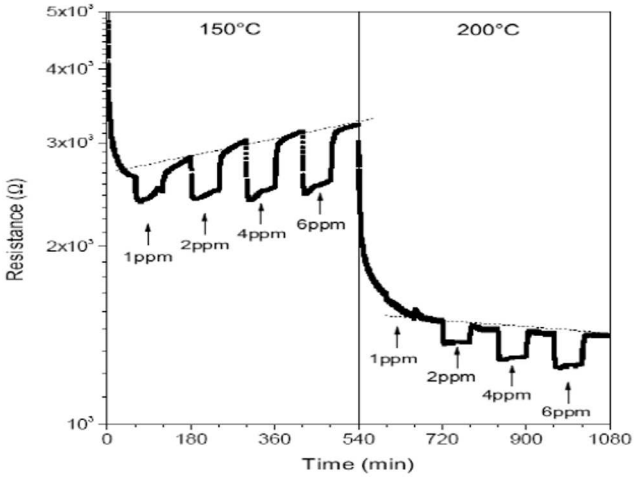

Figure 2: rGO film electrical resistance change at 150°C and 200°C. The NO_2 gas concentration is increased from 1 to 6 ppm in dry air. Dotted lines represent the resistance in dry air (reference base line).

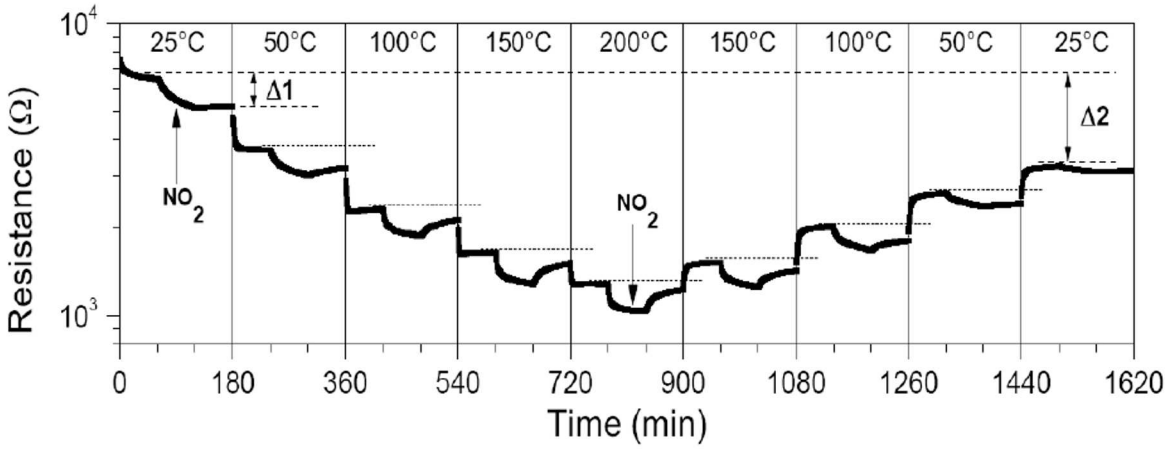

Figure 3: Resistance variation of a rGO film when exposed to 5 ppm NO_2 in dry air and temperatures ranging from 25°C to 200°C. Each temperature step in the picture lasts 180 minutes and comprises a 60' exposure to dry air, 60 min. exposure to 5 ppm NO_2 and 60 min exposure to dry air.

References

[1] L. Valentini, C. Cantalini, *et al.*, Appl.Phys. Letters, 82, (6) (2003) 961.
[2] K.R. Ratinac, W. Yang, *et al.*, Environ. Sci. Technol. 44 (2010) 1167.
[3] F. Schedin, A.K. Geim, *et al.*, Nat. Mater. 2007, 6 (9) (2007) 652.
[4] J. D. Fowler, M. J. Allen, *et al.*, ACS Nano, 3 (2) (2009) 301.