proceedings

Proceedings

A New Method to Prepare Few-Layers of Nanoclusters Decorated Graphene: Nb_2O_5/Graphene and Its Gas Sensing Properties †

Andrea Gaiardo [1,2,*], Nadhira Laidani [2], Hafeez Ullah [2], Giancarlo Pepponi [2], Michele Fedrizzi [2], Vincenzo Guidi [1], Pierluigi Bellutti [2], Barbara Fabbri [1], Cesare Malagù [1], Giulia Zonta [1], Nicolò Landini [1], Soufiane Krik [1], Ruben Bartali [2], Francesca Marchetti [2] and Matteo Valt [1]

[1] Department of Physics and Earth Sciences, University of Ferrara, 44122 Ferrara, Italy; guidi@fe.infn.it (V.G.); fbbbbr@unife.it (B.F.); malagu@fe.infn.it (C.M.); giulia.zonta@unife.it (G.Z.); nicolo.landini@unife.it (N.L.); soufiane.krik@unife.it (S.K.); vltmtt1@unife.it (M.V.)

[2] Center of Materials and Microsystems, Bruno Kessler Foundation, 38128 Trento, Italy; laidani@fbk.eu (N.L.); hafeezullah83@gmail.com (H.U.); pepponi@fbk.eu (G.P.); mfed@fbk.eu (M.F.); bellutti@fbk.eu (P.B.); bartali@fbk.eu (R.B.); fmarchetti@fbk.eu (F.M.)

* Correspondence: grdndr@unife.it; Tel.: +39-0461-314-451

† Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Published: 12 November 2018

Abstract: During the last decade, due to its excellent electrical, mechanical and thermal properties of chemically modified graphene has been extensively studied for many applications, such as polymer composites, energy-related materials, biomedical applications and sensors. The aim of this work is to evaluate the gas sensing performance of niobium oxide (Nb_2O_5) nanoclusters deposited onto few-layers graphene powder by magneton sputtering. Two different samples were prepared by changing electrical power of deposition. The materials were deeply morphologically, structurally and chemically characterized. Finally, they were deposited onto alumina substrates and their sensing properties were investigated vs. different gases, showing good sensing performance vs. ppm concentrations of NO_2 at room temperature.

Keywords: chemoresistive gas sensors; room temperature; functionalized graphene; NO_2 detection

1. Introduction

In the last years, the research in the gas sensor field experienced a significant boost. Gas sensors represent the crucial elements in gas detection systems and olfactory systems for several applications: environmental monitoring, safety and security, quality control of food production, medical diagnosis and so on [1,2]. Among the various innovative gas sensing materials investigated so far, 2D materials shown interesting chemoresistive behaviour, due to their excellent electrical, mechanical and thermal properties [3,4]. Graphene, an allotrope form of carbon, is the most famous 2D-material, consisted of a single layer of carbon atoms arranged in a hexagonal lattice [5]. This configuration rends graphene a zero-band-gap material since it has a small overlap between the valence and the conduction bands [6]. This property confers to the graphene unique chemical-physical characteristics, which have led it to be the most studied material of recent years [7,8]. Among the various advantage of this semiconductor, the high electrical conductivity allowed to explore its gas sensing performance at room temperature, which opens up to the development of ultra-low power consumption gas sensors [9]. However, gas-sensing responses vs. gases resulted to be low and the reaction kinetics slow, giving a high response and recovery times. To counteract these drawbacks, various investigations were carried out to verify the effect of adding functionalization on the graphene sensing properties [10].

In this work, we investigated the gas sensing performance of nanoclusters decorated few layer graphene (Nb_2O_5/graphene). This composite material was obtained by using magnetron-sputtering technique, in which a mixing system allow to deposit homogeneously Nb_2O_5 nanoclusters on graphene powder. Two different samples were prepared to investigate the influence of sputtering power deposition effect on the final Nb_2O_5 decorated graphene samples. The electrically characterization highlighted that Nb_2O_5/graphene sensors showed good and selective sensing properties vs. NO_2 both in dry and wet air, at room temperature.

2. Materials and Methods

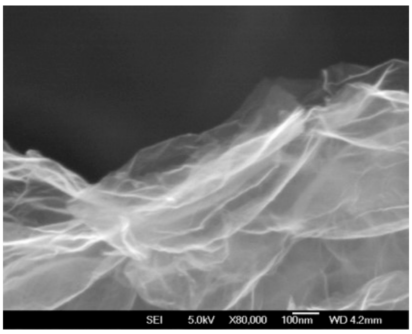
Nb_2O_5 deposits were grown at room temperature on graphene powder of 1.6 nm thickness purchased from Graphene Supermarket, by means of RF magnetron sputtering of a commercially available high purity Nb_2O_5 disc (99.99%) with 5 cm diameter. A powder vibration set up was employed to uniformly coat the graphene powder with Nb_2O_5. The deposition was carried out at a 6 Pa gas pressure, with a powder vibration frequency of 10 Hz, a deposition time of 30 min and varying the electrical power at the target (50 and 80) W.

Then, chemical, structural and morphological characterizations were carried out on samples. The morphology was analysed by Scanning Electron Microscopy (SEM, cold cathode JEOL Microscope, model JSM 7401-F) and Transmission Electron Microscopy (TEM, Hitachi H-800 model). The chemical characterization was performed by using a Kratos AXIS Ultra^{DLD} instrument equipped with a monochromatic Al Kα (1486.6 eV) x-ray source.

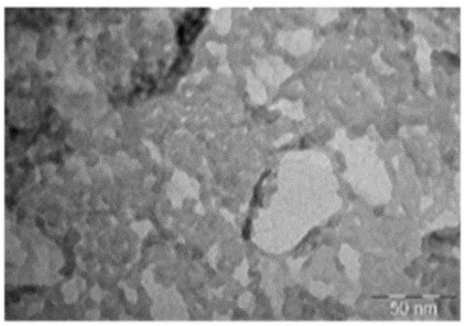
Nb_2O_5/graphene, graphene and Nb_2O_5 nanostructured materials were mixed with ethanol and deposited onto alumina substrates, provided with gold interdigitated electrodes and platinum heater, by means of drop coating technique. Gas sensing performance of devices were investigated in a suitable gas chamber, both in dry and wet conditions, vs. various concentrations of different gases, i.e., CO, H_2S, butanol and NO_2. Gases were from certified cylinder, and they were injected into the gas chamber by using mass flow controller. Gas sensing responses was calculated as $(G_{gas} - G_{air})/G_{air}$ for reducing behaviour and $(G_{air} - G_{gas})/G_{gas}$, where G_{air} is the conductance of sensing material in air and G_{gas} in the presence of gas.

3. Results and Discussion

In the Figure 1 SEM and TEM characterizations are shown. In Figure 1a is reported an image of the graphene flakes before the Nb_2O_5 deposition, meanwhile Figure 1b highlights the change of the sample morphology after the magnetron sputtering deposition, due to the formation of Nb_2O_5 clusters over the graphene flakes surface.



(**a**)



(**b**)

Figure 1. SEM and TEM images of (**a**) graphene and (**b**) graphene decorated with Nb_2O_5 nanoparticles (deposition power 80 W).

The XPS analysis was carried out to investigate how the deposition parameters influenced the Nb_2O_5 concentration on samples (Table 1).

Table 1. Atomic% of niobium on the Nb_2O_5/graphene samples.

Samples \ Parameters	Power (W)	Sample Vibration Frequency (Hz)	Deposition Time (min)	Nb/C Atomic Ratio (%)
Sample 1	50	10	30	3.2
Sample 2	80	10	30	7.3

As it can be seen, the change in the deposition electrical power strongly affected the Nb_2O_5 concentration in the material, giving a major concentration by using 80 W compared to 50 W.

The electrical characterization, in dry air, highlighted that Nb_2O_5/graphene sensors were insensitive to all gases tested, except for NO_2, at room temperature. The same measurements were repeated in presence of wet air, showing that the selectivity of the sensing material to NO_2 was not affected by the presence of moisture. Furthermore, the response values obtained in dry and wet air were comparable up to a relative humidity of 40% (Figure 2).

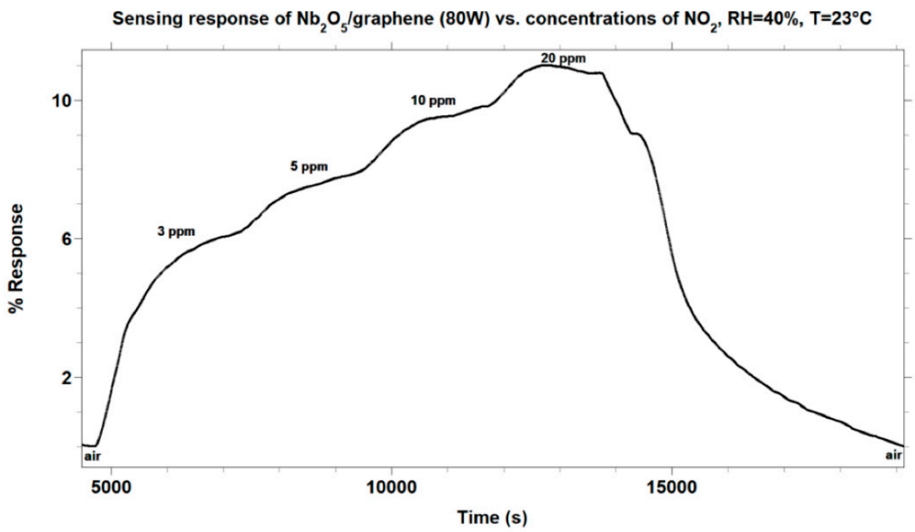


Figure 2. % Sensing response of a Nb_2O_5/graphene sensor (deposition electrical power 80 W) vs. 3, 5, 10, 20 ppm of NO_2, in wet air (RH% = 40%, T = 23 °C).

The response of sensors was strongly influenced by the concentration of Nb_2O_5 on the surface of the graphene flakes. Indeed, the sensor obtained by depositing the sample with the highest concentration of Nb_2O_5 showed responses 1.5 times higher than the less concentrated one (Figure 3).

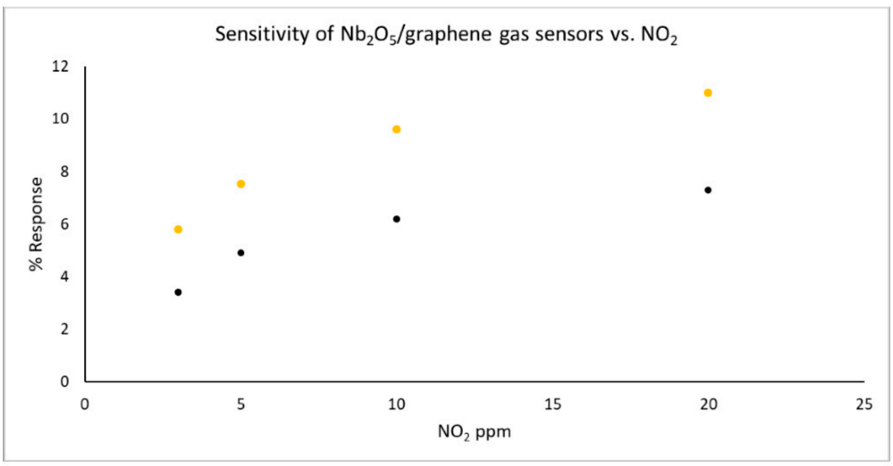


Figure 3. Sensitivity of Nb_2O_5/graphene sensors (yellow point = 80 W, dark points = 50 W) vs. NO_2 concentrations (RH% = 40%, T = 23 °C).

Further electrical characterizations have shown that sensors prepared using separately graphene and Nb_2O_5 showed a strong decrease in the sensing performance compared to Nb_2O_5/graphene sensors.

4. Conclusions

In this work, an innovative method to decorate homogenously graphene with Nb_2O_5 nanoparticles is presented, using magneton-sputtering instrument equipped with a powder mixing system. This material highlighted good sensing properties vs. NO_2 both in dry and wet air, at room temperature. The electrical characterization showed that the gas sensing performance of Nb_2O_5/graphene layers depended on the deposition parameters used in the magnetron sputtering, which were improved by increasing the deposition electrical power and thus the concentration of Nb_2O_5 nanoparticles on graphene flakes.

Author Contributions: A.G., N.L. (Nadhira Laidani) and G.P. conceived and designed the experiments; M.F., M.V., S.K., H.U., R.B. and F.M. performed the experiments; G.Z. and N.L. (Nicolò Landini) analyzed the data; P.B., V.G. and C.M. contributed reagents/materials/analysis tools; A.G., N.L. (Nadhira Laidani) and B.F. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zonta, G.; Anania, G.; Feo, C.; Gaiardo, A.; Gherardi, S.; Giberti, A.; Guidi, V.; Landini, N.; Palmonari, C.; Ricci, L.; et al. Use of gas sensors and FOBT for the early detection of colorectal cancer *Sens. Actuators B Chem.* **2018**, *262*, 884–891, doi:10.1016/j.snb.2018.01.225.
2. Gaiardo, A.; Fabbri, B.; Guidi, V.; Bellutti, P.; Giberti, A.; Gherardi, S.; Vanzetti, L.; Malagù; C; Zonta, G. Metal sulfides as sensing materials for chemoresistive gas sensors. *Sensors* **2016**, *16*, 296, doi:10.3390/s16030296.
3. He, Q.; Zeng, Z.; Yin, Z.; Li, H.; Wu, S.; Huang, X.; Zhang, H. Fabrication of flexible MoS_2 thin-film transistor arrays for practical gas-sensing applications. *Small* **2012**, *8*, 2994–2999, doi:10.1002/smll.201201224.
4. Borini, S.; White, R.; Wei, D.; Astley, M.; Haque, S.; Spigone, E.; Harris, N.; Kivioja, J.; Ryhänen, T. Ultrafast graphene oxide humidity sensors. *ACS Nano* **2013**, *7*, 11166–11173, doi:10.1021/nn404889b.
5. Castro Neto, A.H.; Guinea, F.; Peres, N.M.R.; Novoselov, K.S.; Geim, A.K. The electronic properties of graphene. *Rev. Mod. Phys.* **2009**, *81*, 109–162, doi:10.1103/RevModPhys.81.109.
6. Ho, K.-I.; Boutchich, M.; Su, C.-Y.; Moreddu, R.; Marianathan, E.S.R.; Montes, L.; Lai, C.-S. A Self-Aligned High-Mobility Graphene Transistor: Decoupling the Channel with Fluorographene to Reduce Scattering. *Adv. Mater*. **2015**, *27*, 6519–6525, doi:10.1002/adma.201502544.
7. Geim, A.K.; Novoselov, K.S. The rise of graphene. *Nat. Mater.* **2007**, *6*, 183–191, doi:10.1038/nmat1849.
8. Park, S.; Ruoff, R.S. Chemical methods of the production of graphene. *Nat. Nanotechnol.* **2009**, *4*, 217–224, doi:10.1038/nnano.2009.58.
9. Yoon, H.J.; Jun, D.H.; Yang, J.H.; Zhou, Z.; Yang, S.S.; Cheng, M.M.-C. Carbon dioxide gas sensor using a graphene sheet. *Sens. Actuators B Chem.* **2011**, *157*, 310–313, doi:10.1016/j.snb.2011.03.035.
10. Kodu, M.; Berholts, A.; Kahro, T.; Kook, M.; Ritslaid, P.; Seemen, H.; Avarmaa, T.; Alles, H.; Jaaniso, R. Graphene functionalised by laser-ablated V_2O_5 for a highly sensitive NH_3 sensor. *Beilstein J. Nanotechnol.* **2017**, *8*, 571–578, doi:10.3762/bjnano.8.61.