EFFECT OF THE SYNTHESIS PARAMETERS ON THE DC RESISTANCE OF GRAPHITE NANOPLATELETS THICK FILMS

G. De Bellis[a*], **F. Ruggeri**[a], **A. Broggi**[a]
A. Tamburrano[a], **M. L. Santarelli**[a] and **M. S. Sarto**[a]

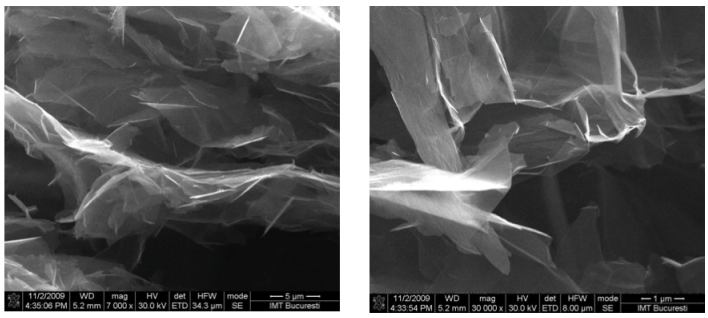
[a] Research Center on Nanotechnology applied to Engineering of Sapienza University (CNIS)
Sapienza University of Rome, via Eudossiana 18, Rome 00184, Italy

Since its first obtainment as a single layer in 2004 [1], graphene has attracted tremendous attention from the research community, who has since then continuously tried out new synthesis techniques with the aim of reducing costs and increasing monolayer graphene yield. The study presented here aims at investigating the effect of the synthesis parameters, like time and temperature, on the final dc electrical properties of thick films made of graphite nanoplatelets (GNPs) produced via thermo-chemical exfoliation. Results show a dependence of the dc resistance from both time and temperature, but with different behaviors at expansion temperatures below or above 1050^{o}C.

GNPs were synthesized through thermal expansion [2] in the CNIS Labs starting from Grafguard 160N-50 (intercalated expandable graphite flakes), provided by Graftech Inc, with a declared mean particle size of 350 μm and a starting flake thickness of 50 μm. The starting Graphite Intercalation Compound (GIC) underwent a thermal shock driven expansion in air at different temperature (i.e. 250^{o}C, 500^{o}C, 750^{o}C, 1050^{o}C, 1150^{o}C, 1250^{o}C) and increasing expansion times of 5 s, 10 s, 30 s, and 60 s. It was observed that no expansion occurred for GIC undergoing thermal shocks at 250^{o}C and 500^{o}C for times up to 60 s and at 750^{o}C for 5 s exposure. For higher temperatures an increase of volume by roughly 200 times of the original one was observed. Furthermore, GIC exposed to 1250^{o}C for 60s reacted completely with atmospheric oxygen giving off carbon oxides, leaving no residue.

After the thermal treatment, expanded graphite (also known as worm-like or accordion-like in this phase) was dispersed in a proper solvent and the suspension was tip sonicated using an ultrasonic processor, thus obtaining GNPs (Fig. 1). Different GNPs suspensions were then subjected to vacuum filtration in order to obtain GNP thick films, having an average thickness of about 200 μm, suitable for the electrical properties investigation. Since no expansion occurred for GIC undergoing thermal shocks at 250^{o}C and 500^{o}C for times up to 60 s and at 750^{o}C for 5 s exposure, it was not possible to obtain paper-like foils allowing the measurement of the dc resistance for these samples. The GNP foils were characterized by means of FTIR spectroscopy using a Bruker Vertex 70 equipped with a Platinum ATR single reflection diamond crystal-based module in the mid IR range (400 to 4000 cm^{-1}). SEM imaging was performed on as-produced samples (without deposition of any conductive coatings) using a Field Emission FEI Nova NanoSEM 630 at IMT (Bucharest). The electrical conductivity of the most meaningful samples was measured through the four probe method at CNIS Labs using a Signatone four point probe station connected to a Keithley power source and a nanovoltmeter.

FTIR spectra of GIC before and after thermal expansion clearly show a severe reduction in the intensity of peaks associated with the O-H stretching from carboxylic groups (around 2950-2850 cm^{-1}), the C=O stretching region (around 1730 cm^{-1}), the epoxy C-O stretching (around 1220 cm^{-1}) and the alkoxy C-O stretching (around 1048 cm^{-1}). Nevertheless below expansion temperatures of 1050^{o}C, time has a much greater effect than temperature on the disappearance of functional groups, indicating the existence of an incubation time for the restoration of the perfect sp^2 conjugated lattice of graphene planes. Above 1050^{o}C, from FTIR analysis, there seem to be no effect on the residual functional groups attached to GNP planes, even with an increase in the time exposure (Fig.2). On the other hand the dc resistance measurements performed on the same samples showed a marked enhancement with values going from 0.19 Ω for 750^{o}C expansion temperature (15 s time exposure) to about 0.09 Ω for 1250^{o}C (5 s time exposure). In conclusion we found that even if FTIR analysis can be a valuable technique for the investigation of chemical-structural variations on GNPs for temperatures below 1050^{o}C, it turns out to be ineffective above this value. However, the measurement of the dc resistance of samples expanded under different time-temperature conditions shows a clear increase, indicating the restoration of the original sp^2 conjugated lattice.



(a) (b)

Figure 1: SEM micrographs of GNPs obtained after thermal expansion and sonication

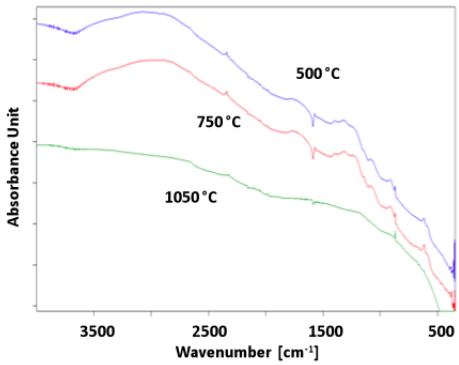


Figure 2: FTIR. spectra of different GNP films. GNP are expanded at increasing temperature for 5 sec. For expansion temperature higher than 1050^{o}C all FTIR spectra are overlapping.

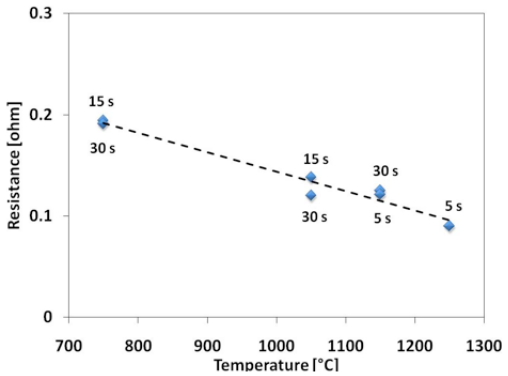


Figure 3: Measured sheet resistance of thick film specimens made of GNP produced at temperature increasing between 750 ^{o}C and 1250^{o}C, and for exposition time between 5 sec and 30 sec.

References

[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos et al. Science 306 (2004) 666.
[2] S. Stankovich, R.D. Piner, S.T. Nguyen, R.F. Ruoff. Carbon 44 (2006) 3342.
[3] The authors greatly acknowledge Dr. Adrian Dinescu for gently providing SEM images of the samples.