Nanoscale Characterization of the Thermal Properties of Supported, Single Flakes of Multilayer Graphene

M. Tortello[1], S. Colonna[2], J. Gomez[3], M. Pavese[1], A. Virga[1], F. Giorgis[1], R.S. Gonnelli[1], G. Saracco[1] and A. Fina[2]*

[1] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, 10129 Torino, Italy
[2] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, 15121 Alessandria, Italy
[3] AVANZARE Innovacion Tecnologica S.L., 26370 Navarrete (La Rioja), Spain
[*] e-mail: alberto.fina@polito.it

The extraordinary electrical, thermal and mechanical properties of a single suspended layer of graphene change, sometimes dramatically, when the number of layers increases considerably or when it is somehow interacting with the surrounding environment as when it is for instance supported by a substrate or employed as a filler in a polymer matrix. Therefore, it is of utmost importance to know and control the properties of graphene in these specific conditions. In particular, as for the thermal properties, it is highly desirable to investigate them also at the nanoscale because it is at this level that the properties of graphene are affected by the interfaces, eventually affecting the properties at the macroscale.

Several measurements of the thermal properties of suspended or supported graphene were reported [1] which employed diverse techniques. For instance, by using an electrical method, the thermal conductivity of graphene has been shown to decrease to 600 $W\cdot m^{-1}\cdot K^{-1}$ when supported on a substrate, due to phonons leaking across the graphene-substrate interface [2]. Atomic Force Microscopy is a very popular characterization technique which usually requires a very simple sample preparation. Moreover, when coupled to a Scanning Thermal Microscopy (SThM) module, it allows obtaining information not only on the topography, but also on the thermal conductivity. The thermal properties of graphene have already been investigated using SThM by Tovee et al. [3] who even integrated the tip with a carbon nanotube in order to enhance its thermal sensitivity. However, systematic studies have not been conducted yet.

Here we present SThM measurements performed using state-of-the-art resistive probes that show, with a resolution of ~ 20 nm: i) that multilayer graphene (MLG) flakes supported by SiO_2/Si substrates feature a noticeable increase of their thermal conductivity after they undergo an annealing process at 1700 °C and ii) that with this technique it will be possible to achieve, thanks to an adequate calibration and modeling of the probes, a quantitative determination of the conductivity of the flakes when they are supported by different substrates and thus determine the influence of the substrate on their thermal conductivity.

SThM measurements were carried out by using an "Innova" AFM from Bruker equipped with an SThM module (VITA module) from Anasys. The tip has a resistive element near its apex. As the tip changes temperature, the resistance of this element changes too. This resistance change is monitored by the hardware to generate an image. Lower temperature means a more

References

[1] A.A. Balandin, Nature Mater. 10 (2011) 569
[2] J.H. Seol et al., Science 328 (2010) 213
[3] P.D. Tovee et al., Phys.Chem.Chem.Phys., 16 (2014) 1174
[4] P.D. Tovee et al., J. Appl. Phys., 112 (2012) 114317
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thermally conducting sample. Two different kinds of flakes were investigated: reduced graphene oxide (RGO) “as received” (AR) and thermally treated (TT) at 1700 °C for 1 h.

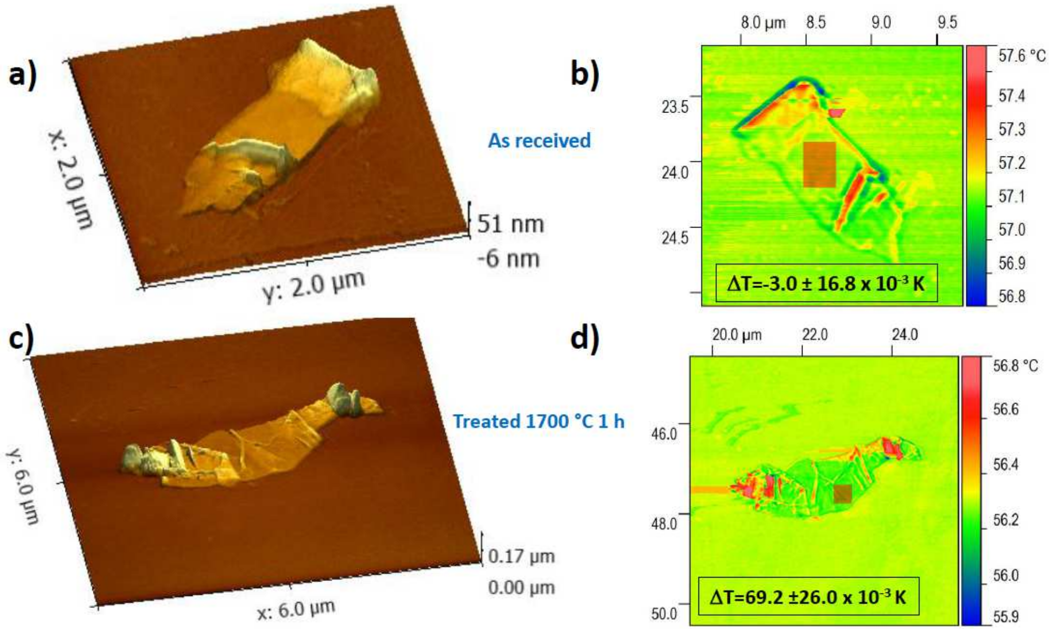

Figure 1: a): Topographic image of an “as received” graphene flake supported on a SiO_2/Si substrate. b): SThM image of the flake shown in a). $\Delta T=T_{substrate}-T_{flake}$. c): Topographic image of a graphene flake supported on a SiO_2/Si substrate and annealed at 1700 °C for 1h. d): SThM image of the flake shown in c). $\Delta T=T_{substrate}-T_{flake}$.

Fig. 1 a) shows an example of topographic image of an AR flake whose thickness in the flat region is ~ 10.3 nm, while Fig.1 b) reports its thermal map. It is possible to notice that the temperature difference between the flake and the substrate is negligible (taking into account the experimental deviation) indicating that, when supported, this flake has almost the same conductivity as the substrate. Fig. 1 c) shows the topographic map of a TT flake, approximately 9.4 nm thick, while panel d) is the corresponding thermal image. In this case, the temperature difference is considerable, thus indicating that the annealing treatment has substantially increased the conductivity of the flake. The vibrational properties of the flakes have been analyzed by Raman spectroscopy, correlating the phonon features to the thermal conductivity properties. The result showed a decrease of the I_D/I_G ratio, due to the reduction of defects in the flakes caused by the thermal treatment, in agreement with SThM findings.

Since it would be highly desirable to quantitatively estimate the thermal conductivity we also performed preliminary tests of three materials of known thermal conductivity, i.e. epoxy, glass and Si, in order to test the sensitivity range the instrument can span. The temperature change the probe experiences when it is brought in contact with the different materials turns out, as expected, to increase with increasing thermal conductivity, although not linearly. Even though, as shown also in ref. [4], the sensitivity of the probe decreases at higher conductivities, this result indicates that an accurate calibration over a wide range of conductivities will allow to reliably extract *quantitatively* the thermal conductivity. Experiments are being carried out in this regard.

In summary, by performing innovative SThM measurements, it has been shown that single multilayer graphene flakes thermally treated at 1700 °C are considerably more conducting than “as received” ones. Moreover, preliminary results on different bare substrates indicate that with proper calibration of the SThM probes and modeling, it will be possible to achieve a quantitative determination of the thermal conductivity at the nanoscale.