CONDUCTIVE-PROBE AFM CHARACTERIZATION OF GRAPHENE SHEETS CHEMICALLY GRAFTED ON GOLD SURFACES

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Electronic transport properties of graphene [1] films have recently attracted extensive interest as it is widely considered as a key material for the development of next generation electronics. In this perspective, it is of major interest to study the electrical and mechanical properties of graphene layers at a nanoscopic scale. Local electronic transport phenomena have been explored by STM [2] and CP-AFM [3] techniques and Lateral Force Microscopy (LFM) has proven to be useful when materials with different surface energies or cohesion need to be characterized [4] in order to study their friction properties. Despite those facts and the numerous theoretical [5] or experimental [6] works on graphene, there is, to our knowledge, no study combining topographical, electrical and frictional measurements of graphene layers grafted on gold coated substrates. In the present paper, we report the first results of the investigations at a nanometric scale of the mechanical, electrical and frictional properties of graphene layers chemically bonded on polyaminophenylene (PAP) films grafted on Au-coated wafers.
The sample preparation can be summarized as follows : (1) the PAP film was synthesized on the gold substrates by the conversion of only one of the two amine groups of p-phenylenediamine to aryldiazonium salt in an aqueous media. (2) The remaining grafted amine groups were converted to grafted aryldiazonium salts (PDP). (3) Direct contact between these few nanometers thick self-adhesive surfaces and the graphite block achieved covalent grafting. The graphite block was then mechanically exfoliated until graphene sheets obtention [7].
On the graphene/PAP/gold assembly, mechanical and electronic measurements were performed using a CP-AFM technique developed at the LGEP since 1996 [8] and called "Resiscope". Two types of measurements were performed : scanning for imaging and spectroscopy for local analysis.
For imaging, the samples surfaces were scanned in contact mode using a minimal constant force ($\sim$10 nN). The topography and the "apparent contact resistance" R were simultaneously acquired measuring respectively the vertical lever deflection D and the tip/sample current I.
The current I was measured by the "Resiscope" device when applying a constant sample

bias voltage of 1 V between the sample and the conducting cantilever tip. The local tip/sample contact resistance R is calculated as V/I. The friction image was obtained by Lateral Force Microscopy, measuring the lever torsion. It was acquired just after the recording of the topographical and electrical resistance images.
In the spectroscopic mode, local Current-Voltage (I-V) and Deflection-Resistance (DRz) curves were recorded at chosen locations of the sample surface. For the I-V curves, the bias voltage was scanned from -1 V to +1 V and back to -1 V at a constant force while I is measured. For the DRz curves,the sample bias voltage V was set at a constant value of 1 V. The deflection of the cantilever D and the resistance R are simultaneously acquired during the approach and withdrawal of the sample thus giving the "Deflection and Resistance" curves as a function of the sample displacement z.
The combination of topology, friction and electrical imaging reveals that different stacked graphene sheets have been successfully distinguished from each other and from the underlying PAP films (Figure 1). Lateral Force Microscopy has shown that the friction is greatly reduced on graphene sheets in comparison with the organic coating. The electrical resistance images show very different local conduction properties which can be linked to the number of underlying graphene sheets, making of this technique is a new approach for the characterization of graphene sheets and a complementary tool to Raman spectroscopy. Furthermore, the resistance decreases very slowly when the normal load increases, indicating a good protection of the organic film by the graphene sheets and I-V curves display characteristics of metal-molecule-metal junctions (Figure 2).

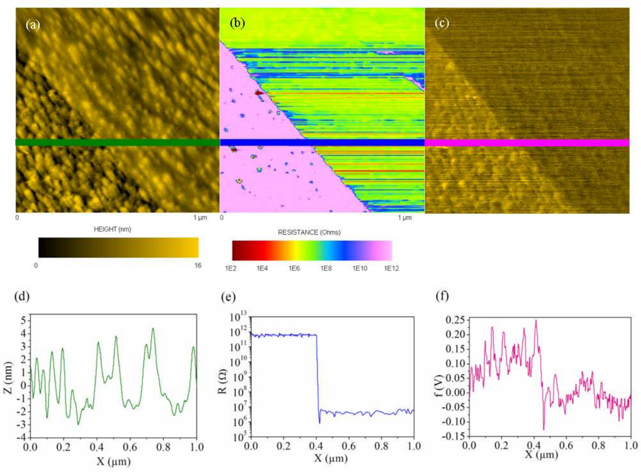

Figure 1: AFM topographical (a), electrical resistance (b) and friction (c) images of a very thin graphene film deposited partially on a PAP film grafted on a Au-coated substrate. Images (a) and (b) were acquired simultaneously. All images are 1 μm x 1 μm in size. Height (d), resistance (e) and friction (f) profiles along the line.

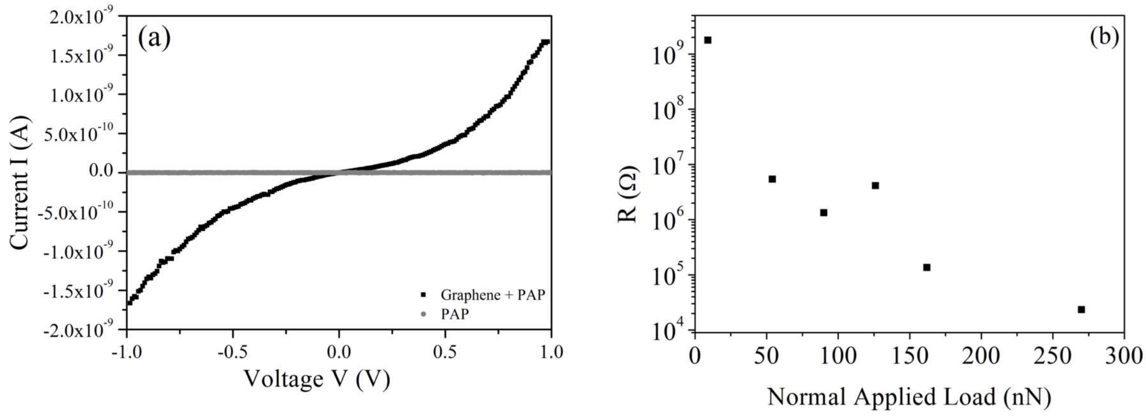

Figure 2: Current-voltage (I-V) curves (a) measured on a very thin graphene film bonded to a grafted PAP film on Au at very low load. Resistance vs normal applied load (b). Resistance was taken to be the reciprocal of the slope of the linear part of the I-V curves.

References

[1] K.S. Novoselov *et al.*, Science. 306 (2004) 666-9.
[2] K.A. Ritter *et al.*, Nat. Mat. 8 (2009) 235-42.
[3] D.J. Wold *et al.*, J. Am. Chem. Soc. 123 (2001) 5549-5556.
[4] S.M. Morgenthaler *et al.*, Langmuir. 22 (2006) 2706-11.
[5] P. Shemella *et al.*, App. Phys. Let. 94 (2009) 032101.
[6] P. Nemes-Incze *et al.*, Carbon. 46 (2008) 1435-1442.
[7] P. Viel *et al.*, J. Mat. Chem. 18 (2008) 5913.
[8] F. Houzé *et al.*, App. Phys. Let. 69 (1996) 1975-1977.