MECHANISM OF WRINKLE FORMATION IN CHEMICAL VAPOR DEPOSITED GRAPHENE AND TUNING ITS MORPHOLOGY BY SUBSTRATES

Mario Lanza [*,**], Yan Wang [*], Haiyi Liang [***] & Huiling Duan [*a)]

[*] *State Key Laboratory for Turbulence and Complex System, Department of Mechanics and Aerospace Engineering, CAPT, College of Engineering, Peking University, Beijing 100871, China*

[**] *Electronic Engineering Department, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain*

[***] *Department of modern mechanics, University of Science and Technology of China, Hefei, Anhu, 230027, China*

Summary Since graphene was discovered, much knowledge about its performance has been reported, but the introduction of new nanostructured materials in the industry requires a previous and intense analysis, not only of its intrinsic properties, but also of its interaction with adjacent layers. The interfacial effects between graphene and other materials have been found to impoverish its genuine properties and, between them, uncontrollable wrinkles formation is one of the most harmful in terms of homogeneity and variability. In this work we present a Scanning Tunneling Microscope and Atomic Force Microscope investigation about wrinkle formation in graphene depending on the substrate used, the corresponding theoretical calculations are also presented. In particular, our results show that the shape, density and size of wrinkles in graphene can be tuned using substrates with different topographic roughness and, following this procedure, we have been able to fabricate the first non suspended free-of-wrinkles sheet of graphene.

INTRODUCTION

An affordable and practical chemical vapor deposition (CVD) method has been recently developed to prepare graphene on both Ni and Cu. One of the characteristics of CVD grown graphene flakes is that they can be transferred to other substrates using an ingenious method [1]. This unusual capability facilitated the appearance of large area graphene field effect transistors [2] and graphene oxide semiconductor capacitors [3], in which the graphene flake is normally placed on SiO_2 [4] and High-k dielectrics [2-3, 5]. But the flakes fabricated by this method contain intrinsic defects that can impoverish the properties of the graphene. Among all of them, wrinkle formation seems to be one of the most harmful in large areas, which can remarkable impoverish the device-to-device variability.

Many reports about CVD graphene sheets on Cu have been published, it is known that substrate-induced roughness can be an important source of wrinkles and lattice distortion [6-9], which can remarkable reduce graphene' performance. But, on the contrary, no reliable statistical information about wrinkles and topographic roughness on the substrate has been previously reported. In this work, we present a scanning tunneling microscope (STM) and atomic force microscope (AFM) study of the amount of defects in as-grown and transferred graphene sheets.

GRAPHENE ON DIFFERENT SUBSTRATES

As-grown graphene on copper

The graphene samples were grown on single-crystalline Cu-(111) substrates via the CVD process recently developed by Li & Bae et al. [10-11].

Figure 1a shows a topographic map obtained when scanning with the AFM tip on as-grown graphene single layer(GSL) by CVD on Cu (fabricated in Peking University). This image clearly displays the typical configuration of graphene on a substrate: the most part of graphene adheres to the Cu substrate (plateaus), whereas, at some specific locations, the higher topographies (wrinkles) can be observed [12]. The wrinkles in figure 1a change their directions and form a quasi-periodic network. Here, the preferred locations for wrinkle formation are substrate steps and rough areas of the substrate.

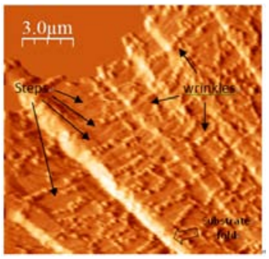

Fig. 1: AFM topographic image of a GSL sheet grown by CVD on a Copper foil (as-grown).

a) Corresponding author. Email: hlduan@pku.edu.cn.

Tune gaphene wrinkles by substrates

We also transferred graphene to different substrates,the corresponding winkle morphologies (density and shape) are different. This may be induced by the roughness and property of substrate.

In order to understand the observed tendencies of wrinkles in as-grown and transferred graphene, we do simulations and theoretical analysis. We performed damped dynamic simulations on the wrinkles morphology of graphene on substrate (see figure 2). These simulations in figure 2 indicate that: wrinkles are prone to align to the substrates.

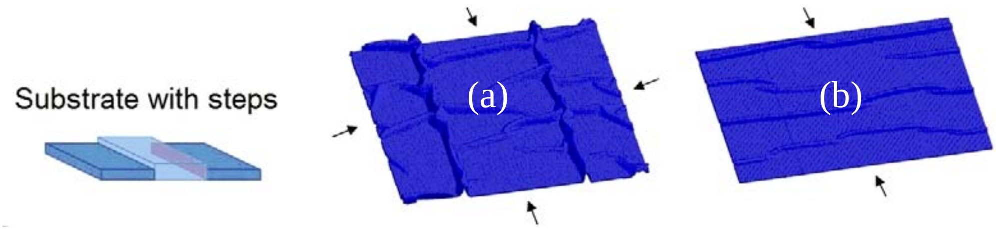

Figure 2: (a) show the typical wrinkles network obtained when applying a biaxial compressive strain (-0.75%) to a GSL sheet which is placed on a substrate with steps. (b) shows the typical wrinkles distribution obtained when applying an uniaxial compressive strain (-0.75%) to a GSL sheet which is placed on a substrate with steps. The arrows indicate the direction of the strain.

Since substrate can affect the formation of wrinkles, we wanted to verify whether it would be possible to create a free-of-wrinkles sheet of graphene by placing it on a very rough substrate. More specifically, we used a 1 µm tall nanowires forest as substrate and we placed a sheet of graphene on it. The results show that the graphene on a nanowire forest substrate has very low topographic RMS roughness which means that we can get a free-of-wrinkle sheet of graphene by choosing substrates. This free-of-wrinkle Graphene/nanowires/Graphene structure can be used for many applications such as piezoelectric field-effect transistors, force/pressure sensors, and resonators [13-15].

CONCLUSIONS

Our measurements indicate the presence of a quasi-periodic network of wrinkles in as-grown CVD graphene flakes on Copper foils. The morphology of substrate affects the wrinkles shape and density. This is also verified by the simulations. Finally, we successfully created a free-of-wrinkles sheet of graphene by placing it on a very corrugated substrate. These results reflect accurate knowledge about wrinkle formation which can be very useful to increase the quality of CVD graphene and, therefore, to reduce variability problems in large area device patterning.

References

[1] Lee Y.; Bae S.; Jang H.; Jang S.; Zhu S. E.; Sim S. H.; Song Y. I.; Hong B. H.; Ahn J. H. *Nano Lett*. **2010**, 10, 490-493.
[2] Lee S.; Lee K.; Zhong Z.; *Nano Lett.* **2010**, *10*, 4702–4707
[3] Park, J. K.; Song, S. M.; Mun, J. H.; Cho, B. J.; *Nano Lett.* **2011**, 355, 305-701.
[4] Liao, Z. M.; Han, B. H.; Zhou, Y.B.; Yu, D.P.; *J. Chem. Phys.* **2010**, 133 , 44-70.
[5] Lin, Y. M.; Jenkins, K. A.; Valdes-Garcia, A.; Small, J. P.; Farmer, D. B. Avouris, P.; *Nano Lett*. **2009**, 9, 422-426.
[6] Zhang, Y. F.; Gao, T.; Gao, Y. B.; Xie, S. B.; Ji, Q. Q.; Yan, K.; Peng, H.; *Nano* **2011**, 5 , 4014– 4022.
[7] Gao, L.; Guest, J. R.; Guisinger. N. P.; *Nano Lett*. **2010**, 10, 3512–3516.
[8] Rasool, H. I.; Song, E. B.; Allen, M. J.; Wassei, J. K.; Kaner, R. B.; Wang, K. L.; Weiller, B. H.; Gimzewski, J. K.; *Nano Lett.* **2011**, 11, 251–256.
[9] Stadler, J.; Schmid, T.; Zenobi, R.; *Nano* **2011**, 5, 8442– 8448.
[10] Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R. D.; *Science* **2009**, 324, 1312–1314.
[11] Bae, S.; Kim, H.; Lee, Y.; Xu, X. ;Park, J. S.; Zheng, Y.; Balakrishnan, J.; Lei, T.; Kim, H. R.; Song, Y. I.; *Nat. Nanotechnol.* **2010**, 5, 574–578.
[12] Xu K.; Cao P.; Heath J. R.; *Nano Lett.* **2009**, 9, 12, 4446-4451.
[13] Choi, D.; Choi, M.Y.; Choi, W.M.; Shin, H. J.; Park,H.; Seo,J. S.; Park, J.; *Adv. Mater.* **2010**, 22, 2187–2192.
[14] Wang, X. D.; Zhou, J.; Song, J. H .; Liu, J.; Xu, N. S.; Wang, Z . L.; *Nano Lett*. **2006**, 6, 2768.
[15] Wang, X. D.; Liu, J.; Song, J. H.; Wang, Z. L.; *Nano Lett.* **2007**, 7 , 24-75.