Directional Etching of Graphene by Catalytic Silver Nanoparticles

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Graphene has a great potential for future high-speed and low-power electronics due to its unique transport properties.[1] The electron mobility is measured as high as 100,000 cm2/Vs at room temperature,[2,3] making ballistic transport possible at submicron scale. The zero-bandgap nature of 2D graphene,[1] however, cannot provide the high current on/off ratio in mainstream electronic switching devices. For field-effect transistors (FETs), a bandgap larger than 400 meV is normally required. Theoretical calculations showed that the quantum confinement effect in a quasi-1D graphene nanoribbon (GNR) could open a bandgap that is inversely proportional to the GNR width and strongly dependent on its edge atomic geometry (crystallographic orientation).[4,5] Current strategies are based on top-down lithographic processes, mainly electron-beam lithography followed by oxygen plasma etching to create narrow structures. The problem is that the resulting ribbon edges contain a mixture of different crystallographic directions which alters the electronic properties of the ribbon. Even when the edges looks atomic smooth by atomic force and scanning electron microscopes (AFM and SEM, respectively), it was shown by Raman spectroscopy that the samples contained disordered edges.[6] The lack of a methodology for the fabrication of atomic smooth graphene edges inhibits the study on such structures. The main goal of this project is to find an alternative method to create graphene nanoribbons with well-defined edge structures. We are studying three different ways for the guided catalytic etching:

1. Catalytic etching along crystallographic directions.

To achieve this, both, thin layer of silver (1-25 nm) was deposited by electron beam evaporation and silver nanoparticles were deposited on highly ordered pyrolytic graphite (HOPG). Then the samples were heated to 450-550ºC in air for few minutes to form nanoparticles that will etch the graphene layers catalytically (We chose silver rather than other metal nanoparticles[7] because of their low catalytic etching temperature). In contrast to previous report,[8] we have observed two etching modes: the etching along crystallographic directions and random etching. We found that the etching modes depend strongly on the nanoparticle diameters, since the trenches created by the etching along the crystallographic directions have a narrow wide distribution comparing to the random etching (Fig. 1).

2. Directional etching along nano-scale features.

In this case, silver lines were deposited by standard photolithography and electron beam evaporation on faceted surfaces, M-plane sapphire after annealing in air at 1200-1500 ºC, perpendicular to the facets (10-50 nm height depending on the annealing conditions). Then, the silver coated sapphire was placed on HOPG and heated as described above. As a result, three different etching modes were observed: random, along crystallographic directions and along the nanofacets. The trench lengths of the random and crystallographic etching are up to 3 μm (Fig. 2a), while the trenches in the direction of the nanofacets are up to 20 μm long (Fig. 2b). The parameters involved in the different etching modes are currently under research. As next steps, we plan to use lithographically defined features and nanowires to guide the etching directions.

3. Nanopatterning by self-assembled nanoparticle monolayers

We recently found that spin coating of colloidal phase silver nanoparticles on HOPG surface could lead to self-assembled monolayer (SAM) structures (Fig. 3). The edges of the SAM patterns were observed to align along some specific directions. We are now in the process to understanding the mechanism of this SAM pattern formation and investigate the correlation of the pattern orientation with the crystallographic directions of underneath graphene surface. We plan to use the SAM patterns to define graphene patterns through controlled local catalytic etching.

[1] Geim, A.; Novoselov, K. *Nature Materials* **2007**, *6*, 183-191.
[2] Bolotin, K. I.; Sikes, K. J.; Jiang, Z.; Klima, M.; Fudenberg, G.; Hone, J.; Kim, P.; Stormer, H. L. *Solid State Communications* **2008**, *146*, 351-355.
[3] Bolotin, K. I.; Sikes, K. J.; Hone, J.; Stormer, H. L.; Kim, P. *Physical Review Letters* **2008**, *101*, 096802.
[4] Son, Y. W.; Cohen, M. L.; Louie, S. G. *Physical Review Letters* **2006**, *97*, 216803.
[5] Yang, L.; Park, C. H.; Son, Y. W.; Cohen, M. L.; Louie, S. G. *Physical Review Letters* **2007**, *99*, 186801.
[6] Casiraghi, C. *et al*. *Nano Letters* **2009,** 9, 1433-1441.
[7] Tomita, A. and Tamai, Y. *J. Phys. Chem.*, **1974**, 78 (22), 2254-2258
[8] Severin, N. et al. *Nano Letters* **2009**, 9, 457-46.

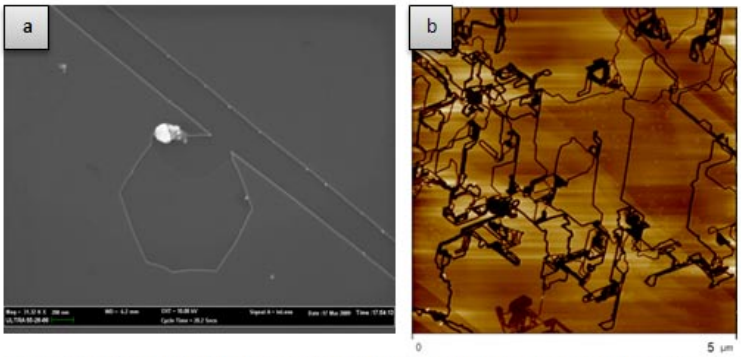

Fig. 1. SEM (a) and AFM (b) images of catalytic etching along the crystallographic directions on HOPG by Ag nanoparticles

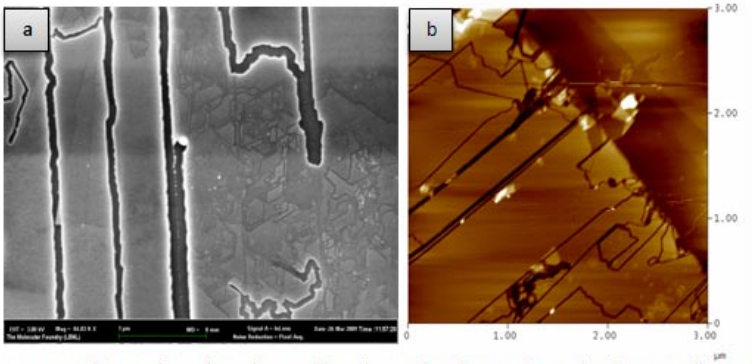

Fig. 2. Catalytic etching along the nanofacet (a, SEM) and crystallographic directions (b, AFM) on HOPG by Ag nanoparticles

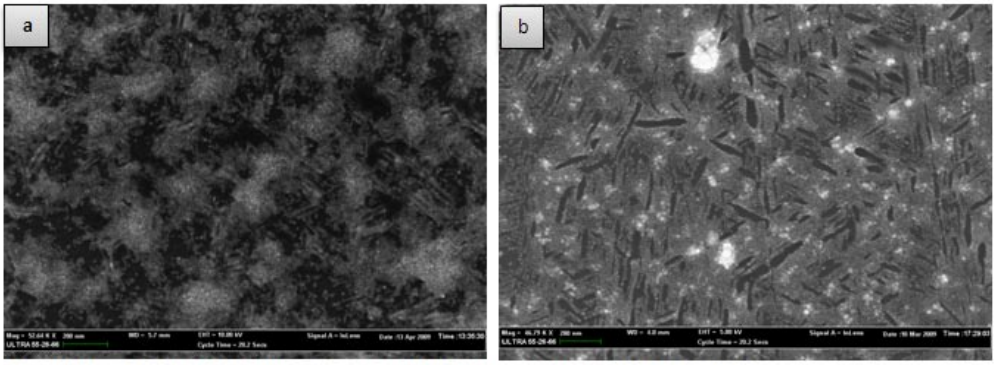

Fig. 3. SEM images of self-assembled Ag nanoparticle Monolayer patterns on HOPG surfaces