Patterning of Graphene by Block Copolymer Nanolithography

Sokol Ndoni, Violetta Shvets, Lars Schulte, José M. Caridad, Sozaraj Rasappa

Technical University of Denmark, Dept. of Micro and Nanotechnology, Produktionstorvet, build. 423, DK-2800, Kgs. Lyngby, Denmark
Center for Nanostructured Graphene (CNG), Technical University of Denmark, Ørsteds Plads, build. 345 Ø, DK-2800, Kgs. Lyngby, Denmark,
sond@nanotech.dtu.dk

Abstract. Nanostructuring of graphene is one of the routes that allows to generate an electronic band gap in graphene [1-2]. We present two methods of fabrication of respectively graphene nanoribbons (GNR) and graphene antidot lattices (GAL). Both methods rely on the preparation of nanolithographic masks from self-assembled block copolymers.

The block copolymers were synthesized by sequential anionic polymerization in our labs [3]. The GNR pattern was generated by utilizing a poly(styrene)-*b*-poly(dimethylsiloxane) block copolymer (PS-*b*-PDMS) with a total molecular mass of 10.5 kg/mol and a volume fraction of PS equal to 0.55. The GAL pattern was generated by utilizing a poly(butadiene)-*b*-poly(dimethylsiloxane) block copolymer (PB-*b*-PDMS) with a total molecular mass of 15 kg/mol and a volume fraction of PB equal to 0.7. The PS-*b*-PDMS shows lamellar bulk morphology, while the PB-*b*-PDMS block copolymer shows bulk morphology of hexagonally packed PDMS cylinders in a PB matrix.

The first method consists of spin-casting of PS-*b*-PDMS directly on graphene, without use of any pre-coating of graphene. After solvo-thermal annealing the PS block and the graphene beneath were selectively removed by oxygen plasma in a single step, thus creating GNR (see Fig. 1). The same oxygen plasma transforms the PDMS block into a hard mask by oxidation, which results in a superior protection of the graphene nanoribbons beneath the PDMS stripes.

In the second method the block copolymer masks were prepared *ex-situ* by microtomy of pre-aligned and cross-linked PB-*b*-PDMS samples [5]. In one variation the pre-aligned block copolymer samples were rendered nanoporous prior to microtomy. This was achieved by selective wet etching of the PDMS cylindrical domains with tetrabutylammonium fluoride. The obtained masks were 30-50 nm thin slices of 100 μm x 200 μm typical size that can be applied directly on graphene. GALs were realized again by oxygen plasma through the masks (see Fig. 1).

The GNRs and GALs were characterized by Raman spectroscopy (Fig. 1). The Raman spectra are consistent with a precise nanopattern transfer onto graphene. Further characterization of the nanopatterned graphene samples and their integration into electronic and sensor devices is ongoing.

References

[1] T. G. Pedersen, C. Flindt, J. G. Pedersen, A.-P. Jauho, A. Mortensen, K. Pedersen, Phys. Rev. B (Cond. Matt. Mat. Phys.) **77**(2008) 245431
[2] J. Bai, X. Zhong, S. Jiang, Y. Huang, X. Duan, Nat. Nanotechnol. **5** (2010), 190-194
[3] S. Ndoni, C. M. Papadakis, F. S. Bates, K. Almdal, Rev. Sci. Instrum. **166** (1995) 1090-1095
[4] S. Ndoni, M. E. Vigild, R. H. Berg, J. Am. Chem. Soc. **125** (2003), 13366-13367
[5] V. Shvets, L. Schulte, L. K. Tschammer, T. Hentschel, A. Cagliani, P. Bøggild, K. Almdal and S. Ndoni, submitted to Langmuir (2015).

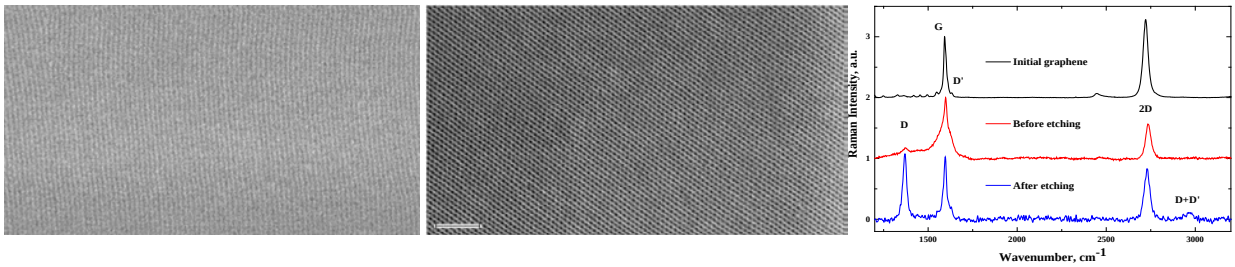

Figure 1. SEM images of two block copolymer masks and Raman spectra of pristine cvd graphene (black curve), of graphene covered with the block copolymer mask before (red curve) and after (blue curve) etching with oxygen plasma. The shown scale bar is 200 nm for both SEM images; the periods are sub-20 nm and the feature sizes are sub-10 nm in both cases.