Patterning of Large-Area Graphene Nanostructures via Holographic Lithography and O_2 Plasma Etching

J. Ding, K. Du, I. Wathuthanthri, C.-H. Choi, F. T. Fisher, and E.-H. Yang
Department of Mechanical Engineering, Stevens Institute of Technology
jding1@stevens.edu

Large-area graphene nanomeshes (GNMs) and graphene nanodots (GNDs) are important nanostructures for gas sensors [1], light harvesting [2], and surface enhanced Raman spectroscopy [3]. Typically GNMs are made using block copolymer [4] or nanosphere lithography [1] approaches, which have limitations in regard to the control of size and throughput. Here, we demonstrate a new technique to fabricate GNMs and GNDs using a unique multi-stack processing approach utilizing negative photoresist (PR), anti-reflective coating (ARC) and positive PR on graphene films (2 cm × 2 cm) deposited on Cu foil as outlined in **Figure 1**. The top negative PR layer, after nanopatterning, acts as an etch mask, while the intermediate ARC is used to eliminate the standing wave effect on the vertical sidewalls of the nanostructures of the top negative PR. The bottom positive PR layer is used as a sacrificial layer for lifting off the mask layers from the graphene film after reactive ion etching (RIE) of oxygen plasma down to the graphene. Detailed procedure is illustrated as follows: First a periodic nanopattern (pore pattern in this study) was created on the top negative PR layer using laser holographic lithography [5]. After etching the ARC, positive PR, and graphene layer through nanopores by using O_2 plasma, the remaining photoresist and ARC layers were then lifted off from the graphene layer by etching the sacrificial layer (positive PR). This lift-off process is important in the graphene layer transfer, because the removal of the negative PR requires strong organic solution, which would oxidize graphene. A PMMA layer was then coated on top of the nanopatterned graphene layer, followed by the etching of Cu foil. The graphene nanostructure was transferred onto a SiO_2/Si substrate, and subsequently the PMMA layer was removed using acetone. As shown in **Figures 2a-c**, GNMs with periods of 500 and 935 nm and with the smallest neck width of 24 nm have successfully been fabricated onto a SiO_2/Si substrate using this approach. The fabrication of GNDs was also demonstrated by etching the sidewalls of mask layers until the neck between two adjacent pores disappeared (**Figure 2d**). The results show that combining holographic lithography and O_2 plasma etching of multi-stack layers, large-area periodic GNMs and GNDs with precise control of their pore sizes and neck widths can be achieved on any flexible (PMMA) and rigid (SiO_2/Si) substrates. This nanopatterning technique offers a flexible and powerful approach to fabricate large-area, nanoscale-size graphene nanostructures on arbitrary substrates.

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[1] R. K. Paul, et al., Analytical Chemistry, 84(19), 8171-8178. (2012)
[2] M. Begliarbekov, et al., Nano Letters, 11(3), 1254–1258. (2011)
[3] J. Liu, et al., The Journal of Physical Chemistry C, 116(29), 15741-15746. (2012)
[4] J. Bai, et al., Nature Nanotechnology, 5(3), 190-194. (2010)
[5] I. Wathuthanthri, et al., Advanced Functional Materials, 23(5), 608-618. (2013)

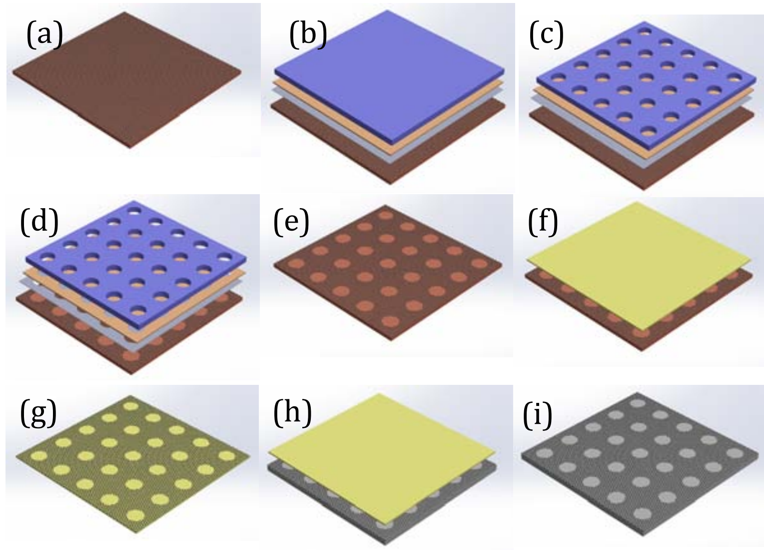

***Figure 1**: Schematic of nanofabrication processes of GNM for arbitrary substrate. (a) A graphene film grown on a copper substrate by CVD. (b) The graphene stack is spin-coated with positive PR, anti-reflective coating (ARC), and negative PR from bottom to top. (c) The top negative PR is patterned by laser holographic lithography. (d) The nanopattern is transferred through the ARC, positive PR, and graphene by reactive ion etching (RIE). (e) The positive PR, ARC, and negative PR are removed by sonication in an acetone bath. (f) The GNM on copper is spin-coated with liquid poly(methyl methacrylate) (PMMA) as a supportive layer for transfer. (g) The copper substrate is wet-etched using a copper etchant. (h) The GNM with PMMA support is placed on an arbitrary substrate (SiO_2/Si substrate in this study). (i) The transfer of GNM is completed after removing the PMMA by using acetone.*

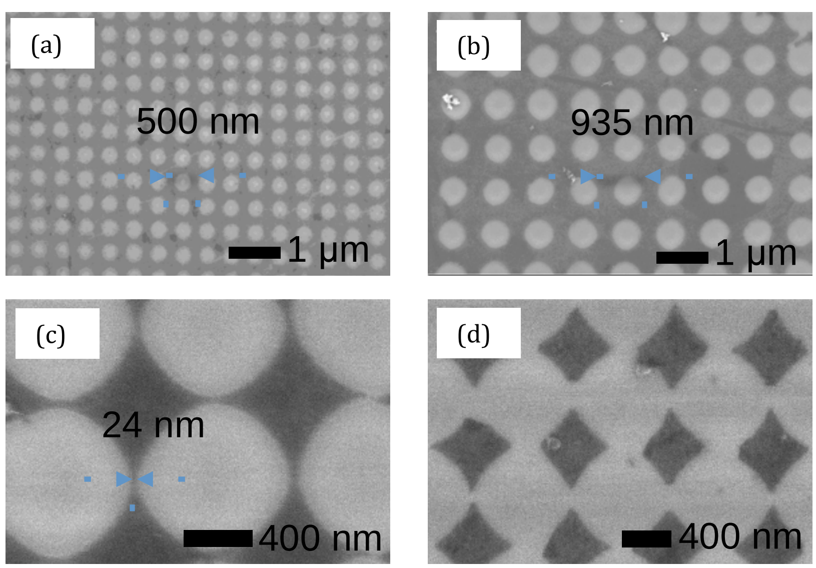

***Figure 2**: (a-b) The GNMs transferred on a SiO_2/Si substrate with period of 500 nm and 935 nm, respectively. (c) The GNM with a neck width of 24 nm. (d) GNDs*