Nanopatterned graphene using spherical block copolymer lithography

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Abstract

The high carrier mobility at room temperature and the possibility of an easy integration with silicon technology makes graphene an attractive candidate for pushing forwards the boundaries of electronics [1]. Unfortunately the absence of a band gap makes it difficult to fabricate FET transistor with a high on-off ratio [1]. Many techniques have been developed to overcome this problem by engineering the graphene properties at the nanoscale. The possibility of creating semiconducting nanoribbons has been extensively investigated, demonstrating that graphene nanoribbons (GNR) with a 2-20 nm width have a band gap useful for FET applications [2][3]. The disadvantage of such narrow structures is a limited maximal current. A possible solution is to fabricate a large number of nanoribbons working in parallel to increase the total current [4]. Pedersen and coworkers [5], suggested graphene anti-dot lattice as an alternative route to bandgap engineering, which was flowingly demonstrated in the form of a graphene nanomesh [6][7]. In this case cylindrical block copolymer lithography has been used, since this approach provides sufficient large areas of nanopatterned graphene with critical dimensions comparable to state-of-the-art GNRs. However, cylindrical block copolymers present several drawbacks. First off, achieving a good uniformity on a large scale is highly challenging (so far limited to 1 cm^2) and the alignment of the cylinders depends strongly on the surface pre-treatment, which is generally a non-trivial procedure. Here we present a method to achieve nanopatterning of graphene with spherical block copolymer in a simpler, more robust and ultimately scalable way, at the cost of reduced ordering of the patterns. Moreover, we show a strong response to small concentrations of NO_2.

The process sequence used to pattern micro-cleaved and CVD graphene is depicted in Figure 1. A 48 nm thick layer of PS-b-PMMA block copolymer is spin cast on top, without any pretreatment of the surface. After annealing, the PMMA spheres segregate at the top of the thin film, forming a hexagonal lattice. The local hexagonal order was found to be robust within a large range of temperatures and annealing times. Moreover, the morphology of the block copolymer after annealing is uniform across an entire 4" inch wafer, with short range hexagonal order everywhere. In order to obtain an etch mask for the SiO_x layer the block copolymer has to be etched (see Figure1 b-c-d). First, the PMMA spheres are removed using a standard UV and acetic acid step, but, in contrast to cylindrical block copolymers, this step is not sufficient to open the nanomask until the SiOx layer and extra plasma etching step is needed [6]. For this reason an O_2/Ar plasma is used to vertically etch the remaining polystyrene layer until the SiO_x layer is reached. As shown in Figure 2 the SiOx layer is not reached for all the polystyrene nanopits at the same etching time. This is most likely due to variation in the diameter of the PMMA spheres. Here we tune the etching time to maximize the number of fully open nanopits, avoiding at the same time overetching of the nanomask. When the nanomask is formed, the SiO_x layer and graphene are etched using a CHF_3/CF_4 plasma and an oxygen plasma. As shown in Figure 3 the process time for the SiO_x etching determines the morphology of the nanopatterned graphene, ranging from few sparse nanoholes to a densely nanoporous, nearly discontinuous graphene layer. The removal percentage for four different etching times is also shown. The size distribution of the holes is much larger compared to typical results with cyclindrical block copolymers and the local order is destroyed for the longest etch time. Thanks to the uniformity of the process samples up to few cm^2 of CVD nanopatterned graphene have been obtained. The response of nanopatterned CVD graphene to small concentrations of NO_2 has been studied by transferring nanopatterned CVD graphene on electrodes and monitoring the change of the resistance for different concentrations. Figure 4 shows a clear improvement compared to unpatterned CVG graphene. This behavior is attributed to the increased number of reactive sites along the edges due to the nanopatterning.

References

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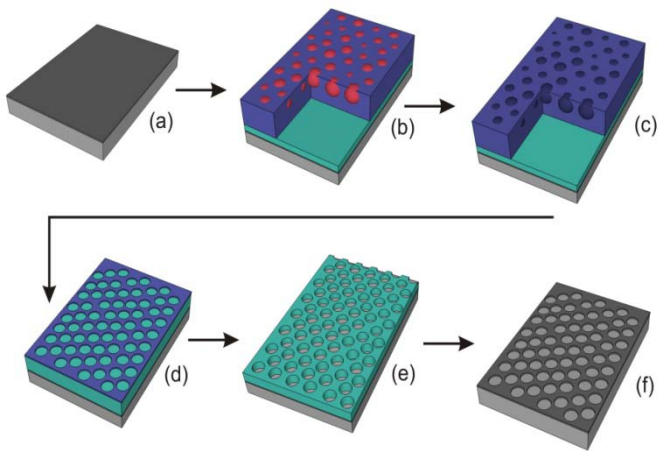
Figures

Figure 1. (a) Graphene is microcleaved on 90 nm SiO₂. (b) Graphene is covered with 15 nm of e-beam oxide. The spherical PS-b-PMMA is spin cast on top and annealed. The crosssectional view shows the inner geometry of the block copolymer. (c) After an exposure to UV light the PMMA sheperes are removed in acetic acid. (c) An oxygen plasma is used to etch the polystyrene nanomask up to the point where the nanopits are all open. (d) A fluorine based plasma is used to etch the SiOx layer. An oxygen plasma removes the residual block copolymer and patterns the graphene. (e) A 5% HF dip removes the remaning SiOx.

Figure 2. (a) SEM micrograph of a spherical block copolymer PS-b-PMMA 48 nm thick layer (inset). The PMMA spheres are the black dots. The local hexagonal order is highlighted in red. The image has been post-processed to enhance the contrast. Large micrograph shows a top view of the polystyrene nanomask after 30 seconds of O₂/Ar etching. (b) After 78 seconds ecthing approximately 50% of the pits are open. (c) Afetr 80 seconds etching 90% of the pits are clear. (d) After 82 seconds etching 95% of the pits reach the SiOx layer and some of the holes are merged. Scale bars are 200 nm (100 nm for inset)
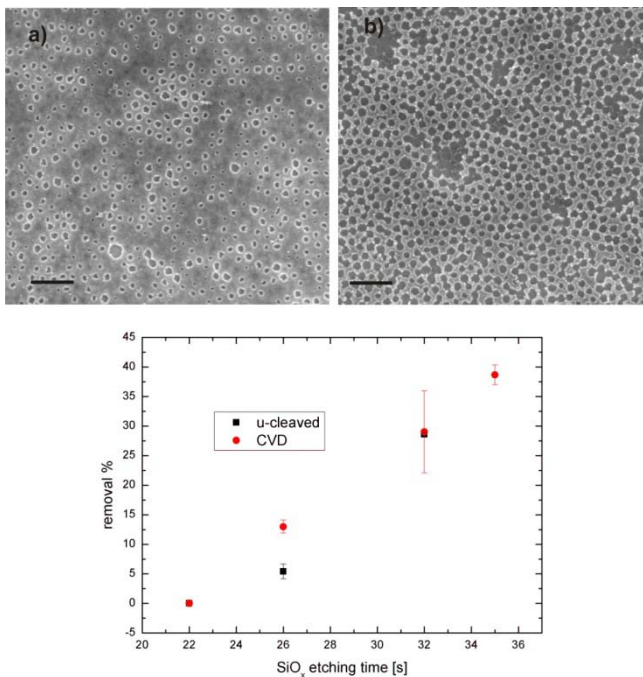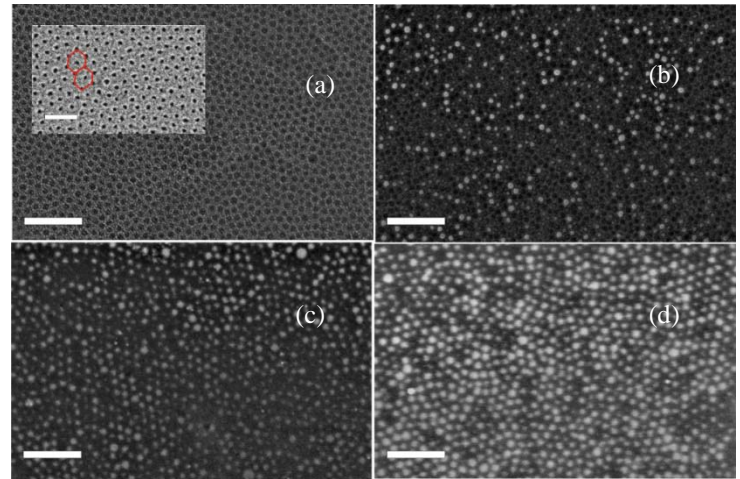

Figure 3. SEM micrographs of microcleaved graphene after nanopatterning. The scale bars are 200 nm. (a) After a 26 seconds etching of the SiOx protective mask. (b) After a 32 seconds etching. (c) Percentage of removed CVD and micro-cleaved graphene per 3 different etching times.
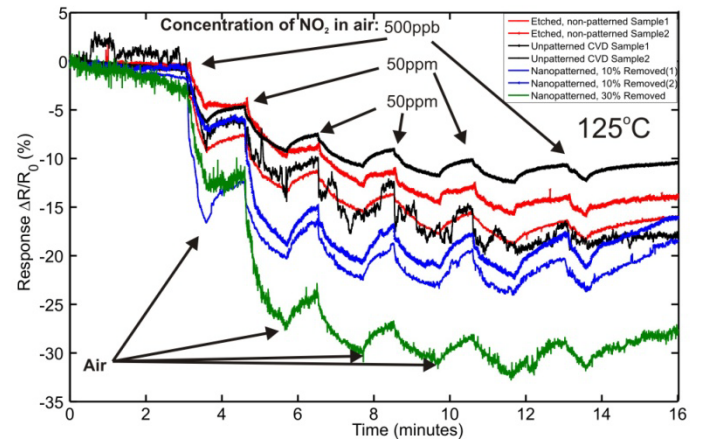

Figure 4. Response of nanopatterned CVD graphene to NO₂. The graph shows a clear improvement in the sensitivity due to the nanopatterning. All samples have been annealed at 230 degrees to remove contaminants.