Large-Area Nanopatterned Graphene For Ultrasensitive Gas Sensing

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Large-Area Nanopatterned Graphene For Ultrasensitive Gas Sensing

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Abstract

Nitrogen dioxide is a highly toxic common air pollutant. It can induce serious breathing related problems if inhaled, and it also contributes to the creation of smog in major cities. Due to the ubiquitous presence of natural and anthropic sources (internal combustion engines, power plants, volcanos, lighting, stoves…) a network of sensors inside large cities would be desirable. International agencies and clinical studies suggest limits of 53 ppb (year average) and 200 ppb (1 hour exposure) to prevent any breathing related issue [1]. This means that the NO_2 should be monitored in a concentration range of 1 to 100 ppb. In recent years, it has been demonstrated that graphene is an extremely sensitive material for gas sensing, thanks to its ultimate surface to volume ratio, low intrinsic noise and the strong dependence of the conductivity on dopants [2][3]. It has been already demonstrated the possibility of detecting single charge adsorbtion/desorption events using exfoliated graphene [3]. Despite these properties as prepared graphene does not reach the sensitivity necessary to monitor the NO_2 concentrations in the required range [2]. Several attempts have been made to improve the sensitivity but so far only UV illuminated graphene gas sensors have demonstrated enough sensitivity [2][4]. On the other hand continuous UV illumination limits portability, cost and in particular, the life span of the gas sensor. At GRAPCHINA 2014 we will present our work on ultrasensitive graphene gas sensors, where concentrations as low as 300 ppt of NO_2 were detected with an ultimate detection limit of tens of ppt. We used CVD graphene nanopatterned by a spherical block-copolymer etch mask and so far, the concentrations we report are the lowest for reusable graphene chemiresistive NO_2 gas sensors [5]. The use of spherical block copolymers, in contrast of cylindrical block copolymers, allows homogeneous and robust nanopatterning of cm-scale areas with nanoholes 10 to 50 nm in diameter without any substrate surface treatment. In Figure 1 the fabrication process is presented. The nanopattern can be tuned from sparse holes (13% graphene removed) to an almost discontinuous network of ribbons (38% graphene removed) by changing the etching time in the reactive ion etching machine (see Figure 2). An important geometrical factor for such nanopatterns is the edge length per unit area, since the edges are considered much more favorable binding sites than the graphene basal plane. The maximal estimated edge length per area is 32 $\mu m/\mu m^2$ (see Figure 3), which is much higher than previously reported for a similar graphene nanomesh [2]. The nanopatterned samples showed sensitivities for NO_2 of more than one order of magnitude higher than for non-patterned graphene in the unprecedented range 300 ppt to 100 ppb (see Figure 4 and Figure 5). This drastic improvement in the gas sensitivity compared to previous works is due to the high adsorption site density, created by controlled generation of edge sites and point defect sites in the graphene crystal lattice. Defects have been reported both theoretically and experimentally to be much more energetically favorable for binding NO_2 gas molecules [5]. Finally, the controlled generation of point defects in the graphene lattice with increasing etching time was studied by Raman spectroscopy. The I(D)/I(G) ratio was recorded as a function of the etching time that defines the patterns and it shows that the characteristic length between two defects is ~7 nm (see Figure 6). Considering the typical dimensions of the neck width between two nanoholes, it is clear that the remaining graphene after nanopatterning is highly damaged. Moreover, the ratio I(D)/I(D') has been recorded as a function of the etching time, since recently this ratio has been associated to the type of point defects [references in Ref.5]. We measured a ratio evolving from 4.2 to 5.5, indicating that boundary like defects and vacancies are generated (see Figure 6). Finally, this work opens the possibility of large area fabrication of nanopatterned graphene with extreme density of adsorption sites for sensing applications.

References

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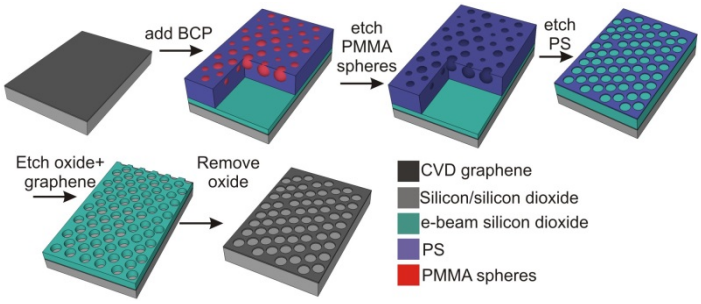

Figure 1. Fabrication sequence of nanopatterned graphene via spherical block copolymer lithography

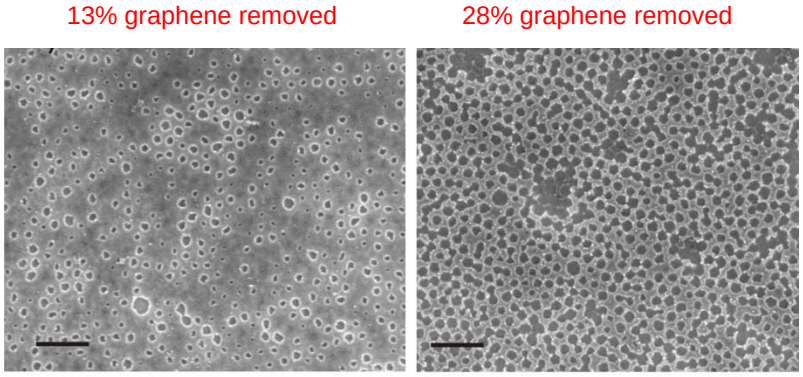

Figure 2. SEM micrographs of nanopatterned graphene. The nanopatterned can be tuned by changing the etching time in the RIE machine. The scale bars are 200 nm.

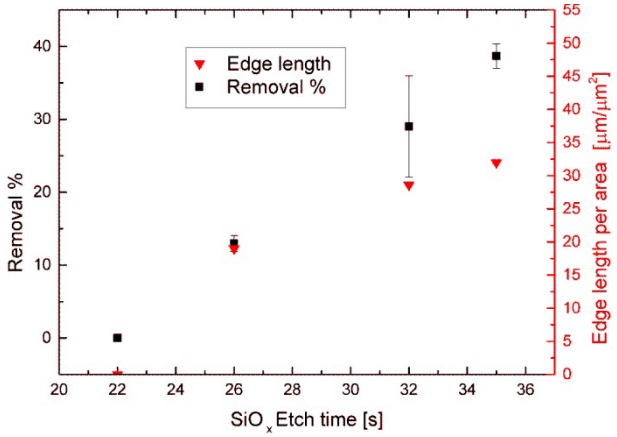

Figure 3. Percentages of removed graphene for 4 etching times of the top silicon oxide layer. The edge length per unit area is also plotted.

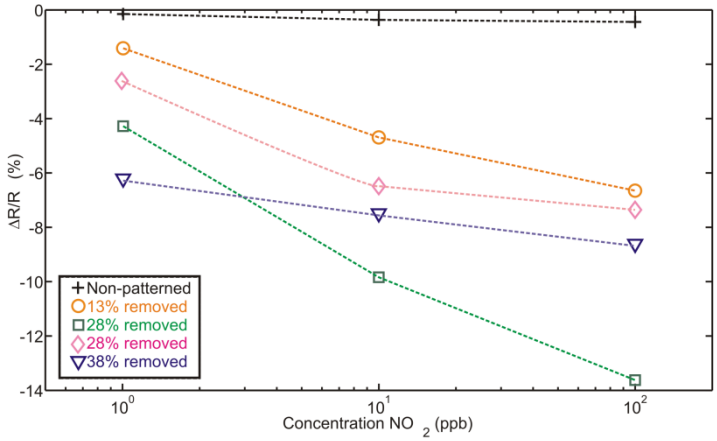

Figure 4. Comparison between the relative change in resistance of non-patterned CVD graphene and nanopatterned CVD graphene upon 2 minutes of NO_2 exposure at different concentrations.

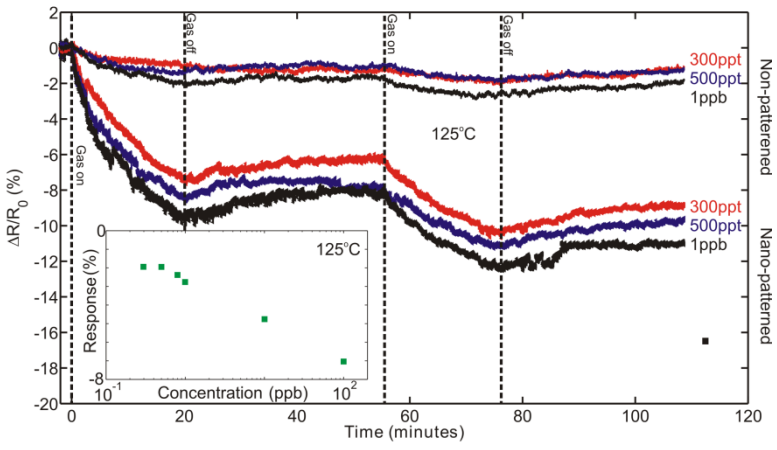

Figure 5. Relative change of resistance for nanopatterned and non-patterned CVD graphene upon sub 1ppb concentrations of NO_2

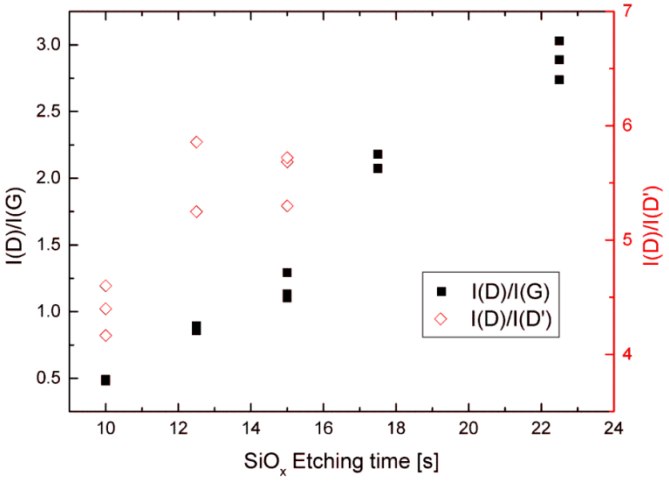

Figure 6. The I(D)/I(G) Raman ratio indicate very high density of point defects