O_2 and H_2O mediated FEBIE for fabrication of sub-10-nm diameter nanopores in few layer graphene

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Low-dimensional carbon based nanomaterials are very attractive due to their good thermal and electrical properties. They constitute ideal components for nanostructures in energy storage and field effect transistors. Focused electron beam induced deposition was recently established as a direct write method for low-resistance connections of carbon nanotubes[1] and ultra-high resolution deposits on graphene-like membranes of a cross-linked biphenyl monolayer[2]. In a previous study we performed Focused Electron Beam Induced Etching (FEBIE) with H_2O and XeF_2 of amorphous carbon membranes[3] and achieved minimum sub-electron-beam diameter hole sizes of around 20 nm.

In this work, we locally etch few-layer graphene by FEBIE [4]. The graphene flakes were produced by sonication of natural graphite[5] and deposited by applying the Langmuir-Blodgett method on a TEM grid. The etching was assisted by the precursors O_2 (Figure 1) and H_2O (Figure 2) introduced with a gas injection system (GIS) into a field emission FIB-SEM from Tescan. Hole arrays were exposed with varying exposure times. The dissociation of surface adsorbed molecules by the focused electron beam (25keV) and the secondary electrons results in highly reactive O, H, and OH radicals which react with the graphene to volatile molecules.

The size of the holes and the etch rate were dependent on precursors, dwell time, electron current and energy. The etch rate with water was higher than with oxygen. This could be explained by a longer residence time of adsorbed dipolar water as well as by formation of volatile CH_x (x=1,…,4) molecules as an additional etching path with water compared to oxygen. The minimum size of the etched holes obtained in these experiments was sub-10-nm. Although being small, this size was still larger than the calculated electron beam diameter of 4 nm used in our experiments.

We will discuss FEBIE hole formation in carbon membranes as function of the precursor regime governed by the residence time, surface diffusion and electron dissociation cross sections and deduce the lower limit of nanopore diameters which can be obtained.

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[1] A. G. Fedorov, S. Kim, M. Henry, D. Kulkarni, and V. V Tsukruk, Appl. Phys. A Mater. Sci. Process. 1659 (2014).
[2] W. F. van Dorp, I. Lazić, A. Beyer, A. Gölzhäuser, J. B. Wagner, T. W. Hansen, and C. W. Hagen, Nanotechnology 22, 115303 (2011).
[3] H. Miyazoe, I. Utke, J. Michler, and K. Terashima, Appl. Phys. Lett. 92, 043124 (2008).
[4] I. Utke, P. Hoffmann, and J. Melngailis, J. Vac. Sci. Technol. B 26, 1197 (2008).
[5] A.V. Alaferdov, A. Gholamipour-Shirazi, M.A. Canesqui, Y.A. Danilov, and S.A. Moshkalev, Carbon N. Y. 69, 525 (2014).

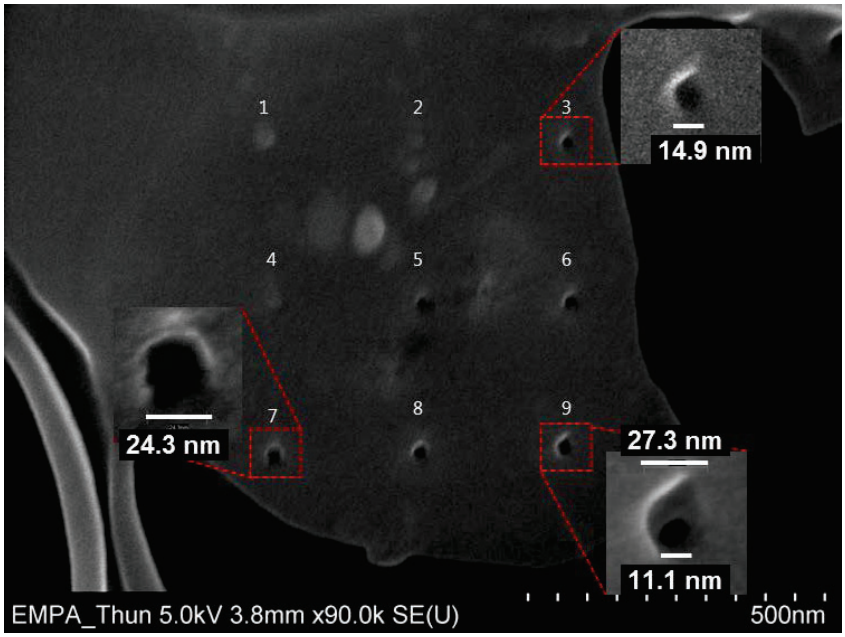

Figure 1: SEM image of a 15-30 layers graphene flake deposited on a holey carbon membrane. The 3x3 hole pattern was obtained by O_2 assisted FEBIE with an oxygen flow rate of 0.6 sccm. The electron current was 500 pA with an energy of 25 keV. The dwell time varied from 1 s (hole 1) to 9 s (hole 9) per pixel. Through hole etching was observed for hole 3 (3s dwell time) and 5 to 9. The hole sizes for specific holes are shown as insets. For hole 9 a funnel geometry can be seen with a smaller hole size at the bottom of the few layer graphene.

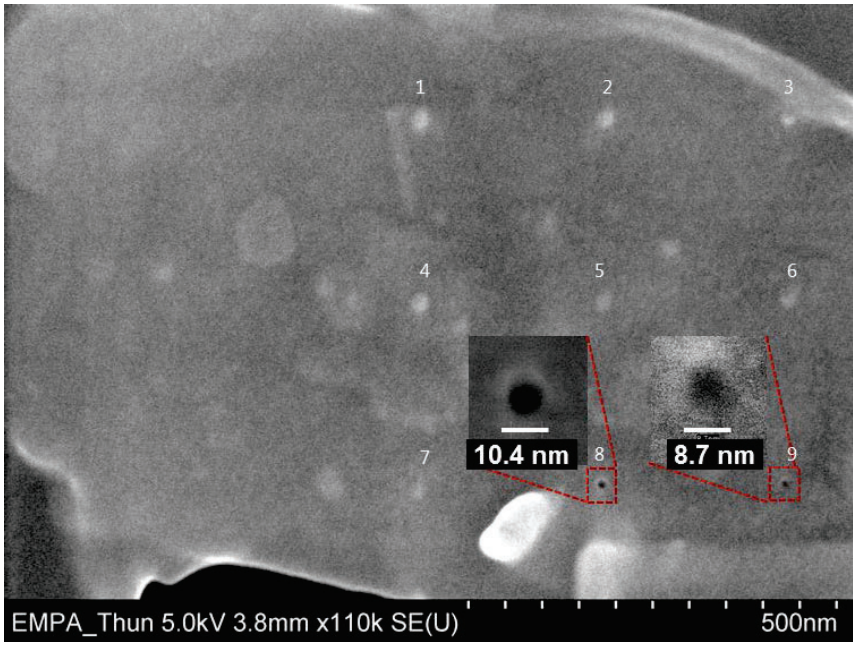

Figure 2: SEM image of a 15-30 layers graphene flake deposited on a holey carbon membrane. A 3x3 pixel pattern was exposed to H_2O and a focused electron beam (500 pA, 25 keV). The dwell time of the electron beam was increased stepwise by 0.25s beginning with 0.25s (hole 1) to 2.25s (hole 9). No ring shape structure could be observed around the holes. Deposits were obtained for pixels 1-7 due to surface contamination and the minimal hole diameters were 10.4 and 8.7nm for the hole 8 respectively 9 .