Patterning of highly oriented pyrolytic graphite by oxygen plasma etching

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Patterning of highly oriented pyrolytic graphite (HOPG) was demonstrated by oxygen plasma etching of lithographically patterned substrates. Periodic arrays of islands, or holes of several microns on an edge, were obtained on freshly cleaved HOPG surfaces which had been prepared with SiO_2 mask stops and then oxygen plasma etched. The etching process is described, including a study of etch rate as a function of rf power, and morphology was characterized with scanning electron microscopy. © *1999 American Institute of Physics.* [S0003-6951(99)03628-1]

The graphite basal plane, also known as graphene, is a hexagonal network of sp^2 covalently bonded carbon atoms.[1] Graphite is very chemically stable in nonoxidizing environments, and is mechanically very stiff (the C_{11} compliance constant is 1060 GPa), and these properties lead to its use in a variety of applications including in high-temperature, high-strength composites.[1] It is well established that the graphite basal plane is inert to chemical reaction with molecular oxygen, while it has limited resistance to atomic oxygen; at only 323 K, attack by atomic oxygen of graphite takes place readily.[2]

Highly oriented pyrolytic graphite (HOPG) is a man-made material which is polycrystalline with highly oriented graphene sheets; the typical domain size in HOPG is 1–10 μm in the basal plane and $>0.1\,\mu$m perpendicular to the basal plane.[3]

We were motivated to pattern HOPG because of our interest in the mechanical strength of graphite in the basal plane, which has not been determined to date. Mechanical strengths as high as ~ 300 GPa for defect-free regions are theoretically predicted from local-density approximation calculations on a truncated graphene sheet,[4] and one might also expect from theoretical calculations on carbon nanotubes (which are graphene sheets wrapped into cylinders) that the graphene sheet strength will be remarkably high;[5] for comparison, the tensile strength of a high-grade tool steel oil quenched from 1143 K and single tempered at 478 K is 2.345 GPa.[6]

One approach we have been recently developing for studying the mechanical properties of graphene is to pattern HOPG and then to manipulate the islands which are formed to obtain very thin sheets. We have reported on these studies separately.[7] Here, we report the creation of patterned islands and holes in HOPG, concentrating particularly on the lithographic patterning of appropriate mask stops and the oxygen-plasma-etching method used.

Beyond our interest in manipulating thin, lithographically prepared graphite islands, there are several other reasons to want to pattern HOPG. First, surface patterning may find application in developing ''graphene origami,'' a technique which may result in novel nanodevices by fabricating carbon by design.[7,8] Second, patterned HOPG surfaces can be used as special substrates for experiments in chemistry, biology, and medical research. Unique micrometer- or nanometer-sized containers can be created by etching small holes into HOPG substrates. As an example, Patrick, Cee, and Beebe studied the behavior of molecules on HOPG surface having etch pits available as containers.[9] These ''molecule corrals,'' as the authors called such etch pits, offered a practical method for confining molecules to small surface regions and allowed statistical analysis of the molecular behavior and the measurement of several other important properties difficult or impossible to determine by other techniques.[9] With the patterning technique outlined here, containers can be created in a designed shape and size and in a desired spatial arrangement, such as a periodic array.

Studies of oxygen plasma etching of HOPG will also help in obtaining better understanding of the resistance of graphite to oxidation by such plasmas, an important issue in material applications. For high-strength composites in some aerospace applications, resistance against attack by low-energy atomic oxygen is required.[2] Graphite is also widely proposed as the first wall material in nuclear fusion devices, where it would be exposed to high dosages of high-energy ions, including oxygen impurities.[10]

Although a lot of research has been done on the ion damage of graphite surfaces,[11] no work has been reported on the deliberate etching of the material to shape it, or to see what will happen under extensive etching. There are studies on etching or modification of the graphite surface with chemical or physical methods, such as thermal oxidation,[9] electrochemical treatment,[12] laser irradiation,[13] ion sputtering,[14] and radio-frequency (rf) plasma treatment.[15] You, Brown, and Al-Assadi[15] studied the surface topography of oxygen-plasma-etched HOPG with scanning tunneling microscopy. Previous research has not addressed the patterning, and the etch rate, of graphite as is discussed below.

The HOPG samples used in this study were obtained from Dr. Arthur Moore. We cut the samples into 1.2 $\times 1.2$ cm plates with a South Bay Technology wire saw. A razor blade was used to cleave the thick plates into ~ 1.5-mm-thick pieces. At the Cornell Nanofabrication Facility, a 200-nm-thick SiO_2 film was deposited onto the freshly cleaved surface of the HOPG substrate with plasma-enhanced chemical-vapor deposition (PECVD) on an IPE

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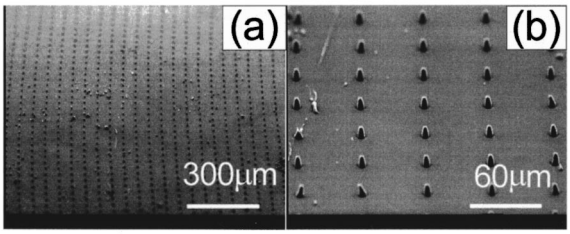

FIG. 1. SEM images of island arrays created on a HOPG surface. (a) and (b) are taken at different magnifications, as shown by the scale bars.

1000 PECVD system. Positive photoresist (Shipley 1813) was then spun coated onto the surface of the SiO_2 film. A proximity photolithography (GCA 6300 DSW Projection Mask Aligner, $5\times$g-line Stepper) was used to yield photoresist islands on the SiO_2 surface. The SiO_2 film was removed by dilute HF solution, except in the areas protected by photoresist islands. After removing the photoresist islands by Shipley photoresist remover 1165, the residual SiO_2 islands were used as mask stops for oxygen-plasma etching of HOPG. Thus, the resulting pattern on the HOPG surface replicated the photomask pattern.

Oxygen-plasma etching was performed with a PlasmaQuest 357 electron cyclotron resonance (ECR) etcher. The sample was attached to a Si wafer, which was maintained in good thermal contact with the chuck by flowing helium gas. The chuck was cooled to 273 K (the HOPG surface temperature might be slightly higher than the measured temperature). The etching system is equipped with an ASTEX 4505 low-profile streaming ECR source. The source can deliver up to 500 W microwave power, and 400 W were used for all the experiments described here. The substrate can, in addition, be biased by applying a rf power (frequency 13.56 MHz). A downstream solenoid magnet is available for further plasma stream confinement. Typical experimental conditions were: oxygen flow rate 20 sccm, oxygen pressure 5 mTorr, temperature of the sample during etching 273 K, and 16 and 60 A current for the upper and lower magnet, respectively. After patterning, the residual SiO_2 islands were removed by dilute HF solution. The etched thicknesses were measured by a Tencor AlphaStep 200 surface profilometer. The sample was then inspected with a Hitachi S-4500 scanning electron microscope (SEM) operated at 15 kV at Washington University.

Figure 1 shows an example of the island arrays fabricated on a HOPG surface. The pattern replicated the photomask quite well, and was uniform over areas as large as the exposed area, $1\,\text{cm}\times1\,\text{cm}$. The debris observed between the islands is most probably due to dust present in the etching chamber. Since graphite substrates can be deformed very easily perpendicular to the surface, it is essential to keep the surface flat in order to get large-area uniformity during all processing steps. We have found that pressing the substrate between two flat hard surfaces is a practical technique to restore the flatness of a deformed substrate prior to photolithographic patterning.

Figures 2(a)–2(c) show individual islands on samples etched under different conditions. The resulting surfaces are very smooth. The lateral shape of the pattern is well defined by the lithography mask, while the vertical dimension can be controlled by etching conditions. These three samples were etched with 200 W rf forward power, which generated about -230 V bias on the samples. The etch times were 30, 5, and 1 min for (a), (b), and (c), respectively, which yielded island heights of 8.62, 1.50, and 0.29 μm, respectively. As expected, the heights of the islands increased with the time duration of etching and the height had a linear relationship with the etch time, as shown in Fig. 3(a). The linear relationship indicated that while keeping all other conditions the same the rf power determined the etch rate.

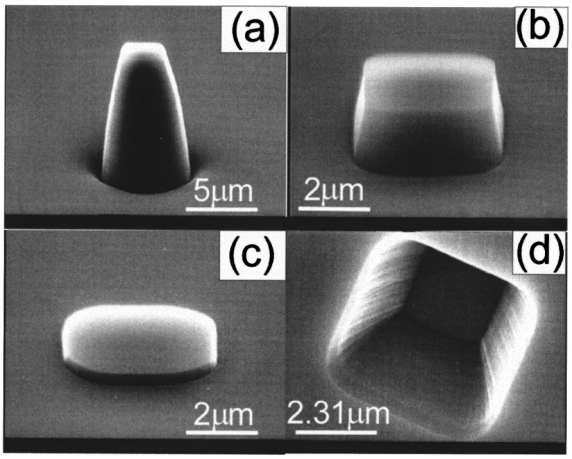

FIG. 2. (a)–(c) SEM images of individual HOPG islands on samples etched under different conditions. (d) SEM image of a hole etched in a HOPG substrate. This hole, if used as a container, could hold a liquid volume of $\sim 20\ \mu\text{m}^3$.

Figure 3(b) shows the heights of the islands etched at different rf powers for a constant etch time of 10 min. There is no significant change in island height until 140 W; the etch rate almost doubled with a rf power of 200 W. No etching was observed with 0 W rf power, while an etch rate of 0.18 μm/min was obtained with rf power as low as 15 W. This etch rate remained almost constant with rf power up to 140 W, indicating that extracting the oxygen radical cations and directing them to the surface is the major role played by the rf power. When the rf power was increased above 200 W, the radical oxygen cations evidently gained enough energy to become more active, and a significant increase in etch rate resulted.

While undercutting was not observed in the etched samples, tapered sidewalls were observed in all the samples. The reason for this is most likely due to the redeposition effect.[16] The sputtered involatile species from the surface of the substrate deposit onto the sidewalls, and shadow the fur-

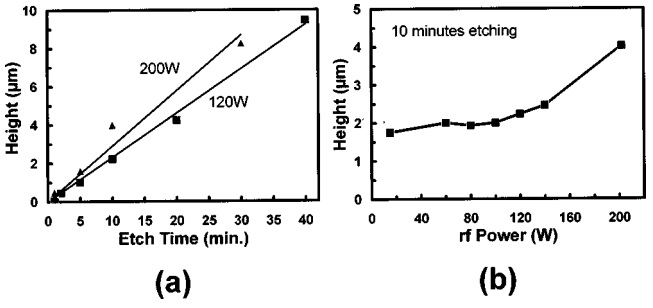

FIG. 3. (a) Etched island height dependence on the etch time. (b) Island height dependence on the rf power for a constant etching time of 10 min.

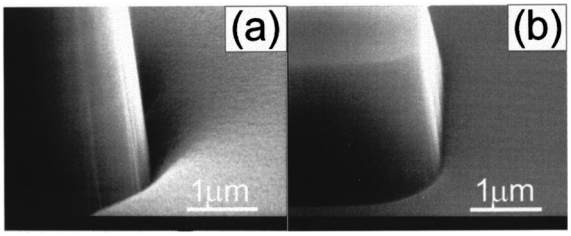

FIG. 4. (a) and (b) show magnified details of small areas of the islands in Figs. 2(a) and 2(b), respectively.

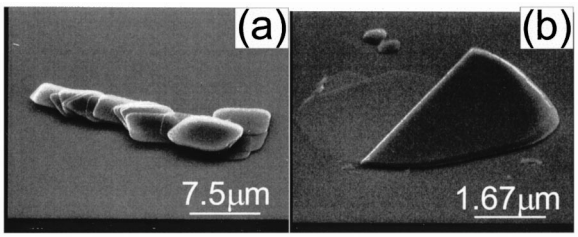

FIG. 5. SEM images of HOPG islands smeared on a Si(001) substrate. (a) Stacked thin platelets. (b) Example of a very thin layer left on the substrate while the platelet folds over.

ther etching of the area immediately beneath this deposited coating, resulting in tapering of the sidewalls. Another possible contribution to this sidewall coating is forward sputtering of the mask material onto the sidewalls.[16] There are vertical lines on the etched walls, as can be seen in Fig. 2. Figures 4(a) and 4(b) show magnified details of small areas of the islands in Figs. 2(a) and 2(b), respectively. These vertical etch lines might be due to the vertical kinetic energy of the impinging oxygen radical cations. Another notable characteristic of the graphite island morphology obtained is that there were always notches along the base of the island perimeters, as can be seen in Fig. 4, and the notch depth increases with the increment of the island height. The notch formation might be a result of the reflection experienced by the incidental ions at the steep sidewalls. This reflection can enhance the energetic particle flux at the base area near the perimeter. In other studies of the plasma etching of materials, sidewall tapering and notch (also referred to as ''trench'') formation often occur together.[16]

Figure 2(d) shows that not only islands can be created on the surface, but also holes can be etched in the substrate with the same quality of smoothness and controllability. As mentioned, such holes may serve as useful containers for chemical solutions.

In summary, patterning of freshly cleaved HOPG surfaces was achieved with lithographic preparation of SiO_2 mask stops and oxygen-plasma etching. Periodic arrays of micrometer-sized HOPG islands or holes were created on HOPG surfaces. These structures may find applications in graphene origami,[7,8] and are proving useful in studies of the mechanical properties of very thin graphite platelets. An example of such thin platelets of graphite is shown in Fig. 5. They may also be used as unique substrates for biological and chemical experiments. Further experiments are needed to achieve understanding of etch rates and control of sidewall morphology.

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[1] B. T. Kelly, *Physics of Graphite* (Applied Science, London, 1981).
[2] N. M. Rodriguez, S. G. Oh, W. B. Downs, P. Pattabiraman, and R. T. K. Baker, Rev. Sci. Instrum. **61**, 1863 (1990).
[3] A. W. Moore, in *Chemistry and Physics of Carbon*, edited by J. Philip, L. Walker, and P. A. Thrower (Marcel Dekker, New York, 1973), Vol. 11, p. 69.
[4] P. Stumm, R. S. Ruoff, and B. Yakobson (unpublished results).
[5] B. I. Yakobson, M. P. Campbell, C. J. Brabec, and J. Bernholc, Comput. Mater. Sci. **8**, 341 (1997).
[6] *CRC Materials Science and Engineering Handbook*, edited by J. F. Shackelford, W. Alexander, and J. S. Park (CRC, Boca Raton, FL, 1994).
[7] X. Lu, M. Yu, H. Huang, and S. R. Ruoff, Sixth Foresight Conference on Molecular Nanotechnology, Santa Clara, CA, 1998.
[8] T. W. Ebbesen and H. Hiura, Adv. Mater. **7**, 582 (1995).
[9] D. L. Patrick, V. J. Cee, and T. P. Beebe, Jr., Science **265**, 231 (1994).
[10] T. Yamashina and T. Hino, Appl. Surf. Sci. **48/49**, 483 (1991).
[11] S. Yugo, T. Kimura, and Y. Kazumata, Carbon **23**, 147 (1985).
[12] A. A. Gewirth and A. J. Bard, J. Phys. Chem. **92**, 5563 (1988).
[13] S. M. Park and J. Y. Moon, J. Chem. Phys. **109**, 8124 (1998).
[14] C. T. Reimann, P. A. Sullivan, A. Türpitz, S. Altmann, A. P. Quist, A. Bergman, S. O. Oscarsson, B. U. R. Sundqvist, and P. Håkansson, Surf. Sci. **341**, L1019 (1995).
[15] H.-X. You, N. M. D. Brown, and K. F. Al-Assadi, Surf. Sci. **284**, 263 (1993).
[16] H. W. Lehmann, in *Thin Film Processes II*, edited by J. L. Vossen and W. Kern (Academic, San Diego, CA, 1991), p. 730.