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Tailoring graphite with the goal of achieving single sheets

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Abstract. We demonstrate the tailoring of highly oriented pyrolytic graphite (HOPG) to obtain uniformly sized islands of up to several microns in size. There has already been some research on manipulating individual sheets on HOPG surfaces with scanning probe microscope tips; such sheets were obtained either accidentally or with a less controllable indenting technique. Here we present a different approach, which is more reliable and controllable. The HOPG surface was first patterned to create an array of small graphite islands by reactive ion etching of the HOPG surface with an oxygen plasma. These islands were then manipulated with an atomic force microscope tip. Carbon nanotubes represent a promising material for nanotechnology and can be considered as a graphene sheet rolled into a seamless cylinder. While carbon nanotubes are synthesized successfully with laser ablation, carbon arc, or chemical vapour deposition techniques, we speculate that it might be possible, by the controlled fabrication of graphene sheets, to form nanotubes or other novel motifs of use for nanotechnology.

1. Introduction

Since the discovery of carbon nanotubes it has been realized that a single sheet of graphite, referred to as graphene, can have three-dimensional forms as well as a planar structure, and its properties can be tailored by controlling its geometry (Mintmire *et al* 1992, Hamada *et al* 1992, Ebbesen and Hiura 1995). This leads to the promising prospect that with the help of nanomanipulation techniques to cut and fold such atomic-layer sheets by design, novel materials with unique properties can be obtained (Ebbesen and Hiura 1995). Manipulating graphene sheets in three dimensions, such as by rolling, bending and folding, will not only provide a route to build new materials and provide an understanding of the relation among geometry, properties, and function of such new structural motifs, but will also provide understanding of the fundamental properties of graphene and therefore graphite. In exploring these possibilities, scanning tunnelling microscope (STM) and atomic force microscope (AFM) tips have been used to tear, and to fold and unfold graphitic sheets on highly orientated pyrolytic graphite (HOPG) surfaces (Hiura *et al* 1994, Roy *et al* 1998). In these studies, the manipulation started at step edges on HOPG surfaces, which were obtained accidentally or with an indenting technique. It should be possible, by taking advantage of present nanofabrication technology, to fabricate and manipulate unique structures in a designed and systematic way. In this paper we present such an approach.

To tailor graphite and obtain tailored graphene for further manipulation an appropriate sample stock is needed. One method of obtaining graphene is to grow it on an appropriate substrate, such as crystal surfaces of transition metals and metal carbides, by decomposing hydrocarbon gases at high temperature (Oshima and Nagashima 1997); it has been shown that a single-layer-thick sheet can be grown on such surfaces, but the average domain size is only several tens of nm (Oshima 1998). Another method is to use existing graphene in graphitic materials. HOPG is a suitable starting material for getting graphene, not only because of its availability in large quantity and in large-size pieces, but also because of its unique structure. It is polycrystalline with highly oriented graphene sheets; the typical domain size in HOPG is 1 to 10 μm in the basal plane and >0.1 μm perpendicular to basal plane (Moore 1973). The domain size in the basal plane was confirmed in our experiments described below.

Before employing manipulation by an AFM tip, the HOPG surface was patterned to create an array of small graphite islands. The subsequent efforts involved attempting to peel graphene sheets from the graphite islands and to further manipulate them with AFM tips. Our study reveals that HOPG can be patterned with oxygen plasma etching in a straightforward way. Preliminary results on HOPG surface patterning, and manipulation of graphite islands, are described and discussed below.

2. Experimental details

The HOPG samples used in this study were obtained from Dr Arthur Moore. We cut the samples into 1.2×1.2 cm^2 plates with a South Bay Technology wire saw. A razor blade was

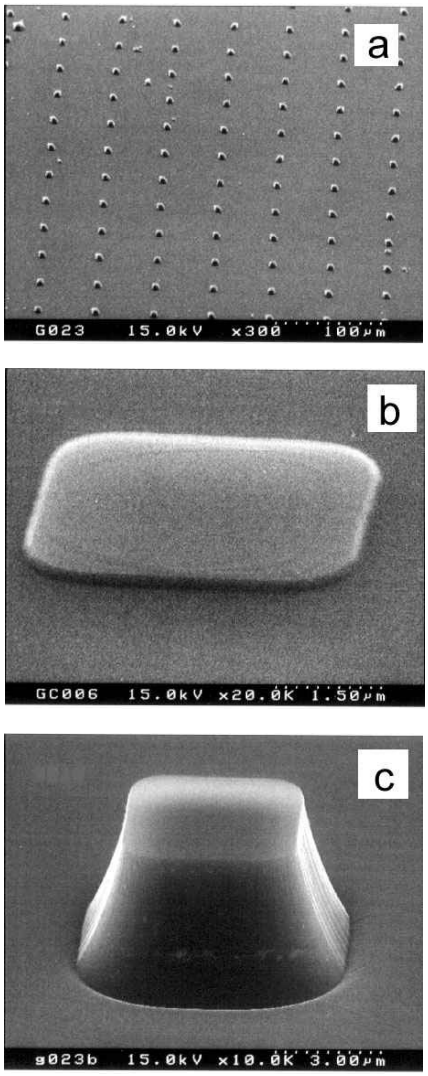

Figure 1. SEM images of graphite islands created by oxygen plasma etching on an HOPG substrate.

used to cleave the thick plates into ∼1.5 mm thick pieces. A 200 nm thick SiO_2 film was deposited onto a freshly cleaved surface of HOPG substrate with plasma enhanced chemical vapour deposition (PECVD). After patterning, the residual SiO_2 islands were used as mask stops for oxygen plasma etching of HOPG. The oxygen plasma etching was performed with a PlasmaQuest 357 electron cyclotron resonance etcher. The details of creating HOPG islands will be published elsewhere. The SiO_2 layers on the resulting HOPG islands were removed with dilute aqueous HF. The islands were then characterized with a Hitachi S-4500 scanning electron microscope (SEM) and a Digital Nanoscope III AFM, and further manipulated with the AFM tip. Some manipulations were performed on islands which were transferred onto a Si(001) substrate surface.

3. Results and discussions

The SEM pictures in figure 1 show the graphite islands created by oxygen plasma etching. A very well-defined array of islands was obtained as shown in figure 1(*a*). The height

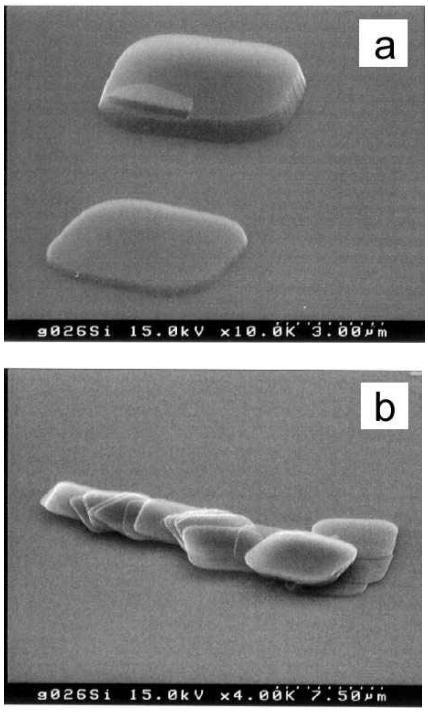

Figure 2. SEM images of graphite plates on the Si(001) substrate.

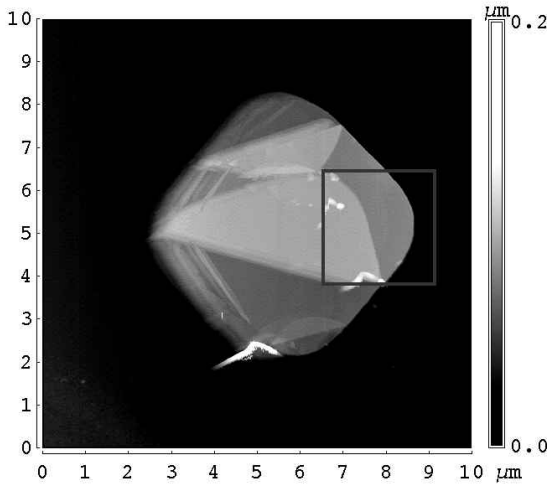

Figure 3. AFM tapping mode image of a graphite plate on the Si(001) substrate.

of the islands can be controlled by etching time and other etching parameters. Islands as low as 200 nm were obtained, a good height range for AFM tip manipulation, as shown in figure 1(*b*). Islands as high as 9 μm can also be obtained. An island of moderate height is shown in figure 1(*c*). The size and shape of the islands can be well defined by the photomask pattern. The smallest size we have prepared to date is 2 μm square, and the largest was 40 μm square.

Since graphite can be easily cleaved along the basal plane, the islands can be transferred to flat surfaces of other substrates, such as mica or Si, simply by rubbing the HOPG surface against the surface of other substrates. Figure 2 shows islands transferred onto a Si(001) substrate. The original islands were 6 μm in height. After being transferred to

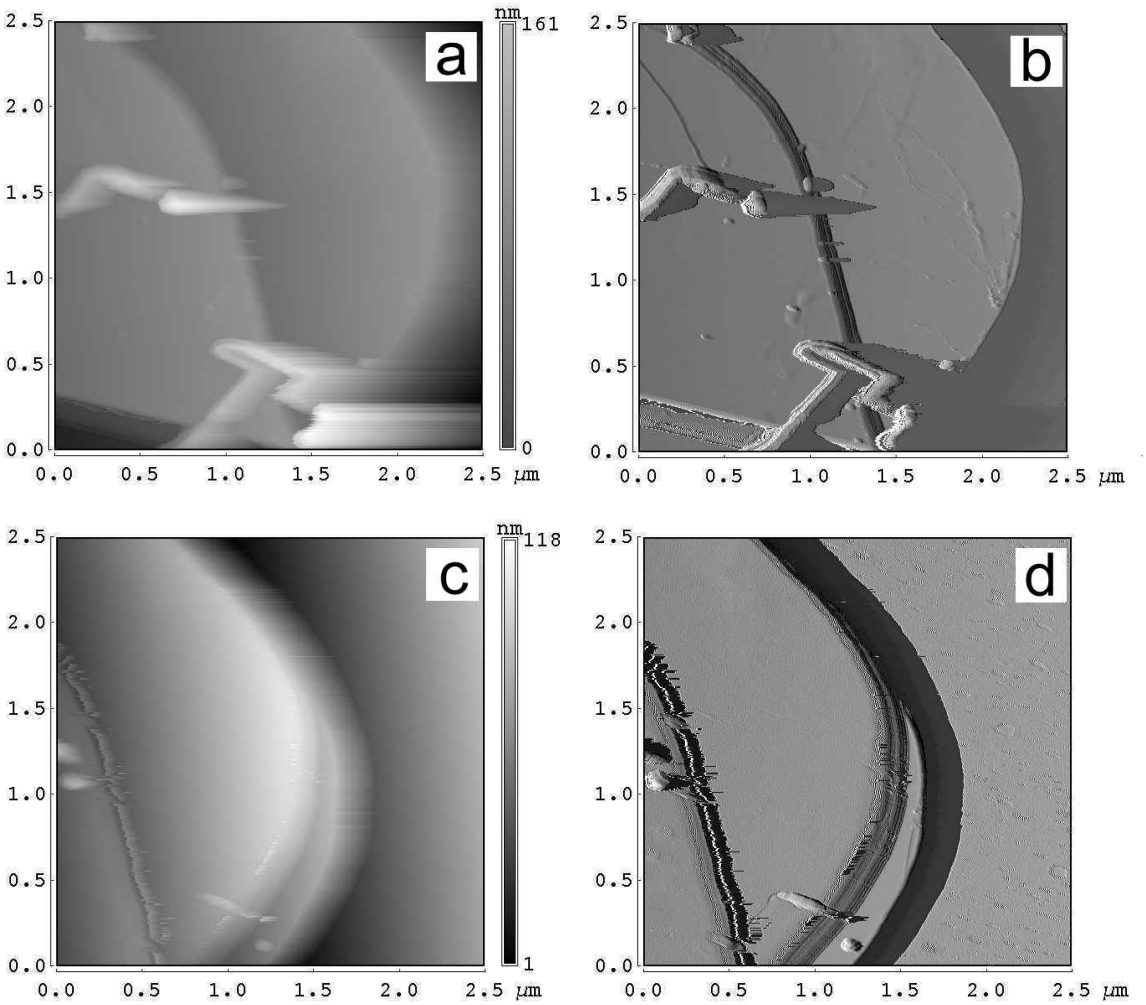

Figure 4. AFM tapping mode images of the corner of a graphite plate before and after AFM tip manipulation. (*a*) and (*c*) are height mode images, (*b*) and (*d*) are amplitude mode images.

a Si(001) substrate, all the islands were 'fanned out' into smaller height pieces. Well-separated as well as stacked plates were found on the surface, as shown in figure 2. It was noticed that some very thin plates were created by this method of transferring from the patterned HOPG surface onto the Si surface. This implies that more extensive rubbing of the patterned (island) HOPG surface against other flat surfaces might be a way to get multiple or even single atomic layers of graphite plates. These thin plates of multiple or single graphite layers can be used as building blocks for fabricating carbon structures by design, as in an approach envisioned by Ebbesen and Hiura (1995).

AFM tip manipulation can be performed either on the original islands on the HOPG substrate, or on the parts transferred to other substrates. Here we present results on transferred islands. Figure 3 shows an AFM image of a graphite plate on the Si(001) surface. The thickness of this plate was found to be 98 nm from the profile plot. The upper layers of the graphite sheets are folded, as shown in the figure. These folds were most likely induced from the tearing and friction which occurred during the transfer process. Although these folds do not happen on the same layers, their axes are either parallel or at an angle of 30° to each other, reflecting the symmetry axes of the graphite hexagonal network. Since folds occur preferentially along the symmetry axes of graphite, as observed by Hiura *et al* (1994), Ebbesen and Hiura (1995) and Roy *et al* (1998), this implies that these layers are in the same single-crystal domain. AFM tip manipulation was initiated at the right corner of the island shown in the black square box in figure 3. A zoom-in image of this area is shown in figures 4(*a*) and (*b*). As the image shows, the island had a very sharp edge at this corner. Since it is now well established that folding can be initiated at step edges, the manipulation was performed in an attempt to create step edges at the corner of the piece, so that the created step edges could, in turn, be used as the starting point for further folding manipulation. By 'knocking' the tip against the island corner, step edges were indeed created as shown in figures 4(*c*) and (*d*). One striking aspect is that, besides small step edges being created, approximately 90 layers of the upper part of this plate was displaced collectively by a distance of 180 nm. It is not quite clear if the tip motion really applied enough energy to make this displacement; another possibility is that the interface created was already the boundary created by whole or partial cleavage during transfer.

We confirmed the large domain size expected for the HOPG samples we were using (1–10 μm) as we found by AFM that there were few and sometimes no step edges on the surface of the plates.

4. Conclusions

The results of the study show that graphite islands of micrometre size can be fabricated on the HOPG surface in a designed way. The islands can be further manipulated by an AFM tip either *in situ* as-created on the HOPG surface, or as-transferred on any other flat surfaces, such as a Si(001) surface. Very thin sections of HOPG plates were found on the substrate to which the islands were transferred. The results have the implication that, by using nanofabrication techniques, single or multiple atomic layers of graphite sheets can be fabricated in any desired shape. These graphite sheets are suitable to be used as building elements for new nanostructral materials and nanodevices. Micrometre- or nanometre-sized graphene sheets can, in principle, be obtained from the graphite islands created from HOPG, within the size range of current nanofabrication techniques. Future work will include trying to obtain graphene rather than multiple-layer thick pieces of graphite, and to understand the physical and chemical properties of graphene and few-layer thick pieces of graphite.

Acknowledgments

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