Controlled nanometre-scale line and symbol formation on graphite in air using a scanning tunnelling microscope

1991 J. Phys.: Condens. Matter 3 7213

(http://iopscience.iop.org/0953-8984/3/37/014)

J. Phys.: Condens. Matter 3 (1991) 7213–7216. Printed in the UK

LETTER TO THE EDITOR

Controlled nanometre-scale line and symbol formation on graphite in air using a scanning tunnelling microscope

C J Roberts, M C Davies, D E Jackson, S J B Tendler and P M Williams
The VG STM Laboratory for Biological Applications†, The Department of Pharmaceutical Sciences, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Received 13 June 1991

Abstract. Here we demonstrate the first reported production of etched lines on a highly oriented pyrolytic graphite surface using a scanning tunnelling microscope. This has been achieved by moving the imaging tip, biased at a minimum of 3.5 V of either polarity, in a controlled fashion over the substrate at a velocity of 10 nm s^{-1} or greater. The potential of the technique to control the width and depth of the lines is investigated. The resultant etched structures may be used to evaluate the performance of the piezo-crystal tube and tip. The potential of this technique in the study of bio-molecules is noted.

The achievement of controllable surface modification at a nanometre-scale has applications in fields such as high-resolution lithography, mass data storage and the provision of binding sites for bio-molecules [1]. In addition, the symmetry and integrity of patterns etched into the substrate can be used as a test for linearity and creep in the piezo-crystal scanner and an analysis of the image of the trough can reveal information concerning the shape of the tip.

At present, lithographic techniques employing electron beams on thin films are commonly limited to 10 nm lateral resolution due to secondary-electron effects [2, 3], whereas scanning tunnelling microscopy has been shown to be capable of surface modifications at an atomic scale [4, 5]. In the wider field of STM surface modification, materials such as gold [6–9], metallic glasses [10] and semiconductors [11] have been modified locally at the 2 to 20 nm range. All these experiments rely to some extent upon raising the voltage bias across the tunnelling gap, usually in a short pulse, to promote a surface fabrication event.

To date, experiments with highly oriented pyrolytic graphite (HOPG) have been limited to the production of pits down to a minimum of 2 nm in diameter by the application of voltage pulses of either polarity from 2 to 8 V and a duration of 1 μs to 2 minutes [1, 12–15]. The features produced are then stable in time, unless defoliation of the upper graphite layers is caused by too much etching around a single area [12, 13]. Rabe *et al* have found that the presence of water is a necessary condition for the

---

† To which any correspondence should be addressed.

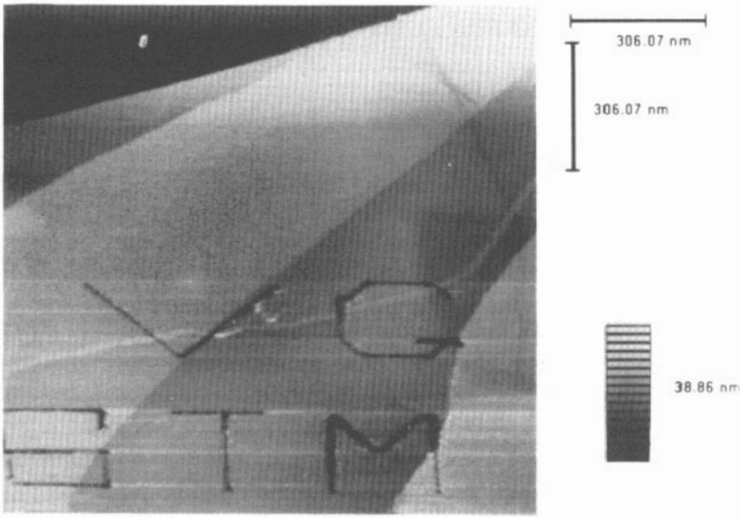

Figure 1. A series of etched lines in HOPG forming the legend VG STM, recorded in the constant-current mode with a tip bias of −330 mV and a current of 360 pA. These lines were formed by moving the tip, biased at −4.26 V, at a velocity of 17 nm s^{-1} over the graphite. Each letter is 150 nm high and 200 nm wide and is made up of lines an average of 9 nm in width and 2.4 nm in depth (i.e. seven graphite layers have been removed).

fabrication process to occur [14], which is thought to be based on the chemical reactions which follow the equations below [13]:

$$C_{(\mathrm{solid})} + H_2O_{(\mathrm{liquid})} + 175.32\ \mathrm{kJ\ mol^{-1}} = CO_{(\mathrm{gas})} + H_{2(\mathrm{gas})}$$

$$C_{(\mathrm{solid})} + 2H_2O_{(\mathrm{liquid})} + 178.17\ \mathrm{kJ\ mol^{-1}} = CO_{2(\mathrm{gas})} + 2H_{2(\mathrm{gas})}.$$

Here we extend this surface modification work to etch troughs reproducibly into a HOPG surface using a scanning tunnelling microscope (STM) in air, with the potential for controllable line widths and depths down to approximately 2 nm and 0.35 nm (i.e. the graphite inter-layer spacing) respectively.

The HOPG for this study (Union Carbide Corporation, OH, USA) was prepared by removing contaminated surface layers with adhesive tape. Initially to ensure a hydrated surface, 30 μl of triple-distilled deionized water was allowed to dry upon the graphite. This approach, however, has proved to be unneccesary as sufficient surface water has been found to be present under ambient conditions to promote the etching reaction. A VG STM 2000 microscope (VG Microtech Ltd, Uckfield, UK) using a cut platinum/iridium tip (80:20) was employed for the STM experiments.

To etch a continuous line in HOPG the tip was moved from a known starting position to a predetermined location at a set velocity, with the voltage bias raised to, or above, the fabrication level. Upon reaching the end point of an etched line the tip voltage was immediately reduced to a normal imaging level (−330 mV in the presented images). The bias threshold is defined as that necessry to produce a clear line in the graphite. This was established for several tips to be at approximately ±3.5 V for a tip velocity of 10 nm s^{-1}. It should be noted that at this voltage level the STM will no longer be operating in a tunnelling regime but a field emission one [16].

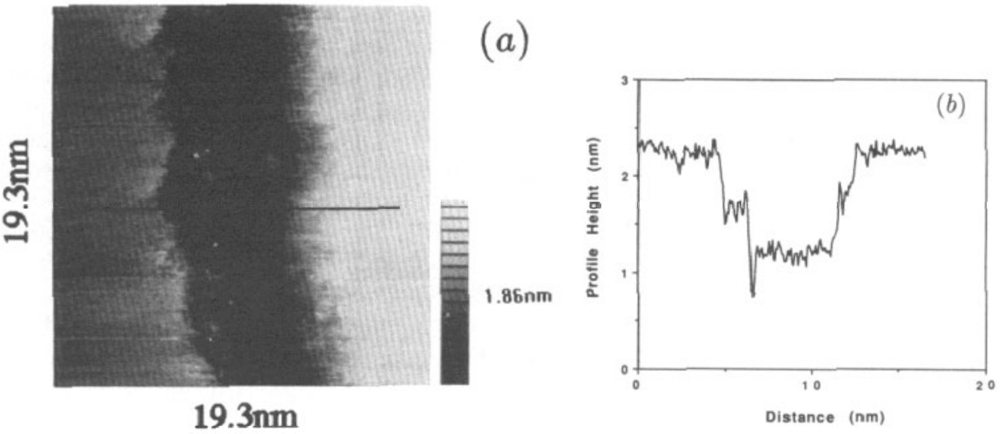

Figure 2. (*a*) A high-resolution scan of a trough produced by a voltage bias of −3.6 V and a tip velocity of 14 nm s^{-1}, whose terraced nature is clearly visible. The width and depth of the line as revealed by the cross-section in (*b*) are approximately 6 nm and 1.0 nm respectively (i.e. three graphite layers have been removed).

The level of control that can be achieved with this as yet semi-automatic process is illustrated in figure 1, where the legend VG STM has been inscribed into the surface. The symbols were written in two five-minute stages, at a tip bias and velocity of −4.26 V and 17 nm s^{-1} respectively. Each letter is 150 nm high and 200 nm wide and is composed of lines of an average width of 9 nm and a depth of 2.4 nm. A higher-resolution scan of an etched trough, produced at −3.6 V and 14 nm s^{-1}, is shown in figure 2(*a*) and a cross-section taken through this feature is presented in figure 2(*b*). These data show the terraced nature of the etched line, due to successive removal of graphite planes. Another common feature observed following the etching of HOPG is debris that lines the edges of the troughs. This may arise from graphite that has failed to oxidize but was disrupted in the fabrication process, possibly by the effects of reflected and secondary electrons [17]. Support for this supposition may be gained from the observation that if a fabrication voltage set just below threshold is employed, some intermittent disruption of the basal plane is noted but no trough is formed (data not shown [18]).

We have found that the line width and depth can be controlled by varying the fabrication voltage and the tip velocity. Increasing the bias voltage causes greater damage and hence larger features, due to the increase in energy flux incident upon the surface and the additional effect it has of broadening the electron beam [17].

Conversely an increase in the tip velocity during etching reduces the energy input over any one point and therefore produces thinner and shallower lines. To date, voltages of magnitude 3.5 to 10 V and tip velocities of between 10 nm s^{-1} and 1 μm s^{-1} (the upper limit we can achieve) have been used. Within these parameters the line widths and depths that have been achieved range from 2 to 100 nm and 0.35 nm to tens of nanometres respectively. The durability of the platinum/iridium tips has been demonstrated by their ability to etch troughs and to supply subsequently good images of these features for a number of days. There was, however, a gradual reduction in line and image quality with time and eventually a failure of the tips to produce any fabricated features. This may be due to the gradual coating of the tip apex in carbon deposits, that thus increases the effective tip area from which field emission can take place. As a result of this, the current density at the surface will eventually fall below that necessary to cause an etch effect.

In conclusion we have demonstrated a technique that produces controlled topographic changes on a graphite surface. The resultant features can be used to test the performance of the piezo-crystal scanner, since any creep or non-linearity effects are made clear by the integrity of the symbol formation. The ability of the tip to image the narrower etched lines may be used in the future to estimate the tip's width and, by the use of deconvolution routines, its profile [19]. The complete automation of this fabrication technique will improve etched pattern definition and make the marking, and hence the unique indentification of specific surface sites, a possibility. Finally the possible use of purpose-built surface features on a HOPG substrate as binding sites for biomolecules is at present under investigation [18].

We would like to thank VG Microtech Ltd for their support.

References

[1] Terashima K, Kondoh M and Yoshida T 1990 *J. Vac. Sci. Technol.* A **9** 581–4

[2] Hatzakis M 1988 *IBM J. Res. Dev.* **32** 441

[3] Broers A N 1988 *IBM J. Res. Dev.* **32** 502

[4] Becker R S, Golovchenko J A and Swartzentruber B S 1987 *Nature* **325** 419–21

[5] Eigler D M and Schweizer E K 1990 *Nature* **344** 524–6

[6] Li Y Z, Vazquez L, Piner R, Andres R P and Reifenberger R 1989 *Appl. Phys. Lett.* **54** 1424–6

[7] Mamin H J, Guethner P H and Rugar D 1990 *Phys. Rev. Lett.* **65** 2418–21

[8] Hoffmann-Millack B, Roberts C J and Steer W S 1990 *J. Appl. Phys.* **67** 1749–52
Roberts C J, Hoffmann-Millack B and Steer W S 1991 *Surf. Sci. Lett.* at press

[9] Sommerfeld D A, Cambron R and Beebe T P Jr 1990 *J. Phys. Chem.* **94** 8926–32

[10] Staufer U, Scandella L and Wiesendanger R 1989 *Z. Phys.* B **77** 281–6

[11] Nagahara L A, Thundat T and Lindsay S M 1990 *Appl. Phys. Lett.* **57** 270–2

[12] Albrecht T R, Dovek M M, Kirk M D, Lang C A, Quate C F and Smith D P E 1989 *Appl. Phys. Lett.* **55** 1727–9

[13] Mizutani W, Inukai J and Ono M 1990 *Japan J. Appl. Phys.* **29** L815–7

[14] Rabe J P, Buchholz s and Ritcey A M 1990 *J. Vac. Sci. Technol.* A **8** 679–83

[15] Bernhardt R H, McGonigal G C, Schneider R and Thomson D J 1990 *J. Vac. Sci. Technol.* A **8** 667–71

[16] Gadzuk J W and Plummer E W 1973 *Re. Mod. Phys.* **45** 487–548

[17] McCord M A and Pease R F W 1987 *Surf. Sci.* **181** 278–84

[18] Roberts C J, Davies M C, Jackson D E, Tendler S J B and Williams P M 1991 in preparation

[19] Williams P M, Davies M C, Jackson D E and Tendler S J B 1991 *J. Mol. Biol.* submitted
Davies M C, Jackson D E, Tendler S J B and Williams P M 1990 *Chem. Indust.* **23** 776–8