Electro-oxidative lithography by STM as a proximity electrode of electrically conducting DLC

T Mühl1,2 and S Myhra1
(1) Department of Materials, University of Oxford, Oxford OX1 3PH, UK
(2) Institute of Solid State and Materials Research IFW Dresden, D-01171, Germany

t.muehl@ifw-dresden.de

Abstract. Carbon-based solids with active surface sites, including electrically conductive diamond-like carbon (DLC), will undergo electro-oxidative conversion to CO₂ in an aqueous phase; the reaction takes place either in a thin film of adsorbed moisture, or in an aqueous fluid cell. The process can be localized by conventional masking, or by a mask-less configuration based on using a scanning tunneling probe as a proximity electrode. In the former case the technology is parallel and spatial resolution is determined by the masking, while in the latter case the technology is serial, but line widths of 10 nm can be obtained.

1. Introduction
Local probe methods have given the scientific community new tools with which to characterize on the nano- and meso-scale the structure and properties of surfaces and interfaces. Recently it has become apparent that the ability to manipulate purposefully those structures and properties may be an even more important attribute of the SPM family.

Several SPM-based nano-technologies for manipulation of surfaces have been described in recent years. While the common element is exploitation of the localized interaction between a sharp tip and a surface for the purpose of carrying out spatially-resolved manipulation of surface structures and/or properties, a large sub-group is based on application of a tip-to-surface bias, with the tip being effectively a local travelling electrode. Oxide structures with line-width resolution better than 10 nm can be written by an SPM probe to a silicon surface by ‘anodic’ oxidation, e.g. [1-3]; the local ferroelectric structure [4] can be manipulated by ‘electrostatic’ force microscopy; and oxidative nano-lithographic patterning of amorphous graphitic carbon films and of electrically conducting diamond-like carbon (DLC) films has been described [5-8]. However, in many cases the underlying mechanism is not fully understood.

DLC is the generic label for materials that can be synthesized by a variety of routes, leading to phases that are diamond-like (e.g., with various degrees of short-and long-range order and/or doping) through to being amorphous and graphite-like. The products are finding increasing industrial usage (e.g., coatings for video tapes and hard drive discs, protective films on razor blades, optical windows, high temperature electronics, etc. [9]). DLC has a number of claimed merits in the context of future nanotechnologies (negligible chemical reactivity with most substrates; hardness and other mechanical properties comparable to those of crystalline diamond; high thermal conductivity, low friction and modest coefficient of expansion; and with surface roughness that can be comparable to that of the substrate [10-12]. It is known that H-termination will result in p-type conductivity in the surface layer.
[13]; it is also known that O-termination will produce an insulating layer. The latter can be ‘written’ to the surface on the nano-scale with a conducting AFM probe. A single hole device has been demonstrated [14, 15]. However, the technological exploitation of DLC has been limited by the lack of a well-developed lithographic technology.

The topicality of diamond/DLC as an ingredient for advanced device technologies provides the immediate rationale for the present project. Patterning of diamond and amorphous carbon films by gas-assisted focused ion beams (FIB) has been reported [16]. While FIB is capable of fabricating sub-100 nm planar features, it is a relatively slow serial technology. A recent study has described amorphous carbon masking in combination with SiO$_2$ capping, as an alternative to resist masking, for a sub-40 nm gate technology [17]. Masking by an amorphous carbon film in combination with lift-off and ion beam milling was used in an earlier study in order to produce YBCO squid devices [18].

This study shows that electro-oxidative nanolithography of DLC can be carried out in the presence of water. The aqueous phase is present either as a thin film of adsorbed moisture or as bulk fluid covering the DLC surface. Water closes the electrical circuit between the STM tip and the DLC film and represents a reaction partner. During local or non-local electrochemical reaction, the carbon-phase is being consumed and the reaction products are volatile gases (earlier work [19] suggests CO$_2$ and H$_2$). Since the anodic electrochemical process can be localized, patterning can be achieved.

2. Experimental details

2.1. DLC films

The DLC process technology was an ion beam assisted variation of the generic chemical vapour deposition route. Details can be found in the literature [10]. The outcome was a wear-resistant diamond-like carbon film, although with considerable graphitic character (inferred from Raman analysis), and with RMS surface roughness of the as-received films in the range 0.25-0.3 nm, inferred from AFM contact mode imaging over fields of view of 1x1 and 2x2 $\mu$m$^2$. Specimens from the same fabrication route have been investigated in earlier studies [2, 10].

2.2. SPM instrumentation and methods

The analysis was carried out with a JEOL JSTM-4200 multi-technique instrument. The JEOL instrument has the particular attribute of allowing analysis within a bell jar; thus the ambient can be controlled and can range from a vacuum of $10^{-3}$ Pa to atmospheric pressure with known humidity. In the latter case a hygrometer was placed within the analysis envelope. As well, the sample can be biased with respect to the tip while scanning in various modes. The instrument also comes supplied with lithographic software. Etched and cut Pt/Ir tips were used for STM lithography and analysis.

2.3. Lithographic methods

2.3.1. Local maskless lithography. The initial state of a particular surface region was determined by STM imaging in the constant current mode, in order to ensure absence of topographical artefacts. The field of view was re-scanned subsequent to electro-oxidative exposure in order to detect the extent of alteration. Even though DLC is hydrophobic there will be present on the surface a thin adsorbed aqueous layer, with a thickness in the nm-range, in a humid atmosphere. After tip approach, the very end of the tip will be located within the aqueous layer. In order to avoid feedback oscillations in the constant current mode, imaging at high relative humidity (RH) had to be performed at low gap voltage, e.g., 100 mV. The system will thus form a local electrochemical cell where the spacing between the electrodes, defined by relative positions of the DLC anode and the probe cathode, will be determined by the length of the meniscus bridge. The cell will be attached to the probe and can thus be transported laterally during a raster. The lateral spatial extent of the cell will be defined by the electrostatic field lines. The sample was biased positively with respect to the tip during lithographic alteration.
2.3.2. *Masked lithography.* Test-patterns were masked on the DLC surface by standard lithographic techniques. A photore sist layer of thickness of ca. 1.3 μm was spin-coated at 4000 rpm, and then cured at 90°C for 90 s. The pattern was exposed for 10 s through a proximity mask in a Quintel Q-4000 system, and subsequently developed at room temperature. The process was terminated by a hard bake at 110°C.

Masking allows parallel processing on the SPM platform. A macroscopic region of the masked surface is submerged in a droplet of distilled and deionized water. The probe electrode is inserted into the aqueous envelope several times 100 μm from the DLC-water interface, followed by establishment of electrochemical conditions. The lithographic pattern can be transferred into the DLC film in a matter of minutes over lateral distances on the mm scale. The mask was removed subsequent to patterning.

3. **Results and discussion**

3.1. *Mask-less lithographic patterning*

Examples of outcomes of mask-less electro-oxidative patterning of a DLC surface, when the STM was a local traveling electrode, are shown in figures 1 and 2. The pattern in figure 1 was obtained with a blunt tip; thus the shape of the pits (evident from the SEM image) was essentially congruent with the tip geometry. The corresponding STM data reveal a depth of the pits of approximately 60 nm.

![Figure 1](image.png)

**Figure 1.** STM (left) and SEM (right) images of an array of pits written to a DLC surface. The SEM image was obtained at an angle of 76°. The STM patterning conditions were: 68% RH, 6 V sample bias, 10 nA tip current, and a dwell time of 500 ms per pit.

The pattern in figure 2, a series of pits, illustrates the resolution of the technique. The spacing and depth of the pits were 20 and 0.75 nm, respectively. The full-width at half maximum pit depth was less than 10 nm, in agreement with previous results for line-width resolution obtained in the contact AFM mode with a conducting probe [8].

Patterning experiments have been carried out for a wide range of conditions. The observed general trends and dependences include: (i) Experiments with opposite bias polarity did not lead to pit formation. (ii) The extent of removal of DLC increased with voltage, tip current, dwell time and RH. Accordingly higher lateral tip speed gave rise to lesser depth and width of a trench arising from a line scan. Below 2 V pit formation could not be observed. However, the latter seems to be due to a decrease in reaction kinetics rather than representing a genuine threshold voltage. (iii) In the absence
of water, i.e., for RH below 10%, pit or trench formation could not be observed. (iv) There is no apparent limitation of the depth of the pattern. Total local removal of the entire DLC film could readily be induced. Appropriate lithographic sequences allow fabricating of desired three-dimensional patterns.

One particular pit in Fig. 1 (second line, fifth column in the pattern) is absent. The reasons are not yet clear but may be due to laterally differentiated surface properties/chemistry (or due to contamination and/or transient tip alteration).

**Figure 2a.** A (300 nm)$^2$ STM image of a line of pits spaced 20 nm apart. The patterning was carried at 78% RH, at 4.5 V bias and 10 nA tip current, and with an exposure time of 10 ms per pit.

**Figure 2b.** The contour line drawn along the line of the pits reveals a depth of ca. 0.75 nm. The spatial corrugation of the pattern is superposed on a local RMS roughness of ca. 0.5 nm of the DLC surface.

**Figure 3.** SEM images of pattern arising from masked electro-oxidative lithography of a DLC surface. The tip was a stationary distant electrode (ca. 0.5 mm displaced from the surface). The exposure conditions were: 8 V bias, 180 s duration.

3.2. **Masked lithographic patterning**

The dependence of the local STM oxidation of DLC films on RH has motivated electro-oxidative experiments with the tip DLC region within a fluid cell defined by a droplet of DDI water. As before, application of a positive sample voltage resulted in removal of DLC. The process is accompanied by gaseous evolution, visible in an optical microscope. The lateral extent of reaction is now macroscopic. In order to write laterally defined pattern, photo-lithographically prepared masks were applied. SEM images in figure 3 show patterns in a 180 nm DLC film.

3.3. **Mechanisms**
Previous work on probe-based patterning of DLC identified outcomes of the process but did not recognize the role of an aqueous phase. The demonstrated significance of a water-to-DLC interface and the application of anodic bias conditions in the case of DLC are similar to observations of SPM-based local oxidation of HOPG [20, 21] and to electrochemical carbon and coal conversion [19, 22, 23]. Thus it is plausible to ascribe DLC removal to a conversion of carbon, water and electric energy into gaseous CO₂/CO and hydrogen. Additional discussion of mechanisms can be found in a companion paper [24].

4. Conclusions
DLC films can be patterned by anodic oxidation in an aqueous environment by means of a local traveling electrode as well as by non-local electrochemical treatment. In the latter case masking allows lateral patterning. The physico-chemical mechanism as well as technological aspects, such as ultimate spatial resolution and optimum process conditions will be addressed in ongoing work.

5. Acknowledgements
The project was funded in part by the Australian Research Council, and by a fellowship awarded to Thomas Mühl by the Deutsche Forschungsgemeinschaft. The work was carried out while the authors were visiting the Department of Materials at the University of Oxford. We wish to acknowledge generous support and hospitality. The DLC material originated with a research programme undertaken at AEA Technology plc.

References
[1] Avouris P, Hertel T and Martel R 1997 Appl. Phys. Letts. 71 285
[2] Myhra S 2003 Appl. Phys. A 76 63
[3] Vullers R J M, Ahlskog M and van Haesendonck C 1999 J. Vac. Sci. Technol. B 17 2417
[4] Shin H, Hong S, Moon J and Jeon J U 2002 Ultramicroscopy 91 103
[5] Mühl T, Brückl H, Weise G and Reiss G 1997 J. Appl. Phys. 82 5255
[6] Mühl T, Brückl H, Kraut D, Kretz J, Mönch I and Reiss G 1998 J. Vac. Sci. Technol. B 16 3879
[7] Mühl T, Kretz J, Mönch I and Schneider C M 2000 Appl. Phys. Letts. 76 786
[8] Myhra S 2005 Appl. Phys. A 80 1097
[9] Sussmann R S, Brandon J R, Pickles C S J and Whitehead A J 2000 Proc. MicroMat 2000, Michel B, Winkler T, Werner M and Feych H (eds) p.129
[10] Crossley A, Johnston C, Watson G S and Myhra S 1998 J. Phys. D: Appl. Phys. 31 1955
[11] Moelle C, Klose S, Szuces F, Fecht H J, Johnston C, Chalker P R and Werner M 1997 Diamond Relat. Materials 6 839
[12] Chalker P R, Johnston C, Crossley J A A, Amobrose J, Ayres J C F, Harper R E, Buckley-Golder I M and Kobashi K 1993 Diamond Relat. Materials 2 1100
[13] Maki M, Shikama S, Komori M, Sakaguchi Y, Sakuta K and Kobayashi T 1992 Jpn. J. Appl. Phys. 31 1446
[14] Taniuchi H, Umezawa H, Arima T, Tachiki M and Kawarada H 2001 IEEE Electron Device Lett. 22 390
[15] Seo H, Tachiki M, Banno T, Sumikawa Y, Umezawa H and Kawarada H 2002 Jpn. J. Appl. Phys. 41 4980
[16] Stanishevsky A 2001 Thin Solid Films 398-399 560
[17] Romero K, Stephan R, Grasshoff G, Mazur M, Ruelke H, Huy K, Klais J, McGowan S, Dakshina-Murthy S, Bell S and M. Wright M 2005 IEEE Trans. Semicond. Manufacturing 18 539
[18] Yi H R, Ivanov Z G, Winkler D, Zhang Y M, Ohlin H and Larsson P 1994 Appl. Phys. Lett. 65 1177
[19] Coughlin R W and Farouquie M, 1979 Nature 279 301
[20] Albrecht T R, Dovek M M, Kirk M D, Lang C A, Quate C F and Smith D P E 1989 Appl. Phys.
[21] Hiura H 2004 Appl. Surf. Sci. 222 374
[22] Binder H, Kohling A, Richter K, and Sandstede G 1964 Electrochim. Acta 9 255
[23] Park S 1984 J. Electrochem. Soc. 131 363C
[24] Mühl T and Myhra S 2006 submitted in this issue