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# Diamond-like-carbon (DLC) master creation for use in soft lithography using the Atomic Force Microscope (AFM)

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**Abstract**. Two and three dimensional polymeric structures at the nano and micro scale are increasingly being incorporated into micro and nano scale devices. Soft lithography can be employed for the creation of templates where a polymer replica can be produced. Obtaining a master is one of the *limiting factors* in the production of such replicas.

This study demonstrates pattern generation on a highly durable and flat diamond-like-carbon (DLC) film with micro/nano-scale resolution using the atomic force microscope (AFM). The AFM is operated in the electrical conductivity mode which induces oxidation on the DLC surface. The technique offers features with line widths less than 20 nm. As a result, highly complex shapes can be produced with a depth being controlled by the DLC film thickness and/or by the bias voltage parameters.

## 1. Introduction

Nano-technologies based on the Scanning probe Microscopy (SPM) family include templating, surface patterning, nano-writing, nanolithography, and nano-machining. Soft lithography is a group of alternative methods which have become utilized for a large variety of applications, some of which include micromolding, microfluidic networks and microcontact printing [e.g., 1]. The method utilizes the formation of stamps and elastomeric elements by way of exposing a suitable polymer to a template. The templates are generally fabricated at the micron scale by well established lithographic techniques used in the microelectronic industry, such as photolithography. Creating templates on the nano-scale however, has been a limiting factor.

Diamond-Like-Carbon (DLC) is a generic term for a class of materials able to be synthesized by a variety of well-established routes, leading to phases that are diamond-like, with hardness and other mechanical properties being also comparable to those of crystalline diamond. DLC is now finding increasing industrial usage, for example coatings for video tapes and hard drive discs, coating on razor blades and high temperature electronics just to name a few.

The transference of a pattern from a master is now possible with the aid of a variety of polymers. One of the most popular polymeric materials utilized is polydimethylsiloxane (PDMS), attributed with a wide range of useful physical, mechanical and chemical properties, some of which include surface hydrophobicity, high electrical resistance, transparency, low toxicity, constant and high ductility over a wide range of temperatures, long-term stability and flexibility [2]. The fabrication and use of micro/nano stamps and fluidic channels using PDMS has been demonstrated in various studies, (e.g., [3-6]). This study demonstrates the use of DLC as a template for producing PDMS micro/nano stamps

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and 3-dimensional polymer structures by Atomic Force Microscopy (AFM) operated in the electrical conductivity mode.

## 2. Experimental details

### *2.1. Materials preparation*

Electrically conductive DLC films were deposited onto polished n-type Si substrates. The process technology was an ion beam assisted variation of the generic chemical vapour deposition route. The substrate was maintained at 80°C at an ambient pressure of $10^{-6}$ Torr, while being exposed to a partial pressure of polyphenyl ether from a source held at 150°C. Simultaneous exposure of the substrate to a 30-80 keV $N^+/N_2^+$ beam at a current density of ca. 7 mA $m^{-2}$ promoted cracking, bond rearrangements, and loss of volatile components. The measured growth rate was of the order of 1 μm/h [7]. The outcome was a wear-resistant diamond-like carbon film, although with considerable graphitic character, and exhibiting low friction (0.1-0.2 for contact loads up to 100 N). RMS surface roughness of the as-received films in the range 0.25-0.3 nm was inferred from AFM imaging over fields of view of 1×1 and 2×2 $\mu m^2$.

The PDMS polymer was supplied by Dow Corning as a two-part silicone elastomer – Sylgard®-184. The two parts consisted of a base and curing agent, mixed at a weight ratio of 10:1. After thorough mixing, the polymer was then deposited directly onto the DLC templates and allowed to cure for 1 hour at a temperature of 100°C. After curing, the hardened polymer was then peeled off the DLC template. The PDMS stamp was then attached to an SPM stub ready for analysis.

### *2.2. SPM instrumentation*

The manipulation of the DLC was carried out with a JEOL JSTM-4200D and JSPM-4200 multi-technique instrument. The instruments have the particular attribute of allowing analysis to be carried out within a bell-jar envelope in a vacuum of $10^{-3}$ Pa. As well, spreading-current I-V analysis with a sensitivity of 30 pA can be carried out routinely with a conducting probe (i.e., electrical conductivity microscopy (ECM)), and the tip can be biased with respect to the sample while scanning in the contact mode. The instruments come supplied with lithographic software.

The consequent surface analysis of the PDMS stamp was carried out in contact mode with the JSPM-4200 instrument with 25×25 and 85×85 $\mu m^2$ tube scanners, with a *z*-range of ca. 3 μm. The experiments were carried out under air-ambient conditions with a relative humidity of 55-75% and a room temperature of 25ºC.

### *2.3. Probes*

The probe consisted of a lever with an integral conical tip attached at its free end. The tip-to-surface point of contact defines the interaction volume, of molecular to micron size, from which information is extracted, (e.g., topography, strength of in-plane and out-of-plane forces, etc.) and through which purposeful manipulation is effected. The beam-shaped Si levers were supplied by Ultrasharp NT-MDT. The length ($L$), width ($w$), thickness ($t$), tip height ($h$) and normal spring constant ($k_N$) values were 350 μm, 35 μm, 1 μm, 15-20 μm and 0.01-0.08 $Nm^{-1}$, respectively, as supplied by the manufacturer. Most of the tips were also characterized by 'reverse' imaging over a grid of spikey features; the radii of curvature were consistent with those claimed by the manufacturer. As well, the probes were subjected to I-V characterization before and during experimental runs by investigation of point-contact resistance on a Si-substrate covered by a gold film.

PDMS stamp surface analysis was carried out using a very soft beam-shaped (Ultrasharp NT-MDT) lever ($k_N$ = ca. 0.03 $Nm^{-1}$) in order to avoid any surface manipulation and/or modification.

## 3. Results and discussion

### *3.1. Oxidation in air*

Manipulation on the nano-scale as a result of tip-induced local prompt oxidation of electrically conductive DLC can result in the creation of well-defined, 3-dimensional lithographic patterns, for example [1, 8]. The results illustrated below were obtained by establishing a bias voltage across the tip, a water layer, the DLC film and the silicon substrate. An insight into the mechanisms responsible for the oxidation are given by Mühl and Myhra [9].

The topographical image in figure 1 (a) shows the outcome of performing single raster scans (various small scan sizes) using a tip with a large radius of curvature. The depth of the pits corresponds to the thickness of the film, ca. 250 nm.

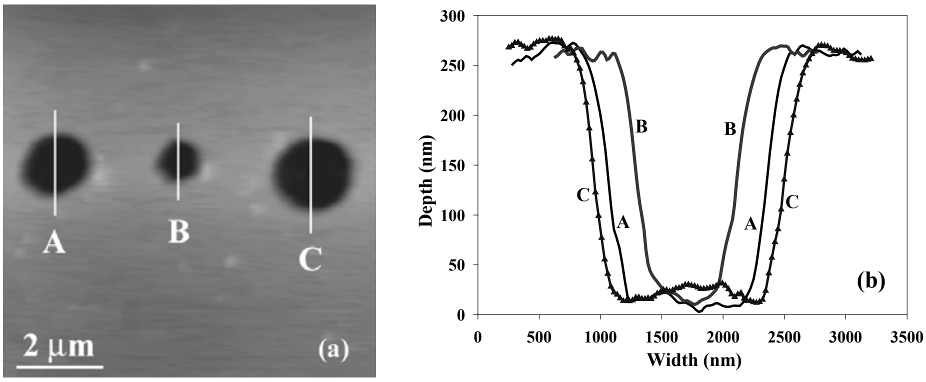


Figure 1. (a) Topographical image of three circular 'holes' created via single raster scans using a tip with a very low aspect ratio. (b) shows the corresponding line profiles across all three holes.

Using a very sharp tip (i.e., small radius of curvature) and allowing it to come into contact on the DLC surface, applying a bias voltage and finally retracting it (as in the case of an f-d curve acquisition), nanometer-scale 'holes' can be formed. Figure 2 is a demonstration of this action. A dwell time of 15 seconds was applied before retracting the tip. Figure 2 (a) shows a topographical image of a single nanometer scale hole created with the line profile shown in (b). The width (half way down) and depth was ca. 17 and 1.5 nm, respectively.

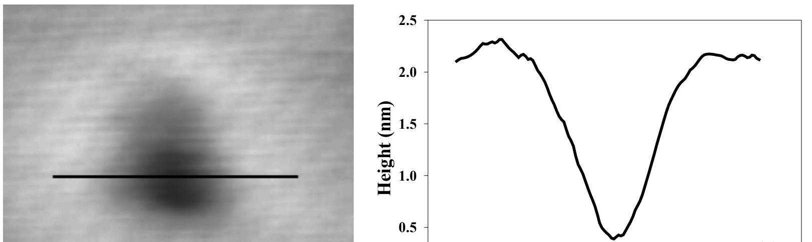


Figure 2. A topographical image (a) showing the creation of a nanometer-scale hole with the corresponding line profile in (b).

Square pits can be produced by utilizing tips with a high aspect ratio and performing a single raster scan. Varying the dwell time and/or scan speed, enables the depth to be controlled. Figure 3 below demonstrates the creation of a pit by scanning over a 100×100 $nm^2$ area at a positive sample bias of 4.5 V, and composed of 256×256 pixels. The bias was applied for 90 seconds, creating a depth of 12 nm. The resultant topographical image is shown in figure 3 (a). A line profile across the pit (defined in (a)) is shown in figure 2 (b). The surface roughness at the bottom of the pit is < 2 nm.

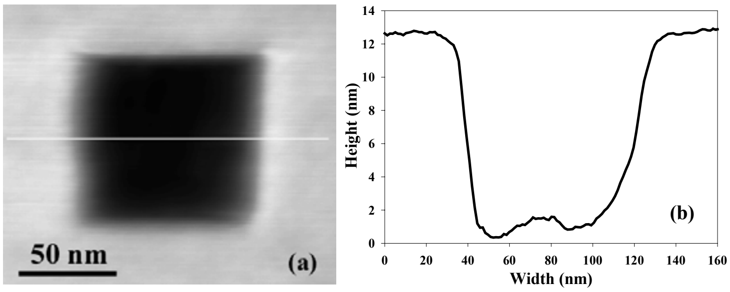


Figure 3. Contact mode image (a), and cross-sectional contour line (c) illustrate a square pit formed as a result of carrying out tip-induced spatially resolved oxidation.

*3.2. Templating*

The formation of various three-dimensional structures on a DLC surface can then be applied to polymeric stamp creation. Figure 4 (a) shows a topographical image obtained after manipulation of an arbitrary pattern created on a DLC surface. PDMS was then deposited onto the surface, cured, peeled off and analysed, with the resultant topographical image shown in figure 4 (b). It can be seen that the pattern transfers with great accuracy.

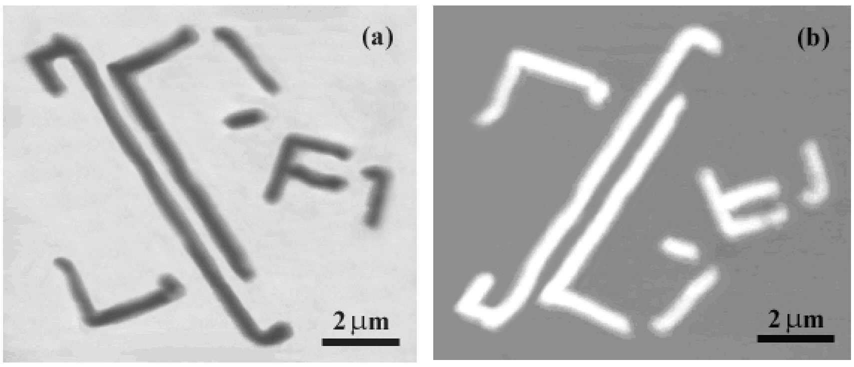


Figure 4. Topographical images of a DLC template (a), and the resultant PDMS stamp (b) showing a high degree of accuracy in the reproduction process.

A three-dimensional representation of the PDMS stamp seen in figure 4 (b) is shown in figure 5 (a) below. The line profile across ‘A’ in figure 5 (a) is shown graphically in (b), revealing a height of ca. 250 nm. It can also been seen that the surface roughness of the top of the feature is in the order of nanometres. The line profiles reveal a high degree of accuracy between the masters and resultant stamps.

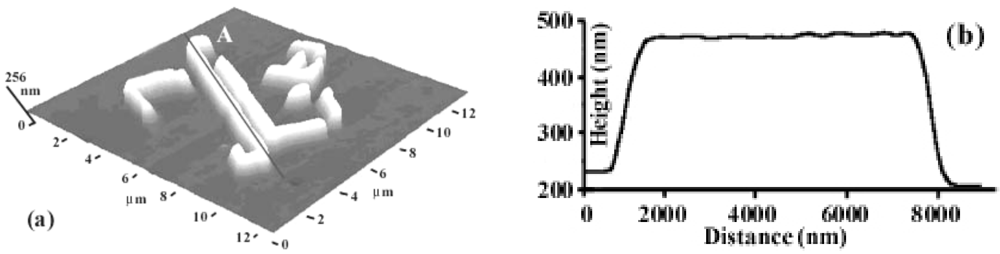


Figure 5. (a) A three dimensional representation of the PDMS stamp. Line profile obtained across sections ‘A’ shown in (a), and the corresponding region on the original DLC template in (b).

## 4. Conclusion

The study demonstrates the ability to produce arbitrary 3-dimensional features on the DLC surface, on the nanometer-scale utilising the SPM tip through which a bias is applied. The DLC can be utilised as a template. Exposing the template to an elastic polymer such as PDMS, stamps with nanometer resolution can be formed. As the formation of nanometer-scale templates is the limiting factor, this technique offers a number of advantages including: the formation of features on the DLC with line widths less than 20 nm is possible; the template edge radius of curvature can be less than 10 nm; various complex shapes can be formed; the depth is controllable either via the bias voltage applied on the DLC film thickness itself; the DLC master is highly durable allowing it to be reused, and; the relief of the master post patterning is extremely flat.

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