Solid-Phase Direct Write (SPDW) of Carbon via Scanning Force Microscopy

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ABSTRACT

The fabrication of carbon nanostructures by direct writing with a scanning force microscope is described. A conductive atomic force tip is used to collect carbon from a glassy carbon substrate and redeposit it onto a gold thin film under voltage control. The resulting patterns are examined with atomic force microscopy and Auger electron spectrometry. Writing of carbon lines with widths as small as 40 nm is demonstrated.

Carbon is a promising material for nanoscale device fabrication due to its range of useful chemical, mechanical, and electrical properties. The ability to deposit controlled 2D and 3D carbon patterns at the nanometer scale adds versatility to nanodevice design and fabrication. Applications include electrodes for electrochemical analysis[1] and resists for etching of nanostructures.[2] This report describes the fabrication of carbon nanostructures by solid-phase direct writing (SPDW) using a scanning force microscope. Although previous work has shown that graphite[3] and amorphous carbon[4] can be controllably etched using voltage-biased scanning probe microscope tips, to the authors' knowledge, this is the first demonstration of direct-write, solid-phase carbon deposition from a coated atomic force microscope (AFM) tip under voltage bias.

Initially, both AFM and STM were developed for imaging the atomic and molecular structure of surfaces. It was quickly discovered that both techniques have considerable potential for atomic manipulations, as demonstrated in the seminal report of the "quantum corral".[5] The introduction of dip-pen lithography[6,7] provided yet another boost in nanofabrication by providing direct write capability to AFM. Dip-pen lithography takes advantage of a well-known problem in AFM imaging, the water meniscus formed at the tip of the AFM probe, to transfer organic "inks" adsorbed on the AFM tip to the substrate. To date, the most common inks are thiol-based organics written on gold surfaces.[8] Although dip-pen lithography is a powerful nanofabrication tool, its utility is limited to select combinations of inks and substrates. Generally, the technique is well suited for lithography where a secondary step is required to etch or otherwise define the nanostructure, however, it is not suited for the direct writing of nanostructural materials in either a deposition or removal mode.
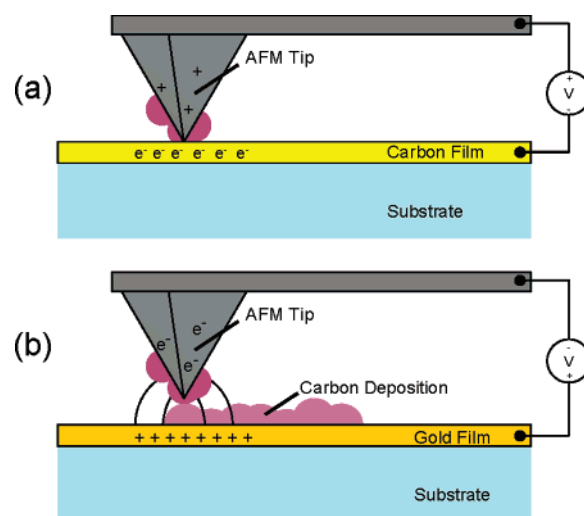

Figure 1. Schematic diagram of solid phase, direct write process. (a) Collecting carbon with a positively biased AFM tip. (b) Depositing carbon onto thin gold film with a negatively biased AFM tip.

Another AFM nanolithography technique utilizes field emission of electrons from the tip to expose an e-beam resist.[9,10] High-field electron emission at AFM tips has also been used to pattern materials such as silicon[11] and titanium[12] by selective anodic oxidation. Although each of the aforementioned techniques have expanded nanoscale imaging and machining capabilities, the full potential of SPM nanomanufacturing has yet to be realized. In this paper, a new AFM-based direct write technique for the deposition and etching of nanostructural materials with nanometer precision is presented. The technique is called solid-phase direct write (SPDW) and can be used to deposit materials directly from the solid phase. In this report, the deposition and etching of

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Figure 2. SEM image of carbon build up on a tip. The thickness of this coating is on the order of 50 nm, and there is evidence of carbon loading as far as 1 μm from the apex of the tip.
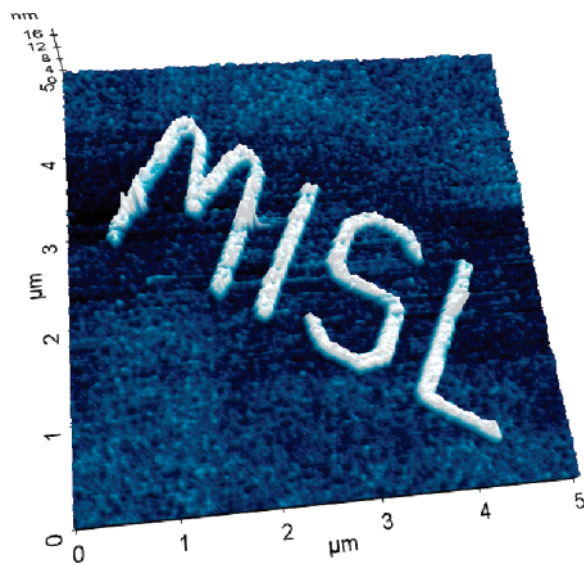

Figure 3. Atomic force micrograph of deposited carbon on gold, using AFM tip biased at -10 V, in air at 0.01 μm/s. Line width is between 200 and 300 nm with height varying from $4-8$ nm.

Figure 4. Example carbon line deposited on thin film gold in a dry nitrogen atmosphere. (a) Atomic force micrograph of two meander lines, left line deposited in one pass at -10 V on tip and at 0.01 μm/s, right line deposited under the same conditions but three passes. (b) Plot showing height profile along white horizontal line from Figure 4a.

carbon is described, although other materials have been similarly demonstrated.

The experimental setup consists of a PSIA XE-100 atomic force microscope and platinum-coated AFM tips (Budget Sensors). Platinum-coated tips were chosen to provide higher conductivity and greater resistance to oxidation than bare silicon tips. Electrical connection was made to the conductive AFM tips using conductive epoxy, and the AFM was operated in contact mode. Both sputter-deposited carbon thin films and commercially available glassy carbon plates (Fischer Scientific) have been used as the carbon source for the SPDW.

The technique is diagrammatically outlined in Figure 1. When a positive voltage is applied to the AFM tip relative to a conducting carbon substrate, the carbon is removed by oxidation to volatile CO_x ($1 \leq x \leq 2$), as previously reported.[4,13] However, under a rather wide range of experimental parameters, elemental carbon is also collected on the tip of the AFM. Figure 2 shows an electron micrograph of a cap of carbon on an AFM tip, extending approximately 1 μm from the apex.

After carbon loading of the AFM tip, the polarity of the tip is reversed (negative) to deposit the carbon onto a conductive substrate. In the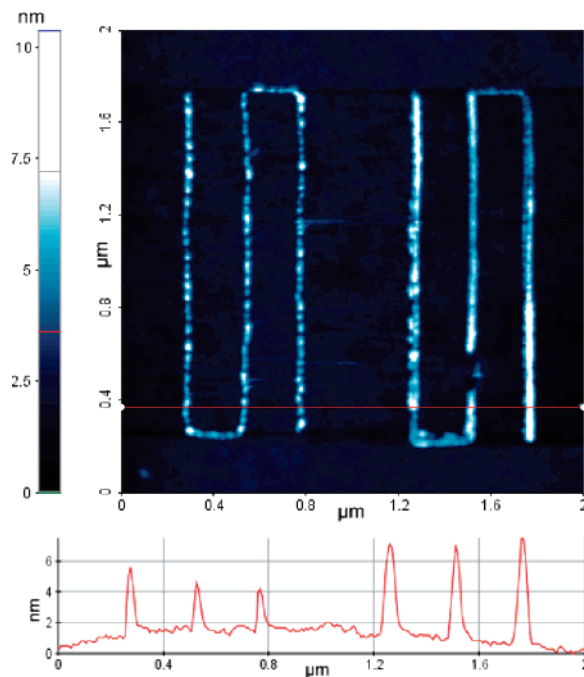 initial studies, a thin gold film was used as a conductive substrate because of its high conductivity and the absence of a native oxide, although other conductive substrates have also been successfully employed. The thickness and relative conductivity of the substrate film does not appear to be a critical variable. Gold thicknesses ranging from 40 nm to 100 nm, as well as other metal and semiconductor films, have yielded similar results. Figure 3 shows an AFM image of a SPDW-patterned carbon structure on gold. Depending on experimental conditions, line widths ranging from 40 to 500 nm with carbon deposition thicknesses ranging from 5 to 20 nm have been achieved. The mechanism of carbon writing is not completely understood, although high-field discharge, electromigration, and surface migration are the more likely mechanisms under consideration. The parameters that are known to affect the line width, height, and continuity of the carbon deposition are voltage magnitude, voltage polarity, current, ambient atmosphere (oxygen and humidity), and writing speed. All experiments reported here were conducted at atmospheric pressure and room temperature using various gas environments. Tip loading and carbon deposition performed under a dry nitrogen environment produced the finest line widths. Lines produced in either wet nitrogen or wet air (gases were passed through a bubbler to saturate with water vapor) tend to be wider (upward of 400 nm) and thicker (upward of 100 nm) than those produced in dry nitrogen given the same write speed and voltage. There is a clear voltage threshold for carbon deposition. Under the conditions presented in this report, no deposition occurs for bias voltages under approximately 6 V dc. Carbon loading and deposition does not
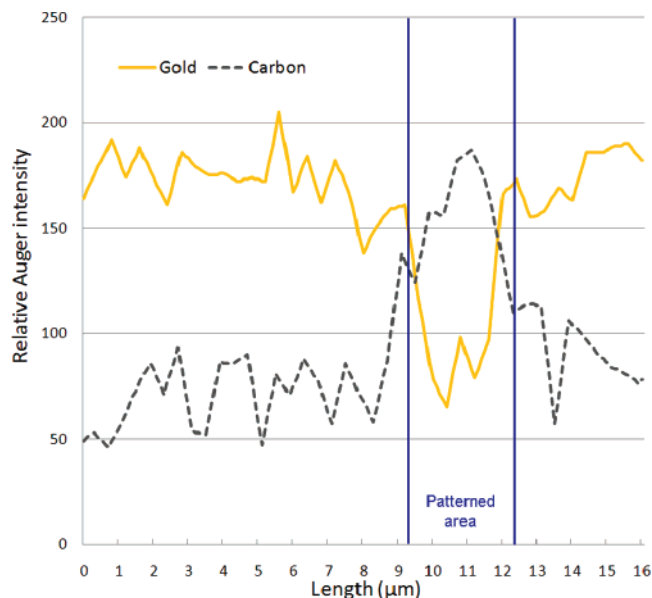
Figure 5. Auger electron line scan across a 3 μm wide section of carbon patterned on a gold surface. The pattern is composed of closely spaced carbon lines with an average height of 30 nm and approximately 80% surface coverage. Carbon Auger intensity is shown with a dashed line. Gold Auger intensity is shown with a solid line. The effective beam width of the Auger electron microscope is estimated to be 1.5 μm, dominated by mechanical noise in the system.

appear to measurably affect the wear characteristics of the AFM tips, and it is possible to write many patterns on the scale presented in this paper from one loading process.

Figure 4 shows an AFM image of two meander carbon lines deposited in a dry nitrogen atmosphere at 10 V. The image on the left was written with a single pass of the AFM and shows line widths of 40 nm and thicknesses of 5 nm. The image on the right is a similar meander line written with three passes of the AFM tip. Multiple deposition passes

increase both the height and line width of the lines, but not proportionally. The specific conditions required for uniform and controlled deposition are still under investigation. Auger electron spectrometry of the deposited carbon films confirmed that the elemental composition of the patterned structures is carbon, with no measurable contribution of materials from the AFM tip, i.e., less than 1% silicon, chromium, or platinum. Figure 5 is an Auger electron line scan across a region where many closely spaced carbon lines were deposited by SPDW onto a gold-coated substrate. The scan beam width is approximately 1.5 μm, which is too large to resolve individual carbon lines and spaces, resulting in an average intensity for gold and carbon within the patterned region.

The deposition process is reversible, such that written carbon patterns can be modified or erased by reversing the polarity of the tip voltage (positive on the tip with respect to the sample). The etching process has a similar resolution as the deposition process for the same write speed and ambient gas environment. Figure 6 shows AFM images of a carbon line (Figure 6a) formed by SPDW and a pair of electrodes formed by removing material from the center section of the carbon line (Figure 6b).

In summary, a technique for solid-phase direct writing and removal of carbon on the nanoscale using an atomic force microscope tip is demonstrated. This technique provides a relatively inexpensive method for nanofabrication. The resulting carbon structures can be either integrated components in sensing structures, e.g., nanoelectrodes, or a chemical etch mask for transferring nanoscale patterns into underlying materials.
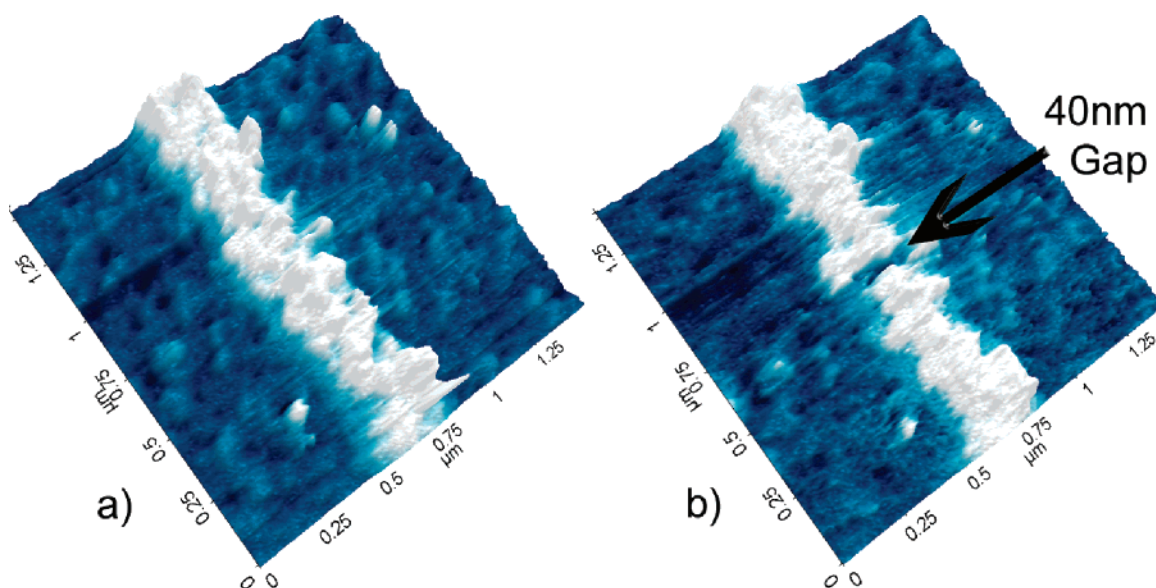
Figure 6. Example of erasing/modifying carbon lines. (a) Atomic force micrograph of carbon line deposited at −10 V on the tip and 0.01 μm/s. (b) Micrograph of same line after it has been modified to form a set of electrodes with +10 V on the tip. The arrow points toward where the line has been modified. The gap created is approximately 40 nm wide at its narrowest point.

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