

## Fountain pen nanochemistry: Atomic force control of chrome etching

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In this report we demonstrate a general method for affecting chemical reactions with a high degree of spatial control that has potentially wide applicability in science and technology. Our technique is based on complexing the delivery of liquid or gaseous materials through a cantilevered micropipette with an atomic force microscope that is totally integrated into a conventional optical microscope. Controlled etching of chrome is demonstrated without detectable effects on the underlying glass substrate. This simple combination allows for the nanometric spatial control of the whole world of chemical reactions in defined regions of surfaces. Applications of the technique in critical areas such as mask repair are likely. © 1999 American Institute of Physics. [S0003-6951(99)02039-2]

In this letter we show that the delivery of a chrome etchant through a force-sensing cantilevered micropipette has the ability to control chemical removal of chrome from a glass surface with the precision of atomic force microscopy (AFM). In addition, the cantilevered micropipette can provide a topographic map of the surface that is chemically altered. The results bode well for achieving similar chemical control and imaging capabilities with any combination of chemical reactions that are presently known.

To place the current work within the perspective of previous studies, it is important to cite a pioneering study<sup>1</sup> in the use of scanned probe microscopy for localized chemistry. This study involved the use of a platinum–rhodium tip in a scanning tunneling microscope to act as a catalyst with the aid of short-voltage pulses for the hydrogenation of carbon clusters on a platinum surface. The first investigation to use AFM for localized chemistry was by Muller *et al.*<sup>2</sup> These workers used a platinum-coated AFM tip to catalyze hydrogenation of terminal azides to amino groups that are amenable to further derivatization. These investigations have inspired the current work which allows for a generalization of these initial studies by the use of cantilevered metal-coated or uncoated micropipettes for the controlled delivery of chemicals in localized regions.

For the experiments reported in this letter the sample was a round 16 mm microscope coverslip on which was deposited a 200 nm chrome layer. The cover slip was placed in a commercial atomic force/near-field optical microscope system, the Nanonics (AFM)/NSOM-100 (Nanonics, Ltd., Jerusalem, Israel) that is fully integrated with conventional optical microscopy.<sup>3</sup> In this arrangement the highly controlled delivery of material could be effectively viewed even with an oil immersion far-field microscope objective (see Fig. 1).

The cantilevered micropipettes used in these experiments were produced based on earlier reports.<sup>4,5</sup> Quartz nanopipettes can have outer diameters at the tip of 10 nm and a hole in the middle that can be as small as 3 nm. In such

structures the capillary is maintained throughout the length of the tip. To prove this we have passed liquid through such tips. The resulting cantilevered glass structures are coated so that there is metal deposited on the glass cantilever to allow for reflection of diode laser light that is used as the standard method of monitoring the bending of the cantilever in all force microscopy systems. To optimize the force-sensing capabilities of these tips the diameter of the capillary in the region of the cantilever was approximately 12  $\mu$  and the cantilever length was 300  $\mu$ . These dimensionalities control the resonance frequency and the force constant of the microcantilever. Resonance frequencies  $f$  can be achieved of up to

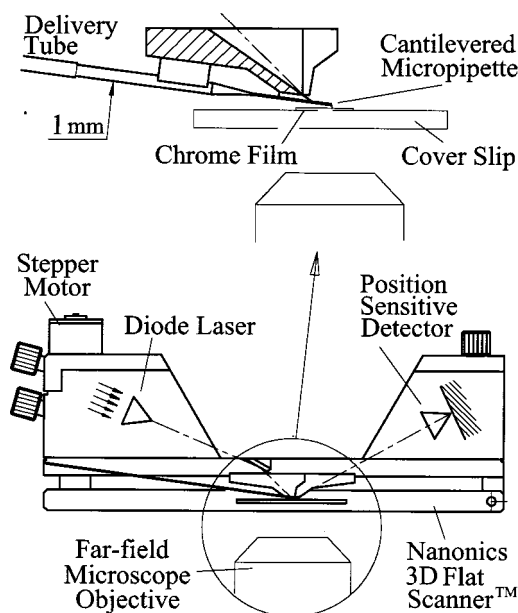


FIG. 1. Diagrammatic representation (bottom of the figure) of the Nanonics scanned probe microscope system that was mounted on the microscope stage of a conventional inverted optical microscope. The upper plate contains the diode laser and a position-sensitive detector for conventional force sensing together with the tip mount. The bottom plate that is hinged on the right to the upper plate is a flat scanning stage with an opening in the middle on which a sample, which in this case is a glass cover slip, is placed. The region of the mounting of the cantilevered micropipette and the associated liquid delivery system is shown at the top half of this figure.

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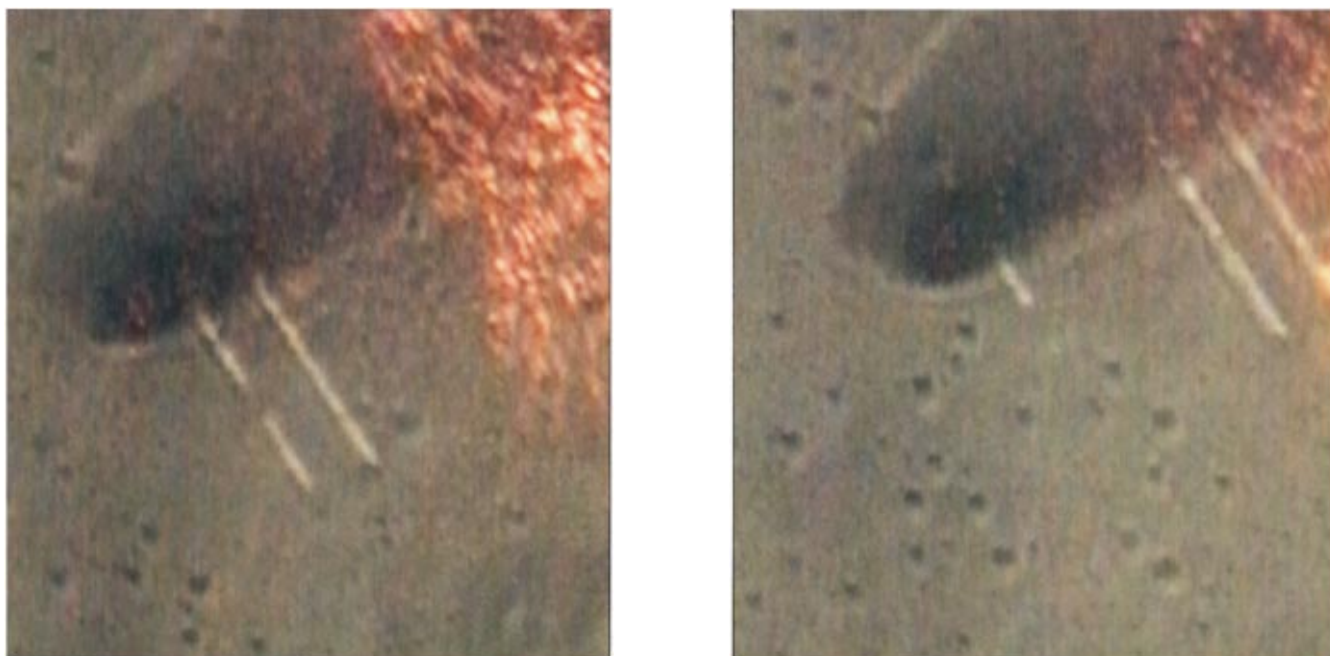


FIG. 2. Frames from a video that show the progress of the controlled etching of a chrome film using cantilevered micropipettes controlled with a Nanonics atomic force microscope system that was fully integrated with a far-field optical microscope. The linewidth of the etched lines in these far-field images are  $\sim 1.45 \mu$ .

400 kHz with a width of the resonance  $\Delta f$  that can be 0.3 kHz. A variety of force constants can also be produced with this tapering and cantilevering technology and the force constants can vary from tenths to tens of N/m.

The etchant is fed into the pipette through a silicon tube (see Fig. 1, top half). One end of the tube is attached to the large end of the cantilevered micropipette, the other end is attached to a pressure regulator. The etchant is introduced into the tube using the pressure regulator and is held at the end of the tube. The pipette is then attached and the etchant enters the pipette due to capillary action. This is helped by the presence of an internal filament in the capillary tube. The hydrostatic pressure in the pipette can be adjusted as required. It is assumed that during etching, the etchant forms a drop at the pipette tip and is held by surface tension. Simple force balance equations show that a pressure increase of  $\approx 1/3$  atmosphere is required for the drop to fall. It can also be shown that for the pipettes under consideration, the viscosity is small compared with the surface tension. For a flow rate equivalent to one drop per second (the diameter of the spherical drop is equal to the tip diameter), the pressure required to overcome surface tension is about four orders of magnitude larger than the overpressure required to maintain a steady flow rate prevented only by viscosity. Gravity  $g$  can be ignored if  $AL \ll 2\gamma/\rho g$  ( $A$ , the tip radius;  $L$ , the length of the tip beyond the bend;  $\gamma$ , the surface tension; and  $\rho$ , the density).

Etchant which leaves the pipette forms globules which solidify on the surface. This hinders the writing process. Globule formation and solidification can be prevented by keeping the surface and tip at absolute humidity. In practice, this is achieved by surrounding the tip with air that is fully saturated with water vapor. The etchant used was a cyanide complex which is fully saturated in water. The solution consists of  $K_3Fe(CN)_6 + KOH$  in a ratio of 3:2 saturated in water.

The tip containing the etchant was engaged using standard contact-mode force microscopy and the sample was then scanned. In order to write a single line, scanning was carried out in only one dimension. The sample was viewed with an optical microscope with a magnification of  $500\times$ , and the scanning was continued until a line could be resolved through the microscope. Two parameters could be changed between writing lines; the pressure on the solution column in the pipette and the set point for the normal force which alters the force with which the pipette tip is held close to the sample. Increasing the pressure on the liquid column can lead to droplets falling from the pipette, but can also be used to unblock any blockages in the tip.

If the linewidth was in the micron regime the writing process could be readily recorded on videotape by attaching a charge-coupled device camera to one of the ports of the fully integrated optical microscope. In Fig. 2 are two frames from a video that was recorded during the writing process. In this sequence of two frames the micropipette force sensor is

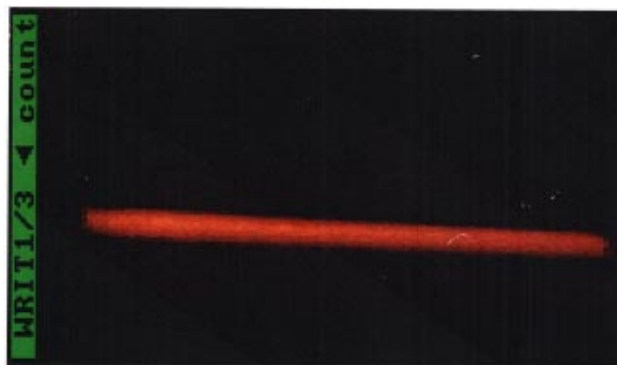


FIG. 3. Near-field scanning optical microscopy of a line etched in the chrome film. The edge sharpness is better than  $0.1 \mu$  in this  $1 \mu$  wide line from the video.

first seen in the engaged position on the sample surface during the writing process [Fig. 2 (left frame)]. In Fig. 2 (right frame) a subsequent frame from this same video sequence is seen showing an additional line in the process of being written with atomic force control.

The lines seen in Fig. 2 are  $\sim 16 \mu$  long. In order to view the progress effectively in the optical microscope, the lines shown in these video frames have dimensions of approximately  $1.15 \mu$ . To completely etch such a  $16 \mu$  long line that is  $1.15 \mu$  wide and 200 nm deep took 40 s at room temperature.

The writing time, in fact, can be increased significantly by the alteration of several parameters. These include the concentration of the chemical in the pipette, the temperature of the surroundings (by simply illuminating through the integrated far-field microscope with a laser beam), and even the pressure of the tip on the surface by finely setting the set point of the pressure of the tip on the surface. This latter parameter can permit the transition from a regime of pure chemical writing to a regime of chemically assisted scratching of the surface. For such scratching to occur the force exerted by the pipette had to be over  $10 \mu\text{N}$ . This is in agreement with a recent study that also measured a similar value for the threshold of scratching a structure of chrome squares for optical memory applications.<sup>6</sup> When the force is less than this value and there is no etchant in the micropipette, no alteration results on the chrome surface even when it is scanned over the surface for 40 min. Another important indication of the direct effect of the chemical change induced by the etchant is the fact that after the tip left a particular region of the line being etched it was possible to view the chemical dissolution of the chrome layer by the etchant even when no tip was present.

One important application of this technique and the particular chemistry that was chosen for its demonstration is in the area of mask repair. The issue of mask repair is becoming a critical technological barrier in the era of  $0.25 \mu$  linewidths. One important parameter for the ultimate utility of the method in mask repair is the uniformity of the transmission of the light through the glass substrate from which the chrome has been etched away. To investigate this we have applied the technique of near-field scanning optical microscopy (NSOM) with the same device as shown in Fig. 1 but with the cantilevered micropipette replaced by a cantilevered optical fiber<sup>3</sup> through which a laser at a wavelength of 514.5 nm is transmitted. In this technique such a cantilevered optical fiber is coated with metal to produce an aperture at the tapered tip with a diameter of  $0.1 \mu$ . This cantilevered optical fiber point light source is then scanned with the control of normal atomic force microscopy. Thus, the aperture is maintained within the near field of the sample at all times while the optical transmission is measured at each point. The results are seen in Fig. 3. In Fig. 3 we see the uniform transmission change in this  $\sim 1 \mu$  wide line from the video. This strongly suggests that all the chrome film was removed in the etched region and the edge sharpness in these images is better than  $0.1 \mu\text{m}$  based on the NSOM results. Thus far, lines have been etched with a linewidth of as small as  $0.1 \mu$  with an etch depth of 120 nm.

Our results indicate that this is not the ultimate resolution of the method. In terms of liquid delivery future improvements can include:

- (i) The application of intermittent contact-mode force microscopy that could act in a form that is similar to an ink jet printer. The resonance frequencies of the micropipettes, in the range of several hundred kHz, are ideal for such a mode of operation.
- (ii) The chemical confinement of the liquid as the pipette tip interacts with the surface, for example, this can be modulated by altering the hydrophobicity or hydrophilicity of the surface and the tip.
- (iii) The geometry of the pipette tip for optimizing delivery of a liquid chemical.
- (iv) The nature of the liquid emanating from the tip that influences its flow, capillary osmosis, lubrication, and wetting properties.

The research that will ensue will indeed be rich in a variety of areas and will also allow for metallic coatings on the pipette to impose voltages on surfaces during chemical reactions. Such a coating would allow for the formation of a subwavelength aperture at the tip of the pipette and this would also allow for illuminating, with the fully integrated optical microscope, only the tip where the liquid is emerging. Such an approach may be particularly important for the photochemical production of free radicals from either fluid or gaseous chemicals emanating from the tip. The lifetime of such a radical would limit the interaction time with the substrate and should further improve the resolution achieved.

In summary, in this letter we have demonstrated a system in which a high degree of spatial control of chemistry is possible by combining force-sensing micropipettes that we have developed with atomic force microscopy. With this relatively simple system we have demonstrated the feasibility of a task, the controlled removal of a chrome film, that is both technically difficult to accomplish by other means and has considerable practical implications. The technology we have described here has wide implications both for the use of the methodology in controlled nanochemistry with liquids or with reactive gases.

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<sup>1</sup>B. J. McIntyre, M. Salmeron, and G. A. Smorjai, *Science* **265**, 1415 (1994).

<sup>2</sup>W. T. Muller, D. L. Klein, T. Lee, J. Clarke, P. L. McEuen, and P. G. Schultz, *Science* **268**, 272 (1993).

<sup>3</sup>K. Lieberman, N. Ben-Ami, and A. Lewis, *Rev. Sci. Instrum.* **67**, 3567 (1996).

<sup>4</sup>S. Shalom, K. Lieberman, A. Lewis, and S. R. Cohen, *Rev. Sci. Instrum.* **63**, 4061 (1992).

<sup>5</sup>K. Lieberman, A. Lewis, G. Fish, T. Jovin, A. Schaper, and S. R. Cohen, *Appl. Phys. Lett.* **65**, 648 (1994).

<sup>6</sup>P. Krauss and S. Y. Chou, *Appl. Phys. Lett.* **71**, 3174 (1997).