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Nanometer-scale manipulation of surfaces is important because subtle changes in surface structure often result in new electronic, magnetic, photonic, and mechanical materials properties. In this brief article we address one aspect of nanometer-scale surface manipulation that is of both technological and fundamental interest: scanning probe microscope (SPM)-induced patterning of surfaces. We begin by discussing traditional methods for submicron patterning, then we address some general aspects of SPM surface manipulation, and finally we present some specific results from our own laboratory.

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Scanning Probe Surface Modification

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Nanometer-scale manipulation of surfaces is important because subtle changes in surface structure often result in new electronic, magnetic, photonic, and mechanical materials properties. In this brief article we address one aspect of nanometer-scale surface manipulation that is of both technological and fundamental interest: scanning probe microscope (SPM)-induced patterning of surfaces. We begin by discussing traditional methods for submicron patterning, then we address some general aspects of SPM surface manipulation, and finally we present some specific results from our own laboratory.

Nanometer-scale surface modification has been approached from two fundamentally different perspectives during the last decade. The first strategy involves the use of high-energy sources such as electron or ion beams and deep-UV or X-ray radiation. By using sequential polymer-resist-based lithography, chemical or physical vapor deposition, and lift-off, this approach has been used to construct structures that have critical dimensions ranging from 20 - 100 nm. Such features have been found to exhibit unique electrical and optical "quantum-confinement" properties that are intermediate between those of atoms and bulk materials.[1]

The second approach, which has been developed more recently and is less well-understood, involves direct or indirect surface modification by scanning probe devices. The proximal probe devices most often used for surface modification are scanning tunneling microscopes (STMs) and scanning force microscopes (SFMs).[2,3] This field has undergone amazing expansion since the first reports appeared in the mid-1980's, and novel SPM-based approaches have been used to fabricate surface features as small as a single atom.[4] The general approaches to SPM-induced surface modification are given in Table I.

The simplest method of SPM surface modification is direct etching, but it is also the most difficult to fully understand because the experimental conditions, particularly the size and shape of the tip and its z-displacement, are extremely difficult to reproducibly control. Nevertheless, some very dramatic examples of direct etching have been presented. For example, Kobayashi et al. used an STM tip in ultrahigh vacuum (UHV) to cut grooves in Si (111) that were a few nanometers wide.[5] They varied the tip material and voltage bias, and concluded that Si-atom removal from the surface arises from field-induced surface-ion emission. The SFM has also been used to directly etch surfaces. In an especially elegant experiment, Delawski and Parkinson created geometrically well-defined pits by using an SFM to remove single atomic layers from a two-dimensional metal chalcogenide.[6] In contrast to direct etching, it is also possible to modify surfaces in the presence of a secondary vapor, liquid, or solid chemical etchant, which is activated by the probe. For example, Schneir and Hansma were able to fabricate holes in a Au surface that had been previously coated with a thin layer of grease; in the absence of the grease, identical surfaces were not modified by the tip.[7]

A third method for inducing surface modification relies on the etching or polymerization of preformed resist materials. These are usually polymeric photo or electron resists, but they may also be Langmuir-Blodgett multilayers or even single monolayers. Most of the early work in this field was done by McCord and Pease who exposed poly(methylmethacralate) and several inorganic alkali-halide resist materials with an STM tip.[8] Marrian et al. have also done elegant and systematic resist-based STM lithography during the last few years.[9] Our group has recently shown that an STM tip can be used to etch features in monolayer resists, which can subsequently be metalized by low-temperature chemical vapor deposition (CVD) methods; these results are expanded upon later in this article.[10,11]

The fourth SPM surface-modification method involves tip-induced deposition of vapor- or liquid-phase precursors. Much of this work has been done by de Lozanne's group; for example, they have recently shown that it is possible to fabricate extremely high-purity Ni features as small as 50 nm across.[12] Several groups have shown that it is possible to directly deposit metals from an STM tip. For example, an IBM group used an Au tip as a miniature solid-state field-evaporation source in both air and vacuum to directly form raised surface features by applying periodic, short-duration voltage pulses between the tip and substrate.[13]

Atom-by-atom manipulation represents the ultimate in high-resolution surface modification, and this level of spatial resolution should permit fabrication of structures and devices with very interesting electronic and photonic characteristics. One of the most dramatic examples of atom-by-atom manipulation was recently described by Eigler and Schweizer, who were able to use an STM tip to pick up individual Ar atoms, move them, and redeposit them in desired locations on Ni surfaces.[4]

Despite the many elegant examples of SPM fabrication that have appeared during the last ten years, it is surprising to note that very little is actually known about the mechanisms that result in surface modification. Several different chemical and physical phenomena have been proposed (Table II), but a definitive understanding of the process or combination of processes responsible for SPM-induced lithography will only be forthcoming when the following aspects of the experiment are well-understood: (1) the size, shape, and surface characteristics of the SPM tip; (2) the spatial relationship between the tip and substrate; (3) the chemical and physical nature of the ambient phase present between the tip and substrate; (4) the nanoscopic chemical and physical nature of the substrate surface. All of these problems present significant challenges that will require chemical and physical solutions.

Another critical issue that must be resolved relates to the chemical and physical characterization of ultrasmall features. At the present time, two approaches to this problem have been used. The STM tip itself can be used to characterize ultrasmall surface features, but this approach has three serious drawbacks: (1) tip structure changes (usually for the worse) during the modification process; (2) tips are not generally chemically sensitive; (3) apparent structural features may actually arise from changes in the electronic nature of the surface. Traditional UHV surface science methods have also been used to evaluate SPM-induced surface structures, but there are significant drawbacks to this approach: (1) UHV methods are usually implemented *ex situ*, and it is often difficult to locate portions of the substrate that were previously modified by the scanning probe; (2) the size of SPM-fabricated surface features can be more than two orders of magnitude lower than the resolution limit of existing surface analytical techniques. Despite these limitations UHV methods are useful if the surface features are sufficiently large.

Recent work in our laboratory serves to illustrate some of the general problems and promises of STM lithography.[10,11] We have used the tip of an STM to lithographically define nanometer-scale features in an ultrathin resist material, and we have subsequently used selective, low-temperature CVD to metalize STM-defined patterns. In our experiments the resists, which consist of monolayers of self-assembled *n*-alkanethiols confined to Au(111) substrates, are approximately 2.5 nm thick. This is thick enough to passivate the Au surface, but it is thin enough to permit tunneling or field emission.[14-16] When an STM tip is positioned near the Au substrate and rastered across the surface, it induces removal of the monolayer resist.

Figure 1A shows three 60 nm x 60 nm STM-defined features confined to a single Au(111) terrace. These features were fabricated by scanning the region to be modified (scan rate = 31.25 Hz) 4 times with the tip biased at +3 V (tip negative) and a tip current of 0.11 nA, followed by 4 additional scans at +0.3 V and the same current and scan rate.[17] The first set of scans removes most of the monolayer resist, but the second set is necessary to completely remove organic material from the bottom of the etched features. We have been able to create geometrically well-defined structures similar to those shown in Figure 2 that are as small as 25 x 25 nm, and it appears that the resolution limit is determined only by the size of the tip and the diameter of the resist molecules. Such structures are dimensionally stable for at least several days at room temperature. Line scans corresponding to the data in Figure 1A are shown in Figure 1B. The important conclusion from these data are that the surface features are structurally uniform and are easily reproduced.

We have also used the STM to fabricate much larger features. An example of a nominally 5 x 5 μm feature is shown in Figure 2. We fabricate large features such as this one by scanning the monolayer-modified surface twice using a bias voltage of +8 V, a tunneling current of 0.11 nA, and a scan rate of 1.34 Hz. Note the debris located parallel to the slow-scan axis of the STM image. We believe this is organic material that has been removed from the pattern and deposited along the edges.

We recently demonstrated that patterns such as that shown in Figure 2 can be metalized with Cu using selective, low-temperature CVD techniques.[11] These experiments involve exposure of a pattern to the Cu CVD precursor hexafluoroacetylacetonatocopper(I)-(1,5-cyclooctadiene), (hfac)Cu(1,5-COD), which disproportionates to deposit Cu on the STM-etched portion of the substrate, but not on the unetched methyl-terminated monolayer resist surface.[18] An example of several metalated features, which have critical dimensions ranging from 0.5 to 5.0 μm, are shown in Figure 3. The important conclusions we derive from this experiment are: (1) Cu only deposits in the etched patterns[19] and (2) the Cu deposits are smooth and homogeneous.

To summarize, we have provided a brief introduction to the field of SPM-induced surface modification, and we have discussed some representative examples. The mechanism or combination of mechanisms responsible for SPM lithography are generally not well-understood at the present time, and good analytical methods for characterizing the smallest features that have been fabricated are not yet available. Both problems require creative solutions. We believe that the methods discussed in this short article are most well-suited for constructing "one-of-a-kind" features or devices to test important theoretical predictions, but it is rather unlikely that such serial approaches to nanofabrication will be commercially useful in the absence of multi-tip SPM devices.

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[17] All experiments were performed using a Digital Instruments NanoScope STM. The image shown in Figure 1A appears somewhat blurred because the tip was damaged during the surface modification step.

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[19] We believe Cu also deposits on the organic material that is deposited along the slow-scan axis of the patterns. Energy dispersive spectroscopy obtained for several different regions of Figure 3 indicate the presence of Cu only in the STM-defined pattern.

TABLES

Table I. General approaches for SPM-induced surface modification

Method

1. Direct substrate etching
2. Direct substrate etching in the presence of a reactive gas, liquid, or solid
3. Etching or polymerization of preformed resists (usually polymers)
4. Tip-induced deposition from a vapor- or liquid-phase precursor
5. Transfer of material from the tip to the substrate or *vice-versa*
6. Direct manipulation of atoms or surface adsorbates

Table II. Phenomena that may be associated with SPM-induced surface modification

Electric Field Effects
- Field-induced electron emission
- Field-induced ion emission (field evaporation)
- Field-assisted diffusion

Joule Heating

Surface Forces (sliding)

Chemical Forces (adsorption or transfer-on-contact)

Mechanical Abrasion

Electrochemistry

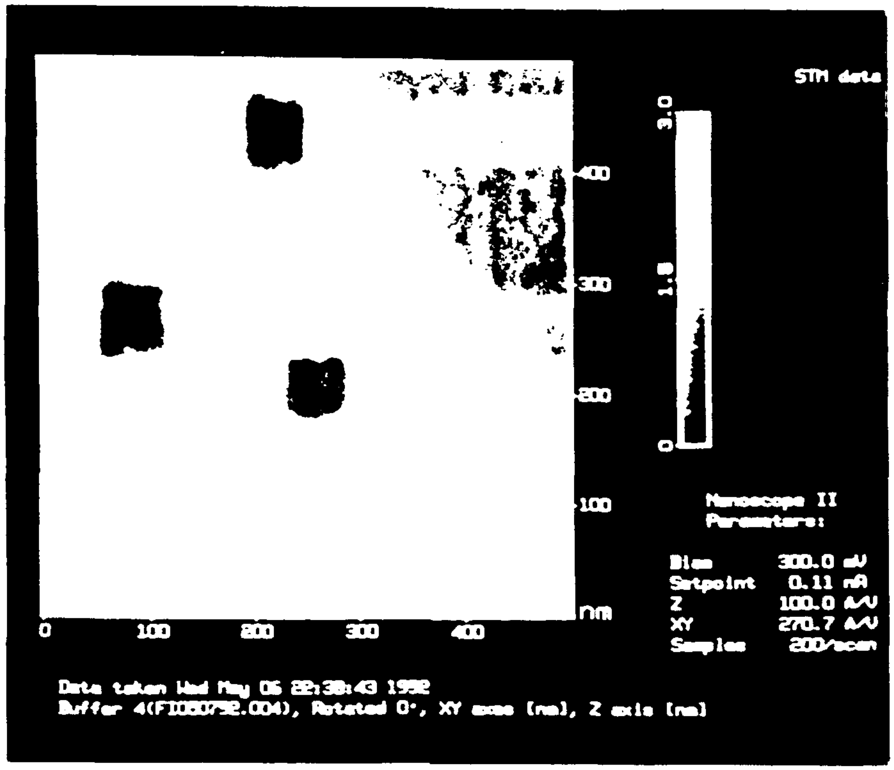
FIGURE CAPTIONS

1. (A) STM image of a Au(111) substrate modified with a monolayer of $HS(CH_2)_{17}CH_3$ after opening three 60 x 60 nm windows. STM etching conditions: 4 scans (bias voltage = +3 V; tunneling current = 0.11 nA; scan rate = 31.25 Hz) followed by 4 additional scans (bias voltage = +300 mV; tunneling current = 0.11 nA; scan rate = 31.25 Hz). (B) STM line scans through the etched regions which are shown in (A) and illustrated schematically to the right of the line scans. The vertical displacement (v. d.) between the arrows (in nanometers) is indicated next to each line scan.

2. Scanning electron micrograph of a 5 x 5 μm (nominal), STM-defined pattern of a $HS(CH_2)_{17}CH_3$ monolayer resist on a Au (111) substrate. This feature was created by scanning the monolayer-modified surface twice (bias voltage = +8 V; tunneling current = 0.11 nA; scan rate = 1.34 Hz).

3. Scanning electron micrograph of Cu features deposited on a Au (111) surface. The square patterns, which range in size from 0.5 to 5.0 μm, were lithographically defined within a $HS(CH_2)_{17}CH_3$ monolayer resist (4 scans: 2.0 Hz, +8 V bias, 0.15 nA; followed by 4 additional scans: 4.0 Hz, +0.3 V bias, 0.15 nA). Following patterning, the features were metalized by exposure to (hfac)Cu(1,5-COD) for 3.5 min at a substrate temperature of 120 °C.

A


STM data
3.0
1.5
0
400
300
200
100
nm
0 100 200 300 400
Nanoscope II
Parameters:
Bias 300.0 mV
Setpoint 0.11 nA
Z 100.0 Å/V
XY 270.7 Å/V
Samples 200/scan
Data taken Wed May 06 22:38:43 1992
Buffer 4(FI060792.004), Rotated 0°, XY axes [nm], Z axis [nm]

B

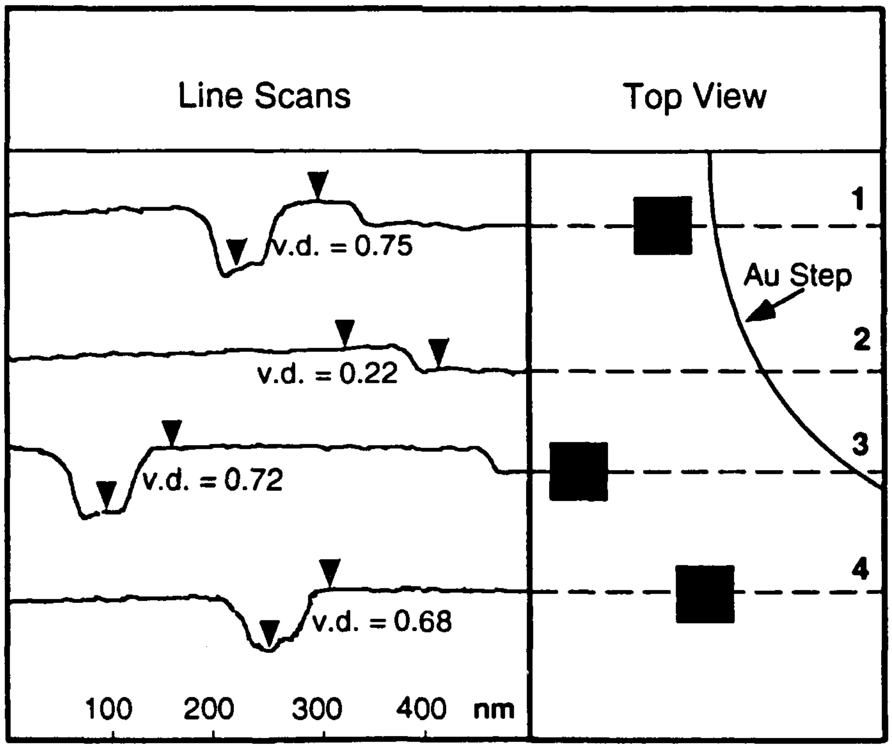

Line Scans
Top View
1
v.d. = 0.75
Au Step
2
v.d. = 0.22
3
v.d. = 0.72
4
v.d. = 0.68
100 200 300 400 nm

Fig 1

Fig 2

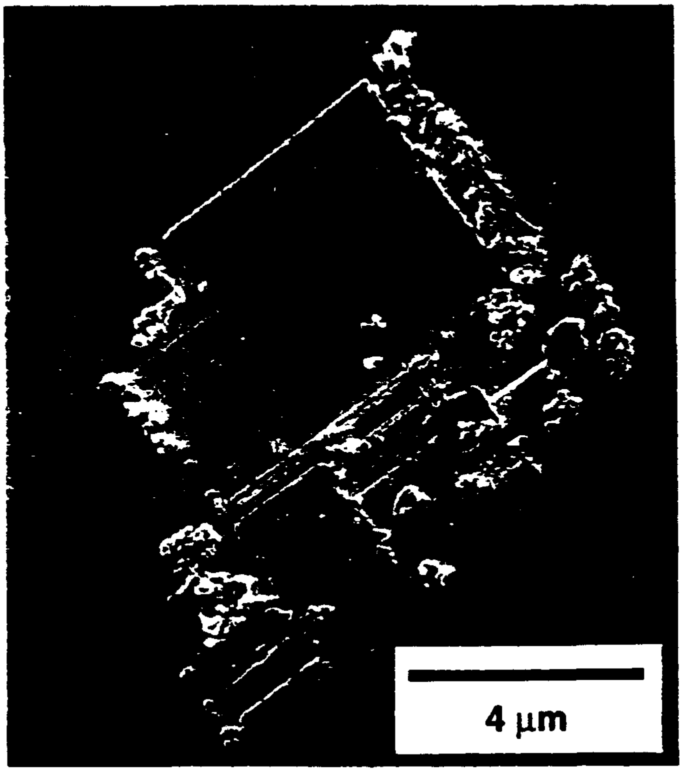


Fig 3