High-resolution deposition and etching of metals with a scanning electrochemical microscope

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A novel method is described which can be used for both the electrochemical deposition of metals in polymer films and the etching of metals with very high resolution. These faradaic processes are controlled using a scanning electrochemical microscope (similar to the scanning tunneling microscope). Patterns of silver and gold deposited in Nafion and poly(4-vinylpyridine), respectively, with a linewidth smaller than 0.5 μm, and high-resolution etching patterns in copper are shown. Extensions of this methodology to depositions of other materials, the use of other conducting polymer films, and possible applications for submicron devices are discussed.

I. INTRODUCTION

The atomic resolution provided by the scanning tunneling microscope[1,2] (STM) has made it a powerful tool for the study of surfaces in UHV chambers, air,[3] or under liquids.[4] Recently, the STM has been used not only to image and determine spectroscopic properties of surfaces, but also to manipulate materials. Surface modifications producing submicron scale structures have been reported using several different approaches, including (i) scratching of interfaces with an STM tip,[5,6] (ii) exposing resist films to an electron beam by applying high voltages between the tip and the substrate,[7,8] (iii) surface deformation by employing a high voltage and/or a high local current density,[9,10] (iv) etching semiconductors in electrolytes using a modified STM,[11] and (v) plasma deposition of metals using organometallic gases.[12]

Research in our laboratory has recently led to the development of a method for the high-resolution deposition of metals in thin ionically conducting polymer films.[13] This technique is based on the scanning electrochemical microscope (SECM) (similar to the STM), which maintains a constant faradaic current between a tip electrode and a substrate electrode. In this case these electrodes are separated from each other by a thin layer of an ionically conducting polymer, which contains anions and/or cations that are not rigidly bonded to the individual molecular chains but instead are free to move within the polymer matrix. The polymer film provides a conductive pathway for the faradaic current to pass between the substrate and the tip and thus negates the need to use any liquid electrolyte solution. Preliminary results using this technique[13] showed that patterns of silver and copper lines could be deposited in a Nafion[14] film. Expanding on these initial studies, we present in this paper results obtained using different conducting polymer films and metal substrates. It will be shown that this methodology is not only useful in producing fine deposition lines in conducting polymer films, but also provides a means for the high-resolution etching of substrate materials. Finally, some possible technical applications will be discussed.

II. EXPERIMENTAL

The STM apparatus used has been described previously.[15] Tip electrodes were made from either 25-μm tungsten or platinum wire, which were first sealed in glass capillaries to increase mechanical stability, and then sharpened to a point < 0.1 μm in diameter by heating in a flame (tungsten) or by electrochemical etching (platinum).

Sample fabrication in all cases followed the same general procedure: First, a smooth metal surface was prepared. A solution containing the ionically conducting polymer was then made and drops of this spin coated onto the surface of the metal. Finally, ions were incorporated into the thin polymer film by soaking in the appropriate solution. Smooth silver and gold samples were prepared by vacuum deposition onto glass slides and silicon wafers, respectively. Copper samples were made by mechanically and electrochemically polishing a ≈2-mm-thick piece of copper plate.

Nafion films were prepared using a 1 wt. % solution in ethanol. Drops of this were spin coated at 3800 rpm onto the appropriate metal surface.[13] Thin films of poly(4-vinylpyridine) (PVP) were obtained by spin coating (6000 rpm) drops of a 2-propanol solution containing 2 wt. % of PVP and 0.2 wt. % of a cross-linking agent (1,6-dibromohexane). The film-coated electrodes were then maintained at 80 °C for ~18 h to promote the desired cross-linking reaction.[16] For both Nafion and PVP the final film thicknesses were in the range 0.1–1 μm. For this study, the solutions used for incorporating ions into the polymer films were as follows: silver (20 mM $AgNO_3$), gold (42 mM $AuCl_4^-$ in 1M HCl), copper (20 mM $CuSO_4$), and methyl viologen (40 mM MV^{2+}). All solutions were prepared from water purified using a Milli Q system (Millipore).

All SECM measurements described here were carried out under atmospheric conditions.

III. RESULTS AND DISCUSSIONS

A. Technique

The work described here is concerned with the deposition and etching of metals using a modified STM. The principle behind the technique[13] is illustrated in Fig. 1 and involves passing a faradaic current between a tip electrode and a metal substrate electrode. These electrodes are separated from each other by a thin film of an ionically conducting polymer which contains mobile metal ions. The current is driven through the polymer film by applying a potential between the tip and the metal substrate (tip negative). Under these
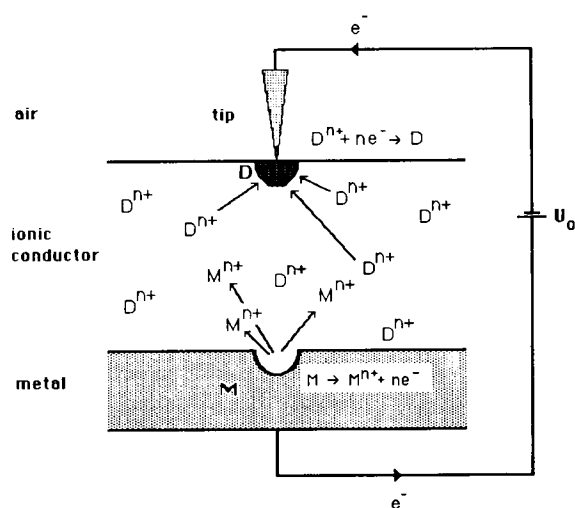
FIG. 1. Schematic representation of a method to simultaneously deposit species D in an ionic conductor and etch the substrate M. Both the deposition and etching processes result as a consequence of passing a current through an ionic conductor. Metal deposition occurs in the film at the tip electrode and localized etching is observed on the metal substrate.

conditions metal ions (D^{n+}) are reduced at the tip to form the metal D, while the metal substrate (M) is oxidized to form ions (M^{n+}). Within the polymer film, charge is carried by the movement of ions (in this example, D^{n+} and M^{n+}). Electrons are transferred across the two boundaries of the polymer by means of electrochemical reactions that take place at the interface between the polymer and each of the two electrodes. The electrochemical reaction that occurs at the tip/polymer interface is

$$D^{n+} + ne^- \rightarrow D,$$
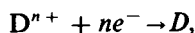
while at the metal substrate/polymer interface, the following reaction occurs:

$$M \rightarrow M^{n+} + ne^-.$$
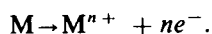
The net result of these processes is therefore the deposition of the metal D in the film at the tip electrode and the etching of the metal substrate electrode M (Fig. 1).

The tip electrode position is held such that only the very end is in contact with the surface of the ionically conducting polymer film. This is achieved by means of a conventional STM feedback loop which is used to maintain a constant faradaic current between the tip and the metal substrate. When the tip is above, and not in contact with, the polymer film, no current will flow, because of the high resistance of the air gap. The feedback circuit progressively lowers the tip until current just begins to flow, signaling the initial contact between the bottom of the tip and the polymer film. At this point the constant current is maintained, and as the tip electrode is moved in a lateral direction, a metal line is deposited at the polymer/air interface with the associated production of an etched line in the metal underlayer. Predefined patterns of both deposition and etching structures can be produced by controlling the x and y movements of the sample with a computer.

The contact area between the tip electrode and the ionic conductor is determined by the magnitude of the reference current used in the STM feedback loop combined with either the concentration and mobility of the ions in the polymer film, or, at lower applied bias potential between the tip and the substrate, the electrode kinetics. In general, ionic conducting polymers contain a high concentration of mobile ions. Although the diffusion coefficients of these ions are often lower than they are in solution, the applied voltage combined with the short separation distance between the tip and the substrate results in field assisted migration of positive ions to the tip electrode. By setting a low value of the STM reference current (≈ 50 pA), the contact area is maintained in the order of a few nm^2. This indicates that a very high resolution of both deposition and etching should be achievable by this novel technique.

B. Deposition of metal structures

Figure 2 shows a scanning electron micrograph (SEM) of a small area of a pattern of silver lines deposited in a Nafion film using the technique described above. As can be seen, a resolution of better than 0.5 μm is obtained. The variation in the width of the deposited silver lines (Fig. 2) is attributed to some mechanical instability in the SECM apparatus. This problem is presently being addressed by improving the SECM design. Direct evidence that the depositions in the films are indeed formed by the postulated electrochemical processes has been described in our earlier publication.[13] For example, a silver film substrate coated with Nafion was soaked with a solution containing copper ions. After deposition of lines using the scanning electrochemical method, elemental analysis under the SEM clearly showed that copper was present in the deposits.[13] The presence of silver in the deposited lines could not be ascertained, since silver served as a substrate.

High-resolution deposition of gold structures has been achieved using films of PVP coated on gold surfaces. In contrast to Nafion, which is a cation exchanger, PVP contains mobile anions. Figure 3 shows an example of gold lines that have been deposited by this technique. Again the width of the structures is smaller than 0.5 μm with the best obtained so far being smaller than 0.2 μm.
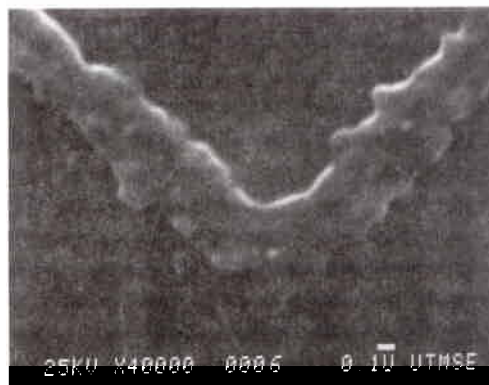

FIG. 2. SEM picture of a pattern of silver lines deposited in a Nafion film. Tip material = tungsten, bias = 5 V, tip current ≈ -0.5 nA, and scan rate ≈ 900 Å/s. Tip reaction, $Ag^+ + e \rightarrow Ag$; substrate reaction, $Ag \rightarrow Ag^+ + e^-$.
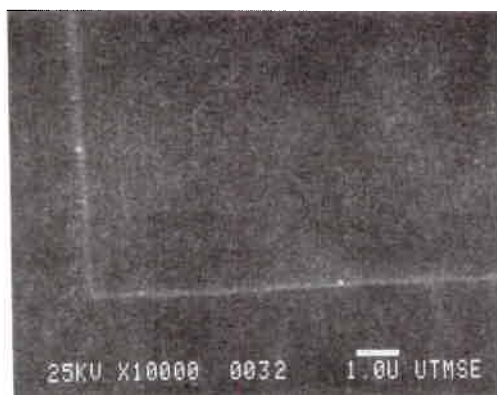
FIG. 3. SEM picture of a gold line deposited in a poly(4-vinylpyridine) film. Tip material = tungsten, bias = 4 V, tip current $\approx$ − 0.2 nA, and scan rate $\approx$ 900 Å/s. Tip reaction, $AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$. Substrate reaction is Au oxidation.

FIG. 4. SEM picture of a copper surface showing etched traces. Tip material = tungsten, bias = 3 V, tip current $\approx$ − 0.4 nA, and scan rate $\approx$ 1000 Å/s.

In general, the thickness of the deposited structures are strongly affected by such factors as the bias voltage applied between the tip and the substrate, the SECM feedback current, the speed at which the tip is scanned over the surface, and the shape of the tip. For metal deposition, the potential applied between the tip and the substrate has to be above a certain threshold value. The exact magnitude of this lower potential limit is a function of both the electrochemical processes and the potential drop across the film. For example, in the case of 2-μm-thick Nafion films, the deposition of silver structures occurs only with applied potentials above 200 mV. For lower bias voltages, the tip electrode penetrates the polymer film producing scratched lines. At the other extreme for very high voltages ($\geqslant$ 7 V) the tip no longer moves smoothly over the surface of the polymer but instead moves erratically in a series of bounces. The thickness of the deposited lines ultimately depends on the number of Coulombs passed per unit distance of tip movement. This is a function of both the set current and the tip scan rate. To date, scan rates of up to 1 μm/s have been used. Faster speeds than this are still possible but will be limited to a few tens of microns per second because of factors such as the resonance frequency of the piezoelectric ceramics, the speed of the STM feedback loop, and the uniformity of the coatings. It should also be noted that lines thinner than 1 μm can only be obtained using very sharp, needle-like, tip electrodes.

C. Etching of metal surfaces

As indicated in Fig. 1, passing a current through the ionic conducting polymer not only results in the electrochemical deposition of metals at the tip/ionically conducting polymer interface, but also causes a localized etching of the metal substrate. To investigate this, the polymer film containing metal deposits (see above) must first be removed from the surface of the metal. For this purpose Nafion films were dissolved with an ethanol/water mixture at 80 °C,[17] and PVP films were washed off with an alkali solution. Figure 4 shows a SEM of a copper surface which has been etched using this technique. These lines were produced by moving the tip electrode over the Nafion coated metal surface.
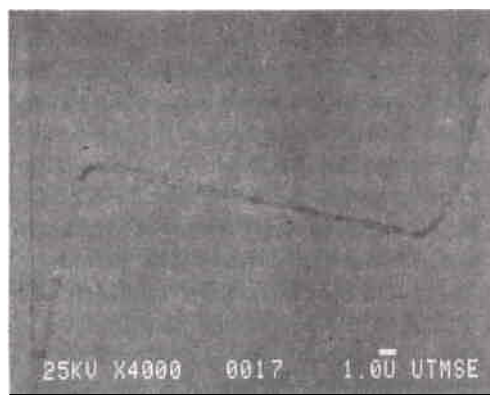
Again, the resolution of the structures is in the submicron range. In this particular case the Nafion film contained methyl viologen (4,4'-dimethyl bipyridinium) ions (MV^{2+}) as the species reduced at the tip. In this case reduction of MV^{2+} occurs at the tip ($MV^{2+} + e^- \rightarrow MV^+$) to produce a soluble cationic species. Initially, experiments were performed with copper ions in the film, but analysis of the structures formed proved to be difficult, because the high exchange current between ions in the film and the metal (resulting in the reaction $Cu + Cu^{2+} \rightleftharpoons Cu^{2+} + Cu$) produced considerable roughening of the copper surface. A similar effect was observed when the soaking solutions used to incorporate the ions into the Nafion film were not rigorously deoxygenated. Here the surface roughening is caused by corrosion processes resulting from the oxidation of the copper metal. It can be seen from Fig. 4 that some pitting of the surface still took place, even though nitrogen was bubbled through the methyl viologen solution for more than 30 min prior to soaking. The soaking process itself was performed in a nitrogen atmosphere. Better results should be obtained by placing the SECM apparatus in an oxygen-free chamber. Even when the Nafion film contained methyl viologen, copper deposition lines were still observed. These were produced by the reduction of copper ions that were released as a result of the etching process.

We have also investigated the etching patterns that accompanied the depositions of both silver in Nafion and gold in PVP. Our results so far suggest that a poorer resolution of etching lines is obtained for these two systems than is observed on copper surfaces. At the moment the reason for this difference in resolution is unclear. However, one would expect that for all systems the thickness of the etching lines should be governed by the same factors that determine the resolution of the depositions (see above).

A previous report from our laboratory showed that high-resolution etching of GaAs could be achieved in a liquid electrolyte solution using a modified STM.[11] Further work has been performed on similar systems with the aim of etching or depositing metals in liquid solutions. Research in this area has, however, proved to be considerably less successful in terms of resolution and reproducibility as compared with

the results described here. The use of a substrate coated with an ionically conducting polymer film has the following advantages over immersing the substrate in a liquid electrolyte:

(i) In both systems the resolution of the structures produced is affected by the magnitude of the gap between the tip and substrate electrodes. In electrolyte solutions the faradaic current is not very sensitive to fluctuations in this distance. This makes it impossible to accurately control the interelectrode spacing. Using the polymer film technique, the tip electrode is held on the air/polymer interface. The contact area and therefore the penetration depth of the tip in the polymer film depend on the reference current set by the STM feedback loop. Hence, the tip/substrate electrode distance is always constant, providing the films are uniform. Therefore, the technique described here should produce more homogeneous structures.

(ii) In the liquid electrolyte systems the resolution of the structures is determined largely by the exposed area of the tip. It is very difficult to fabricate tip electrodes of area in the μm^2 to nm^2 range. In contrast, the tip electrodes for the studies described here are very easy to fabricate, since it is the area of the tip in contact with the polymer film that is important (see Sec. III A above).

(iii) In the liquid electrolyte system, deposits tend to form on the tip electrode, resulting in a large increase in the size of this electrode, with rapid deterioration in resolution (see above). According to SEM analysis, the deposition processes that occur at the tip/polymer interface remain within the film and no change in the tip structure was observed.

In a very recent report, other authors used the liquid electrolyte technique to deposit gold lines on a gold surface.[18] A maximum resolution of $0.3\,\mu m$ was described, but structures were only produced twice out of 20 attempts. This same deposition of metal on the metal substrate is achievable using a polymer film, with a positive potential applied to the tip (where chloride or water oxidation occurs). Results have already been obtained in this area and will be the subject of a later publication.

IV. TECHNICAL APPLICATIONS

We are currently considering possible practical applications of this technique. Because of the constraints on the speed with which the tip can be rastered over the surface, the main area of interest might be for mask fabrication, in particular, for x-ray lithography. For this purpose the polymer film containing the deposited metal structures will first have to be supported by a transparent material (e.g., polyimide) and then separated from the substrate.

Other possible applications might be in the repair of broken contacts in integrated circuits or mask defects. This might be achieved by first covering the circuit or mask with a thin film of an ionically conducting polymer, and then depositing a metal line between the edges of the broken contact. Further, the mass production of some devices might be possible using multiple tip[8] or pattern tip arrangements. In the

latter, a structure of the desired shape can be used to produce the whole pattern. With a modified SECM, the pattern can be repeatedly transferred to the surface of ionic conductors.

V. CONCLUSION

We have shown that a modified STM (a SECM) can be used to etch and deposit metals by using thin ionically conductive polymer films coated on a metal surface. The resolution of the structures produced are smaller than $0.5\,\mu m$. The results illustrate the scope of the technique which can be applied to deposit or etch a variety of different metals. In principle, many other ionic conductors can be employed to serve as media for the desired electrochemical reactions.

The excellent resolution of lines deposited using this technique combined with the low cost of the experimental apparatus and the advantage of being able to work at atmospheric pressure could lead to its possible use in the fabrication of submicron devices.

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