Scanning Electrochemical Microscopy

High-Resolution Deposition and Etching of Metals

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ABSTRACT

Electrochemical methods for the high resolution etching of metals as well as the deposition of metals in polymer films and on conducting substrates are presented. These faradaic processes were carried out with a scanning electrochemical microscope (SECM) (similar in design to the scanning tunneling microscope) and different ionically conducting polymer films such as Nafion, poly(4-vinylpyridine), and poly(bis-(methoxyethoxyethoxide)phosphazene) on the substrate. Continuous patterns of silver, gold, copper, and palladium were deposited, and copper, silver, and gold were etched with widths in the submicron range. The use of polymer-coated substrate electrodes to deposit and etch metals is compared to depositions and etchings performed in electrolyte solutions.

Soon after the introduction of the scanning tunneling microscope (STM) (1, 2) researchers began to investigate the possibility of utilizing it for fabrication. The aim of this work was to take advantage of the high spacial resolution of the STM to produce submicron scale structures. To achieve this goal, a variety of different strategies were employed. For example, metal surfaces were scratched by passing a high current between the STM tip and the metal substrate (3). A similar type of mechanical deformation was achieved by using an STM in the tunneling mode on a silicon substrate coated with a thin film of a metal halide (4). A slightly different approach has been successfully employed, where surfaces were deformed by applying a high-voltage and/or a high local current density (5, 6). McCord and Pease (7,1 8) demonstrated that resist films such as PMMA can be exposed to an electron beam by applying high voltages between the tip and the conducting substrate. A similar method involving plasma deposition of organometallic compounds on the surface of metals has been described by Silver and co-workers (9). Finally, a non-vacuum technique has been described in which semiconductors were photoetched in electrolytes (10) and gold was deposited on gold in a commercially available electro-

plating solution (11) using a modified STM. More recent reports describing surface modifications with the STM apparatus are mostly based on the ideas previously summarized, with improvements in the resolution obtained, or in application to other material systems.

Recently, in a communication from this laboratory (12, 13), a method was described for the high-resolution deposition of metals in polymer films. This technique is based on the scanning electrochemical microscope (14) (SECM), which is similar in design to the STM. The principle behind this technique is illustrated in Fig. 1 and involves passing a faradaic current between a tip electrode and a metal substrate electrode. A bias voltage is applied between these two electrodes, which are separated from each other by a thin film of an ionically conducting material. The magnitude of the faradaic current that passes through the ionic conductor is kept constant by means of a conventional STM feedback control that monitors the current and adjusts the interelectrode spacing accordingly. By choosing a reasonably low value for this reference current (in the order of nanoamps), the position of the tip electrode can be held so that it is positioned on top of the film with only a very small area actually in contact with the surface. If reducible metal ions are present in the ionic conductor and the tip electrode is poised negative with re-

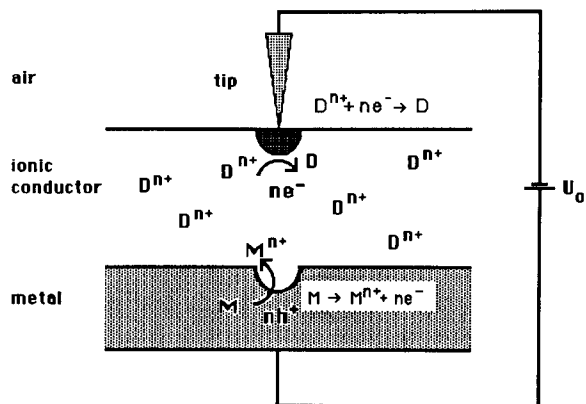* Electrochemical Society Active Member.

Fig. 1. Schematic representation of the method used to simultaneously deposit a species, D, and etch a conducting substrate, M. This is achieved by applying a potential between a tip electrode and a substrate electrode (M), which are separated by a polymer film containing a mobile ion D^{n+}. The result is the passage of a faradaic current with a reduction process at the tip/polymer interface (deposition) and an oxidation reaction at the substrate (*e.g.*, etching).
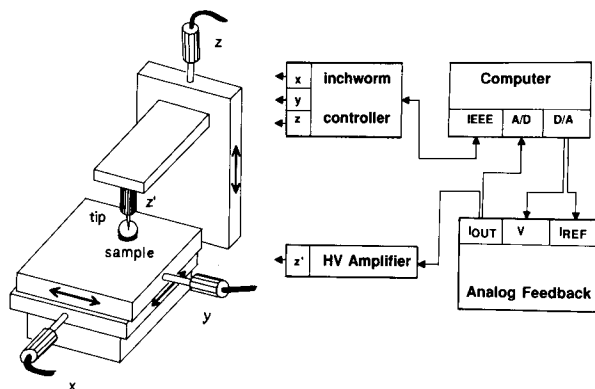

Fig. 2. Block diagram of the experimental setup. X, y, z are piezoelectric drivers (inchworms), z' is a piezoelectric pusher, V = bias between the tip electrode and the conducting sample, I_{REF} = current set by the computer and I_{OUT} = effective current output adjusted by the analog feedback.

spect to the substrate electrode, then the faradaic current that is passed results in the deposition of metal in the film at the tip electrode. By moving the tip electrode in a lateral direction across the surface of the ionic conductor, while still maintaining a constant current, metal lines are deposited at the surface of the film. In our previous communication (12), we demonstrated this technique by depositing micron thick lines of silver in Nafion films.

As shown in Fig. 1, in addition to the deposition of materials at the tip electrode, the current flow can also cause localized changes in the substrate electrode. When the films of the ionic conductor are very thin (a few microns or less), the applied field will cause the electrochemical process that takes place at the metal substrate/polymer interface to occur preferentially directly under the tip. Thus, the same techniques used to deposit metal lines in polymer films also produced localized etching (Fig. 1) or the deposition of structures on the substrate electrode.

In this paper we describe the high-resolution deposition of metals in polymer films, the etching of metals, and the deposition of metal on conducting substrates with the SECM. We show that the method can be applied with a number of different ionically conducting polymers and for the deposition and etching of a variety of different materials. Finally, we compare the use of polymer films to liquid electrolyte solutions and discuss possible practical applications of this technique for submicron lithography and device fabrication.

Experimental

The scanning electrochemical microscope used for all of the experiments presented in this paper is illustrated in Fig. 2. The sample holder is attached to an x-y stage whose position is controlled by a pair of piezoelectric drives (inchworms) (Burleigh Instruments). The motion of the stage on which the tip is mounted is also controlled by a piezoelectric driver, with fine adjustment of the vertical position carried out using a second piezoelectric pusher regulated by a high-voltage amplifier (Burleigh Instruments, expansion *ca.* 50 Å/V). All three piezoelectric drivers are controlled by a motor controller that is interfaced (IEEE) to a personal computer. The drivers have a dynamic range of *ca.* 2.5 cm with programmable speeds between 10 nm/s and 2 mm/s. A conventional STM analog feedback loop is used in conjunction with the high-voltage amplifier to adjust the tip height so as to maintain a constant current between the tip and the conducting substrate.

The fabrication of the platinum and tungsten tip electrodes has been described previously (13).

Samples were prepared by spin coating drops of a solution of a polymer onto the surface of a conducting substrate. The conducting substrates used in this study were copper, silver, gold, platinum, graphite, and ITO (indium

tin oxide). Copper substrates were made either by mechanically and electrochemically polishing copper plates or by sputtering copper on glass slides. The silver surfaces were obtained by vacuum deposition onto glass slides. Gold and platinum samples were prepared by sputtering the corresponding materials on glass slides. Graphitic layers were prepared by spin coating colloidal graphite (Ted Pella, Incorporated) (diluted 2:1 in isopropanol) at 5000 rpm on quartz slides and baking the samples at 400°C for 30 min. The ITO was coated on glass (CG-901N, Delta Technologies, Limited).

Nafion (registered trademark of E.I. du Pont de Nemours and Company, Incorporated), poly(4-vinylpyridine) (PVP) and poly(bis-(methoxyethoxyethoxide)-phosphazene) (MEEP) served as the ionically conducting polymers. Nafion films were prepared using a 1% w/w solution in ethanol. Drops of this were spin coated at 3800 rpm onto the appropriate conducting surface. PVP films were obtained by spin coating (5000 rpm) drops of a 2-propanol solution containing 2% w/w of PVP (Scientific Polymer Products, Incorporated) and a 0.2% w/w of a cross-linking agent (1,6-dibromohexane) (Aldrich). The desired cross-linking reaction was achieved by placing the film-coated electrodes in an oven at 80°C for about 18h (15). The polymer MEEP was obtained from Professor H. R. Allcock (Pennsylvania State University) and was dried before use by heating for 24h in a vacuum oven at ~75°C. Solutions of this polymer were prepared by dissolving the polymer and a small quantity of silver trifluoromethanesulfonate (Aldrich) in THF. The concentration of MEEP in this coating solution was 2%, with sufficient silver salt added to give approximately one silver ion for every 5 repeat units of the polymer chain. Samples were formed by spin coating (4000 rpm) drops of this solution onto the surface of a silver-covered microscope slide. Prior to use in the SECM apparatus, these samples were placed in a vacuum oven overnight at ~75°C to remove any residual moisture. (Note that, whenever possible, care was taken not to expose the samples to light.)

Results

Deposition of metals in Nafion.—In our first publication describing this technique (12), preliminary results showing the deposition of silver in Nafion films were presented. The results were obtained using samples composed of a silver substrate coated with a Nafion film containing silver ions; silver was deposited in the film using a platinum tip electrode. The resolution of the lines shown were on the order of 1-2 μm. Figure 3 shows an SEM of some recent results obtained using this same system. Note that the resolution of the deposition lines has now been improved, with structures as thin as 0.3 μm obtained. The variation in line thickness observed (Fig. 3) is caused by a small degree of mechanical instability in the SECM apparatus.

Initially, the evidence that the observed structures were formed by the postulated electrochemical method (see in-
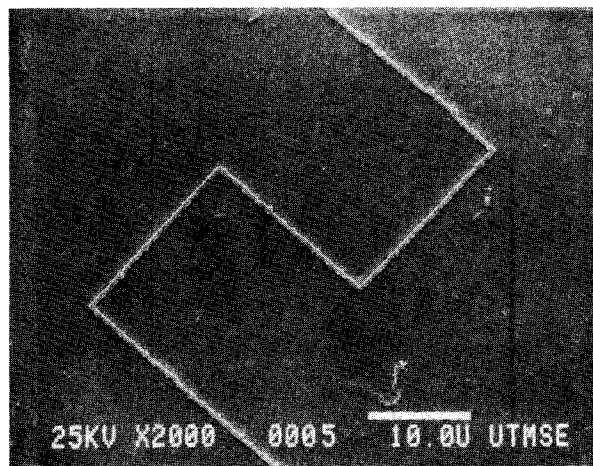
Fig. 3. SEM picture of a pattern of silver lines deposited in a Nafion film. Tip material, tungsten bias 5V; tip current, 0.5 nA; and scan rate, 900 Å/s. Tip reaction, $Ag^+ + e^- \rightarrow Ag$. Substrate reaction $Ag \rightarrow Ag^+ + e^-$.

Fig. 5. EDS analysis of the sample shown in Fig. 4. Top figure: electron beam focused on the deposition structures. Bottom figure: electron beam focused near the deposits (representative data).

troductory paragraphs) came from experiments performed on samples with copper ions in the Nafion film in the place of silver ions (12). X-ray analysis, EDS (energy dispersive spectroscopy), of the structures produced using these samples showed that copper was present in the deposition lines. Recently, however, we have been able to remove the Nafion films containing the deposition lines from the surface of the silver substrate and analyze these lines for the presence of silver. The films were removed by first coating the sample with a layer of polyimide (~100 μm thick) and then peeling this layer away. The Nafion film containing the deposition lines is picked up along with the polyimide, leaving the silver substrate behind. Figure 4 shows an SEM picture of a deposition structure produced using a silver-coated Nafion sample in which the Nafion film contained silver ions. The Nafion and deposition lines were then removed from the silver substrate using polyimide, and this film was mounted on a glass microscope slide. As can be seen from Fig. 4, the deposition of the polyimide and its subsequent removal have caused some structural damage to the lines, which now have jagged edges. Nevertheless, the lines do appear to be continuous, which was further verified by conductivity measurements performed by placing two SECM tungsten tips on top of the deposits using micromanipulators in conjunction with a microscope. The resistance between the two tips, measured with an ohmmeter, was finite only when both tips

were placed directly on the deposited lines. Because it was impossible to contact the deposited lines without touching the silver substrate, conductivity measurements of this type could only be performed when the deposits were removed from the substrate by the method described above. Figure 5 shows an EDS analysis of one of these polyimide-supported metal structures taken in a SEM with the electron beam focused on the line (top figure) and on an area on another part of the sample (bottom figure). These results clearly demonstrate that the deposition lines are composed of silver, which once again supports the postulated deposition mechanism. (The gold lines in the EDS spectra are present because the sample was first sputtered with gold to make it conducting before it was introduced into the SEM chamber.)

Deposition lines similar to those shown in Fig. 3 and 4 have also been obtained by soaking the Nafion films with either copper ions (soaking with 20 mM $CuSO_4$ or 20 mM $Cu(NO_3)_2$) or chromium ions (soaking with 20 mM $Cr(NO_3)_3$).

Deposition of metals in PVP.—Figure 6 shows high-resolution gold structures deposited at the air/poly(4-vinylpyridine) interface using the SECM. These structures
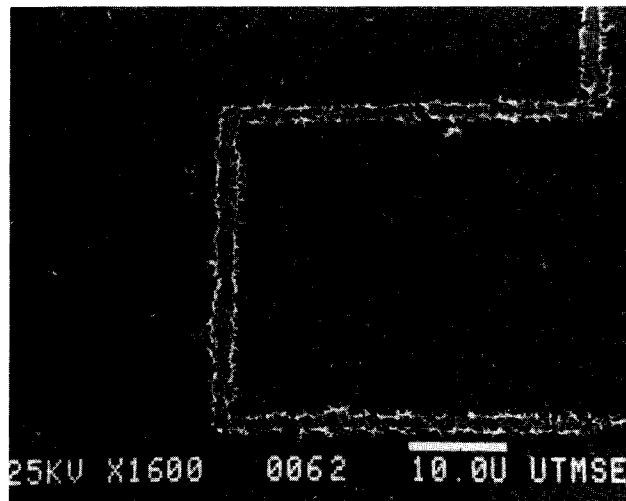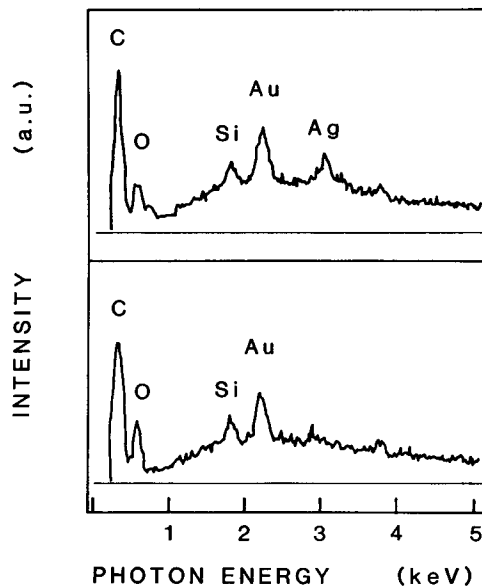

Fig. 4. SEM of silver structures on polyimide. The silver was first deposited in Nafion using a tungsten tip, applying 5V bias, 3 nA, and a scan rate of 1170 Å/s. After the deposition, the Nafion film was first coated with polyimide and then separated from the substrate (Ag).
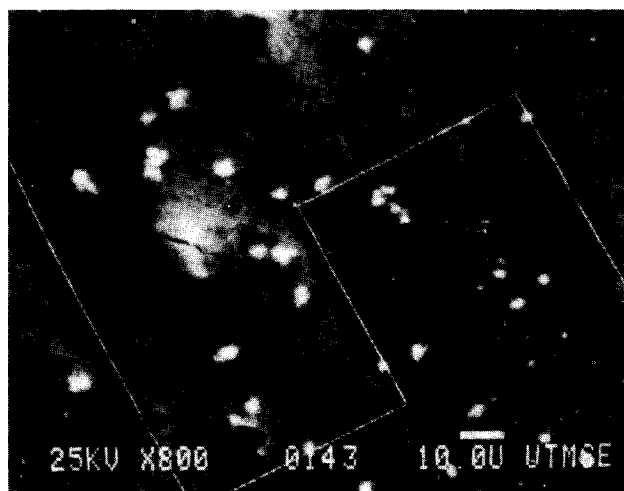

Fig. 6. SEM of a gold line deposited in a poly(4-vinylpyridine) film. Parameters: bias, 5V; current, 1.0 nA; speed, 1000 Å/s; tip material, platinum. Tip reaction, $AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$. Substrate, quartz slide coated with colloidal graphite.

were obtained using a sample consisting of colloidal graphite coated with PVP containing $AuCl_4^-$ (anion incorporated into the film by soaking the sample in a solution containing 42 mM $AuCl_4^-$ and 1M HCl). Graphitic layers as the conducting substrates were chosen to clearly distinguish the deposits from the substrate by EDS (*e.g.*, the x-ray energies of gold and platinum could not be separated). It can be seen from Fig. 6 that the graphite surface is not as smooth as the surfaces obtained by sputtering or vacuum deposition. Similar experiments performed on sputtered platinum and gold substrates yield lines of widths smaller than 0.2 μm (13).

The electrochemical reactions that take place when the tip electrode makes contact with the PVP film are similar to those described for Nafion: at the tip electrode, $AuCl_4^-$ ions are reduced to gold and chloride

$$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$$
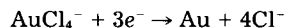
while the oxidation reaction that occurs on the gold substrate, for example, leads either to the formation of Au(III) or to the decomposition of water to O_2.

We have also found that narrow lines are also produced when the $AuCl_4^-$ in the PVP film is replaced by $PdCl_4^{2-}$. The exact composition of these lines has not yet been elucidated, but it is expected that they will contain both gold and palladium.

Deposition of silver in MEEP.—In both the case of Nafion and PVP, ions are only mobile within the film if there is a high concentration of solvent species present. For the cases described above, this solvent was water. It is likely, especially when using higher voltages, that some of the current passed while scanning the tip electrode over the surface of these polymers results from the decomposition of water at either the tip or the substrate electrodes. There are a number of different polymers that do not require solvent to be present for the ions to be mobile. An example of such a polymer is MEEP (16, 17), which, after doping with salts of either lithium, sodium, or silver, shows conductivity on the order of 1×10^{-5} Ω^{-1} cm^{-1} at room temperature. We have used samples of silver-doped MEEP coated on a silver substrate, as described in the Experimental section, to deposit lines of silver with the SECM (platinum tip). Figure 7 shows an SEM picture of some of the structures produced. It can be seen that the lines are not very uniform or continuous and the resolution is much lower than that obtained with Nafion or PVP. With similar settings for the bias potential and reference current, the silver depositions in MEEP (see Fig. 3 and 7) show a more dendritic growth than the corresponding structures produced in Nafion films. Dendritic growth of the deposited structures in Nafion films was observed only at low bias potentials (less than 3V). In MEEP, lines were only observed if the bias voltage was above 1V. The reason that the lines produced in MEEP were so poor is that there were considerable

Fig. 7. SEM picture of silver deposited in MEEP. Tip material, platinum; bias, 5V; tip current, 0.5 nA; scan rate, 250 Å/s.

problems associated with stabilizing the SECM feedback loop. This resulted in the tip electrode moving over the surface of the film in a series of bouncing steps rather than the normal, relatively smooth motion. This erratic motion might be explained in terms of the rubbery and "sticky" nature of the MEEP polymer, which could cause the film to move up and down with the tip electrode.

Deposition of structures containing different metals.—In the previous sections we presented results that show that very thin metal deposition lines of a single material can be produced by reducing ions within a polymer film. In the case of both Nafion and PVP, the ions present in the polymer films can be changed by soaking the sample in the appropriate solution. This, in principle at least, should allow the production of structures made of individual lines, each of which can have a different composition.

In all of the work we have described to date, the ionic species present in the polymer film, and hence the composition of the lines deposited at the tip electrode, were of the same material as the metal substrate on which the polymer were coated. The experiments were designed in this way because any ions produced as a result of the oxidation process at the metal polymer interface rapidly diffuse across the thin polymer film and subsequently reduce back to metal at the tip electrode. So, for example, if a sample composed of silver metal coated with Nafion containing copper ions is used, then the lines deposited at the tip electrode using the SECM would be composed of a mixture of both copper (formed by the reduction of the ions in the film) and silver (formed by the reduction of ions that are produced as a result of the anodic process at the silver/Nafion interface).

To produce deposition lines composed solely of the species present in the film requires the use of a sample composed of a polymer film coated on an inert electrode that will not release metal ions on oxidation. With this view in mind, we have used platinum as a substrate material and made samples by coating this with Nafion containing the appropriate metal ion. The oxidation process that accompanies the electrochemical deposition at the tip electrode under these conditions involves the decomposition of water present in the Nafion films (producing O_2) and/or the formation of platinum oxide with no metal ions being released into the polymer.

With Nafion films containing either silver or copper ions coated on a platinum substrate, it is possible to deposit lines of silver and copper, respectively. These structures were produced only if thin films of Nafion were employed (ca. 0.1 μm). If the Nafion film thickness was on the order of 1-2 μm, the motion of the tip electrode became highly irregular, resulting in deposition structures that were discontinuous and nonuniform. We attribute this behavior to problems associated with gas formation at the platinum/Nafion interface. In addition to producing deposition lines composed entirely of either silver or copper, we have also performed experiments where the ion incorporated into the film is changed after an initial deposition, so that lines of this different material could be deposited. Here, substitution of the ion in the film was achieved by first moving the tip a short distance away from the surface of the polymer film (ca. 30 μm), disconnecting the SECM feedback electronics, and then soaking the sample in a solution containing the desired ion for 20 min. Finally, the solution was removed from the surface of the sample, which was then left for 10 min to dry before reconnecting the electronics and bringing the tip back to the surface of the polymer. Throughout this process, the lateral position of the tip was not changed; therefore, subject to drift, the tip should return to the surface of the polymer at the same position as it was before being removed. Figure 8 shows an SEM of deposition lines in a Nafion film that was coated on a platinum substrate. Here, the first set of S-shaped lines (S shape on the top left side) were produced with silver ions in the film. Copper ions were then incorporated into the film in the manner described (soaking in copper nitrate), after which the next set of S-shaped lines (S shape on the bottom right side) were produced. Note that although the tip electrode was removed from the sample for about 30 min to allow
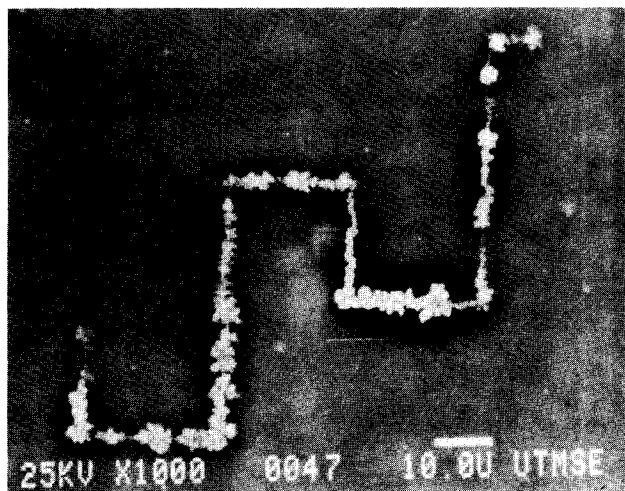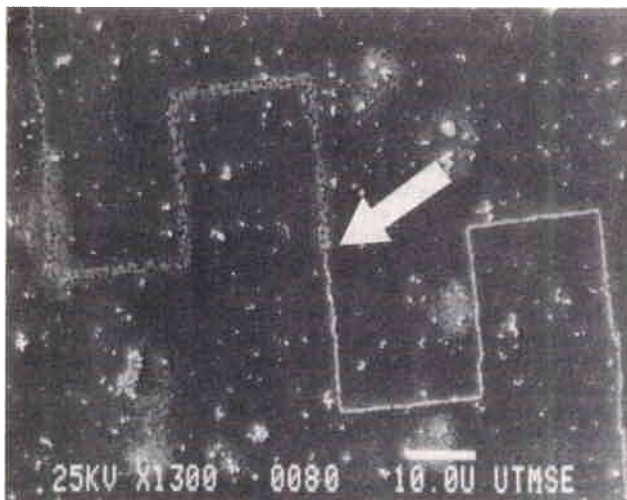
Fig. 8. SEM picture of a sample where silver structures were first deposited (upper left side) followed by copper (right side). Parameters: bias, 4V; current, 0.2 nA; speed, 423 Å/s. A tungsten tip and a platinum substrate were used. The arrow indicates the change of the materials.

the ions present in the film to be exchanged, the two S-shaped structures were still connected. This shows that the SECM instrument showed little drift, at least on the micron scale, over this period of time. Figure 9 shows EDS spectra taken with the SEM of lines made in exactly the same way as described above. These spectra show clearly that the lines produced with silver ions in the film (Fig. 9, top figure) contain silver and no copper, whereas the lines produced after the sample is soaked in copper nitrate solution (Fig. 9, center figure) contain copper and no silver. In each of these two spectra, the large peaks located at approximately 2000 and 9400 keV and the small peak at about 8500 keV represent platinum, the substrate material. These peaks are also present on the EDS spectrum of a region of the sample away from the deposition lines (Fig. 9, bottom figure). These results show conclusively that it is possible to change the deposition species without changing the position of the tip so that it is possible to produce metallic deposition structures that contain lines of different materials.

Etching of conducting substrates.—As indicated in Fig. 1, passing a current through the ionic conducting polymer film 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 study the etched traces on the conducting substrates, the polymer film, including any deposits, has to be removed. In the case of Nafion, films were removed by placing the sample in an ethanol/water mixture at 80°C (18), while PVP films were washed off in an alkaline solution.

Figure 10 shows an SEM of a sputtered copper surface containing etched structures that were obtained using this technique. These structures were formed by moving a tip electrode over a copper surface coated with a Nafion film containing methyl viologen (4,4-dimethyl bipyridinium) (MV^{2+}) ions. In this case, the tip reaction involved the reduction of MV^{2+} to MV^{+}. SECM experiments performed with Cu^{2+} ions in the Nafion film proved hard to analyze because the high exchange current between ions in the film and the copper metal caused considerable roughening of the surface that masked the etched lines. A similar effect was observed when the solutions used to incorporate the MV^{2+} ions or to dissolve the Nafion were not properly deoxygenated. Roughening was caused by surface corrosion resulting from the reaction between oxygen and the copper metal. Even with mechanically and electrochemically polished copper samples in well-deoxygenated solutions, some pitting of the surface still occurred (13). Better results should be obtained by performing the experiments in an oxygen free chamber. For sputtered copper surfaces, no difference of the surface structure before and after the experiment could be observed, indicating a homogeneous oxidation of the copper (Fig. 10). Even when the Nafion film contained methyl-violgen, some copper deposition occurred at the tip electrode because of reduction of copper ions that were released as a result of the etching process. We have also used this technique to etch silver and gold surfaces which, for this purpose, were coated with Nafion and PVP polymer films, respectively.

Because of the field distribution inside the polymer films, the etched lines should be of lower resolution than the corresponding deposition structures. In fact, depending on the parameters such as the bias potential between the tip and the substrate electrodes, the reference current
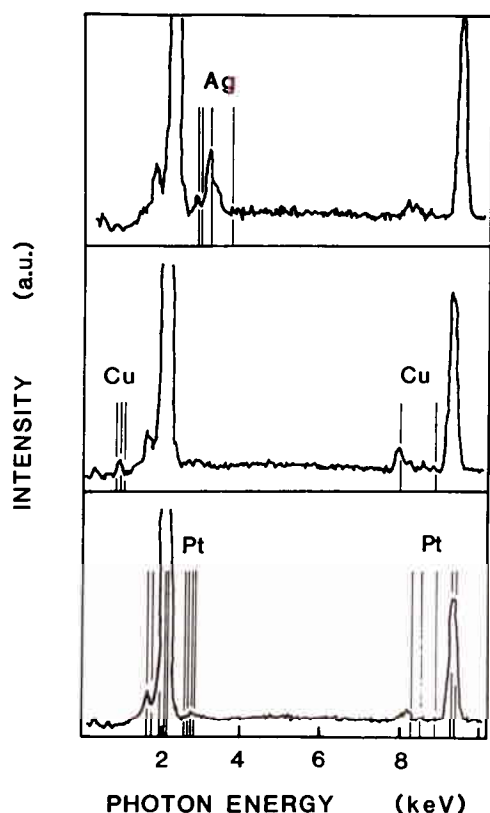

Fig. 9. EDS analysis of structures similar to those shown in Fig. 8. Top figure: electron beam focused on the Ag deposits (elapsed time 5s), center figure; e⁻-beam focused on Cu deposits (elapsed time 43s), and bottom figure: analysis of the Nafion-coated platinum substrate (elapsed time 33s).
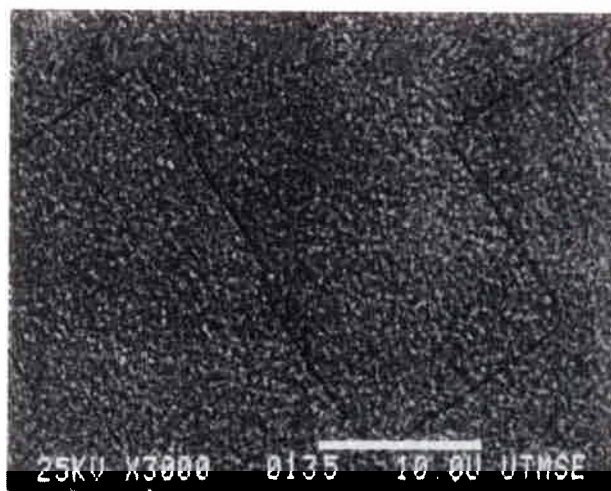

Fig. 10. SEM picture of a sputtered copper surface showing etched traces. Tip material, tungsten; bias, 4V; tip current, 3 nA; scan rate, 200 Å/s.

set by the SECM feedback electronics, and the speed that the tip moves over the surface of the polymer, a decrease in resolution of etching lines up to a factor of two was observed.

*Deposition of metals on conducting substrates.—*Changing the polarity of the tip and substrate electrodes (*i.e.*, tip electrode positive) will result in an oxidation process at the tip/polymer interface and a reduction reaction at the polymer/substrate interface. Thus, taking the case where there are metal ions incorporated in the ionically conducting polymer films, (*e.g.*, Ag^+ or Cu^{2+} in Nafion, or $AuCl_4^-$ or $PdCl_4^{2-}$ in PVP), the result should be the deposition of the metal directly on the conducting substrate.

Figure 11 shows an SEM of gold deposited on a colloidal graphite substrate. Here, a sample consisting of graphite coated with PVP containing $AuCl_4^-$ ions was used, with the lines obtained using the SECM (tip electrode positive). In this case, the oxidation process that occurred at the tip electrode involved either the formation of chlorine gas or the decomposition of water. Elemental analysis of the lines under the SEM clearly proved the presence of gold in the deposits. Again, as in the case of the etching of metals, the resolution of the deposits on the conducting substrate is, as expected, less than for the same process at the tip polymer interface (compare Fig. 11 to Fig. 6, same sample and tip). With ITO as the substrate, optical microscopic examination showed that the tip had slightly penetrated into the PVP film, producing a scratch on the surface. The gold deposits were clearly visible only after the PVP film had been removed from the ITO surface. In the case of ITO, the resolution was much poorer than the resolution obtained on the graphite substrates.

Despite our ability to deposit gold on graphite and ITO, the deposition of other metals on conducting substrates has been less successful. Though we have recently been able to produce structures on metals coated with either Nafion containing copper, silver, or nickel ions, or PVP containing Pd ions, we have been unable to verify the nature of these deposits by EDS. Therefore, it apparently is more difficult to deposit metals at the polymer/metal interface than at the air/polymer interface (*i.e.*, at the tip electrode).

Discussion

We have demonstrated that the high-resolution deposition and etching of metals can be achieved by coating a conductive substrate with a thin polymer film and then using a modified scanning tunneling microscope, the SECM. Metals can be electrochemically deposited either on the surface of the polymer film or directly on the conductive substrate. There is no evidence, except at very high applied fields (*ca.* 8V over about 1 μm film thicknesses), to suggest that any of the deposition products formed at the tip electrode actually grow on this electrode.

Fig. 11. SEM picture of gold deposited on a graphitic layer. Bias, −5V; other parameters are identical to the parameters in Fig. 6.

There are several possible reasons for this. One is that the metal atoms, formed as a result of the electrode process at the tip, preferentially nucleate and grow at sites within the polymer matrix rather than on the electrode itself. In certain cases it may be possible to initiate the deposition process at some distance from the electrode (a few Å) via a relay reaction involving moieties in the polymer chain or within the polymer, *e.g.*

tip reaction	$A + e^- \rightarrow A^-$
relay reaction	$Ag^+ + A^- \rightarrow Ag + A$
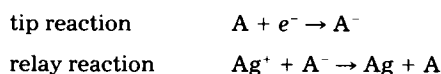
where A is a species within the polymer. Alternatively, the metal can initially deposit on the tip electrode, but as the amount of material formed increases, the contact between the tip and the metal becomes weak compared to the forces holding the metal within the film. Thus, when the tip is removed from or moved across the surface of the polymer, the contact between it and the metal is broken. For example, consider the deposition of metals in Nafion films. Here, the SECM feedback control is unable to maintain a strictly constant current, and a series of current spikes representing the tip making contact with and subsequently being removed from the surface of the polymer film is observed. The response of the SECM feedback loop is on the order of 1 kHz and is limited by the resonance frequency of the piezo ceramic that controls the z motion of the tip. With a set current of about 0.1 nA, an approximation for the amount of charge that is passed each time that the tip makes contact with the surface of the polymer is somewhere on the order of 10^{-13}C. The molecular weight and density of silver translate into a corresponding volume of about 10^4 nm^3. The area of the tip that actually makes contact with the surface of the polymer film can be estimated from the expression for the steady-state current obtained at a microelectrode given by (19, 20)

$$i = 4\pi n FCDr \qquad [1]$$

where C and D are, respectively, the concentration and diffusion coefficient of the electroactive species, F is Faraday's constant, n is the number of electrons involved in the electrode reaction, and r is the radius of the electrode. For the polymers described in this study, all of which have a high ion exchange capacity, the concentration of ions within the film will be high [greater than $1M$ (21)]. The diffusion coefficient of these ions within polymer films tends to be less than for the same ion in solution. However, because of the low separation distance between the tip and metal electrodes, the field across the polymer film will be very large (10^4-10^5 V/cm), and hence, migrational effects will probably increase the overall rate of transport of ions to the tip electrode. Moreover, in the case of silver ions in Nafion, the relatively low partition coefficient of the ions within these films as compared with other cationic species indicates that there is only a small interaction between the silver ions and the SO_3^{2-} groups that are bound to the polymer chain. Thus, one would not expect the diffusion coefficient of this species within the film to be much smaller than its value in aqueous solution. With a diffusion coefficient and concentration of silver ion of 10^{-6} cm^2/s and $1M$, respectively, tip current of 0.1 nA would require a contact area of less than 20 nm^2 (Eq. [1]). This suggests that the contact area between the tip and the polymer is fairly small compared to the actual volume of material formed each time the electrode makes contact with the film. The metal deposits are probably well-anchored to the polymer matrix, so that given the relative sizes of the contact area and deposited volume, the explanation for the lack of deposition products at the tip electrode in terms of relative binding forces seems plausible.

Several factors govern the resolution attainable by this technique. As described above, we have had some success in improving the resolution of the silver structures produced as compared to an earlier report (12). The major factor contributing to this improvement was a change in the STM feedback control, which adjusts the vertical position of the tip as it is moved across the surface of the polymer. In our initial studies (10, 12), the feedback was controlled

digitally with a microcomputer (Apple IIe) linked to the current amplification electronics and vertical piezoelectric positioner by way of a standard interface (Isaac 91A). In the experiments reported here, this was replaced by an entirely analog system (described in the Experimental section), which has the advantage of providing a much faster response. This increase in response time allowed the tip to be moved across the surface at much faster speeds while still retaining the same control. By building a more stable SECM apparatus and using higher scan speeds, even thinner and more uniform lines might be obtained. At this point, however, we can only speculate what level of resolution might be attainable. Certainly, the lines produced cannot be any thinner than the contact area between the tip and the surface of the polymer film, which imposes a limit on the order of a few tens of nanometers. In practical terms, however, the amount of silver deposited ultimately depends on the amount of charge passed per unit area traveled. This is governed by both the current used in the STM feedback loop and the speed that the tip is moved over the surface of the polymer film. At the moment, the maximum speed that the tip is moved is on the order of 0.5 μm/s. This does not represent an upper limit, but it is unlikely that speeds much above 10 μm/s can be used; this limit is set by such factors as the resonance frequency of the piezoelectric ceramics, the speed of the STM feedback loop, and the uniformity of the coatings. Ultimately, the size and structure of the tip will probably limit the thickness of the lines that can be obtained with this technique. Certainly, the best results obtained to date have been achieved using uninsulated, very sharp, needle-like tip electrodes.

So far, we have been unable to determine the exact profiles of the deposited lines within the Nafion or PVP films. These profiles will vary depending on the experimental conditions. The major determining factor will probably be the magnitude of the applied field across the polymer, which will determine the relative importance of diffusional and migrational processes within the film. This parameter is a function of both the applied voltage and the thickness of the polymer layer. At very low applied fields (~200 mV across a 2 μm thick Nafion film at a tip current of 0.1 nA), the tip electrode is unable to follow the surface of the polymer and instead penetrates into the film producing a scratched line. At the other extreme, at high fields (ca. 7V across a 0.1 μm thick film), the motion of the tip electrode becomes highly erratic due to problems in stabilizing the SECM feedback electronics. The profiles of the deposition lines in PVP are expected to be different from those obtained in Nafion. This is because the mobile ions in PVP are anions and thus have to diffuse to the tip electrode against the applied field.
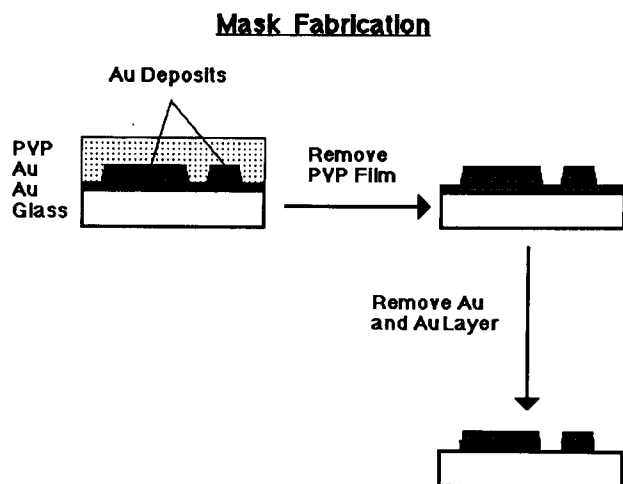
Mask Fabrication

Fig. 12. Schematic representation of a procedure to fabricate a lithographic mask by the deposition of metals directly on a conducting substrate using the polymer film technique (tip positive) followed by controlled etching of the substrate. The example shown is the deposition of gold on a thin gold layer.

The etching and deposition of metals has also been achieved using an SECM where the tip and substrate electrodes are immersed in a liquid electrolyte (10, 11). However, the use of polymer films has several advantages over the liquid electrolyte technique. 1. The resolution of the structures produced strongly depends on the distance between the tip electrode and the surface of the substrate. In liquids the faradaic current is sensitive only to fluctuations in this distance when it is of the order of the tip diameter (22). This makes it difficult to control the interelectrode spacing precisely. When a polymer film is used, the depth to which the tip penetrates into the polymer-film strongly depends on the contact area, which is turn depends on the current set by the analog feedback loop. As a consequence, the distance between the tip and the substrate is always constant, providing the films are uniform. 2. In all of the experiments described in this paper, no deposition of materials at the tip electrode or etching of the tip electrode was observed. In contrast, experiments performed in our laboratory with liquid electrolytes always resulted in either the passivation of the tip electrode or an increase in its size with a corresponding decrease in the resolution of the surface modifications. 3. As mentioned above, the area of the tip exposed to the polymer or liquid electrolyte could ultimately determine the resolution and the deposition or etching patterns. It is still difficult to insulate tips in such a way that less than a μm² is exposed to the liquids (23). With the polymer films, the tips are easy to fabricate, as no insulation is required, since it is the area of the tip in contact with the ionically conducting film that is important.

The techniques described here are currently extended to the deposition of polymers and semiconductors in experiments underway in our laboratory. Possible practical applications of the technique described here include the fabrication of lithographic masks (e.g., for x-ray lithography) and the repair of broken contacts in integrated circuits or mask defects. Masks can be produced simply by removing the deposition structures (preferrably of gold because of high x-ray absorption coefficient) in the polymer film using polyimide as previously described. An alternative method of mask fabrication is shown schematically in Fig. 12. Here, a material with a high absorption coefficient is directly deposited on a thin layer of a nonabsorbing conducting material. After the deposition process, the polymer film is then removed to leave the desired pattern.

Conclusion

It has been shown that a scanning electrochemical microscope can be used to deposit and etch materials with a resolution in the submicron range. The technique described, which involves the use of ionically conducting polymer films, has a wide range of possible applications, allowing the deposition and etching of a variety of different metals and probably also semiconductors and polymers. The high resolution obtained, the low cost of the instrument, and the advantage of being able to work at atmospheric pressure rather than vacuum might lead to its possible use in the fabrication of submicron devices.

REFERENCES

1. G. Binnig and H. Rohrer, Helv. Phys. Acta, 55, 726 (1982).

2. G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, *Phys. Rev. Lett.*, **50**, 120 (1983).
3. D. W. Abraham, H. J. Mamin, E. Ganz, and J. Clarke, *IBM J. Res. Dev.*, **30**, 492 (1986).
4. M. A. McCord and R. F. W. Pease, *Appl. Phys. Lett.*, **50**, 569 (1987).
5. R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, *Nature* (London), **325**, 419 (1987).
6. U. Staufer, R. Wiesendanger, L. Eng, L. Rosenthaler, H.-R. Hidber, H.-J. Güntherodt, and N. Garcia, *J. Vac. Sci. Technol.*, **A6**, 537 (1988).
7. M. A. McCord and R. F. W. Pease, *J. Vac. Sci. Technol.*, **B4**, 86 (1986).
8. M. A. McCord, Ph.D. Dissertation, Stanford University, Stanford, CA (1987).
9. R. M. Silver, E. E. Ehrichs, and A. L. de Lozanne, *Appl. Phys. Lett.*, **51**, 247 (1987).
10. C. W. Lin, F.-R. F. Fan, and A. J. Bard, *This Journal*, **134**, 1038 (1987).
11. J. Schneir, P. K. Hansma, V. Elings, J. Gurley, K. Wickramasinghe, and R. Sonnenfeld, *Proc. SPIE—Int. Soc.*, **897**, 16 (1988).
12. D. H. Craston, C. W. Lin, and A. J. Bard, *This Journal*, **135**, 785 (1988).
13. O. E. Hüsser, D. H. Craston, and A. J. Bard, *J. Vac. Sci. Technol.*, **B6**, 1873 (1988).
14. A. J. Bard, F.-R. F. Fan, J. Kwak, and O. Lev, *Anal. Chem.*, **61**, 132 (1989).
15. B. Lindholm, M. Sharp, and R. D. Armstrong, *J. Electroanal. Chem.*, **235**, 169 (1987).
16. P. M. Blonsky, D. F. Shriver, P. Austin, and H. R. Allcock, *Solid State Ionics*, **18** and **19**, 258 (1986).
17. P. M. Blonsky, D. F. Shriver, P. Austin, and H. R. Allcock, *J. Am. Chem. Soc.*, **106**, 6854 (1984).
18. R. B. Moore III and C. R. Martin, *Anal. Chem.*, **58**, 2569 (1986).
19. K. B. Oldham, *J. Electroanal. Chem.*, **122**, 1 (1981).
20. K. Aoki, K. Akimoto, K. Tokuda, H. Matsuda, and J. J. Osteryoung, *J. Electroanal. Chem.*, **171**, 219 (1984).
21. H. S. White, J. Leddy, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 4811 (1982).
22. J. Kwak and A. J. Bard, *Anal. Chem.*, **61**, 1221 (1989).
23. A. A. Gewirth, D. H. Craston, and A. J. Bard, *J. Electroanal. Chem.*, **261**, 477 (1989).