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High Resolution Deposition of Silver in Nafion Films with the Scanning Tunneling Microscope

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Since its introduction, the scanning tunneling microscope (STM) (1,2) has been used mainly to determine surface topography and structure at the atomic level. However, there have also been several reports of its use in vacuum or air for surface modification and submicron lithography (3-8). A recent paper from this laboratory (9) described a similar technique, based on the scanning electrochemical and tunneling microscope (SETM) (10), for the high resolution etching of semiconductors immersed in a liquid. We describe here a novel method for the deposition of metal structures within a polymer film based on the STM. The principle behind this technique is shown in Figure 1. A thin (e.g., ca. μm) film of an ionic conductor containing the metal ion of interest is formed on a conductive substrate. This is placed in the usual STM-type apparatus (in air), in which the sample can be moved in the X-Y direction and the fine metal tip can be moved in the Z-direction with nm-level resolution. A bias voltage is applied between the tip electrode (negative) and the substrate. When point contact is made between the tip and the surface of the ionic conductor, a faradaic current passes, with metal ions being reduced to metal at the tip-ionic conductor interface. The tip follows the surface of the ionic conductor by means of a conventional STM feedback control, which maintains a constant current between the tip and the substrate. It is thus possible to produce metal structures by scanning the tip along the surface of the substrate. If it is assumed that the bias voltage is suffciently large that the kinetics of the electrode reactions are not rate limiting, then the current obtained when the tip makes contact with the surface of the ionic conductor will depend on the rate of mass transport of metal ions to the tip. Therefore, by setting a low value for the reference current, it should be possible to maintain a contact area on the order of a few nm^2, provided that both the diffusion coefficient and the concentration of the metal ions within the ionic conductor are not too low. Hence we believe that very high resolution of deposition can be obtained by this technique. The work described here illustrates the above principle and involves the deposition of silver in Nafion (11) films.

The STM apparatus used and the method of tip preparation (platinum) have been described previously (10). The sample was made by first vacuum depositing silver onto the surface of a glass slide. Drops of a 1% w/w solution of Nafion (E. W. 970) in ethanol were then spin coated at 3800 rpm on to the silver surface with a total of 40 drops added to give a film thickness of ca. 2.5 μm, as measured with a surface profilometer. Prior to use, the sample was first soaked in Millipore water for 1 h and then in 50 mM silver nitrate solution for 15 min. Experiments were performed at various bias voltages between ca. 200 mV and 8 V. Below ca. 200 mV the tip can no longer follow the surface of the Nafion and instead penetrates the film producing a scratched line. This is presumably due to either slow electrode kinetics at these voltages or IR drop in the Nafion film. The reference current used for the STM was approximately 15 pA. However, during the experiment the current oscillated between zero and ca. 1 nA, the exact value being dependent on the bias voltage. This current oscillation is ascribed to either vibrations of the system (estimated to be on the order of ca. 1 nm) or to an on/off mechanism for the faradaic process with no current observed before the tip touches the surface and larger currents obtained upon contact. This differs from the exponential dependence of the current as a function of the distance between the tip and substrate normally observed in STM.

Figure 2 shows an example of the types of structures that have been produced as observed with a scanning electron microscope (SEM). In general, the larger the applied voltage and the faster the tip is scanned over the surface, the higher the resolution that can be obtained, with lines of ca. 0.5 μm thickness observed under optimum conditions. Up to now the scan rate has been limited to speeds below ca. 500 Å sec^{-1}, with dotted lines being produced at higher scan rates. Increasing the response time of the STM feedback control should permit faster scan rates and thereby obtain even higher resolution. Indirect evidence that the lines shown are indeed silver comes from applying the same technique to other types of substrate. Lines can also be drawn with samples consisting of silver coated with Nafion containing copper ions (Figure 3). Elemental analysis of these lines under the SEM shows that they contain copper. In addition, no structures are observed when platinum coated with Nafion containing only potassium counter ions was used as the sample. In this case, the current between the tip and sample is probably maintained by the electrolysis of water at both the tip/Nafion and the platinum/Nafion interfaces.

We are currently investigating, both

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experimentally and theoretically, the effect ot bias voltage and Nafion film thickness on the resolution of the silver deposit. Further work is also in progress at our laboratory with different ionic conductors (polymer and solid state) and metal ions. With adaptation, this technqiue might be useful in the production of lithographic masks, which, to our knowledge, would be the first time this has been acheived by an electrochemical method.

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11. Nafion is a registered trademark of E. I. duPont de Nemours and Co., Inc.
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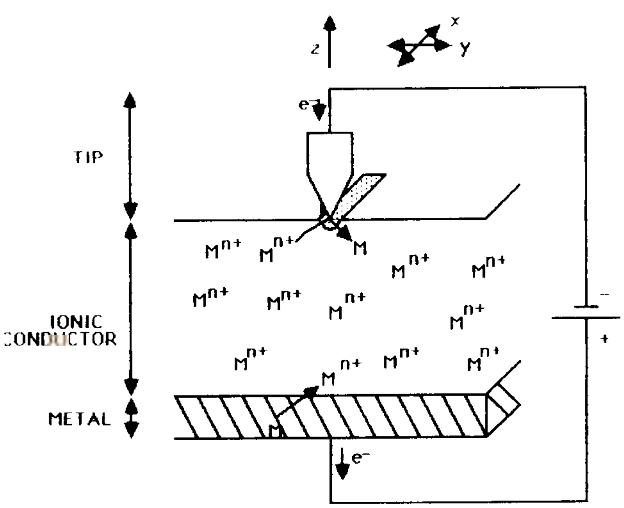

Fig. 1. (a, above) Schematic representation of a method for the general case of metal deposition in ionic conductors.

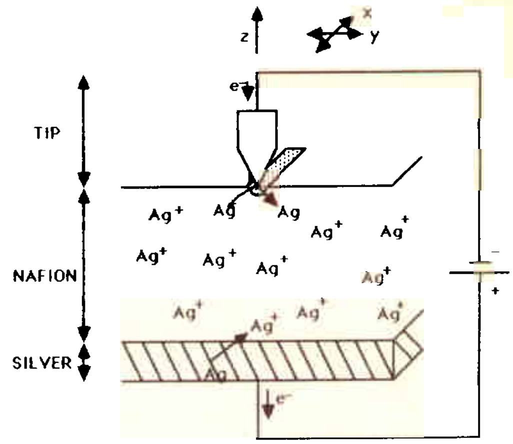

Fig. 1. (b, above) Schematic representation of a method for the deposition of silver in Nafion films as described in the text.

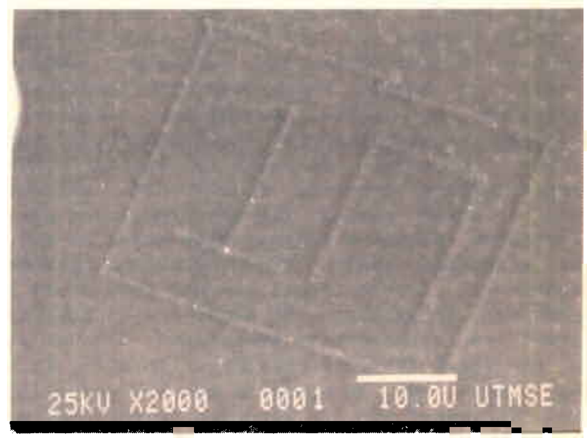

Fig. 2. Scanning electron micrograph of a pattern of silver lines deposited in a Nafion film. The bias voltage was 3V, with a tip scan rate of ca. 400A s^{-1}. Marker, 10 µm.

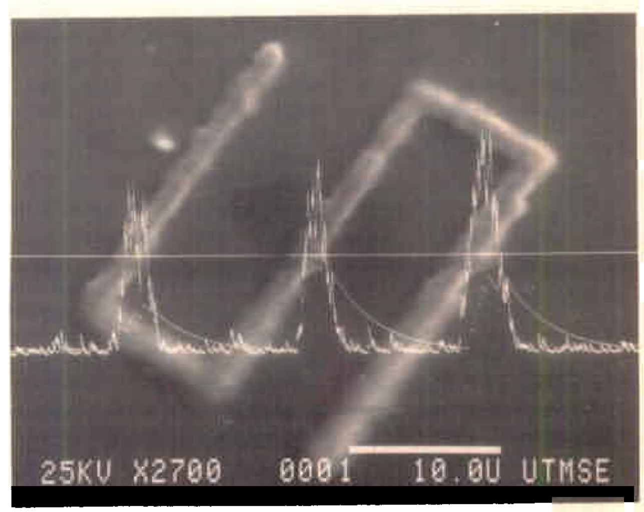

Fig. 3. Scanning electron micrograph of a copper pattern deposited in a Nafion film. The bias voltage was 3V, and the tip scan rate was ca. 100A s^{-1}. The trace represents the intensity of x-rays emitted from the sample with an energy indicative of the presence of copper, taken while scanning across the upper line. Marker, 10 µm.