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High Resolution Deposition of Polyaniline on Pt with the Scanning Electrochemical Microscope

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The fabrication of electronic devices based on organic materials has been investigated for possible use in memory devices (1), in molecular based transistors (2), as wiring (3), and for the fabrication of p-n junctions (4). In particular, organic electronically conducting polymers, e.g., polyaniline, polypyrrole and polythiophene (5,6) are important as materials for such applications, because these polymers can be formed electrochemically and show conductivities that depend on their state of charge. We describe here a method for the high resolution deposition of polyaniline on a Pt substrate based on an apparatus similar to the scanning tunneling microscope (STM). The STM has been used not only to determine surface topography and structure at the atomic level (7,8) but also to modify surfaces and for submicron lithography (9-13). Research in this laboratory recently has led to the development of a method for the high resolution deposition of metals with line widths better than 0.5 μm in thin polymer films (14,15). The principle behind the technique is illustrated in Figure 1. This technique is based on the scanning electrochemical microscope (SECM) (16), which maintains a constant faradaic current between a tip electrode and a metal substrate electrode. In this case these electrodes are separated by a thin layer of an ionically conductive polymer, which serves as the electrolyte and contains cations that are free to move within the polymer matrix. The Nafion (17) film thus provides an ionically conductive pathway for the current between the substrate and the tip and thus removes the need to use any liquid electrolyte solution. The current is driven by applying a potential between the tip and the metal.

The apparatus used and the methods of tip preparation (platinum or tungsten) have been described previously (14,15). The sample was made by first vacuum sputtering Cr (ca. 50 Å) then Pt (ca. 2 μm) onto the surface of a glass slide. Nafion films were prepared using a 1% w/w solution in ethanol. Drops of this were spin-coated at 3800 rpm onto the Pt surface. The final Nafion film thicknesses were approximately 0.1 μm. The sample was soaked in 0.1 M anilinium sulfate solution (prepared from Millipore water) for 40 min.

There are several reasons for using protonated aniline. First, cations can be readily incorporated into Nafion films via ion exchange. Second, electroactive polyaniline is formed in water only from acidic solutions, e.g., with aniline and H_2SO_4 or $HClO_4$ (18). Third, the reduction of protons provides the cathodic reaction at the tip during polyaniline deposition on the substrate. The resulting faradaic processes are:

$$2n\ C_6H_5NH_2 \rightarrow (\text{-}C_6H_5NH\text{-})_{2n} + 2n\ H^+ + 2n\ e^-$$
(at the Pt substrate/Nafion interface)

$$H^+ + e^- \rightarrow 1/2\ H_2$$
(at the tip/Nafion interface)

The potential applied between the tip and the substrate must be above a threshold value. The magnitude of this potential is a function of both the electrochemical processes and the iR drop in the Nafion film. For example, with 0.1 μm thick Nafion films, the deposition of polyaniline structures only occurred with applied potentials above 5 V. For lower bias voltages, the tip electrode penetrated the Nafion film producing scratch lines. The feedback current, which maintains the tip position so that only the very end is in contact with the surface of the ionically conducting polymer film, was about 1 nA.

Figure 2 shows an example of the type of structures that have been produced as observed with a scanning electron microscope (SEM) at a resolution of better than 2 μm. The thin dotted line on top of the polyaniline line is generated by the cathodic reaction (hydrogen generation) at the tip/Nafion interface). This was proved by soaking the sample in 0.1 M sulfuric acid solution and carrying out the same deposition operations. Only the dotted line in the Nafion film was formed. Most of the dotted line can be removed by rinsing the sample with methanol, which slowly dissolves the top layers of the Nafion films. After this treatment, the polyaniline lines were readily observed with SEM. The resolution obtained so far for polyaniline deposition is not as good as in metal depositions, where a resolution of better than 0.5 μm was found (15). The resolution for metal deposition in Nafion films (at the tip/Nafion interface) is controlled mainly by the tip size. In contrast, the resolution for polyaniline deposition on the Pt substrate (at the Nafion/Pt interface) is controlled not only by the tip size but also by the thickness of Nafion films and the electric field distribution.

In principle, narrower polyaniline lines should be produced by applying a positive potential to the tip (opposite to the polarization shown in Fig. 1). However, under these conditions, only scratch lines in the Nafion were observed. This might be caused by the growth of polyaniline at the tip. The relatively low conductivity of the polyaniline would cause the feedback circuit to push deeper into the Nafion film, resulting in a scratch line.

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Keywords: microfabrication, conductive polymer, scanning tunneling microscope, scanning electrochemical microscope

In conclusion, an SECM can be used to deposit polyaniline on a substrate by using thin, ionically conductive Nafion films coated on a Pt surface. The resolution of the patterns produced are smaller than 2 µm. Further work is in progress at our laboratory with different ionic conductors and electroactive materials (conductive polymers, organic metals and semiconductors).

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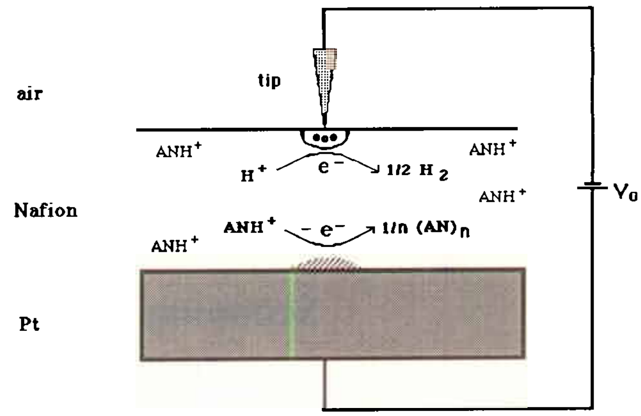

Fig. 1. Schematic representation of a method for the deposition of polyaniline on Pt as described in the text.

Fig. 2. Scanning electron micrograph of a pattern of polyaniline lines deposited on Pt in a Nafion film. Tip material = tungsten; bias voltage = 7.5V (tip negative); tip current = 1 nA; scan rate = 400 Å/s.