Reprinted from JOURNAL OF THE ELECTROCHEMICAL SOCIETY
Vol. 136, No. 10, October 1989
Printed in U.S.A.

Scanning Electrochemical Microscopy: The Application of the Feedback Mode for High Resolution Copper Etching

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We report here the successful etching of copper with high resolution using the scanning electrochemical microscope (SECM). Electrochemical copper dissolution has been studied extensively (1,2) as a means of understanding and preventing copper corrosion, while copper etching has been of interest (3) in microdevice fabrication, e.g., integrated circuit production. The SECM is based on the measurement or control of the faradaic current that flows at an ultramicroelectrode (UME) as it is moved near (ca. μm) a substrate surface and can be used for either surface characterization (4) or modification (5). Previous surface modifications, e.g., metal deposition or etching, have been carried out mainly by the direct method, where the applied potential between tip and substrate causes the desired reaction at the substrate (5). However, an alternative approach, recently applied to the deposition of metals, such as Au and Pd in a polymer film on an electrode (6), is to employ a redox species (a mediator) in solution to cause a reaction at the substrate. This is called the feedback mode (4a,b), because the current at the UME is affected by the electron transfer that occurs at the substrate.

We demonstrate here that metal etching via the feedback mode offers several advantages over the direct mode. A major problem in the direct method is control of the cathodic electrode reaction at the UME. Formation of gas bubbles or metal deposition leads to changes in UME tip geometry and loss of resolution. Moreover, the fact that the substrate is held at potentials that are positive with respect to the UME promotes corrosion of the substrate with concomitant roughening and formation of oxide films. Thus, direct etching by this approach in liquid media generally has been unsuccessful (7), although etching of Cu covered by a polymer film has been possible (5b,c).

The principle of etching via the feedback mode is shown in Figure 1. Specifically, the system consists of a 1-2 mM redox couple, e.g., $Fe(phen)_3^{2+}$ or $Os(bpy)_3^{2+}$ (phen=1,10-phenanthroline, bpy=2,2'-bipyridyl) in a 10 mM acetate buffer (pH 4.0) solution. The UME is mounted on a piezoelectric device, while the copper substrate is placed in a Teflon cell that is attached to an x-y micropositioning device (5). A platinum counter electrode and a saturated calomel reference electrode are introduced into the cell as well. No electrical connection is made to the substrate, which is maintained at a potential governed by the solution redox couple. When the UME that is held far (several UME diameters) from the surface is biased (1.0 V vs. SCE with $Fe(phen)_3^{2+}$ or 0.7 V vs. SCE with $Os(bpy)_3^{2+}$), a constant steady-state current is established within several seconds. However, when the UME approaches the surface, an increase in the steady-state current (a positive feedback current) is observed due to the regeneration of the reduced species via electron transfer at the surface. As a result, copper dissolution occurs, which is strictly limited to the diffusional range of the oxidized mediator. Moreover, the magnitude of the UME current compared to that at large separation, allows sensing and control of the tip-substrate distance (4,6). Figure 2a shows a scanning electron micrograph of three etching spots made by holding a 25 μm Pt UME at a constant distance for various periods of time. The profiles of these etching spots are depicted in Figure 2b. Notice that the upper width of the etching crater matches almost precisely the UME diameter and that a continuous electrolysis leads to deeper etching profiles. The width of the etching pattern reflects the diameter of the UME, because the UME is held at a small distance, d, from the copper surface, compared to the electrode diameter. Indeed, the etching profile depends critically on d; i.e., longer distances between the UME and the surface resulted in shallower and wider etching profiles. Sputtered copper films (thickness 0.15-2 μm) over 50 Å sputtered chromium on quartz disks were used as substrates, and profilometry (Figure 2b) showed that the copper was continuously etched down to the chromium base. Since the current is very sensitive to changes in UME-surface distance, the distance could be easily monitored. Therefore, a UME that scanned over the surface at constant d yielded an etching line whose profile depended on the scanning rate as well as d (Figure 2c).

This feedback mode of etching, utilizing an oxidant generated at a positive electrode, has a number of advantages over the direct method: (a) The etching profile depends upon the diffusion of UME-generated species rather than the electric field and current distribution between UME and substrate. At small values of d, this should produce higer aspect ratios in etched patterns. (b) Operating in the feedback mode allows straightforward control of d, a factor that critically affects the etching profile. (c) Since the UME is held at a positive potential, dissolved copper will not be deposited on the electrode tip, leading to a constant area UME. Moreover, bubble formation (e.g., hydrogen) at the tip is not a problem. (d) On the other hand, the substrate surface itself is not biased directly, but its potential is controlled by the solution species. Thus, as long as oxidants are only generated at the UME, the surface

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Keywords: scanning electrochemical microscope, ultramicroelectrode

will not corrode elsewhere. In addition, no contacts need to be made to the substrate. (e) The disk UME is not as prone to damage by surface crashing as the tip electrodes, which are sometimes used in the other approaches. Although a rather large UME diameter was employed in this initial study, so that larger patterns which could be easily characterized by profilometry could be obtained, very small UME (down to 0.6 μm) have already been fabricated, implying that much smaller patterns should be possible. Characterization of the different steps involved in the etching processes and examination of the various factors that affect the etching profile are currently being studied.

References

1. (a) D. J. G. Ives, A. E. Rawson, *This Journal*, 109, 447 (1962); (b) Ibid, p. 452; (c) Ibid, p. 458; (d) Ibid, p. 462.
2. (a) H. P. Leckie, *This Journal*, 117 1478 (1970); (b) D. Kinneke, R. Lacmann, *Electrochim. Acta*, 28, 967 (1983); (c) L. Kiss; J. Farkas, *Acta Chim. Acad. Sci. Hung*, 66, 395 (1970).
3. C. F. Coombs, Jr.; Printed Circuit Handbook, 3rd Ed., McGraw-Hill, New York, 1988, p. 148.
4. (a) A. J. Bard, F-R. F. Fan, J. Kwak, O. Lev, *Anal. Chem.*, 61, 132 (1989); (b) J. Kwak, A. J. Bard, *Anal. Chem.*, 61, 1221 (1989); (c) J. Kwak, A. J. Bard, *Anal. Chem.*, in press.
5. (a) D. H. Craston, C. W. Lin, A. J. Bard *This Journal*, 135, 785 (1988); (b) O. H. Hüsser, D. H. Craston, A. J. Bard, *J. Vac. Sci. Technol*, B6, 1873 (1988); (c) O. H. Hüsser, D. H. Craston, A. J. Bard, *This Journal*, in press.
6. D. Mandler, A. J. Bard, submitted.
7. C. W. Lin, Y. M. Wuu, A. J. Bard, unpublished experiments.

8. Support of this research by the Texas Advanced Research Program is gratefully acknowledged. We are indebted to the Chaim Weizmann Fellowship committee for support of D. Mandler in this work. We thank Mr. J. Cook for making the sputtered samples.

Manuscript received June 22, 1989.

The University of Texas assisted in meeting the publication costs of this article.

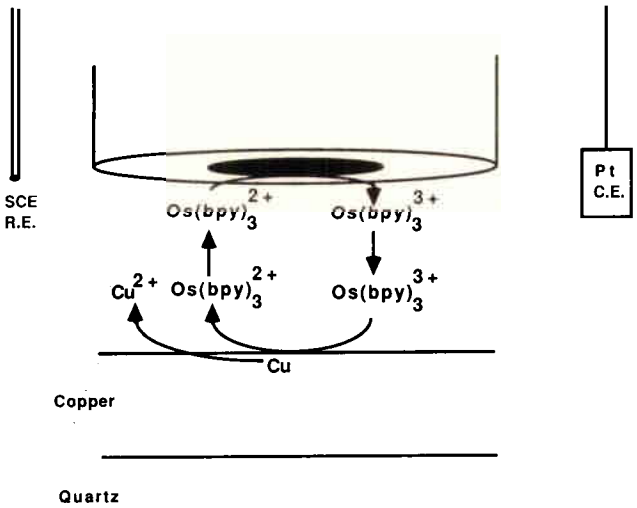
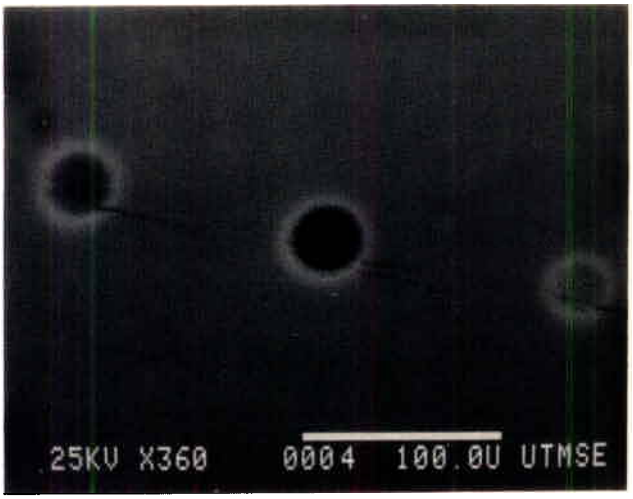
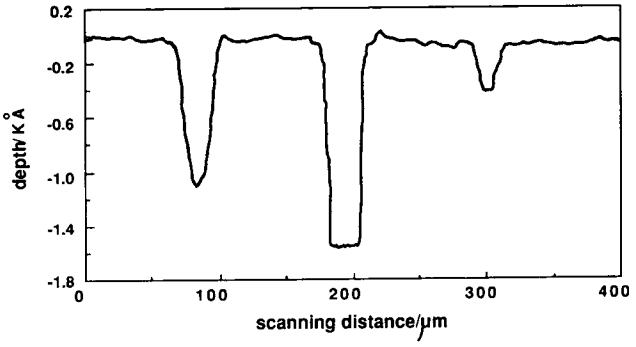


Fig. 1. Principles of copper etching by the SECM in the feedback mode.





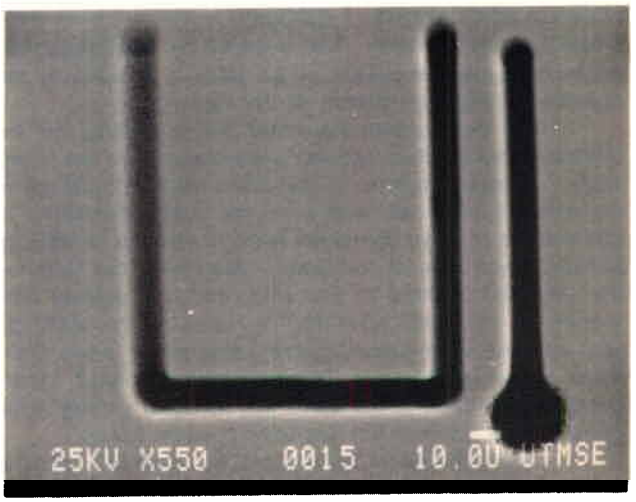


Fig. 2. (a, top) Scanning electron micrograph (SEM) of a copper surface etched in three places for 5, 10, and 20 min with a 25 μm Pt UME in a 2 mM $Os(bpy)_3(ClO_4)_2$ and 10 mM acetate buffer solution (pH 4.00) held at d = 9 μm. (b, middle) Profile of the copper surface over the etching patterns. (c, bottom) SEM of an etching line made by a 10 μm Pt UME that scanned over a copper surface at 0.05 μm/s in a 2 mM $Os(bpy)_3(ClO_4)_2$ and 10 mM acetate (pH 4.00).