High Resolution Etching of Semiconductors by the Feedback Mode of the Scanning Electrochemical Microscope

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ABSTRACT

High resolution (~μm) etching of semiconductors has been achieved by applying the scanning electrochemical microscope (SECM) in the feedback mode. Strong oxidants, such as bromine, were electrogenerated *in situ* at an ultramicroelectrode (UME) and used as etchants. The current flowing at the UME was also used to monitor the distance between the UME and the surface. The variables that affect the size and shape of the etched pattern, the required properties of the redox couple, and the mechanism of the etching process are discussed. This approach was successfully applied to several III-V and II-VI semiconductors: gallium arsenide, gallium phosphide, cadmium telluride, and mercury cadmium telluride.

We have recently described the application of the scanning electrochemical microscope (SECM) in the feedback mode for metal deposition (1) and metal etching (2) with high resolution. Here we present the utilization of the SECM for the high resolution etching of semiconductors. High resolution etching and modification of semiconductor surfaces is of technological importance in the fabrication of microelectronic devices (3, 4) and is usually carried out by photolithography through several consecutive steps that include coating with photoresist, x-ray or UV-irradiation, etching, and stripping. Wet etching of semiconductors is generally carried out with strong oxidants, such as bromine (5), hydrogen peroxide (6), and nitric acid (7), and by dissolving metal oxides, *e.g.*, SiO_2, mainly with hydrofluoric acid (8).

As discussed below, the SECM enables the high resolution etching process to be carried out in a single step. In the SECM experiment, a biased ultramicroelectrode (UME), which is immersed in a solution containing an appropriate electroactive species, is moved close to the surface to be etched (Fig. 1). The potential applied to the UME causes either the reduction or the oxidation of the redox species and results in a steady-state current. However, when the UME is brought close (of the order of the UME diameter) to the surface, fluxes at the tip are perturbed from those at longer distances by the presence of the substrate, and the steady-state current reflects processes occurring on the substrate. Namely, if an electron transfer reaction occurs between the redox species and the surface, an increase in the steady-state current (a positive feedback current) is produced. A decrease in the steady-state current (a negative feedback current) results when electron transfer does not occur between the mediator and the surface. In other words the distance between the UME and the surface can be determined and controlled by measuring changes in the UME current. The motion of the UME toward and away from the surface (the z-direction) and across the surface (x- and y-directions) is controlled by piezoelectric micropositioners. This feedback mode of operation (9) has been used to image conductive and insulator surfaces (10) and to modify surfaces with high resolution (1, 2). The same approach has now been applied successfully to semiconductors.

Experimental

The construction of the SECM and its general features have been described previously (1, 2, 9-11). A micropositioning device (Burleigh Instruments, Fishers, New York) that controlled the movement of three piezoelectric drivers (inchworms, 100 Å/s-2 mm/s) was used as the base of the SECM. The cell, which consisted of a Pt counterelectrode, a saturated calomel reference electrode (SCE), and the substrate, was attached to the x-y stage, while the UME was mounted on the z piezoelectric drive. The SECM and cell were placed on an air table (NRC pneumatic isolation mount, Newport Corporation, Fountain Valley, California) and shielded with a Faraday cage.

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The UME was biased either with a PAR Model 173 potentiostat or by a home-built bipotentiostat (for small currents) and the current was recorded as a function of time on a strip-chart recorder. The profiles of the etching patterns were determined by an Alpha-step 200 profilometer (Tencor Instruments, Mountain View, California) and the electron micrographs were taken with a scanning electron microscope (SEM, JEOL, JSM-35C).

Gallium arsenide(100) doped with chromium (a semi-insulator) and undoped mercury cadmium telluride were obtained from Texas Instruments. Undoped highly polished cadmium telluride(III) was purchased from II-VI Incorporated (Saxonburg, Pennsylvania) while undoped gallium phosphide was obtained from Atomergic Chemetals Corporation (Farmingdale, New York) and was polished mechanically (with 0.25 μm diamond paste) before use. Tris(1, 10-phenanthroline)ruthenium(II)chloride was obtained from Alfa Products (Danvers, Massachusetts). All other chemicals were purchased from Fisher Scientific (Fair Lawn, New Jersey). Platinum (disk ultramicroelectrodes 2-50 μm diam) sealed in a glass capillary were fabricated as described previously (9a).

In a typical experiment a small single-crystal of GaAs was fixed in the SECM cell and the UME was manually brought close (~0.5 mm) to the semiconductor. Then a solution of the redox couple, *e.g.*, 0.02*M* HBr in 0.5*M* HCl, was added. Note that the GaAs was not connected to any external voltage source so that its potential was largely determined by the solution potential. The current as a function of time was recorded while the UME approached the surface, and later transformed into a current-distance curve (9b). In addition, the UME current was integrated with time to yield the charge that passed when the UME was left biased at a constant distance above the substrate. As discussed below, this charge is a measure of the amount of reaction occurring at the substrate.

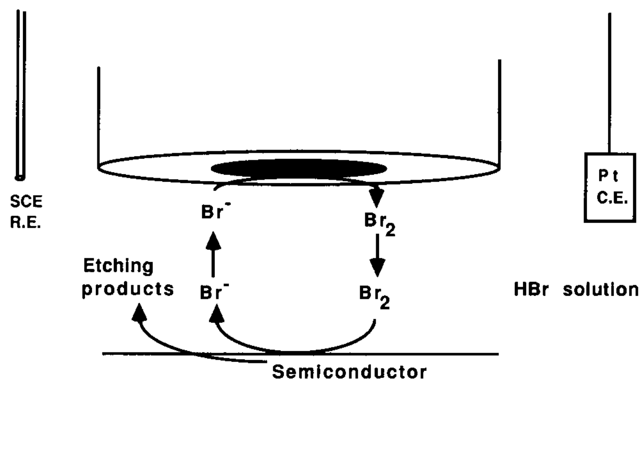


Fig. 1. Overall scheme for the etching of semiconductors using the SECM.

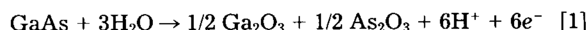
Results and Discussion

Etching of GaAs with electrogenerated bromine.—Bromine is widely used to etch III-V semiconductors such as GaAs (5). Thus, we anticipated that application of the SECM to generate electrochemically, *in situ*, strong oxidants like bromine, would lead to the etching of the semiconductor substrate, with a resolution governed by the UME diameter and UME/substrate distance. Indeed, a positive feedback current was observed when an UME (biased at 1.0V *vs.* SCE) approaches a GaAs surface immersed in a 0.02*M* HBr solution, indicating that the oxidized form of the redox couple, bromine, is reduced by a surface reaction (Fig. 1). However, the current tended to decrease rapidly, when the electrode was left biased several micrometers above the surface. This means that the electron transfer from the surface to the bromine became blocked, evidently by formation of an insulating layer on the GaAs. This blockage, as discussed below, was overcome upon adding 0.1*M* HCl to the solution. Under these conditions GaAs was etched continuously, as shown by the scanning electron microscope (SEM) picture of three etched spots that were produced by holding a 25 μm UME at a constant distance from a GaAs sample for different durations (Fig. 2a). The profiles of these spots, scanned by a profilometer, are shown in Fig. 2b. Note that the length scales are different on the x and y axes of all profilometer scans.

Parameters affecting the etching size and shape.—The parameters that affect the width and the depth of the etched spots include the UME size, the distance between the UME and the surface, and the electrolysis time, *i.e.*, the charge passed through the UME. Figure 3 shows a SEM micrograph and the profiles of etch spots made with UMEs of different diameters. Clearly, smaller electrodes resulted in smaller etch spots. Electrodes as small as 2 μm diam were successfully used (Fig. 3c) resulting in spots that were too small to scan with a profilometer (~2.5 μm stylus radius). However, such small electrodes required very stable instrumentation as well as very stable redox reactions to detect the small changes in the steady-state current.

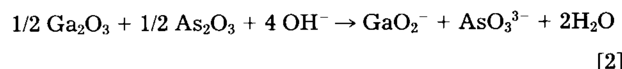
Figure 4 shows a profile of three etch spots made by holding a 50 μm Pt UME for the same duration and at several distances from a GaAs substrate. The closer the electrode was held to the surface, the greater was the depth and the higher the aspect ratio of the etched spot. The charge that passes through the UME is a measure of the total amount of oxidant generated at the UME and is a function of two additional parameters: the concentration of the redox couple and the electrolysis time. Figure 5 shows the profiles of three different experiments in which the concentrations of the redox couple and the electrolysis times were varied to keep the total charge passed constant. For these conditions, the etching times were inversely proportional to the HBr concentration so the electrolysis durations in Fig. 5c were about one-fifth of those in Fig. 5a. Note that the etch profiles obtained for different electrolysis durations were almost the same, suggesting that faster etching is possible without loss of resolution by increasing the concentration of the oxidant and electrolysis current. In all of the experiments shown in Fig. 5 the distance between the UME and GaAs was identical.

Mechanism of etching process.—The first step in the etching process involves the oxidation of bromide to bromine at the UME. The heterogeneous electron transfer reaction of this redox couple is rapid in acidic solution (12), and both forms of the couple are stable, yet under long term electrolysis a continuous decrease in the steady-state current was observed, even when the UME was held far from the surface. This instability is probably due to the relatively low solubility of bromine in acidic solutions or to the changes in the surface of the electrode (12). Since a very stable current is essential to detect the small changes in the current upon approach of the UME to the surface, acetonitrile was added to the aqueous solution containing the redox couple ($MeCN:H_2O$ 1:1). This resulted in a completely stable steady-state current. To be a useful etchant system, the redox couple must exhibit the reversibility and stability to produce stable currents for judging the UME position, while the oxidized form of the redox couple must be thermodynamically and kinetically capable of oxidizing the semiconductor surface. The oxidation mechanism of GaAs by bromine is not fully understood and is believed to proceed through a chemical decomposition (13) rather than by hole injection via the valence band (14). Whatever the mechanism, the positive feedback current indicates that a fast electron transfer occurs between the GaAs surface and bromine. Detailed examination (9b) of the feedback current reveals that Nernstian conditions exist at the surface, *i.e.*, the bromide is regenerated on the GaAs surface in a fast electron transfer process. The direct oxidation of GaAs in the presence of water yields (15) Ga_2O_3 and As_2O_3 (Eq. [1]), which are both electrochemically inactive



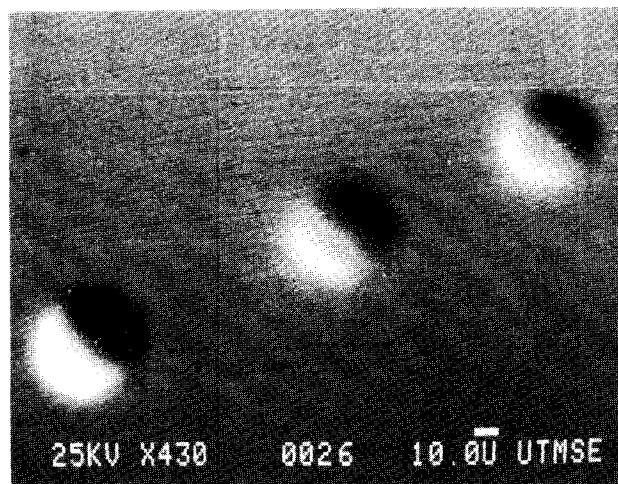
$$GaAs + 3H_2O \rightarrow 1/2\, Ga_2O_3 + 1/2\, As_2O_3 + 6H^+ + 6e^- \quad [1]$$

The dissolution of the etching products, *e.g.*, Eq. [2], plays an important role in the overall rate and can be the rate-limiting step of the overall process



$$1/2\, Ga_2O_3 + 1/2\, As_2O_3 + 4\, OH^- \rightarrow GaO_2^- + AsO_3^{3-} + 2H_2O \quad [2]$$

Moreover, oxide layers of GaAs are insoluble in aqueous solution only at pHs of 7 to 3 (16) and therefore it is obvious that pH affects the etching rate. Thus the positive feedback current decreases rapidly in 0.02*M* HBr solution whereas it stays constant when 0.1*M* HCl is added. In other words, the oxidation of the surface in 0.02*M* HBr, leads to



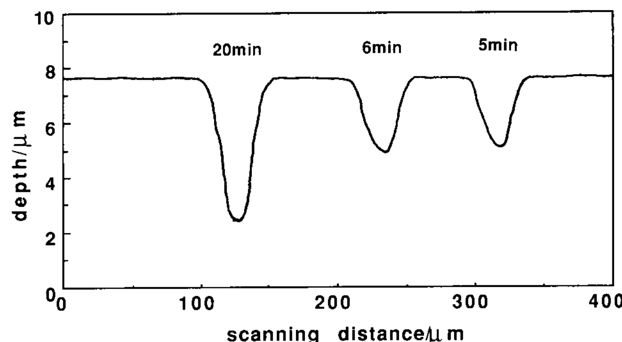
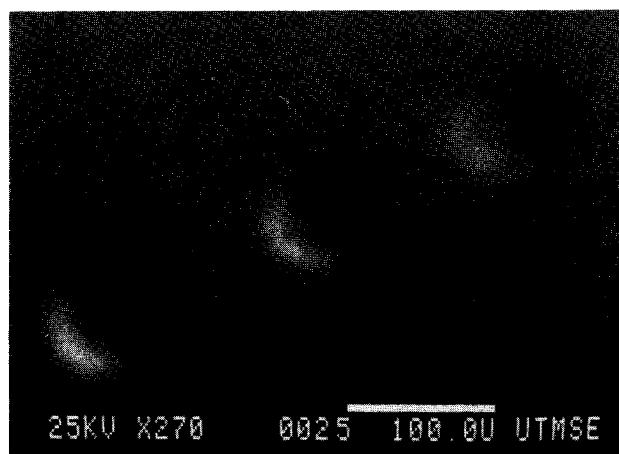
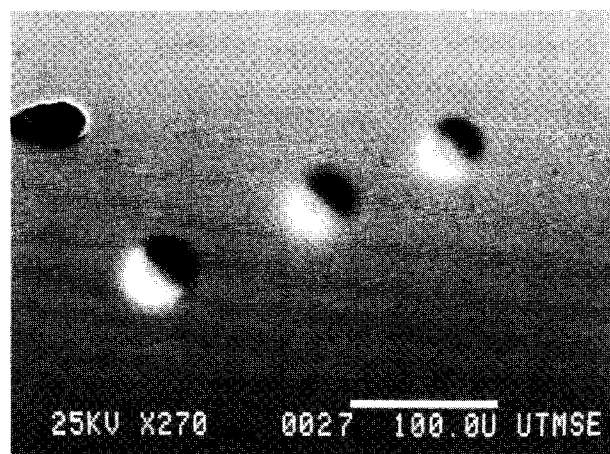


Fig. 2. (a, left) Scanning electron micrograph (SEM) of single crystal of GaAs etched in three places for 5, 6 and 20 min in a 0.02M HBr/0.1M HCl solution with a 25 μm Pt UME. (b, right) Profile of the GaAs surface at the etching spots.





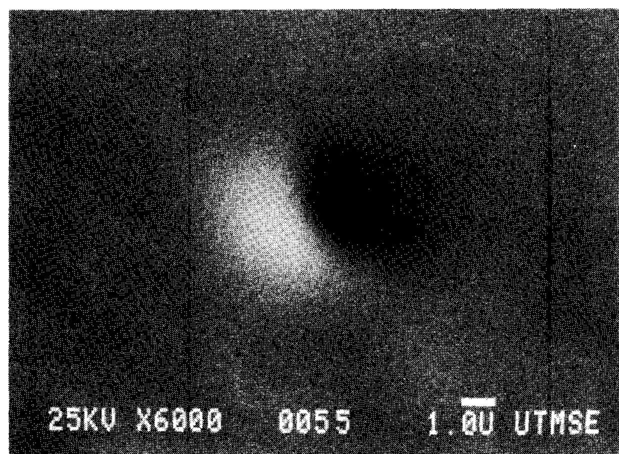


Fig. 3. Effect of UME diameter: SEM pictures of etching spots made with (a, top left) 50, (b, above) 25, and (c, left) 2 μm Pt UME.

passivation to further oxidation by bromine at that location. Under these conditions a colored spot is produced on the surface rather than an etched spot.

Etching of other semiconductors.—Since most of the III-V and II-VI semiconductors are etched via an oxidation process we have examined several other semiconductors. Figure 6 shows SEM pictures and profilometer measurements of GaP, CdTe, and $Hg_{1-x}Cd_xTe$ that were etched by the same approach.

Attempts to etch GaP with electrogenerated bromine yielded poor results which were in accordance with a previous report (5a). A negative feedback current was observed when an UME generating bromine approached a polished GaP single crystal. This indicates that bromine is not sufficiently powerful to oxidize GaP rapidly, and with the bromide/bromine couple, the GaP behaves as an insulating substrate. Indeed, substitution of a couple involving a better oxidant compared to the Br_2/Br^- couple ($E^\circ = 1.09V$ *vs.* NHE), $Ru(phen)_3^{2+/3+}$ ($E^\circ = 1.27V$ *vs.* NHE) resulted in a positive feedback response and deeper etching patterns (Fig. 6a). Even with $Ru(phen)_3^{3+}$ as the etch-

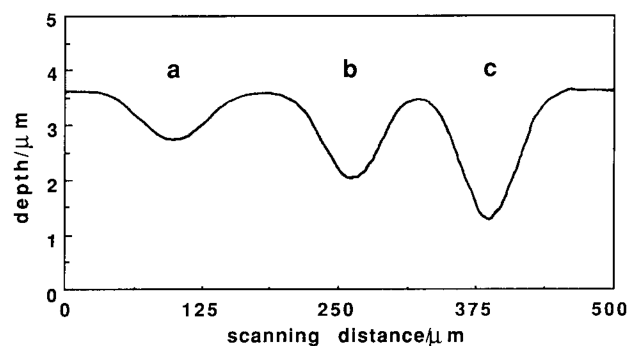


Fig. 4. Effect of UME/substrate distance: profile of single crystal of GaAs etched with a 50 μm Pt UME held at (a) 26, (b) 20.5, and (c) 17 μm from the surface.

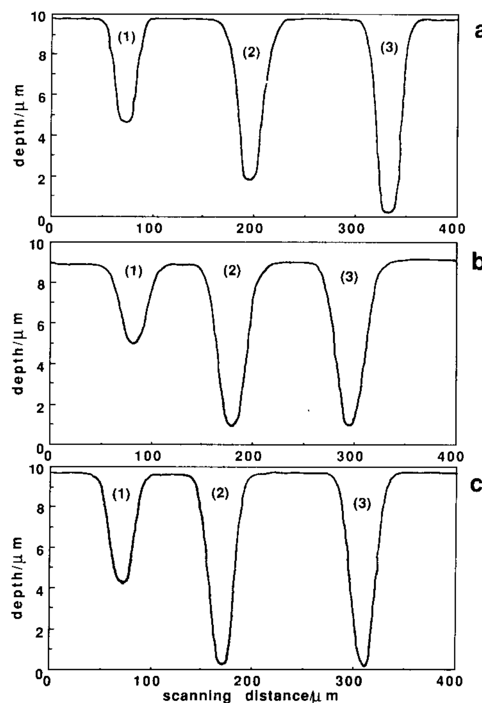
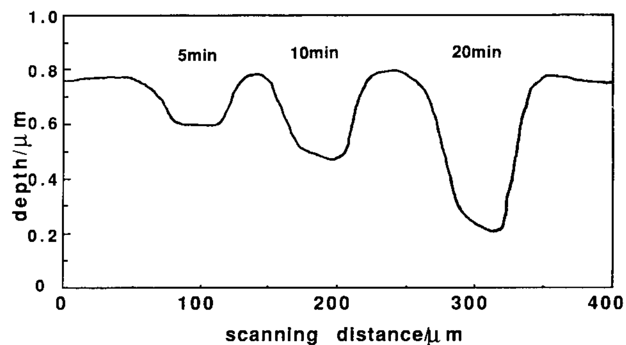
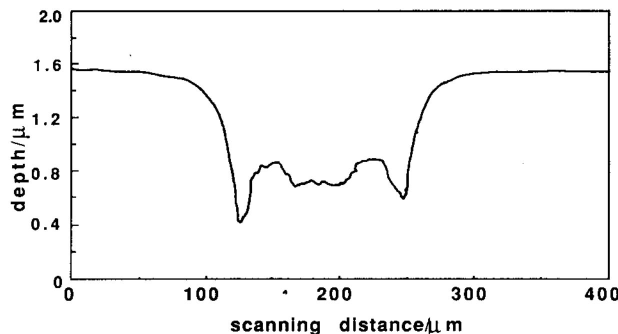
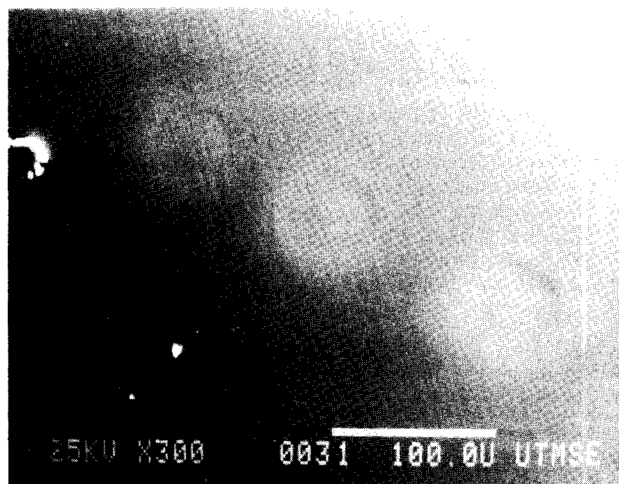
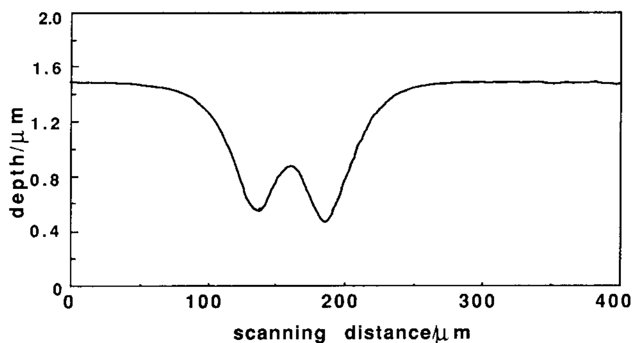


Fig. 5. Effect of charge passed and solution composition: profile of a single crystal of GaAs etched with a 25 μm Pt UME in three spots that correspond to (1) 1×10^{-4}, (2) 2.7×10^{-4}, and (3) 2.98×10^{-4}C in 0.5M HCl containing (a) 0.02, (b) 0.05, and (c) 0.1M HBr.









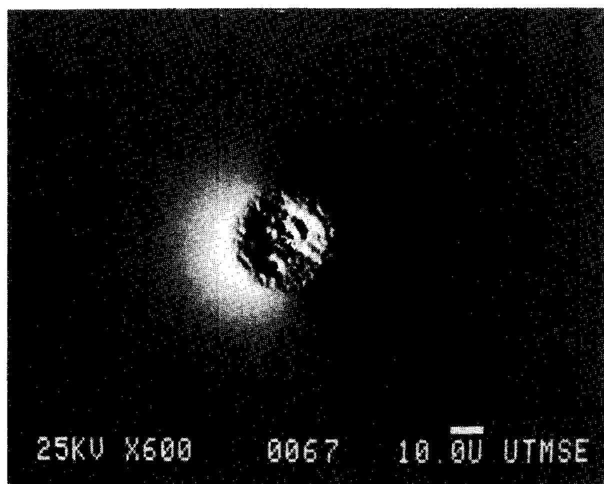


Fig. 6. SEM pictures and profilometer scans of: (a, top left) single crystal of GaP etched with a 50 μm Pt UME in a 0.01M $Ru(phen)_3Cl_2$/0.5M HCl solution (E = 1.1V vs. SCE) for 5 min (1.4×10^{-5}C), 10 min (2.4×10^{-5}C) and 20 min (4.3×10^{-5}C). (b, above) Single crystal of CdTe etched with a 25 μm Pt UME (E = 1.2V vs. SCE) in a 0.1M HBr solution for 5 min (3.5×10^{-4} C). (c, left) Single crystal of $Hg_{1-x}Cd_xTe$ etched with a 25 μm Pt UME (E = 1.2V vs. SCE) in a 0.1M HBr solution for 10 min (2.9×10^{-4}C).

ant, etching was still much slower than that of Br_2 and of GaAs. This is presumably due to slow product dissolution, although we cannot exclude that in this case a different mechanism, *i.e.*, hole injection into the valence band, takes place. To increase the etching rate of GaP, not only a powerful oxidant like $Ru(phen)_3^{3+}$ must be applied, but also a

suitable solvent is important. Indeed, better results were obtained when a mixture of H_2O:acetonitrile (1:1) was used.

CdTe and $Hg_{1-x}Cd_xTe$ exhibited similar behavior. While a positive feedback current was found, when an UME immersed in a 0.1*M* HBr approached the semiconductor surface, the current then showed a rapid decrease. This decrease in the current was caused not only by precipitation of the insoluble products on the semiconductor surface, but also by the filming of the UME tip, as indicated by the fact that the current did not increase when the UME was backed away from the surface. Note that the high concentration of the redox couple, Br_2/Br^-, caused the formation of much wider etch patterns. In addition, the etching process resulted in small pits and craters in the etched pattern (Fig. 6b, c) which might suggest that either a preferential etching occurs, when the overall process is chemically controlled and not diffusion controlled (4), or the pits are formed as a result of etching through pin holes in a resistant surface layer (17).

Conclusions

The high resolution etching of semiconductors has been accomplished using the SECM in the feedback mode. Strong oxidants generated *in situ* at an UME serve both as the etchants of the semiconductor and as surface sensors allowing control of the distance between the electrode and substrate. This allows the formation of well-defined small etch structures. To achieve etching of semiconductors with high resolution, the extrinsic parameters, *e.g.*, the distance between UME and surface, that affect the size of the etching features must be controlled. In addition, the control of the solution composition and the chemistry of the surface reactions is important in the design of the etching process. The results also suggest that by monitoring the UME current as a function of time and tip/substrate distance, useful information about the rate and nature of the substrate surface processes can be obtained. Further studies of these applications of the SECM are currently under way.

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REFERENCES

1. D. Mandler and A. J. Bard, *This Journal*, In press.
2. D. Mandler and A. J. Bard, *ibid.*, **136**, 3143 (1989).
3. (a) W. Kern and C. A. Deckert, in "Thin Film Process," J. L. Vossen and W. Kern, Editors, p. 401, Academic Press, Orlando (1978); (b) S. K. Ghandhi, "VLSI Fabrication Principles," p. 475, John Wiley & Sons, Inc., New York (1983).
4. B. Tuck and *J. Mater, Science*, **10**, 321 (1975).
5. (a) C. S. Fuller and H. W. Allison, *This Journal*, **109**, 880 (1962); (b) A. Sagar and W. Lehmann, *J. Appl. Phys.*, **39**, 5336 (1968); (c) M. V. Sullivan and G. A. Kolb, *This Journal*, **110**, 585 (1963).
6. (a) S. Iito and K. Ito, *ibid.*, **118**, 768 (1971); (b) W. Primak, R. Kampwirth, and Y. Dayal, *ibid.*, **114**, 88 (1967).
7. (a) B. Tuck and A. J. Baker, *J. Mater. Sci.*, **8**, 1559 (1973); (b) T. H. Yeh and A. E. Blakeslee, *This Journal*, **110**, 1018 (1963).
8. (a) J. S. Judge, in "Etching for Pattern Definition," H. G. Hughes and M. J. Rand, Editors, pp. 19-36, The Electrochemical Society Softbound Proceedings Series, Princeton, NJ (1976); (b) V. Harrap "Semiconductors Silicon 1973," H. R. Huff and R. R. Burgess, Editors, pp. 354-362, The Electrochemical Society Softbound Proceedings Series, Princeton, NJ (1973).
9. (a) A. J. Bard, F.-R. Fan, J. Kwak, and O. Lev, *Anal. Chem.*, **61**, 132 (1989); (b) J. Kwak and A. J. Bard, *ibid.*, **61**, 1221 (1989).
10. (a) J. Kwak and A. J. Bard, *ibid.*, **61**, 1794 (1989); (b) J. Kwak, C. Lee, and A. J. Bard, *This Journal*, **137**, 1481 (1990).
11. (a) O. E. Hüsser, D. H. Craston, and A. J. Bard, *J. Vac. Sci. Technol. B.*, **6**, 1873 (1989); (b) O. E. Hüsser, D. H. Craston, and A. J. Bard, *This Journal*, **36**, 3222 (1989).
12. (a) J. Llopis and M. Váquez, *Electrochim. Acta*, **6**, 167 (1962); (b) G. Raspi and F. Pergola, *J. Electroanal. Chem.*, **15**, 35 (1967); (c) W. Cooper and R. Parsons, *Trans. Faraday Soc.*, **66**, 1698 (1970); (d) B. H. Loo and Y. G. Lee, *Appl. Surf. Sci.*, **18**, 345 (1984); (e) M. W. Breiter, *Electrochim. Acta*, **8**, 925 (1963); (f) D. C. Johnson and S. Bruckenstein, *This Journal*, **117**, 460 (1970); (g) G. Dryhurst and P. J. Elving, *Anal. Chem.*, **39**, 606 (1967).
13. H. Gerischer and W. Mindt, *Electrochim. Acta*, **13**, 1329 (1968).
14. (a) H. Gerischer, in "Advances in Electrochemistry and Electrochemical Engineering," Vol. 1, P. Delahay and C. W. Tobias, Editors, p. 139, Interscience, New York (1961); (b) F. Decker, B. Tettinger, and H. Gerischer, *This Journal*, **130**, 1335 (1983).
15. (a) H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, **69**, 578 (1965); (b) F. Decker, *Electrochim. Acta*, **30**, 301 (1985).
16. S. Menezes and B. Miller, *This Journal*, **130**, 517 (1983).
17. J. W. Faust, Jr., in "The Surface Chemistry of Metals and Semiconductors," H. C. Gatos, Editor, pp. 151-173, John Wiley & Sons Inc., New York (1959).

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