Measurement of Concentration Distribution of Etchant Using an Electrochemical Probe

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Concentration distribution of electrogenerated etchant bromine as close as 8 micrometer to the surface of the macrodisk is studied quantitatively with an electrochemical probe technique. The feasibility of micro-fabrication using the confined etchant layer technique is further verified.

The measurement of an electrogenerated etchant in a close vicinity of macrodisk, such as the life time and the concentration distribution of etchant, can provide useful information for the Confined Etchant Layer Technique(CELT).[1] Bromine generated in situ on the surface of macrodisk can be used as etchant.[2] In the transient generation/constant potential collection mode, the possibility of using a microelectrode(diameter, 10 μm) to probe concentration profile for simple oxidation reduction reaction near a macrodisk electrode for $4 < z < 150$ μm was demonstrated.[3,4] In the ac generation/constant potential collection mode, concentration distribution of electrogenerated bromine as close as 8 micrometer to the surface of the macrodisk is studied quantitatively with an electrochemical probe technique.

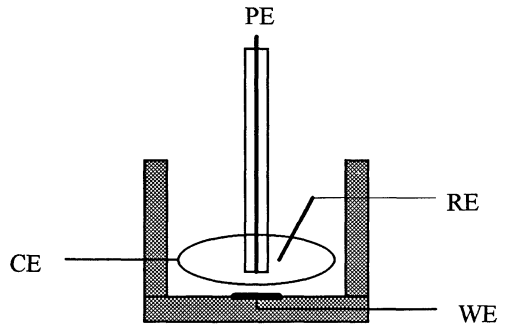

Figure 1. Schematic diagram of electrochemical cell for detecting electrogenerated etchant. WE: Macrodisk electrode; PE: Microdisk detecting electrode; CE: Counter electrode; RE: Reference electrode.

The electrochemical cell for detecting electrogenerated etchant is shown schematically in Figure 1. An electrochemical probe electrode was constructed using 7 micrometer tungsten microdisk. The radius of the microdisk was estimated according to the steady state current.[5] The probe electrode was positioned in the close vicinity to the surface of the macrodisk electrode(platinum disk diameter, 1 mm) using a three dimensionally piezoelectric micro-manipulator system. The manipulator system is similar to Scanning Tunneling Microscopy(STM). The potentials of both the macrodisk electrode and the probe electrode were controlled independently using a dual potentiostat. As a square wave potential from 0.2 V to 0.9 V(The frequency of the square wave is 0.5 Hz.) was applied to macrodisk electrode that resulted in an

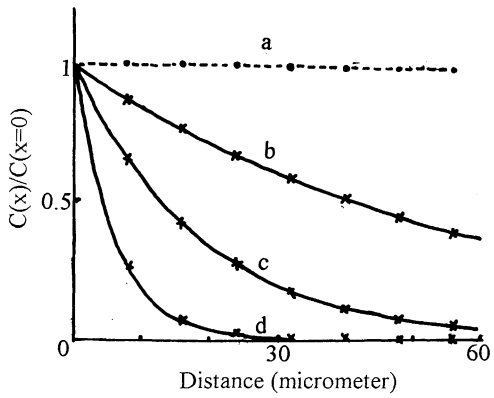

Figure 2. Experimental(dots) and theoretical(lines) electrogenerated bromine concentration profiles in 10 mmol/L KBr + 0.05 mol/L Na_2SO_4 + 0.5 mol/L H_2SO_4 solution containing various concentrations of arsenious acid(a, b, c, d: 0, 0.001, 0.01, 0.1 mmol/L, respectively).

electrochemical reaction($2Br^- - 2e \Rightarrow Br_2$), the bromine created in the reaction was free to diffuse to the probe electrode. The change of the probe current at a given potential(0 V) at which the bromine was itself electroactive($Br_2 + 2e \Rightarrow 2Br^-$) was measured with a lock-in amplifier(or signal averager) referenced to the macrodisk signal. Pt and Ag/AgCl were used as counter electrode and reference electrode, respectively. The experiment was performed in the ambient temperature. The probe current(I) corresponding to reduction of the electrogenerated bromine depended upon the distance between the macrodisk and the probe electrode. The probe current decreased generally while the probe electrode moved away from the macrodisk, which corresponded to the concentration of electrogenerated bromine decreasing generally(line a in figure 2). It showed that the diffusion characteristics of the electrogenerated bromine can be monitored using the electrochemical probe measurement system. If arsenious acid was added to the electrolyte solution, the current of the probe electrode far away from the surface of microdisk decreased obviously in comparison with in the solution that does not contain arsenious acid. Since arsenious acid is not oxidized on the macrodisk electrode it can scavenge the electrogenerated bromine according to $Br_2 + H_3AsO_3 + H_2O \Rightarrow H_3AsO_4 + 2Br^- + 2H^+$.[6] The current of the probe is proportional to the local concentration of bromine in solution. The concentration at the surface of the macrodisk can be obtained by extrapolating from relationship between current and distance in the solution that does not contain arsenious acid. Under the steady state condition the following relationship between concentration and distance was found.[1]

$$C(x) = C(x=0)\exp(-x/\mu)$$

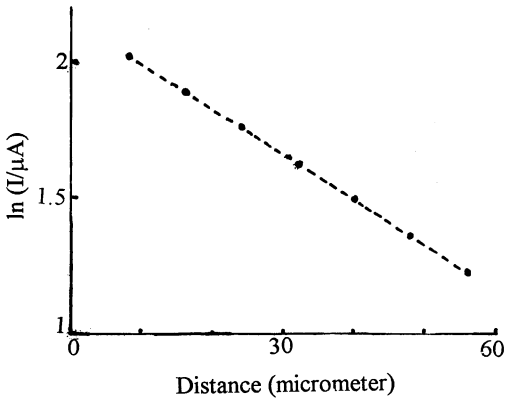

Figure 3. Relationship plot of ln I vs distance in 0.001 mmol/L arsenious acid + 10 mmol/L KBr + 0.05 mol/L Na_2SO_4 + 0.5 mol/L H_2SO_4 solution.

Where C(x=0) is the concentration of the surface of the macrodisk electrode; μ is the reaction layer thickness. Thus, the electrogenerated bromine concentration profiles(dots in Figure 2) within the diffusion layer in 10 mmol/L KBr + 0.05 mol/L Na_2SO_4 + 0.5 mol/L H_2SO_4 solution containing various concentrations of arsenious acid(a, b, c, d: 0, 0.001, 0.01, 0.1 mmol/L, respectively) were obtained by neglecting any distortion of the diffusion layer caused by the probe electrode. They agreed with the theoretical concentration profiles(line b, c and d in Figure 2) quite well. The feasibility of microfabrication using CELT is further verified. Relationship between ln I and distance is shown in Figure 3. From the slope(-1/μ) of straight line the thickness of the confined etchant layer(60 μm) can be worked out.

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References and Notes

1 Z. W. Tian, Z. D. Feng, Z. Q. Tian, X. D. Zhuo, J. Q. Mu, C. Z. Li, B. Ren, Z. X. Xie, and W. L. Hu, *Faraday Discuss*, **94**, 37(1992).
2 D. Mandler and A. J. Bard, *J. Electrochem. Soc.*, **7**, 467(1992).
3 R. C. Engstrom, T. Meaney, R. Tople, and R. M. Wightman, *Anal. Chem.*, **59**, 2005(1987).
4 R. C. Engstrom, B. Small, and L. Kattan, *Anal. Chem.*, **64**, 241(1992).
5 G. Che and S. Dong, *Electrochim. Acta*, **38**, 1345(1993).
6 L. Y. Su, J. Luo, Z. H. Lin, and Z. W. Tian, *Chin. Chem. Lett.*, **6**, 24(1995).