

Scanning Electrochemical Microscopy

XXIX. *In Situ* Monitoring of Thickness Changes of Thin Films on Electrodes

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ABSTRACT

Film thickness changes occurring at substrates immersed in solutions can be measured by scanning electrochemical microscopy (SECM). The measurement is based on the SECM feedback method in which the tip-substrate separation is determined. Two different approaches, with or without a mediator, were employed to demonstrate the applicability of SECM for these measurements with selected model systems (AgBr on Ag; Cu deposition; TiO₂ formation on Ti). The measurement resolution of this technique was 10 nm to 1 μm depending on the size of the tip electrode. The advantages and disadvantages of this technique and the factors affecting resolution are discussed.

Introduction

Applications of scanning electrochemical microscopy (SECM) have increased rapidly in recent years, and reviews are available.¹⁻³ In SECM, a small tip electrode (with a radius of less than 10 to 20 μm) is scanned in close proximity (usually the order of a few tip diameters or less) near a substrate surface. The tip current as a function of tip position is used to obtain topographic and chemical information about the surface. It can also be used to study electrochemical and chemical processes occurring at the tip and substrate electrodes. Usually, SECM is used in the feedback mode where a mediator (a component of a redox couple that undergoes a Nernstian reaction at the tip) is added to the solution in which the tip, substrate, and counter- and reference electrodes are immersed. The tip electrode is held at a potential where the tip current is determined by the rate of diffusion of the mediator species to the tip. The tip current i_T is a function of the substrate separation (taken as the z direction). The nature of the substrate, such as its electrical conductivity and chemical reactivity, also affect tip response. For example, the tip current decreases as the tip approaches an inert insulating surface (negative feedback), but increases as it approaches a conductive surface (positive feedback).⁴ Compared to other types of scanning probe microscopy, one advantage of SECM is that the tip current can be calculated from known theoretical equations. Moreover, as discussed below, the tip current normalized with respect to that when the tip is far from the substrate is a function only of the tip-substrate spacing, d . This allows absolute determination of d . By such an approach, SECM has been employed previously to measure the rate of dissolution of inorganic crystals.^{5,6} In this paper we describe the use of SECM for the *in situ* monitoring of thickness changes of thin films formed on electrodes during various electrochemical processes.

Experimental

Chemicals.—KBr, CuSO₄, Na₂PO₄ (Fisher Scientific, Fair Lawn, NJ), KCl and H₂SO₄ (95%) (J. T. Baker, Phillipsburg, NJ), and Ru(NH₃)₆Cl₃ (Strem Chemicals, Newburyport, MA) were used as received. Fe(Cp)₂COONa was synthesized from ferrocene monocarboxylic acid [Fe(Cp)₂COOH, Strem Chemicals] by reaction with NaOH in methanol and was recrystallized before use. All experiments were performed in aqueous solutions prepared from deionized water (Milli-Q, Millipore Corp.).

Tips and substrates.—Platinum wires (25, 10, and 2 μm diam, Goodfellow, Cambridge, England) were heat-sealed in glass tubes under vacuum and then were beveled to produce SECM tips as described previously.¹ These electrodes were polished with 0.05 μm alumina before each experiment. Rods of silver (1 mm diam, 99.99%, Aldrich, Milwaukee, WI), copper (2 mm diam, 99.999%, Aldrich) and titanium (5 mm diam, 99.6%, Goodfellow) were employed as substrates for the formation of AgBr, Cu, and TiO₂ thin

films. For AgBr deposition, the silver substrate was held at 0.15 V *vs.* an Ag/AgCl reference electrode in 0.1 M KBr solution to oxidize Ag to AgBr. The solution was presaturated with AgBr to prevent dissolution of AgBr from the substrate surface. Electrodeposition of copper was performed in a 0.1 M CuSO₄, 0.01 M H₂SO₄ solution by holding the copper substrate at -0.7 V *vs.* an Hg/Hg₂SO₄ reference electrode. For TiO₂ film formation, the Ti substrate was oxidized in 10% Na₃PO₄ solution by applying a dc voltage (1 to 90 V) between the substrate and a Pt counterelectrode using a dc power supply (KEPCO, Flushing, NY).

SECM apparatus.—The basic apparatus used for the SECM experiments has been described previously.⁷ A CE-1000 micropositioning device (Burleigh Instruments, Fishers, NY) connected to a PC via a DAC was used to control the movement of the tip via three piezoelectric inchworm motors. An electrochemical cell with the substrate of interest was placed in the middle of the base and mounted on a vibration-free horizontal stage. An EI-400 bipotentiostat (Ensmann Instruments, Bloomington, IN) was used for potential control and measurement. A lock-in amplifier (EG&G Instruments, Princeton Applied Research, Model 5210, Princeton, NJ) was used for ac impedance measurements. The oscillator output of the lock-in amplifier was connected to an Hg/Hg₂SO₄ auxiliary electrode and the tip was held at virtual ground. A home-built ac current follower was used in conjunction with the lock-in amplifier to measure the response at the tip electrode. The real and imaginary components of the tip current were fed into an ADC and collected by the personal computer (PC). The SECM cell was made of Teflon with a volume of about 4 ml. The reference electrode was either Ag/AgCl or Hg/Hg₂SO₄, and the auxiliary electrode was a Pt wire in all experiments except the ac impedance measurements in which Hg/Hg₂SO₄ was used.

SECM procedures.—The measurement of thin film thickness is based on the determination of the absolute tip-substrate separation using SECM feedback theory. For the measurement of AgBr film thickness, a 10 μm diam Pt tip was used with 5 mM Fe(Cp)₂COONa as the mediator. While AgBr was electrochemically deposited at the Ag substrate and the corresponding electrical charge was monitored, the tip electrode was held away from the substrate surface (>50 μm) to minimize possible blocking of Br⁻ diffusion to the substrate by the tip electrode. To determine the absolute tip-substrate separation, i_T *vs.* d curves were recorded as a function of time following AgBr electrodeposition by scanning the tip from bulk solution to a reference position near the AgBr surface. The thickness of the AgBr film deposited was then computed from the change in the tip-substrate separation, Δd , obtained from the approach curves. A similar procedure was used in thickness measurements of electrodeposited Cu films using a 25 μm diam Pt tip, except that approach curves acquired in this case were based on solution resistance measurements of the tip electrode in which a mediator was not necessary. For the meas-

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urement of TiO₂ thin film thickness, complete approach curves were not recorded because the change in the thickness of the TiO₂ film was small, in the range of tens of nanometers to less than one micrometer. Instead, a 2 μm diam Pt tip was placed in close proximity (~0.6 μm) to the substrate surface to monitor feedback current as a function of the film thickness. In this experiment, TiO₂ films were formed in 10% Na₃PO₄ solution,⁸ and the corresponding thickness measurements were performed in a 10 mM Ru(NH₃)₆Cl₃, 0.1M KCl solution.

Results and Discussion

Thickness measurements with a mediator.—In amperometric SECM with an ultramicroelectrode tip and a mediator, i_T can be recorded as a function of d as the tip approaches the substrate. Analytical expressions for i_T as a function of d are available for both conducting and insulating substrates.⁹ For a conductive substrate with diffusion-controlled reactions at both tip and substrate

$$i_T(L)/i_{T,\infty} = 0.68 + 0.78377/L + 0.3315 \exp(-1.0672/L) \quad [1]$$

For an insulating substrate

$$i_T(L)/i_{T,\infty} = 1/[0.292 + 1.5151/L + 0.6553 \exp(-2.4035/L)] \quad [2]$$

where $L = d/a$ is the normalized tip-substrate distance, a is the tip radius, and $i_{T,\infty}$ is the tip current with the tip far from the substrate. These expressions apply to an inlaid microdisk electrode with a ratio of glass sheath diameter to electrode diameter (denoted RG) of 10. From the normalized tip current and a known tip radius, an absolute value of d can be found, and from this, the thickness of the thin films deposited at the substrate surface can be determined. First, a reference position is chosen at which the tip electrode is close enough to the substrate to see the feedback effect. Then the absolute distance between the substrate and the reference position is determined both before (d_1) and after (d_2) the film formation using the feedback theory, and the film thickness can be directly related to the change in d

$$\Delta d = d_1 - d_2 \quad [3]$$

In principle, any process in which a change in thin film thickness occurs at a substrate can be monitored *in situ* using the procedure described above, as long as the thin film is not porous or penetrated by the mediator. The film should also be inert to the mediator during the measurements. The advantage of this method is that the measured thickness change is not based on any assumptions about the film density, faradaic efficiency, or substrate geometry, nor is the film touched by the tip, as in profilometry.

AgBr/Ag.—Figure 1A shows the approach curves obtained at an AgBr substrate as a function of time during the electrodeposition of AgBr. The Ag substrate was biased at 0.15 V vs. Ag/AgCl in a 0.1M KBr solution saturated with AgBr to form the AgBr film. Voltammetric studies have shown that AgBr is the predominant product of Ag oxidation under these conditions. For all these approach curves, the tip traveled the same distance (50 μm) from a predetermined reference position. Before the first approach curve was acquired at $t = 0$ min, a thin layer of AgBr was performed at the substrate surface by polarizing the substrate at 0.15 V for a short time (<1 min). As seen in Fig. 1A, the absolute tip-substrate separation systematically decreased with time due to the deposition of AgBr at the substrate surface. Control experiments yielded five overlapped approach curves over the unbiased substrate under the same conditions (Fig. 1B) since the substrate surface was unchanged in this case. This experiment also indicated that the dissolution of AgBr from the substrate surface was negligible under the experimental conditions. The experimental approach curve fit the SECM negative feedback theoretical curves very well (Fig. 2A); thus absolute tip-

substrate distances could be measured, and from these values, the change in the AgBr film thickness at the substrate could be determined. Since previous work showed that AgBr films deposited under similar conditions were fairly smooth on the micrometer scale,¹⁰ the Δd determined by SECM can be related to the electrical charge passed at the substrate electrode

$$\Delta d = Q(M_{AgBr}/\rho_{AgBr} - M_{Ag}/\rho_{Ag})/FA \quad [4]$$

where Q is the electric charge passed for the AgBr deposition, A is the substrate surface area, F is the faraday constant, and M_{AgBr} , M_{Ag} , ρ_{AgBr} , and ρ_{Ag} are the corresponding molecular weights and densities of AgBr and Ag. Figure 2B is a plot of Δd as a function of electrodeposition time of AgBr. Clearly, the Δd measured by SECM is in good agreement with that calculated from Eq. 4, demonstrating that SECM can be applied to measure the thickness changes of micrometer thick films at substrates. The applicability of SECM for thin film thickness measurements is strongly dependent on the selection of proper mediators. In addition to the mediator's stability and good redox behavior, its tip-generated product should not perturb the chemistry of the system under investigation. For the Ag/AgBr system using Fe(Cp)₂COONa as the mediator, (i) the mediator did not react with or at the substrate during substrate processes, (ii) no species formed at the substrate or added to the solution to yield the substrate reaction (e.g., Br⁻) reacted at the tip, and (iii) the tip-generated species did not react at the substrate. By changing the mediator from Fe(Cp)₂COONa to Ru(NH₃)₆Cl₃, the current increased as the tip approached the substrate, instead of decreasing as shown in Fig. 1A. As discussed elsewhere,¹⁰ this positive feedback is due to a chemical reaction between the tip-generated species and

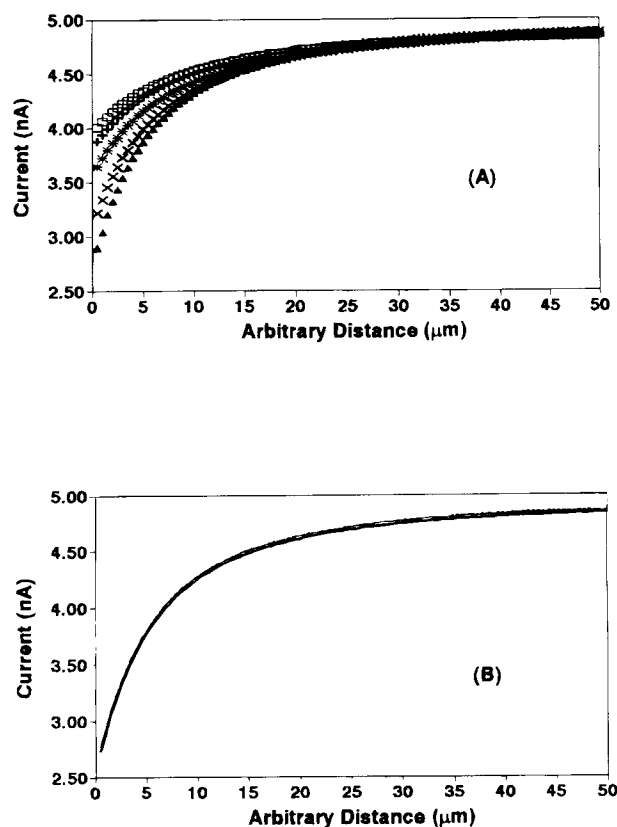


Fig. 1. SECM approach curves with a 10 μm Pt tip over an AgBr substrate. The solution was 0.1M KBr, and the mediator was 5 mM Fe(Cp)₂COONa saturated with AgBr. The tip was held at 0.4 V vs. Ag/AgCl and approached the substrate at 1 μm/s. (A) Substrate was held at 0.15 V for (□) 0, (+) 6, (*) 21, (×) 41, and (▲) 52 min. The approach curves had the same starting and ending positions in each case. (B) Control experiments with the substrate unbiased yielded five overlapping approach curves for periods up to 30 min.

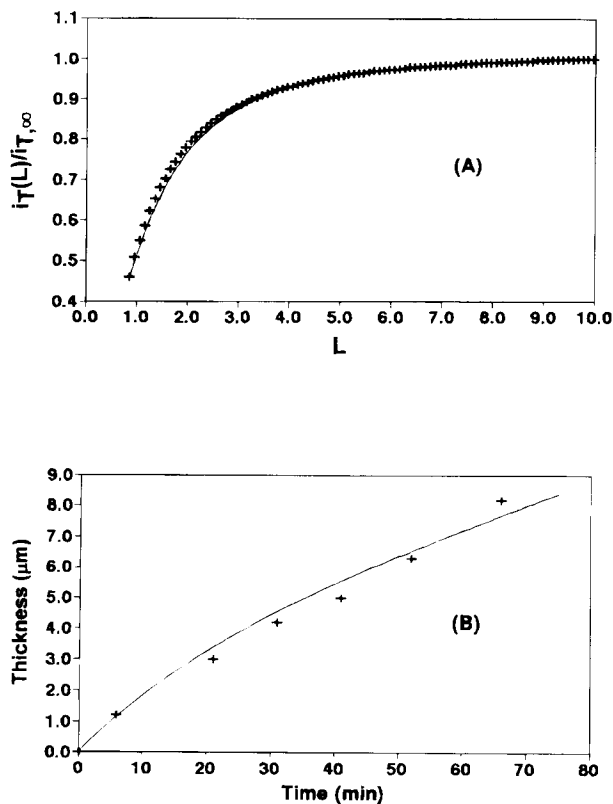
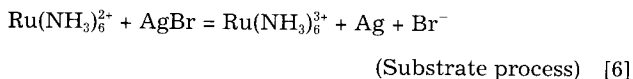
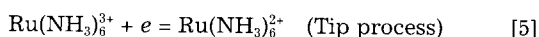


Fig. 2. (A) Typical fit to SECM feedback theory of approach curves obtained with a 10 μm Pt tip over the AgBr substrate. (—) Theoretical; (+) experimental data. Experimental conditions were the same as in Fig. 1. (B) Plot of Δd as a function of time. (—) Computed from electric charge; (+) SECM data. The 1 mm diam substrate was held at 0.15 V vs. Ag/AgCl.

the AgBr substrate in which the mediator $\text{Ru}(\text{NH}_3)_6^{3+}$ was regenerated at the substrate surface



Thickness measurements without a mediator.—When the system under investigation contains tip active species, it is difficult to select a mediator which does not perturb the chemistry of the system and can be used for thin film thickness measurements. For example, in the electrodeposition of metal films, the choice of mediator is limited by the fact that either the reduced form of the mediator can reduce the metal ion in solution or the oxidized form can oxidize the metal film at the substrate. However, a mediator-free method based on ac impedance measurement of the tip electrode can be used in this case. By applying an alternating potential (frequency 120 kHz) to the tip, the solution resistance between the tip and auxiliary electrode can be measured.⁷ The solution resistance increases as the tip approaches an insulating substrate due to the blocking effect of the substrate to ion movement to the tip. The solution resistance decreases as the tip approaches a conducting substrate because the substrate capacitatively couples to the solution and the alternating current flows more readily through the conductive substrate than the thin solution layer. The relationship between measured resistance and the diffusion-controlled feedback current has been given previously⁷

$$R(\infty)/R(L) = i_T(L)/i_{T,\infty} \quad [7]$$

where $R(\infty)$ and $R(L)$ are the solution resistance with the tip far from the substrate and at the normalized distance L . Thus the tip-substrate distance can be correlated with the

solution resistance for both insulating and conductive substrates by Eq. 1, 2, and 7. It is assumed that no faradaic processes occur at the tip electrode.

Cu deposition.—Electrodeposition of Cu on a Cu substrate was employed as a model system to test the mediator-free method. Figure 3A shows the approach curves at a Cu substrate based on ac solution resistance measurements in 0.1M CuSO_4 and 0.01M H_2SO_4 in which both 0° and 90° current components change with tip-substrate separation. To assure no faradaic processes (*e.g.*, Cu deposition and stripping) occurred at the tip electrode, an alternating potential (120 kHz) with a small amplitude (2 mV) was applied between the tip and the $\text{Hg}/\text{Hg}_2\text{SO}_4$ auxiliary electrode. Since the potential of the $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode was fixed, the potential at the tip electrode was also well defined, and no significant faradaic processes occurred at the tip. The corresponding experimental approach curves show good agreement with theory (Fig. 3B). In this case, the solution resistance was computed based on a simple series resistance/conductance (RC) equivalent circuit. Thus the measured tip-substrate distance can be used to estimate the Cu film thickness. The thickness of the Cu film can also be expressed as a function of electrical charge Q passed for the Cu electrodeposition

$$\Delta d = QM_{\text{Cu}}/2FA\rho_{\text{Cu}} \quad [8]$$

where M_{Cu} and ρ_{Cu} are the molecular weight and density of Cu. A plot of Δd as a function of electric charge passed shows the linear dependence (Fig. 4). However, the resulting slope yields a density of 7.2 g/cm^3 for the electrodeposited film, significantly smaller than its documented value of 8.9 g/cm^3 .¹¹ This difference can probably be attributed to the roughness of the deposited film.

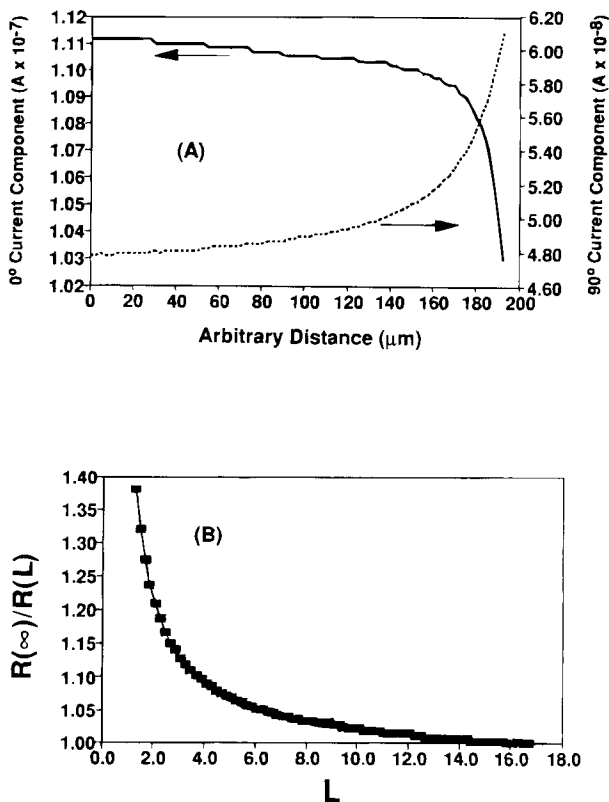


Fig. 3. (A) SECM approach curves based on ac resistance measurements. The tip was 25 μm diam Pt, and the substrate was 2 mm diam Cu. The solution was 0.1M CuSO_4 and 0.01M H_2SO_4 . The applied ac potential between the tip and an $\text{Hg}/\text{Hg}_2\text{SO}_4$ auxiliary electrode was 2 mV in amplitude with a frequency of 120 kHz. Solid line, 0° current component; dashed line, 90° current component. (B) The corresponding fit of the solution resistance as a function of distance. (—) Theoretical; (■) experimental data.

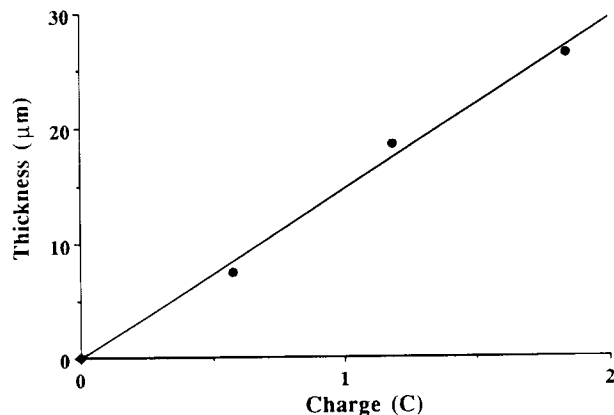


Fig. 4. Thickness of an electrodeposited Cu film as a function of the electric charge passed. The 2 mm diam Cu substrate was held at -0.7 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$. Solution as in Fig. 3.

While this method has the advantage of not requiring a mediator, it becomes less applicable when a smaller tip is used to yield a higher measurement sensitivity. The small tip double-layer capacitance contributes a higher capacitive reactance, even at high ac frequencies, and may become dominant to the impedance contribution. In this case, the change of solution resistance as a function of tip-substrate separation cannot be obtained from the approach curves. This effect will eventually limit the measurement sensitivity, although the situation can be improved by using high frequency ac.⁷

Measurement sensitivity-TiO₂/Ti system.—For SECM measurements of thin film thickness, the measurement sensitivity (resolution) is affected by several factors including d , a , and RG . Since the tip current changes more steeply as the tip approaches the substrate (*i.e.*, at small L), the measurement sensitivity is higher with a tip of small a close to the substrate. Although Eq. 1 and 2 were simulated for a tip with $RG = 10$, a size commonly used in SECM, the size of RG does not affect the positive feedback current and has a small effect in the negative feedback region.⁹ However, while a tip with small RG ($\ll 10$) is difficult to fabricate, a large RG may limit the attainment of small d , because the sheath can touch the substrate due to slight misalignment. Figure 5 shows approach curves of two 2 μm diam tips with different RG values at a TiO₂ substrate. For the tip with the larger RG (Fig. 5A), the tip current starts leveling off near $L = 1$, because of the contact between the glass sheath and the substrate. For the tip with the smaller RG (Fig. 5B), the tip current does not deviate significantly from the theory even at $L = 0.5$. Clearly, a tip with smaller RG will be easier to orient for thin film thickness measurements. For a conventional SECM tip with $RG = 10$, a tip-substrate separation of $L = 0.4$ can usually be achieved quite readily. If a 3% change of tip current caused by a change in L can be resolved, *i.e.*, if

$$[i_T(L_1) - i_T(L_2)]/i_T(L_1) = [f(L_1) - f(L_2)]/f(L_1) \geq 3\% \quad [9]$$

where $f(L_1)$ and $f(L_2)$ are the right side values of Eq. 1 or 2 at normalized distances L_1 and L_2 , this would require that $\Delta L = 0.02$ at $L \approx 0.4$, based on Eq. 1 and 2. (The more exact change of tip current for $\Delta L = 0.02$ at $L = 0.4$ is 3.5% for a conductive substrate and 4.4% for an insulating substrate.) Thus the measurement sensitivity can be approximated as $\Delta d \approx 0.02a$ or 10 nm to 0.25 μm for SECM tips of 0.5 to 12.5 μm radii.

Measurement resolution was tested by forming oxide films of different thickness on a Ti substrate and monitoring these with a 2 μm diam Pt tip and $\text{Ru}(\text{NH}_3)_6^{3+}$ as mediator (Fig. 6). The Ti substrate with the native oxide film was placed in the cell and an approach curve was obtained in a 10 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, 0.1 M KCl solution; insulator behavior was observed. The tip was then held at -0.4 V and moved

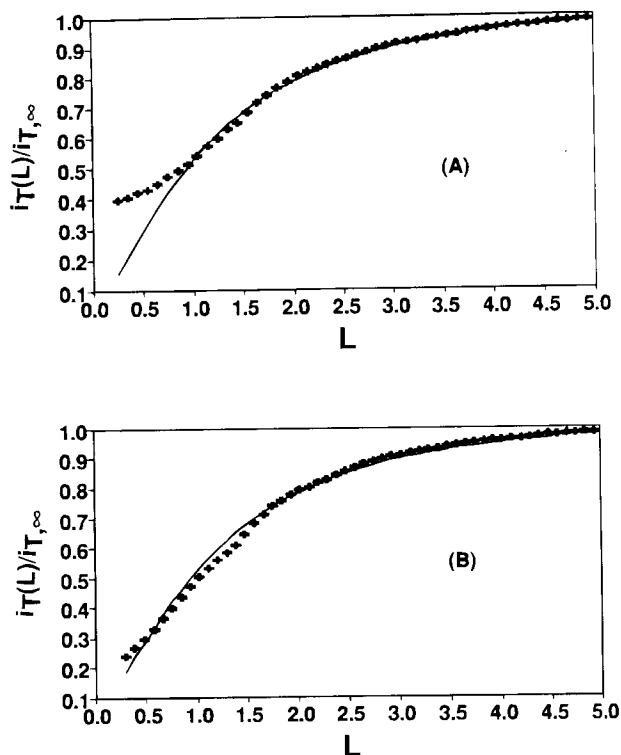


Fig. 5. SECM approach curves obtained over a TiO₂ substrate with 2 μm Pt tips with $RG =$ (A) 80 and (B) 12. (—) Theoretical; (+) experimental data. The solution was 10 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ and 0.1 M KCl. The tip was held at -0.4 V vs. Ag/AgCl and approached the substrate at 20 nm/s.

to a position above the Ti where i_T was about $0.32i_{T,\infty}$ (about 0.6 μm from the surface). The mediator solution was carefully removed with a syringe, the surface was flushed with a 10% Na_3PO_4 solution, and the Ti was anodized at 1 V for several minutes (without changing the tip position). The Na_3PO_4 solution was then removed and replaced with mediator solution, and the tip current was monitored (Fig. 6A). The current showed a small drift over the observation time of 1 min. This procedure was repeated without changing the tip position with anodizations at 40 V (curve B) and 70 V (curve C). As expected, the tip current decreased with the growth of the TiO₂ film. A quantitative estimate from curves B and C yields TiO₂ film thicknesses of 74 and 172 nm, in reasonable agreement with literature

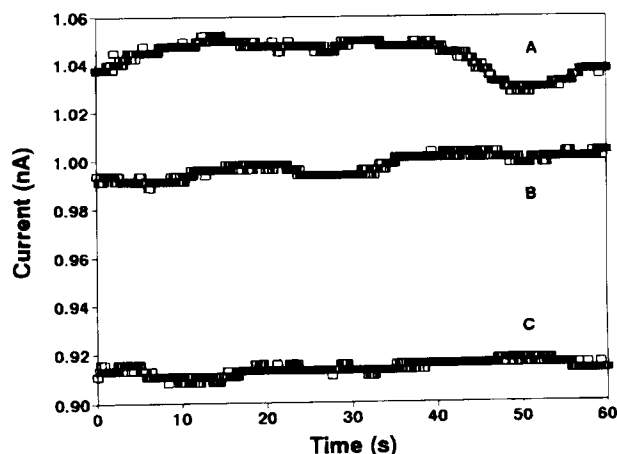


Fig. 6. Tip current for TiO₂ films of different thickness. The 2 μm diam Pt tip was placed in close proximity (~ 0.6 μm) to the TiO₂ substrate. The anodizing voltage for TiO₂ film formation in a 10% Na_3PO_4 solution was (A) 1, (B) 40, (C) 70 V. Other experimental conditions as in Fig. 5.

values, based on the thickness *vs.* anodization voltage relation, of 66 and 130 nm.⁸ This experiment demonstrates that with a suitable tip, SECM can be used to measure thickness changes within the range of tens of nanometers to micrometers.

Conclusions

SECM can be used to measure thickness changes of thin films, both electrically conductive and insulating, during various electrochemical processes. For measurements with a mediator, thickness changes are reflected by changes in the feedback current. With different tip sizes, the measurement sensitivity ranged from 10 to 250 nm. A mediator-free method based on the measurement of resistance between tip and counterelectrode can also be applied to thickness measurements, but with a lower measurement sensitivity.

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