THE ELECTRODEPOSITION OF Al-Cu ALLOYS FROM ROOM-TEMPERATURE CHLOROALUMINATE ELECTROLYTES

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ABSTRACT

The electrodeposition of Cu-Al alloys, as well as the underpotential deposition (UPD) of Al onto Cu(111), were investigated in acidic aluminum chloride/1-methyl-3-ethylimidazolium chloride ambient temperature molten salt. It was shown that it is possible to produce Cu-Al alloy deposits at potentials positive of that corresponding to the electrodeposition of bulk Al. The onset of Al codeposition was found to occur at approximately 0.30 V versus the Al(III)/Al couple, and the Cu-Al alloy composition was found to be independent of the Cu(I) concentration, reaching a maximum value of 43% atomic fraction Al at 0 V. Alloy deposition potentials based on free energy calculations are in good agreement with those observed experimentally for Zn-Al, Cu-Al, Co-Al, and Fe-Al deposited at room temperature and Ni-Al deposited at 150 °C from an aluminum chloride/sodium chloride melt. Cyclic voltammograms recorded on Cu(111) clearly indicate that UPD of Al commences at about 0.30 V vs. Al and is characterized by two distinct surface processes. In-situ scanning tunneling microscopy (STM) examination indicates that an ordered ad-layer appears on the Cu(111) surface at potentials positive of the first UPD wave. A possible model representing this structure corresponds to a layer of tetrachloroaluminate ions, oxidatively adsorbed on the Cu(111) surface, with the face of the tetrahedra adjacent to the copper surface.

INTRODUCTION

Aluminum alloys can be electrodeposited from chloroaluminate molten salts with the addition of the solute metal ions to the electrolyte. This can be accomplished by either anodic dissolution of the solute metal directly into the melt or by the addition of the appropriate chloride salt. The formation of Al-transition metal alloys is also possible even though the deposition potential of the transition metal may be several hundred millivolts more positive than that of Al. The mechanism leading to the formation of these alloys is a variant of underpotential deposition (UPD) phenomena whereby alloy formation proceeds by co-deposition of Al during the mass-transport-limited electrodeposition of the transition metal. Such interesting alloy formation has been demonstrated for Al-Ni (1) from AlCl3:NaCl electrolyte as well as Al-Ni (2-4), Al-Co (5,6) and Al-Cu (7,8) from the room-temperature chloroaluminates. In this article, we describe the electrodeposition of Cu and the underpotential co-deposition of Al with Cu to form Cu-Al alloys from solutions of Cu(I) in the Lewis acidic AlCl3-MeEtimCl melt. Alloy deposition potentials independently derived from the free energy of alloy formation are compared to those observed experimentally for several aluminum alloy systems. In addition we examine the
UPD of Al onto Cu(111) by means of linear sweep voltammetry and in-situ scanning tunneling microscopy.

EXPERIMENTAL

Methyl-ethylimidazolium chloride (MeEtimCl) was synthesized from ethyl chloride and 1-methylimidazole (Aldrich, 99%)* and recrystallized from acetonitrile-ethyl acetate mixtures as described in the literature (9). Protonic impurities were removed from the melt by pre-electrolyzing the melt between Al electrodes (Alfa/ESAR, puratronic, 99.999%) for several days while the melt was stirred. The melt was filtered through a medium porosity glass frit to remove any Al debris that may have detached from the cathode during the electrolysis step, and it was then evacuated to 1.3 x 10⁻³ Pa for 24 h.

Chronoamperometric and electrodeposition experiments were conducted in the 60:40 mole ratio AlCl₃:MeEtimCl melt at 40 ± 1 °C. The working electrode was a stationary platinum disk having a geometric area of 0.196 cm². Aluminum was used as the counter and reference electrodes. All potentials are referenced to the Al(III)/Al couple in this melt. The electrochemical instrumentation and cell were identical to those employed during a previous investigation (6). Cu(I) was introduced into the melt by the electrodissolution of a Cu wire anode at a potential of 0.85 V. The weight loss of the Cu anode was determined after the passage of a given charge, and calculations based on these measurements confirmed that Cu(I) was the anodization product.

The underpotential deposition of aluminum was examined on a Cu(111) single crystal electrode (Monocrystals Company) in 55:45 mole ratio AlCl₃:MeEtimCl. The Cu(111) electrode was mechanically polished on fine grade emery papers (1200, 2400 and 4000) with subsequent polishing on polishing cloths impregnated with suspensions of alumina with particle dimensions of 1 μm, 0.3 μm and 0.05 μm. After mechanical polishing, the Cu single crystal was electrochemically polished in a solution of 85 % phosphoric acid at a constant voltage of 1.7 V (vs. Pt counter electrode) until the current density dropped to a value of about 18 mA cm⁻². The copper electrode was then thoroughly washed with distilled water, dried in a nitrogen stream and then transferred into the glove box. The surface area of the Cu(111) single crystal exposed to the electrolyte was 2.84 cm².

The Cu(111) surface was examined by in-situ scanning tunneling microscopy (STM) in 55:45 mole ratio AlCl₃:MeEtimCl using a Molecular Imaging STM. Tungsten tunneling probes were fabricated by etching in 1.0 mol L⁻¹ KOH followed by coating with polyethylene in order to minimize Faradaic background currents. The sample chamber and electrolytes were purged with argon before each experiment. An aluminum wire was used as a reference electrode in the STM experiments.

* Certain commercial materials and instruments are identified in this report to adequately specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material identified is necessarily the best available for this purpose.
RESULTS AND DISCUSSION

Electrodeposition of Cu-Al alloys

Figure 1(a) shows a series of sampled-current or pulse voltammograms constructed from chronoamperometric current-time transients that were recorded at a platinum disk electrode in unstirred 0.010 mol L\(^{-1}\), 0.025 mol L\(^{-1}\), and 0.050 mol L\(^{-1}\) solutions of Cu(I) in the 60.0:40.0 mole ratio AlCl\(_3\)-MeEtimCl melt. The data used to construct these voltammograms were obtained by stepping the electrode potential from an initial value of 1.50 V, where no Faradaic reaction takes place, to the potential of interest. The current was sampled at 10 s following the application of the potential pulse. The resulting electrodeposition was then stripped from the electrode by holding the potential at 1.50 V for 30 s while the solution was stirred, and then the entire process was repeated at another potential. All three voltammograms exhibit well-defined limiting currents due to the mass-transport-controlled deposition of Cu. In addition, these voltammograms show a rise in current beginning at about 0.25 V, which is due to the co-deposition of Al with Cu to produce a Cu-Al alloy, Cu\(_x\)Al\(_{1-x}\), where 1 > x > 0. The overall deposition reaction is shown in Equation [1].

\[\text{xCu}^+\text{(solv)} + 4(1-x)\text{Al}_2\text{Cl}_7^- + (3-2x)e^- \leftrightarrow \text{Cu}_x\text{Al}_{1-x} + 7(1-x)\text{AlCl}_4^-\]  \[\text{[1]}\]

The limiting currents of the voltammograms in Figure 1(a) were found to vary linearly with the Cu(I) concentration. The diffusion coefficient of Cu(I), \(D_{\text{Cu(I)}}\), was calculated from these limiting currents by using the Cottrell equation. The average value of \(D_{\text{Cu(I)}}\) is \((3.6 \pm 0.5) \times 10^{-7} \text{ cm}^2 \text{s}^{-1}\), and the Stokes-Einstein product, \(D_{\text{Cu(I)}}\eta/T\), where \(\eta\) and \(T\) are the absolute viscosity and temperature, respectively, is \(1.9 \times 10^{-9} \text{ g cm} \text{s}^{-2} \text{K}^{-1}\).

The Cu-Al alloy composition, represented for convenience as the fraction of Al in the alloy, \(1 - x\), was estimated from the voltammograms in Figure 1(a) by using the following expression

\[1 - x = 1/\left[1 + 3\left(\frac{i_j}{i} - 1\right)\right]\]  \[\text{[2]}\]

where \(i\) is the limiting current for the copper deposition reaction depicted in Figure 1(a), and \(i_j\) is the total current observed at potentials where the co-deposition of Al is observed. Plots of \(1 - x\) versus \(E\) based on these calculations are given in Figure 1(b) for three different Cu(I) concentrations. Examination of the data in this plot reveals that the Cu-Al alloy composition is independent of the Cu(I) concentration over the range of concentrations that were examined in this study.

Taken together, the results presented above suggest that at a fixed potential the rate of alloy formation is determined by the mass-transport-limited reduction of Cu(I) and, as a result, the rate of alloy formation increases in direct proportion to an increase in the Cu(I) concentration. Thus, under the conditions of the present study, the concentration of Al\(_2\)Cl\(_7^-\) does not play a role in determining the rate of alloy formation because the concentration of this ion is in large excess (1.95 mol L\(^{-1}\)) over the Cu(I) concentration, i.e., the reaction depicted in Equation [1] can be considered to be pseudo-first order in Cu(I). Somewhat different results were found during previous investigations involving the UPD of Co-Al (6) and Ni-Al (4) in acidic AlCl\(_3\)-MeEtimCl. At a fixed potential, the compositions of these alloys varied with the concentrations of the respective transition
Figure 1: (a) Sampled-current voltammograms recorded at a stationary Pt electrode in solutions of Cu(I) in the 60.0:40.0 mole ratio AlCl₃:MeEtimCl at 40±1 °C. The Cu(I) concentrations were: (●) 0.010 mol L⁻¹; (■) 0.025 mol L⁻¹; and (♦) 0.050 mol L⁻¹. The current was sampled at 10 s following the application of each potential pulse; (b) Fraction of Al in Cu-Al alloy, 1 - x, as a function of potential from Figure 1(a): (○) 0.010 mol L⁻¹ Cu(I); (□) 0.025 mol L⁻¹ Cu(I); and (△) 0.050 mol L⁻¹ Cu(I); (●) AAS analysis of bulk electrodeposits.
metal ions in the deposition solution, even though the transition metal ions were undergoing reduction at the mass transport limited rate during alloy formation. This suggests that in the case of both Co-Al and Ni-Al, the Al co-deposition process is kinetically hindered.

Several bulk electrodeposits were prepared on 0.10 cm nickel wire at potentials ranging from 0.40 V to 0 V at 25 °C from 60.0:40.0 mole ratio AlCl₃:MeEtimCl melt containing 0.10 mol L⁻¹ Cu(I) at 25 °C. Based on the charge passed, the nominal thickness of these deposits ranged from 10 to 15 μm. The compositions of some of these deposits were determined by atomic absorption spectrophotometry (AAS) after the deposits were dissolved from the substrates with 1:1 HNO₃:HCl. Prior to dissolution, the deposits were examined by EDS to ensure that no chloride was present. Within the detection limits of EDS, all of the deposits were found to be either pure Cu or Cu-Al alloy. The AAS results, which are shown in Figure 1(b), are in excellent agreement with the alloy compositions determined by sampled current voltammetry.

Free Energy Analysis

The electrodeposition of Cu-Al, Ni-Al and Co-Al alloys at potentials considerably positive of that for the bulk deposition of aluminum is consistent with the observations of Nicol and Philip (10) who postulated that the steady-state underpotential deposition of a bulk alloy on a foreign substrate is possible when the work function of the less noble alloy component is smaller than that of the more noble component. Although UPD studies have shown that the potential difference between monolayer and bulk deposition of metal atoms onto foreign metal substrates is closely related to the difference in the work functions of substrate and deposit (11), the general application of this relationship to the deposition of bulk alloys may not be justified. For example, based on the difference in work functions (12), one would expect Zn-Al and Sb-Al alloys to deposit at potentials positive of the aluminum deposition potential. This has not been observed (13,14) and in fact the microstructure of Sb-Al alloys formed at potentials negative of aluminum show the face-centered cubic (fcc) Al and hexagonal close-packed (hcp) Sb to be completely segregated (14). Although aluminum and antimony have a 0.37 eV difference in work function, the energetics for bulk alloy formation are presumably unfavorable.

In order to examine a possible relationship between the bulk thermodynamics of a binary aluminum alloy and its tendency to form at underpotentials, the room-temperature free energy of several binary aluminum alloys was calculated as a function of composition using the CALPHAD method (15). The Gibbs energy of a particular phase, $G^*$, was calculated using Equation [3],

$$G^* = G^0 + G^{id} + G^{ss} \quad [3]$$

The first term, $G^0$, corresponds to the Gibbs energy of a mechanical mixture of the constituents of the phase,

$$G^0 = x_A G_A^0 + x_B G_B^0 \quad [4]$$

where $x_A$ and $x_B$ are the mole fractions and $G_A^0$ and $G_B^0$ are the reference states of elements A and B, respectively. For these calculations, the fcc structure was taken as the

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reference state. The second term of Equation [3], $G^{id}$, corresponds to the entropy of mixing for an ideal solution and is expressed as,

$$G^{id} = RT[x_A \ln x_A + x_B \ln x_B]$$

[5]

The third term of Equation [3], $G^{xs}$, is the excess term of the free energy. Although several of the aluminum alloys considered here form ordered intermetallic compounds, a regular-solution type model was used to describe the excess free energy. $G^{xs}$ is described by the following Redlich-Kister polynomial,

$$G^{xs} = x_A x_B \sum_{i=0}^{n} G_i (x_A-x_B)^i$$

[6]

where literature values of the coefficients, $G_i$, were used (16).

The free energy calculations for the Zn-Al and Cu-Al systems, as a function of composition, are shown in Figure 2(a). Because the fcc structure was used as the reference state, the free energy for hcp zinc (equilibrium structure) has a negative value while that for hcp aluminum has a positive value. It is clear that the incorporation of aluminum into fcc copper lowers the free energy of the system up to a concentration of about 35% atomic fraction aluminum. For this reason, an fcc copper solid solution is the equilibrium crystal structure for alloy compositions ranging from 0% to 15% atomic fraction aluminum (17). In this composition range, the aluminum atoms alloy substitutionally into the copper fcc lattice. The linear increase in the lattice parameter of fcc copper with increasing aluminum composition is well documented (18). In contrast, the addition of aluminum to the hcp Zn lattice results in an increase in free energy, Figure 2(a). An examination of the Zn-Al phase diagram indicates that the room-temperature solubility of aluminum in zinc is 0.07% (17). The sign and magnitude of the free energy change with aluminum addition is likely the driver for alloy deposition at aluminum underpotentials.

The activity of aluminum, $a_{Al}$, in a given phase can be calculated as a function of alloy composition by first evaluating the partial molar free energy, $\mu_{Al}$, using the following expressions,

$$a_{Al} = \exp \left( \frac{\mu_{Al}}{RT} \right)$$

[7]

where

$$\mu_{Al} = G^\Phi + (1-x_{Al}) \frac{\partial G^\Phi}{\partial x_{Al}}$$

[8]

The potential for alloy formation can be calculated by substituting the aluminum activity
Figure 2: (a) Free energy as a function of alloy composition for the hcp Zn-Al and fcc Cu-Al systems calculated using Equation [3]; (b) Alloy composition versus $\Delta E$ calculated using Equations [8] and [12] and the free energy curves from Figure 2(a).
into the Nernst equation for the aluminum deposition reaction (Equation [1] where x = 0),

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{Al}_2\text{Cl}_7]^4}{a_{\text{Al}}[\text{AlCl}_4]^7}$$ \[9\]

The Nernst potential for the aluminum reference electrode is

$$E_{\text{ref}} = E^0 + \frac{RT}{nF} \ln \frac{[\text{Al}_2\text{Cl}_7]^4}{[\text{AlCl}_4]^7}$$ \[10\]

Because the aluminum reference is placed in an electrolyte of identical composition to that in the working compartment, the difference in potential between the alloy electrode and the aluminum reference is simply,

$$\Delta E = E - E_{\text{ref}} = -\frac{RT}{nF} \ln a_{\text{Al}}$$ \[11\]

If one substitutes Equation [7] for $a_{\text{Al}}$ into Equation [11], one obtains the familiar expression

$$\Delta E = -\frac{\mu_{\text{Al}}}{nF}$$ \[12\]

where the potential at which a particular alloy deposits is directly proportional to the partial molar free energy of aluminum in the alloy.

Figure 2(b) is a plot of alloy composition versus $\Delta E$ for the deposition of fcc Cu-Al and hcp Zn-Al alloys. The $\Delta E$ values were calculated from Equations [8] and [12] using the free energy curves from Figure 2(a). In the case of Cu-Al, aluminum incorporation should commence at a potential of about 0.35 V. It is further predicted that an alloy containing 50% atomic fraction aluminum can be deposited at a potential of 0.02 V. The composition-potential curve in Figure 2(b) is quite similar to that seen experimentally for Cu-Al in the 60:40 mole ratio AlCl₃:MeEtimCl melt, Figure 1(b). In contrast, the Zn-Al system shows completely different behavior. The potential for depositing a hcp Zn-Al alloy is negative of that for depositing pure aluminum. This suggests that deposits formed at negative potentials will consist of segregated hcp zinc and fcc aluminum rather than a hcp Zn-Al alloy. This has yet to be verified experimentally; however, zinc films electrodeposited from a 60:40 mole ratio AlCl₃:MeEtimCl melt containing 0.025 mol L⁻¹ Zn(II) in the potential range of 0 V to 0.2 V contain no aluminum (13). The fact that Zn-Al alloy deposition has not been observed is consistent with the free energy results in Figure 2.

Calculations similar to those presented for fcc Cu-Al and hcp Zn-Al were performed for fcc Ni-Al, fcc Ag-Al, body-centered cubic (bcc) Fe-Al, hcp Co-Al and body-centered tetragonal (bct) Sn-Al. Figure 3 shows a plot of experimentally observed co-deposition potentials versus the calculated $\Delta E$ values for alloys having a composition of 10⁻⁴ atomic
fraction aluminum; i.e., an alloy composition arbitrarily chosen to represent the beginning of alloy formation (the difference in $\Delta E$ between an aluminum atomic fraction of 10⁻² and 10⁻¹ is approximately 0.1 mV). The experimentally observed co-deposition potentials in Figure 3 were obtained from composition-potential curves derived from sampled-current voltammograms appearing in the literature (1,4,6,13,19,20), similar to that shown in Figure 1(b). The curve extrapolated to 1-$x = 0$ was taken as the potential at which alloy formation begins. The calculated alloy deposition potentials are quite similar to that observed experimentally for the Cu-Al, Co-Al and Fe-Al. The experimentally observed co-deposition potential for Ni-Al alloys deposited at room temperature was about 0.14 V less than the calculated value while the potential reported from AlCl₃:NaCl at 150 °C (1) is consistent with the calculated value. This is likely due to a kinetic limitation in the Al co-deposition reaction which has been reported for Ni-Al in the room-temperature melt (4).

As shown in Figure 2, the calculated deposition potential for the hcp Zn-Al alloy is negative of the aluminum deposition potential, which is consistent with the experimental data. The free energy-derived alloy deposition potentials predict that no alloy formation would be expected for bct Sn-Al whereas some degree of alloying has been observed (19). The co-deposition potential observed for fcc Ag-Al is also significantly more positive than that predicted by free energy (20). These discrepancies may be due to surface energy contributions which have not been included in this treatment.

**UPD of Al onto Cu(111)**

**Cyclic Voltammetry.** Cyclic voltammograms recorded on Cu(111) in the 55:45 mole ratio AlCl₃:MeEtimCl melt at a sweep rate of 20 mV s⁻¹ are shown in Figure 4. The underpotential deposition of Al onto Cu(111) is characterized by two pairs of voltammetric peaks, Figure 4(a), indicating that two distinct surface processes occur in the UPD region. If the negative potential limit is restricted to 0.18 V (dashed line), a single reversible redox couple (Ic, Ia) is observed. The charge associated with this surface process is approximately 0.22 mC cm⁻². A weak set of voltammetric waves (Ic', Ia') is
Figure 4: Cyclic voltammograms recorded on Cu(111) in 55:45 mole ratio AlCl₃:MeEtimCl at a sweep rate of 20 mV/s; (a) cathodic limits of 0.180 V (dashed line) and -0.015 V (solid line); (b) cathodic limits of -0.020 V (solid line); and -0.080 V (dashed line).
also apparent just positive of the reversible (Ic, Ia) wave. If the cathodic limit is lowered to -0.015 V (solid line), then the second set of voltammetric waves (IIc, IIa) is observed. The total charge associated with Ic and IIc combined is approximately 0.70 mC cm\(^2\) which is consistent with a fully discharged monolayer of aluminum on the surface. It is interesting to note that after cycling the Cu(111) electrode in the potential region of peaks IIc and IIa, the anodic peak Ia becomes less sharp, while peak Ia' becomes more pronounced.

Bulk deposition of aluminum starts at about -0.05 V vs. Al, Figure 4(b) (dashed line). This process requires an appreciable nucleation overpotential, which is responsible for the hysteresis in the deposition current observed when the potential sweep is reversed. The shape of the anodic portion of the voltammogram changes significantly after the overpotential deposition of aluminum. The transient is dominated by the dissolution of bulk aluminum, peak IIIa. Peaks IIa and Ia, which are associated with the UPD layer of aluminum, are poorly defined while peak Ia' becomes much more prominent. A common feature in all voltammograms is a poorly defined redox couple which appears at 0.5 V, somewhat more negative than the potential for copper dissolution.

**Scanning Tunneling Microscopy.** STM has been used to examine the UPD of aluminum on Cu(111) in 55:45 mole ratio AlCl\(_3\) : MeEtimCl. In these experiments, attention was focused on the surface processes accompanying the near reversible wave (Ic, Ia). High resolution imaging at 0.455 V revealed an ordered adlayer as shown in Figure 5. A possible model representing this structure corresponds to a layer of tetrachloroaluminate ions which have been oxidatively adsorbed on the Cu(111) surface with the face of the tetrahedra adjacent to the copper surface. In this instance the STM image reveals the protruding chloride ion of the adsorbed tetrahedral ionic complex. The outlying chloride exhibit a nearest neighbor spacing ranging from 0.62 to 0.711 to 0.81 nm depending on the particular direction. Interestingly, the chloride species on the face of the tetrahedral chloroaluminate ion (21) have a spacing comparable to that observed for the nearest neighbor spacing of a compressed c(p x √3)R30° chloride monolayer on Cu(111) (22). In the latter case, the close packed direction of the halide layer tends to align with the <211> direction (23). Importantly, the adlayer of tetrachloroaluminate ions adsorbed in this geometry yields the nearest neighbor distance of the protruding chloride ion aligned in the <110> direction as shown in the Figure 5 schematic.

Sweeping the potential in the negative direction to 0.20 V results in the disruption and desorption of the adlayer. The charge involved in the process is approximately 0.22 mC cm\(^2\). A brief assessment suggests that this quantity may be ascribed to the reductive decomposition of the adsorbed tetrachloroaluminate species, releasing free chloride from the surface which is quickly consumed by AlCl\(_3\) to form 2 AlCl\(_4^-\). Pursuing the analogy between an ordered chloride adlayer and the chloride species on the face of the tetrahedral chloroaluminate species, the desorption of a chloride monolayer corresponds to ~0.094 to 0.128 mC cm\(^2\) (depending on the degree of compression) while the charge associated with reduction of the complexed aluminum ion would yield ~1/3 (0.094 to 0.128) x 3e\(^-\) or about 0.094 to 0.128 mC cm\(^2\). This crude description of the overall process, yields a total charge of 0.188 to 0.256 mC cm\(^2\), in reasonable agreement with the voltammetric data.

The reverse process of aluminum desorption and tetrachloroaluminate adsorption was also examined. A sequence of images is shown in Figure 6 as the potential was stepped from 0.204 to 0.354 V. At 0.204 V, Figure 6(a), limited evidence of step faceting along the <110> direction is observed. However as the potential is increased in the positive direction to 0.324 V (not shown) the step orientation becomes more disordered and imaging of the terraces is noticeably streaky indicating significant interaction between the tip and the dilute aluminum atoms on the terrace. The fluctuations within the terrace adlayer exert little influence on the step dynamics. As the potential is increased further to
**Figure 5**: A 30 x 30 nm image of an ordered adlayer on Cu(111) at 0.455 V vs. Al/Al$^{3+}$ in 55:45 mole ratio AlCl$_3$:MeEtimCl. A schematic of the proposed tetrachloroaluminate adlayer structure is shown.
Figure 6: A sequence of 100 x 100 nm images of the Cu(111) surface in 55:45 mole ratio AlCl₃:MeEtimCl as the potential was stepped from (a) 0.204 V to (b) - (d) 0.354 V revealing the moving interface/step demarking the boundary between aluminum desorption and tetrachloroaluminate adsorption.

0.354 V, Figure 6(b,c,d), dissolution of the aluminum adlayer is apparent as the step edge recedes. Surprisingly, the step orientation of the receding adlayer is well defined despite the significant fluctuation in the remaining aluminum adlayer terrace. This suggests that transformation proceeds with a well defined interface orientation between the growing ordered anion adlayer and the dissolving aluminum UPD layer. Thus, the receding step edge may be more accurately viewed as the moving interface between the two adlayer phases. Another feature of interest is the decoration of the substrate step edges following dissolution of the aluminum UPD layer, Figure 6(d). This is thought to be associated with Cu-Al alloy formation which occurs preferentially at step sites. Presumably the alloyed clusters would be removed at a more positive potential. These alloy clusters may also account for some of the aging effects seen in the voltammetric analysis. An alternative explanation for the step decoration follows from analogous observations of intralayer mass transport that reportedly accompany the anion-induced reconstruction of Cu(111) in acid sulfate solution (24). Further work is underway to address these questions.
ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of Ursula Kattner to the thermochemical treatment used in this paper. Research carried out at the University of Mississippi is supported by AFOSR Grant No. F49620-00-1-0123.

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