NUCLEATION AND MORPHOLOGY STUDIES OF ALUMINUM DEPOSITED FROM AN AMBIENT-TEMPERATURE CHLOROALUMINATE MOLTEN SALT

Richard T. Carlin, Wayne Crawford, and Tea-Lane Liu
Department of Chemistry
University of Alabama
Tuscaloosa, AL 35487

Michael Bersch
School of Mines and Energy Development
University of Alabama
Tuscaloosa, AL 35487

ABSTRACT

Thin, continuous aluminum coatings can be electrodeposited onto a tungsten substrate from a 1.1:1.0 AlCl_3:MEIC (1-methyl-3-ethylimidazolium chloride) ambient-temperature molten salt using controlled potential deposition. At deposition potentials negative of -0.2 V versus an Al(III)/Al reference electrode, the resulting coating consists of nuclei (or cluster) sizes below optical microscopic resolution (< 0.5 μm). At less negative potentials, the microscopic structure consists of larger (> 0.5 μm), optically observable nuclei. Chronoamperometric analyses performed at 250-μm tungsten electrodes indicate that the deposition process involves progressive nucleation with diffusion-controlled growth of the three-dimensional nuclei. Calculated nuclear site densities and average nuclei sizes are in agreement with images obtained with optical microscopy, scanning electron microscopy (SEM), and scanning tunneling microscopy (STM).

INTRODUCTION

The ambient-temperature chloroaluminate molten salts derived from the combination of AlCl_3 with the organic salts N-butylpyridinium chloride (BuPyCl) or 1-methyl-3-ethylimidazolium chloride (MEIC) are promising electrolyte baths for industrial aluminum electroplating (1,2), and in fact, a continuous plating process has been recently reported (3,4). Aluminum deposition proceeds by reduction of the Al_2Cl_7^- ion which is present at high concentrations in melts with AlCl_3:MCl (MCl = organic chloride) molar ratios greater than one, termed acidic melts.

\[ 3 \text{e}^- + 4 \text{Al}_2\text{Cl}_7^- \rightleftharpoons \text{Al} + 7 \text{AlCl}_4^- \] [1]
In melts with AlCl$_3$·MCl molar ratios less than one, termed basic melts, the Al$_2$Cl$_7^-$ concentration is extremely small, and the dominant chloroaluminate anion, AlCl$_4^-$, is not reducible within the electrochemical window of the melt (5).

The salient feature of the aluminum deposition process is a nucleation phenomenon with diffusion-controlled growth of the three-dimensional centers (6-9). At tungsten and platinum electrodes an underpotential deposition (UPD) of aluminum is also observed (6,7). The deposition/stripping efficiencies approach 100% indicating the production of stable, adherent aluminum deposits (6,10); however, in AlCl$_3$·BuPyCl melts, the N-butylpyridinium cation slowly reacts with the freshly deposited aluminum metal (6,7). The morphology of aluminum deposits produced using a 2:1 AlCl$_3$·MEIC molten salt is reported to be dense, smooth, and corrosion resistant (3,4). From published SEM images, the aluminum deposits appear to consist of crystallites or platelets ranging in size from 1 to 10 μm (4,10).

To better understand the parameters influencing the aluminum deposition process, we have undertaken studies employing an inverted optical microscope to perform in situ observations of the coating morphology. A small (250-μm diameter) tungsten disk electrode was chosen as the working electrode because tungsten is an excellent substrate for aluminum deposition (6-9). Also, the small size of the electrode has several benefits including 1) minimal errors resulting from IR-drop, 2) a uniform potential distribution over the electrode surface due to the negligible IR-drop, 3) reproducible current density distributions with somewhat higher current densities being observed at the electrode edge, and 4) easy observation of the entire electrode area at high magnification during the deposition process.

**EXPERIMENTAL**

The preparation of MEIC was performed as previously described (11). Melts were prepared by the addition of sublimed AlCl$_3$ to MEIC with stirring. All melt preparations and manipulations were performed under a purified N$_2$ atmosphere in a Vacuum Atmosphere glove box. All experiments were performed at ambient temperature, ca. 25 °C.

Electrochemical experiments not requiring in situ optical observations were performed in the glove box using an electrochemical cell consisting of a glass vessel fitted with a Teflon cap in which holes were drilled for the electrodes. For the in situ optical observation of the deposition process, a sealed cell with an optically transparent bottom was employed. This cell was assembled in the glove box and transferred to the optical microscope stage where it was supported by a small Flexframe assembly. For all electrochemical experiments, the tungsten working electrodes were constructed by first sealing a length of 250-μm diameter W wire (Alfa) in Pyrex capillary glass (25 mm O.D., 1 mm I.D.) under vacuum. The glass was cut at the seal to expose a circular W disk which was then polished consecutively with 1, 0.3, and 0.05 μm alumina polishing compounds (Buehler). The reference and counter electrodes consisted of aluminum wires dipped directly into the analyte melt; therefore, measured potentials are true overpotentials.
A Nikon Epiphot metallurgical inverted microscope equipped with brightfield/darkfield optics and with a 35mm Nikon N6006 camera was used for optical observations and photographs. Extra-long-working-distance objectives provided magnifications up to 400x. Using darkfield illumination, we estimate that this optical system allows us to discern structural features down to approximately 0.5 μm in size, although resolution at these dimensions is poor. All electrochemical experiments were performed using an EG&G PARC Model 273 Potentiostat/Galvanostat controlled with a Dell System 310 computer using the EG&G PARC Model 270 software package.

The scanning tunneling microscopy was a Digital Instruments Nanoscope II STM fitted with the electrochemical option and so is termed an electrochemical scanning tunneling microscope (ECSTM). The electrochemical cell used in this investigation was supplied by Digital Instruments. The tungsten substrate was a tungsten foil (0.127 mm thick, Aldrich) which constituted the bottom of the electrochemical cell. The reference and counter electrodes were aluminum wire (0.25 mm diameter, Aldrich). The counter electrode was bent into a loop to provide more uniform current densities, while the reference electrode was a short length of wire. The imaging tip was 0.010" tungsten wire coated with glass to minimize background faradaic currents and was purchased from FHC, Brunswick, ME. An Eppendorf pipette was employed to introduce approximately 50 μl of the melt into the ECSTM electrochemical cell. Because the chloroaluminate molten salts are moisture sensitive, it was necessary to place the entire ECSTM microscope inside a glove bag filled with nitrogen. The glove bag provided only a marginally moisture-free environment, so some reaction with moisture was observed at the surface of the melt. Because relatively large imaging scans (not atomic level) were collected, it was not necessary to take extreme measures for vibration isolation; instead, the microscope assemble was positioned on a ca. 1' x 1' concrete slab placed in the glove bag which was in turn situated on a standard lab bench.

RESULTS AND DISCUSSION

Voltammetric studies and optical observations.

Staircase cyclic voltammetric studies indicated an overpotential for aluminum deposition which was dependent upon the electrochemical treatment of the tungsten electrode. By scanning to +3.0 V, the AlCl₄⁻ ion is oxidized to elemental chlorine, and an electrochemical cleaning occurs which lowers the overpotential for aluminum reduction. Therefore, prior to all chronopotentiometry and chronamperometry experiments, the tungsten electrodes were electrochemically cleaned by scanning to +3.0 V (500 mV/s) until consistent staircase cyclic voltammograms were obtained (see Figure 1). The electrochemical cleaning process also clearly revealed the Al underpotential deposition (UPD) at +0.22 V reported by other workers (see Figure 2). Integration of the current under the UPD wave gave a quantity of charge passed corresponding to 84% of a complete monolayer - higher than the values of 1/3 and 1/2 reported previously on tungsten (6,7).

Using the 1.1:1.0 AlCl₃:MEIC melt, efforts to produce smooth, continuous aluminum coatings using chronopotentiometry melt were unsuccessful as judged by in situ
optical observations. The deposits were not dendritic, but they consisted of nuclei with dimensions > 1 μm. Application of an initial pulse to -1.0 V to initiate the nucleation process prior to constant current deposition failed to improve the morphology of the Al deposits. During all chronopotentiometric experiments, the deposition potential remained below -0.1 V. The non-dendritic, larger-nuclei (> 1 μm) morphology is in agreement with previous studies (3,4,10).

Chronoamperometry and in situ optical observations were then employed to study the deposition of Al from 1.1:1.0 AlCl3:MEIC. Under potentiostatic conditions, the resulting coatings consisted of smaller nuclei than seen for coatings obtained under galvanostatic conditions. Therefore, the potential of deposition is a critical parameter for determining the final coating morphology. At a deposition potential of -0.1 V, the coatings had optically resolved nuclei (> 0.5 μm), while at potentials ≤ -0.2 V, the nuclei could not be discerned when the electrode was viewed through the bottom of the electrochemical cell.

To view the deposits with improved resolution, the electrodes were plated with aluminum at a constant potential in the glove box, removed, and immediately washed with methanol. The chronoamperograms were recorded to permit determination of the thickness of the resulting aluminum coating. Deposition times were chosen so that a coating of ca. 0.1 μm was achieved at all potentials; longer deposition times were required for lower overpotentials. Electrodes prepared in this manner were then examined on the inverted microscope employing darkfield illumination. As in the in situ studies, deposits made at -0.1 V exhibited optically resolved nuclei; however, with the higher resolution, nuclei were seen for the -0.2 V deposits as well, albeit the nuclei were smaller than for -0.1 V deposits. A deposition potential of -0.3 V was required to produce an aluminum coating for which no nuclei could be discerned at a magnification of 400x.

Figures 3 and 4 show photographs (darkfield illumination, 400x) of 250-μm tungsten disks having calculated aluminum coating thicknesses of 0.093 and 0.094 μm produced at overpotentials of -0.1 and -0.4 V, respectively. It should be noted that darkfield photographs of an uncoated tungsten electrodes are almost completely black with only scratches in the tungsten surface showing as bright lines. The presence of discernable nuclei are indicated by the bright features seen in Figure 3 while few such features are observed in Figure 4. Therefore, based on our microscope resolution, the nuclei sizes for the -0.4 V coating are estimated to be < 0.5 μm, while they are > 0.5 μm for the -0.1 V coating. It is noteworthy that the scratches in the tungsten substrate are still visible in Figure 4 indicating that these coatings are able to conform to small structures on the substrate surface. The scratches are obscured by the coating in Figure 3.

To examine in more detail the electrocrystallization process, chronoamperograms were collected over a range of overpotentials, and the curves were analyzed following the method of Scharifker and Hills (12). In this analysis, the nucleation process may be instantaneous or progressive while the growth of the individual nuclei is limited by diffusion of the electroactive species to the growing nuclei. The diffusion layer profile at each nucleus is initially hemispherical; however, after sufficient time, the individual diffusion zones overlap forming a diffusion layer characteristic of semi-infinite linear diffusion.

In the method of Scharifker and Hills, an initial analysis of the chronoamperograms can be performed by plotting log(i) vs. log(t) for the rising portion of the curves; the slope
of this log-log plot will be 1/2 for instantaneous nucleation and 3/2 for progressive nucleation (12). A more stringent analysis of the nucleation process is obtained by comparing the chronoamperometric curves to the theoretical curves for instantaneous, Eq. [2], and progressive, Eq. [3], nucleation processes

\[
\left(\frac{i}{i_m}\right)^2 = 1.9542\left(\frac{t}{t_m}\right)^{-1}\left(1 - \exp[-1.2564(\frac{t}{t_m})]\right)^2 \tag{2}
\]

\[
\left(\frac{i}{i_m}\right)^2 = 1.2254\left(\frac{t}{t_m}\right)^{-1}\left(1 - \exp[-2.3367(\frac{t}{t_m})^2]\right)^2 \tag{3}
\]

where \(i_m\) and \(t_m\) are the current density and time, respectively, at the peak in the chronoamperograms (12). The comparison of experimental curves to theoretical curves is done by plotting \((i/i_m)^2\) versus \(t/t_m\), the dimensionless current and time parameters.

Chronoamperometric data collected for deposition potentials from -0.075 to -0.20 V are shown in Figure 5, and the comparisons of the -0.075 and -0.175 V experimental curves to theoretical curves are shown in Figure 6. Plots of \(\log(i)\) vs. \(\log(t)\) have slopes ranging from 1.5 to 2.0 reflecting a progressive nucleation process. Confirmation of this progressive nucleation process is provided by the similarity of the experimental curves to the theoretical progressive nucleation curve in Figure 6.

After determining that the nucleation process is progressive, Eq. [4] and [5] are employed to calculate the product \(AN^\infty\), where \(A\) is the steady state nucleation rate constant per site, \(N^\infty\) is the number density of active sites on the electrode, and \(M\) and \(\rho\) are the atomic weight and density of aluminum (12).

\[
i_m = 0.4615nFD^{3/4}C(kAN^\infty) \tag{4}
\]

\[
k = \frac{4}{3}(8\pi CM/\rho)^{1/2} \tag{5}
\]

Finally, the saturation number density sites, \(N_s\) (i.e., the nuclear site densities observed at long time) is calculated with Eq. [6]. The important parameters are summarized in Table I.

\[
N_s = (AN^\infty/2kD)^{1/2} \tag{6}
\]

From the analysis of the nucleation process, some predictions can be made regarding the final morphology of the aluminum coating. If the completed coating is assumed to result from the eventual overlap of individual nucleation sites, then the average
nucleus size will be inversely proportional to the number of nucleation sites. Also, for hemispherical growth, the individual nuclei of the completed surface can be approximated as have a two-dimensional circular geometry on the electrode surface with a radius given by Eq. [7].

$$r = \left(\frac{1}{\pi N_s}\right)^{1/2}$$

[7]

The average nucleus radius will decrease with increasing overpotential because the higher overpotential increases the number of nucleation sites per unit area. As seen in Table I, the calculated radius varies from 0.2 to 2.0 μm for the deposition potentials studied. These calculated radii are consistent with the optical observations discussed above. At deposition overpotentials negative of -0.2 V, no nuclei were observed implying the average nucleus size is < 0.5 μm, while in Table I, the radius is calculated to be < 0.5 μm for depositions performed negative of -0.150 V. Clearly, this method of calculating the average nucleus size is only an approximation; however, it provides a qualitative picture of how the nucleation process can influence the morphology of the final deposit.

The density of bright features in Figure 3 were measured by projecting a slide of the figure onto a white screen and counting the number of features in a given area of the projected image; a value of 50 x 10^6 features cm^-2 was obtained. These bright features should represent the presence of individual nuclei in the coating and can be taken as representative of the number of individual nucleation sites produced at -0.1 V. Therefore, this number corresponds to the nuclear site density and is close to the theoretical values of 18.4 x 10^6 sites cm^-2 and 42.1 x 10^6 sites cm^-2 predicted from the chronoamperograms obtained at overpotentials of -0.1 V and -0.125 V, respectively.

Electrochemical scanning tunneling microscope investigations.

For aluminum depositions performed at potentials negative of -0.2 V, the in situ optical images did not have sufficient resolution to estimate the size of the Al nuclei. To overcome this problem, we have recently begun investigating the aluminum deposition process using electrochemical scanning tunneling microscopy (ECSTM).

The application of standard scanning tunneling microscopy (STM) and ECSTM to the study of surfaces in a variety of environments is an exploding field (13,14). Of particular interest to us is the ability to image surfaces under solutions during surface corrosion (15), electrochemical deposition (16), and anodic dissolution (17).

Cyclic voltammetry at the tungsten foil substrate in the ECSTM cell showed an onset of aluminum deposition at -0.6 V; the Al/Al(III) equilibrium potential, $E_{eq}$, was estimated to be -0.52 V from the zero-current crossover following scan reversal. Initially, the uncoated tungsten substrate was imaged under the melt, then the tungsten potential was stepped to -1.1 V (overpotential = $E - E_{eq} = -0.6$ V) for increasing times to deposit increasing quantities of aluminum on the tungsten substrate. During Al deposition, the imaging tip was withdrawn several microns from the surface to prevent interference with
diffusion of $\text{Al}_2\text{Cl}_7^{-}$ to the substrate. Images of aluminum coatings formed following total deposition times of 30 and 90 s are shown in Figures 7 and 8 (constant-current mode, bias voltage = +1.713 V, setpoint current = 0.5 nA). The two photographs have the same x, y, and z scalings to clearly show the changes in the morphology of the surface with longer aluminum deposition times. The aluminum coatings display features resembling ridges which may correspond to Al plates. These appear as parallel ridges in Figure 7. Importantly, the structural features in the two figures have dimensions in the 20-100 nm range (0.02-0.1 μm). These sizes are below the optical resolution discussed above and are in reasonable agreement with the average nucleus size predicted in Table I for aluminum deposited at more negative potentials.

The surface roughness was quantitated with an option in the Digital Instrument software which provides a mean roughness ($R_a$), a ten-point mean roughness ($R_z$, calculated from the five highest and five lost points), and a maximum roughness ($R_{\max}$). Theses values are presented in Table II for the uncoated tungsten, for Figures 7 and 8, and for a 390 s deposition. For short deposition times, the aluminum deposit remains smooth and regular indicating formation of a continuous, small-nuclei deposit. At longer deposition times, the thicker Al deposits exhibit an increasing roughness. Such increases in roughness may be due to the development of larger aluminum clusters on top of the smoother aluminum undercoating.

CONCLUSIONS

Thin, continuous aluminum coatings can be produced on a tungsten substrate from the 1.1:1.0 $\text{AlCl}_3$:MEIC molten salt at room-temperature using constant-potential deposition. The average nucleus size of the deposit is estimated to be < 0.5 μm when the deposition potential is negative of -0.2 V versus Al(III)/Al. Analysis of the nucleation process gives calculated nuclear site densities and estimated nuclei sizes in agreement with optical microscopy and STM images. The growth process for thick Al coatings (> 0.1 μm) may involve the formation of larger aluminum clusters on top of a smooth Al undercoating.

ACKNOWLEDGEMENTS

This work was supported by the Air Force Office of Scientific Research under the Research Initiation Program and by the National Science Foundation through the Research Experience for Undergraduates Program. We would like to thank 3M Corporation for the funds used to purchase the ECSTM.

REFERENCES

1. C. L. Hussey, in “Advances in Molten Salt Chemistry,” Vol 5, p. 185, G. Mamantov, Editor, Elsevier Science Publishers, Amsterdam (1983).
2. R. A. Osteryoung, in “Molten Salt Chemistry,” p. 329, G. Mamantov and R. Marassi, Editors, D. Reidel Publishing, Holland (1987).

3. S. Takahashi, I. Kazuhiko, and M. Shoichiro, in “Molten Salts,” PV 90-17, C. L. Hussey, S. N. Flengas, J. S. Wilkes, and Y. Ito, Editors, p. 661, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1990).

4. S. Takahashi, I. Saeki, I. Kazuhiko, and M. Shoichiro, Extended Abstracts, Abstract No. 889, 177th Meeting of the Electrochemical Society, Montreal, Quebec, Canada, May 6-11, 1990.

5. R. T. Carlin and R. A. Osteryoung, J. Electrochem. Soc., 136, 1409 (1989).

6. J. Robinson and R. A. Osteryoung, J. Electrochem. Soc., 127, 122 (1980).

7. P. K. Lai and M. Skyllas-Kazacos, Electrochim. Acta, 32, 1443 (1987).

8. Y. Chryssoulakis, J.-C. Poignet, and G. Manoli, J. Appl. Electrochem., 17, 857 (1987).

9. P. K. Lai and M. Skyllas-Kazacos, J. Electroanal. Chem, 248, 431 (1988).

10. J. J. Auborn and Y. L. Barberio, J. Electrochem. Soc., 132, 598 (1985).

11. J.S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., 21, 1263 (1982).

12. B. Scharifker and G. Hills, Electrochim. Acta, 28, 879 (1983).

13. P. K. Hansma and J. Tersoff, J. Appl. Phys., 61, R1 (1986).

14. L. L. Soethout, H. van Kempen, and G. F. A. van de Walle, in “Advances in Electronic and Electron Physics,” Vol. 79, 155 (1990).

15. Representative Articles: (a) F.-R. F. Fan and A. J. Bard, J. Electrochem. Soc., 136, 3216 (1989); (b) O. Lev, F.-R. F. Fan, and A. J. Bard, J. Electrochem. Soc., 135, 783 (1988); (c) F.-R. F. Fan and A. J. Bard, J. Electrochem. Soc., 136, 166 (1989).

16. Representative Articles: (a) M. P. Green, K. J. Hanson, R. Carr, and I. Lindau, J. Electrochem. Soc., 137, 3493 (1990); (b) M. Szklarzczk and J. O’M. Bockris, J. Electrochem. Soc., 137, 452 (1990).

17. Representative Articles: (a) A. A. Gewirth and A. J. Bard, J. Phys. Chem., 92, 5563 (1988); (b) T. P. Moffat, F.-R. F. Fan, and A. J. Bard, J. Electrochem. Soc., 138, 3224 (1991); (c) I. C. Oppenheim, D. J. Trevor, C. E. D. Chidsey, P. L. Trevor, and K. Sieradzki, Science, 254, 687 (1991).
Table I. Analysis of chronoamperometric data for aluminum deposition from 1.1:1.0 AlCl₃:MEIC at a 250-μm diameter tungsten electrode.

| E (V) | tₘ (ms) | iₘ x 10^2 (A cm⁻²) | AN∞ x 10⁻⁶ (sites cm⁻² s⁻¹) | Nₛ x 10⁻⁶ (sites cm⁻²) | r (μm) |
|-------|---------|---------------------|-----------------------------|------------------------|--------|
| -0.075 | 378     | 2.27                | 32                          | 8.94                   | 1.89   |
| -0.100 | 200     | 3.26                | 137                         | 18.4                   | 1.31   |
| -0.125 | 83      | 4.93                | 719                         | 42.1                   | 0.87   |
| -0.150 | 35      | 7.64                | 4149                        | 101                    | 0.56   |
| -0.175 | 30      | 9.44                | 9640                        | 154                    | 0.45   |
| -0.200 | 18      | 12.1                | 25768                       | 252                    | 0.36   |
| -0.250 | 11      | 17.4                | 111068                      | 523                    | 0.25   |
| -0.300 | 6       | 23.2                | 350620                      | 929                    | 0.19   |

Table II. Surface roughness for Al deposited on tungsten substrate at -0.6 V

| Deposition Time (s) | Rₐ (nm) | R₂ (nm) | Rₘₐₓ (nm) |
|---------------------|---------|---------|-----------|
| 0                   | 0.53    | 2.5     | 4.2       |
| 30                  | 1.0     | 4.2     | 8.6       |
| 90                  | 1.3     | 6.0     | 12        |
| 390                 | 3.0     | 15      | 38        |
Figure 1. Staircase cyclic voltammograms for aluminum deposition and stripping at a 250-\(\mu\)m tungsten disk electrode in a 1.1:1.0 AlCl\(_3\):MEIC molten salt following successive scans to +3.0 V.

Figure 2. Staircase cyclic voltammetry showing aluminum underpotential deposition at a 250-\(\mu\)m tungsten disk electrode in a 1.1:1.0 AlCl\(_3\):MEIC molten salt: (a) following electrode pretreatment; (b) prior to electrode pretreatment. Integration of the charge under the peak at ca. 0.2 V indicates formation of a monolayer.
Figure 3. Darkfield illumination of 0.093-μm thick aluminum coating on a 250-μm diameter tungsten disk electrode. Deposition potential: -0.1 V. Magnification: 400x.
Figure 4. Darkfield illumination of 0.094-μm thick aluminum coating on a 250-μm diameter tungsten disk electrode. Deposition potential: -0.4 V. Magnification: 400x.
Figure 5. Chronoamperograms for aluminum deposition at a 250-μm tungsten disk electrode in a 1.1:1.0 AlCl₃:MEIC molten salt. Deposition potentials (V): (a) -0.075, (b) -0.1, (c) -0.125, (d) -0.150, (e) -0.175, (f) -0.20.

Figure 6. Comparison of (a) experimental aluminum nucleation processes at overpotentials of -0.075 V and -0.175 V to theoretical (b) progressive and (c) instantaneous nucleation processes.
Figure 7. STM image of an aluminum deposit produced after 30 s at $E - E_{eq} = -0.6$ V.

Figure 8. STM image of an aluminum deposit produced after 90 s at $E - E_{eq} = -0.6$ V.