



Ultrathin Copper Films Grown at the Interface Between Two Immiscible Liquids

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Here we report the discovery of ultrathin copper films electrodeposited at a heptane/CuSO₄ aqueous solution interface. The films consist of two layers; one is a very thin layer growing along the organic side of the interface, and the other is an aggregate of dendrites growing from the organic-side layer into the solution bulk. The thinnest film obtained in this study is composed of only the organic layer less than 1 μm in thickness, and it is transparent. Here we discuss how the interface is associated with the growth of the deposit.

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Here, we report the growth dynamics of an ultrathin copper film, electrodeposited at the interface between two immiscible liquids. Kaneko and coworkers used an interface to prepare electrochemical metallic films,¹⁻⁶ electro-conductive oxides,⁷ and polymers.^{8,9} The advantages of this method are that no solid substrate for electrodeposition is required to make a thin film, and that by controlling experimental conditions, a variety of morphologies can be obtained if deposits can be obtained from the electrolyte solution electrochemically. Studies about a century ago by Mylius and Fromm¹⁰ and Freundlich and Novikow¹¹ hinted at this method. They observed the growth of a leaf-like deposit, a so-called Metallblätter (metal leaf), at the interface between natural oil and an electrolyte solution during electrolysis. In 1980, Tamamushi and Kaneko¹ investigated these studies and made two types of deposits depending on experimental conditions: metal leaf and filmy deposits. In addition, many researchers have investigated the formation of a metal leaf as a typical fractal phenomenon. Matsushita *et al.*¹² and Sawada *et al.*¹³ analyzed the fractal dimension of a metal leaf in relation to the diffusion-limited aggregates model (DLA) of Witten and Sander.¹⁴ At present, however, the mechanism of filmy growth remains unclear.

The morphologies of electrochemical deposits grown in two-dimensions have been observed in a Hele Shaw cell, which consists of two glass plates separated by a few hundred μm using a spacer, with a circular anode, and a rod cathode.¹⁵⁻²³ In a Hele Shaw cell, growth in the cross-sectional direction is limited to the space between the two glass plates. Unlike a Hele Shaw cell, using the electrodeposition method shown here, a deposit can grow semi-two-dimensionally. Although the growth of a deposit is not limited in the direction below the interface of two liquids, and the deposit grows in two dimensions along the interface; the interface behaves just like a substrate. Therefore, the surface between the two immiscible liquids has an important role in the two-dimensional growth. It is intriguing to identify the unusual characteristics of the liquid interface. Furthermore, we can obtain a very thin filmy deposit by using the characteristics of the interface. In this paper, we examine the electrodeposition of an ultrathin copper film at the interface between two immiscible liquids. We focus on the process of film growth, how the structure of the film is constructed, and why the film grows at the interface. Finally, we discuss the growth mechanism of a very thin copper film.

Experimental

To produce thin two-dimensional copper films, an interface was prepared between two immiscible liquids as a virtual reaction field; the interface was built with *n*-heptane and an aqueous CuSO₄ electrolyte as shown in Fig. 1. The *n*-heptane was used without further

distillation. The concentration of the CuSO₄ electrolyte was varied from 0.001 to 1 M. The electrolytic cell used in this study was a glass beaker (6.2 cm in i.d. and 5.5 cm in depth) with a water-jacket to circulate thermostated water (25°C). The cell was put on a silicon rubber sheet (5 mm thick) to prevent from vibration. The cell was filled with an electrolyte (100 mL) and then *n*-heptane (10 mL) was poured onto the electrolyte. Electrodeposition was performed using the conventional three-electrode method to keep the ohmic resistance as low as possible. The counter electrode used as an anode was a copper ring (38 mm i.d., 50 mm o.d., and 0.2 mm thick). The copper ring was held 5 mm lower from the interface with a hook attached to a stand. The reference electrode was Ag/AgCl in saturated KCl (silver-silver chloride electrode in saturated KCl: SSE). All the electrode potentials are referred to SSE ($E_{SSE} = +0.197$ V vs. SHE at 25°C). The working electrode used as the cathode was a Pt wire (0.5 mm diam). The tip of the working electrode was set at the center of the interface. The spacing between the tip of the Luggin capillary and the tip of the working electrode was ~2 mm. After setting the electrode potential, which was less than that required for the cathodic reduction of Cu²⁺, a copper film started to grow in two-dimensions in the radial direction along the interface from the cathode. Applied voltages were input from a potentiostat. The data of potential and current were recorded in a personal computer through a digital multimeter. The personal computer and the digital multimeter were controlled with a program written in Basic. For scanning electron microscopy (SEM) observations of copper films deposited at the interface, the film was scooped from the interface with a copper plate (*ca.* 1 cm²). Then the film was immersed for 30 s in 0.25 M benzotriazole solution to be prevented from corrosion and washed gently with distilled water. After dried in a desiccator, the film on the plate was applied to SEM observation. To investigate the mechanism of interfacial growth of copper films, the growth was chased in a cell of a Petri dish (8.6 cm diam and 2 cm deep) with a transmitted microscope. A growing film was illuminated from the bottom of the cell and observed by the transmitted light.

Results and Discussion

To determine the potential needed for the cathodic reduction of Cu²⁺ at the interface, the current-potential curves were measured in the CuSO₄ electrolyte by locating the tip of the working electrode at the interface. The current-potential curves increased at *ca.* 0.1 V, depending on the Cu²⁺ concentration. This increase indicates the onset of the cathodic reduction of Cu²⁺. In these curves, a diffusion-limited region was observed at cathodic potentials exceeding -0.5 V. We visually confirmed that the interfacial growth of copper occurred at a potential within this region. This suggests that the diffusion of Cu²⁺ is associated with the growth mechanism at the interface.

In general, branching morphologies are observed when the diffusion field affects the growth of deposits, as shown previously.¹²

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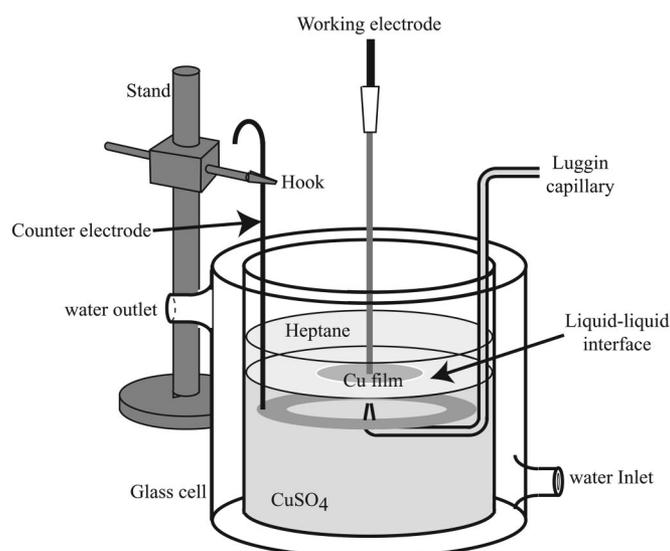


Figure 1. Experimental setup for electrodeposition of copper films at the interface between two immiscible liquids.

Figure 2 shows copper deposits obtained at various CuSO_4 concentrations. In this experiment, the copper deposits clearly show a compact, radial morphology with no branching. A glass capillary, located *ca.* 2 mm below the interface, can be seen through the deposits in (c) and (d); the thickness of the deposits decreases with decreasing electrolyte concentration. The deposit in (d) is very thin and transparent.

The changes in the radius of the deposit as a function of electrolyte concentration during electrodeposition are shown in Fig. 3. Above 150 s, the radius of the deposits tended to decrease with decreasing electrolyte concentration. For example, after growing for 180 s, the radius was *ca.* 17.5, 16.1, and 13.9 mm in 1, 0.1, and 0.01 M CuSO_4 , respectively. Furthermore, if the growth velocity of the deposits is approximated to be constant during electrodeposition, the average velocity of interfacial growth was 97.2, 89.4, and 77.2 $\mu\text{m/s}$ in 1, 0.1, and 0.01 M CuSO_4 , respectively. Therefore, the interfacial growth velocity decreases with the electrolyte concentration, although the differences are slight. Moreover, we can estimate the apparent thickness of the deposits using Faraday's law, assuming

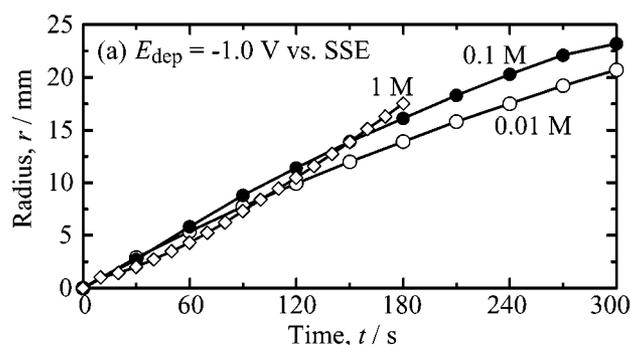


Figure 3. Changes in the radius of copper films growing at -1 V in several CuSO_4 solutions.

that the overall density of the deposits equals that of bulk copper (8.93 g/cm^3).²⁴ The apparent thickness of the deposit was *ca.* 1.8, 0.3, and 0.04 μm , respectively, and the apparent thickness decreased with the CuSO_4 concentration. This trend matches the visual observations in Fig. 2. Thus, interfacial growth is favored over growth in the cross-sectional direction of the deposits with decreasing CuSO_4 concentration.

The structure of the film was investigated using SEM. Figure 4 shows a cross-section of deposits grown in 0.1 M CuSO_4 . The deposit consisted of two layers: a very thin film and many fiberlike branches perpendicular to the thin film. The thin film had a compact structure less than 1 μm thick. By contrast, the branches grew quite densely into the electrolyte and they were not entangled; this may be due to a screening effect during branch growth.¹² Furthermore, the branches were roughly the same length, *ca.* 30 μm . As shown in Fig. 4, the length of the branches determined the overall thickness of the deposit, because the thickness of the very thin film is negligibly small. However, the overall thickness obtained from Fig. 4 is much larger than the apparent thickness estimated above (in this case 0.3 μm). The difference between the observed and estimated thickness is due to the difference in the density of the deposits, because the deposit is not compact and its density is much lower than the bulk value of copper.

A growing deposit was observed using a transmitted light microscope (Fig. 5). In Fig. 5a, dark spots are distributed on the filmy deposit; the number of spots decreases gradually towards the growth front of the deposit. Note that no spots are observed around the

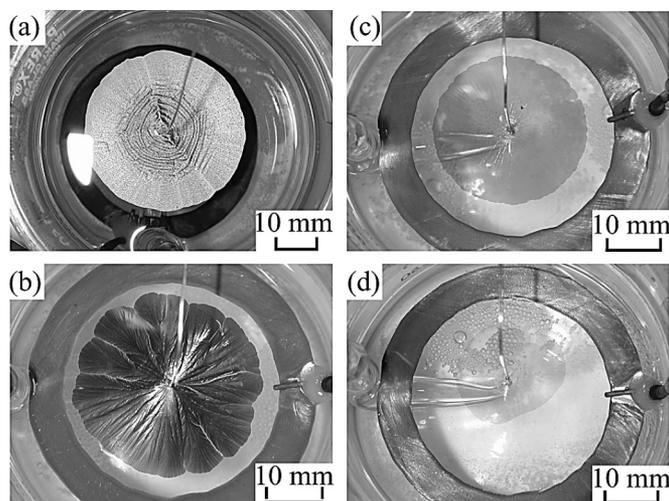


Figure 2. Copper films grown at the two liquid interface for 180 s after applying potential of -1 V: (a) 1, (b) 0.1, and (c) 0.01 M CuSO_4 . (d) Taken for 600 s after applying potential of -1 V in 0.01 M CuSO_4 .

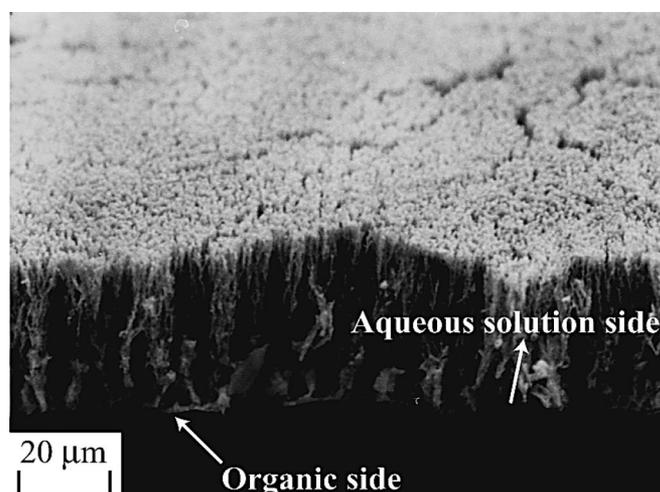


Figure 4. SEM image of cross-section of a film electrodeposited at -1 V in 0.1 M CuSO_4 . This figure was taken with turning the film upside down. Many branches grow from the organic side of the film.

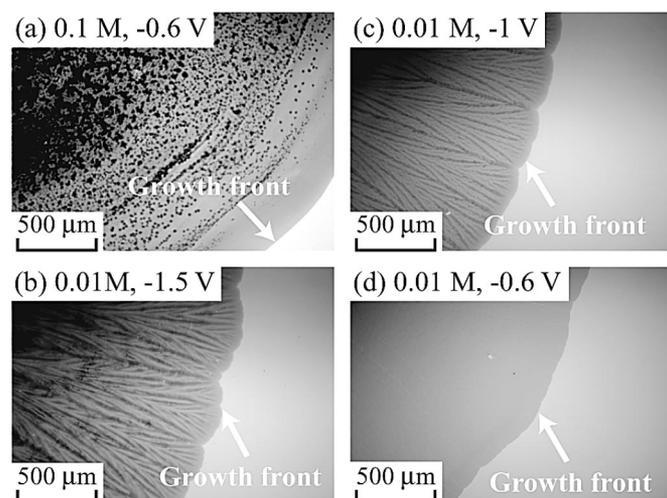


Figure 5. Transmitted light microscope images of copper films grown at the interface under several conditions. The elapsed times of the images were (a) 105, (b) 15, (c) 24, and (d) 73 s.

growth front of the deposit, only a bright filmy deposit is observed. The dark spots increased with electrolysis time. The spots and filmy deposit correspond to the branches and the very thin film, respectively, as shown in Fig. 4. These results strongly suggest that the very thin film always grows along the interface before branch formation and the branches grow from the very thin film. The films became thinner with decreasing the CuSO_4 concentration (compare Fig. 5a and d) and the applied potential (compare Fig. 5b and c with Fig. 5d). In Fig. 5d, no dark spots are seen in the deposit, indicating that the growth of branches is inhibited and only a very thin film grows along the interface. The very thin film electrodeposited in 0.01 M CuSO_4 at -1 V was observed using transmission electron microscopy (TEM), which revealed that the thin film was polycrystalline, with crystals tens of nm in size.

What is the mechanism that explains these experimental results? With the electrodeposition method shown here, the very thin film always advances primarily along the interface between the two immiscible liquids, and then the branching deposits grow towards the bulk solution from the advancing thin film, which acts as a substrate for nucleation. This unique growth is thought to result from the difference between the reaction rates in the interfacial and vertical directions below the interface (downwards). Here, we roughly estimate the relative reaction rates in the two directions. If the growing deposit is modeled as a homogeneous disk, the electric current flowing through the deposit can be divided into two components: one in the interfacial direction and the other in the vertical direction below the interface. In this case, the electric current, I , is approximated as a function of the radius and is expressed as follows

$$I = \pi r^2 J_V + 2\pi r h J_H \quad [1]$$

where r and h are the radius and thickness of the disk, respectively, and J_V and J_H are the respective current densities in the vertical and interfacial directions. In this estimate, h can be regarded as a constant because the change in h during the growth of the deposit is very low at electrolytic concentrations less than 0.1 M. By fitting the current-radius relation, the fraction J_H/J_V is estimated as 1.6×10^7 and 4.7×10^5 for 0.01 and 0.1 M CuSO_4 , respectively. Therefore, the reaction rate in the interfacial direction is much higher than that in the vertical direction and this trend is enhanced with decreasing electrolyte concentration. In general, because the nucleation rate is accelerated as the concentration of reductive ions and overvoltage increase, the branches growing below the very thin

film are suppressed by decreasing the electrolytic concentration and overvoltage. In other words, nucleation for branches is less likely to occur below the film than at the interface.

Why does interfacial growth between the two immiscible liquids occur before growth below the film? As mentioned above, the growth of the deposits occurs under diffusion-limited conditions for the reduction of copper ions: $\text{Cu}^{2+} + 2e^- = \text{Cu}$. Under this condition, the current density at the surface of the deposit depends not on the applied voltage, but on the concentration gradient next to the deposit. Therefore, the reaction rate should be constant as long as the diffusion field around the deposit is maintained at a steady state. As estimated above, however, the reaction rate in the interfacial direction is much higher than in the direction normal to the interface. This suggests that different growth dynamics affect morphological selection in the interfacial and vertical directions. This is emphasized by the fact that the deposit grown along the interface has two different structures: a thin-film structure and a branching structure. This suggests that at least two different mechanisms involving these two structures are associated with the growth of the deposit.

If the diffusion field affects interfacial growth, the deposit assumes a dense branching morphology (DBM) or a fractal pattern related to DLA. In this experiment, unlike previous studies,¹² a compact, radial filmy deposit grew along the interface and moss-like branches grew vertical to the film. Therefore, we think that the dominant effect causing the growth of the filmy deposit is not the diffusion field, whereas the dominant effect causing branch growth is the diffusion field.

If the diffusion field affects branch growth, the branch length should be related to the diffusion length.¹⁵⁻¹⁸ We estimated the diffusion length using $l = D/v$, where D is the diffusion coefficient and v is the growth velocity. Substituting $D = 9.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in Ref. 15 and $v = 89 \mu\text{m s}^{-1}$ obtained for 0.1 M CuSO_4 , then $l \approx 10 \mu\text{m}$. This estimated length is the same order of magnitude as the length (*ca.* 30 μm) of the branches growing below the thin film. Therefore, the diffusion field affects growth below the interface and gives rise to the branching morphology.

What is the dominant process producing interfacial growth? Matsushita *et al.*¹² attributed the deposit with a dense branching morphology growing at the interface between two immiscible liquids to the diffusion field. As shown above, however, we found that the growth of a compact deposit differs from that of a diffusion-limited aggregate. We think that the interfacial growth observed in this study is associated with the physico-chemical characteristics of the interface.

When a deposit grows rapidly in the interfacial direction, it is necessary to supply Cu^{2+} rapidly to the growth front at the interface. However, it is most unlikely that the diffusion rate of Cu^{2+} at the interface is 10^5 to 10^7 times greater than that in the bulk electrolyte, based on the fraction J_H/J_V . We attribute the rapid supply of Cu^{2+} to the Marangoni effect²⁵ at the interface, as follows. At the growth front at the interface, the Cu^{2+} concentration must be zero, because electrodeposition occurs here under perfectly diffusion-limited conditions. By contrast, at the interface distant from the growth front, the Cu^{2+} concentration at the interface reaches an equilibrium value. Therefore, a concentration gradient builds at the interface, which corresponds to the gradient in interfacial tension and produces a convective motion. Recently, we confirmed that the interfacial tension changed with the growth of a Zn film at the interface between *n*-butyl acetate and ZnSO_4 solution. Simultaneously, we observed Marangoni convection occurring in the ZnSO_4 solution just below the growing front of the Zn film. Hence, we believe that this convection motion supplies Cu^{2+} to the growth front on the surface because this convection can enhance mass transfer as compared to normal diffusion and surface diffusion.²⁶

Conclusion

In summary, we explored the growth dynamics of copper electrodeposited at the interface between two immiscible liquids. The film deposit consisted of two structures: a very thin film growing at the interface and many branches growing from the very thin film perpendicular to the interface. Furthermore, the interfacial growth is due to the Marangoni effect, while the branching growth is due to the diffusion field in the electrolyte below the very thin film. The unique character of a “liquid interface” as a reaction field should be investigated in more detail.

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