In Situ Transmission Electron Microscopy Study of Nucleation and Growth During Electrochemical Deposition of Copper on Gold

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The mechanism of nucleation and growth in electrochemical deposition of bulk films is usually determined from analysis of electrochemical experiments, such as current – time transients, in conjunction with *ex situ* imaging of the surface. Such techniques do not reveal the rates of growth of individual islands or the spatial correlations between islands. We have studied nucleation and growth processes during electrochemical deposition of copper using *in situ* transmission electron microscopy. This is a real-time, high resolution imaging technique that allows us to study the evolution of individual islands with time, as well as the spatial and temporal correlations between islands. Furthermore, this *in situ* technique allows us to compare electrochemical parameters commonly used to determine growth mechanisms, such as current – time transients, with real time images of island growth.

Figure 1 shows a series of TEM images recorded simultaneously with current-time transients during deposition of copper from 100 mM $CuSO_4$ solution (pH = 1) at -0.08 V (vs Cu wire). The images show that copper deposition under these conditions occurs through Volmer-Weber island growth. The island density increases with time (not shown) and reaches a maximum of 1×10^9 cm^{-2} after 0.75 s.

The current – time transient associated with the series of images shown in Figure 1 exhibits an initial increase in deposition current and reaches a maximum after about 0.75 s. At longer times the deposition current decreases with time according to the Cottrell equation. These features are characteristic of nucleation and diffusion limited growth of hemispherical islands.

The growth of individual islands can be analyzed by plotting the island radius versus time. Figure 2 shows an example of island growth at –0.08 V (Cu wire). Two linear regions can be seen on the log-log plot: an initial fast growth regime with a slope of about 0.56 and a later slower growth regime with a slope of about 0.13. These two regimes correspond to the current rise and current decay portion of the macroscopic current – time transient shown in Figure 1. Since $R(t) \propto Q^{1/3}$, it is easy to show that the initial regime is consistent with 3D diffusion limit growth of a hemispherical island and that the later regime corresponds to 1D diffusion limited growth.

Figure 3 shows the dependence of the average exponents for the two growth regimes plotted versus deposition potential. From this plot it is seen that the exponents asymptotically approach the limiting values with increasing overpotential. At more positive potentials deposition is under mixed control and hence the exponents are slightly higher than the diffusion limited values.

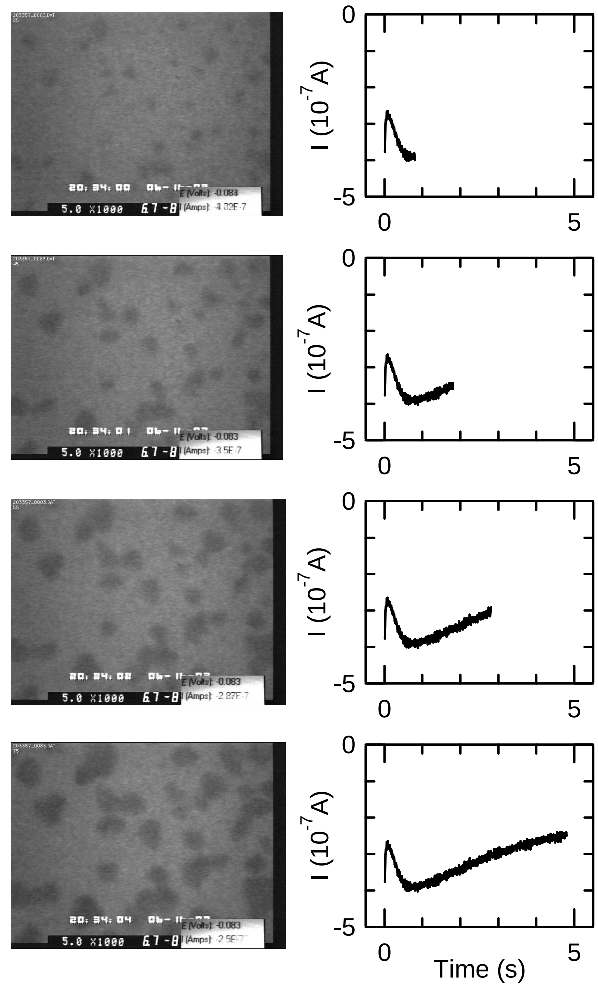

Figure 1. A series of TEM images and the corresponding current-time transient for deposition at –0.08 V.

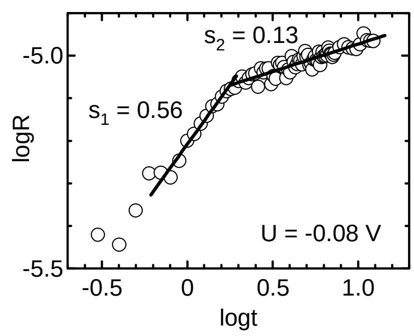

Figure 2. A typical log(radius) versus log(time) plot for an island at -0.08 V.

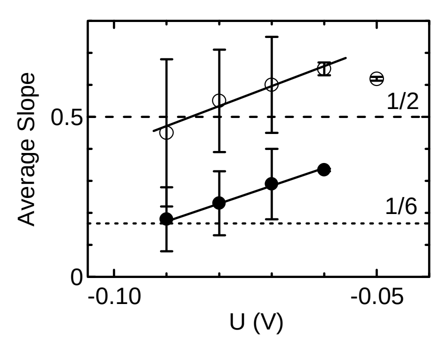

Figure 3. Potential dependence of the average time exponent for the two growth regimes: (o) fast growth regime and (•) slow growth regime.