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Formation of a Core/Shell Microstructure in Cu–Ni Thin Films

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Electrodeposition of Cu–Ni thin films can result in phase separation characterized by the formation of nodular features that exhibit a uniform columnar core/shell structure with a copper-rich core and nickel-rich shell. Here, we show that the core/shell micro-structure is the result of differences in the nucleation and growth rates of the two components. In the potential range where the core/shell structure is observed, copper deposition is fast, resulting in the formation of a relatively low density of large hemi-spherical islands. Nickel deposition is characterized by slower kinetics, resulting in the formation of a high density of small islands surrounding the copper islands. These results provide a basis for understanding the formation of this core/shell microstructure in binary alloy systems.

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The microstructure of thin films can be influenced by both thermodynamic and kinetic parameters associated with the deposition process. For binary alloy systems this can lead to a rich array of microstructures. Due to the similarity in lattice parameters ($a_{\rm Ni}$ =0.3524 nm, $a_{\rm Cu}$ =0.3615 nm) Cu–Ni is predicted to exhibit a broad range of solid solubility.¹⁻⁵ However, calculations show a miscibility gap below about 600 K.^{6,7}

Electrodeposition in the Cu–Ni system has focused primarily on the deposition of multilayer thin films or nanowires from solution containing both Cu(II) and Ni(II). In this case pure copper is deposited at more positive potentials and a Cu–Ni alloy at more negative potentials. To minimize the amount of copper in the nickel layer, the Ni(II)/Cu(II) ratio is usually ≥ 100 .⁸⁻¹² Under these conditions, the nickel layer is a single-phase Ni–Cu solid solution with the mole fraction of copper usually less than about 5%. Intermediate Cu–Ni alloy compositions can be accessed by deposition from solution with lower Ni(II)/Cu(II) ratios.¹³ While solid solutions have been reported at intermediate compositions using pulse plating,⁵ phase separation has been reported for deposition at constant potential,¹³ indicating that the equilibrium state can be achieved in electrodeposition.

In previous work, we have shown evidence for the miscibility gap in electrodeposited Cu–Ni thin films that exhibit a remarkable core/shell columnar microstructure characterized by nodular features with a copper-rich core and a nickel-rich shell.¹⁴ By confining deposition in a patterned structure with dimensions corresponding to the size of the nodular features, the core/shell microstructure can be exploited for the formation of individual ferromagnetic rings and tubes.¹⁴ The core/shell structure is of particular interest for the synthesis of ferromagnetic rings^{15,16} and tubes,¹⁷⁻²⁰ and for applications in bioseparations²¹ and magnetoresistance random access memory devices.²²

While thermodynamics provides a driving force for phase separation, it does not explain the columnar core/shell structure. Here, we report on the kinetics of copper and nickel deposition and show that differences in the nucleation and growth rates are essential for the formation of the core/shell structure.

Experimental

Electrochemical deposition was performed on Au films sputter deposited onto Si(111) wafers in a three-electrode cell with a platinum mesh (99%, Sigma Aldrich) counter electrode and a Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems). All potentials are reported vs the Ag/AgCl reference ($U_{eq} = 0.200$ V vs standard hydrogen electrode). Thin films were deposited in the potential range from -0.7 to -1.1 V from solution containing 400 mM

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Ni(H₂NSO₃)₂·4H₂O (99.99% Aldrich), 50 mM CuSO₄·5H₂O (98%, Aldrich), and 0.65 M HBO₃ (Alfa Aesar) at pH 3.8. In all cases the deposition charge was 3 C cm⁻², corresponding to a film thickness of about 1 μ m with a deposition efficiency of \geq 0.95. The electrochemical etching of copper was performed at +0.5 V for 20 min in the same solution.

The kinetics of copper nucleation and growth was studied by depositing copper from solution containing 50 mM $CuSO_4$ ·5H₂O and 0.65 M HBO₃. The nickel deposition kinetics was studied by depositing nickel from solution containing 400 mM Ni(H₂NSO₃)₂·4H₂O and 0.65 M HBO₃. In both cases, current–time transients were recorded at different potentials and the island size and density were determined using scanning electron microscopy (SEM).

The morphology of Cu–Ni thin films before and after etching the copper was characterized by SEM (JEOL 6700F). After etching, the back side of the thin films was imaged by using conductive tape to peel the films from the substrate. The near-neighbor pore and island distributions were obtained from analysis of SEM images using NIH Image. The microstructure of the films was characterized by X-ray diffraction (Phillip's X Pert 3040) with a Cu K α source.

Results and Discussion

Core/shell microstructure of Cu–Ni thin films.— In previous work, we have shown that phase separation in Cu–Ni thin films is dependent on the deposition potential and the Cu(II)/Ni(II) concentration ratio in solution.¹⁴ Figure 1 shows X-ray diffraction (XRD) patterns for Cu–Ni thin films deposited at potentials from -0.7 to -1.1 V. In this potential range the copper deposition rate is diffu-



Figure 1. XRD patterns for Cu–Ni thin films deposited from solution containing 0.4 M Ni(N_2 HSO₃)₂, 0.05 M CuSO₄, and 0.65 M HBO₃. The dotted lines show the positions of the Cu(111) and Ni(111) peaks.

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Figure 2. Cu–Ni phase diagram (adapted from Ref. 7). (\blacksquare): The mole fraction of Cu in Cu–Ni thin films where phase separation is observed.

sion limited and hence effectively independent of potential. However, nickel deposition is in the kinetic regime and the deposition rate increases exponentially as the deposition potential becomes more negative. At -0.7 V, where the nickel deposition rate is low, a single broad peak close to the Cu(111) peak $(2\theta = 43.41^{\circ})^{23}$ is seen, indicating a single-phase Cu_xNi_{1-x} alloy with $x \approx 0.97$.¹⁴ At -0.8 V, two peaks are observed, indicating phase separation into a Cu-rich phase and a Ni-rich phase. As the potential becomes more negative, the nickel deposition rate increases and the intensity of the Ni-rich peak increases. The mole fraction of copper in the films where phase separation is observed is in the range 0.3–0.8, consistent with the miscibility gap in the Cu–Ni phase diagram,^{7,24} as shown in Fig. 2.

Figure 3 shows plan-view SEM images of Cu–Ni thin films before and after etching the copper-rich phase. Thin films were deposited from 50 mM Cu(II) and 400 mM Ni(II) at -0.8, -0.9, and -1.0 V where phase separation is observed. Before etching, the as-deposited thin films exhibit nodular features with an average size that decreases slightly as the potential becomes more negative.

The distribution of the copper- and nickel-rich phases cannot be determined from the SEM images of the as-deposited films; however, this can be conveniently accomplished by selective etching of the copper-rich phase.^{8,13,14} In sulfamate solution, copper can be selectively etched at positive potentials where nickel is passivated



Figure 3. Plan-view SEM images of Cu–Ni thin films. Film deposited at -0.8 V (a) as deposited, (b) after etching, and (c) the back side of the film after etching. Film deposited at -0.9 V (d) as deposited, (e) after etching, and (f) the back side of the film after etching. Film deposited at -1.0 V (g) as deposited, (h) after etching, and (i) the back side of the film after etching.



Figure 4. (Color online) Distributions of near-neighbor distances for films deposited at -0.9 V: (a) nodular features in as-deposited films, (b) pores on the top of the film after etching, and (c) pores on the back side of the film after etching. (d) Summary of near-neighbor distances vs deposition potential: (\bigcirc) before etching, (\square) after etching (top), and (\triangle) after etching (back side).

by the formation of a thin oxide layer.⁸ As shown in Fig. 3, after etching, the thin films have uniform pores. Cross-section images show that the pores are cylindrical and uniform throughout the film. At the bottom of the film there is a thin, approximately 50 nm thick, transition region with a higher density of pores.

Comparison of the thin films before and after etching the copperrich phase reveals that each individual nodular feature is correlated with each individual pore. This can be demonstrated quantitatively from the near-neighbor distributions, as shown in Fig. 4 for the film deposited at -0.9 V. From the distribution of the nodular features we obtain an average near-neighbor distance of 230 ± 59 nm, which is very close to the near-neighbor distance (242 \pm 50 nm) of the cylindrical pores on the top side of etched thin films. On the back side of the films the near-neighbor distance is 133 ± 29 nm, somewhat smaller than the average spacing on the top of the films. This is consistent with the higher density of pores on the bottom side in the transition region (see Fig. 5). Because the pores are derived from the copper-rich phase, it is clear that each individual nodule is characterized by a columnar structure with a copper-rich core and a nickel-rich shell. The near-neighbor distances are only weakly dependent on the deposition potential, as shown in Fig. 4d.

The SEM images of the Cu–Ni thin films reveal a uniform core/ shell microstructure. The miscibility gap provides a thermodynamic driving force for phase separation, but does not explain the separation into nodular features with a copper-rich core and a nickel-rich shell. We show that the growth kinetics of the individual components is key to the evolution of this unique core/shell structure.

Kinetics of copper and nickel deposition.— The influence of nucleation and growth on the evolution of film microstructure in alloy deposition is poorly understood. To provide insight into the evolution of the core–shell microstructure observed here, we analyze the nucleation and growth of each component individually. As we show below, the nucleation and growth kinetics provides important clues into the formation of the core–shell microstructure in this system.



Figure 5. SEM images of the Cu–Ni thin film cross section deposited at -1.0 V after etching the Cu-rich phase.

Figure 6a shows a cyclic voltammogram for gold in 400 mM Ni(II) solution. The equilibrium potential for the Ni(II)/Ni couple in this solution is -0.48 V. The onset for nickel deposition is about -0.9 V, corresponding to a nucleation barrier of 0.22 V. In the potential range from -0.8 to -1.1 V where phase separation is observed in the Cu–Ni films, nickel deposition is kinetically limited, as evidenced by the exponential increase in current with potential. On the reverse scan, there is no stripping peak due to the formation of the nickel passivation layer.^{8,13}

For copper deposition, the onset potential is close to the equilibrium potential ($U_{eq} = 0.04$ V), as shown in Fig. 6b. In the potential range from -0.8 to -1.1 V where phase separation is observed, copper deposition is diffusion limited and hence independent of potential. In the positive scan, a large striping peak is observed.

Figure 6c shows cyclic voltammetry (CV) for gold in a solution containing 400 mM Ni(II) and 50 mM Cu(II). The onset potential around 0.04 V is followed by a constant current due to the diffusionlimited deposition of copper, as can be seen by comparison with Fig. 6b. At -0.7 V, the onset of nickel deposition results in an exponential increase in current, as seen by comparison with Fig. 6a. The CV of Cu–Ni solution reveals similar features of individual Cu(II) and Ni(II) solution, and hence the independent deposition of Cu and Ni can be used to understand the formation mechanism of Cu–Ni codeposition.

Figure 7a shows current-time transients for copper deposition from 50 mM Cu(II) solution. Up to about 50 ms, the current associated with copper nucleation and growth is very high whereas at longer times the current decreases. As shown in the inset of Fig. 7a, the initial current is approximately constant and independent of potential with an average value of 130 mA cm⁻². Due to the low bulk Cu(II) concentration (50 mM), the concentration at the surface is quickly depleted and copper growth becomes diffusion limited after about 50 ms. For a diffusion-limited process the current is given by the Cottrell equation

$$i = \frac{n \text{FD}^{1/2} c}{\pi^{1/2} t^{1/2}}$$
[1]

where *F* is Faraday's constant, *D* is the diffusion coefficient, *c* is the bulk ion concentration, and *n* is the number of electrons evolved. The current–time transients are replotted as i^{-2} vs *t* in Fig. 7b showing a linear region from about 50 ms to 1 s, consistent with Eq. 1. The diffusion coefficient, obtained from the slopes, is $7.7 \pm 0.3 \times 10^{-6}$ cm² s⁻¹, in excellent agreement with values of 6-8 $\times 10^{-6}$ cm² s⁻¹ reported.²⁵⁻²⁷

Figure 8a shows current–time transients for nickel deposition from 400 mM Ni(II) solution at -0.8, -0.9, and -1.0 V. The initial current for nickel deposition is much lower than the initial current



Figure 6. Current–voltage curve for gold in solution containing (a) 0.4 M $Ni(N_2HSO_3)_2$ and 0.65 M HBO₃, (b) 0.05M CuSO₄ and 0.65 M HBO₃, and (c) 0.4 M $Ni(N_2HSO_3)_2$, 0.05M CuSO₄, and 0.65 M HBO₃. The equilibrium potential for the Ni(II)/Ni couple is –0.48 V and for the Cu(II)/Cu couple is +0.04 V. The scan rate was 20 mV s⁻¹.

for copper deposition, even though the Ni(II) concentration is almost an order of magnitude larger [Ni(II)/Cu(II) = 8]. This indicates that the kinetics for copper deposition is initially much faster than for nickel deposition. After about 5 s, when the gold surface is almost completely covered with nickel, the current is exponentially dependent on the applied potential, as shown in Fig. 8b. The inverse slope gives a Tafel coefficient of 0.09 V per decade, close to published values.²⁸ The results presented in Fig. 7 and 8 confirm that, in the potential range of interest, copper deposition is diffusion limited while nickel deposition is kinetically limited. The current density for copper during the early stages of nucleation and growth is much higher than for nickel, even though the Ni(II) concentration is much larger [Ni(II)/Cu(II) = 8].

Figure 9 shows plan-view SEM images of copper and nickel islands deposited at different potentials. After 100 ms, copper forms relatively large hemispherical islands with a relative low island density. These results are typical for the deposition of copper from



Figure 7. (a) Current–time curves for deposition of copper from 50 mM Cu(II) at -0.8, -1.9, and -1.0 V. The inset shows the initial current vs potential. (b) Current–time transients replotted as i^{-2} vs t: (solid line) -0.8 V, (dotted line) -0.9 V, and (dashed line) -1.0 V. The inset shows the diffusion coefficient, calculated from the slopes of the linear regions vs deposition potential.

different solutions.^{25,26,29-33} As shown in Fig. 10, the island density is independent of deposition time. The first measurement at 50 ms corresponds to the shortest time where the copper islands can be easily imaged. Analysis of the distribution of copper islands results in a near-neighbor distance of 447 nm, within a factor of 2 of the near-neighbor distance of the nodular features in the Cu–Ni thin films, and is in good agreement with the near-neighbor distance value of nodular features.

The initial rate of deposition of nickel is much slower than for copper, as described above, and hence the nickel islands can only be imaged after longer deposition times. After 5 s, nickel forms very small islands with a high island density ($>5 \times 10^{11}$ cm⁻²) which is 3 orders of magnitude than the island density of copper.

The results from the analysis of copper and nickel deposition reveal two important features. First, the initial copper current is very high with a low island density, resulting in the fast formation of large copper islands. Second, the initial nickel current is relatively low and the island density is very high, resulting in the formation of small islands.

Figure 11 shows the difference in current from the independent experiments of copper and nickel deposition. At short times (50 ms), the copper growth rate is much larger than the nickel growth rate. The difference in growth rates then decreases as the copper ions at the surface are depleted. At longer times, after about 10 s, steady-state growth is achieved, which is consistent with the 50 nm transition region described above.

From these independent measurements of the nucleation and growth of pure copper and pure nickel, we can provide new insight into Cu–Ni codeposition, as shown schematically in Fig. 12. At short times, copper growth is very fast and the island density is relatively low, resulting in the formation of relatively large copper



Figure 8. (a) Current–time curves for deposition of nickel from 400 mM $Ni(N_2HSO_3)_2$ and 0.65 M HBO₃. (b) Current at -0.8, -0.9, and -1.0 V after 5 s vs potential.

islands. Nickel has a much higher island density that, coupled with the phase separation, results in relatively small nickel islands surrounding the large copper islands. As described above, during the first 50 ms (35 equivalent ML), the copper growth rate is much



Figure 9. (Left) Plan-view SEM images of Cu islands deposited from 50 mM Cu(II) solution after 100 ms at -0.8, -0.9, and -1.0 V. (Right) Plan-view SEM images of Ni islands deposited from 400 mM Ni(II) solution after 5 s at -0.8, -0.9, and -1.0 V.



Figure 10. Cu island density vs time at -0.8, -0.9, and -1.0 V.

faster than the nickel growth rate, even though the Ni(II) concentration in solution is almost an order of magnitude larger. At longer times, the Cu deposition rate decreases, and steady-state growth is achieved after about 10 s, corresponding to the transition region described above (see Fig. 5). The miscibility gap provides the driving force for phase separation and leads to the formation of a columnar microstructure.

On the basis of our results, we can summarize the conditions required to form a core/shell microstructure in a binary alloy system. First, the system must exhibit a miscibility gap in the composition range of interest, providing a thermodynamic driving force for phase separation. Second, to form the core requires a material with a high initial current and low island density. The fast initial kinetics results in the formation of a low density of relatively large islands at short times. Third, the shell requires a material with a relatively low initial current and high island density, resulting in the formation of relatively small islands. Based on these considerations, it should be possible to extend the core/shell structure to other systems such as Co-Cu.

Conclusion

Phase separation in electrodeposited Cu-Ni thin films results in nodular features with a copper-rich core and nickel-rich shell. We show that the evolution of this microstructure can be explained by differences in nucleation and growth between copper and nickel. At short times, copper deposition is initially fast and exhibits a relatively low island density, resulting in the formation of large hemispherical islands that become the cores in the nodular features. In contrast, the kinetics of nickel deposition is initially slow but the







Figure 12. (Color online) Schematic illustration of the evolution of the core/shell microstructure. Initially, the growth rate of copper is very fast compared to nickel and the relatively low island density results in the formation of large copper islands surrounded by smaller nickel islands. As the copper growth rate slows down, the core/shell microstructure evolves as steady state is reached.

island density is relatively large, resulting in the formation of a high density of nickel islands surrounding the larger copper islands. At longer times, the copper growth and nickel growth reaches steady state due to the decreased rate of copper deposition. The differences in nucleation and growth kinetics, coupled with the miscibility gap, result in this unique core/shell microstructure.

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