Abstract #2353, 224th ECS Meeting, © 2013 The Electrochemical Society

Comparison of Structural Properties of Copper Deposits from Sulfate and Pyrophosphate Electrolytes

[1]Burcu Arslan, [2]Nilüfer Ülgüdür, [1]Metehan Erdoğan,
[2]İpek İmamoğlu and [1]İshak Karakaya
[1]Department of Metallurgical and Materials Engineering,
[2]Department of Environmental Engineering,
METU Ankara 06531, Turkey

Aluminum has wide use in structural and electronic applications due to its light weight, high strength and relatively low price. However, it is easily corroded when it is not passivated. Aluminum is relatively soft and not easily welded or soldered. Therefore, it is quite often plated. Furthermore, electroplating of aluminum is commonly practiced in electroforming because it is relatively easy to remove aluminum to obtain the final electroformed structure.

In spite of above advantages, plating on aluminum substrates necessitates close controlled pretreatment steps because native oxide of aluminum hinders the adhesion of the subsequent deposition. Pretreatment steps consist of alkali cleaning, acid activation and zinc layer deposition (zincate) to avoid reoxidation of the surface until deposition. Copper is generally deposited on aluminum from copper cyanide and copper pyrophosphate strike electrolytes after zincate treatment. Since potentials of zincate layer and complex ions in the electrolytes are approximately equal, immersion deposition is prevented [1] and adhesive copper layer is produced. Further development of coating over adhesive thin layer of copper reduces the overall stress induced by the structural differences.

In this study, copper strike platings of 2 micron thickness were applied from cyanide and pyrophosphate baths to obtain good adhesion between copper and aluminum. Even though copper cyanide strikes are generally used in industry, environmentally safer practice, longer life and superior surface roughness provides advantages for copper pyrophosphate strike electrolyte. SEM images of aluminum surfaces coated by copper cyanide and copper pyrophosphate strike electrolytes are shown in Figure 1. About 50 micron thickness copper deposition on the strike plated aluminum surface, from acid copper sulfate and copper pyrophosphate electrolytes were prepared to compare structural properties of copper. Comparison and characterization of copper electrodeposits from two different electrolytes were performed by potentiometry, SEM, XRD, and roughness analyses.

The linear sweep voltammetry (LSV), between platinum working electrode and Ag/AgCl reference, within the range 0.1 to -1.6 V was performed at 30 mV/s scan rate both in acid copper sulfate and copper pyrophosphate electrolytes. The results are shown in Figure 2. It can be seen that deposition of copper form sulfate bath starts at relatively low cathodic potentials than pyrophosphate bath. Furthermore, the corresponding cathodic current density of pyrophosphate electrolyte is smaller than acid copper sulfate bath. Therefore, different structural properties are expected for copper deposited from these electrolytes.

The variation of texture for two electrolytes can be seen from XRD results given in Figure 3. The (111) direction was favored when copper was deposited from copper pyrophosphate but deposition from copper sulfate electrolyte favored (220) growth. Normally, growth direction of (111) is expected for fcc structure; however, preferential (110) planes of copper deposits may be obtained in highly strained films [2] because their strain energy densities were reported as the lowest [3].

Roughness measurements revealed that there was a direct correlation between roughness of copper, obtained from copper pyrophosphate electrolyte, and current density. Roughness of copper deposits increased with increase in current density. However, there was no such correlation for copper deposits obtained from copper sulfate electrolyte (See Figure 4).

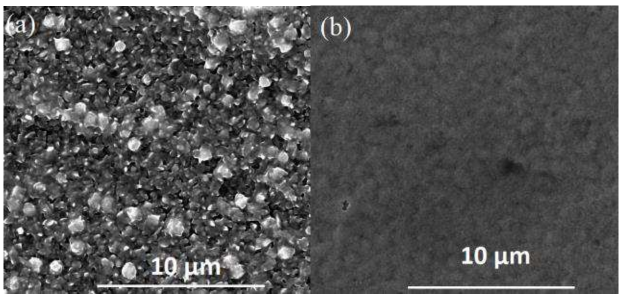

Figure 1: SEM images of aluminum surfaces coated by (a) copper cyanide and (b) copper pyrophosphate strikes.

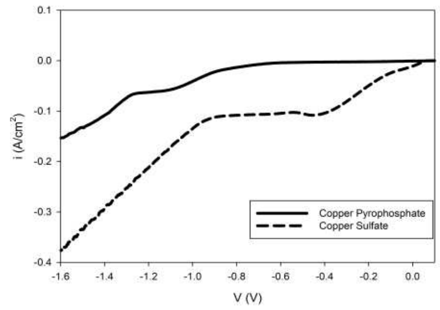

Figure 2: LSV between platinum working electrode and Ag/AgCl reference at room temperature.

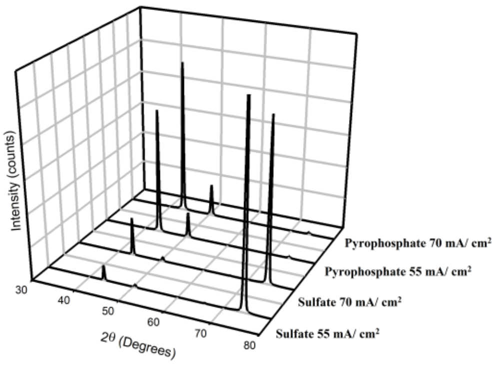

Figure 3: XRD results of copper coatings.

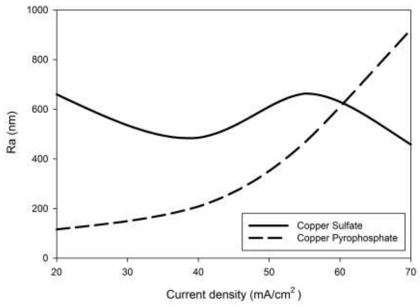

Figure 4: Surface roughness of copper coatings as a function of current density.

References

1. M. Schwartz, Handbook of Deposition Technologies for Films and Coatings 2nd Edition, N.J., (1994).
2. B. Hong, C. Jiang, X. Wang, Materials Transactions, 47, 2299, (2006).
3. J. M. Zhang and K. W. Xu, Acta Phys. Sin-CH ED. 51, 2563, (2002).