Presented at IPC Printed Circuits Expo®
SMEMA Council APEX®
Designers Summit 04

Deposition of Gold and Silver Surface Finishes Using Organic-Based Solutions

Jinghua Sun, Eric Dahlgren, Dian Tang, Thomas O'Keefe, and Matthew O'Keefe
University of Missouri-Rolla, Materials Research Center
Rolla, MO

Keryn Lian and Manes Eliacin
Motorola Advanced Technology Center
Schaumburg, IL

Abstract

A novel electrochemical plating process for depositing gold and silver surface finishes using environmentally benign, organic-based solutions as the plating bath is being investigated. The plating bath solution consists of an extractant and a diluent of the types used in conventional organic solvent extraction. The organics are very poor electrolytic conductors and can sustain only short range electrochemical reactions. The deposition mechanism involves the dissolution of a less noble substrate metal with the simultaneous deposition of more noble metal particles on the surface of the substrate, similar to immersion plating in an aqueous solution. Feasibility of the concept was demonstrated by loading the organic extractants with gold or silver in the form of complexed ions. The metal bearing organic liquid was then placed in contact with blank or patterned copper and nickel surfaces commonly used in the printed circuit board industry. Deposition of a continuous, adherent gold and silver surface finishes from the organic liquid was achieved with the proper processing conditions. Gold and silver films were deposited only on the exposed metallic surfaces of the substrate, indicative of a selective area deposition process similar to immersion plating. Scanning electron microscopy (SEM) indicated that the films were composed of nanometer sized particles.

Introduction

A new immersion plating process based on organic solvent extraction solutions that could replace existing processes used in applications such as electroless nickel – immersion gold (ENIG) is being developed. The unique aspect of the process is that the plating is conducted in an organic medium rather than in a conventional aqueous medium or a polar organic liquid such as alcohol. The organic medium features good stability over long time periods, low volatility, low toxicity, high flash point, low electrical conductivity, low surface tension, very low solubility in the aqueous phase, low cost, and commercial availability. The organic solvents used in the organic immersion process were originally developed for solvent extraction processes used to separate metal ions from aqueous solutions. The organic liquid is generally composed of a metal extractant mixed with a diluent. There are three main classifications of extractants: anion exchange, cation exchange, and solvating extractants. The diluent, which usually makes up the major part of the organic liquid, may range from essentially aliphatic to essentially aromatic compounds. Both the extractant and the diluent are insoluble in the aqueous phase. The selection of the extractant and the diluent is a key factor in the success of a solvent extraction process. It is equally important for the metal deposition process.

The organic deposition process currently under development was derived from an earlier process termed galvanic stripping.[1] The process was originally developed for removing impurities from organic solvents used commercially in the metals recovery industry. Galvanic stripping is a spontaneous electrochemical process in which a solid metal is used as a reducing agent to remove a more noble metal ion loaded in the organic liquid. In previous studies, galvanic stripping of cations such as Fe^{3+}, Cu^{2+}, Pb^{2+} and Au^{3+} from organic solvents using solid metal reductants was successfully demonstrated.[2-4] Utilizing the electrochemically driven reactions with the unique properties of conventional organic solvents extended the technology to metal deposition processes. Preliminary studies on the deposition of metals from organic liquids focused on producing Cu or Pd nano-sized particles as a seed layer for the subsequent deposition of electroless copper on a thin diffusion barrier material.[5-6]

Additional studies led to the development of processes to deposit gold and silver onto nickel and copper surfaces commonly used in the printed circuit board industry. Gold or silver ions can be loaded into the organic bath by mixing with an aqueous solution containing dissolved gold or silver compounds such as $AuCl_3$ or $AgNO_3$. The organic and aqueous phases are then allowed to settle before separating the metal bearing organic phase for use in the deposition process. Another method for loading metal ions into the organic bath is to directly dissolve metal salts in the organic solution.

The metal deposition mechanism from an organic liquid is a spontaneous, immersion displacement process. More noble metal ions (i.e. Au^{3+}, Ag^{+}) are electrochemically reduced and deposited on a less noble substrate surface (i.e. Ni, Cu). The overall reaction, depicted in Equation 1, is similar to oxidation and reduction half-reactions for an aqueous displacement reaction.

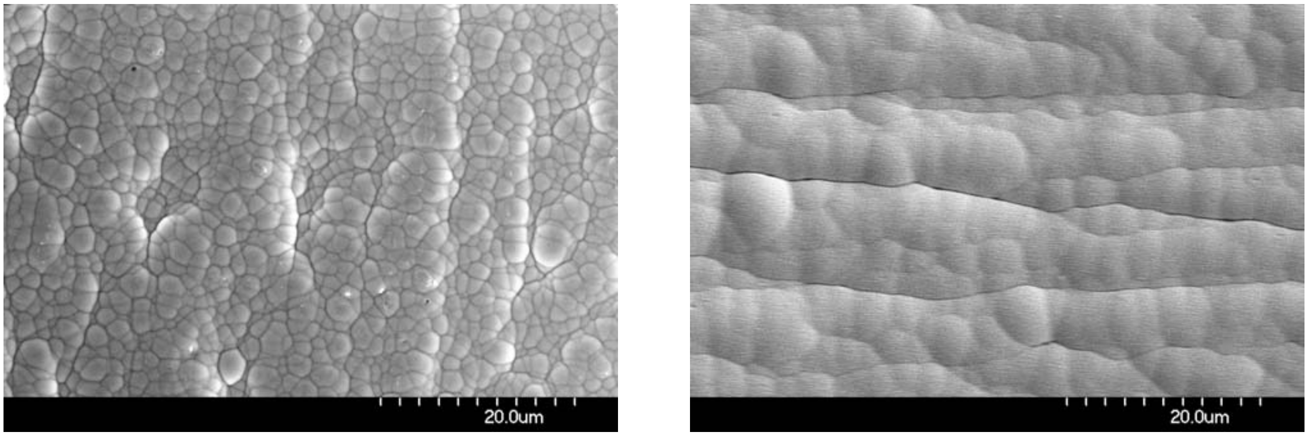
$$[RM_2]_{(organic)} + M_{1(solid)} \longrightarrow [RM_1]_{(organic)} + M_{2(solid)} \quad (1)$$

Where M_1 is the less noble metal substrate and RM_2 is the organic compound containing the more noble metal to be deposited. Reactions of the type in Equation 1 were previously demonstrated for a number of different metals. Since the process depends on the oxidation of the less noble metal surface to supply electrons for the reduction of the more noble metal from solution, dissolution of the substrate metal and a balanced reduction of the metal ion occur simultaneously, driven by the thermodynamic potential difference between them. In the case of gold and silver surface finishes on nickel and copper substrates, the nickel or copper is oxidized and dissolved into the organic solution while the gold or silver in the liquid is reduced to metal and deposited on the nickel and copper surfaces, respectively.

Precious metal coatings such as gold, silver, and palladium are important to microelectronic applications because of their good chemical stability, good solderability, compatibility with wirebonding, and good surface flatness. Electrochemical deposition methods for precious metal coatings have been developed and refined over the years for such applications.[7-8] The alternative organic immersion process features a selective and nanoscale particle size finish with good uniformity, conformality, and adherence. Another characteristic of the organic immersion process is the capability of producing a uniform reaction interface that allows very complex structures and geometries to be evenly coated. An additional aspect of the organic immersion process is its environmentally friendly nature. Most immersion plating baths for gold and silver contain cyanide complexes, such as $[Au(CN)_2]^-$ or $[Ag(CN)_2]^-$, and releases free cyanide ions during plating. The free cyanide is not only highly toxic but also attacks photoresists. In spite of the efforts to formulate non-cyanide baths, only relatively unstable gold sulfite based systems have been found as a viable alternative.

Gold Deposition

ENIG has been used as a microelectronic component surface finish to attain good solderability and bondability for many years. The reducing agents used in electroless nickel baths contain phosphorus or boron that are incorporated into the nickel film. The presence of phosphorous in the film promotes dissolution of the nickel which is required for immersion gold plating to occur. Figure 1a shows a typical surface morphology of the electroless nickel deposit produced on a copper PWB substrate. Figure 1b presents an SEM image of a commercial immersion gold coating on nickel. It shows that the gold film is conformally deposited over the nickel surface. Chemical analysis using energy dispersive spectroscopy (EDS) showed 92 wt% gold for this specific sample.



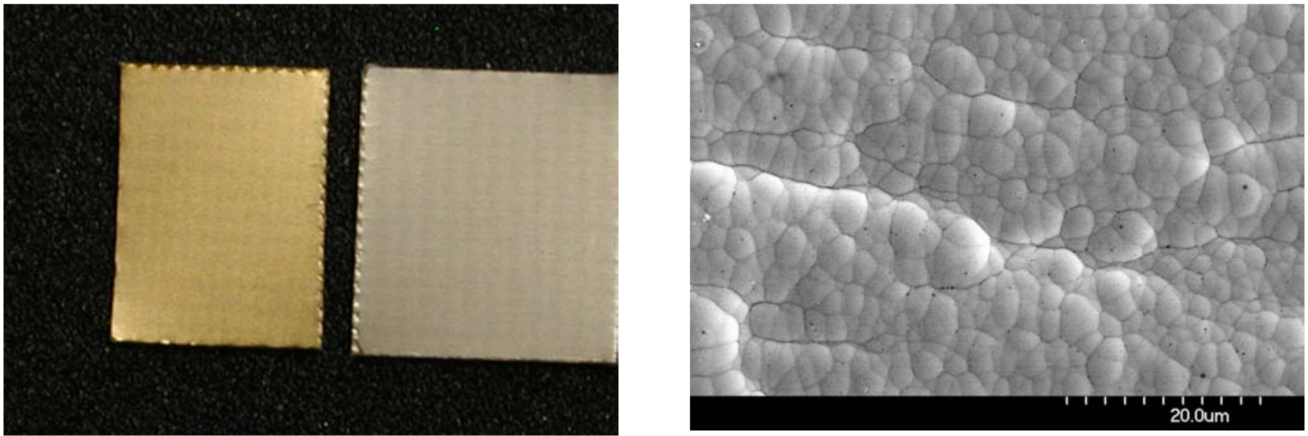
(a) (b)

Figure 1 - SEM Images of Commercial (a) Electroless Nickel and (b) Immersion Gold on Electroless Nickel

In this study sputter deposited pure nickel films and commercial electroless nickel-phosphorous layers were coated with gold using the organic immersion process, demonstrating that pure Ni and Ni-P films can be gold immersion coated using the organic solution process. Initial experiments focused on identifying organic extractants and diluents that meet requirements of high solvency for the gold species and readily allows gold deposition. Deposition experiments were carried out to establish processing conditions for producing gold films that were uniform, nonporous, and adherent. Gold salts, such as $AuCl_3$, AuCl, $Au(OH)_3$, and $Na_3Au(S_2O_3)_2 \bullet 2H_2O$, and pure gold powder were investigated as sources for the gold ions.

The organic immersion gold bath consists of the organic solvents, i.e. extractant and diluent, and the gold complex. No physical or chemical surface pretreatment for nickel substrates was performed prior to deposition. The operating parameters were usually a few minutes immersion time in an ultrasonically agitated solution near room temperature.

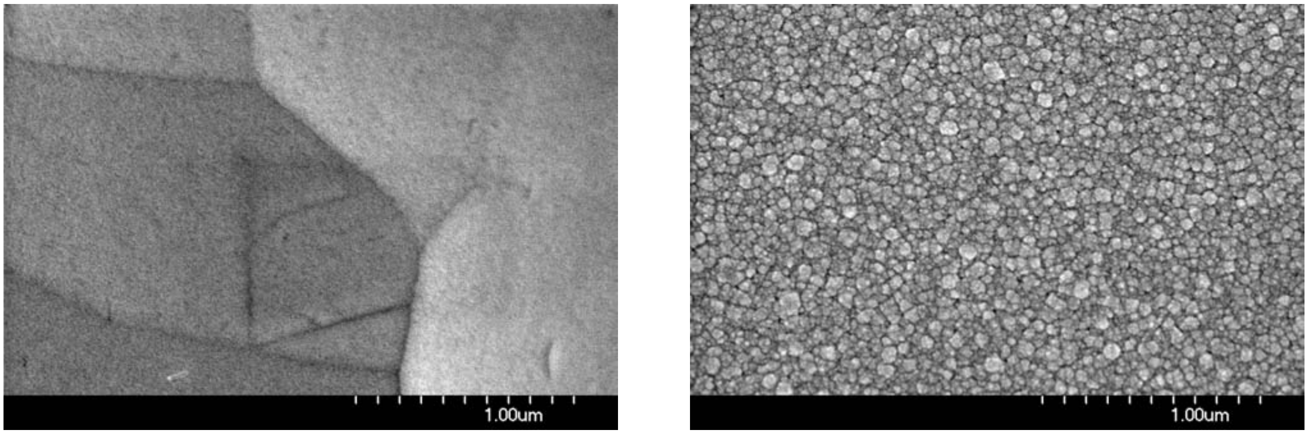
An electroless Ni film on a PWB substrate was plated in a Au loaded organic solution for immersion plating. Figure 2a shows a gold coated sample using the organic immersion process and an initial electroless nickel sample. The gold film is visually bright, uniform, and completely covered the electroless nickel substrate. Tape testing indicated good adhesion of the gold film on the nickel substrate. Figure 2b is a SEM image of the sample after deposition of gold from the organic solution. The SEM image shows that a continuous, conformal gold film covers the nickel surface. EDS analysis indicated 25 wt% gold after three minutes in the organic immersion plating bath.



(a) (b)

Figure 2 – (a) Digital Image of Initial Electroless Nickel Substrate (right) and Gold Coated Substrate (left); (b) SEM Image of Sample Surface after Immersing in a Gold Organic Immersion Bath

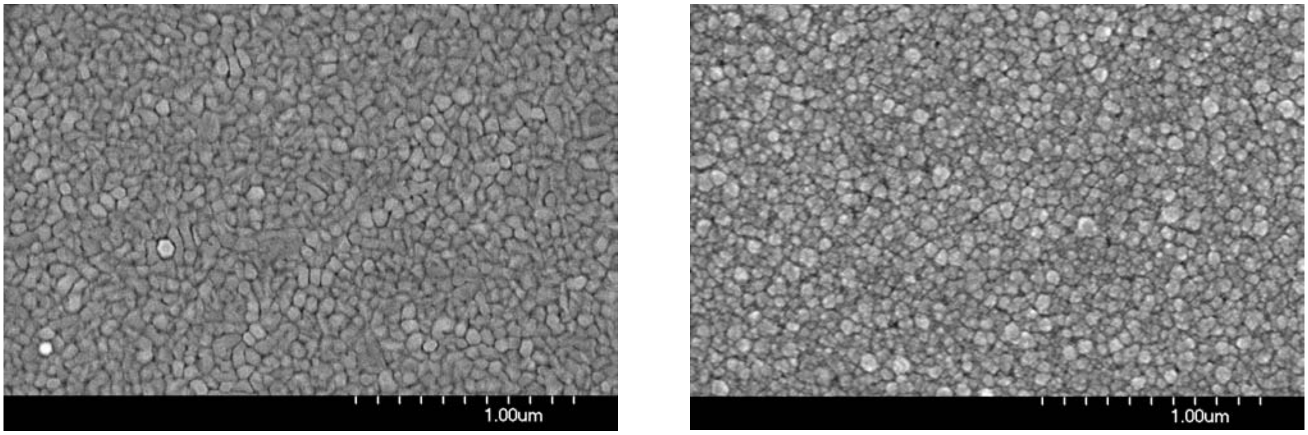
Process parameters for organic immersion plating such as bath organic composition, gold concentration, gold loading method, deposition time, temperature, and agitation were studied to identify their effects on gold film uniformity, morphology and deposition rate. Since the electrolyte (or immersion) medium itself is an important factor to control the gold film deposition rate and uniformity, organic solvents that promote an over-aggressive attack of the nickel substrate were avoided. The organic composition of the bath and agitation were found to be the most significant parameters responsible for morphology changes. Figure 3 shows an electroless nickel substrate before and after immersion in the organic bath. For this specific sample, gold deposition was carried out at room temperature for three minutes under ultrasonic agitation. SEM images indicated a gold particle size of approximately 10 to 20 nm, although the agglomeration of the individual gold grains resulted in 60 nm particles. EDS data indicated a gold concentration of 46 wt%.



(a) (b)

Figure 3 – SEM Images of (a) Electroless Nickel Substrate and (b) Gold Coated Substrate

Figure 4 shows a pure sputtered nickel film (a) and a sputtered nickel film coated with gold (b). The morphology of the gold film on a sputtered nickel is similar to the electroless nickel substrate, indicating that the deposited film morphology is not significantly affected by the initial substrate morphology. Concentration of gold ion, deposition temperature, and deposition time are the key factors in controlling the rate and uniformity of deposition. The effects of immersion time and temperature on the amount of gold deposited are presented in Figure 5. The gold immersion experiments were performed on sputtered nickel substrates at 20, 30, and 40°C for times from one to ten minutes. Results from the study indicate that, in general, the higher the temperature the faster the deposition rate. This trend continues until the entire substrate is covered, after which no further increase in gold was observed. This supports a deposition mechanism similar to the electrochemical galvanic displacement reaction of immersion plating.



(a) (b)

Figure 4 – SEM Images of (a) Sputtered Nickel Substrate and (b) Gold Coated Substrate

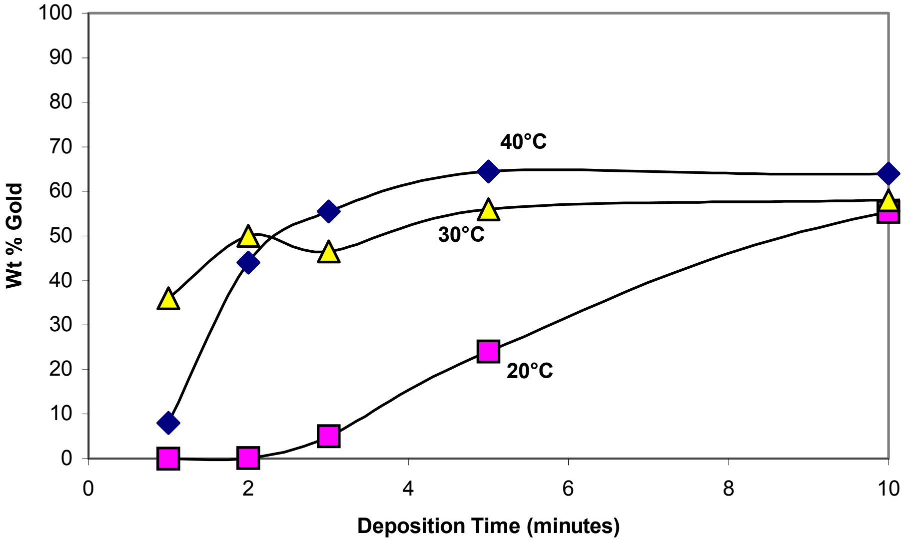


Figure 5 – Plot of the Weight Percent Gold Deposited on Sputtered Nickel Films as a Function of Time and Temperature

Silver Deposition

The feasibility of immersion plating silver from organic solutions onto copper surfaces was also investigated. Electrochemical deposition of silver on copper substrates has been widely investigated [9,10] with more recent work focusing on its potential use for nanometer size features for advanced silicon integrated circuit applications. [11,12] As in the case with gold, cyanide based plating baths are commonly used for immersion Ag plating. In this study, silver was loaded into a neutral extractant organic solvent and diluent by contacting the organic liquid with an aqueous solution containing silver from dissolved $AgNO_3$. Substrates used in the investigation included copper foil, copper foil laminated to a PWB, and sputtered copper films on silicon substrates. The typical substrate size was 1cm^2.

After one minute in a room temperature and ultrasonically agitated Ag bearing organic solution, the substrate visually changed color from copper (Figure 6a) to highly reflective metallic grey (Figure 6b) suggesting Ag deposition on Cu. Due to the relatively short time required to deposit a continuous silver film, a series of films were deposited on samples from ten to 120 seconds and the amount of deposited Ag was measured using EDS and then converted to mass per unit area. Figure 7 shows a linear increase in silver content from 10 to 60 seconds, but after 60 seconds of immersion time only a slight increase in deposited silver was observed. This result is consistent with a displacement reaction in which the deposition stops when the less noble substrate has been completely covered with the more noble deposited film, as was observed for the gold deposition (Figure 5).

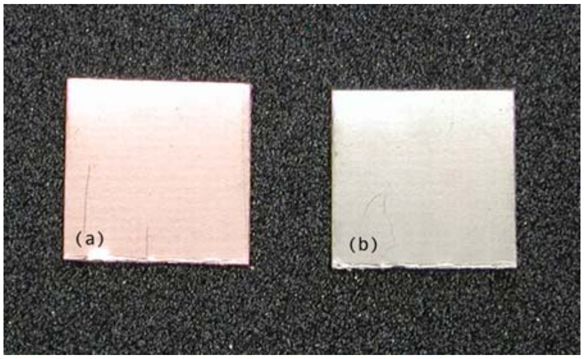


Figure 6- Digital image of the Surfaces of Cu PWB Samples (a) before and (b) after Organic Solution Immersion Silver Plating

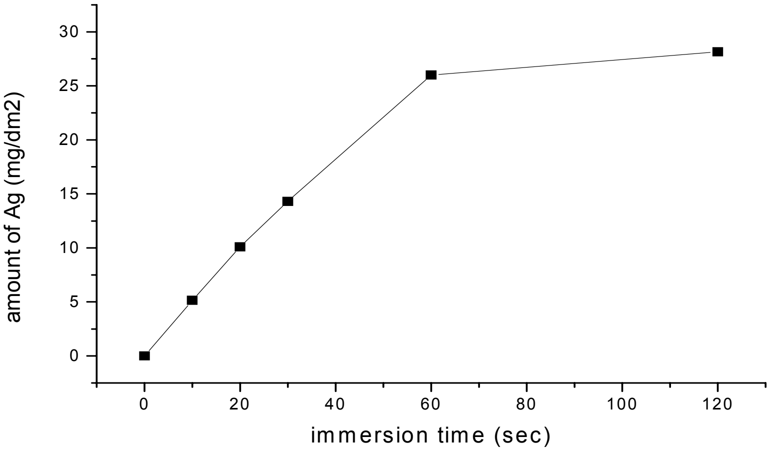
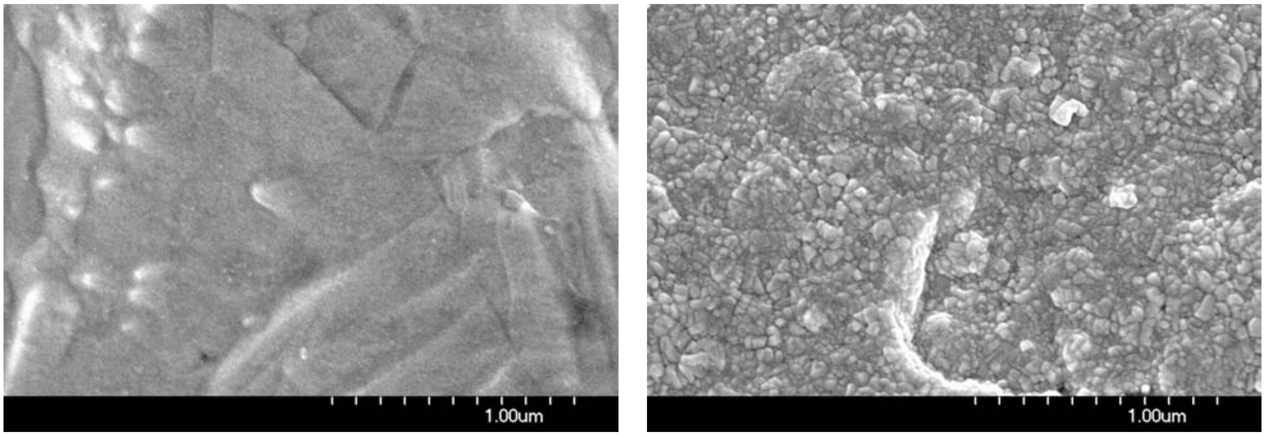


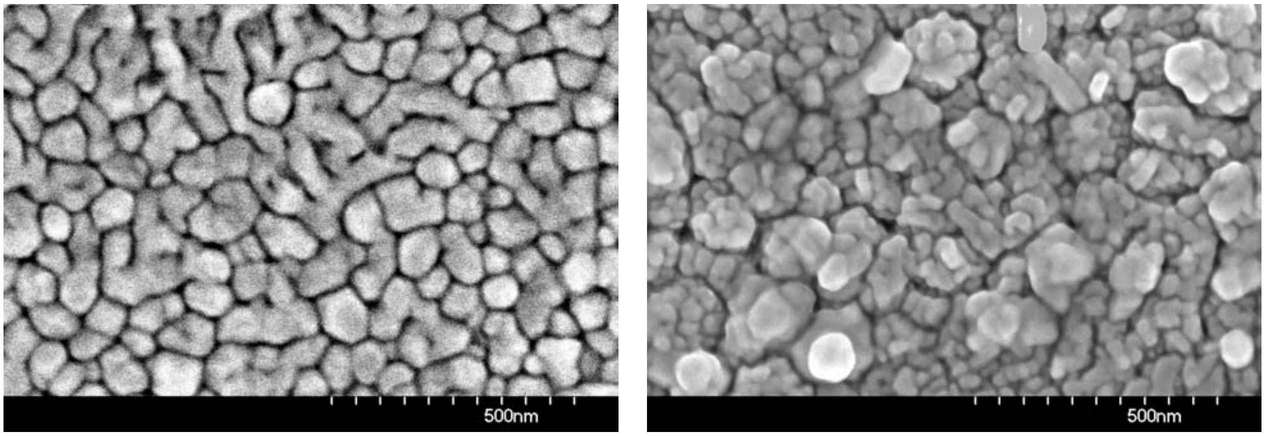
Figure 7- Plot of the Amount of Silver Deposited on a Cu PWB Substrate vs. Immersion Time

Characterization of the silver deposits using SEM revealed that, similar to the gold films, the silver grain size was very small, on the order of 20 to 40 nm in diameter regardless of the original copper substrate surface. As shown in Figure 8, the starting copper surface on a PWB sample was not uniform in grain size or topography (Figure 8a). However, a very dense, fine grained silver deposited was observed after one minute in the organic solution (Figure 8b) that had little similarity to the original surface. When a smooth sputter deposited copper film was used as the substrate (Figure 9a) the immersion silver coating was also fine grained with agglomerations of nano-sized particles densely packed across the entire surface (Figure 9b). In both cases, the immersion silver film was adherent to the substrate surface when tape tested.



(a) (b)

Figure 8-SEM Images of Copper Foil (a) before and (b) after One Minute Immersion in a 25°C Ag Loaded Organic Solution



(a) (b)

Figure 9 – SEM Images of Sputtered Copper (a) before and (b) after One Minute Immersion a 25°C Ag Loaded Organic Solution

Summary

Gold films were successfully deposited on sputtered pure nickel or electroless nickel – phosphorous substrates using a unique organic solution immersion plating bath. Silver immersion plating from organic solutions onto copper substrates was also demonstrated. The deposited gold and silver films were continuous, smooth, bright, and adherent. Typical deposition conditions were a few minutes of immersion time in an ultrasonically agitated, room temperature solution. Scanning electron microscopy characterization revealed that the films were composed of nanometer sized particles. Gold and silver film morphology was not affected by initial starting substrate surface. It was determined that gold and silver deposition increased at a linear rate until the entire substrate surface was covered, after which no measurable increase in deposition occurred. This result is consistent with an immersion plating process. The approach has the potential to replace cyanide based immersion plating processes in the PCB industry.

Acknowledgements

Funding for this study was provided by the Defense Advanced Research Projects Agency (DARPA) through the Air Force Research Laboratory Sensors Directorate, F33615-00-2-1718, and the Dept. of Education Graduate Assistance in Areas of National Need (GAANN) Fellowship program (ED). The support and encouragement of Dr. Rebecca Cortez and Mr. Alan Tewksbury of the Sensors Directorate is gratefully acknowledged. Special thanks are extended to Marshall Bishop of Chevron Philips Chemical Company LP and Jerry Tabor of Rhodia for supplying the diluents and solvent extraction solutions.

References

1. O'Keefe, T. J., U.S. Patent, No. 5,228,903, (1993).

2. Belew, B., Harlanovs, J.R., O'Keefe, T.J., and Watson, J.L., *Hydrometallurgy Fundamentals, Technology, and Innovations,* 817-830, (1994).
3. Moats, M.S., Chang, C-M, and O'Keefe, T.J., *Recycling of Metals and Engineered Materials,* ED PlB. Queneau and R.K. Peterson, The Extraction & Process Division and The Light Metals Division of The Minerals, Metals & Materials Society, Point Clear, AL, 545-562, (1995).
4. Chang, C-M, Gu, H., and O'Keefe, T.J., *HSRC/WERC Joint Conference on the Environment,* HSRC/WERC, Albuquerque, NM, 164-175, (1996).
5. Fang, R., Gu, H., O'Keefe, M.J., O'Keefe, T.J., Shih, W-S., Leedy, K.D., and Cortez, R., *J. Electr. Mater.,* **30**(4). 349-354, (2001).
6. Sun, J-H., Johnson, B. O'Keefe, T.J., and O'Keefe, M.J., *Advanced Metallization Conference*, (2003).
7. Safranek, W.H., *The Properties of Electrodeposited Metals and Alloys,* 2nd Edition, 163-195, (1986).
8. Mallory, G.O., and Hajdu, J.B., *Electroless Plating,* 401-421, (1990).
9. Parker, Lee J., Proceedings AESF SUR/FIN Annual Technical Conference, 761-770 (2000).
10. Walsh, D., Milad, G., Gudecaauskas, D., *Metal Finishing*, **101**(1), 25-26, (2003).
11. Moffat, T. P., Baker, B, Wheeler, D, Bonevich, J E, Edelstein, M; Kelly, D R; Gan, L, Stafford, G R; Chen, P J, Egelhoff, W F, and Josell, D., *J. Electrochem. Soc.,* **149**(8,) C423-C428, (2002).
12. ten Kortenaar, M. V., De Goeij, J. M., Kolar, Z. I., Lusse, P. J., Ziuddam M. R., and Van der Driff, E., *J. Electrochem. Soc.,* **148**(1), C28-C33, (2001).