Technical Article

Spontaneous Electrochemical Deposition of Gold Coatings from Organic Solutions

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Thin gold films less than 100 nm thick were deposited onto copper and nickel substrates using a unique immersion gold plating bath.** The plating bath was prepared with poor-electrically conductive organic solvents that are typically used in the metal recovery industries. These solvents are commonly used for concentrating both base metals and precious metals by extracting them from aqueous solutions. Although the gold films deposited in this study were thin, they were continuous, free of pores, smooth, bright, and adherent. Scanning electron microscopy and x-ray diffraction showed the films were composed of nanometer-sized crystalline gold particles. X-ray photoelectron spectroscopy was used to confirm that the films consisted of metallic gold. Additionally, cross-sectional transmission electron microscopy was used to measure the thickness of a gold coating deposited on a copper substrate and to investigate the film/substrate interface. A deposition mechanism that is similar in nature to an aqueous immersion plating process is proposed.

Surface finishes are applied to a printed circuit board (PCB) to protect the copper surface from oxidation and to provide a solderable surface for subsequent attachment of PCB components. Gold is commonly used as a final finish for electronic components because of its low electrical resistance and its ability to resist oxidation. In the PCB industry, gold is applied as a final surface finish over electroless nickel and is referred to as electroless nickel/ immersion gold (ENIG).¹ ENIG surface finishes are being investigated as an alternative to hot air solder leveling (HASL) for PCBs incorporating fine pitch surface mount technology (SMT).^{2,3} It is interesting to note that in the

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The work is an interesting and novel study to produce gold from organic solutions. Using liquid ion exchange extractants more commonly used in the mining industry, this work describes the "spontaneous" deposition of remarkably pore-free gold films. "Spontaneous" here is closer to electroless deposition than immersion plating, but there are elements of both. This work could be the seed from which forests grow. 1960s the majority of multilayer and double-sided PCBs utilized an ENIG surface finish.⁴ Then, in the early 1970s, this method was largely abandoned as a conventional surface finish due to the high cost of gold.⁴

HASL is currently the standard surface treatment utilized for PCBs because it produces surfaces that have excellent solderability and it uses low cost materials. However, as the components that are mounted to PCBs have decreased in size, the copper PCB feature size has also decreased. This has resulted in PCBs with copper lines that are narrower and spaced closer together. Additionally, SMT requires a surface finish that results in planar surfaces that are conformal to the original copper trace. These surfaces are not effectively produced with HASL and this is the principle reason alternatives are being considered.^{1,5} Other deleterious side effects produced by HASL surface finishes include the incorporation of lead into the PCB, the incompatibility with aluminum or gold wire-bonding and the requirement of the PCB to undergo a thermal excursion during processing.² Thus, the traditional use of HASL is no longer an optimal solution for producing solderable surfaces on PCBs incorporating fine pitch devices.

ENIG plating is a suitable alternative surface finish for PCBs incorporating fine pitch SMT because solderable surfaces with a planarity equivalent to that of the original copper trace are produced.² Additionally, the use of ENIG as a surface finish for PCBs is advantageous because the finish is highly selective and no bridging between closely-spaced copper lines occurs.⁶ ENIG surface finishes are also free of lead, provide a contact surface with low electrical resistance and do not require the PCB to undergo a thermal excursion during processing.

The ENIG plating process consists of four major process steps: copper surface preparation, copper surface activation, electroless nickel deposition, and immersion gold deposition. Micro-etches and acid cleaning are used to prepare the copper surface by removing surface oxides. A

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palladium activator is then applied to the cleaned copper surface to act as a catalyst for subsequent electroless nickel deposition. The electroless nickel film is generally deposited using a hypophosphite bath and is typically 2.5 to 5.0 μ m (98 to 197 μ -in.) thick.² Finally, a thin gold film less than 125 nm (5 μ -in.) thick is deposited using an immersion plating bath.² The immersion baths used for gold plating typically contain cyanide, although some sulfite-based baths are also available.

Based on the advantages that ENIG surface finishes offer, a unique non-cyanide immersion gold plating bath prepared from organic solvents is being developed. The organic solvents used in the plating bath are commonly used in large quantities in metal recovery operations such as solvent extraction. However, the solvents are not designed to support macro-scale electrochemical reactions. Thus, the process that is being developed is unique because spontaneous micro-scale reactions have been shown to be feasible. Preliminary results have indicated the plating bath has characteristics similar to a traditional cyanide immersion gold plating bath, whereby gold is selectively deposited only on active metal areas of the substrate. The gold films deposited from the organic plating bath are uniform and have a surface roughness characteristic of the initial starting substrate. That is, if the initial surface is highly reflective, then the final gold film is also highly reflective. Additionally, the deposited films are comprised of metallic gold and are free of pores.

Background

The organic deposition process currently under development was derived from an earlier process termed galvanic stripping.⁷ This process was developed for removing impurities from the organic solvents commonly used in the metals extraction industry. The impurity removal studies focused on reducing the oxidation state of iron contained in solvent extraction process streams from Fe⁺³ to Fe⁺² using metallic zinc or iron as reducing agents.^{8,9} During the course of this investigation it was found that other metal ions that were more noble than the active metal reducing agent would also be removed from the organic solution. The more noble metal ions were electrochemically reduced and deposited on the surface of the active metal by means of a galvanic displacement reaction. A process for recovering gold from organic solutions utilizing zinc, iron, aluminum and copper powders was subsequently demonstrated.¹⁰

Further development of the galvanic stripping process led to studies focusing on the use of an organic immersion plating bath, which has numerous applications, including several in the microelectronics industry. Unlike the galvanic stripping process where the composition of the organic solution is controlled by its ability to remove metals from an aqueous leaching solution, the composition of the organic solution used for plating can be tailored to obtain the type of film morphology required. With this in mind, different organic solvents that are commonly used in the solvent extraction industry such as anion exchange extractants^{***}, cation exchange extractants (di-ethylhexyl phosphoric acid), chelating extractants (5,8 diethyl-7-hydroxy-dodecane-6-one-oxime) and solvating extractants (tri-butyl phosphate) were investigated as possible components for an organic solution immersion plating bath. The initial studies focused on identifying the conditions necessary for depositing solderable metals onto aluminum bond pads using organic solvents. These studies focused primarily on depositing Cu onto Al bond pads and depositing Cu and Pd onto Al and Al(Cu) thin films.¹¹⁻¹³ An important outcome of these studies was the identification of surface activating agents that could be added to the organic solutions. Incorporation of the activating agents into the organic solvents effectively allowed metallization of electronic components, many of which generally cannot be metallized using an immersion type plating process. Additional process development has led to the adaptation of the organic plating baths for the deposition of copper or palladium nanometer-sized particles onto diffusion barrier layers for the subsequent deposition of electroless copper. The copper or palladium particles were deposited on Ti, Ti(N), Ta and Ta(N) barrier layers.^{14,15}

Modification of the galvanic stripping process has led to the current process which is being developed for depositing gold onto copper and nickel substrates. This process has the potential for replacing aqueous based gold immersion processes.

Experimental

A literature survey was performed to identify which of the four major classifications of organic solvents should be pursued for use in the development of the gold organic plating bath. Based on the survey, a solvating extractant combined with an organic diluent was chosen as the base component for the plating bath. It should be noted that all of the organic solvents employed in this study are commonly used in large quantities by various metal recovery operations and are readily available.

Gold was loaded into the organic solvent by vigorously mixing the organic solvent for five minutes with an aqueous solution containing gold chloride ions in a separatory funnel. The gold was transferred into the organic solution because the organic solution had a greater affinity for the gold ions than the aqueous solution. After mixing, the organic and aqueous phases were allowed to separate. Separation of the two phases occurred naturally due to mutual immiscibility. The gold-depleted aqueous phase was drained from the separatory funnel and the gold loaded organic phase was passed through silicone-treated phase separating filter paper to remove any entrained water.

The gold deposition experiments were carried out on 500-nm thick (~20 μ -in.) copper and nickel films that were deposited on silicon wafers using physical vapor deposition. Following deposition of the copper and nickel films, the wafers were cut into 1.0 cm × 1.0 cm square (~0.4 × 0.4 in.) substrates. The copper substrates were immersed in a 10 vol% sulfuric acid solution prior to gold plating. They were then rinsed with deionized water and acetone. Compressed air was used to remove the acetone from the surface of the copper. No pretreatment was used for the nickel substrates. Rather, an *in-situ* activating agent was added to the organic solution to promote plating of the nickel.

Gold films were deposited on both the copper and nickel substrates by placing them in a glass reaction vessel containing the organic plating solution. The glass reaction vessel was then immersed in an ultrasonic water bath, which was modified to enable control of the bath temperature. The reaction times used for depositing the gold films were varied from one up to 20 min and the temperature of the water bath was held constant at $30^{\circ}C$ ($86^{\circ}F$). Following deposition of gold on the substrates, the samples were rinsed with deionized water and acetone. Compressed air was used to remove the acetone from the gold plated surface.

Scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and cross-sectional transmission electron microscopy (XTEM) were used to analyze the deposited films. The adherence of the gold films was qualitatively tested by placing a piece of ScotchTM tape on the gold film and rapidly removing it. If no gold was removed from the plated surface, the gold film was considered to be adherent.

^{***} Alamine 336, Cognis Corporation, Cincinnati, OH.

^{****} LIX 63, originally developed by General Mills Chemicals in 1963.

The adherence and ability of solder to wet sputtered nickel substrates with gold films deposited from an organic solution was examined. Three sputtered nickel substrates were coated with gold for three, five and seven min. After deposition of the gold film, solder paste[†] was applied to each substrate. Solder paste was also applied to an uncoated nickel substrate. All of the substrates were then heated in a solder reflow oven with a peak temperature of 224°C (435°F). Wetting angle measurements were made by first cutting the solder bead and substrate in half using a diamond saw. A digital image of the substrate cross-section was acquired. The contact angle between the solder bead and the substrate was measured using a digital image analysis program.^{††} Ten measurements were collected and averaged for each substrate.

Results and discussion

Based on the literature survey, several screening experiments were conducted. The initial experiments suggested that a solution containing tributyl phosphate, a solvating extractant, combined with an organic diluent would produce gold deposits. Furthermore, secondary electron images collected while performing SEM studies showed the deposition of gold only occurred on the active metal surfaces of the substrates, *i.e.*, gold was only deposited on the copper or nickel films, not on the unmetallized parts of the silicon wafer. It was found that the morphology of the deposited gold changed significantly when various kinds of solvating extractants were used. Surprisingly, it was also found that significant changes to the gold morphology occurred when different organic diluents were used. This result was unexpected because of the similar compositions of the organic diluents used in this study. Additionally, the results of the screening test indicated that different diluents

worked better for different substrate metals. Thus, conditions for two different gold deposition baths were identified. The first gold deposition bath utilized odorless kerosene as the diluent and was used for depositing gold onto copper substrates. A commercial solvent extraction diluent^{†††} was used to prepare the gold deposition bath for depositing gold onto nickel substrates.

Copper substrates

Adherent gold films that were as highly reflective as the initial copper surface were deposited from an organic plating bath having a gold concentration of 0.1 g/L. The organic solvent utilized for the bath consisted of 20 vol% tributyl phosphate (solvating extractant) and 80 vol% odorless kerosene (diluent). No other additives were required to initiate the deposition of gold on the copper. However, it was found that the addition of di-ethylhexyl

phosphoric acid, a cation exchange extractant, improved the adhesion of the gold film in some cases.

A SEM analysis of the initial copper surface and the surface of a deposited gold film produced after 10 min in the organic bath was performed. Secondary electron images of both surfaces were collected. Figure 1(a) shows a secondary electron image of the initial copper surface. The surface is composed of equiaxed grains that have an average diameter of approximately 90 nm (3.5 μ -in.). Figure 1(b) shows the morphology of the gold film deposited on



Figure 1—Secondary electron images illustrating (a) initial sputtered copper substrate and (b) gold coated copper substrate.



Figure 2–TEM cross-section showing the gold film deposited on a sputtered copper substrate.

the copper substrate. The film is continuous and consists of gold particles with diameters of 20 nm (0.8 μ -in.) or less. Additionally, it can be seen from Fig. 1(b) that the film is pore-free.

XTEM was performed to determine the gold film thickness and to gain an understanding of what occurred at the interface between the gold and copper layers. The film was deposited by immersing a copper substrate in the organic solution for 10 min. The thickness of the gold film was measured from the XTEM image shown in Fig. 2 and was found to be approximately 64 nm (2.5 μ -in.). An interaction layer was observed underneath the gold film and appeared to penetrate into the sputtered copper surface to a depth of 50 to 200 nm (~2 to 8 μ -in.). The interaction layer was believed to be caused by partial dissolution of the substrate during deposition of the gold, similar to immersion plating. Initially, it was believed that the

[†] Locktite™ Multicore M00078 Sn 62, Henkel Loctite Corporation, Düsseldorf, Germany.

^{††} Scion Image, Scion Corporation, Frederick, MD.

^{†††} ORFOM® SX-1, Chevron Phillips Chemical Company LP, The Woodlands, TX.



Figure 3—Secondary electron images illustrating a) initial sputtered nickel substrate and b) gold coated nickel substrate.

interaction layer contained large voids, but closer inspection of the light areas in the interaction layer confirmed the presence of some contrast indicating that not all of the copper within the interaction layer was dissolved.

Nickel substrates

Bright, reflective gold films were successfully deposited on nickel substrates using an organic plating bath having a gold concentration of 0.5 g/L. The plating bath was prepared from an organic solvent containing 10 vol% tributyl phosphate and 90 vol% of the commercial diluent.^{†††} A 1.0 vol% addition of concentrated hydrochloric acid was also added to the bath to activate the sur-



Figure 4-X-ray diffraction pattern of a) sputtered Ni film on a Si substrate and b) Au film deposited on a sputtered Ni film with the organic plating bath.



face of the nickel. By using this bath composition, it was found that continuous, adherent gold films could be produced when the substrate was immersed in the bath for five min. The initial nickel surface was characterized by SEM. Fig. 3(a) shows a secondary electron image of the sputter-deposited nickel surface. The nickel grains appeared to be equiaxed and the average diameter was found to be approximately 60 nm (2.4 μ -in). Scanning electron microscopy was also used to characterize the gold film deposited on the nickel substrate. Figure 3(b) shows a secondary electron image of the gold film. From the figure it can be observed that the film was continuous and pore-free. Additionally, it can be seen that the film was composed of gold particles with diameters less than 20 nm (0.8 μ -in.). An XRD analysis was also performed on an uncoated nickel substrate and a gold-coated nickel substrate. Figure 4 shows the resulting diffraction patterns. As expected, the nickel substrate exhibited sharp peaks on both patterns due to the thinness of the gold film. However, gold peaks can clearly be seen and labeled, indicating the deposited film was crystalline. A gold coated nickel substrate was also analyzed using XPS to determine the type of gold deposited on the surface of the nickel using the organic deposition bath. Figure 5 shows the region in the x-ray photoelectron spectrum where gold is present. Only two peaks were present, the $Au4f_{5/2}$ and the $Au4f_{7/2}$. Both peaks are indicative of metallic gold and not an organic-metallic compound.

The ability of solder to wet and adhere to nickel substrates coated with gold deposited from the organic plating bath was examined. A digital image of the resulting solder bead on the uncoated nickel substrate is shown in Fig. 6(a). From the figure it can be seen that the solder did not spread across the entire substrate and numerous solder spatters were present. Figure 6(b) shows a digital image of the resulting solder bead on a nickel substrate that was placed in the organic gold plating bath for seven min. The solder bead spread across the substrate without spattering. Similar results were observed for the samples immersed in the organic plating bath for three and five min. However, it should be noted that solder spreading increased as the immersion time was increased. The adherence of the solder beads was qualitatively tested by applying a shearing force to them with a razor blade. It was concluded that the solder beads were adherent, as none of them could be removed.

The contact angle made by the solder bead with the substrate was measured for the two substrates presented in Fig. 6. An angle of $21 \pm 3^{\circ}$ was measured for the solder bead shown in Fig. 6(a) and an angle of $21 \pm 1^{\circ}$ was measured for the solder bead shown in Fig. 6(b). It was not surprising that the angle was the same for both as a solder paste containing flux was used for this experiment. However, results from this experiment showed that the gold plated from the organic plating bath did improve the solder wetting characteristics of the nickel substrates. This conclusion was based on the presence of solder spatter on the uncoated nickel substrate opposed to the absence of solder spatter on the gold coated sub-



Figure 6–Digital photographs showing the solderability of a) uncoated sputtered nickel substrate and b) Au coated sputtered nickel substrate.

strate. Furthermore, Fig. 6(b) shows that improved solder wetting occurred on the gold coated substrate.

Plating mechanism

Depositions from the organic plating bath are believed to occur by an electrochemical galvanic displacement reaction. The thermodynamic driving force for these types of reactions is a result of the difference between the reduction potential of the more noble metal ions in solution and the reduction potential of the less noble metal substrate. Figure 7 illustrates the proposed deposition mechanism. The figure shows the metal substrate dissolving at a micro-anode



Compound

Figure 7—Illustration of the proposed mechanism for deposition of noble metals from an organic solution onto a less noble metal substrate.

resulting in the availability of electrons, which can travel a short distance through the conductive metal substrate and effectively form a micro-cathode. The noble metal ions are reduced at these sites. Equation 1 shows the proposed reaction:

$$R-M_1 + M_2 \rightarrow M_1 + R-M_2 \tag{1}$$

where $R-M_1$ is the organic compound complexed with the more noble metal ion, M_2 is the less noble metal substrate, M_1 is the reduced more noble metal and $R-M_2$ is the organic compound complexed with the less noble metal ion. Because the deposition mechanism relies on the dissolution of the substrate, deposition reactions cease once all of the active anode sites have been covered with the noble metal film similar to an aqueous solution immersion solution process.

The primary difference between the organic deposition bath developed in this study and a typical aqueous immersion plating bath is the method by which the noble metal ions are complexed. In an aqueous solution, the metal cations are complexed with water in a hydration sheath, while in the organic plating bath the metal cations are in solution as an organic complex. Another important difference is that the organic solvents used to prepare the organic plating baths have very low electrical conductivity. Consequently, the electrochemical reactions occur over a very short range, which imparts a high degree of polarization to the system.¹⁶ As a result, the potential exists to produce unique microstructures for different applications.

Conclusions

Conditions for depositing metallic gold films from an organic plating bath were established. The gold films were adherent, continuous and free of pores. Characterization of the films showed that they were crystalline and composed of particles with diameters of 20 nm (0.8 μ -in.) or less. Transmission electron microscopy analysis of the gold film deposited on the copper substrates indicated that the gold film was approximately 64 nm thick (2.5 μ -in.). Additionally, it was found that the gold film deposited from an organic solution improved the solderability of a nickel substrate. Further studies delineating the affects of varying the gold concentration in the plating bath and identifying other possible organic solvents as bath components are currently in progress.

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