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**METAL DEPOSITION FROM
ORGANIC SOLUTIONS FOR
MICROELECTRONIC
APPLICATIONS**

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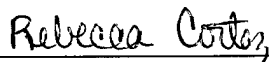
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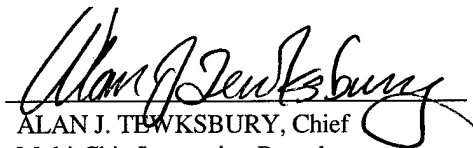
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14. ABSTRACT A unique method for electrochemically depositing metal films from organic solutions was previously demonstrated. It was shown that by plating with this method, metallic particles and layers could be deposited on metals commonly used in the microelectronics industry. The deposition mechanism involved the dissolution of a less noble substrate metal and the simultaneous deposition of more noble metal particles on the surface of substrate, similar to immersion plating in aqueous solutions. This process was also shown to be capable of producing selectively deposited seed layers only on exposed reactive metal surfaces for subsequent electroless and electrolytic metal depositions. This process was highly selective and was compatible with film depositions onto patterned and unpatterned substrates, including printed circuit boards and silicon wafers. Refinement and optimization of the process have resulted in extending the technology to include the deposition of Cu and Pd seed layers from organic solutions onto TiSiN barrier films using in situ activating agents. Additionally, the process was modified to selectively deposit continuous Au films on Cu laminated FR-4 substrates and sputter-deposited Cu films. In this study, the ability to selectively deposit adherent Au thin films and Cu or Pd seed layers from an organic solution onto patterned and unpatterned substrates is demonstrated. The results from process development and microstructural characterization of the deposits are presented.					
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Metal Deposition from Organic Solutions for Microelectronic Applications

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ABSTRACT

A unique method for electrochemically depositing metal films from organic solutions was previously demonstrated. It was shown that by plating with this method, metallic particles and layers could be deposited on metals commonly used in the microelectronics industry. The deposition mechanism involved the dissolution of a less noble substrate metal and the simultaneous deposition of more noble metal particles on the surface of the substrate, similar to immersion plating in aqueous solutions. This process was also shown to be capable of producing selectively deposited seed layers only on exposed reactive metal surfaces for subsequent electroless and electrolytic metal depositions. The process was highly selective and was compatible with film depositions onto patterned and unpatterned substrates including printed circuit boards and silicon wafers. Refinement and optimization of the process have resulted in extending the technology to include the deposition of Cu and Pd seed layers from organic solutions onto TiSiN barrier films using *in situ* activating agents. Additionally, the process was modified to selectively deposit continuous Au films on Cu laminated FR-4 substrates and sputter deposited Cu films. In this study, the ability to selectively deposit adherent Au thin films and Cu or Pd seed layers from an organic solution onto patterned and unpatterned substrates is demonstrated. The results from process development and microstructural characterization of the deposits are presented.

INTRODUCTION

Earlier research on metal deposition from an organic solution focused on depositing adherent metal thin films and metallic particles onto sputter deposited Al(Cu) [1], Ti(N), and Ta(N) [2]. It was shown that plating from an organic solution allowed selective deposition of metal films or particles onto substrates that typically are not amenable to non-vacuum deposition techniques. The plating method utilized a galvanic displacement reaction whereby an ion with a reduction potential more positive than the substrate was loaded into an organic solution using conventional liquid-liquid ion exchange techniques. The substrate to be plated was immersed in the loaded organic solution and noble ions from the organic solution were deposited onto the surface of the substrate. Substrate ions were simultaneously transferred into the organic solution. Metal particles were selectively deposited only onto active metal regions with a lower or more negative reduction potential. Thus, this process is compatible with both patterned and unpatterned substrates and can be used for a variety of microelectronic applications. Refinement and optimization of this technique have advanced the technology to selectively deposit continuous Au films onto Cu and to deposit Cu or Pd seed layers on TiSiN for subsequent electroless or electrolytic Cu plating.

Gold is commonly used in the microelectronics industry as a protective coating because of its corrosion properties, low contact resistance, good electrical conductivity, and solderability.

Electrochemical methods are commonly used to deposit Au from cyanide solutions onto Cu substrates. These solutions contain free cyanide, which can pose health and environmental risks. Non-cyanide plating baths are also used, but they work best if preceded by a cyanide based-gold strike [3]. Organic solution deposition techniques were investigated as an alternative to a cyanide based gold strike bath. A continuous and adherent Au film was electroplated from a non-cyanide bath onto a Cu substrate initially seeded with Au using an organic solution. The deposition technique was also investigated as a post-treatment method of selectively depositing Au onto the Cu surfaces of microelectromechanical systems (MEMS). MEMS structures used as microswitches benefit from specialized reproducible contact surfaces with controlled morphologies [4], which could possibly be obtained by depositing the Au from an organic solution.

Copper is rapidly becoming the standard material for interconnects in the microelectronics industry due to its low electrical resistance [5]. Although methods and processes currently exist to deposit Cu on barrier materials, i.e., physical vapor deposition and chemical vapor deposition, electrochemical methods are seen as advantageous for economic and process integration reasons. The electrochemical process must be compatible with the barrier film between the Cu and dielectric diffusion barrier; layers of interest include Ta, TaN, and TiSiN. In this study, Cu seed layers and Pd seed layers were deposited from an organic solution onto a chemical vapor deposited TiSiN barrier. An adherent copper film was then deposited using a standard aqueous electroless Cu deposition process. Seed layer deposition from an organic solution is a viable alternative because *in situ* etching agents that remove the oxide layer on the surface of the barrier film can be incorporated into the organic solution. Therefore, the number of process steps can be minimized.

EXPERIMENTAL

Organic solutions were prepared from a mixture of anion exchange extractants, cation exchange extractants, solvating extractants, and diluents. Metals were loaded into the organic solution by contacting an acidic aqueous solution containing noble metal ions with the organic solution in a separatory funnel for five minutes. The organic and aqueous phases were allowed to separate; the organic solution was then passed through hydrophobic filter paper to remove water entrained in the organic solution. Organic and non-organic activating agents were also added to the organic deposition solutions. The concentration of each organic reagent and activating agent was varied to change the deposition characteristics of the deposited seed layer or metal film. Additionally, *in situ* etching agents were added to the organic solution when the Cu or Pd seed layers were deposited on the TiSiN.

Substrate materials, with the exception of the sputter deposited Cu, were obtained from commercial sources. Selected specimens were made by sputter depositing Cu onto a Si wafer with a Denton Discovery 18 sputter deposition system. Deposition experiments were conducted with 1cm x 1cm square sections of substrate material. Copper substrates were prepared by briefly immersing them in a solution containing 5% sulfuric acid + 100g/L Na₂S₂O₈ to remove the oxide layer. The initial surface oxide layer on the TiSiN was removed by chemical etching and provided a reproducible starting surface. After the initial oxide layer was removed, the samples were immersed in the organic solution and displacement plated from 2 to 20 minutes.

The deposited Cu or Pd seed layers and Au film were analyzed with a Hitachi S-4700 field emission scanning electron microscope (SEM) equipped with an energy dispersive x-ray

spectrometer (EDS). Some samples were also analyzed with a SEM equipped with a FEI 620 dual beam focused ion beam (FIB) to examine the cross section of the deposited films. The adherence of the Au film and Cu or Pd seed layers was qualitatively tested by applying tape and rapidly removing it. Secondary electron (SE) images, EDS data, and adherence data were collected.

RESULTS

Gold Plating on Copper Substrates

Adherent, sub-micron sized Au particles were uniformly deposited on a printed circuit board Cu signal trace by deposition from an organic solution. Figure 1 illustrates the selectivity of the process. EDS analysis confirmed Au was deposited only on the Cu signal trace and not on the FR-4 substrate. Additionally, no apparent damage was caused by the organic solution to the FR-4 substrate, which is an important consideration if the process is used for microelectronics applications.

The use of additives or activating agents to the organic solution can modify the microstructure of the deposited Au, similar to Au plating in aqueous electrodeposition systems. Changes in the composition of the organic solution resulted in significant changes to the microstructure of the Au deposits. Figure 2 illustrates the different microstructures obtained by varying the relative amounts of the extractants and diluents comprising the organic solution. It was found that adherence became a problem, i.e., the Au film failed the tape test, when deposition times were longer than 20 minutes or if the organic solution composition was changed from the established optimum composition.

The thickness of the gold film deposited from an organic solution was approximately $0.2\mu\text{m}$ after a 20 minute deposition time. Thickness variations, determined from cross sections of the Au film, were minimal due to the self-regulating nature of immersion plating processes. Small voids occurred at the interface between the gold film and the sputter deposited Cu film (Figure 3). These voids may have been caused by small pinholes in the initial Au deposit which may have been present at highly anodic sites where significant Cu dissolution occurred.

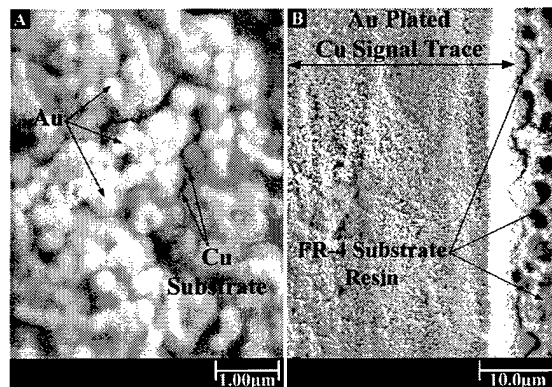


Figure 1. SE images magnifications showing particles deposited on a printed circuit board Cu trace; no Au was deposited on the FR-4 substrate.

taken at different sub-micron sized gold

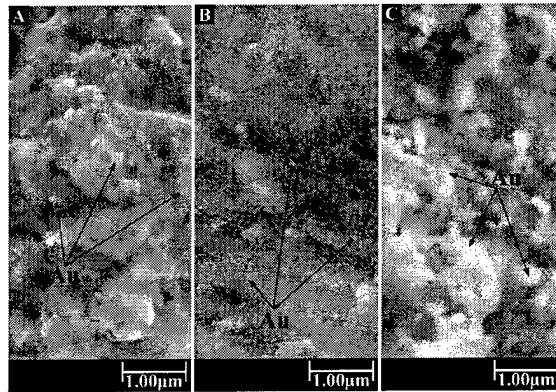


Figure 2. SE images illustrating different Au microstructures obtained by varying the organic solution composition; plated on Cu foil laminated FR-4.

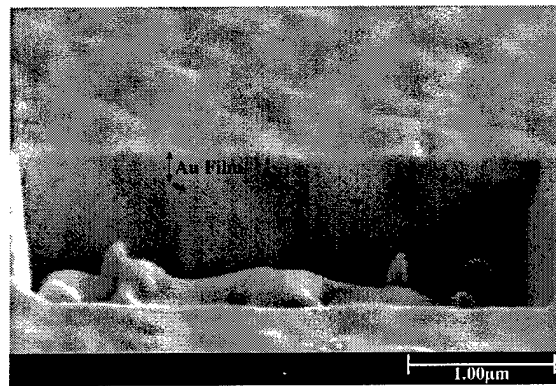


Figure 3. Cross sectional SE image of a Au film deposited from an organic solution onto a sputter deposited copper film with a silicon substrate.

The Au thickness was increased on some samples by electroplating from a non-cyanide Au plating bath. A thin Au film was initially deposited from an organic solution onto both sputter deposited Cu samples and Cu foil laminated FR-4 samples to act as a seed layer for electrolytic plating. The resulting electroplated Au on both the sputter deposited Cu samples and the copper foil laminated FR-4 samples, was highly reflective with minimal defects. The electroplated Au film was also adherent and passed the tape test. Therefore, it was demonstrated that Au deposited from an organic solution can act as a seed layer for electroplating Au.

Copper or Palladium Seeding on TiSiN

Figure 4 illustrates a Pd seeded TiSiN sample before and after electroless Cu plating. The seed layer was deposited from an organic solution containing an *in situ* etching agent to remove the native oxide layer from the surface of the TiSiN. After processing in the organic solution, a uniform distribution of Pd particles was deposited across the surface of the TiSiN.

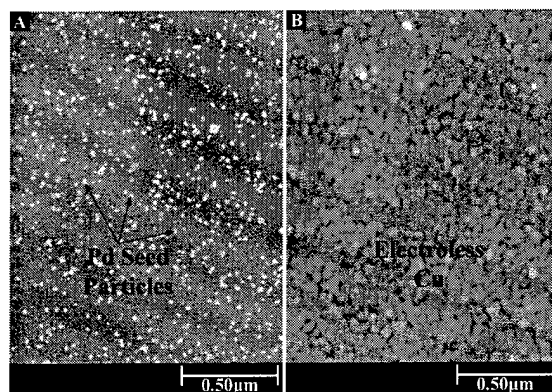


Figure 4. SE image of Pd seeded TiSiN a) before plating with electroless Cu and b) after plating with electroless copper.

This facilitated the use of a standard electroless Cu bath to deposit an adherent Cu film. Similar results were obtained when a Cu seed layer was deposited from an organic solution prior to electroless Cu deposition.

CONCLUSIONS

A method of selectively depositing Au films and Cu or Pd seed layers from an organic solution was demonstrated. Gold deposits with different microstructures could be obtained by varying the composition of the organic solution or by adding activating agents to the organic solution. Cross sectional SE images illustrated that a continuous Au film with minimal thickness variations was deposited. Additionally, results showed that a Au film could be electroplated from a non-cyanide Au plating bath after an initial Au film was deposited from an organic solution. Furthermore, it was demonstrated that uniform Cu or Pd seed layers could be deposited on TiSiN from an organic solution containing an *in situ* etching agent.

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