



## Electroless Deposition of Copper on Organic and Inorganic Substrates Using a Sn/Ag Catalyst

Nathan Fritz,\* Hyo-Chol Koo,\* Zachary Wilson, Erdal Uzunlar, Zhongsheng Wen, Xinyi Yeow, Sue Ann Bidstrup Allen, and Paul A. Kohl\*\*<sup>z</sup>

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100, USA

In this study, the electroless deposition of copper and silver was investigated on epoxy and silicon dioxide-based substrates. A cost-efficient, Sn/Ag catalyst was investigated as a replacement for the Sn/Pd catalyst currently used in board technology. The surface of the epoxy based polyhedral oligomeric silsesquioxane (POSS) films was modified by plasma and chemical etching for electroless activation without the creation of a roughened surface. The electroless copper deposited on the modified POSS surface exhibited excellent adhesion when annealed at 180°C in nitrogen for 90 min or at room temperature for 24 hr. Electroless copper deposition was also demonstrated on oxidized silicon wafers for through silicon via sidewall deposition.  
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Transistor scaling has improved the performance of integrated circuits, however, on-chip and off-chip interconnect have not kept pace in terms of bandwidth and energy per function. Mechanical anchoring is achieved on organic boards by roughening the surface. This degrades the electrical performance because it causes electron scattering.<sup>1</sup> Hence, there is a critical need to transition from high loss, roughened organic substrates to smooth inorganic substrates (e.g. silicon) using low dielectric constant insulators.<sup>1</sup> In addition, the elimination of the expensive palladium catalyst would reduce the cost of electroless copper plating.

In general, electroless metallization is cost-effective because it does not require vacuum equipment, such as sputtering, evaporation and chemical vapor deposition, or power supplies and seed layers, such as in electroplating. The electroless deposition of metal is based on the incorporation of a chemical reducing agent into the electrolyte. The electroless process is initiated by a catalyst on the insulating surface. Once the metal nuclei have been initiated, the process transitions into an autocatalytic process where the metal itself serves as the site for oxidation of the reducing agent. In addition to initiating the deposition of the first metal nuclei, the catalyst sites serve as the adhesive link between the depositing metal and the insulating surface.<sup>2,3</sup>

Thus, a key metric in achieving a reliable electroless film is the adhesion between the deposited metal copper and the dielectric material on the substrate. Copper is the metal of choice for interconnect in integrated circuits and electronic packages because it has low resistivity and high electromigration resistance. The interface between the insulator and metal usually has high interfacial energy resulting in poor adhesion strength between the catalyst and the deposited metal film. The surface of an epoxy-based FR-4 board is typically modified to enhance the adhesion of the catalyst and/or deposited metal to the insulating substrate. There are two general approaches taken: physical and chemical adhesion. The chemical method involves modification of the insulating surface producing chemical groups on the surface that can form covalent or ionic bonds between the insulating surface and the catalyst and/or electroless metal. Physical adhesion involves mechanical anchoring of the deposited metal to a roughened substrate where film delamination may occur through cohesive failure of the substrate in the region surrounding the roughened cavity which the metal has filled. Epoxy roughening is often achieved by the swell-and-etch process so as to induce anchoring of metal onto small cavities created in the insulator surface.<sup>4-8</sup> The swell-and-etch process currently used to activate phenolic novolac epoxy, found in printed wiring boards (PWB), provides an efficient method for creating a catalyst-friendly surface with excellent adhesion. Mechanical anchoring is a dominant form of adhesion.

The swell-and-etch process incorporates three steps.<sup>4-8</sup> First, the samples are placed in a swelling solvent which rearranges polar groups in the polymer into packets for etching. Second, the substrate is etched in a strong oxidizing agent, such as potassium permanganate, which preferentially attacks the ether-linkages within the packets to form pores or micro-cavities in the epoxy surface. Last, a neutralizing bath is used to remove the residual etchant from the substrate before catalyst deposition. Figure 1 shows the mechanism for this process which results in the creation of a micro-porous surface for electroless copper seeding and deposition.

Although the micro-cavities are responsible for the excellent anchoring of the metal to the substrate, they create the above-mentioned problem of electron surface scattering in the metal, especially at high frequency. High-frequency signals in the gigahertz range travel in the skin of the conductor due to the interaction with its own magnetic field.<sup>1</sup> The skin depth of the metal is given by Equation 1.<sup>9</sup>

$$\delta = \sqrt{\frac{2\rho}{\omega\mu}} \quad [1]$$

Where  $\delta$  is skin depth,  $\rho$  is the resistivity of the conductor,  $\omega$  is the angular frequency of current, and  $\mu$  is the magnetic permeability of the conductor. At frequencies above a few GHz, the skin depth is on the same order as the roughness in the metal surface produced by the swell-and-etch process. Thus, the surface roughness can cause excessive signal loss within the metal.<sup>9</sup> It would be desirable to shift from primarily mechanical adhesion to chemical adhesion between the electroless metal and a smooth insulator. This would enable the use of smooth surfaces, reducing electron scattering at the metal-insulator surface. Further, there is interest in lowering the dielectric constant (both permittivity and loss) below that of epoxy.

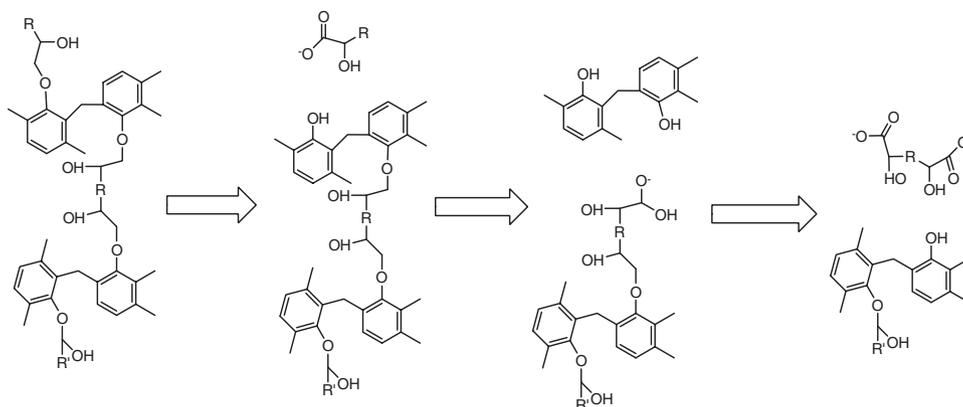
The critical parameters for the catalyst include the size, density and adhesion of the catalyst site or moiety. Once the insulating surface has been pretreated, it is important to form a high density of catalytic particles which are adherent to the substrate. This seeding of the surface with a catalytic metal activates the reducing agent in the electroless bath, initiating electroless metal deposition. In addition, the cost of the catalyst on the insulating surface is a critical parameter, especially for high-volume, cost-sensitive electronic components.

Tin sensitization followed by palladium activation is an important route to the formation of the catalyst on a variety of substrates, including epoxy boards. The surface is activated by immersion in an acidic Sn(II)-Pd(II) chloride solution. The catalytic surface is composed of palladium particles created through the reduction of Pd<sup>2+</sup> to Pd, and oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup>.<sup>10-12</sup> The Pd activation process uses a colloidal tin solution, originating from the presence of Sn(IV) formed during the reduction of Pd(II).<sup>13</sup> Chloride ions are important in stabilizing the palladium/tin colloid in solution and on the epoxy surface.<sup>13</sup>

\*Electrochemical Society Student Member.

\*\*Electrochemical Society Fellow.

<sup>z</sup>E-mail: kohl@gatech.edu



**Figure 1.** Mechanism of phenol-novolac etching prior to Sn-Pd activation.<sup>2</sup> The polymer is rearranged using a swelling agent. Packets of polymer are then etched at ether sites using a strong oxidizing agent.

Stannic chloride has been shown to form a stabilizing colloid around the Pd particles which assists in adhesion of the ionic colloid to the surface. The deposited copper film is adherent to the palladium catalyst. While there is no clear explanation of the mechanism or colloid adhesion, it is reasonable to assume that electrostatic interactions at acidic conditions contribute to ionic bonding of the colloid to the surface and hold the negatively charged colloids to the positively charged surface created during the swell-and-etch process.<sup>14</sup>

Since the adhesion of the electroless metal originates with the catalyst nano-particles on the surface, the adhesion strength for the deposited film should be related to the density and size of the catalyst site on the surface, and adhesive force of each catalyst particle to the substrate. Most research on improving the adhesion of the catalyst to the surface has focused on surface modification (i.e. control adhesion of the catalyst particles by changing interfacial energy) and optimizing the bath formulation to obtain better adhesion and higher nucleation density. This includes the addition of surfactants, surface modification by chemical or plasma treatment, and adsorption of adhesion promoters on the surface.<sup>15-17</sup>

Due to the high cost of palladium, non-palladium catalysts are of current interest for electroless copper on organic and inorganic substrates. However, the critical aspect of the process is how to form and adsorb catalytic particles on the substrate, where the particles have excellent uniformity and adhesion. Furthermore, the candidate catalyst should have a relatively positive reduction potential, with respect to the reduction potential of copper, so that it is easily reduced on the surface and remains stable in the presence of the electroless copper plating. That is, a corrosion couple is not setup where the catalyst is oxidized by copper ions in the bath. The traditional reducing agent in electroless copper has been formaldehyde whose oxidation can be catalyzed by many metals, including Au, Ag, Pt, Ru, Ni, and Co.<sup>18-20</sup> Among them, silver is an interesting choice because it is a relative noble with a reduction potential similar to Pd, and can be easily produced electrolessly. The price of silver is ca. 5% of that of palladium because of its plentiful abundance. Although previous silver catalyst baths generally have a short shelf-life, the unused metal in the catalyst bath can be easily reclaimed. Further, advances in silver catalyst technology may lead to catalyst baths with longer lifetimes.

Inorganic substrates have attracted interest as epoxy board replacements due to their low dielectric constant and low coefficient of thermal expansion (CTE). The electroless deposition of silver on glass has been used to form adherent, smooth layers, especially in the production of mirrors.<sup>2,3</sup> However, the approach has usually been to spray a solution onto the surface in thin layers. The process has generally not been used in the microelectronics industry because of the tendency of silver conductors to form dendrites under the influence of an electric field.

On the other hand, if silver proves to be an effective catalyst and bridge between the inorganic substrate and electroless copper, there is

little danger of forming silver dendrites because it is not present on the exterior surface of the copper line. In addition, there are applications where little adhesive strength between the metal and dielectric surface is needed, such as in the case of geometrically restricted regions of an electronic package. Via holes through boards or through silicon vias (TSV) sometimes have metallized side walls. The side wall metal forms the general shape of a cylinder with the contours following the micro-structure of the etched hole. It is difficult to extract the metal cylinder out from the via hole because of the mechanical constraints of the hole micro-structure. The metallized via hole can be later thickened to form a conductive path from one side of the substrate to the other, or the hole can be fully filled with metal, as in the case of a TSV.

This investigation focuses on improvements in the copper electroless process for both organic and inorganic substrates. Ultra-thin silver layers were investigated as catalytic sites for the subsequent electroless deposition of copper. The silver catalyst could replace the palladium catalyst, thus reducing the cost of the electroless copper process, as used in integrated circuits, packaging substrates, or printed circuit boards. Silver was selected for investigation due to its catalytic properties, cost, and adhesion to silicon oxide-based surfaces. The electroless bath properties were optimized to improve the deposition rate and adhesion. Three types of surfaces were investigated. First, a roughened FR-4 board was activated with silver catalyst and compared to the traditional Pd catalyzed epoxy surface. Second, an epoxy POSS coated FR-4 board was used where the goal is to improve the interaction between POSS surface and the electroless copper. POSS films have a high silicon oxide content which can be used to promote adhesion with the silver catalyst without roughening the surface. The smooth POSS surface should lead to smooth copper and lower signal loss in the interconnect. Finally, oxidized silicon wafers were used in the electroless deposition experiments in an effort to metallize TSVs for interposer applications.

## Experimental

An FR-4 board was used as a substrate for Ag and Cu electroless plating. Electroless films were then deposited onto oxidized silicon wafers and POSS coated surfaces. The Cu layer on a Cu-clad FR-4 board was etched in concentrated nitric acid, rinsed in DI water, and dried. The surface had a rough finish with pores created from the swell and etch process used to metallize the board. The deposition process consisted of Sn sensitization, Ag activation, and electroless plating. The samples were rinsed carefully in DI water between each step to avoid cross-contamination of the solutions during the process.

A similar process was used for the silicon wafers and POSS-coated samples. Silicon dioxide was grown on silicon wafers followed by the electroless deposition of copper. Once the electroless bath was optimized, the electroless copper process was used to deposit metal on the sidewalls of the TSVs.

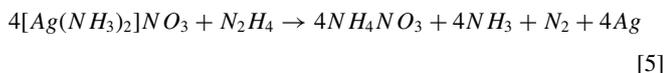
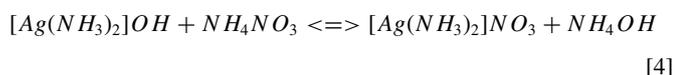
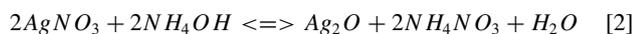


**Table I. Bath formulations for electroless silver.**

	Water	AgNO <sub>3</sub>	NH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub>	NH <sub>4</sub> OH	Triton X-100	H <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S	Average Plating Rate
Ag-A	180 mL	0.2 g	10 g	15 mL	0.2 mL	0.25 g	40 nm/min
Ag-B	180 mL	0.4 g	10 g	15 mL	0.2 mL	0.25 g	20 nm/min
Ag-C	180 mL	0.7 g	10 g	20 mL	0.2 mL	0.25 g	10 nm/min

were seen when the sample was transferred from the silver seeding bath into the electroless deposition bath after a 30 second DI water rinse.

Three electroless plating baths with different deposition rates were investigated for copper and silver, as described in Tables I–II. The deposition rate of the plating baths was changed by adjusting the concentration of the components. The concentration of the base (i.e. pH) is important because hydroxide is consumed in oxidizing the reducing agent. The concentration of metal ions is also important in the electrochemical reaction. Equations 2 to 5 show the reactions for electroless silver deposition with hydrazine as the reducing agent.<sup>22</sup> In the reaction, silver nitrate and ammonium hydroxide form the silver ammonia nitrate, which is consumed in the deposition reaction, Eq. 5. By controlling the concentration of these silver nitrate and ammonium hydroxide, the deposition rate of the bath can be controlled through the equilibrium reactions, Eq. 2 to 4.

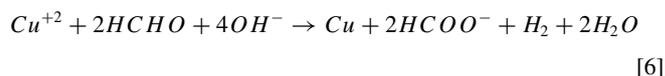


The deposition rate generally has a strong influence on the density, grain size, and surface texture of the deposited metal. The deposition rate of the metal can also affect the adhesion of the metal to the surface. If the metal catalyst is the anchor for adhesion of the deposited layer to the surface, then slow plating with island growth, where a high density of catalyst sites which evolve into a full surface film, is preferred. If the plating rate is too fast, a sufficient number of catalyst sites may not be used which leads to poor adhesion.

The electroless baths shown in Tables I–II had limited shelf life once the hydrazine sulfate was added. The baths were active for several hours before spontaneous oxidation of the reducing agent and metal ion reduction occurred. The slowest deposition rate silver bath, Ag-A, produced an 800 nm layer of silver in 20 min. The medium speed silver bath, Ag-B, produced the same quantity of metal in half the time, ca. 10 min. The fastest bath, Ag-C, was about twice the rate of Ag-B. If the catalyst seed layer was defective or deactivated, a slower overall deposition rate occurred.

The electroless copper baths shown in Table II were operated at 55°C. The overall reaction for copper plating is shown in Equation 6.

Copper ions and base are consumed allowing for a similar control of the deposition rate by changing the concentrations.<sup>4</sup>



The average deposition rates for Cu-A, Cu-B, and Cu-C were 60, 30, and 15 nm/min, respectively.

The A and C bath for copper and silver were tested on the FR-4 board after silver activation. The films deposited for 45 min had a uniform thickness and matte finish, suggesting a somewhat rough surface. The speed of the bath (A and C) produced the same finish and adhesion for silver and copper on the FR-4 board.

The adhesion of the electroless films to the substrates was investigated using a traditional tape test, ASTM D3359. A cross-hatch of 1 mm squares was scribed into the sample to test the peel strength at the corners of the cross-hatched pattern. The film adhesion was found to be excellent with no film peel-up or damage of the electrodeposited film. The FR-4 surface roughness before deposition was found to be 200 to 500 nm (root mean square value of peaks-to-valleys). Since the Sn/Ag catalyst with electroless plating passed the tape-test, similar to the Sn/Pd catalyst, we conclude that the Sn/Ag is an effective and adherent catalyst for the electroless deposition on FR-4 boards.

The electroless deposition was then tested on epoxy-cyclohexyl POSS coated substrates. A POSS film was spin coated onto FR-4 boards, prepared as described above. The films were soft baked for 5 min followed by exposure to 365 nm radiation at a dose of 250 mJ/cm<sup>2</sup>. The POSS film formed a smooth, hydrophobic surface. The organic component of the POSS likely contributed to its hydrophobic nature. An oxygen plasma was used to change the surface properties of the POSS. The reactive ion etch conditions include 310 mTorr pressure and 100 W power for 1 min. The reactive ion etch likely removed the organic component of the POSS at the surface leaving a predominantly silicon oxide surface. The POSS surface changed from hydrophobic with a water contact angle of 88° to hydrophilic with a water contact angle of 13°. The effect of oxygen plasma etching on the electroless seeding was investigated using the silver activation and plating process. The plasma etched sample showed uniform deposition over the entire sample whereas the unetched POSS surfaces showed little or no deposition. It was found that the silver bath with the slowest deposition rate, Ag-A, produced films with the highest adhesion. The samples produced using the fastest plating bath, Ag-C did not pass the tape test.

In an effort to improve the metal adhesion to the POSS surface, a variety of cleaning steps were investigated. It is possible that organic material remained on the POSS surface after oxygen plasma treatment. Several different cleaning baths were tested including (i)

**Table II. Bath formulations for electroless copper.**

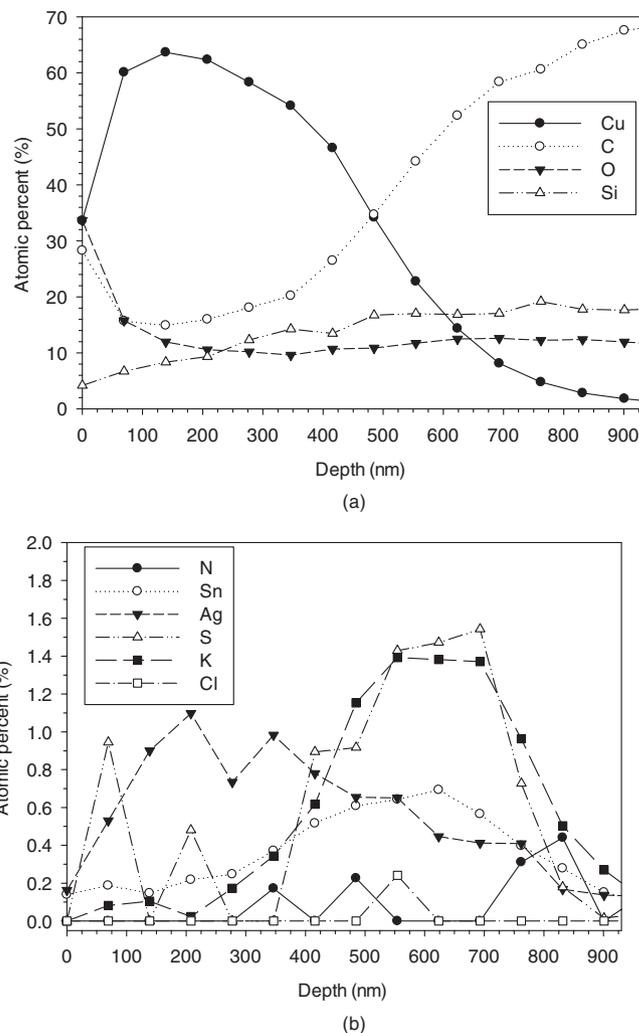
	Water	CuSO <sub>4</sub> * 5H <sub>2</sub> O	EDTA	KOH	Triton X-100	HCHO	Average Plating Rate
Cu-A	200 mL	0.25 g	0.63 g	0.86 g	0.2 mL	0.58 g	60 nm/min
Cu-B	200 mL	0.75 g	1.89 g	2.58 g	0.2 mL	0.58 g	30 nm/min
Cu-C	200 mL	1.26 g	3.16 g	4.3 g	0.2 mL	0.58 g	15 nm/min

3 vol% sulfuric acid bath, (ii) 1:1:2 vol. ratio of acetone, isopropyl alcohol, and water, and (iii) citric acid and peroxide bath. These baths generally improved the adhesion of the electroless metal, especially if the samples were left in the cleaning solution for extended periods of time, e.g. 50 min. However, none of these cleaning solutions was fully effective at providing complete adhesion over the entire POSS surface. All samples were tin sensitized for 30 min, followed by silver activation for 1 min. XPS was used to investigate the surface composition, in atomic percent, after activation but before electroless plating. The surface roughness was found to be 30 to 50 nm, which was about 10% of the surface roughness on the FR-4 surface. Thus, the etching processes used to create a suitable POSS surface did not roughen the surface in the same manner as used to create mechanical adhesion to the epoxy board. The untreated POSS surface was found to be composed of 68% carbon, 11% silicon, and 23% oxygen. The etched/catalyzed POSS surface was composed of 32% carbon, 25% silicon, and 38% oxygen. This decrease in carbon content on the surface was due to the plasma treatment. The surface also contained 3% Ag (zero valence state) and 1% Sn(IV) with no Sn(II) observed. This confirms that the Sn(II) was oxidized to Sn(IV) during the Ag seeding process. Any remaining Sn(II) could have been air oxidized by air after the silver process was complete.

Based on the three cleaning baths described above, it was concluded that the surface contaminants responsible for blocking adhesion were not simply adsorbed species on the surface since these baths did not dissolve away the contaminants. Thus, a strong oxidant was chosen in an attempt to improve the chemical bonding of the metal film to the POSS surface. Previously, dichromate has been used to oxidize surface films and etch epoxy boards to improve the chemical bonding of electroless metal to the surface.<sup>21</sup> The chromic acid etch investigated here consisted of 40 mL DI water, 75 mL sulfuric acid, and 1.3 g potassium dichromate, and was maintained at 90°C. The chromic acid etch led to the deposition of an adherent, electroless copper layer on the POSS substrate; however, the results were sometimes difficult to reproduce. It was found that a similar solution without the potassium dichromate, containing only the sulfuric acid (i.e. 40 mL DI water, and 75 mL sulfuric acid, at 90°C) led to more reproducible adhesion results. The adhesion of the copper film on the activated POSS surface was investigated as a function of post-plating aging or annealing conditions.

Freshly made copper samples using plasma etching followed by hot sulfuric acid cleaning, Ag/Sn activation, and electroless copper plating were allowed to sit at room temperature or annealed at 180°C in a nitrogen oven. It was found that if the POSS samples were plasma etched immediately before the sulfuric acid treatment, excellent adhesion was obtained after sitting for one day at room temperature or 90 min at 180°C. If there was a time lag between the plasma etching and sulfuric acid treatment, then it required more than a week at room temperature to obtain excellent adhesion. However, it is clear that the samples allowed to sit at room temperature for an extended period or annealed at 180°C showed dramatically improved adhesion compared to samples that were not annealed or allowed to sit at room temperature for a short period of time.

XPS surface analysis was used to examine the compositional changes at the copper/catalyst/substrate interface. The copper was deposited onto the plasma/sulfuric acid treated POSS surfaces followed by Sn/Ag activation. Copper was deposited using the Cu-B bath at 55°C for 3 to 5 min. One sample was examined directly after copper plating, Figure 4. A second sample was annealed at 180°C for 90 min in nitrogen, Figure 5. The annealed sample did show a dramatic improvement in adhesion compared to the unannealed sample. The depth scale in these experiments was obtained by measuring the thickness of the copper film by surface profilometry. The copper thickness, 4850 Å for the unannealed sample and 4700 Å for the annealed, are correlated with the sputtering etching time values from the XPS experiments on the x-axis of the plots in Figures 4 and 5. The etching rates were assumed to be the same for each layer in the samples. The copper-POSS interface was located at the intersection of the Cu and C signals in Figure 4a and Figure 5a.

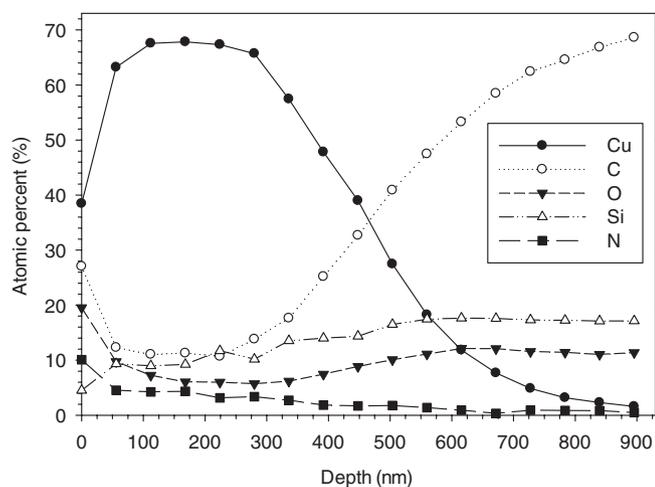


**Figure 4.** XPS depth profile of unannealed Cu/POSS sample. a) Major constituents in unannealed sample. b) Minor constituents in unannealed sample.

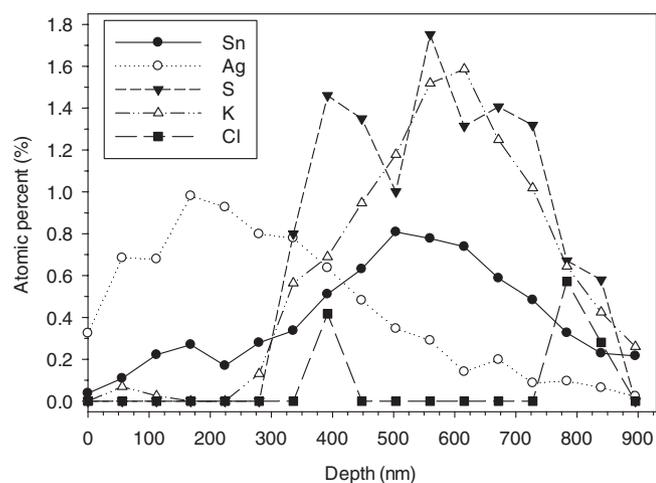
The XPS depth profile for the unannealed sample, Fig. 4a, shows a copper film on the surface of the sample and a transition region at the interface with the POSS at approximately 480 nm. The distribution of the N, Sn, Ag, S, K, and Cl are shown in Fig. 4b. It is clear that there is Sn, S, K, and Cl at the copper/POSS interface. The S and K most likely result from neutralization of the sulfuric acid with KOH in the electroless copper bath. The presence of Sn and Cl also mark the transition region from the substrate to the copper. Ag is interesting because it not only exists at the POSS/Cu interface, but a small amount also dissolves in the copper film. There is little Ag at the copper/air interface.

Figure 5a shows that the profile of the major constituents after annealing the sample at 180°C for 90 min in nitrogen. The sharpness of the transition region from Cu to Si/C is essentially the same as the unannealed sample, Fig. 4a. The distribution of the minor constituents, Fig. 5b, is also similar for the two samples. The presence and location of Sn, S, K, and Cl show that the effect of annealing, and the resulting adhesion improvement, did not come from a gross redistribution of the species at the Cu/POSS interface. It is possible that copper grain growth, and/or dehydration could be responsible for the adhesion improvement.

The dielectric constant, relative permittivity, of the POSS film was measured for use as an interlevel dielectric in board buildup technology to be used with electroless metallization. For an interconnect, the dielectric loss becomes increasingly important at high frequency



(a)

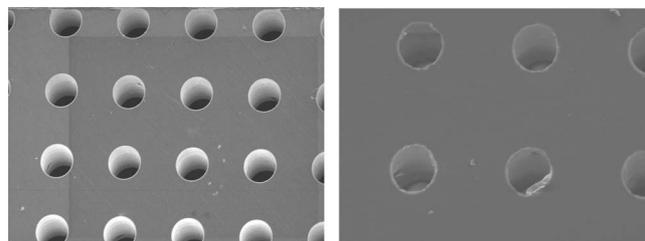


(b)

**Figure 5.** XPS depth profile of annealed Cu/POSS sample. a) Major constituents in annealed sample. b) Minor constituents in annealed sample.

because the loss scales linearly with frequency above 10 GHz.<sup>23</sup> The optimum metal-insulator configuration includes a smooth POSS/metal interface with a low permittivity and loss insulator. Capacitance and conductance values were measured using parallel plate capacitors at 10 kHz and 100 kHz using a Hewlett Packard 4236 LCR meter on a Karl Suss probe station. No correction was needed for fringing fields due to the high capacitor area-to-thickness ratio (>1000). The dielectric constant of the POSS film depended on the shape of the silica cage, and free volume created through the cage-to-cage cross-linking. The relative permittivity of the POSS film was found to be 3.03. The loss tangent was 0.019 at 100 kHz. The relative permittivity is well below the value of dense silicon dioxide,  $\epsilon_r = 3.9$ ,<sup>24</sup> due to the free volume in the POSS cage structure. Typical FR-4 materials have a dielectric constant between 4.2 and 5.5.<sup>23</sup> The combination of a low dielectric constant and adhesion of electroless copper on a smooth POSS surface provides an improved, low-loss alternative to current epoxy board technology.

The electroless deposition of copper directly on a native silicon oxide layer was also attempted. There are advantages to electrolessly depositing copper on an oxidized wafer, especially in cases such as TSVs and other applications. The deposition of metal on the sidewalls of high aspect ratio TSVs is difficult by sputtering or evaporation because of the line-of-sight nature of those processes. The ability to



**Figure 6.** SEMs of electroless copper deposited on the sidewalls of 120  $\mu\text{m}$  diameter TSVs. The copper on the top surface was removed by polishing.

metalize sidewalls can improve processing for chip packaging and microelectromechanical devices.

The electroless Cu deposition on silicon dioxide surfaces and in a TSV-containing wafer involved the same four steps as used above: (i) cleaning, (ii) Sn sensitization, (iii) Ag activation, and (iv) electroless Cu deposition. The cleaning solution used was 3 vol%  $\text{H}_2\text{SO}_4$  in DI water. The tin sensitization solution and silver activation baths were the same as discussed above. The Cu-B bath was used for copper electroless plating. It was found that baths with higher deposition rates, e.g. Cu-C, produced hydrogen gas at too high of a rate causing poor film uniformity. The slow deposition rate of the Cu-A bath was inconsistent and produced non-uniform films on the silicon oxide surface.

A 520  $\mu\text{m}$  thick wafer containing an array of 120  $\mu\text{m}$  diameter TSVs was fabricated. After fabrication, plasma enhanced vapor deposition was used to deposit a 500 nm thick silicon dioxide layer. The sample was cleaned for 10 min on an inclined plane in the bath for better flow into the vias. The sample was rinsed and placed in the Sn sensitizer for 15 min. It was then placed in the Ag activation solution for 1 min followed by copper deposition in the Cu-B solution for 3 min. The 500 nm thick Cu film was uniform and had specular reflectance. The inside of the TSVs were coated with copper, as shown in Figure 6. The copper was polished from the front and back surfaces to better show the metallization of the TSVs. The copper film had modest adhesion to the top of the surface of the substrate, however, the adhesion inside the TSVs was excellent due to the mechanical anchoring, as described above. The adhesion was significantly improved after sitting at room temperature for 24 hr, consistent with the results described above. Thus, the Sn/Ag activation step was effective for activating the silicon dioxide surface as well as producing an adherent coating to the substrate and TSVs.

## Conclusions

An improved electroless deposition process for silver and copper was developed. The Sn/Pd activation was replaced by a cost-efficient Sn/Ag catalyst. The copper and silver films were adherent to the roughened epoxy boards, POSS coated surfaces, and silicon dioxide. Silver deposition on POSS showed poor adhesion; however, the adhesion of copper on smooth POSS was dramatically improved by the addition of oxygen plasma cleaning and acid etching steps. The electrical permittivity and loss at 100 kHz for a POSS film was 3.03 and 0.019, respectively. Electroless copper deposition was used to plate a thin copper film on the oxidized sidewalls of TSVs.

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