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.

The swell-and-etch process incorporates three steps.4,5 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.1 The skin depth of the metal is given by Equation 1.

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

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.9 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 is modified, 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.4 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 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.

© 2012 The Electrochemical Society. [DOI: 10.1149/2.09206jes] All rights reserved.

Manuscript submitted December 12, 2011; revised manuscript received April 2, 2012. Published April 13, 2012.
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 charge surface created during the swell-and-etch process.14

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.15–17

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.18–20 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.3,4 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.

![Figure 1. Mechanism of phenol-novolac etching prior to Sn-Pd activation](image-url)
POSS films were formulated using epoxycyclohexyl POSS cage mixture (Hybrid Plastics Inc.). POSS consists of a silicon oxide cage structure with an epoxycyclohexyl group on each corner, \((C_9H_{13}O_2)\_n(SiO_{1.5})\_n\) where \(n = 8, 10, \) or 12. An example of the 8 cornered POSS functionalized with an epoxy group is shown in Figure 2. POSS film formulations and processing were completed as described previously.\(^{21}\) The POSS samples were spin-coated onto the FR-4 boards and then soft-baked on a hotplate at 85°C for 5 min to remove the solvent from the polymer film. A 1 kW Hg-Xe lamp with a broad band filter (350 to 380 nm wavelength) was used for exposure with an optimal dose of 250 mJ/cm\(^2\).

The mechanical and photolithographic properties of POSS for use in the fabrication of microstructures and microelectromechanical systems were previously reported.\(^{21}\) However additional properties and processes, such as the dielectric properties and metallization of the POSS film, were necessary for the films to be used in substrate technologies.\(^{21}\) In this study, the electrical permittivity of the POSS film was measured for use in board-level packaging as a dielectric. The dielectric measurements were performed by fabricating parallel-plate capacitors. The bottom plate of the capacitors was a full-surface metal film of sputtered Ti/Au/Ti (300 Å/4000 Å/300 Å) using the Unifilm sputtering system. A 5 μm POSS film was processed on top of the lower electrode. The top electrode consisting of Ti/Au/Ti (300 Å/4000 Å/300 Å) was patterned by photolithography using a resist into 2 mm diameter circular pads. The metal film in field was wet etched and the resist was removed. Capacitance and conductance were measured at 10 kHz and 100 kHz using a Hewlett Packard 4236 LCR meter on a Karl Suss probe station.

Electroless copper plating on POSS required surface modification of the film to promote deposition and metal adhesion. The POSS film was reactive ion etched in an oxygen plasma at 310 mTorr pressure and 100 W power for 1 min to remove a fraction of the organic content near the surface before electroless treatment. Several cleaning steps were also investigated on the POSS surfaces prior to the Sn sensitization to ensure the surfaces were clean and oxidized.

Substrates were characterized with a profilometer to determine surface roughness. Surface hydrophobicity was tested using water contact angle measurements with a Rame-Hart CA goniometer. A Thermo K-alpha XPS was used to analyze the metal seeding of the surface. Metalization was examined for plating quality and adhesion. The bath concentration and time were adjusted to improve the metal quality. The deposited copper film thickness was measured by patterning and etching a hole into the Cu film and measuring step change with a profilometer. The metal was cross hatched and tape tested, according to ASTM D3359, for adhesion. Based on the ASTM five-point scale for adhesion, this study described the film adhesion being poor if the ASTM resulted in a 1 or 2, modest for 3 or 4, and excellent or passing for a 5.

Results and Discussion

There are two goals in this study. The first is to replace the palladium catalyst used in electroless copper deposition with a less expensive catalyst. The second goal is to achieve acceptable adhesion of the catalyst and electroless copper metal on smooth silicon dioxide surfaces, or surfaces which are primarily composed of silicon dioxide (e.g. POSS). The two goals are simultaneously addressed because the catalyst plays a critical role in achieving adhesion of the metal film to the insulating surface. Thus, the development of a suitable catalyst, such as for the oxidation of formaldehyde in electroless copper, with excellent adhesion strength to the surface is the central topic of this study. Silver was chosen as the catalyst metal of choice since it can be electrolessly deposited on glass surfaces with good adhesion, and is a Group IB metal (as is copper) which should provide a catalytic surface for electroless copper.

Since the Sn(IV) colloid is an integral part of the formation and adhesion of the palladium catalyst to surfaces, a similar tin-colloid route was chosen with silver. A Sn/Ag catalyst seeding was tested on the organic and inorganic substrates, as described in the Experimental Section, for potential use on epoxy-based boards and silicon dioxide containing surfaces.

The electroless deposition was first tested on an FR-4 board and POSS coated FR-4 board in an attempt to determine whether the Sn/Ag catalyst can be used to replace the Sn/Pd catalyst on organic and organic/inorganic hybrid surfaces. The FR-4 board was prepared for electroless deposition by etching the copper from a copper-clad board with nitric acid. One sample was seeded for electroless plating directly after stripping the copper, and a second sample was spin-coated with POSS on the roughened epoxy surface, which will be discussed in later in this section. The seeding process consisted of the two-step activation process with the first step being tin sensitization followed by silver seeding. The tin bath served to seed the POSS surface with tin ions that anchor the silver-tin colloid to the POSS surface. The tin sensitization step consisted of a 30 min immersion in a bath consisting of 180 mL of deionized (DI) water, 2.4 g of tin (II) chloride dihydrate, and 2 mL of hydrochloric acid. Other concentrations and immersion times were also investigated. While some deposition of the catalyst, as measured by the subsequent deposition of electroless copper, occurred with the other catalyst formulations, this formulation and immersion time were found to give the best coverage and most reproducible results.

The Sn(II) colloid on the FR-4 surface was used to reduce Ag(I) so as to form adherent silver islands on the surface to serve as the catalyst for electroless copper. After immersion for 30 min in the tin chloride bath, the sample was rinsed with DI water and immersed in the silver nitrate bath. Silver/tin catalyst colloids are formed through the oxidation of Sn(II) ions (producing Sn(IV)) and reduction of the silver nitrate bath. Tin sensitization step consisted of a 30 min immersion in a bath consisting of 180 mL of deionized (DI) water, 0.7 g of Sn(II) chloride dihydrate, and 2 mL of hydrochloric acid. Other concentrations and immersion times were also investigated. While some deposition of the catalyst, as measured by the subsequent deposition of electroless copper, occurred with the other catalyst formulations, this formulation and immersion time were found to give the best coverage and most reproducible results.

The Sn/Pd catalyst can be used to replace the Sn/Pd catalyst on organic and inorganic surfaces, except for potential use on epoxy-based boards and silicon dioxide containing surfaces.
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.25 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.

$$2\text{AgNO}_3 + 2\text{NH}_4\text{OH} \rightleftharpoons \text{Ag}_2\text{O} + 2\text{NH}_4\text{NO}_3 + \text{H}_2\text{O} \quad [2]$$

$$\text{Ag}_2\text{O} + 4\text{NH}_4\text{OH} \rightleftharpoons 2\text{[Ag(NH}_3\text{)_2]}\text{OH} + 3\text{H}_2\text{O} \quad [3]$$

$$[\text{Ag(NH}_3\text{)_2}]\text{OH} + \text{NH}_3\text{NO}_3 \rightleftharpoons [\text{Ag(NH}_3\text{)_2}]\text{O} + \text{NH}_3\text{H}_2\text{O} \quad [4]$$

$$4[\text{Ag(NH}_3\text{)_2}]\text{O} + \text{N}_2\text{H}_4 \rightarrow 4\text{NH}_4\text{NO}_3 + 4\text{NH}_3 + \text{N}_2 + 4\text{Ag} \quad [5]$$

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.

$$\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu} + 2\text{HCOO}^- + \text{H}_2 + 2\text{H}_2\text{O} \quad [6]$$

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).

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 epoxycyclohexyl 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/cm². 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 lowest 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>
<thead>
<tr>
<th>Table I. Bath formulations for electroless silver.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Ag-A</td>
</tr>
<tr>
<td>Ag-B</td>
</tr>
<tr>
<td>Ag-C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table II. Bath formulations for electroless copper.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Cu-A</td>
</tr>
<tr>
<td>Cu-B</td>
</tr>
<tr>
<td>Cu-C</td>
</tr>
</tbody>
</table>
3 vol% sulfuric acid bath, (ii) 1:1:2 vol. ratio of acetone, isopropanol 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 on the epoxy boards. The etched 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.\(^\text{21}\) 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 surface.\(^\text{21}\) 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 on the epoxy boards. The etched 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.

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.

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.
dielectric constant between 4.2 and 5.5. The combination of a low volume in the POSS cage structure. Typical FR-4 materials have a because of the line-of-sight nature of those processes. The ability to of high aspect ratio TSVs is difficult by sputtering or evaporation oxide layer was also attempted. There are advantages to electrolessly POSS surface provides an improved, low-loss alternative to current dielectric constant and adhesion of electroless copper on a smooth epoxy board technology.

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% H2SO4 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 μm thick wafer containing an array of 120 μm 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 metalization 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 replaced the 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.

References