Metal-to-glass interfaces commonly encountered in electronics and surface finishing applications are prone to failure due to intrinsically weak interfacial adhesion. In the present work, an ‘all-wet’ process (utilizing solution-phase process steps) is developed for depositing nucleation- and adhesion-promoting layers that enhance the interfacial adhesion between glass substrates and electrochemically-deposited copper (Cu) films. Adhesion between thick (>10 μm) Cu films and the underlying glass substrates is facilitated by an interfacial Pd-TiO₂ layer deposited using solution-phase processes. Additionally, the proposed interfacial engineering utilizes self-assembled monolayers to functionalize the glass substrate, thereby improving surface wettability during Pd-TiO₂ deposition. Resulting Pd-TiO₂ deposits catalyze direct electroless plating of thin Cu seed layers, which enable subsequent electrodeposition of thick (>10 μm) Cu coatings. The present work provides a viable route for high-throughput, cost-effective metallization of glass and ceramic surfaces for electronics and surface finishing applications.

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The interfacial adhesion between metallic films and insulating substrates, e.g., glass, is intrinsically poor. This is a major roadblock in numerous electronics applications, particularly the manufacturing of printed circuit boards (PCBs) and integrated circuits (ICs).

Interfacial adhesion between metallic thin films deposited on glass substrates can be improved using functionalized polymers or self-assembled monolayers (SAMs). SAMs provide interfacial ‘anchor- ing’ by chemically bonding to the substrate (SiO₂) as well as the deposited metal film. While SAMs have been shown to enable deposition of sub-micron scale, adherent Cu films on SiO₂, they do not provide adequate interfacial strength to enable thick (>10 μm) Cu coatings on glass. The Cu-to-SiO₂ interfacial adhesion may also be improved by utilizing metallic adhesion layers or mixed-metal oxides. Metallic adhesion promoters, e.g., titanium or titanium-nitride, are deposited using ‘dry’ methods such as physical vapor deposition (PVD). ‘Dry’ techniques are not desirable for high-volume manufacturing given their low throughput and high cost of ownership. On the other hand, mixed-metal oxides maybe deposited using sol-gel methods in which a metal alkoxide is co-deposited with a catalytic metal salt in a polar-organic solvent, resulting in a mixed-metal oxide adhesion layer with catalytic activity for electroless plating. The methods by which the sol-gel catalyst may be deposited include dip-coating, printing, spin-coating, or brushing.

In the present work, we demonstrate an ‘all-wet’ process for depositing adhesion-promoting layers that enhance the interfacial adhesion between glass substrates and electroless-deposited copper (Cu) films. Adhesion between electrochemically-deposited thick (>10 μm) Cu coatings and the underlying glass substrates is facilitated by an interfacial Pd-TiO₂ layer fabricated using solution-phase processing. Our interfacial engineering approach utilizes self-assembled monolayers (SAMs) to functionalize the glass substrates before applying the Pd-TiO₂ coating. The SAM layer improves surface wettability during Pd-TiO₂ deposition as shown below. Pd-TiO₂ deposits effectively catalyze electroless plating of thin Cu seed layers, which enable subsequent electrodeposition of thick (>10 μm) Cu coatings.

**Experimental**

This section describes the materials and methods used for cleaning the glass slides, functionalizing them with SAMs, depositing Pd-TiO₂ adhesion-promoting layers, depositing electroless and electroplated Cu films and characterizing their adhesion.

**Glass slide cleaning** — Eagle XG glass slides (alkaline earth boroaluminosilicate) manufactured by Corning were employed as substrates. Glass slides were cleaned using a protocol described by Cras. First, glass slides were rinsed with deionized (DI) water and then dried using a stream of nitrogen. Next, the glass slides were submerged in a 1:1 volume ratio of concentrated hydrochloric acid and methanol for 30 min followed by a DI rinse. The glass slides were then submerged in concentrated sulfuric acid for 30 min followed by a thorough DI rinse and drying under nitrogen.

**Silanization of cleaned glass surfaces** — After cleaning, glass slides were immersed in a 5 mM solution of APTES (3-aminopropyltriethoxysilane, Acros Organics) in toluene solvent at 25 °C for 60 min. Slides were then rinsed with toluene, then with ethanol, and finally with DI water before drying under nitrogen.

**Deposition of Pd-TiO₂ ink** — An ink solution containing 1.1 mM titanium (IV) butoxide (Acros) and 1.1 mM PdCl₂ in n-butanol solvent was prepared. The ink was dropped on the glass surface via a transfer pipette. Ink volume dropped was approximately 0.1 mL per 1 cm² of the glass surface area. The ink was then dried in air at 130 °C for 15 min in a Thermo Scientific Heraeus OGS 60 oven. Next, the dried ink was sintered in air at 450 °C in a Hoskins electric tube furnace for 30 min. After cool down, samples were immersed in a 2 M sulfuric acid solution for 2 min followed by a DI rinse. Finally, samples were immersed in a reductant solution of 0.5 mM dimethylamine borane (DMAB) for 2 min and then rinsed with DI water.

We note that our aforementioned stepwise procedure of applying the Pd-TiO₂ adhesion-promoting layer differs from the sol-gel technique described elsewhere. First, our procedure does not utilize chemical hydrolysis of the titanium butoxide in solution but rather relies on its reaction with moisture in air to induce oxidation (shown below). The DMAB reductant treatment then facilitates chemical reduction of the oxidized Pd to metallic Pd catalyst. Furthermore, we utilize dilute inks that enable thinner Pd-TiO₂ adhesion layers to be formed. Finally, our ink application procedure hinges on utilizing a SAM-terminated glass surface, which improves surface wettability and enables uniform Pd-TiO₂ deposition as also discussed below.

**Electroless Cu deposition** — Proprietary electroless Cu plating chemistry from Atotech, USA was employed. This alkaline

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electroless plating solution consisted of the following components: copper sulfate, tartrate-based complexing agent and formaldehyde-based reducing agent. The electroless Cu deposition process was operated at 35°C. After electroless plating, samples were rinsed with DI water and then annealed in a Hoskins electric tube furnace under flowing argon at 400°C for 60 min.

**Cu electroplating.**—Following electroless seed layer deposition, samples were electroplated with Cu using a high-throw plating solution described by Dini and Snyder. The composition of the bath was 100 g/L CuSO4·5H2O (Fisher Scientific), 270 g/L H2SO4 (Fisher Scientific), and 0.1 g/L NaCl. A large area (70 cm²) Cu foil counter electrode was used, which was placed at a distance of 10 cm from the working electrode. Samples were electroplated at a current density of 10 mA/cm².

**Materials characterization.**—The scotch tape test was used to qualitatively assess the adhesion of electrochemically-deposited Cu on glass with or without the Pd-TiO2 adhesion promoter layer. Scotch Matte Finish Magic tape from 3 M was used for all tape tests. During tape testing, the applied scotch tape was removed at roughly a 90° angle relative to the sample. In some cases, prior to applying the tape, the Cu was scratched in perpendicular directions using a diamond-tip scriber. For quantitative adhesion testing, a 90° peel strength test was performed at a peel rate of 50 mm/min and the force required to peel unit width of the plated Cu was recorded. X-ray photoelectron spectroscopy (XPS) was performed using a PHI Versaprobe 5000 Scanning X-ray photoelectron spectrometer with a monochromatic AlKα anode X-ray source. Surface roughness of deposited Pd-TiO2 layer was measured using a profilometer (KLA-Tencor P-6 Stylus) and surface morphology was imaged using a high-resolution optical microscope (Leica DM2500M).

**Results and Discussion**

Figure 1 is a process flow diagram detailing the sequence of glass surface preparation, nucleation and adhesion promoter deposition, and Cu metallization used in the present work. Fig. 1a shows a cleaned, hydroxyl-terminated glass surface, which promotes the deposition of 3-aminopropyltriethoxysilane (APTES) self-assembled monolayer (SAM) using procedure described above. APTES self-assembly is mediated by a condensation reaction that provides amine-terminated glass as shown in Fig. 1b. APTES deposition plays an important role in improving the surface wettability, as discussed below.

Ink containing titanium butoxide and palladium chloride dissolved in n-butanol is then applied to the amine-terminated glass surface, following procedure described in the Experimental section above. Upon drying at 130°C for 15 min, the ink leaves a composite mixture of PdCl2-TiO2 on the glass surface (Fig. 1c). A prolonged (30 min), high temperature (450°C) sintering step in air converts the PdCl2 to PdO-TiO2; (e) PdO is reduced to Pd via reaction with DMAB; (f) Electroless Cu seed layer deposition catalyzed by Pd; and (g) Cu electroplating on electroless seed layer to achieve functional thickness (>10 μm).

**Wettability of APTES-modified glass surfaces.**—Fig. 2 demonstrates the improved wettability of butanol ink on an APTES-modified glass slide. A 10 μL volume of ink (composition described in Experimental section above) was dropped onto the surface of APTES-modified glass slide. The droplet spread, which in a qualitative measurement of the surface wettability, was measured and compared to a glass slide without APTES termination. In the case of APTES-modified glass (Fig. 2a), the ink droplet spreads out nearly covering the entire surface of the glass indicating a low contact angle and good wettability.
In absence of APTES (Fig. 2b), the ink droplet shows a higher contact angle and thus poor surface wetting. The improved wettability of the glass surface with APTES-termination is critical for the subsequent uniform deposition of the Pd-TiO$_2$ adhesion-promoting layer.

**Pd-TiO$_2$ deposition mechanism.**—To better understand the formation of the Pd-TiO$_2$ adhesion-promoting layer on the SAM-terminated glass surface, we performed XPS at various stages of ink application, drying, sintering and reduction. Fig. 3 shows the observed XPS spectra at each of these stages. Fig. 3a is XPS spectra of an APTES-modified glass slide. In Fig. 3a, the nitrogen 1s peak observed at around 400 eV indicates presence of APTES on the glass substrate. This peak is absent in the baseline XPS spectra of a glass slide without APTES termination. Fig. 3 also shows XPS spectra of APTES-terminated glass substrate after ink deposition and drying (Fig. 3b), ink sintering (Fig. 3c) and reduction (Fig. 3d), respectively. Titanium 2p$_1$ and 2p$_3$ peaks, observed at 464 eV and 458 eV respectively, confirm the presence of titanium on the surface after ink drying, sintering and reduction steps. Presence of palladium too is confirmed by the Pd 3d$_{3/2}$ and 3d$_{5/2}$ peaks observed around 341 eV and 336 eV, respectively.

After the initial drying step (Fig. 3b), strong chlorine 2s peak is observed at 269 eV indicating that Pd is present as its chloride in the dried ink. Upon sintering at elevated temperature (Fig. 3c), the intensity of the chlorine peak is significantly reduced. After ink reduction (Fig. 3d), the chlorine peak is absent. Further insights into the transitions occurring during the drying, sintering and reduction steps can be gained by observing the Pd 3d$_{5/2}$ XPS spectra (Fig. 4). Figs. 4a, 4b and 4c show the XPS spectra for samples with: (a) dried PdCl$_2$-TiO$_2$ ink; (b) sintered PdO-TiO$_2$ ink; and (c) reduced Pd-TiO$_2$. The shift of binding energy of the Pd 3d$_{5/2}$ peaks is evidence for the transition from PdCl$_2$ to PdO during sintering, and for the transition from PdO to Pd during reduction by DMAB.

**Surface characteristics of Pd-TiO$_2$ deposits.**—To characterize the surface during Pd-TiO$_2$ deposition, we collected surface
profilometer scans at the various stages of deposition, i.e., for the untreated glass substrate (Fig. 5a), after drying the PdCl₂-TiO₂ ink (Fig. 5b), after sintering to form PdO-TiO₂ (Fig. 5c), and finally after reduction to form the Pd-TiO₂ adhesion layer (Fig. 5d). Profilometer scans indicate that the underlying glass substrate is fairly smooth with RMS roughness of ~7 nm. However, after ink application, sintering and reduction, sub-micron sized roughness elements are detected on the glass substrate as highlighted by arrows in Figs. 5b–5d. To observe the surface structure after Pd-TiO₂ formation, we used high-resolution optical microscopy (Fig. 5e), which confirmed the presence of sub-micron sized particles uniformly distributed on the glass substrate. While high-resolution SEM imaging and EDS compositional mapping were attempted, reliable results could not be obtained because of ‘charging’ on account of the poorly conducting glass surface. Nonetheless, XPS analysis (reported above – Figs. 3 and 4) provided valuable compositional information. The presence of Pd-TiO₂ particles provides anchoring sites that enhance interfacial adhesion while catalyzing subsequent electroleless deposition as discussed below. We believe that the Pd-TiO₂ particle density may be modulated via the ink application, drying and sintering process conditions; however, further studies are required to understand how the particle density can be precisely controlled.

Adhesion characterization of Cu films.—The Pd-TiO₂ adhesion-promoting layers formed above served as catalysts for electroleless seed-layer deposition followed by electroplating of Cu. Electroleless Cu seed layers were favored over other metals such as Ni and Co because of the high electrical conductivity of Cu, which is essential for promoting uniform current distribution during the subsequent Cu electrodeposition step. Fig. 6 shows results of tape tests for Cu films deposited on a glass substrate modified with SAM and Pd-TiO₂ following the process outlined above (see Fig. 1 schematic). Tape tests were conducted using the procedure described above. Figs. 6a and 6b are images after tape testing of an electroleless Cu plated glass substrate and the tape fragment, respectively. In this case, the ~440 nm thick electroleless Cu film remained attached to the substrate without interfacial failure. Figs. 6c and 6d are images after tape testing of a glass substrate modified with SAM and Pd-TiO₂ after electroleless Cu seeding and thick (~100 μm) Cu electroplating. Additive-free Cu electroplating baths were employed (which contained ppm-levels of chloride) because these baths are known to minimize stress in electroplated films. Additives-containing electrolytes may be used after optimization of the plating conditions that provide minimal stress in thick deposits. The tape test results, even after aggressive cross-hatching, confirm the superior adhesion of thick (~100 μm) electroplated Cu films to glass. The above results demonstrate the adhesion enhance-

![Figure 6](image_url)
Figure 6. Qualitative tape test results of Cu films on SAM/Pd-TiO₂ modified glass: (a) 440 nm electroleless Cu on glass showing majority of Cu remaining adherent after tape test; (b) tape fragment after tape test of sample in (a) showing almost no Cu removed; (c) electroplated Cu (~100 μm) on glass showing majority of Cu remaining adherent after cross-hatched tape test; and (d) tape fragment showing no Cu removed after tape testing sample in (c).

![Figure 5](image_url)
Figure 5. Surface profilometer scans for samples with: (a) Untreated glass substrate; (b) Dried PdCl₂-TiO₂ ink; (c) Sintered PdO-TiO₂; (d) Reduced Pd-TiO₂ adhesion layer. Profilometer scans indicate formation of sub-micron sized particles (instead of a uniform film) during Pd-TiO₂ deposition on the glass substrate (particles highlighted by arrows). This is also supported by high-resolution optical microscopy (e), which indicates that the adhesion-promoting particles of Pd-TiO₂ are uniformly distributed over the glass substrate. These particles subsequently catalyze electroleless deposition.
with ~400 nm electroless Cu seed-layer and 15 μm electroplated Cu. Fig. 7 shows results of a 90° peel strength test. The average observed peel strength was 1.4 N/cm and the maximum peel strength was 1.8 N/cm. These peel strength values are comparable to those reported by Shen and Dow for adherent Cu films on AlN substrates enabled using chemical grafting.15 While the above adhesion testing establishes the basic feasibility of an ‘all-wet’ route for depositing thick, adherent Cu films on glass substrates, further process optimization and characterization is needed to implement the process on large-area substrates and on patterned surfaces.

Conclusions

An ‘all-wet’ process for Cu metallization of glass substrates has been demonstrated. In this process, interfacial adhesion is promoted through the use of SAM/Pd-TiO2 adhesion layer that also catalyzes electroless deposition of a Cu seed layer. The mechanism for Pd-TiO2 adhesion layer formation involves stepwise reduction of Pd(II) to metallic Pd embedded in a TiO2 matrix. Electrodeposition of Cu onto the electroless Cu seed layer enables thick (>10 μm), adherent Cu films. The proposed ‘all-wet’ strategy provides a significant adhesion enhancement as observed in tape tests and 90° peel strength tests. Owing to its low-cost and ease of integration, the ‘all-wet’ process offers promise in numerous metallization applications where insulator-metal interfaces are encountered.

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References

1. W. J. Dressick, C. S. Dulcey, J. H. Georger, G. S. Calabrese, and J. M. Calvert, “Covalent Binding of Pd Catalyst to Ligating Self-Assembled Monolayer Films for Selective Electroless Metal-Deposition,” Journal of the Electrochemical Society, 141(1), 210 (1994).
2. A. M. Caro, S. Armini, O. Richard, G. Maes, G. Borghs, C. M. Whelan, and Y. Traval, “Bottom-Up Engineering of Sub-nanometer Copper Diffusion Barriers Using SiH4-Derived Self-Assembled Monolayers,” Advanced Functional Materials, 20(7), 1125 (2010).
3. Z. Kong, Q. Wang, L. A. Ding, and T. Wu, “Study on chemical vapor deposited copper films on cyano and carboxylic self-assembled monolayer diffusion barriers,” Thin Solid Films, 518(17), 4852 (2010).
4. W. Su, L. B. Yao, F. Yang, P. Y. Li, J. Chen, and L. F. Liang, “Electroless plating of copper on surface-modified glass substrate,” Applied Surface Science, 257(18), 8067 (2011).
5. S. Armini and A. M. Caro, “Materials Engineering for Future Interconnects: Catalyst-Free Electroless Cu Deposition on Self-Assembled Monolayer Alternative Barriers.” Journal of the Electrochemical Society, 157(1), D74 (2010).
6. S. Gandikota, S. Voss, R. Tao, A. Dubont, D. Cong, L.-Y. Chen, S. Ramaswami, and D. Carl, “Adhesion studies of CVD copper metallization,” Microelectronic Engineering, 50(1–4), 547 (2000).
7. R. D. Stolk and M. R. Rahe, Sol-gel Catalyst for Electroless Plating, US Pat. 6,344,242 B1 (2002).
8. J. J. Cras, C. A. Rowe-Taitt, D. A. Nivens, and F. S. Ligler, “Comparison of chemical cleaning methods of glass in preparation for silanization.” Biosensors & Bioelectronics, 14(8), 683 (1999).
9. J. W. Dani and D. D. Snyder, “Electrodeposition of Copper,” in Modern Electroplating, 2010, John Wiley & Sons, Inc. p. 33.
10. J. A. Howarter and J. P. Youngblood, “Optimization of Silica Silanization by 3-Aminopropyltriethoxysilane,” Langmuir, 22, 11142 (2006).
11. F. Bozoz-Verduraz, A. Omar, J. Escard, and B. Pontvianne, “Chemical state and reactivity of supported palladium: I. Characterization by XPS and uv-visible spectroscopy.” Journal of Catalysis, 53(1), 126 (1978).
12. K. S. Kim, A. F. Gossmann, and N. Winograd, “X-ray photoelectron spectroscopic studies of palladium oxides and palladium oxide-electrode,” Analytical Chemistry, 46(2), 197 (1974).
13. J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bohen, Handbook of X-ray Photoelectron Spectroscopy, 1992, Chanhassen, Minnesota: Physical Electronics USA, Inc. 261.
14. D. D. Gandhi, M. Lane, Y. Zhou, A. P. Singh, S. Nayak, U. Tisch, M. Eizenberg, and G. Ramanath, “Annealing-induced interfacial toughening using a molecular nanolayer,” Nature, 447, 299 (2007).
15. S. P. Shen and W. P. Dow. “Adhesion Enhancement of a Plated Copper Layer on an AlN Substrate Using a Chemical Grafting Process at Room Temperature,” Journal of the Electrochemical Society, 161(10), D579 (2014).