ENHANCED COPPER ADHESION ON GLASS VIA ADHESION PROMOTION COATING

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Abstract

Seed copper metallization on glass has been achieved by simple wet chemistry methods that involve deposition an adhesion promoting organic material which enables metallization without any special or high-temperature treatment of the glass substrate. The coating is catalytically activated by depositing atomic palladium using $LMI_x^{®}$, a Liquid Metal Ink organic precursor of palladium with a low contact angle, in which the "x" subscript denotes formulaic tailoring to specific substrate applications. Catalytic atomic palladium was generated on the organic coating by thermal processing at <230°C or in fact at room temperature by using an appropriate reducing agent. The catalytic layer/s of atomic palladium respond faithfully to commercial electroless copper chemistries furnishing a conductive copper layer. The adhesion of the copper layer was tested using conventional cross-hatch testing and nano-scratch testing methods. AFM was used as a tool to monitor changes in surface roughness during multiple process steps. FESEM/EDX spectra were taken after catalytic palladium and SEM of electroless copper deposition. Also, XPS imaging was used to further understanding the chemical conversion of atomic palladium. DSC/TG runs of the atomic palladium ink formulation in air were used to suggest appropriate thermal processing parameters. Sheet resistance of electroless copper was assessed by the 4-point probe method. Glass substrates with high aspect-ratio Through Glass Vias were subjected to BIB/FIB followed by SEM/EDS analysis to determine coverage and conformality of electroless copper deposition in the vias.

Key words

Atomic Palladium, Electroless Copper, Glass Core IC-Substrates, TGV (Through Glass Vias), $LMI_x^{®}$ (Liquid Metal Ink^{TM}).
Throughout the remainder of this paper, trademarks and sub-scripts will be removed for readability.

I. Introduction

Glass has gained considerable interest as a substrate for advanced semiconductor packaging and interposer applications due to its exceptional properties, including high dimensional stability, low coefficient of thermal expansion (CTE), low dielectric loss, and excellent surface smoothness. These features make it well suited for high-density redistribution layers, RF interconnects, and optoelectronic integration. Despite these advantages, metallizing glass remains a significant challenge. Glass is chemically inert and lacks surface functional groups, which makes direct metal adhesion difficult without additional surface modification.

Several methods have been explored in the literature to address this issue. One widely adopted approach uses physical vapor deposition (PVD) techniques—typically sputtering of a titanium/copper seed layer—followed by electrochemical deposition (ECD). These methods have demonstrated some promise for low aspect-ratio Through Glass Vias (TGVs) but require expensive vacuum deposition equipment, involve multiple process steps, and are limited in their ability to conformally coat high-aspect-ratio through-glass vias (TGVs) [1], [2]. Other approaches have relied on polymer lamination and patterning to facilitate metallization, but these introduce additional materials and thermal expansion mismatches that can complicate reliability [1].

More recent work has focused on laser-assisted surface modification, particularly through techniques like Selective Surface Activation Induced by Laser (SSAIL). This method uses short-pulse lasers to locally modify the surface of glass or transparent polymers, enabling site-selective electroless copper deposition [3]. SSAIL is attractive for producing narrow metal traces with reasonable adhesion, but it typically

requires separate chemical activation steps (e.g., silver nitrate baths) and does not scale easily to large-area or 3D structures such as TGVs.

Nanoparticle-based catalysts, especially those using silver or palladium colloids, have also been proposed to initiate electroless copper deposition. One recent example demonstrated the use of silver nanoparticles stabilized by polyethyleneimine and glutaraldehyde on grit-blasted glass, which resulted in continuous copper coverage and good electrical performance [4]. However, nanoparticle systems tend to suffer from agglomeration, limited dispersion stability, and relatively low catalytic efficiency per unit mass. They also generally require surface roughening or chemical primers, such as silanes, to improve adhesion to glass [1].

In contrast to these approaches, the present method is based on the use of atomic-scale palladium deposition from molecular precursor inks, not nanoparticles. The palladium ink herein discussed—referred to as LMI, Liquid Metal Ink—is applied over a proprietary adhesion-promoting organic coating, LIQUECOAT. This coating introduces polarity onto the glass surface, improving interaction with the palladium/copper and enabling better adhesion of the subsequent copper layer. Upon mild thermal treatment (≤230 °C in air), the ink decomposes cleanly to form atomically dispersed palladium that serves as an efficient catalyst for electroless copper plating. This method does not require plasma activation, surface roughening or vacuum deposition.

The atomic ink methodology used here has its origins in earlier patents, e.g., US Patent 5,894,038 describes the use of palladium carboxylates and related compounds that decompose at low temperatures to generate catalytic surfaces [5]. US Patent 5,980,998 outlines selective patterning techniques using such inks to produce metal features on insulating substrates [6]. Unlike colloidal systems, these inks are shelf-stable, and allow better control over film formation.

The process we present is particularly effective for metallizing smooth glass surfaces and for achieving conformal coverage in through-glass vias. This paper does not aim to provide a comprehensive survey of all prior methods but focuses on establishing the viability of this alternative approach. The cited references and references therein provide reasonable background of different arts of metallization of glass. The method and overall process has been studied using a range of analytical techniques—TG/DSC for thermal behavior of the atomic palladium ink, AFM and FESEM for surface morphology, and XPS for chemical characterization of the resulting atomic palladium film from LMI. Adhesion performance has been evaluated using the nano-scratch test. Preliminary data of laser direct writing experiments are also presented.

II. Methodology

A. General Process

Soda-lime microscope glass slides (Corning™, 75 mm × 25 mm x thickness 0.9–1.1 mm), Corning™ Eagle XG (50 mm x 50 mm x thickness 0.65mm) and Schott BOROFLOAT® 33 glass slides (55 mm x 25 mm x thickness 0.65mm) were used as experimental substrates. These were not subjected to any special chemical pre-treatment except for wiping with methanol to remove dust and handling smudges.

The processing steps are as follows:

1. Substrates were cleaned by methanol wiping and dried at 80°C for 5 minutes.
2. A proprietary adhesion-promoting formulation was applied to the cleaned glass substrates using a wire-wound rod. Coated samples were then dried and thermally baked at 200°C to mature the film.
3. (a) A layer of the palladium ink was applied on top of the proprietary adhesion-promoting formulation layer by dip coating. Catalyst activation was then performed by either:
   (b) Thermal activation, at temperatures below 230°C, or
   (c) Chemical activation using a proprietary solution, or
   (d) Selective laser cure
4. Following activation, the samples were rinsed with deionized water at room temperature for 2 minutes and air-dried.
5. Copper metallization was achieved using commercial electroless plating baths: MKS Atotech Printoganth MV TP2 or McDermid VIA DEP 4550.

B. Laser Direct Processing

For laser patterning experiments, the substrates underwent steps 1–3(a) above. A CO_2 laser (Model: Mophorn 80W CO_2 laser engraving and cutting machine) was used to selectively cure the palladium ink coating on microscope glass slides. The laser-developed patterns were then washed with an organic solvent to remove uncured palladium ink, dried, and subjected to the same electroless copper deposition protocol. Additionally, Kaneka PI 1-mil sheets were used for laser direct writing of the palladium ink, and the resulting palladium film was examined by FESEM.

C. General Conditions

All chemicals used were commercially available (COTS). Processing was performed in ambient (non-cleanroom) conditions, with precautions taken to minimize dust and contaminants

D. Characterization Techniques

Atomic Force Microscopy (AFM): Park Systems EX7 AFM. Sheet Resistance: 4-point probe with Signatone SP4 probe and Keithley 580 Micro-Ohmmeter. Cross-section TEM, High resolution FESEM (400K and 500K), XPS, and nano-scratch tests. was obtained from commercial laboratories. Thermal analyses were performed using PerkinElmer TGA and DSC instruments. The cross-hatch adhesion test was carried out using commercially available tool kit.

III. Results and Discussion

The glass metallization process using the atomic palladium ink and an organic adhesion-promoting coating was monitored using spectroscopic and physical characterization tools. LIQUECOAT, an organic polar coating, enhances copper adhesion on glass by modifying its inherently non-polar surface. Palladium deposited via LMI, was used to catalyze electroless copper deposition.

Following thermal maturation of the organic adhesion-promoting coating below 230°CTM, the palladium ink was applied and activated thermally or chemically to produce atomic palladium. The process is summarized in the flow diagram (Fig. 1).

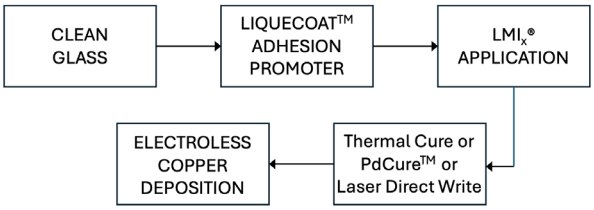

Fig. 1. Process Flow-Chart for copper deposition on glass (PdCure™, Thermal and Laser processing)

LMI, is a liquid formulation that generates atomic palladium (1), upon thermal or chemical decomposition. The generation of atomic palladium using the palladium ink is independent of the nature of substrate, provided it is solid, not chemically reactive, and tolerates the <230°C activation temperature.

$$\text{LMI} \xrightarrow{Thermal/Chemical/Photothermal} Pd_{atomic} + \text{Products} \quad (1)$$

Fig. 2 presents the DSCs of the palladium ink in quartz sample holders and in organic adhesion-promoting formulation coated quartz sample holders. The thermal collapse temperatures of the palladium ink in quartz sample holder and in organic adhesion-promoting formulation coated quartz sample holder are within ±5-7°C. Also, the overall profile of the two DSC curves nearly duplicates of each other lending support to the premise that atomic palladium generated by LMI is independent of the nature of the substrate. Fig. 3 shows the TGA of the palladium ink in air. The weight loss cut-off is close to 192°C and matches with the thermal profiles exhibited by DSCs. The FESEM of a thermally matured palladium film on glass is shown in Fig. 4 illustrating nano domains of palladium reflecting the diffusion of atomic palladium. This film is modestly textured, in contrast with the precipitated aggregates of nano particle that result from palladium nanoparticle precursors. Fig. 5 is the cross section of palladium film showing the bcc planes of the quasi-2D palladium film. Fig. 6 shows the FESEM of laser cured palladium ink on polyimide. Comparing the FESEMs of the palladium ink by laser and thermal curing prosses, it's concluded that atomic palladium was generated by both methods.

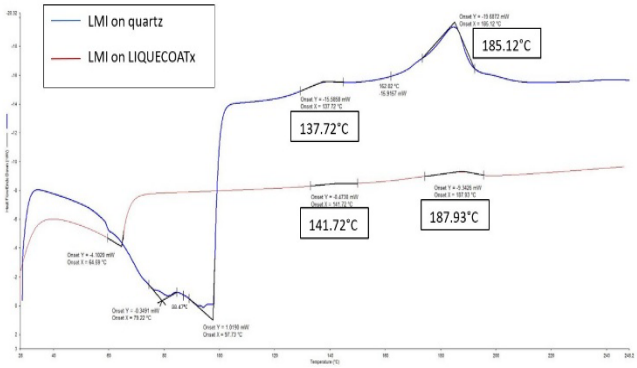

Fig. 2. DSC of the palladium ink in quartz sample holder

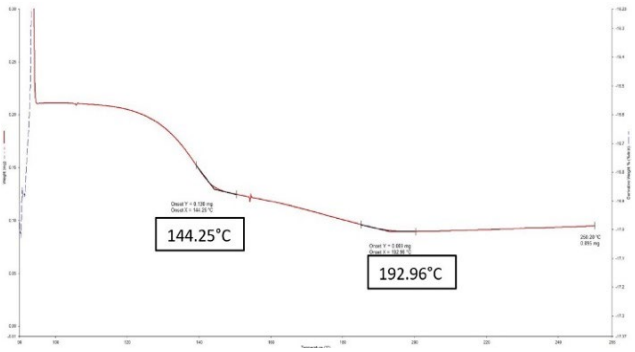

Fig. 3. TGA of the palladium ink in air

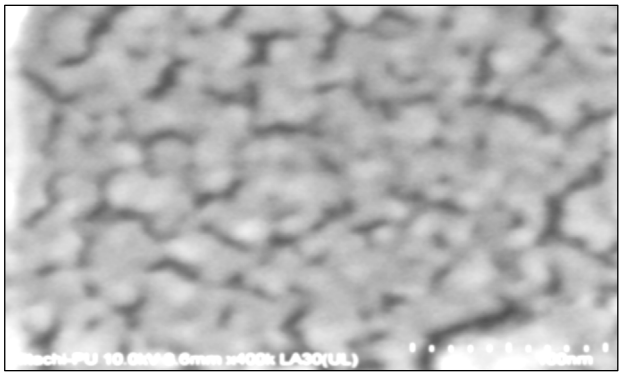

Fig. 4. FESEM of quasi-2-dimensional film

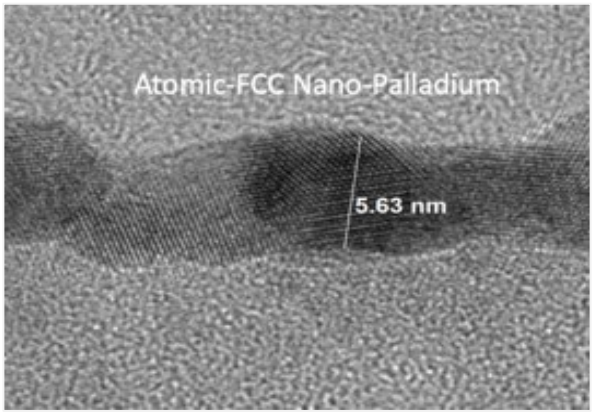

Fig. 5. TEM Cross-section of the palladium film

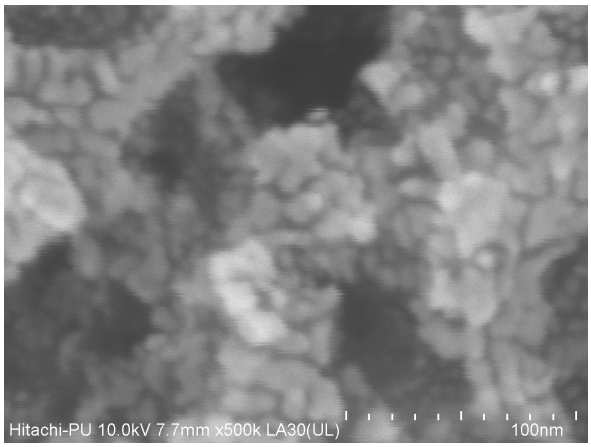

Fig. 6. FESEM of Laser cured palladium film

Upon thermal processing of the palladium ink, a sub-nanometer oligomeric organic polar coating forms on the substrate surface which is coated with atomic palladium on it. This layer is believed to enhance substrate compatibility of atomic palladium for subsequent metallization by electroless copper. XPS analysis (Table. 1) reveals the presence of multiple polar organic functionalities, labeled here as Polar Groups 1, 2,3 and 4 for simplicity and Pd^0 in addition to PdO_m (m represents non- stoichiometric composition). The relative amounts in each category (organic and palladium) are shown. The atomic palladium generated through thermal or chemical treatment conforms to the nanoscale contours of the substrate enabled by the sub nano organic oligomeric layer thereby replicating the topography with high fidelity. This effect is corroborated by AFM imaging of the substrate at various stages, confirming nanoscale replication prior to copper metallization. The surface profile of Schott BOROFLOAT® 33 glass was obtained using AFM before and after the organic adhesion-promoting formulation coating. Two representative AFM images and data are shown in Fig. 8-9.

Table.1 XPS analysis of the palladium film on glass

Functionality	Polar Organic Group 1	Polar Organic Group 2	Polar Organic Group 3	Polar Organic Group 4	Pd^0, PdO_m
Relative Amounts within each category	67	12	13	8	100

The glass substrates were subjected to electroless copper deposition in MKS Atotech Printoganth MV TP2. The deposition of copper was monitored by sheet resistance at different intervals of time. The drop in sheet resistance with dip time in electroless solution is shown in Fig. 7.

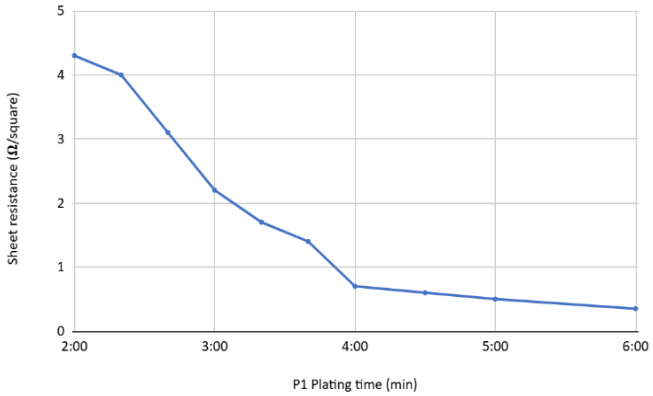

Fig. 7. Sheet resistance as a function of dip time in electroless copper bath.

Post electroless copper deposition the samples were baked as described above. The adhesion of copper was qualitatively assessed by cross-hatch test which shows adhesion of category 5B. Nano scratch test showed a peel of 16 milli Newtons (mN).

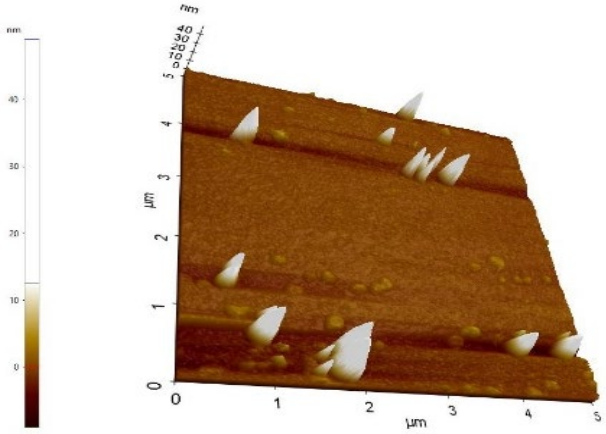

Fig. 8. AFM after Methanol wipe (Sa: 1.1 nm)

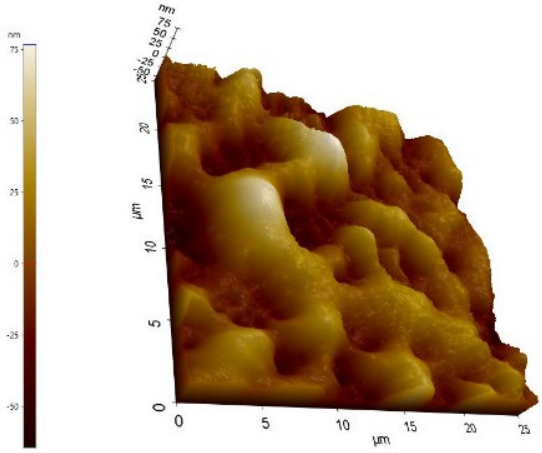

Fig. 9. AFM after electroless copper (Sa: 16.8 nm)

The metallization of glass by electroless copper is complete and has good adhesion as checked by cross-hatch and nano adhesion tests.

An important feature of the palladium ink/ copper layers is the ability to coat smoothly within vias. This was substantiated by plating vias in glass with copper. The SEM images of the vias exhibited good conformality and coverage of both copper and the palladium ink as shown in Fig. 10. It is worth an emphasis that efficient coverage of electroless copper is enabled by the atomic palladium generated by LMI.

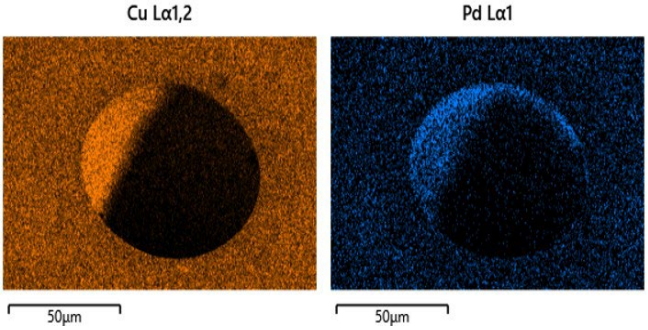

Fig. 10. SEM-EDS shows uniform and good coverage around the vias and inside the vias.

Fig. 11(a) shows a cross-section view of TGV electroless copper on Schott Borofloat 33 Glass with 100x lens magnification and Fig. 11(b) shows a close-up view with higher magnification of 2500x. Fig. 12(a)-(c) show a cleave done by FIB followed by Dual Beam PFIB analysis at 50kx on side wall on top, middle and bottom of the via shown in Fig. 11(a). The layers from top to bottom are glass, the organic adhesion-promoting formulation coating, electroless copper (the shiny area) and an Ir protective layer for conducting purpose.

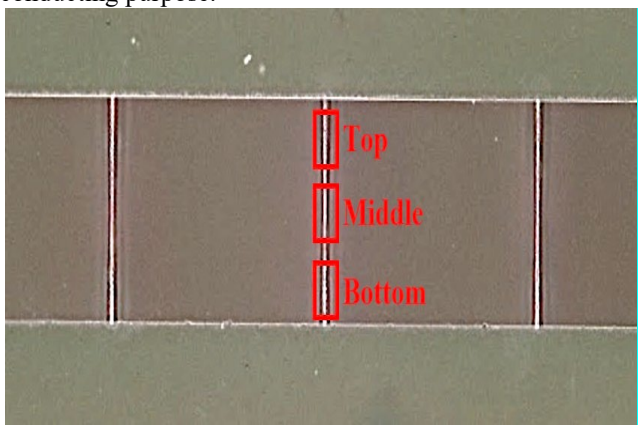

Fig. 11(a). A cross-section view of TGV electroless copper on Schott Borofloat 33 Glass with100x lens magnification

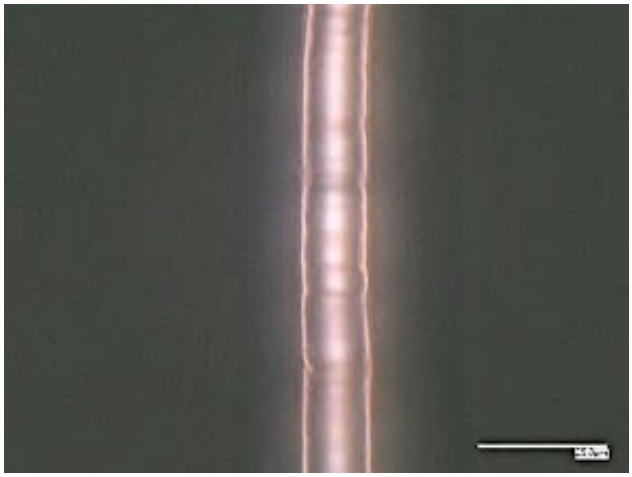

Fig. 11(b) A cross-section view of high aspect-ratio (>13:1) TGV electroless copper on Schott Borofloat 33 Glass with 2500x lens magnification

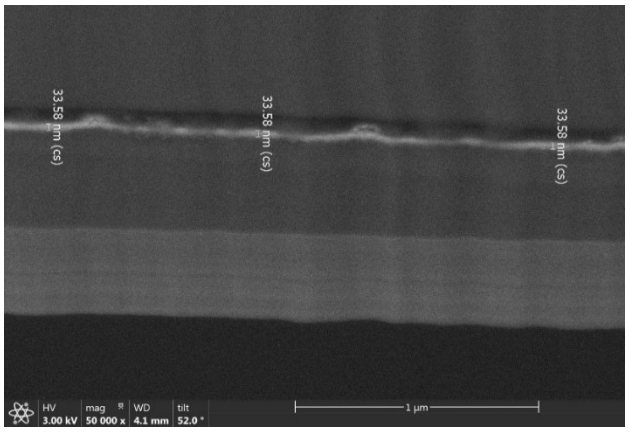

Fig. 12(a). Dual Beam PFIB analysis of top view of a cleaved via of Schott Borofloat 33 glass

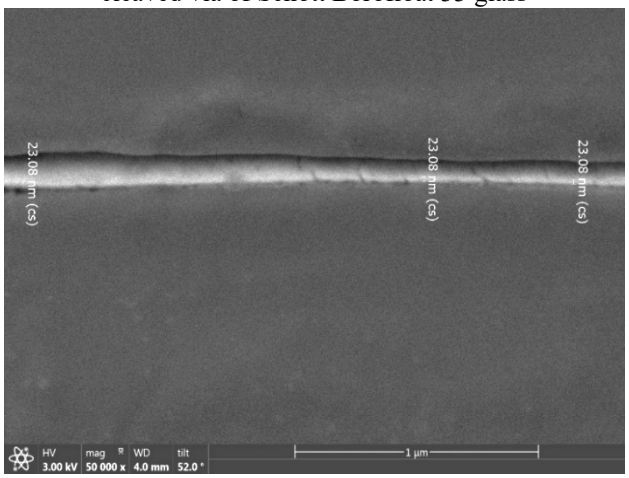

Fig. 12(b). Dual Beam PFIB analysis of middle view of a cleaved via of Schott Borofloat 33 glass

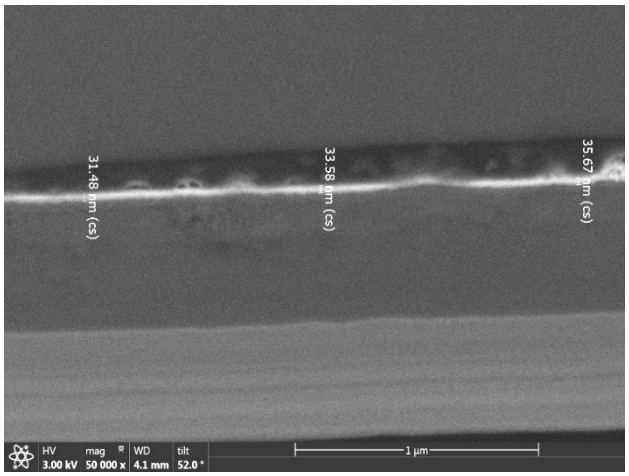

Fig. 12(c). Dual Beam PFIB analysis of bottom view of a cleaved via of Schott Borofloat 33 glass

Initial results of electroless copper deposition by laser curing are also encouraging, showing the presence of electroless copper only in the areas where the palladium ink was cured by the laser (Fig. 13-14).

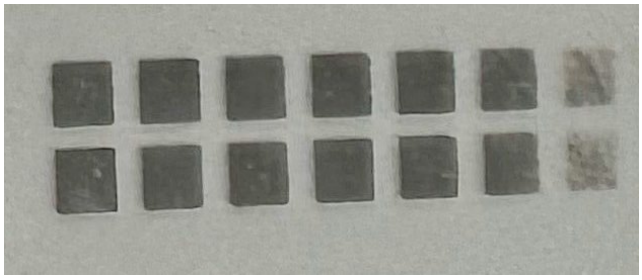

Fig. 13. Pattern of the palladium ink cured by Laser

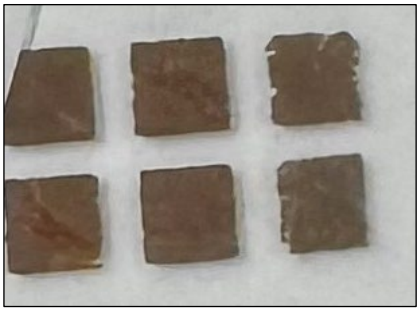

Fig. 14. Electroless copper after the organic adhesion-promoting coating and laser curing of the palladium ink

The work on the palladium ink and the organic adhesion-promoting formulation for metallization of glass is under active and continued investigation.

IV. Conclusion

This study demonstrates a simple, reliable, low-temperature wet chemical process for copper metallization on glass using an organic adhesion-promoting coating (LIQUECOAT™) and atomic palladium generated from a palladium ink (LMI_x®), both developed by LQDX. The adhesion-promoting organic layer provides a polar surface, while LMI delivers atomic palladium via thermal, chemical, or laser activation. Characterization by DSC, TGA, XPS, and FESEM confirms the formation of a quasi-two-dimensional palladium film that conforms to complex substrate topology. Electroless copper deposition on these activated surfaces shows highly acceptable conductivity and adhesion measurements, confirmed by 4-point probe, cross-hatch (category 5B), and nano-scratch testing. AFM profiling further supports nanoscale topographic replication. Sheet resistance measurements validate continuous copper growth. The method also enables conformal adherent plating in high aspect-ratio (>13:1) Though Glass Vias (TGV). Initial laser direct-write results are promising, facilitating selective patterning on glass core substrates.

References

[1] T. Huang, B. Chou, V. Sundaram, H. Sharma, and R. Tummala, Novel Copper Metallization Schemes on Ultra-Thin, Bare Glass Interposers with Through-Vias," *Proc. Electronic Components and Technology Conference (ECTC)*, 2015.

[2] K. Demir et al., "First Demonstration of Reliable Copper-plated 30μm Diameter Through-Package-Vias in Ultra-thin Bare Glass Interposers," *Proc. ECTC*, 2014.

[3] M. Sadauskas et al., "Laser-induced microscale copper trace deposition on glass and PET substrates," *Optics & Laser Technology*, vol. 183, 2025.

[4] T.-L. Chiang, A.-Y. Cheng, J.-L. You, C.-P. Chang and M.-D. Ger, "Efficient copper plating on glass substrates through amine-functionalized nanocomposite-immobilized silver nanoparticles," *Colloids and Surfaces A*, vol. 688, 202.

[5] S. Sharma, "Deposition of substances on a surface," U.S. Patent 5,980,998

[6] S. Sharma, "Direct deposition of palladium," U.S. Patent 5,894,038