DIRECT ELECTROLESS COPPER PLATING ON GLASS MEDIATED BY SOLUTION-PHASE DEPOSITION OF NUCLEATION AND ADHESION PROMOTERS

By

ALEXANDER T. MILLER

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Thesis Advisor: Professor Rohan Akolkar

Department of Chemical Engineering

Case Western Reserve University

August 2015
We hereby approve the thesis of

Alexander T. Miller

Candidate for the degree of Master of Science in Chemical Engineering*

Committee Chair

Prof. Rohan Akolkar

Committee Members

Prof. Chung-Chiun Liu

Prof. Heidi B. Martin

Date of Defense:  May 7, 2015

*We also certify that written approval has been obtained for any proprietary material contained therein
Contents

List of Tables and Figures................................................................. iv

Acknowledgements...................................................................... vi

Abstract ....................................................................................... 1

Chapter 1: Introduction ................................................................. 2

1-1 Review of Copper Metallization Methods for Insulating Substrates...... 4
1-2 Review of Adhesion Promotion of Copper films on Glass substrates........ 5
1-3 Relevant Patent Literature .......................................................... 7
1-4 Objectives ................................................................................. 9
1-5 Scope of Thesis ......................................................................... 9
1-6 References ............................................................................ 10

Chapter 2: Experimental Procedures .............................................. 14

2-1 Glass Substrate Preparation ....................................................... 14
2-2 Glass Substrate Cleaning .......................................................... 15
2-3 Silane Deposition ..................................................................... 16
2-4 Activation for Electroless Copper Plating ..................................... 17
   2-4.1 Ionic Palladium Activation ............................................... 17
   2-4.2 Pd-TiO₂ Ink Activation ..................................................... 17
2-5 Methods of Cu Seed layer Deposition ......................................... 18
   2-5.1 Physical Vapor Deposition (PVD) Cu ................................... 18
   2-5.2 Electroless Cu Deposition .................................................. 18
2-5.3 Annealing of Cu Seed Layers ................................................................. 19

2-6 Electrolytic Cu Deposition ........................................................................... 19

2-6.1 Electrodeposition of Small Scale (1.00 cm × 1.27 cm) Samples ................. 19

2-6.2 Electrodeposition of Large-scale (7.62 cm × 1.27 cm) samples .................. 20

2-7 Evaluation of Film Thickness Using Four-Point Probe ................................. 21

2-8 Evaluation of adhesion ............................................................................... 21

2-8.1 Scotch Tape Test ..................................................................................... 21

2-8.2 Cross-Hatched Tape Test ..................................................................... 22

2-8.3 Quantitative 90° Peel Strength Tests ......................................................... 22

2-9 X-ray Photoelectron Spectroscopy (XPS) ..................................................... 23

2-10 References ............................................................................................... 25

Chapter 3: Theory ........................................................................................... 26

3-1 Four-Point Probe Theory ............................................................................ 26

3-2 Pd-TiO₂ ink deposition mechanism ............................................................... 28

3-2.1 Pd-TiO₂ ink deposition mechanism: Drying step .................................... 28

3-2.2 Pd-TiO₂ ink deposition mechanism: Sintering step ................................. 28

3-2.3 Pd-TiO₂ ink deposition mechanism: Pd^{2+} reduction step ....................... 28

3-3 Electroless Cu Metallization ....................................................................... 29

3-4 Electroplating of Cu .................................................................................... 30

3-5 References .................................................................................................. 32

Chapter 4: Observations, Results, and Discussion .......................................... 33
List of Figures

Table 1-1. Summary of Adhesion Promotion Strategies for Cu films on SiO₂ .............. 6

Figure 1-1. Cross-sectional schematic of IC, interposer, PCB assembly. The role of the interposer is to provide a robust integration of the nano-scale connections of ICs into the micro-scale connections of PCBs. .................................................................................................................. 2

Figure 2-1. Process flow diagram outlining the sequence of sample preparation, adhesion promoter application, electroless Cu deposition, Cu electroplating, and adhesion testing. Sections of the thesis detailing procedures are shown in parentheses. ........................................ 14

Figure 2-2. Basic mechanism for formation of APTES SAM on Glass. APTES adsorbs to hydroxylated glass surface and bonds to surface through condensation reactions. ..... 16

Figure 2-3. Method of masking of 1.00 cm × 1.27 cm electroless Cu on glass samples defining circular electrode area of 0.317 cm² for Cu electroplating. ..................... 20

Figure 2-4. Schematic of 90° peel test. Cu films peeled at 90 degree angle relative to the substrate at 50 mm/min. ........................................................................................................ 23

Figure 3-1. Schematic of Four-Point Probe Measurement of a Rectangular Thin-film. .. 27

Figure 4-1 XPS Spectra of glass slides before and after silanization. a) Clean glass surface. b) APTES modified glass surface. The presence of a nitrogen 1s peak and increased intensity of the carbon 1s peak after modification indicate the presence of an adsorbed APTES layer on the glass surface. ........................................................................ 34

Figure 4-2. Stages of Pd-TiO₂ ink deposition. a) Dried deposit after 15 min at 130°C in air. b) Sintered deposit after 30 min at 450°C in air. c) Reduced deposit after 2 min in 0.5M DMAB. The oxidation state of Pd species incorporated in TiO₂ is tracked at each stage of deposition. ........................................................................................................... 35

Figure 4-3. XPS spectra at various stages of Pd-TiO₂ deposition on APTES modified glass. a) APTES modified glass. b) Dried Pd-TiO₂ ink. c) Sintered Pd-TiO₂ ink. d) Reduced Pd-TiO₂ ink. ........................................................................................................ 36

Figure 4-4. XPS of Pd 3d₃/₂ and 3d₅/₂ peaks for a) APTES modified glass, b) dried Pd-TiO₂ ink, c) sintered Pd-TiO₂ ink, and d) reduced Pd-TiO₂ ink. The shift of the Pd 3d₅/₂ peaks is evidence for the change of PdCl₂ to PdO, and then to metallic Pd. ........................................ 38

Figure 4-5. APTES ‘wetting layer’ for Pd-TiO₂ Ink deposition and its effect on electroless Cu plating. a1-a3 are representative images of APTES modified glass substrates, while b1-b3 are representative images of clean glass substrates (without APTES). Images a1 and b1 show a 10 µl Pd-TiO₂ ink droplet on the substrate surface. Profile images of droplet are shown in a2 and b2. Images a3 and b3 show 400 nm electroless Cu on Pd-TiO₂ modified glass substrates. The improved wettability of ink on APTES modified glass results in a more uniform Pd-TiO₂ deposit than ink dried on glass without APTES. Uniformity of Pd-TiO₂ deposits is demonstrated by the uniformity of electroless Cu deposited. ........................................................................ 40
Figure 4-6. Tape test results for electroless Cu seed layers of various thicknesses on 30 nm Pd-TiO₂ coated glass. Electroless Cu thickness: a) 100 nm. b) 250 nm. c) 440 nm. d) 540 nm. e) 800 nm. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test showing the amount of Cu removed from the substrate onto the tape. ...... 42

Figure 4-7. Images after tape test for electroless Cu of various thicknesses on Pd activated APTES modified glass. Electroless Cu thickness: a) 50 nm. b) 100 nm. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test. ............ 44

Figure 4-8. Images after tape test for PVD Cu seed layers of various thicknesses on APTES modified glass. PVD thickness: a) 70 nm. b) 300 nm. c) 400 nm. d) 500 nm. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test. PVD Cu on APTES fails tape tests at Cu thicknesses exceeding 400 nm....................................... 46

Figure 4-9. The effect of Pd activation on the adhesion of PVD Cu films to APTES modified glass. a) 300 nm PVD Cu on APTES modified glass. b) 300 nm PVD Cu on Pd activated APTES modified glass. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test. ................................................................................ 47

Figure 4-10. Tape test results for electroplated Cu films on electroless Cu seed layers on Pd-TiO₂ ink modified glass. a) 30 μm electroplated Cu. b) 100 μm electroplated Cu. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test. Samples survive tape tests despite aggressive crosshatching. ............................................... 50

Figure 4-11. 90° peel strength test results for the stack: 15 μm electroplated Cu / 300 nm electroless Cu / Pd-TiO₂ / glass. Cu film breaks before traveling the complete length of the sample. ........................................................................................................ 51

Figure 4-12. 5000 × zoom SEM/FIB Cross-Section Image of Electroplated Sample. Image was collected using ICE detector at an accelerating voltage of 5 kV at a tilt angle of 52°. The image shows coalesced electroless and electroplated Cu layers. The combined thickness of Cu layers corresponds to a thickness of 14.4 μm. The Pd-TiO₂ interface was not able to be discerned. ................................................................. 52

Figure 4-13. XPS of failure interface after 90° Peel Test showing presence of Ti and Pd. a) Peeled Cu interface. b) Glass Substrate. The presence of Ti and Pd on both interfaces suggest that interfacial failure mechanism is one of Pd-TiO₂ de-cohesion. .................... 53
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Direct Electroless Copper Plating on Glass Mediated by Solution-Phase Deposition of Nucleation and Adhesion Promoters

By: ALEXANDER T. MILLER

Abstract

Metal-to-dielectric interfaces are commonly encountered in numerous electronics applications, including printed circuit boards and integrated devices. While applications demand strong interfacial adhesion, the intrinsic adhesion between metallic films and dielectric substrates is often inferior as compared to metal-to-metal adhesion. In the present work, nucleation and adhesion promoters are employed to enhance the interfacial adhesion between glass and electrochemically deposited copper (Cu) layers. Adhesion enhancement of thick (>10 μm) Cu films on glass substrates is facilitated by an interfacial Pd-TiO$_2$ layer deposited using an all-wet deposition sequence. This sequence employs self-assembled monolayer functionalized glass substrates to improve surface wettability during Pd-TiO$_2$ deposition. Resulting Pd-TiO$_2$ deposits are also catalytic towards direct electroless deposition of thin Cu seed layers. The seed layers then enable electrodeposition of thick (> 10 μm) Cu films. The present work provides a viable route for high-throughput, cost-effective metallization of glass and ceramic surfaces for high-end microelectronics applications.
Chapter 1: Introduction

The interfacial adhesion between metallic films and dielectric materials is intrinsically weak. This is an important problem for numerous electronics applications, particularly the manufacturing of printed circuit boards (PCBs) [1] and integrated circuits (ICs) [2, 3]. As electronic devices have become increasingly miniaturized, limitations have arisen with interposer technologies, which distribute the many nm-sized connections of high-end ICs into PCBs. Specifically, these problems include electromagnetic interference (EMI) [4] and thermo-mechanical failure of weak interfaces [5]. This thesis addresses the specific interface between a glass substrate and a Cu film. Specifically, it outlines an all-wet strategy for depositing adherent Cu films of functional thicknesses (>10 μm) on glass substrates.

Figure 1-1. Cross-sectional schematic of IC, interposer, PCB assembly. The role of the interposer is to provide a robust integration of the nano-scale connections of ICs into the micro-scale connections of PCBs.

Although many applications would benefit from the all-wet metallization of glass, through-glass-vias (TGVs) interposer technology will be perhaps the most impacted [6-8]. Figure 1-1 is a cross-sectional schematic of an interposer implemented between silicon ICs and a PCB. The interposer’s Cu vias are used to distribute the nano-scale connections of IC chips to the micro-scale connections of the PCB board. The role of the
interposer is important for future devices where feature sizes of ICs are becoming increasingly miniaturized and feature sizes of conventional PCBs have reached practical limits of miniaturization.

The use of a glass substrate is an important distinction from conventional interposer technologies which primarily rely on organic substrates [7]. This is because organic substrates lack the dimensional and chemical stability required for ultrafine via formation [7]. To overcome this, considerable efforts have been made to develop a through-silicon-via (TSV) approach. Silicon is an ideal material for interfacing with silicon based ICs, however, the high material and processing cost of silicon limits its widespread implementation [6, 7]. Additionally, the semiconducting properties of silicon lead to high electrical losses within the interposer layer [7]. Alternatively, the relatively inexpensive glass substrate is sought due to its high dimensional stability and low dielectric constant [6-8].

However, technical challenges still exist when using glass as a substrate for metal films. The low roughness of glass requires the adhesion of Cu to SiO₂ to be dominated by chemical interaction rather than mechanical anchoring. The chemical stability of SiO₂ makes this inherently difficult. Also, differences between the coefficient of thermal expansion (CTE) of Cu and SiO₂ are considerable (16.6 ppm/°K versus 4.0 ppm/°K) [9]. As a result, temperature fluctuations may lead to huge amounts of stress at the interface of the two materials leading to thermo-mechanical failure. Finally, all of these challenges are encompassed and confounded by the challenge of depositing a metallic film on an insulating substrate such as glass.
1-1 Review of Copper Metallization Methods for Insulating Substrates

The deposition of adherent Cu films on glass substrates can be accomplished using ‘dry’ or ‘wet’ methods. ‘Dry’ deposition methods typically utilize a high-vacuum to deposit films from the vapor phase. Examples include physical vapor deposition [2, 7, 10-13] (PVD, or sputtering), chemical vapor deposition (CVD) [14], and thermal evaporation deposition (TED). These techniques are extremely versatile in that they can deposit metals on virtually any substrate. However, the ‘dry’ deposition methods require large capital investments and have relatively slow throughput [6, 8, 15]. In contrast, ‘wet’ techniques such as electroless deposition or electrodeposition for the metallization of insulators do not require large capital investments, are highly scalable, and operate at a very high throughput [6, 8, 15].

In the context of insulating substrates like glass, the term ‘wet’ deposition typically refers to electroless plating. Although many variations of electroless metal plating chemistries exist, all operate using the same reaction scheme: A catalytic substrate is immersed in an electroless plating solution containing a reducing agent and metal ions. At the substrate surface, the reducing agent oxidizes while metal ions are reduced to metal deposits that adhere to the substrate [16].

In most cases, the surface of an insulator, such as glass, is not directly catalytic for electroless reactions. For this reason, most substrate surfaces must be modified to become catalytic for electroless deposition. These modifications serve the dual purpose of catalyzing the electroless reaction as well as promoting the adhesion between the deposited metal film and the substrate surface. Various ways of promoting adhesion for ‘wet’ and ‘dry’ methods of metallization are reviewed in the following section.
When discussing the adhesion of a film to a substrate, a distinction must be made between chemical and mechanical adhesion. Chemical adhesion describes the adhesive strength due to chemical bonding of film and substrate, while mechanical adhesion describes the geometric interlocking of roughened surfaces. Chemical adhesion and mechanical adhesion are often difficult to completely decouple. With that caveat, the remainder of this section describes primarily methods of chemical adhesion.

Adhesion promotion of Cu films to SiO$_2$ substrates can be categorized into two groups: organic and inorganic. Organic adhesion promotion utilizes functionalized polymers [17] or self-assembled monolayers (SAMs) [2, 10, 12, 18, 19]. Inorganic methods of adhesion promotion include metallic adhesion layers [7, 20], and mixed-metal oxides [8, 21]. Table 1 summarizes the various methods surveyed for Cu metallization of SiO$_2$. 

---

1-2 Review of Adhesion Promotion of Copper films on Glass substrates
Table 1-1. Summary of Adhesion Promotion Strategies for Cu films on SiO₂

<table>
<thead>
<tr>
<th>Adhesion Promotion Strategy</th>
<th>Method of Cu Deposition</th>
<th>Cu Thickness</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Functionalized Polymers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethyleneimine</td>
<td>Electroless Cu</td>
<td>Unknown</td>
<td>17</td>
</tr>
<tr>
<td><strong>SAMs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-aminopropytrimethoxy silane</td>
<td>Electroless and PVD Cu</td>
<td>70 nm</td>
<td>19</td>
</tr>
<tr>
<td>3-aminopropytrimethoxy silane</td>
<td>PVD Cu</td>
<td>70 nm</td>
<td>10</td>
</tr>
<tr>
<td>3-mercaptopropytrimethoxy silane</td>
<td>PVD Cu</td>
<td>50 nm</td>
<td>12</td>
</tr>
<tr>
<td><strong>Metalic Adhesion Layer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta ~ 20 nm</td>
<td>CVD Cu and PVD Cu</td>
<td>100 nm</td>
<td>20</td>
</tr>
<tr>
<td>Ti ~ 20 nm</td>
<td>CVD Cu and PVD Cu</td>
<td>100 nm</td>
<td>20</td>
</tr>
<tr>
<td><strong>Mixed Metal Oxide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sol-gel (No composition reported)</td>
<td>Electroplated Cu and</td>
<td>&gt; 10 μm</td>
<td>8</td>
</tr>
<tr>
<td>Many compositions</td>
<td>Electroless Cu</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electroless Cu</td>
<td>Unknown</td>
<td>21</td>
</tr>
</tbody>
</table>

Organic adhesion layers, particularly SAMs, are thought to work by creating chemical bonds to both the substrate (SiO₂) and the deposited metal film. Silanes are particularly useful as SAMs because of their bifunctionality: having a silanol group and an organic functional group (typically an amine [2, 10, 14, 19] or a mercapto group [15]). A single molecular layer (mono-layer) self-assembles on the substrate surface where silanol groups bond covalently to hydroxylated SiO₂ via a condensation reaction. When a metallic film is deposited, the organic functional groups are thought to coordinate with the metal over-layer.

Inorganic adhesion layers are commonly used for ‘dry’ methods of Cu deposition. Both reactive metallic adhesion layers and mixed metal oxides are thought to enhance chemical adhesion with SiO₂ substrates by competing with Si for oxygen contained in the
substrate [20]. This can be illustrated best by considering the surface of Ti metal in air. When exposed to an oxidizing environment, the reactive metal of Ti will oxidize to form a protective TiO$_2$ layer on the surface. However, when deposited in an inert environment on SiO$_2$ surface, the Ti will compete with the Si atom for the available oxygen. The mechanisms by which inorganic adhesion layers interact with metallic films vary from case to case. Reactive metal adhesion layers often inter-diffuse with the metallic films they support, producing an alloy transition at the interface [20]. With mixed metal oxides deposited using sol-gel methods, the interaction with metal films is often mechanical in nature due to the porous nature of sol-gel films [8].

Of the organic adhesion layers surveyed, none have reported adhesion enhancement of Cu films with thicknesses of greater than 100 nm on SiO$_2$. Furthermore, none of the electroless deposition methods have commented on the effect of Pd activation on the resulting adhesion of the films. The only report of thick Cu films (>10 μm) on glass using an electroless seed layer utilize a mixed metal oxide adhesion scheme [8]. In this publication, the sol-gel composition used is not explicitly reported.

1-3 Relevant Patent Literature

Patent literature for sol-gels is extensive; however, one with particular relevance to the present work was identified [21]. In this patent, metal alkoxides are co-deposited with a catalytic metal salt in a polar-organic solvent. The result is a mixed metal oxide adhesion layer with catalytic activity for electroless plating. A broad range of metals alkoxides are claimed including Si, Al, Ti, Zr, Ce, Sn, Ta, and In. The patent also claims a broad range of catalytic metal salts including the chlorides and nitrates of Pd, Pt, Ni,
Co, Au, and Ag. The methods by which the sol-gel catalyst may be deposited include dip-coating, printing, spin-coating, or brushing.

In the present work, a catalytic adhesion layer for electroless Cu plating is deposited using similar ingredients and procedures to the above patent. A metal alkoxide [titanium(IV)-butoxide] and a catalytic metal salt [PdCl$_2$] are co-deposited in a butanol ink similar to the sol-gel method described above. However, many key differences exist between the described patent and the procedure used herein. First, the ink used in this work is approximately 1000 times more dilute than the patented sol-gel. This allows for much thinner adhesion layers to be deposited. Second, water is not added to the ink used, as in the case of the sol-gel. Third, in the present work, the glass substrate is first modified with a SAM (an essential step for depositing a smooth and even electroless layer as will be demonstrated in section 4-2.2). This is in contrast to the patent, which does not require any substrate conditioning prior to deposition. Finally, the patent requires the incorporation of an acid into the sol-gel to facilitate the hydrolysis of the metal alkoxide, while the Pd-TiO$_2$ ink does not. The low Pd-TiO$_2$ ink concentration enables it to utilize the moisture in air for hydrolysis of the titanium(IV)-butoxide.
1-4 Objectives

The objectives of the present research are:

- To develop an all-wet process that yields adherent Cu films on glass substrates at functional thicknesses greater than 10 μm;
- To characterize the adhesion of deposited Cu films as a function of their thickness and as a function of the properties of the nucleation and adhesion promoters employed.

1-5 Scope of Thesis

- Chapter 2: Describes materials and methods used to deposit adhesion/nucleation promotors, and Cu films. Methods of surface and adhesion characterization are also described.
- Chapter 3: Describes the theory of various tools and techniques used for characterization and deposition.
- Chapter 4: Discusses experimental results characterizing the deposition of adhesion/nucleation promotors, as well as the adhesion enhancement of Cu films at the glass-Cu interface.
- Chapter 5: Describes the key conclusions and recommended next steps for optimization and scale-up.
1-6 References


Chapter 2: Experimental Procedures

Figure 2-1 is a process flow diagram outlining the sequence of sample preparation, adhesion promoter application, electroless Cu deposition, Cu electroplating, and adhesion testing. Sections of the thesis that detail the experimental procedures are noted in parentheses.

2-1 Glass Substrate Preparation

7.62 cm × 2.54 cm Eagle XG glass substrates, made by Corning, were used in all experiments. These alkaline earth boro-aluminosilicate glass slides are much smoother
than standard polished glass slides as reported by Wang [1] (Boro-aluminosilicate average roughness = 1.7 Å, versus polished glass average roughness = 6.0 Å). The glass slides were sectioned using a straight edge and a diamond scribe into two sample geometries: 1.00 cm × 1.27 cm samples for tape tests and screening purposes, and 7.62 cm × 1.27 cm samples used for quantitative peel strength measurements. After scribing, the glass was cleaved using a pair of Fletcher “Gold Tip” glass nipping plyers. A single scribe mark was made on the downward face of each sample so that the upward face remained pristine and recognizable during subsequent treatments.

2-2 Glass Substrate Cleaning

The following glass cleaning protocol is described by Cras in preparation for silanization [2]. All cleaning treatments were carried out at 25°C. Deionized water (DI H₂O) was made in-house using a Direct-Q 3UV deionization system by Millipore. Concentrated HCl, methanol, and concentrated H₂SO₄ were purchased from Fisher Scientific. After being cleaved to the desired sample dimension, glass samples were rinsed with DI H₂O and blown dry under a stream of nitrogen. Next, the samples were submerged in a 1:1 volume ratio of concentrated HCl to methanol solution for 30 min. The purpose of this step is to degrease and remove any organics from the surface of the sample. After again being thoroughly rinsed with DI H₂O and dried under a stream of nitrogen, the samples were then immersed in concentrated H₂SO₄. After 30 min, the H₂SO₄ was decanted off the glass samples. The samples were then rinsed aggressively with DI H₂O, and dried under a stream of nitrogen. The purpose of the concentrated H₂SO₄ treatment was to hydroxylate the glass samples in preparation for following
treatments. Cleaned glass samples were stored in covered petri dishes no longer than 60 min before being used in subsequent treatments.

2-3 Silane Deposition

The chosen silane, 3-Aminopropyltriethoxysilane (APTES, Acros), was deposited from a 5mM APTES solution in toluene (ACS grade, Fisher Scientific). Deposition was performed at 25°C for 60 min. Samples were then rinsed twice with toluene, rinsed twice with ethanol (190 proof, Fisher Scientific), rinsed twice with DI H₂O, and finally dried under a stream of nitrogen. A basic mechanistic representation of the formation of an APTES SAM to a hydroxylated glass surface is shown in Figure 2-2.

Figure 2-2. Basic mechanism for formation of APTES SAM on Glass. APTES adsorbs to hydroxylated glass surface and bonds to surface through condensation reactions.
2-4 Activation for Electroless Copper Plating

2-4.1 Ionic Palladium Activation

This method of activation was used for select samples in section 4-3.2. Ionic Pd activation of samples was done in two steps at 25°C. First, samples were immersed in a 200 ppm PdSO₄ solution for 5 min (Proprietary solution from Atotech). Then, samples were gently rinsed with DI H₂O and immersed in a 0.5M dimethlyamine-borane (DMAB) solution for 1 min (Proprietary solution from Atotech). Finally, samples were again gently rinsed with DI H₂O.

2-4.2 Pd-TiO₂ Ink Activation

Palladium-Titanium Inks were made using solutions of Titanium (IV) Butoxide (Acros) and PdCl₂ salt using 1-butanol (ACS grade, Fisher Scientific) as the solvent. PdCl₂ salt was isolated from an aqueous 5 g/l PdCl₂ solution in dilute HCl (Fisher Scientific). The solid PdCl₂ hydrate salt was obtained by evaporation of the aqueous solution in a Thermo Scientific Heratherm OGS 60 oven at 130°C in air. The ink concentrations used were 1.1 mM Titanium (IV) butoxide and 1.1 mM PdCl₂.

Inks were dropped on the sample surface via transfer pipette at volumes of approximately 0.1 mL/cm² based on sample area. Inks were then dried in air at 130°C for 15 min in a Thermo Scientific Heratherm OGS 60 oven. Next, samples were sintered in air at 450°C in a Hoskins electric tube furnace for 30 min. After cooling for 5-10 min,
samples were dipped in 2M H$_2$SO$_4$ for 2 min and rinsed in DI H$_2$O. Finally, samples were dipped in 0.5 M DMAB for 2 min and rinsed with DI H$_2$O.

2-5 Methods of Cu Seed layer Deposition

2-5.1 Physical Vapor Deposition (PVD) Cu

Deposition of PVD Cu: Samples were coated with PVD Cu in a Discovery 18 sputter system at a base pressure of 3×10$^{-6}$ torr and an argon deposition pressure of 2×10$^{-3}$ torr. The 99.99% purity Cu target used was purchased from Angstrom Sciences. Deposition thickness was determined by time using a calibrated deposition rate of 6.4 Å/s.

2-5.2 Electroless Cu Deposition

Printoganth SBP Electroless Cu plating chemistry was obtained from Atotech, USA. The proprietary plating solution consists of CuSO$_4$ supported by a tartrate complexing agent using formaldehyde as the reducing agent. The electroless Cu deposition process was operated at 35°C. Samples were immersed in the bath directly for 5-40 min depending on the desired thickness. After electroless plating, samples were rinsed with DI H$_2$O.
2-5.3 Annealing of Cu Seed Layers

After Cu seed layers are deposited, samples were annealed in a Hoskins electric tube furnace under flowing argon at 400°C for 60 min. After annealing, samples were allowed to cool to 25°C under flowing argon for an additional 60 min.

2-6 Electrolytic Cu Deposition

All samples were electroplated at 25°C in a high-throw plating solution reported by Dini and Snyder [3]. The composition of the bath was 100 g/L CuSO\(_4\)·5H\(_2\)O (Fisher Scientific), 270 g/L H\(_2\)SO\(_4\) (Fisher Scientific), 0.3 g/L polyethylene glycol [molecular weight = 4000 g/mol] (Alfa Aesar) and 0.1 g/L NaCl (Fisher Scientific).

2-6.1 Electrodeposition of Small Scale (1.00 cm × 1.27 cm) Samples

Small-scale samples, 1.00 cm × 1.27 cm, were used for qualitative adhesion testing described in section 2-8.2. Samples were electroplated (using the electrolyte described above) at a current density 15 mA/cm\(^2\). To establish electrical contact and obtain a well-defined surface area, a double layer of tape was applied to the Cu seed layer on each sample as shown in Figure 2-3. First, insulating ‘Fisherbrand™ High-Low Temperature Tape’ (Fisher Scientific) was placed over 1 cm strips of ‘Conductive Copper Tape with Conductive Adhesive’ (McMaster-Carr). Then, a 0.635 cm diameter hole was punched through both layers. The copper adhesive tape was then positioned on the
glass sample such that a 0.317 cm² circular exposed electrode area was defined (Figure 2-3).

![Diagram](image)

Figure 2-3. Method of masking of 1.00 cm × 1.27 cm electroless Cu on glass samples defining circular electrode area of 0.317 cm² for Cu electroplating.

2-6.2 Electrodeposition of Large-scale (7.62 cm × 1.27 cm) samples

Large-scale, 7.62 cm × 1.27 cm, samples were required for adhesion quantification using the 90° peel strength test described in section 2-8.3. Samples were electroplated (using the electrolyte described above) at a current density 10 mA/cm². Electrical contact was made using conductive copper tape along the length of the electrode defining an area plated of approximately 7.62 cm². A large area (70 cm²) Cu foil counter electrode was used, which was placed at a distance of 10 cm from the working electrode.
2-7 Evaluation of Film Thickness Using Four-Point Probe

To estimate Cu film thickness, a Lucas Labs Model S-302-4 Resistivity Test Stand with four-point probe was used. A Keithley 2400 Source Meter was used to supply current and measure resistance at a resolution of ±0.0001 Ω. Probe spacing was 1.0 mm. The practical range for estimation of Cu film thickness is between 50 nm and 2000 nm.

2-8 Evaluation of adhesion

2-8.1 Scotch Tape Test

Scotch Matte Finish Magic™ tape by 3M was used for all tape tests. First, samples were placed face up on a clean benchtop. Fresh tape was applied to the plated surface of samples extending 3 cm beyond the edge of the sample in both directions. Light pressure was applied to the taped sample using forceps to smoothly attach the tape along the sample surface. After waiting approximately 1 min, the tape was removed at a 90° angle relative to the sample using forceps to hold the glass sample in place. Photographs, taken before and after peeling, were used to determine the relative amount of Cu film remaining on the sample surface. The percentage area of Cu remaining on the glass samples was recorded.
2-8.2 Cross-Hatched Tape Test

Cross-hatched tape tests were used to characterize electroplated Cu films on electroless seed layers. These more aggressive tape tests were used to characterize the adhesion of electroplated Cu on glass. Prior to applying tape, samples were scored in four perpendicular directions using a diamond scribe. After cross-hatching, samples were subjected to the same tape test described in section 2-8.1.

2-8.3 Quantitative 90° Peel Strength Tests

The adhesion of electroplated Cu on electroless seed layers was quantified using a 90° peel strength test. A schematic of the peel test is shown in Figure 2-4. Peel strength tests were conducted at a peel rate of 50 mm/min. The force required to peel the sample was recorded as the peel propagates along the length of the sample. Peel strengths are given as force/unit width of sample (N/cm).
Figure 2-4. Schematic of 90° peel test. Cu films peeled at 90 degree angle relative to the substrate at 50 mm/min.

2-9 X-ray Photoelectron Spectroscopy (XPS)

XPS spectra of samples were taken using a PHI Versaprobe 5000 Scanning X-Ray Photoelectron Spectrometer with a monochromatic AlKα anode X-ray source. Survey scans were taken from 1100 eV to 0 eV for 8 cycles. The step size was 0.4 eV/step at a dwell time of 200 ms/step. Peak identification and quantifications were performed using PHI Multipak software. Charge compensation of approximately +1.6 eV was applied to non-metallic samples using the C1s peak at 284.4 eV as a reference [4].
SEM/FIB images of cross-sectioned samples were obtained using a FEI Helios NanoLab™ 650. Samples were cross-sectioned using FIB at 90° normal to the sample surface while images were collected at a tilt of 52°. Images were collected using an ion conversion and electron detector (ICE) at an accelerating voltage of 5 kV. The working distance was 4.2 mm.
2-10 References


Chapter 3: Theory

3-1 Four-Point Probe Theory

As stated in the section 2-7, four-point probe measurements were used to characterize the thickness of Cu on glass substrates. Figure 3-1 is a schematic of a typical four-point probe measurement showing the relevant geometries of a centered probe on a rectangular film. During the sample measurement, a current, $I$, is passed through the outermost probes while the potential, $V$, is measured between the innermost probes. The spacing between each successive probe, $s$, is constant for the measurement.

In order to calculate the film thickness, $t$, equation E1 is used [1, 2].

$$ t = \frac{I \rho}{V G} = \frac{\rho}{R_m G} $$  \hspace{1cm} [E1]

$\rho$ is the known resistivity of the film material, and $R_m$ is the measured resistance. $G$ is a correction factor that depends on the geometric arrangement of the probe on the film and the thickness of the film.

In the case of an infinite ($a=b=\infty$) thin film ($t \ll s$), Equation E1 and an exact value of $G$ can be derived [1]. This is done by considering the differential resistance, $\Delta R$, at radial distance, $x$, from the a probe where current emanates as shown in equation E2.

$$ \Delta R = \rho \frac{dx}{A} = \rho \frac{dx}{2\pi xt} $$  \hspace{1cm} [E2]

In this case, $A$ is the area of the ring at distance $x$ from a single probe. The thickness, $t$, is constant. Integrating from $x_1 = s$ to $x_2 = 2s$ we get equation E3.

$$ R = \frac{\rho}{2\pi t} \left[ x_2 \frac{dx}{x} - \frac{\rho}{2\pi t} \ln x \right]_{x_1}^{x_2} = \frac{\rho}{2\pi t} \ln \frac{2s}{s} = \frac{\rho}{2\pi t} \ln 2 $$  \hspace{1cm} [E3]
Due to the superposition of the probes, \( R = \frac{V}{2I} \). Substituting this into equation E3, and solving for \( t \), we get equation E1 with \( G = \frac{\pi}{\ln 2} = (4.532) \).

![Figure 3-1. Schematic of Four-Point Probe Measurement of a Rectangular Thin-film.](image)

In the present work, the sample dimensions are large enough to be considered semi-infinite and adjustments to \( G \) must be made. Correction factors for the four-point probe measurement of thin films with rectangular geometries (length \( a \), width \( b \), and spacing, \( s \)) have been tabulated by Smits [1]. Based on these values, the correction factors used in this thesis were \( G = 4.225 \) for \( 1.27 \text{ cm} \times 1.00 \text{ cm} \) samples and \( G = 4.321 \) for \( 7.62 \text{ cm} \times 1.27 \text{ cm} \) samples.
3-2 Pd-TiO₂ ink deposition mechanism

3-2.1 Pd-TiO₂ ink deposition mechanism: Drying step

PdCl₂ and titanium(IV) butoxide in n-butanol solutions are deposited on glass substrates resulting in a catalytic heterogeneous Pd-TiO₂ adhesion layer. In the first step, the homogeneous ink is dropped on the surface and dried at 130°C. During this step, butanol is evaporated allowing PdCl₂ to crystalize and titanium(IV) butoxide to react with moisture from the air. For the drying step, the crystallization reaction is shown in equation E4 and the hydrolysis of titanium(IV) butoxide is shown in equation E5.

\[ \text{Pd}^{2+} + 2\text{Cl}^- \rightarrow \text{PdCl}_2(s) \]  \[ \text{E4} \]

\[ \text{Ti}(\text{C}_4\text{H}_9\text{O})_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2(s) + 4\text{C}_4\text{H}_9\text{OH}(v) \]  \[ \text{E5} \]

3-2.2 Pd-TiO₂ ink deposition mechanism: Sintering step

In the sintering step, the deposit of TiO₂ and PdCl₂ is heated to 450°C in air. In this step, TiO₂ is thought to remain intact. However, PdCl₂ reacts with oxygen as shown in equation E6.

\[ \text{PdCl}_2(s) + \frac{1}{2}\text{O}_2 \rightarrow \text{PdO}(s) + \text{Cl}_2 \]  \[ \text{E6} \]

3-2.3 Pd-TiO₂ ink deposition mechanism: Pd²⁺ reduction step

Prior to electroless plating, the oxidized Pd must be reduced to be an effective catalyst. This occurs in the final step of Pd-TiO₂ ink preparation when the substrate is
immersed in an alkaline solution of dimethylamine-borane (DMAB). The reaction begins by DMAB dissociation as shown in equation E7 [4].

\[
(CH_3)_2NH \cdot BH_3 + OH^- \rightarrow BH_3OH^- + (CH_3)_2NH
\] [E7]

In the next step of the reaction, the hydroxytrihydroborate anion is oxidized supplying electrons for the reduction of PdO. This occurs via a series of hydrolysis reactions, as shown in equations E8 and E9 [4].

\[
BH_3OH^- + 3OH^- \rightarrow B(OH)_4^- + \frac{3}{2}H_2 + 3e^-
\] [E8]

\[
BH_3OH^- + 6OH^- \rightarrow B(OH)_4^- + 3H_2O + 6e^-
\] [E9]

The supplied electrons are then consumed in the reduction of PdO as shown in equation E10.

\[
PdO + 2e^- \rightarrow Pd + \frac{1}{2}O_2
\] [E10]

Additionally, the hydroxytrihydroborate anion can decompose with water in the side reaction shown in equation E11[4].

\[
BH_3OH^- + 3H_2O \rightarrow B(OH)_4^- + 3H_2
\] [E11]

3-3 Electroless Cu Metallization

Electroless plating is an electrochemical process where both oxidation of a reducing agent and reduction of a metal ion occur simultaneously on a single electrode. This occurs without any externally applied current. The electroless Cu plating bath used in this work operates under alkaline conditions using the reduced Pd (section 3-2.3) as a catalyst. The reducing agent was formaldehyde, and the complexing agent was potassium sodium tartrate. In this case, the role of potassium sodium tartrate is to ligate
Cu$^{2+}$ ions in the alkaline solution preventing Cu hydroxide precipitation. The oxidation half-reaction of formaldehyde is shown in equation E12 [5].

$$2\text{CH}_2\text{O} + 4\text{OH}^- \rightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2e^- \quad [\text{E12}]$$

The electrons produced by this reaction are then transferred via the Pd catalyst to reduce Cu$^{2+}$ ions on the surface as shown in equation E13 [5].

$$\text{Cu}^{2+} + 2e^- \xrightarrow{\text{catalyst}} \text{Cu} \quad [\text{E13}]$$

Once the process is initiated, the reduced Cu is also able to self-catalyze the electroless reaction.

3-4 Electroplating of Cu

Unlike electroless deposition where oxidation and reduction reactions occur concurrently on the same electrode surface, electroplating separates the oxidation and reduction reactions which occur on separate electrodes. An oxidation reaction occurs at the anode while reduction, or ‘plating,’ occurs on the cathode. The reaction is driven externally using a power supply or potentiostat. In this work, Cu electroplating occurs galvanostatically, \textit{i.e.}, at a constant current. When the electrode area, \(A\), is fixed, the current density, \(i\), remains constant. The current density is analogous to the plating rate. The mass of a given deposit (\(m\)) plated at a constant current over time, \(t\), is governed by Faraday’s law [6]:

$$m = \frac{iAtn}{Fn} \quad [\text{E14}]$$
Where $m$ is the mass of Cu deposited, $M$ is its atomic weight, and $n$ is the oxidation state of the ionic species being reduced ($n=2$). Faraday’s constant, $F$, is equal to 96485 Cb/equivalent. The thickness of a deposit can be calculated by dividing the mass of the deposit by its density and area.

In many cases an additional factor accounting for the current efficiency of the reaction is included. However, in the case of acid Cu plating at relatively low current densities (as used herein), a current efficiency of 100% is expected.
3-5 References


Chapter 4: Observations, Results, and Discussion

4-1 Silanization of GlassSlides

Figure 4-1 shows the XPS spectra of clean glass slides and APTES modified glass slides. The figure emphasizes the spectral peaks of the nitrogen 1s, and carbon 1s, which were observed at binding energies of 400 eV, and 284 eV respectively. The observed calcium peak and magnesium peaks are secondary species incorporated in the glass during production, and thus remain largely unaltered before and after APTES deposition.

As the APTES molecule contains nitrogen, carbon, silicon, and oxygen atoms, evidence of an APTES SAM layer on the glass surface is provided by XPS spectra of any of these elements. However, a spectral difference of silicon and oxygen, before and after APTES deposition, was not observed due to the large background signal of the glass substrate, which is primarily made up of SiO$_2$. For this reason, nitrogen and carbon peaks were chosen to confirm the presence of APTES. As noticed in Figure 4-1, both the nitrogen and carbon peaks become much more prominent after APTES deposition. This provides evidence confirming the presence of the APTES self-assembled monolayer on the glass surface.
Figure 4-1 XPS Spectra of glass slides before and after silanization. a) Clean glass surface. b) APTES modified glass surface. The presence of a nitrogen 1s peak and increased intensity of the carbon 1s peak after modification indicate the presence of an adsorbed APTES layer on the glass surface.

4-2 Pd-TiO₂ ink deposition

Pd-TiO₂ ink was deposited on APTES modified glass slides to serve as a nucleation layer for electroless Cu plating. This section focuses on the deposition and analysis of the ink layer prior to metallization. Additionally, the role of the APTES as a wetting layer for ink deposition on the glass surface is explored.
4-2.1 Pd-TiO₂ ink deposition mechanism

Figure 4-2 is a schematic showing the proposed structural evolution of a Pd-TiO₂ deposit (procedure described above in section 2-4.2) after drying, sintering, and reduction. Figure 4-2a, illustrates the structure of the initial stage of Pd-TiO₂ ink deposition consisting of a dried TiO₂ layer encapsulating co-deposited PdCl₂ salt. This dried layer is deposited on an APTES monolayer represented by the amine groups on the glass substrate (SiO₂). Figure 4-2b shows the structure of this layer after sintering at 450°C. After sintering, the APTES monolayer has been volatilized, and the PdCl₂ is reacts with oxygen to form PdO. Figure 4-2c shows the structure of a sintered layer where PdO which has been reduced to metallic Pd using DMAB as a reducing agent.

![Diagram showing stages of Pd-TiO₂ ink deposition](image)

Figure 4-2. Stages of Pd-TiO₂ ink deposition. a) Dried deposit after 15 min at 130°C in air. b) Sintered deposit after 30 min at 450°C in air. c) Reduced deposit after 2 min in 0.5M DMAB. The oxidation state of Pd species incorporated in TiO₂ is tracked at each stage of deposition.

Figure 4-3 shows the observed XPS spectra after each of these stages. Figure 4-3a is the XPS spectra of an APTES modified glass slide, and Figure 4-3b, 4-3c, and 4-3d show the XPS spectra of samples after drying, sintering, and reduction respectively. Titanium 2p₁ and 2p₃ peaks are observed at 464 eV and 458 eV respectively confirming the presence of titanium in each step after drying. The presence of palladium is
confirmed by the Pd 3d_{3/2} and 3d_{5/2} peaks observed around 341 eV and 336 eV respectively.

The nitrogen 1s peak observed at 400 eV confirms the presence of APTES on the glass substrate (Figure 4-3a) as reported above. After Pd-TiO_2 ink placement and drying (Figure 4-3b), a weak nitrogen 1s peak is still observed indicating the presence of some APTES molecules on the glass surface. The disappearance of this nitrogen 1s peak after sintering suggests that the APTES monolayer is volatilized or decomposed at the higher temperature during sintering. This is consistent with other reports of similar silanes leaving the surface of SiO_2 substrates above temperatures of 400°C [1, 2].

![Figure 4-3. XPS spectra at various stages of Pd-TiO_2 deposition on APTES modified glass. a) APTES modified glass. b) Dried Pd-TiO_2 ink. c) Sintered Pd-TiO_2 ink. d) Reduced Pd-TiO_2 ink.](image-url)
Another important transition occurring during the sintering step is the conversion of PdCl$_2$ to PdO. After the initial drying step (Figure 4-3b), strong chlorine 2s and 2p peaks are observed at 269 eV and 199 eV respectively. When the sample is sintered at high temperature (Figure 4-3c), the intensity of the chlorine peaks is significantly reduced. After ink reduction (Figure 4-3d), the chlorine peaks are not observed at all.

Further evidence of the transition from PdCl$_2$ → PdO → Pd is found in Figure 4-4, which provides a detailed look at the Palladium 3d$_{5/2}$ and 3d$_{3/2}$. Figure 4-4a shows the APTES modified glass slide without palladium, while Figure 4-4 b, c, and d show the Pd-TiO$_2$ deposits after drying, sintering, and reduction respectively. The shift of the 3d$_{5/2}$ peaks after each stage is consistent with a change in palladium oxidation state [3]. Figure 4-4b shows the highest binding energy observed of the palladium 3d$_{5/2}$ at 338.0 eV after drying the Pd-TiO$_2$ ink. This binding energy, along with the chlorine peaks observed in Figure 4-3b, suggests the presence of PdCl$_2$ in the dried deposit [3-4].

After sintering, the Pd 3d$_{5/2}$ peak in Figure 4-4c was observed at 336.4 eV which is consistent with PdO [5]. This binding energy shift, along with the disappearance of chlorine peaks in Figure 4-3c, suggests that the PdCl$_2$ of the dried deposit transitions to PdO during the high temperature sintering [3]. When the sintered Pd-TiO$_2$ ink is reduced in DMAB, the palladium 3d$_{5/2}$ peak shifts to approximately 335.0 eV as observed Figure 4d. This shift is consistent with the transition of PdO to metallic Pd [3-5].
Figure 4-4. XPS of Pd 3d$\text{3/2}$ and 3d$\text{5/2}$ peaks for a) APTES modified glass, b) dried Pd-TiO$\text{2}$ ink, c) sintered Pd-TiO$\text{2}$ ink, and d) reduced Pd-TiO$\text{2}$ ink. The shift of the Pd 3d$\text{5/2}$ peaks is evidence for the change of PdCl$\text{2}$ to PdO, and then to metallic Pd.

4-2.2 APTES Wetting Layer for Pd-TiO$\text{2}$ Ink Deposition

Figure 4-5 illustrates the improved wettability of Pd-TiO$\text{2}$ ink on an APTES modified glass slide as compared to a clean, unmodified glass slide. Figure 4-5 also shows how the wettability of the Pd-TiO$\text{2}$ ink impacts the plating of electroless Cu (after drying, sintering, and reduction.) Figure 4-5a1 is an image of a 10 μl droplet of Pd-TiO$\text{2}$ ink on the surface of an APTES modified glass slide (profile image shown Figure 4-5a2). The low contact angle of the ink droplet is an indication of its good wettability to the APTES modified surface. In contrast, Figure 4-5b1 is an image of a 10 μl droplet of Pd-TiO$\text{2}$ ink on the surface of a clean, unmodified glass slide (profile image shown Figure 4-5b2). The relatively high contact angle observed is an indication of poor wettability of the Pd-TiO$\text{2}$ ink on unmodified glass surfaces.
When Pd-TiO$_2$ ink dries, the improved wettability on an APTES modified glass results in a more even deposit of Pd-TiO$_2$ than compared to the analogous deposit on unmodified glass substrates. Although the uniformity of the Pd-TiO$_2$ deposit cannot be visually discerned after drying the ink, it is evident after electroless Cu plating. The electroless Cu in Figure 4-5a3 is smooth and uniform across the surface of the sample. However, the electroless Cu in Figure 4-5b3 does not cover the glass substrate uniformly and contains blisters. It can be concluded that the APTES ‘wetting layer’ allows for a more uniform deposition of Pd-TiO$_2$ using the methods described in section 2-4.2.
Figure 4-5. APTES ‘wetting layer’ for Pd-TiO₂ Ink deposition and its effect on electroless Cu plating. a1-a3 are representative images of APTES modified glass substrates, while b1-b3 are representative images of clean glass substrates (without APTES). Images a1 and b1 show a 10 μl Pd-TiO₂ ink droplet on the substrate surface. Profile images of droplet are shown in a2 and b2. Images a3 and b3 show 400 nm electroless Cu on Pd-TiO₂ modified glass substrates. The improved wettability of ink on APTES modified glass results in a more uniform Pd-TiO₂ deposit than ink dried on glass without APTES. Uniformity of Pd-TiO₂ deposits is demonstrated by the uniformity of electroless Cu deposited.
4-3 Adhesion of Cu seed layer to activated glass substrates

4-3.1 Glass metallization: Adhesion of Electroless Cu seed layers on Pd-TiO₂ ink

Results of tape tests of electroless Cu seed layers of various thicknesses deposited on glass substrates modified by APTES followed by Pd-TiO₂ are shown in Figure 4-6. The Pd-TiO₂ thickness for these samples was estimated to be 30 nm, based on the volume and concentration of PdCl₂ and Ti(IV)-butoxide in the ink solution. In each case, samples were annealed after electroless deposition. The images in the left column of Figure 4-6 (a1-e1) are the metallized glass substrates after the tape test. The images in the right column of Figure 6 (a2-e2) are the tape fragments showing Cu detached from the metallized sample onto the tape.
Figure 4-6. Tape test results for electroless Cu seed layers of various thicknesses on 30 nm Pd-TiO$_2$ coated glass. Electroless Cu thickness: a) 100 nm. b) 250 nm. c) 440 nm. d) 540 nm. e) 800 nm. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test showing the amount of Cu removed from the substrate onto the tape.
At electroless Cu thicknesses below 500 nm, little Cu is removed during the tape. The Cu that is removed is primarily small fragments at the imperfect edges of the samples. However, when the electroless Cu thickness is increased beyond 500 nm, the adhesion to the substrate begins to deteriorate. At a thickness of 800 nm, nearly all of the electroless Cu is removed. This provides an upper bound on the Cu seed layer thickness to be used in building the stack described above in Figure 2-1.

4-3.2 Glass metallization: Adhesion of Cu seed layers on APTES modified glass without Pd-TiO₂ adhesion promoter

Figure 4-7 shows tape test results for two thicknesses of electroless Cu deposited on APTES modified glass without Pd-TiO₂ adhesion promoter. Since electroless deposition suffers from poor nucleation on APTES modified glass, ionic Pd activation was employed. It is important to note that this Pd activation results in a very thin layer (sub-nm) of Pd nanoparticle catalysts that is very different in morphology and composition than the Pd-TiO₂ adhesion promoter described above. This Pd activation procedure is detailed in section 2-4.1 and is a conventional method of Pd activation. In this procedure, aqueous Pd²⁺ ions adsorb onto an APTES monolayer on glass. Finally, the adsorbed Pd²⁺ ions are reduced to metallic nanoparticles in DMAB. The now activated glass slides are then plated in the same electroless Cu plating solution described in section 2-5.2.

When electroless Cu films are plated at a thickness of 50 nm, the Cu film is discontinuous, but adherent (Figure 4-7a1-a2). However, at thicknesses beyond 50 nm,
the electroless Cu film is removed with the tape test (Figure 4-7). In many cases, when the electroless Cu film grew beyond 100 nm, delamination would occur even before removing the substrate from the electrolyte. The poor adhesion of electroless Cu films on APTES modified glass is thought to be due to the weak adhesion promotion properties of the conventionally applied Pd activation procedure.

![Figure 4-7](image)

Figure 4-7. Images after tape test for electroless Cu of various thicknesses on Pd activated APTES modified glass. Electroless Cu thickness: a) 50 nm. b) 100 nm. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test.

Silane base SAMs have been reported as adhesion promoters for PVD Cu films [1, 2, 6] deposited on SiO₂. However, this process suffers from two drawbacks: (i) It introduces a ‘dry’ deposition method and does not provide an ‘all-wet’ integrated process; and (ii) It does not yield adherent Cu films of thicknesses needed for PCB and interposer applications. This is shown in the tape test results of Figure 4-8 where
70-400 nm adherent PVD Cu films were deposited on glass. However, the PVD Cu films failed the tape test at thicknesses beyond 400 nm. While the failure mechanism is not presently known, it is likely to be the increased stress developed in thicker PVD films that compromises the interfacial adhesion thereby resulting in failed tape testing.
Figure 4-8. Images after tape test for PVD Cu seed layers of various thicknesses on APTES modified glass. PVD thickness: a) 70 nm. b) 300 nm. c) 400 nm. d) 500 nm. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test. PVD Cu on APTES fails tape tests at Cu thicknesses exceeding 400 nm.
To better understand the poor adhesion of electroless Cu on APTES, 300 nm PVD Cu was deposited on APTES modified glass slides with and without Pd activation. Figure 4-9 summarizes the results of tape tests after annealing. As shown in Figure 4-9a, PVD Cu passes the tape test when using APTES alone as the adhesion promoting layer. However, when PVD Cu is deposited on Pd activated APTES modified glass, the sample fails the tape test (Figure 4-9b). These results suggest the weak link for poor adhesion of electroless Cu on Pd activated APTES is the Pd activation layer. Fundamental insights into the failure mechanism are, as of yet, not available.

![Figure 4-9](image)

**Figure 4-9** The effect of Pd activation on the adhesion of PVD Cu films to APTES modified glass. a) 300 nm PVD Cu on APTES modified glass. b) 300 nm PVD Cu on Pd activated APTES modified glass. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test.

The detrimental effect of conventional Pd activation treatment on the adhesion of Cu films on APTES modified glass has been demonstrated above. Adhesion
enhancement of PVD Cu films deposited directly on APTES modified glass was demonstrated by passing tape tests at thicknesses up to 400 nm. However, this enhancement is inferior when compared to electroless Cu films deposited on Pd-TiO$_2$ modified glass which tape tests beyond 500 nm thickness.

4-4 Cu Electrodeposition on Electroless Cu Seed Layers

The above discussion shows that glass substrates using Pd-TiO$_2$ adhesion promoting layers can be coated with up to 500 nm of electroless Cu seed layers. However, numerous applications require thicker (10-20 μm) Cu coatings. To achieve such Cu thickness, the route of Cu electrodeposition on electroless Cu seed layers was chosen because electrodeposition offers high throughput and ease of processing.

A simple optimization of current density was conducted for the minimum magnitude of film stress after electroplating Cu to thickness of 10 μm. The magnitude of Cu film stress was determined by electroplating dual-leg stress test strips from Specialty Testing & Development Co. (PN 1194). After electroplating at a given current density, the legs of the test strips would bend outward if the electroplated Cu film contained stress, while the legs would remain straight if the electroplated Cu films did not contain stress. The lowest observed stress was when test strips were electroplated between 10-20 mA/cm$^2$. At higher current densities (>20 mA/cm$^2$), Cu films contained tensile stress, while at lower current densities (<10 mA/cm$^2$), Cu films contained compressive stress. For electroplating onto electroless Cu seed layers on small samples (1.00 cm × 1.27 cm) a current density of 15 mA/cm$^2$ was chosen. However, when this current density was used to electroplate Cu on large samples (7.62 cm × 1.27 cm), the
electroplated Cu was powdery and dendritic. For this reason, large samples shown herein were electroplated at 10 mA/cm$^2$ which produced much smoother films.

4-4.1 Adhesion of Electroplated Cu on Electroless Cu Seed Layers

Figure 4-10 shows the cross-hatched tape test results for samples electroplated with thick Cu layers. These samples were prepared by electroplating Cu at a current density of 15 mA/cm$^2$ from an acid bath (described in section 2-6 above). The substrate for electroplating was APTES-modified glass pre-coated with a 30 nm thick Pd-TiO$_2$ adhesion layer and 450 nm electroless Cu. The electroplated Cu passes tape tests even at an electroplated Cu thickness of more than 100 μm despite aggressive cross-hatching with a diamond scribe.
Figure 4-10. Tape test results for electroplated Cu films on electroless Cu seed layers on Pd-TiO₂ ink modified glass. a) 30 μm electroplated Cu. b) 100 μm electroplated Cu. ‘1’ denotes glass substrate after tape test. ‘2’ denotes tape fragment after tape test. Samples survive tape tests despite aggressive crosshatching.

In order to quantify the adhesion of electroplated Cu films on electroless Cu seed layers the sample size was scaled up to 7.62 cm × 1.00 cm. These samples were prepared by electroplating Cu at a current density of 10 mA/cm² from an acid bath (described in section 2-6) for 68 minutes yielding a Cu thickness of approximately 15 μm. Figure 4-11 shows the results of a 90° peel strength tests. 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 for Cu films on AlN substrates [7].
Figure 4-11. 90° peel strength test results for the stack: 15 μm electroplated Cu / 300 nm electroless Cu / Pd-TiO₂ / glass. Cu film breaks before traveling the complete length of the sample. Peel Strength testing was performed by Dr. Zhiming Liu of Atotech USA, Denver, CO.

Figure 4-12 shows an SEM/FIB image of a typical sample. The total Cu thickness in this image was measured to be approximately 14.4 μm. Prior to electrodeposition, the electroless Cu thickness for this sample was measured to be 0.3 μm using the previously described four-point probe technique. Using the difference of total Cu thickness and electroless Cu thickness a columbic efficiency of approximately 94.0% was calculated. This is in agreement with the measured mass of the electrodeposit which gave a columbic efficiency of 96.6%.
Figure 4-12. 5000 × zoom SEM/FIB Cross-Section Image of Electroplated Sample. Image was collected using ICE detector at an accelerating voltage of 5 kV at a tilt angle of 52°. The image shows coalesced electroless and electroplated Cu layers. The combined thickness of Cu layers corresponds to a thickness of 14.4 μm. The Pd-TiO₂ interface was not able to be discerned.

4-5 Investigation of Failure Interface

After 90° peel testing, the failure interface of a selected Pd-TiO₂ was examined using XPS. The selected spectra of the peeled Cu and glass substrate are shown in Figure 4-13a and Figure 4-13b respectively. Peaks consistent with titanium 2p₁ and 2p₃, as well as palladium 3d₃/₂ and 3d₅/₂, are observed on both sides of the interface [3]. This suggests that the failure mechanism for the peeled Cu films is a de-cohesion of the Pd-TiO₂ adhesion layer.
Figure 4-13. XPS of failure interface after 90° Peel Test showing presence of Ti and Pd. 
a) Peeled Cu interface.  b) Glass Substrate. The presence of Ti and Pd on both interfaces 
suggest that interfacial failure mechanism is one of Pd-TiO$_2$ de-cohesion.
4-6 References


Chapter 5: Conclusions and Future Work

5-1 Summary and 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 a Pd-TiO$_2$ adhesion layer that also catalyzes electroless deposition of a Cu seed layer. The mechanism for Pd-TiO$_2$ adhesion layer formation involves stepwise reduction of Pd-ions to metallic Pd particles embedded in a TiO$_2$ matrix. Electrodeposition onto the Cu seed layer enables thick (>10 μm) adherent Cu films. The proposed ‘all-wet’ strategy provides a significant adhesion enhancement when compared to electroless Cu deposited on conventional Pd-activated APTES modified glass. This ‘all-wet’ process also offers low-cost and ease of integration in numerous applications where dielectric-metal interfaces are encountered.

5-2 Future Work

In order for the ‘all-wet’ process investigated in this thesis to be implemented at an industrial scale, future work should be focused on the development and further understanding of the Pd-TiO$_2$ adhesion layer. Specifically, developmental work should focus on the optimization of Pd-TiO$_2$ deposition conditions to achieve higher peel strengths. An investigation of structure and morphology of the Pd-TiO$_2$ adhesion layer, and their effect on adhesive strength, would improve fundamental understanding of how to improve the process. Finally, the proposed process for the ‘all-wet’ Cu metallization
of glass substrates should be evaluated on patterned glass substrates before implementation at an industrial scale.
Chapter 6: Complete List of References

6-1 Chapter 1 References


6. Wang, B.K., Y.A. Chen, A. Shorey, and G. Piech, Thin Glass Substrates Development and Integration For Through Glass Vias (TGV) With Copper (Cu)


6-2 Chapter 2 References


6-3 Chapter 3 References


6-4 Chapter 4 References


