2005

Chemical vapor deposition of thin films for ULSI interconnect metallization

Lidong Wang
Louisiana State University and Agricultural and Mechanical College, wang_lidong@yahoo.com

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations

Part of the Chemical Engineering Commons

Recommended Citation

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Doctoral Dissertations by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
CHEMICAL VAPOR DEPOSITION OF THIN FILMS FOR ULSI INTERCONNECT METALLIZATION

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
The Gordon A. and Mary Cain Department of Chemical Engineering

by
Lidong Wang
B.S., Tianjin University, P.R. China, 1994
M.S., Tianjin University, P.R. China, 1997
May, 2005
To our lord – Jesus Christ
ACKNOWLEDGEMENTS

This dissertation was finished under the guidance of Dr. Gregory L. Griffin, Professor of Chemical Engineering. I would express my deepest appreciation to Dr. Griffin for his constant advice, encouragement, and enthusiasm through the whole research. I have learnt a great deal from him during these years, like his unique way of organizing research activities.

I would also thank Dr. Kerry M. Dooley, Dr. Elizabeth J. Podlaha-Murphy, Dr. Douglas P. Harrison from Chemical Engineering, Dr. Andrew W. Maverick from Chemistry, and Dr. Kenneth Matthews from Physics for their time and energy devoted for serving on my examination committee.

I appreciate all the help on the resistivity measurements from Dr. Pratul K. Ajmera and Dr. Golden Huang from the Department of Electrical and Computer Engineering. I also appreciate all the help on AFM analysis from Dr. Robin L. McCarley of the Chemistry Department, the XPS and SEM analysis from Dr. Jiechao Jiang of the Department of Mechanical Engineering, and the SEM analysis from Dr. Xiaogang Xie of the Department of Geology.

I would like to thank Dr. Jed Aucoin and Miss Mariah Mcmasters for their help on AFM measurement. I also would like to thank all the undergraduate students (Kyle Thomas, Christina Canright, Thomas Miller, Ryan Fontenot, James Michiels, and Katherine Levy) for helping me do the experiments.

Finally, I would like to extend my appreciation to my family who are always encouraging and supporting me. I would also like to thank Don and Lynda Stewart for their love and friendship during the past five years.
# TABLE OF CONTENTS

DEDICATION ................................................................................................................................. ii

ACKNOWLEDGEMENTS ................................................................................................................... iii

LIST OF TABLES ............................................................................................................................... vi

LIST OF FIGURES .............................................................................................................................. viii

ABSTRACT ......................................................................................................................................... xi

CHAPTER 1 INTRODUCTION ............................................................................................................. 1

CHAPTER 2 LITERATURE REVIEW ................................................................................................. 9
  2.1 Interconnect Metallization ........................................................................................................... 9
    2.1.1 The Advantages of Copper as Metal Interconnects in ULSI ..................................................... 10
    2.1.2 Dual Damascene Process ...................................................................................................... 11
    2.1.3 Overview of Chemical Vapor Deposition .............................................................................. 13
  2.2 Copper CVD Using Cu(hfac)$_2$ ............................................................................................... 15
    2.2.1 Cu(hfac)$_2$ Reduced by $\text{H}_2$ ............................................................................................ 15
    2.2.3 Alcohol Additives in Copper CVD ........................................................................................ 21
    2.2.4 Film Properties ..................................................................................................................... 23
  2.3 Tantalum as Copper Diffusion Barrier ....................................................................................... 26
  2.4 Palladium Seed Layer for Electroless Copper Deposition ............................................................. 28
    2.4.1 Overview of Electroless Copper Deposition .......................................................................... 28
    2.4.2 Deposition of Pd Seed Layer ................................................................................................. 32
  2.5 Palladium CVD Using Pd(hfac)$_2$ ............................................................................................ 38
    2.5.1 Precursors for Pd CVD ......................................................................................................... 38
    2.5.2 CVD Thin Pd Films from Pd(hfac)$_2$ .................................................................................... 38

CHAPTER 3 EXPERIMENTAL: APPARATUS AND PROCEDURE ................................................. 43
  3.1 Copper CVD ................................................................................................................................ 43
    3.1.1 Warm Wall Low Pressure LDS CVD System ....................................................................... 43
    3.1.2 Operating Procedure .............................................................................................................. 50
  3.2 Tantalum CVD .............................................................................................................................. 54
    3.2.1 Tantalum CVD System .......................................................................................................... 54
    3.2.2 Operating Procedure .............................................................................................................. 59
  3.3 Palladium CVD ............................................................................................................................. 61
    3.3.1 Pd CVD Apparatus ............................................................................................................... 61
    3.3.2 Operating Procedure .............................................................................................................. 67
  3.4 Film Characterization .................................................................................................................... 71

CHAPTER 4 RESULTS AND DISCUSSION ABOUT COPPER CVD .............................................. 76
  4.1 Baseline Results ........................................................................................................................... 76
  4.2 Reaction Order Experiments ....................................................................................................... 87
    4.2.1 Cu(hfac)$_2$ Effect ................................................................................................................ 87
<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Properties of Tantalum</td>
<td>27</td>
</tr>
<tr>
<td>2-2</td>
<td>Solution Composition for Electroless Cu Deposition</td>
<td>31</td>
</tr>
<tr>
<td>2-3</td>
<td>The Reaction Orders for the Rate Law of ELD Cu</td>
<td>32</td>
</tr>
<tr>
<td>2-4</td>
<td>Studies about Pd CVD</td>
<td>40</td>
</tr>
<tr>
<td>3-1</td>
<td>Operating Conditions for Copper CVD</td>
<td>53</td>
</tr>
<tr>
<td>3-2</td>
<td>Operating Conditions for Batch Pd Activation</td>
<td>69</td>
</tr>
<tr>
<td>3-3</td>
<td>Operating Conditions for Continuous Pd CVD without Activation</td>
<td>70</td>
</tr>
<tr>
<td>4-1</td>
<td>Operating Conditions for Baseline Copper CVD</td>
<td>77</td>
</tr>
<tr>
<td>4-2</td>
<td>Baseline Results of Cu CVD on Glass</td>
<td>78</td>
</tr>
<tr>
<td>4-3</td>
<td>Steady State Growth Rate and Induction Time</td>
<td>80</td>
</tr>
<tr>
<td>4-4</td>
<td>Operating Conditions for Cu(hfac)$_2$ Reaction Order Experiments</td>
<td>87</td>
</tr>
<tr>
<td>4-5</td>
<td>Experimental Results with Different Cu(hfac)$_2$ Partial Pressure</td>
<td>88</td>
</tr>
<tr>
<td>4-6</td>
<td>Steady State Kinetic Results with Different Cu(hfac)$_2$ Partial Pressure</td>
<td>90</td>
</tr>
<tr>
<td>4-7</td>
<td>Operating Conditions for isopropanol Reaction Order Experiments</td>
<td>91</td>
</tr>
<tr>
<td>4-8</td>
<td>Summary of Experimental Results with Different i-PrOH Partial Pressure</td>
<td>92</td>
</tr>
<tr>
<td>4-9</td>
<td>Steady State Kinetic Results with Different i-PrOH Pressures</td>
<td>93</td>
</tr>
<tr>
<td>4-10</td>
<td>Operating Conditions for H$_2$ Reaction Order Experiments</td>
<td>95</td>
</tr>
<tr>
<td>4-11</td>
<td>Summary of Experimental Results with different H$_2$ Partial Pressure</td>
<td>96</td>
</tr>
<tr>
<td>4-12</td>
<td>Steady State Kinetic Results with Different H$_2$ Partial Pressures</td>
<td>98</td>
</tr>
<tr>
<td>4-13</td>
<td>Operating Conditions for Copper CVD using N$_2$ as Carrier Gas</td>
<td>100</td>
</tr>
<tr>
<td>Page</td>
<td>Title</td>
<td>Section</td>
</tr>
<tr>
<td>------</td>
<td>----------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>4-14</td>
<td>Cu CVD Results using N₂ as Carrier Gas</td>
<td></td>
</tr>
<tr>
<td>4-15</td>
<td>Steady State Growth Rate and Induction Time</td>
<td></td>
</tr>
<tr>
<td>5-1</td>
<td>Proposed Reaction Mechanism for i-propanol-assisted Reduction of Cu(hfac)₂</td>
<td></td>
</tr>
<tr>
<td>6-1</td>
<td>Operating Conditions for Tantalum CVD</td>
<td></td>
</tr>
<tr>
<td>7-1</td>
<td>Operating Conditions for Pd CVD without activation</td>
<td></td>
</tr>
<tr>
<td>7-2</td>
<td>Operating Conditions for Activation Step</td>
<td></td>
</tr>
<tr>
<td>7-3</td>
<td>Operating Conditions for Continuous CVD Step</td>
<td></td>
</tr>
<tr>
<td>7-4</td>
<td>Measured Film Thickness of Slide 1 and 2</td>
<td></td>
</tr>
<tr>
<td>7-5</td>
<td>Operating Conditions of Activation Step for ELD Cu</td>
<td></td>
</tr>
<tr>
<td>7-6</td>
<td>Operating Conditions of Activation Step for Temperature Effects</td>
<td></td>
</tr>
<tr>
<td>7-7</td>
<td>Operating Conditions of Activation Step for Evaporation Time Effect</td>
<td></td>
</tr>
<tr>
<td>7-8</td>
<td>Surface Quantitative Analyses of Pd Seed Layers using XPS</td>
<td></td>
</tr>
<tr>
<td>7-9</td>
<td>Surface Morphology Analyses of Pd Seed Layers using AFM</td>
<td></td>
</tr>
<tr>
<td>7-10</td>
<td>Operating Conditions of Activation Step for Additive Effect</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF FIGURES

2-1  Dual Damascene Copper Deposition ................................................................. 13

2-2  Relationship between Thickness and Resistivity of CVD Cu Film ............... 24

3-1  Schematic of Solution Delivery System for Copper CVD ......................... 44

3-2  Schematic of Pedestal Reactor ..................................................................... 49

3-3  Schematic of Warm Wall Low Pressure Tantalum CVD System .............. 55

3-4  Schematic of Pedestal Reactor ..................................................................... 58

3-5  Schematic of Cold Wall Pd CVD System ..................................................... 63

3-6  Schematic of Pd APCVD Reactor ................................................................. 65

3-7  Schematic of Four Point Probe ................................................................... 74

4-1  Steady State Growth Rate using Baseline Deposition Conditions .............. 80

4-2  SEM Images of Copper Films with Different Deposition Times ............... 83

4-3  AFM Images of Copper Films with Different Deposition Times ............... 84

4-4  RMS Roughness vs. Film Thickness ............................................................. 85

4-5  Resistivity vs. Equivalent Thickness for Baseline Films ......................... 86

4-6  Mass Loading vs. Deposition Time under Different Cu(hfac)$_2$ Partial Pressure .... 89

4-7  Resistivity vs. Equivalent Thickness for Cu(hfac)$_2$ Reaction Order Experiments .... 90

4-8  Mass Loading vs. Deposition Time under Different isopropanol Pressures .......... 93

4-9  Resistivity vs. Equivalent Thickness for isopropanol Order Experiments .......... 94

4-10 Mass Loading vs. Deposition Time under Different H$_2$ Partial Pressure ........... 97
<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-11</td>
<td>Influence of H(_2) Partial Pressure on Growth Rate</td>
</tr>
<tr>
<td>4-12</td>
<td>Resistivity vs. Equivalent Thickness for H(_2) Reaction Order Experiments</td>
</tr>
<tr>
<td>4-13</td>
<td>Steady State Growth Rate using N(_2) as Carrier Gas</td>
</tr>
<tr>
<td>4-14</td>
<td>Resistivity vs. Equivalent Thickness using N(_2) as Carrier Gas</td>
</tr>
<tr>
<td>5-1</td>
<td>Copper Deposition Rate as a Function of Cu(hfac)(_2) Partial Pressure</td>
</tr>
<tr>
<td>5-2</td>
<td>Copper Deposition Rate as a Function of i-PrOH Partial Pressure (low Cu(hfac)(_2) partial pressure)</td>
</tr>
<tr>
<td>5-3</td>
<td>Copper Deposition Rate as a Function of i-PrOH Partial Pressure (high Cu(hfac)(_2) partial pressure)</td>
</tr>
<tr>
<td>6-1</td>
<td>Thermodynamic Product Yields as a Function of SiH(_4)/TaF(_5) molar ratio</td>
</tr>
<tr>
<td>6-2</td>
<td>XPS Depth Profile of a CVD Ta Film</td>
</tr>
<tr>
<td>7-1</td>
<td>Thickness Profile of Pd Film using Mass-Transfer Limited Model</td>
</tr>
<tr>
<td>7-2</td>
<td>Resistivity of Pd Films with Activation Step</td>
</tr>
<tr>
<td>7-3</td>
<td>Effects of Batch Holding Time on Cu ELD Time</td>
</tr>
<tr>
<td>7-4</td>
<td>Effects of Batch Holding Time on ELD Cu Film Thickness</td>
</tr>
<tr>
<td>7-5</td>
<td>Effects of Batch Holding Time on ELD Cu Film Growth Rate</td>
</tr>
<tr>
<td>7-6</td>
<td>ELD Cu Film Appearance Time using 150°C as Activation Temperature</td>
</tr>
<tr>
<td>7-7</td>
<td>ELD Cu Film Thickness using 150°C as Activation Temperature</td>
</tr>
<tr>
<td>7-8</td>
<td>ELD Cu Film Growth Rate using 150°C as Activation Temperature</td>
</tr>
<tr>
<td>7-9</td>
<td>ELD Cu Film Appearance Time using 210°C as Activation Temperature</td>
</tr>
<tr>
<td>7-10</td>
<td>ELD Cu Film Thickness using 210°C as Activation Temperature</td>
</tr>
<tr>
<td>7-11</td>
<td>ELD Cu Film Growth Rate using 210°C as Activation Temperature</td>
</tr>
</tbody>
</table>
7-12 Cu Deposition Rates with Different Pd Activation Temperature ............................... 149
7-13 Effects of Precursor Evaporation Time on ELD Cu Film Appearance......................... 153
7-14 Effects of Precursor Evaporation Time on Cu ELD Time ........................................... 154
7-15 Effects of Precursor Evaporation Time on Cu Film Thickness .................................. 155
7-16 Effects of Precursor Evaporation Time on Cu Film Growth Rate ............................. 156
7-17 Effects of Precursor Evaporation Time on Cu Film Resistivity ................................. 157
7-18 XPS Spectra of CVD Pd Activated Glass Substrates................................................. 160
7-19 Effects of Precursor Evaporation Time on Pd Atomic Percent .................................... 163
7-20 Plan-view SEM Images of Pd Seed Layers using Different Evaporation Time ........ 164
7-21 AFM Images of Pd Seed Layers using Different Evaporation Time ............................ 165
7-22 Effects of Precursor Evaporation Time on Pd Particle Size ....................................... 166
7-23 Effects of Precursor Evaporation Time on Pd Coverage ........................................... 168
7-24 Comparison of Intensity Ratio of Pd and Si from XPS and AFM ............................... 169
7-25 Effects of H$_2$O Vapor on Cu ELD Time ................................................................. 172
7-26 Effects of H$_2$O Vapor on Cu Film Thickness............................................................ 173
7-27 Effects of H$_2$O Vapor on Cu Film Growth Rate ......................................................... 173
7-28 Effects of i-PrOH Vapor on Cu ELD Time ................................................................. 174
7-29 Effects of i-PrOH Vapor on Cu Film Thickness........................................................... 175
7-30 Effects of i-PrOH Vapor on Cu Film Growth Rate ..................................................... 176
A-1 Precursor Concentration Profile using Mass-Transfer Limited Model ....................... 196
ABSTRACT

We have studied the kinetics of copper chemical vapor deposition (CVD) for interconnect metallization using solution delivery of Cu(hfac)$_2$ (Cu(II) hexafluoroacetylacetone) dissolved in isopropanol. We observe a growth rate of 17.7 ± 1.5 nm/min at reference conditions of 300°C substrate temperature, 0.025 Torr Cu(hfac)$_2$ partial pressure, 1.6 Torr isopropanol (reducing agent), and 80 Torr H$_2$ (carrier gas). The film resistivity approaches the bulk value of copper for film thickness greater than 100 nm. Reaction order experiments show first-order kinetics with respect to Cu(hfac)$_2$ partial pressure and zero-order with respect to isopropanol.

A series reaction mechanism including three kinetically significant steps (adsorption of Cu(hfac)$_2$, dissociation of (hfac) ligand, and desorption of (hfac)) is used to describe the observed kinetic results. The proposed rate determining step is the dissociation of (hfac) ligand when the pressure ratio of Cu(hfac)$_2$ to isopropanol is low, and becomes the desorption of (hfac) when the pressure ratio is high.

We also examined a low temperature chemical vapor deposition process for the growth of tantalum thin films using SiH$_4$ reduction of TaF$_5$. Using a temperature of 350°C and reactant partial pressures of 0.2 Torr TaF$_5$ and 0.3 Torr SiH$_4$, we obtain a growth rate of 2.2 ± 1.7 nm/min. The XPS analysis results show that the Ta film is Si free, but contains relatively high oxygen concentration because of residual gas contamination.

Lastly, we have studied a batch CVD process for palladium seed layer deposition using H$_2$ reduction of Pd(hfac)$_2$ (Pd(II) hexafluoroacetylacetone). Nano-sized Pd particles with nuclei density between 1 to 14 clusters/µm$^2$ are observed using AFM. The quality of the Pd seed layer is examined by depositing electroless copper film. We have investigated the
influence of CVD operating conditions (deposition time, activation temperature, and precursor concentration) on the activity of the Pd seed layers (i.e., by monitoring visual appearance and deposition rates of the ELD Cu films). At the optimized conditions we can deposit uniform Cu films at a rate of $3.4 \pm 1.4$ nm/s. Additional work is needed to improve the resistivity and adhesion of the films.
CHAPTER 1 INTRODUCTION

The demand for manufacturing semiconductor integrated circuit (IC) devices with high circuit speed and high packing density requires the shrinking scale of feature sizes in ultra-large-scale integration (ULSI) structure. The minimization of interconnect feature size will meet the trend of smaller chip sizes and increased packing density. However, it will also increase interconnect resistance and reliability concerns like electromigration. Both of these problems can be overcome by replacing aluminum with copper as IC metal interconnects.

Compared with aluminum, copper offers several intrinsic property advantages over Al. It has lower resistivity (1.67 vs. 2.67 $\mu\Omega\cdot$cm for Al), which means wires can be smaller and packed more tightly, but still carry the same current. It also means fewer levels of metal for the same duty and lower production costs. A second advantage is that copper has up to 4 orders of magnitude greater electromigration resistance than Al (Shingubara, 1991), which will improve the performance and reliability of device. Third, with its higher melting temperature vs. Al, copper has increased resistance to stress-induced voids (Jain, 1993). All in all, copper is said to provide better yield than aluminum-based devices of the same design (Singer, 2002). Over the past five years, many semiconductor companies have moved to use copper as metal interconnects.

However, copper cannot be patterned using well-understood plasma etching because the halide reaction products are not volatile. Thus, copper wiring is achieved by the Damascene process, which consists of copper deposition into patterned dielectric trenches or vias, followed by chemical mechanical polishing (CMP) of the copper. One critical issue associated with the Damascene process is the filling of vias and trenches with copper, a process that can leave voids and seams. Electrochemical deposition (ECD) is currently the
preferred method for depositing bulk copper. ECD requires deposition of a thin seed layer of about 200 Å for electrode before the plating fill step. The main requirement for the seed layer is that it must be continuous but as thin as possible in openings with a high aspect ratio.

There are several techniques for copper seed layer deposition, such as chemical vapor deposition (CVD), ionized metal plasma (IMP), and physical vapor deposition (PVD). PVD is the currently seed layer deposition method. However, as a “line-of-sight” deposition technique, PVD is not suitable for the node below than 100 nm according to the ITRS roadmap. Because of its advantages of superior step coverage and excellent gap-filling capacity for high aspect-ratio vias and trenches, CVD method is expected to take the place of PVD below 100 nm geometries.

Two basic types of reaction chemistries have emerged for performing copper CVD according to the oxidation state of the Cu precursors. The highest deposition rates to date have achieved using the disproportion of various Cu⁺ mono-β-diketonates, notably $\text{Cu(hfac)(VTMS)}$:

$$2\text{Cu}^+ (\text{hfac})(\text{VTMS}) \rightarrow \text{Cu}^0 + \text{Cu}^{II} (\text{hfac})_2 + 2\text{VTMS} \quad \text{(Eq. 1-1)}$$

Here, $H(\text{hfac}) = 1,1,1,5,5,5$-hexafluoro-2,4,-pentandione = hexafluoroacetylacetone, and $\text{VTMS} = $ vinyl trimethyl silane. The alternate route is based on $H_2$ reduction of Cu⁺ bis-β-diketonates, notably $\text{Cu(hfac)}_2$:

$$\text{Cu}^{II} (\text{hfac})_2 + H_2 \rightarrow \text{Cu}^0 + 2H(\text{hfac}) \quad \text{(Eq. 1-2)}$$

The potential advantage of the latter chemistry is that the Cu⁺ precursors are generally more stable and somewhat easier to handle than their Cu⁺ counterparts. The primary disadvantage is a slower growth rate.
Understanding the reaction mechanism of Cu(hfac)$_2$ reduction process is essential for efforts to increase the growth rate. Several qualitative studies of the growth rates and proposed reaction mechanisms have been reported. Awaya and Arita (1992) originally reported a mechanism involving competitive adsorption between adsorbed (hfac) ligands and H atoms based on their observation of maximum rate as a function of Cu(hfac)$_2$ concentration. Lai et al (1991) confirmed this saturation behavior at high Cu(hfac)$_2$ concentration under atmospheric pressure conditions, and further showed that H(hfac) will inhibit the growth rate. They derived a rate expression using an irreversible, two-step mechanism involving adsorption of (hfac) ligands produced by dissociative adsorption of Cu(hfac)$_2$. Borgharkar et al (1998a) examined the growth rate extensively as a function of the composition of the reactant mixture (i.e., the partial pressure of Cu(hfac)$_2$, H$_2$, and H(hfac)). The results were fitted using an optimized Langmuir-Hinshelwood rate expression with a numerator that is first order in Cu(hfac)$_2$ and half-order in H$_2$, and a third-order denominator that includes adsorption terms for Cu(hfac)$_2$, H$_2$ and H(hfac). In contrast, Kim et al (1993) reported half-order behavior with respect to both Cu(hfac)$_2$ and H$_2$ pressure. They developed a rate expression based on reversible, noncompetitive adsorption of Cu(hfac)$_2$ and H$_2$ on separated reaction sites.

There have been several reports that the growth rates for Cu(hfac)$_2$ reduction can be improved using alcohols as co-reactant. Two enhancement effects by alcohols have been reported. Chiang et al (1993) reported that ethanolates are substantially more volatile than the pure precursor, thus increasing the delivery rate of solvent-coordinated complexes to the substrate. The same transport enhancement is reported by Maverick et al (1999). The alternative interpretation is that alcohols give an enhanced intrinsic kinetics. Cho et al (1992)
reported that addition of isopropanol or other alcohols increases the nucleation and growth rates. Borgharkar et al. (1998b) reported that six times higher growth rate was obtained when 5 Torr of isopropanol vapor was added to the H\(_2\) carrier gas as co-reactant, compared to the direct reduction of Cu(hfac)\(_2\) using pure H\(_2\) under the same operating conditions (i.e., 300°C and 40 Torr H\(_2\) pressure).

In the first part of this dissertation, a new liquid delivery system was built around a high pressure liquid chromatography pump to study the thermal copper CVD using Cu(hfac)\(_2\) dissolved in isopropanol solution as the precursor. This technique provides the ability to introduce the reactant at an accurate and precisely controlled rate, while avoiding the requirement to handle the precursor at its high melting point. We observed a growth rate of 17.7 ± 1.5 nm/min at reference conditions of 300°C substrate temperature, 0.025 Torr Cu(hfac)\(_2\) partial pressure, 80 Torr H\(_2\) partial pressure, and 1.6 Torr isopropanol. This growth rate is similar to those observed using conventional delivery by solid sublimation while adding alcohol as co-reactant (Maverick et al., 1999), with the additional benefit that this growth rate is achieved using a much lower partial pressure of Cu(hfac)\(_2\) in the reactor (about 2 order magnitudes lower than Maverick et al., 1999).

The film resistivity approaches the bulk value of copper for film thickness greater than 100 nm. This critical thickness value is lower than that reported by Lecohier (1992) of 300 nm and by Kim et al. (1992) of 500 nm, both of which were obtained without adding isopropanol as co-reactant. Surface roughness was analyzed using atomic force microscopy (AFM) to determine the root mean square (RMS) values. From the results of films deposited by 4, 7.5 and 15 minutes, we find the shorter the deposition time, the smoother the film is.
The kinetic experiments were also performed using different reactant partial pressures. These are 0.0063 to 0.05 Torr for Cu(hfac)$_2$ partial pressure, 0.8 to 3.2 Torr for isopropanol partial pressure, and 40 to 160 Torr for H$_2$ partial pressure. The observed growth rates initially increased linearly with partial pressure of Cu(hfac)$_2$, then a saturated growth rate is reached when the pressure of Cu(hfac)$_2$ is higher than 0.025 Torr. Meanwhile, the growth rates are nearly independent of isopropanol and H$_2$. Copper CVD experiments were also performed using N$_2$ as carrier gas with baseline conditions for other reactants, i.e., 0.025 Torr Cu(hfac)$_2$ partial pressure, 1.61 Torr isopropanol partial pressure, 80 Torr N$_2$ pressure and 300°C substrate temperature. Similar growth rate is obtained compared to the rate with H$_2$ gas, but the visual appearance of films is much worse than those using H$_2$ as carrier gas. Both of the results suggest that using H$_2$ as the carrier gas improves the nucleation behavior of the copper growth process.

A series reaction mechanism with two intermediates was proposed to describe the reaction kinetics. Adsorbed Cu(hfac)$_2$ molecule and (hfac) ligand were determined to be the two kinetically significant intermediates. The model can account for the positive-order kinetics with respect to Cu(hfac)$_2$ and zero-order kinetics with respect to isopropanol observed in the current study, which uses a relatively low Cu(hfac)$_2$ partial pressure. The proposed reaction mechanism can also account for the positive-order kinetics with respect to isopropanol that were reported in a previous study using a higher Cu(hfac)$_2$ partial pressure (Borgharkar et al, 1998b).

The proposed mechanism begins with a Cu(hfac)$_2$ molecule reacting at the clean surface to form an adsorbed Cu(hfac)$_2$ molecule. The second step of the process is the dissociation of adsorbed Cu(hfac)$_2$ to produce an adsorbed (hfac) ligand and Cu(hfac) species.
The latter species are rapidly transformed through a Cu(I) disproportionation reaction, which produces Cu(hfac)$_2$ as a desorbing gas molecule and leaves Cu deposited on the desired solid film. The last step is the desorption of (hfac) ligand, which reacts to form H(hfac) via proton transfer between isopropanol and (hfac). The residual isoproproxide is decomposed rapidly to acetone and H$_2$ at the current deposition temperature.

The ligand dissociation will be the rate determining step in the series mechanism at low ratios of Cu(hfac)$_2$ to isopropanol partial pressures, as in the present work. Thus the kinetics will be near first-order with respect to Cu(hfac)$_2$ partial pressure and zero-order to isopropanol. The ligand desorption step becomes rate determining step at high ratios of Cu(hfac)$_2$ to isopropanol partial pressures, as in Borgharkar et al (1998b). The kinetics then become first-order with respect to isopropanol and zero-order with respect to Cu(hfac)$_2$.

The second part of this dissertation is tantalum CVD using TaF$_5$ and SiH$_4$ as reactants. The integration of copper interconnects requires a barrier layer to prevent copper from diffusing into the contact devices. Tantalum and Ta-based materials are currently the leading candidates for barrier layers in the copper metallization technology because of their excellent barrier and adhesion properties (Ryu, 1999). CVD of tantalum will be necessary for the 2005 technology node (i.e., 65 nm feature size) according to ITRS roadmap forecast.

A pedestal reactor system has been built in-house to study thermal tantalum CVD. The TaF$_5$ reactant is introduced into the He carrier gas using a stainless steel evaporator, while 5% SiH$_4$ in He is used as the reducing agent. Using a temperature of 350°C and reactant partial pressures of 200 mTorr TaF$_5$, and 300 mTorr SiH$_4$, we obtained a growth rate of 0.215 ± 0.168 mg cm$^2$ h$^{-1}$ (ca. 2.2 ± 1.7 nm min$^{-1}$). X-ray photoelectron spectroscopy (XPS) depth profiling analysis showed that Ta film was Si free, but contained relatively high oxygen
concentration because of residual gas contamination. These preliminary experiments indicated that CVD of Ta from TaF$_5$ and SiH$_4$ is a candidate deposition method for diffusion barrier applications in copper integrated circuit.

The final part of this dissertation describes the studies about CVD palladium seed layer for electroless Cu deposition. Cu film on Pd seeds had a smooth surface and good adhesion (Cho et al, 1995). Colloidal Pd has been widely deposited using wet chemistry on dielectric, semiconductor, barrier layer or metal surfaces for electroless copper deposition (Dubin, 1992; Hsu, 2001, 2002). However there are no publications about Pd seed layer using CVD method for electroless Cu deposition to our knowledge.

A cold wall APCVD reactor using a flat strip heater as thermal energy source and substrate holder was built to study the CVD Pd seed layer. A batch CVD activation process was applied after an attempt using continuous flow process failed because of the nucleation barrier for continuous Pd CVD on glass substrates. The batch activation process was completed by heating the substrates after the Pd precursor and reducing agent (H$_2$) have been delivered into the reactor.

Continuous CVD Pd films deposited on the batch Pd activated glass substrates were also obtained in the same reactor. The batch CVD step succeeds in reducing the nucleation barrier and improves the local uniformity of the final films. However, the subsequent continuous CVD process deposits Pd films under mass transport limited conditions, which leads to globally non-uniform deposition profiles. We developed a simple reactor transport model to simulate the axial thickness profile along the flow direction of the reactants. The model not only predicts the observed rapid axial decay profile, but also gives a reasonable quantitative agreement with observed results for the activated deposition process.
Electroless Cu was deposited directly on the batch CVD Pd seeds. An optimized combination of activation conditions was also obtained as the baseline procedure for future work after we studied the effects of activation temperature, holding time, and precursor evaporation time with a fixed evaporation temperature (70°C) on the visual properties and kinetic growth rate of ELD Cu films. These parameters are: holding time = 5 min, activation temperature = 180°C, and precursor evaporation time = 15 s. The ELD Cu films using baseline conditions were smooth, shiny, and continuous in the electrolyte solution but with some cracking after the drying, and the deposition rate was about 3.38 ± 1.43 nm/s.

In order to solve the cracking issues of the Cu films, we also tried adding H_2O or isopropanol into the CVD reactor to improve the quality of Pd seed layer. Water and alcohols are widely accepted as co-reactants to improve the film nucleation quality and growth rate for Cu CVD process using the reduction of Cu(hfac)_2 (Lecohier et al, 1991; Chiang et al, 1993). Unfortunately, we found that neither of the additives has a significant effect on the Pd seed layers after we compared the visual qualities and the growth rates of electroless copper films.

We also examined the atomic composition and morphology of the Pd seed layer using XPS and AFM, respectively. The samples were prepared using the baseline activation temperature and holding time, but with 4, 7.5 and 15 seconds precursor evaporation times at 70°C evaporation temperature. The amount of Pd seeds on the substrate increase linearly as a function of the amount of the precursor delivered into the reactor (i.e., the precursor evaporation time) as suggested by XPS analysis. AFM results shows that the precursor evaporation times have no significant effects on the grain size and height of Pd seeds. However, the nucleus densities of Pd seeds increase from about 1 cluster/µm² to 14 clusters/µm² when the evaporation time is increased from 4 to 15 s.
CHAPTER 2 LITERATURE REVIEW

This chapter reviews the important papers that are related to the current research. Section 2.1 overviews the process of copper as metal interconnect in ULSI. We present the main work about copper CVD using Cu(hfac)$_2$ reduction by H$_2$ or alcohol in section 2.2. Section 2.3 is about tantalum barrier layer for copper interconnect. We discuss the formation methods of palladium seed layer for electroless copper deposition in section 2.4. In section 2.5 we review some results about palladium CVD using Pd(hfac)$_2$ reduction by H$_2$.

2.1 Interconnect Metallization

Because of its lower resistance and better electromigration resistance compared to aluminum, copper has replaced aluminum as the preferred interconnect material at the 130 nm technology node. Dual Damascene is the patterning method used in current IC fabrication due to the difficulty of etching copper. In this technique, trenches and vias are etched into the dielectric and then filled with copper. Electrochemical deposition (ECD) is currently the preferred method for depositing bulk copper. ECD requires deposition of a thin metal seed layer about 200Å before the plating fill step. The seed layer, usually copper itself, provides a low resistance electrode for conducting current that facilitates the process, and also controls the subsequent film nucleation.

The main requirement for the seed layer is that it must be continuous but as thin as possible, especially in the openings with high aspect ratio. Physical vapor deposition (PVD) is currently the main seed layer deposition method. However, chemical vapor deposition (CVD) of the copper seed layer may replace PVD methods below 100 nm geometries because of its capability of nearly 100% step coverage. Furthermore, CVD is a promising candidate for bulk copper deposition in future microprocessor manufacture. In this section, the roles of copper in
2.1.1 The Advantages of Copper as Metal Interconnects in ULSI

The demand for manufacturing semiconductor integrated circuit (IC) devices with high circuit speed and high packing density requires the shrinking scale of feature sizes in ultra-large-scale integration (ULSI) structure. The minimization of interconnect feature size will meet the trend of smaller chip sizes and increased packing density. However, it will also increase interconnect resistance and reliability concerns like electromigration. In general, such structures use silicon wafer with SiO₂ being the dielectric material, and openings are patterned in the dielectric layer in shape of vias and trenches, which are then filled with metals forming the interconnects. Increased minimization is reducing the openings to nanometer sizes (e.g. 130 nm for the Pentium® 4 CPU) and increasing the aspect ratio of the features, i.e., the ratio of the depth of the trench or via to the width of its opening.

For many years, aluminum has been the metal choice for integrated circuits because of its relatively low resistivity and ease of manufacturability. With the decrease of the design rule to dimensions of 0.18μm and below, the interconnect RC time constant, which is the product of the metal resistance and the dielectric capacitance, significantly limits microprocessor clock speed. Meanwhile the worsening electromigration resistance (movement of metal atoms during current flow) in smaller devices will also begin to deteriorate the performance and reliability of aluminum as interconnect. Both of these problems can be overcome by replacing aluminum with copper as IC metal interconnects.

Compared with aluminum, copper offers many benefits. It has lower resistivity (1.67 vs. 2.66 μΩ-cm for Al), which means wires can be smaller and packed more tightly while still
carrying the same current. This means fewer levels of metal are required to achieve the same
duty and lower production costs. Lower resistivity also provides faster speed. Also, copper
has higher resistance to electromigration, which will improve the performance and reliability
of the device. All in all, copper is said to provide better yield than aluminum-based devices of
the same design (Singer, 2002). Over the past five years, many semiconductor companies
have moved to use copper as metal interconnects. The most familiar device to us is Pentium®
4 CPU, which is manufactured using 130 nm copper technology.

However, copper also has some disadvantages compared to aluminum. Plasma etching
is usually used to pattern the aluminum wiring in traditional metallization process. Because
copper has no volatile etching products, an alternative patterning methodology called dual
Damascene has been developed for copper wiring. The limiting factor in the dual Damascene
process is the requirement of depositing a uniform and continuous thin barrier layer and a
copper seed layer in high aspect ratio trenches and vias. The Damascene process will be
described in the next sub-section. Copper is also a known fast impurity diffuser into SiO₂ and
silicon. Thus a robust barrier layer to prevent copper diffusion is also required to encapsulate
the copper interconnect. The barrier layer will be discussed briefly in section 2.3.

2.1.2 Dual Damascene Process

The practice of creating patterns by metal inlays was first invented by the ancient
artisans of Damascus. Today, thousands of years later, a similar process is being adopted by
the semiconductor industry. The dual Damascene process is one of the two variations of the
Damascene process. It involves etching and filling both trenches and vias in a single
combined step. The opposing process is the single Damascene process, which involves
separate steps for filling interconnect lines and vias. In both cases, the following step is planarization of the surface by chemical mechanical polishing (CMP).

The dual Damascene process now is widely adopted by most leading-edge semiconductor fabrications. This process starts with the deposition of a thin silicon nitride stop layer on the top of the first metal layer (Fig. 2-1) (Teschler, 2001). Silicon dioxide or low-k dielectric layer is deposited on the top of the SiN$_x$. Then the dielectric layer is patterned for vias and etched down to the metal layer. Etching goes through the dielectric layer and stops at the SiN$_x$. Next another thin SiN$_x$ layer is deposited and then another layer of dielectric materials. The trenches, which are for copper wiring, are etched through second dielectric layer and stopped at the second SiN$_x$ layer. Once the openings for vias and trenches for metal connections have been patterned, the process next deposits a thin film of barrier layer, such as tantalum/tantalum nitride, by a PVD method, such as sputtering. Then a thin copper seed layer is deposited by PVD or CVD for ECD of copper metal. The wafer then goes through CMP before repeating the process for the next copper wiring level.

The main advantage of Damascene processing is that it eliminates the need for metal etch. This is an important concern in copper technology since copper is extremely hard to etch. A second advantage is that it eliminates the need for dielectric gap fill, which is seen as one of the industry’s greatest challenges in the drive to smaller dimensions (Singer, 1997). However, the Damascene process also has its disadvantages. One critical issue is the filling of vias and trenches with the thin copper seed layer and barrier layer, a process that can leave voids and seams, especially in small devices. Therefore, CVD of copper seed layer is being proposed to take the place of PVD methods, which are currently used for seed layer deposition, because CVD is capable of nearly 100% step coverage for geometries below 100 nm.
2.1.3 Overview of Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a versatile process, which is suitable for producing thin films, powders, and monolithic components. Chemical vapor deposition may be defined as the deposition of a solid on a heated surface by chemical reactions of precursors from the vapor phase. Unlike traditional chemical reactions, in which reactions usually occur in homogenous solution or gas, CVD reactions take place on a two-dimensional solid surface, i.e., the substrate.

CVD is normally performed in a low pressure vacuum reactor, which consists of the following parts: a reactor chamber; gas carrier; source materials; and the needed energy source for the chemical reactions to occur, either thermal heating or plasma energy. The carrier gas flows through the source reactants that are usually solids, and picks up some quantity of the material. Sometime the carrier gas will also be a reactant. These materials are mixed in a mixing chamber and then injected into the reaction chamber. In the reaction
chamber, the reactants in the carrier gas flow across the substrate(s) on which chemical reaction(s) that deposit a suitable film take place as a result of some external energy provided by thermal heaters or a plasma discharge.

CVD has several important advantages that make it the preferred deposition technology in many applications (Pierson, 1999). These can be summarized as follows:

- It is not restricted to a line-of-sight deposition, which is a typical feature of sputtering, evaporation and other PVD methods. So CVD has high throwing power that is suitable to coat complex surface features, such as deep via holes, trench and other difficult three-dimensional configurations. For example, tungsten plugs can be completely filled in an integrated circuit (IC) via with an aspect ratio of 10:1.

- CVD has relatively high deposition rate. For thick coatings, in some cases centimeter thick, CVD process is generally competitive and, in some cases, more economical than PVD processes.

- CVD has the potential to perform selective deposition, which refers to the preferential deposition of a film on one surface in the presence of another. For example, copper often more easily deposits on conductive surfaces than on dielectric ones.

However, CVD is not a universal coating panacea. One major disadvantage is that it may need high reaction temperatures of 600°C or above; many substrates are not thermally stable under these temperatures. Fortunately, the development of plasma CVD and metallo-organic CVD partially offsets this problem. The other disadvantage is that pure films can be difficult to obtain by CVD because many side reactions occur, especially in metal-organic CVD. This problem can be controlled by depositing film under optimized conditions.
2.2 Copper CVD Using Cu(hfac)$_2$

Cu(hfac)$_2$, i.e. Copper(II) bis(hexafluoroacetylacetonate), is one of the most promising Cu(II) β-diketonate precursors for copper CVD. The present study of copper CVD is performed by using this compound. The main advantage of Cu(hfac)$_2$ over Cu(I) β-diketonates is that Cu(hfac)$_2$ is very stable. The major shortcoming of Cu(hfac)$_2$ is its relatively low deposition rate compared to Cu(hfac)(VTMS), the most popular Cu(I) diketonate precursor. Several previous studies (Cho, 1992; Awaya, 1995; Borgharkar, 1998b) have shown that the copper deposition rate can be increased using Cu(hfac)$_2$ with some co-reactant, such as isopropyl alcohol or water. In the present study, copper CVD is studied using Cu(hfac)$_2$ dissolved in isopropanol as a liquid phase precursor. In this chapter, Section 2.2.1 presents the results on Cu(hfac)$_2$ reduction using H$_2$. Section 2.2.2 is about the alcohol enhancement on copper CVD using Cu(hfac)$_2$ as precursor. Section 2.2.3 presents some results of CVD copper film properties, including resistivity and film morphology.

2.2.1 Cu(hfac)$_2$ Reduced by H$_2$

This sub-section presents some of the previous research on copper CVD using Cu(hfac)$_2$ reduced by H$_2$. The first kinetic study was reported by Van Hemert and coworkers (1965) using Cu(hfac)$_2$⋅H$_2$O and H$_2$. Recent studies by Awaya et al (1989) and Borgharkar et al (1998a) are also included. The first comprehensive quantitative rate expression for this reaction was published by Lai et al (1991) and later expanded by Wang (1995). Other works by Awaya et al (1992) and Kim et al (1993) are also presented, as well as Borgharkar et al (1998a).

- Previous Kinetic Studies. Van Hemert et al (1965) reported the first kinetic study of copper CVD using Cu(hfac)$_2$⋅H$_2$O. Films were deposited on a heated flint glass substrate in
a warm-wall horizontal tube reactor using H\(_2\) at atmospheric pressure as the carrier gas and reducing agent. Optimum film quality was obtained using a substrate temperature of 250\(^\circ\)C and precursor evaporated at temperature of 90\(^\circ\)C. The same process was also performed in an inert carrier gas of nitrogen, but the deposition temperature was higher and there was more impurity in the films. The stoichiometry of the deposition reaction was reported to be:

\[
\text{Cu(hfac)}_2 \cdot H_2O + H_2 = \text{Cu(s)} + 2\text{H(hfac)(g)} + H_2O \quad \text{(Eq. 2-1)}
\]

Awaya et al (1989) published the selective deposition of copper on several substrates. The experiments were carried out in a cold wall, low pressure reactor. The pressure in the reactor was kept at about 15 Torr, and the deposition temperature was 350\(^\circ\)C. The Cu(hfac)\(_2\) precursor was evaporated between 40 – 70\(^\circ\)C. A growth rate about 10 nm/min was observed on metals (W, Cr, Al, Zr) and metal silicide (TiSi\(_2\)). Copper only deposited on metal and metal silicides, but not on the SiO\(_2\) and Si\(_3\)N\(_4\) surface, when the authors tried to deposit copper into patterned via holes.

Borgharkar et al (1998a) reported copper CVD by using H\(_2\) reduction of Cu(hfac)\(_2\). A growth rate of 9 nm/min was observed at reference conditions of 300\(^\circ\)C substrate temperature, 40 Torr H\(_2\) partial pressure, and 1.8 Torr Cu(hfac)\(_2\) partial pressure. A hot wall reactor built on a TGA microbalance was used. The substrates were stainless steel to reduce the nucleation barrier and to ensure the weight change of the substrate reflected the steady state growth rate. The Cu(hfac)\(_2\) precursor was evaporated at 90\(^\circ\)C to get a partial pressure of Cu(hfac)\(_2\) about 1.8 Torr with 40 Torr H\(_2\) carrier gas.

- **Mechanism and Rate Expression.** The rate expression represents the quantitative relationship between deposition rate on the substrate surface and the concentration of
reactants in the gas phase near the substrate surface. An activation energy with one or two coefficients can be included in a rate expression if information about temperature dependence is also available. There are two methods to determine the rate expression. The first one is empirical way, in which case a power law or similar equation is developed to correlate measured deposition rates with reactants concentration (and temperature). The alternative one is semi-theoretic, in which case a rate expression is derived on the basis of a proposed reaction mechanism and the coefficients are determined by judging the agreement between calculated and measured growth rates. In this sub-section, we prefer to discuss the second way.

Lai et al (1991) published the first rate expression about Cu(hfac)$_2$ reduction by H$_2$ in atmospheric pressure from our lab. Their rate expression was derived from the three experimental results:

1) The growth rate is nearly independent of Cu(hfac)$_2$ concentration at the inlet of the reactor. This zero order reaction kinetics suggests that a saturation effect by the adsorption of intermediate at the inlet conditions.

2) The growth rate decreases when the mole fraction of H$_2$ in the inlet reactant stream is decreased. This means that H$_2$ is also involved in the rate-limiting step.

3) The growth rate decreases when H(hfac) was added to the inlet reactant stream. This suggests that there exits a competitive adsorption on vacant surface sites between H(hfac) and Cu(hfac)$_2$.

A Langmuir-Hinshelwood mechanism with the regeneration of vacant sites by H(hfac) desorption being the rate-limiting step was derived based on these observations:
The parameters in Eq. 2-2 were optimized from experimental results:

\[ k_{ads} = k_{ads,1} = k_{ads,2} = 0.1\text{cm-s}^{-1}; \]
\[ k_{des} = 2.2 \times 10^{23} \exp(-80\text{kJ-mol}^{-1}/RT) \text{molecule-cm}^{-2}\text{-s}^{-1}\text{-atm}^{-1}. \]

Awaya and Arita (1992) presented quantitative results for the influence of Cu(hfac)$_2$ concentration on growth rate over a wider range of conditions than the above work (Lai, 1991). Their experiments were carried out in a cold-wall, low pressure apparatus with total pressure about 15 Torr. The precursor was evaporated between 50 – 100°C and delivered by H$_2$ to reactor. Substrate temperature was maintained between 350 – 390°C. Maximum deposition rates of about 10 nm/min were obtained at a substrate temperature of 350°C. Their main observations were:

1) Growth rate increases linearly at low Cu(hfac)$_2$ concentration and then saturates at higher concentration, which is consistent with the observation by Lai et al (1991).

2) Growth rate has a positive order dependence on H$_2$ pressure at high Cu(hfac)$_2$ concentration, but is independent of H$_2$ at low precursor concentration.

These observations support the assumption of a Langmuir-Hinshelwood mechanism but also suggest that a mixed second order rate expression should be used to account for competitive adsorption between Cu(hfac)$_2$ and H$_2$ on the same surface sites.

Kim et al (1993) reported an alternate Langmuir-Hinshelwood, dual-site non-competitive mechanism for Cu(hfac)$_2$ reduced by H$_2$. The copper CVD experiments were
performed in a cold wall, vertical flow, bell jar reactor system with 2 – 20 Torr of H\textsubscript{2} and
temperatures between 280 to 400\textdegree C. A half-order dependence on Cu(hfac\textsubscript{2}) partial pressure
over a range of 0.25 – 0.7 Torr and an half order on H\textsubscript{2} with pressure over a range of 2 – 10
Torr were observed. Adsorption of H\textsubscript{2} and Cu(hfac\textsubscript{2}) species on two different sites was
assumed. A complex rate expression was provided from the proposed mechanism with no
individual rate constants. Instead, with some reasonable assumptions, a simplified version of
rate expression was published:

\[
\begin{align*}
    r &= 5.7 \times 10^7 \exp\left(-\frac{75000 J \cdot mol}{RT}\right) P_{\text{Cu(hfac)}_2}^{0.5} P_{H_2}^{0.5} \text{ nm-min}^{-1} \\
    &\quad \text{(Eq. 2-3)}
\end{align*}
\]

Wang et al (1995) in our lab extended the atmospheric copper CVD experiments by
Lai et al (1991) to low-pressure conditions (i.e. 40 Torr). The operating conditions were: 40 –
760 Torr partial pressure of H\textsubscript{2}, 250 – 350\textdegree C substrate temperature, 76 – 90\textdegree C Cu(hfac\textsubscript{2})
evaporator temperature. A deposition rate of 15 nm/min was observed under 40 Torr H\textsubscript{2}
partial pressure, 2.3 Torr Cu(hfac\textsubscript{2}) partial pressure, and 350\textdegree C substrate temperature. The
measured growth rates were analyzed using a 2-D reactor transport model. The rate
expression of Lai et al (1991) above was used in their transport model, but the kinetic
constants were optimized to agree closely with the experimental rates. Based on the literature
values of sticking coefficients of Cu(hfac\textsubscript{2}) and H(hfac) (Dubois,1992; Girolami, 1993),
Wang et al increased the value of adsorption coefficients in the Lai et al (1991) rate
expression about two orders of magnitude to make the adsorption coefficients more physically
realistic:

\[
\begin{align*}
    k_{ads,1} &= 40 \text{ cm-s}^{-1} \\
    k_{ads,2} &= 65 \text{ cm-s}^{-1};
\end{align*}
\]
Next, the deposition rate constant was optimized using the above adsorption rate constants:

\[ k_{des} = 4.4 \times 10^{23} \exp(-80 \text{kJ-mol}^{-1}/\text{RT}) \text{ molecule-cm}^{-2} \text{-s}^{-1} \text{-atm}^{-1}. \]

Borgharkar et al (1998a) did extensive research on reduction kinetics of copper using H\(_2\) reduction of Cu(hfac)\(_2\) in our lab. The reaction conditions were changed with reference conditions of 300°C substrate temperature, 40 Torr H\(_2\) and 1.8 Torr Cu(hfac)\(_2\) partial pressures. The reaction mechanism analysis was based on three major observations from their experiments:

1) The growth rates initially increase with increasing Cu(hfac)\(_2\) pressure, passing through a maximum value near \(P_{\text{Cu(hfac)2}} = 2\) Torr. This suggests a bimolecular surface reaction mechanism with competitive adsorption of reactants.

2) The growth rates on H\(_2\) pressure show about half-order kinetics, which is associated with the dissociative adsorption of H\(_2\) on metal surface (Campbell, 1991).

3) The growth rates decrease with the addition of H(hfac), which acts as an inhibitor of copper nucleation.

The rate expression is:

\[
 r = \frac{k_1 K_{\text{Cu(hfac)2}} K_{H_2}^{1/2} P_{\text{Cu(hfac)2}}^{1/2} P_{H_2}^{1/2}}{\left[1 + K_{\text{Cu(hfac)2}} P_{\text{Cu(hfac)2}} + \left(K_{H_2} P_{H_2}\right)^{1/2} + K_{H(hfac)} P_{H(hfac)}\right]^3} \quad \text{(Eq. 2-4)}
\]

The optimized kinetic parameters are:

\[ k_1 = 1.1 \times 10^{17} \text{ molecule-cm}^{-2} \text{-s}^{-1}; \quad K_{\text{Cu(hfac)2}} = 0.312 \text{ Torr}^{-1}; \]

\[ K_{H_2} = 2.9 \times 10^{-4} \text{ Torr}; \quad K_{H(hfac)} = 0.138 \text{ Torr}^{-1}; \]
2.2.3 Alcohol Additives in Copper CVD

As mentioned in the previous section, the growth rate of copper using Cu(hfac)$_2$ is only about 10 times lower compared to the copper (I) precursors. Therefore many studies have been performed to increase the growth rate of Cu(hfac)$_2$ reduction by H$_2$. The most widely accepted method is to add specific co-reactants, such as water or alcohols. A tenfold increase in deposition rate for Cu(hfac)$_2$ under H$_2$ was reported in the presence of water vapor by Awaya and Arita (1995). The film morphology is also improved by water, i.e., films were more smooth and reflective with finer grain size. Lecohier et al (1991) showed that adding water vapor to the feed stream eliminated the selectivity toward deposition on Pt that had been observed in the study of H$_2$ reduction of Cu(hfac)$_2$. Instead, the addition of H$_2$O activated the neighboring SiO$_2$ surface for deposition.

The enhancement effects of adding alcohols into Cu(hfac)$_2$ and H$_2$ reactants were first reported by Cho (1992). The addition of isopropanol, methanol, or isobutyl alcohol as a co-reactant led to a significant reduction of the temperature at which deposition occurred on SiO$_2$ substrate. Meanwhile, the quality of copper on Si and SiO$_2$ was also improved significantly. The author concluded that the addition of isopropanol and other alcohols increased the nucleation and growth rates.

Zheng et al (1992) reported that pure and dense films could be deposited on various substrate by plasma-assisted CVD using a liquid delivery method that exploits the high solubility of Cu(hfac)$_2$ in selected solvents, such as isopropanol and ethanol. Copper films were produced at substrate temperatures in the range 160 – 170°C and at a reactor pressure and plasma power density of 1.0 – 1.7 Torr and 0.13 – 0.25 W/cm$^2$, respectively. Film characterization by Rutherford backscattering spectroscopy (RBS) and cross-section scanning
electron microscopy (SEM) indicated that the films were pure, dense and highly uniform with resistivity of 1.7 – 1.9 µΩ-cm by four-point resistivity probe. However, a relatively low growth rate around 25 nm/min was obtained over large area substrate.

Chiang et al (1993) investigated the vapor phase and surface chemistries of Cu(hfac)₂ dissolved in alcohols (methol, ethanol and isopropyl alcohol) by molecular beam/mass spectrometry, nuclear magnetic resonance (NMR), and reflection-absorption infrared spectrocope. They reported that the adduct between Cu(hfac)₂ and alcohol is substantially more volatile than the pure precursor, thus increasing the delivery rate of these solvent-coordinated complexes to the substrate. Meanwhile, the alcohols also lowered the reaction barrier energy of Cu(hfac)₂ reduction by H₂ to aid the production of copper metal.

Borgharkar et al (1998b) in our lab reported the influence of various alcohols (ethanol, methanol and isopropyl alcohol) on the transport mechanism and reaction kinetics of Cu(hfac)₂ reduction for copper CVD. A variety of transport experiments were performed by thermogravimetric analysis (TGA), all of which indicated no increase of Cu(hfac)₂ vapor phase transport rate by the presence of alcohols. In contrast, steady-state kinetic measurements showed a significant increase in copper growth rates. They concluded that alcohols act primarily to enhance the intrinsic kinetics of Cu(hfac)₂ reduction. For the series of alcohols studied, the enhancement factor increase in the order of MeOH<EtOH<i-PrOH.

Later, the same authors demonstrated that growth rates of up to 50 nm/min can be obtained using the alcohol-assisted reduction of Cu(hfac)₂ in a capillary-based liquid delivery system (Borgharkar et al, 1999). The experimental conditions were substrate temperature of 300°C, and reactant partial pressure of 0.65 Torr Cu(hfac)₂, 8.5 Torr isopropanol, and 40 Torr
H₂. The growth rate is several times faster than that observed using direct reduction of Cu(hfac)₂ by H₂ alone and is comparable to rates reported for Cu(I) disproportionation.

Maverick et al (1999) reported copper CVD using various alcohol adducts of Cu(hfac)₂·ROH as precursors, where ROH is methanol, ethanol, or isopropyl alcohol. The authors found some Cu(hfac)₂·ROH adducts have low melting points, which allow them to be used as liquid precursors at the common precursor evaporation temperature (ca. 80°C). Metallic Cu films were obtained using most of these adducts as precursors under either H₂ or N₂ mixed with corresponding alcohol vapor. The authors proposed a reaction scheme in which the alcohol acts as a reducing agent in the deposition of the Cu films. The authors found that Cu(hfac)₂·i-PrOH is the most effective precursor for Cu CVD. An average growth rate of 21.7 ± 8.0 nm/min was obtained for films deposited using Cu(hfac)₂·i-PrOH and N₂ carrier gas with i-PrOH vapor. The experimental conditions were: 200°C substrate temperature, 80°C precursor evaporation temperature, 760 Torr total pressure, and 13 ml/min N₂ gas flow rate.

2.2.4 Film Properties

- Resistivity. Resistivity is one of the most important indexes to reflect the quality of metal film. Usually, the resistivity of thin deposited film is compared to that of bulk metal. For copper, ρₜₚₚ = 1.67 μΩ-cm. The closer the film value is to the bulk copper resistivity, the higher the purity of deposited film is. In addition, it has been observed that the thickness of film must be larger than a critical value.

Kaloyerros et al (1990) reported copper CVD using H₂ reduction of Cu(hfac)₂ with film resistivity of less than 2 μΩ-cm over a range temperatures of 300 – 450°C. The purity of deposited films was greater than 99%. In contrast, Temple et al (1989) were only able to
obtain the copper films with resistivity of 3 – 6µΩ·cm. They deposited films by thermal decomposition of Cu(hfac)₂ in Ar at atmospheric pressure and temperatures of 420°C and higher. Using Auger electron spectroscopy (AES) analysis for the deposited films, they found significant impurity concentrations of carbon and oxygen from the decomposition of ligands. The same results were reported by Awaya and Arita (1989), i.e., that film resistivity increased when Ar instead of H₂ was used as the carrier gas in Cu(hfac)₂ CVD experiments.

Awaya and Arita (1989) also showed that the film thickness may have to exceed a critical value in order for the film resistivity to reach the bulk value. They could get films approaching bulk resistivity only thicker than 300 nm. A similar value for the critical thickness was obtained by Lecohier et al (1992), while a higher value of 500 nm was reported by Kim et al (1992). Figure 2-2 is a plot of resistivity as a function of film thickness from Kim et al (1992).

Fig. 2-2 Relationship between Thickness and Resistivity of CVD Cu Film (Kim, 1992)
• **Morphology.** As mentioned in section 2.1, thin copper seed-layer about few hundreds Å thick is needed for the bulk copper filling by ECD. For this thin seed-layer, the major morphological issue becomes film continuity to provide a low-resistance conductor for ECD current. The fact that a critical minimum film thickness is needed to achieve bulk resistivity values (see Fig. 2.2) suggests that thinner films may be discontinuous. Since nucleation period is the initial deposition stage of copper CVD, improving the conditions of this stage can obtain more uniform and continuous copper film.

Lai et al (1991) reported that films thinner than 100 nm consisted of isolated clusters. The SEM images suggested that the lateral dimensions of these clusters were comparable to the vertical dimensions (based on step profilometry). The discontinuous structure was independent of the conditions that produced the thin films; similar morphology was observed at the inlet of their reactor where the growth rate was limited by low temperature and also at the end of the reactor where the growth rate was limited by low Cu(hfac)$_2$ concentration.

It is widely reported that the addition of water will improve the film morphology because of H$_2$O improving the copper nucleation behavior. Awaya and Arita (1992) reported that the reflectivity of the film increased, and a smoother surface was obtained when H$_2$O was added to the reactant stream. Together with their evidence that the addition of H$_2$O also activated non-selective surfaces for copper growth, they drew a conclusion that H$_2$O acts to increase the nucleation rate of new crystallites. This results in smaller grain sizes and smoother films.

Kim et al (1998) reported the effect of water vapor on the surface morphology of the copper films from Cu(hfac)$_2$. The deposition experiments were carried out in a cold-wall, vertical system with 15 Torr pressure and temperature range of 310-390°C. SEM images
revealed that the films appeared smooth with well-connected grains and reduced porosity due to fast deposition with high water vapor flow rate (2 sccm). In the lower water vapor flow rate region (0.5 sccm), many pores were observed between the large granular grains. The authors proposed that water changed the growth mechanism of copper from the Volmer-Weber island mechanism at low water flow rate to some degree of layer by layer growth at high water flow rate.

2.3 Tantalum as Copper Diffusion Barrier

As implied by the name, a diffusion barrier must prevent copper penetrating the barrier sufficiently to degrade the device performance. Some typical requirements include (Pierson, 1999): good adhesion both to the dielectric material and copper, low resistivity, good step coverage, and good chemical mechanical polishing (CMP) compatibility. The thin film barrier’s surface condition and microstructure can strongly affect the texture and grain size of deposited copper (Ryu, 1999), which are the critical factors in determining electromigration reliability. Thus, the barrier is essential to seeding the desired copper microstructure, (e.g., films with Cu<111> orientation are the preferred structure).

Tantalum is a refractory metal with similar properties to tungsten, which is a material already used as diffusion barrier in aluminum-silicon devices. The physical properties of tantalum are listed in Table 2-1 (Pierson, 1999).

As a refractory metal, tantalum does not react with copper, so a Cu-Ta contact should be stable to high temperatures. Hu et al (1986) reported that there is no diffusion of copper through tantalum deposited on oxidized silicon substrates up to 750°C. The diffusion constant of copper in tantalum has been measured by radiotracer study with an expression (Holloway, 1992): $D = 9 \times 10^{-4} \exp\left(\frac{-2.3\times V}{k_B T}\right) \text{cm}^2/\text{s}$ at 400–700°C. A diffusion coefficient of copper in
Table 2-1 Properties of Tantalum

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure</td>
<td>B.C.C.</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>16.65</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>2996</td>
</tr>
<tr>
<td>Thermal Expansion (×10⁻⁶/°C)</td>
<td>6.5</td>
</tr>
<tr>
<td>Electrical Resistivity (µΩ·cm)</td>
<td>12.45</td>
</tr>
</tbody>
</table>

tantalum at 400°C calculated from this expression is about 5.44×10⁻²¹ cm²/s, which is about 10¹⁵ times lower than the diffusion coefficient of copper in silicon at the same temperature, which is about 1.35×10⁻⁵ cm²/s (Istratov, 2002).

An important issue concerning tantalum as diffusion barrier for copper metallization is the adhesion between the dielectric and the copper. Good adhesion plays an important role for both the mechanical strength and electrical conduction. The adhesion between two adjacent solid films is the result of either physical interaction or chemical bonds at the interface. Van der Waals force is the typical example of physical force. Diffusion both of substances into each other to form a thin transition region is an example of chemical bond, which will provide better adhesion than physical forces. Ryu et al (1999) reported that there is a small degree of atomic mixing, an amorphous interlayer region of 2 ~ 3 nm thickness observed by TEM at the copper-tantalum interface. This interlayer obviously provides good adhesion between the contacting copper and tantalum films.

Because the copper layer is deposited on the barrier layer, the surface properties of the tantalum layer will strongly influence the nucleation mode and texture pattern of the copper
film. A thin and continuous copper seed layer will be formed if nucleation is easy on the tantalum barrier layer. Also, copper films with the desired <111> texture have been obtained by CVD on tantalum barrier layer (Ryu, 1999).

2.4 Palladium Seed Layer for Electroless Copper Deposition

This section reviews the deposition of Pd seed layers for the electroless Cu deposition on non-conducting substrates. We will first review the fundamentals about electroless deposition of Cu, including thermodynamics, plating solution, and kinetics. Next we will present some Pd seed layer deposition methods and the properties of the Cu films on these Pd seed layers from the literature.

2.4.1 Overview of Electroless Copper Deposition

The process of ELD Cu is assumed to involve two reactions which occur simultaneously on a catalytic surface including the reduction reaction of Cu ions and the oxidation reaction of a reducing agent. Formaldehyde is the most widely used reducing agent in ELD Cu solution. The overall reaction of ELD Cu deposition in formaldehyde-based plating solution with ethylenediaminetetraacetic (EDTA) as a chelating agent is (Lukes, 1964):

\[
[CuEDTA]^{2-} + 2HCHO + 4OH^- \rightarrow Cu^0 + 2HCOO^- + 2H_2O + H_2 + EDTA^{4+} \quad (\text{Eq. 2-5})
\]

The anodic oxidation of formaldehyde for Eq. (2-5) is:

\[
2HCHO + 4OH^- \rightarrow 2HCOO^- + 2H_2O + H_2 + 2e \quad E_{\text{an}}^o = 1.14 V \quad \text{(Eq. 2-6 a)}
\]

The cathodic reduction of Cu ions for Eq. (2-5) is

\[
Cu^{2+} + 2e \rightarrow Cu \quad E_{\text{red}}^o = 0.337 V \quad \text{(Eq. 2-6 b)}
\]

Here \( E^o \) is the standard redox potential of the related reduction or oxidation half reactions, and the potential values are from Shacham-Diamand and Dubin (1995).
• Thermodynamics. The thermodynamic possibility for carrying on a reaction is determined by its Gibbs free energy. The definition of the Gibbs free energy change in the electrochemical terminology is:

\[ \Delta G_0 = -nF(E_{ox}^0 - E_{red}^0) \]  

(Eq. 2-7)

Here \( n \) is number of the exchanged electrons during the reaction, and \( F \) is Faraday constant. With the redox potential values given in Eq. (2-6), the calculated Gibbs free energy change for electroless Cu deposition is -155 kJ/mol. With this relative large negative Gibbs free energy change, the electroless Cu deposition is a thermodynamically favorable process.

Although the electroless Cu deposition is a thermodynamically favorable process, its potential barrier, which exists between the reactants and products, prevents the homogenous solution decomposition to form Cu particles. To perform the heterogeneous steady-state deposition of Cu on copper surface, the potential barrier must be reduced by the formation of reactive intermediate species on the catalytic surface. The estimated activation energy (\( \Delta E \)) for this process is about 60.9 kJ/mol (0.63eV) (Shacham-Diamand and Dubin 1995).

• Deposition Solution. An electroless Cu plating bath usually contains a cupric ion source, a reducing agent for the cupric ion source, a chelating agent for the cupric source and a pH adjuster. In addition, some additives are also added to the solution, in order to increase the stability of the plating bath and improve the properties of the obtained electroless Cu film.

Cupric sulfate (\( \text{CuSO}_4 \)) is the most common source for the electroless Cu film. Formaldehyde is the most widely used reducing agent for Cu ions. EDTA is applied as a chelating agent for the Cu ions. We can use sodium or potassium hydroxide as the pH adjuster, but the introduction of alkali metal ions into the integrated circuit (IC) will result in the
possible circuit failure. People have found several suitable organic bases as the pH adjuster for a formaldehyde-based plating solution. Tetramethylammoniumhydroxide (TMAH) is considered as the best choice as a provider of hydroxide ion for the electroless Cu deposition in Si-based IC manufacture.

Many additives have been tested for application in electroless Cu deposition solution. We may classify them according to their different functions during the ELD Cu process. Stabilizer, such as 2-2′-dipyridyl, is used to prevent the homogenous decomposition of the plating solution. Surfactant or wetting agent, such as polyethylene glycol (PEG), is used to decrease the surface tension of the plating solution and reduce the formation of H₂ bubbles on the deposited Cu film. Ductility promoter, such as potassium ferricyanide or 2-2′-dipyridyl, is used to lower the film tensile strength and to lead a crack-free deposited Cu film.

A typical electroless Cu deposition solution is listed in Table 2-2 (Shacham-Diamand and Dubin 1995, Chang 2003).

- **Kinetics.** The growth rate of the ELD Cu can be affected by the concentration of Cu ions \([C_{Cu}^{2+}]\), formaldehyde \([C_{HCHO}]\), hydroxide ion \([C_{OH}^-]\), and chelating agent \([C_{EDTA}^{4-}]\) as well as temperature according to the overall reaction of ELD Cu (Eq. 2-5). Thus the overall rate law for ELD Cu can be expressed as (Dubin and Shacham-Diamand, 1997):

\[
R = A \cdot \exp\left(-\frac{\Delta E}{RT}\right) \cdot [C_{Cu}^{2+}]^a[C_{HCHO}]^b[C_{OH}^-]^c[C_{EDTA}^{4-}]^d
\]  

(Eq. 2-8)

Here \(A\) is the Arrhenius pre-exponential factor, and \(\Delta E\) is the activation energy (\(\Delta E = 60.9\) kJ/mol). The values of \(a, b, c,\) and \(d\) in Eq. (2-8) are the reaction orders for the related reactants.
Table 2-2 Solution Composition for Electroless Cu Deposition

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper Sulfate ((\text{CuSO}_4 \cdot 5\text{H}_2\text{O}))</td>
<td>Cu ions Supplier</td>
<td>0.05 – 0.1 mol/L</td>
</tr>
<tr>
<td>Formaldehyde ((\text{HCHO}))</td>
<td>Reducing Agent</td>
<td>0.01 – 0.1 mol/L</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetate ((\text{EDTA}))</td>
<td>Chelating Agent</td>
<td>0.1 mol/L</td>
</tr>
<tr>
<td>Tetramethylammonium Hydroxide ((\text{TMAH, N(CH}_3\text{)}_4\text{OH}))</td>
<td>pH value adjuster</td>
<td>Adjust pH to 12.5 – 12.6</td>
</tr>
<tr>
<td>2-2’-dipyridyl ((\text{C}_5\text{H}_4\text{N})_2)</td>
<td>Stabilizer / ductility promoter</td>
<td>$6.4 \times 10^{-4}$ mol/L</td>
</tr>
<tr>
<td>Polyethylene glycol ((\text{PEG, H(OCH}_2\text{CH}_2\text{)}_n\text{OH}))</td>
<td>Surfactant</td>
<td>((0.25–2.5) \times 10^{-3}) mol/L</td>
</tr>
<tr>
<td>Potassium ferricyanide ((\text{K}_4[\text{Fe(CN)}_6]))</td>
<td>Ductility promoter</td>
<td>$1.4 \times 10^{-4}$ mol/L</td>
</tr>
</tbody>
</table>

The reaction orders of the reactants are dependent on the experimental conditions. The experimental results about main reactant orders are listed in Table 2-3 (Ohno and Haruyama, 1981; Sviridov et al, 1987; Dubin et al, 1997).

It is worth to discuss the role of the hydroxide ion in the reaction of electroless Cu deposition. From the reaction kinetics, increasing hydroxide ion can increase the Cu plating rate, i.e., the higher pH value, the higher plating rate. However, the extent of coordination between copper ion and the chelating agent will be greater when the pH value of the plating solution is higher. Thus thermodynamically, the reduction of copper(II) chelating ion is more difficult at higher pH value (Hung and Chen, 1989). Dubin and Shacham-Diamand (1997)
found an optimum pH value in the range of 12.5 to 12.6, when the formaldehyde and EDTA are used as the reducing agent and chelating agent, respectively.

Table 2-3 The Reaction Orders for the Rate Law of ELD Cu

<table>
<thead>
<tr>
<th>Reactant Concentration Range</th>
<th>Deposition Temperature</th>
<th>Reactant Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.015 \leq C_{Cu}^{2+} \leq 0.1 \text{ mol} / L$</td>
<td>$0.05 \leq C_{HCCHO} \leq 0.5 \text{ mol} / L$</td>
<td>$0.07 \leq C_{OH}^- \leq 0.3 \text{ mol} / L$</td>
</tr>
<tr>
<td>$a = 0.78$</td>
<td>$b = 0.13$</td>
<td>$c = 0.02$</td>
</tr>
</tbody>
</table>

| $0.02 \leq C_{Cu}^{2+} \leq 0.04 \text{ mol} / L$ | $0.17 \leq C_{HCCHO} \leq 0.34 \text{ mol} / L$ | $0.03 \leq C_{OH}^- \leq 0.04 \text{ mol} / L$ | $0.05 \leq C_{EDTA}^4 \leq 0.09 \text{ mol} / L$ | $75 – 80^\circ C$ |
| $a = 0.9$ | $b = 0.3$ | $c = 0.0$ | $d = 0.0$ |

| $0.003 \leq C_{Cu}^{2+} \leq 0.03 \text{ mol} / L$ | $0.03 \leq C_{HCCHO} \leq 0.4 \text{ mol} / L$ | $0.5 \leq C_{OH}^- \leq 2 \text{ mol} / L$ | $21^\circ C$ |
| $a = 0.37$ | $b = 0.00$ | $c = 0.37$ |

2.4.2 Deposition of Pd Seed Layer

The electroless Cu deposition is an auto-catalytic process, which means if there is an initial Cu layer, the reaction can continue indefinitely. However, if Cu is to be electrolessly deposited on a non-metallic surface, it is difficult to start this first layer of Cu. Thus catalytic sites, or seed layer, should be created on the non-metallic surface for initiating the electroless plating.

Various materials, including Ti, W, TiN, Al, Au and Pd, have been evaluated as the seed layer for electroless Cu deposition (Cho et al, 1995). No deposition was found on Ti because of its easy oxidization. The Cu films on TiN or W were rough and had poor adhesion. The thin Al seed layer will be etched away right after the substrate is immersed into the
solution because of its high hydroxide concentration. The best results were obtained on a layer of Pd or Au, on which Cu films had a smooth surface and good adhesion. Pd becomes the most frequently used seed layer for electroless Cu deposition instead of Au, because gold is a deep-level dopant in a silicon-based advice.

Two different methods, classified as wet and dry activation, have been applied to deposit a Pd seed layer on non-conductive substrates prior to electroless Cu deposition. In wet activation, the substrate is treated by immersing into a solution containing Pd ions (Pd$^{2+}$) to obtain numerous Pd seeds. In dry activation, an ultra-thin Pd film is deposited using sputtering (physical vapor deposition) or chemical vapor deposition.

- **Wet Activation.** Two major wet activation processes have been developed: sensitization-activation and displacement-activation. In sensitization-activation, Sn$^{2+}$ ions are adsorbed on the substrate and then oxidized to Sn$^{4+}$, thereby providing electrons to reduce Pd$^{2+}$ ions to Pd atoms. In displacement-activation, the substrate is oxidized and dissolved by the activation solution, and in this way electrons are provided for the reduction of Pd$^{2+}$ to Pd atom.

  - **Sensitization-Activation Process.** This is a two-step process. The sensitization step is to adsorb Sn$^{2+}$ onto the substrate, which is performed by immersing the substrate into the SnCl$_2$/HCl solution. The activation step is to deposit Pd catalytic sites on the substrate, which is performed by immersing the substrate into the PdCl$_2$/HCl solution. The reaction mechanism during the latter step is thought to be (Sard 1970):

\[
Sn^{2+} + Pd^{2+} \rightarrow Pd^0 + Sn^{4+}
\]  

(Eq. 2-9)
which means that the adsorbed stannous ions provide the sites and electrons for the adsorbing palladium ions.

Several papers about Pd seed layers deposited by sensitization-activation have been published. Sard (1970) investigated the catalytic behavior of Pd on a carbon substrate, and found that particle-like structures with size less than 2 nm were formed. These particles tended to agglomerate to form dense clumps which were an order of magnitude larger in size. Hsu et al (2002) reported Pd was composed of an agglomerate of small particles on TaN substrate using AFM. These agglomerates had sizes of several tens to hundreds of nanometers in diameter and several to tens of nanometers in height due to the various catalyzation times. The catalytic sites contained Sn and Pd with a ratio of Sn/Pd about 1.3. Fong et al (2003) revised the sensitization activation process from two-step to one step by mixing the sensitization and activation solution together. They found that the density of Pd nuclei was about $5.8 \times 10^7/\mu m^2$. Chang et al (2004) found that Pd clusters with size of 5 – 10 nm were distributed uniformly on the whole TiN substrate using TEM cross-sectional analysis. They also observed that the Pd nucleus density was in an order of $10^3$ to $10^4/\mu m^2$.

The above papers also included some discussion of the growth mechanism and the properties of electrolessly deposited Cu on the sensitization activated Pd seed layer. Sard (1970) believed that Cu was initiated on the Pd seed sites in a three-dimensional way, and then these Cu nuclei aggregated to large unstable grains before a re-crystallization process took place. This repeated nucleation and re-crystallization process resulted a continuous Cu film. After that, the Cu film thickness gradually increased with increasing deposition time. Hsu et al (2002) deposited a uniform and smooth Cu film with a thickness of 210 nm and a surface roughness of 6.2 nm. The lowest Cu resistivity was about 2.5 $\mu \Omega$-cm. Chang et al
were able to deposit void free ELD Cu film with a thickness of 20 nm in 1 min. The lowest resistivity was 4.08 \( \mu\Omega \)-cm, which was measured from a 30 nm Cu film.

- **Displacement-Activation Process.** This is a one-step process using an activation solution that contains mainly HF and PdCl\(_2\). In this activation solution, two galvanic half-cell reactions including Pd deposition and removal of substrate simultaneously occur. For the deposition of Pd on a metal or silicon surface, the following two typical reactions are considered (Nagahara et al 1993):

\[
Pd^{2+} + 2e \rightarrow Pd \quad \text{(Eq. 2-10)}
\]

\[
PdCl_2 + 2e \rightarrow Pd + 2Cl^- \text{ (presence of HCl in the solution)} \quad \text{(Eq.2-11)}
\]

The electrons required for the displacement deposition are supplied by the oxidization of substrate (\( M \)). The following reaction possibly takes place and leads to the dissolution of substrate by HF:

\[
M + 4F^- \rightarrow MF^{4-} + 4e^- \quad \text{(Eq. 2-12)}
\]

Several papers regarding to the displacement activation on different substrates have been published. Nagahara et al (1993) investigated the influence of the HF concentration on the initial stages of Pd deposition on a \( p \)-Si wafer. They found that the rate of Pd deposition correspondingly increased as the HF concentration in the activation solution increased, because the reaction involved fluorine ions. Karmalkar et al (1997) reported that the addition of NH\(_4\)F into PdCl\(_2\)/HF solution improved the Pd activation efficiency for Si. The authors believed that the improvement in the activation was due to the generation of a palladium amine complex and HF\(_2^-\) ions. Pd deposition from complex metal ions resulted in a superior quality. Similar phenomena were also observed by Oh et al (2005). Hsu et al (2001b)
published a study about Pd activation on a Ta diffusion barrier using a PdCl\textsubscript{2} buffered oxide etch (BOE, 34.9% NH\textsubscript{4}F + 7.2% HF)/HNO\textsubscript{3}. The authors concluded that the activation solution with a ratio of BOE/HNO\textsubscript{3} of 3:2 gave the substrate the best distribution of Pd particles and the least damage to the barrier layer as confirmed by SEM and AFM. Hong et al (2002) found the nuclei density of Pd on the TaN\textsubscript{x} (0 ≤ x ≤ 1) was approximately 10\textsuperscript{2}/\mu\text{m}\textsuperscript{2}, and the Pd nuclei had size of 30 to 40 nm in diameter. XPS spectra of Pd 3d\textsubscript{5/2} showed that the deposit was pure metallic Pd without chemical shift.

Different authors obtained Cu films with similar properties on substrates which were activated using the displacement activation method. Hsu et al (2001b) found that Cu grains grew on the catalytic Pd nuclei first, and the Cu growth rate in the horizontal direction was faster than that in the vertical direction. The typical Cu surface roughness values were between 24 – 40 nm, and the electrical resistivity values were 1.9 – 2.5 \(\mu\Omega\)-cm. Ee et al (2004) deposited Cu films with similar surface roughness (23 – 26 nm), while with high electrical resistivity values (7.57 – 9.6 \(\mu\Omega\)-cm) for 84 nm Cu films. Oh et al (2005) reported a growth rate of 1.83 nm/s for ELD Cu on TiSiN. The authors also found that the as-deposited Cu film had a resistivity below 3 \(\mu\Omega\)-cm.

- **Dry Activation.** Physical vapor deposition (PVD) or chemical vapor deposition (CVD) also can deposit an ultra thin Pd seed layer for electroless Cu deposition. We categorize them as dry activation methods because of the absence of activation solution. One of the main advantages of the dry activation, especially for PVD, is the absence of introducing extra metals into the activation layer, such as Sn in sensitization activation. These metals will increase the resistivity of the Cu seed layer, and in turn increase the resistivity of the deposited interconnect Cu line.
**Physical Vapor Deposition.** Johnson et al (1998) published the only study about electroless Cu deposition on a PVD Pd seed layer. The Pd layer was created by sputtering onto a (100) Si wafer and plasma etching the Pd back to 100 nm thickness. Using grazing incidence x-ray diffraction, the authors determined the Pd seed layer had a (111) texture without radial orientation. The authors also found that the Pd particles had spheroidal shapes with an average grain size in a range of 30 – 50 nm, using AFM and STM analyses. Electroless Cu deposition was performed using deposition times from 1 – 300 s to determine the growth spectrum of the Cu film from its initial grain nucleation to micron sized features. AFM analyses revealed that the nucleation of ELD Cu was not homogeneous across the homogeneous Pd seed layer. Multiple nucleation sites were found on the Pd seed layer, and the final Cu film produced row-like structures. The texture of the ELD Cu was determined to be (111).

**Chemical Vapor Deposition.** To our knowledge, there are no publications about Pd seed layer using CVD method for electroless Cu deposition. The properties of the Pd seed layer mainly determine the quality and morphology of thin electroless Cu film. The continuous shrinkage of the feature size in dual damascene processing requires a smooth Cu seed layer with good step coverage in both the feature’s bottom and side surfaces. One of the merits of CVD is its high step coverage. Provided that acceptable film properties can be achieved using a low enough deposition temperature, then CVD may become a promising alternative method for depositing a thin and smooth Pd activation layer for electroless Cu deposition in the future semiconductor application.
2.5 Palladium CVD Using Pd(hfac)$_2$

In this section, we review the deposition of thin Pd films using CVD method. We will first present the available precursors for the Pd deposition. Next we will review the kinetics and the properties of thin Pd films grown by CVD using Pd(hfac)$_2$, i.e., palladium(II) bis(hexafluoropentanedionate).

2.5.1 Precursors for Pd CVD

Palladium thin films have several technological applications such as inorganic membranes for H$_2$ gas separation (Tsapatsis et al, 2000), supported catalysts for CO oxidation (Dossi et al, 1993), and multilayer magneto-optical data storage device (Gurney and Seymour, 1991). Thin films of Pd have also been used in the fabrication of microelectronic devices: Ohmic and Schottky contacts in compound semiconductors (Chen et al, 1992; Leigh et al, 1994), and Pd silicides in silicon based MOS device structures (Gurney and Seymour, 1991).

In order to deposit Pd films with high purity and high deposition rates, the basic requirements for the Pd precursors are high vapor pressure, thermal stability and reactivity. Many new organometallic and metal-organic complexes of Pd precursors have been studied, the results of which are listed in Table 2-4. Among all these precursors, Pd(hfac)$_2$ seems to the most favorable precursor to use, since highly pure Pd films with relatively fast deposition rate can be obtained provided that H$_2$ is introduced during the deposition.

2.5.2 CVD Thin Pd Films from Pd(hfac)$_2$

In this subsection, we will include some previous studies about CVD thin films from thermal decomposition or H$_2$ reduction of Pd(hfac)$_2$. The selective deposition of Pd has been investigated due to its particular relevance in microelectronic devices (Lin et al, 1993; Jeon et al, 1997). A reaction mechanism for selective deposition of Pd thin film on Cu surface has
been published by Lin et al (1996a, b). The deposition kinetics of Pd thin films has been studied by Bhaskaran et al (1997) and Wunder et al (2002).

Lin et al (1993) prepared high-purity Pd (< 1 mass% C, O and F) on several substrates (glass, silicon, copper, tungsten, aluminum, nickel) from Pd(hfac)$_2$ in the presence of H$_2$ using a deposition temperature between 200 and 425°C and a system pressure of 10$^{-4}$ Torr. While under vacuum and without the assistance of H$_2$, Pd films were selectively deposited only on copper substrate. Jeon et al (1997) selectively deposited high purity Pd films from Pd(hfac)$_2$ in presence of H$_2$ on various substrate surfaces, which were patterned by a microcontact method using octadecyltrichlorosilane (OTS). The tested substrates which could be selectively Pd deposited included titanium nitride(TiN), indium tin oxide(ITO), silicon dioxide on silicon (SiO$_2$/Si), sapphire, and borosilicate glass. The authors found that the selective deposition occurred at all studied temperature and pressure ranges (175 – 275°C, and 0.1 – 5 Torr, respectively), when the deposition rate was lower than 40 nm/min. A growth rate using deposition temperature of 250°C was measured to be about 20 nm/min, and the film resistivity about 25 $\mu$Ω-cm.

Lin et al (1996a, b) studied the reaction pathway and the kinetics for the selective deposition of Pd on polycrystalline Cu foil from Pd(hfac)$_2$ by means of reactive molecular beam-surface scattering. The surface selectivity of the deposition process was considered to be a consequence of a “redox transmetalation” reaction, in which Pd(hfac)$_2$ molecules were reduced by surface Cu atoms to give Pd deposits while the Cu substrate was etched away as the volatile byproduct Cu(hfac)$_2$. The redox reaction could be described by the stoichiometric equation:
<table>
<thead>
<tr>
<th>Precursor</th>
<th>Deposition Temperature (°C)</th>
<th>Co-reactant</th>
<th>Deposition Rate (nm/min)</th>
<th>Impurities</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(allyl)$_2$</td>
<td>250</td>
<td>–</td>
<td>–</td>
<td>Thermally unstable</td>
<td>Gozum et al, 1988</td>
</tr>
<tr>
<td>Pd(Me-allyl)$_2$</td>
<td>250</td>
<td>–</td>
<td>–</td>
<td>Thermally unstable</td>
<td>Gozum et al, 1988</td>
</tr>
<tr>
<td>Pd(allyl)(hfac)</td>
<td>330 – 370</td>
<td>O$_2$</td>
<td>1.1 – 6.6</td>
<td>&gt;99% mass Pd</td>
<td>Yuan et al, 1994a</td>
</tr>
<tr>
<td>Pd(Me allyl)(hfac)</td>
<td>330 – 370</td>
<td>O$_2$</td>
<td>1.1 – 6.6</td>
<td>&gt;99% mass Pd</td>
<td>Yuan et al, 1994a</td>
</tr>
<tr>
<td>Pd(Me allyl)(acac)</td>
<td>330 – 370</td>
<td>O$_2$</td>
<td>1.1 – 6.6</td>
<td>&gt;99% mass Pd</td>
<td>Yuan et al, 1994a</td>
</tr>
<tr>
<td>PdMe$_2$(PMe$_3$)$_2$</td>
<td>130 – 300</td>
<td>H$_2$</td>
<td>3.3</td>
<td>C free, 12% mass P</td>
<td>Yuan et al, 1994b</td>
</tr>
<tr>
<td>PdMe$_2$(PEt$_3$)$_2$</td>
<td>130 – 300</td>
<td>H$_2$</td>
<td>3.3</td>
<td>C free, 10% mass P</td>
<td>Yuan et al, 1994b</td>
</tr>
<tr>
<td>PdMe$_2$(tmeda)</td>
<td>130 – 300</td>
<td>H$_2$</td>
<td>15</td>
<td>11% mass C</td>
<td>Yuan et al, 1994b</td>
</tr>
<tr>
<td>CpPd(allyl)</td>
<td>30 – 60</td>
<td>H$_2$</td>
<td>–</td>
<td>High purity</td>
<td>Hierso et al 1996</td>
</tr>
<tr>
<td>Pd(acac)$_2$</td>
<td>350 – 400</td>
<td>H$_2$</td>
<td>–</td>
<td>C and O free</td>
<td>Meng et al 1997</td>
</tr>
<tr>
<td>Pd(hfac)$_2$</td>
<td>80 – 200</td>
<td>H$_2$</td>
<td>100 – 400</td>
<td>Free of C, O, F</td>
<td>Bhaskaran et al, 1997</td>
</tr>
<tr>
<td>Pd(hfac)$_2$</td>
<td>200 – 375</td>
<td>He (carrier)</td>
<td>139 – 3600</td>
<td>25 – 35% C</td>
<td>Wunder et al, 2002</td>
</tr>
</tbody>
</table>

Here: Me = Methyl; Cp = cyclopentadiene; acac = acetylacetonate; tmeda = tetramethyl-ethylenediamine;
\[ Pd(\text{hfac})_2 + Cu \rightarrow Pd + Cu(\text{hfac})_2 \]  
(Eq. 2-13)

The authors found that this transmetalation reaction was favored to produce \( \text{Cu(hfac)}_2 \) from the \( \text{Cu} \) surface when its temperatures were between 400 and 600\(^\circ\)K. At temperatures above 600\(^\circ\)K, the yield of \( \text{Cu(hfac)}_2 \) decreased and eventually fell to zero at 800\(^\circ\)K as the thermolytic decomposition of the \( \text{hfac} \) ligands on the surface became kinetically competitive. The above phenomena could be explained by the activation energies for these two processes: 13 kcal/mol for the transmetalation reaction (Eq. 2-13) and 36.8 kcal/mol for the decomposition of \( \text{hfac} \) ligands.

Bhaskaran et al (1997) published a comprehensive kinetics study about \( \text{Pd} \) thin films grown from \( \text{Pd(hfac)}_2 \) reduced by \( \text{H}_2 \). The deposition experiments were carried out over a substrate temperature range of 80 – 200\(^\circ\)C and a system pressure of 50 mTorr. The deposited \( \text{Pd} \) films were free of \( \text{C, F, and O impurities within the detection limits (≈1 at. %) of AES} \). The growth rates were independent of substrate temperatures over the tested range if the concentration of \( \text{Pd(hfac)}_2 \) in the reactor was fixed. The average growth rate was a function of the inlet concentration of precursor, i.e., the rate increased from 100 nm/min to 400 nm/min when the evaporation temperature increased from 65\(^\circ\)C to 75\(^\circ\)C. The authors concluded that the film growth was a mass-transfer limited process under low system pressure. The deposited \( \text{Pd} \) films were polycrystalline and the resistivity values ranged from 20 – 50 \( \mu \Omega \)-cm without annealing.

Wunder et al (2002) investigated the decomposition of \( \text{Pd(hfac)}_2 \) in helium as a carrier gas. The kinetic experiments were performed using the following conditions: He flow rate = 100 sccm; concentration of \( \text{Pd(hfac)}_2 = 0.001 – 0.1 \text{ mol/m}^3; \) deposition temperature = 200 –
375°C; system pressure = 20 – 720 mTorr. The authors found that the Pd deposition rate initially increased with increasing the Pd(hfac)$_2$ concentration, passing through a maximum value (3600 nm/min) near $c[\text{Pd(hfac)}_2] = 0.01 \text{ mol/m}^3$. The authors proposed a Langmuir–Hinshelwood reaction mechanism to interpret this kinetic behavior, and obtained a hyperbolic law rate with four kinetic parameters. The effects of temperature on the Pd deposition rate were also investigated. Four regions with different apparent activation energies were listed: 200 – 250°C, surface reaction controlled, $E_{\text{aI}} = 150 \text{ kJ/mol}$; 250 – 275°C, both surface reaction and mass transport controlled, $E_{\text{aII}} = 100 \text{ kJ/mol}$; 275 – 325°C, mass transport controlled, $E_{\text{aIII}} = 16 \text{ kJ/mol}$; > 325°C, homogeneous gas phase reaction. The authors believed that the absence of H$_2$ led to Pd films with high carbon content (Pd/C = 0.65 – 0.75, independent of the process parameters).
CHAPTER 3 EXPERIMENTAL: APPARATUS AND PROCEDURE

This chapter describes the reactor systems built-in-house and the operating procedures for studying the chemical vapor deposition of metal thin films (Cu, Ta, Pd). Section 3.1 presents the pedestal reactor system for copper CVD using Cu(hfac)$_2$ precursor dissolved in isopropanol solution. Section 3.2 describes the pedestal reactor system for tantalum CVD using TaF$_5$ and SiH$_4$ as reactants. Section 3.3 describes the APCVD reactor system for depositing Pd seed layers or continuous Pd films using Pd(hfac)$_2$ as precursor. Lastly, section 3.4 briefly describes the techniques used to characterize the film properties (morphology, composition, and resistivity).

3.1 Copper CVD

In this section we describe the experimental apparatus and operating procedures for depositing Cu films using liquid precursor delivery. We will first present the details about the CVD reactor and carrier gas flow system. We then discuss the operating procedure for Cu deposition.

3.1.1 Warm Wall Low Pressure LDS CVD System

This subsection describes the reactor system built to study Cu CVD using liquid precursor delivery. Figure 3-1 shows an overview of the system, which is comprised of four main components: the gas delivery section (GDS), the liquid delivery system (LDS), the pedestal reactor, and the vacuum pump. The GDS meters the H$_2$ gas from the cylinder to the system, where H$_2$ play the role of carrier gas. The LDS, which contains a solution reservoir and an isocratic pump (Hewlett Packard, 1100 series), delivers the solution of Cu(hfac)$_2$ dissolved in isopropanol (i-PrOH) into the carrier gas stream. The gas mixture flows into the
Fig. 3-1 Schematic of Solution Delivery System for Copper CVD
reactor through heated stainless steel tubing. The copper is deposited onto the hot substrate that is mounted on the pedestal. Finally, the gas mixture is pumped out of the system after passing through a collection trap where the unconsumed Cu(hfac)$_2$ condenses out. The details of the GDS, LDS, reactor and pump are given below.

- **Gas Delivery System (GDS).** Ultra high purity hydrogen gas is used as the carrier gas. One mass flow controller (MFC, Omega®, FMA-1912, 500 sccm capacity) meters the flow of hydrogen into the system tubing, where the Cu(hfac)$_2$ : i-PrOH solution enters the stream and is heated to evaporate. A four-way switching valve is used to direct the flow either into the reactor or into the bypass line. The bypass line is engaged when the CVD reaction is not in progress. The system pressure is measured using a capacitance manometer (MKS Instrument, model 122AA-01000AC), which is connected to a digital readout (MKS Instrument, model PDR-D-1).

  The flow system tubing from the solution injection point up to the reactor is heat-traced with heating tapes (VWR) to keep the temperature high enough (120°C) to prevent the Cu(hfac)$_2$ precursor from condensing and plugging the lines. Several variable voltage transformers are used to control the temperatures. Temperatures at seven locations on the heat-traced line are measured using thermocouple wires. The thermocouple wires are connected to a 12 point selector switch (Omega Instruments, model no. M141 0689), which displays the selected temperature on a temperature indicator (Omega Instruments, model no. 115KC). The temperature locations are indicated in Fig. 3-1.

- **Liquid Delivery System (LDS).** There are several methods to deliver a MOCVD precursor into the reaction system according to its state under room temperature. Usually solid
precursors are introduced by carrier gas into system through heating an evaporator, while liquid sources can be introduced into system by a micro pump. The direct sublimation of precursors has the drawback of variation in transport rate because the evaporation of solids suffers from mass transfer resistance at the gas-solid surface. The evaporation rate may also become smaller by a decrease in surface area of precursor particles over time. Direct delivery of a liquid precursor into a system has no such problem, and the precursor flow rate can be controlled precisely.

If a suitable solvent can be found to dissolve the solid precursor, then the precursor solution can be transported into reaction system directly using a micro pump. The solvent should have following features (Zheng, 1992): (a) the source precursor can be easily dissolved in it without adversely changing its chemistry, (b) it is easily vaporized at low temperature to allow for ease in the transportation of mixtures of precursor and solvent into reactor, and (c) it can either easily decouple from the precursor in the gas phase in the reactor so as not to affect its decomposition pathways and the quality of the deposited films or, alternatively, the solvent may enhance the nucleation or growth rate of solid film.

The solubility of Cu(hfac)$_2$ in alcohols is high. Several studies (Borgharkar, 1998b; Raman, 2000) have found that alcohols can improve the copper deposition rate and film properties on different substrates. So in this research we use i-PrOH as a solvent to provide highly accurate, reproducible, and controllable flow rates of Cu(hfac)$_2$:i-PrOH mixtures to the reaction zone using the isocratic liquid pump. The stable flow range of the pump is 0.001–10 ml/min, in 0.001ml/min increments. Reservoirs containing Cu(hfac)$_2$:i-PrOH solution and pure i-PrOH are used to supply the inlet feed for CVD experiment and for intermediate purge periods. A four-way valve (Upchurch Scientific Inc.) is used to direct the pumped solution
either to the injection point or to a bypass reservoir. The solution flows through a small
diameter capillary tubing (0.1 mm ID, 35 cm length, Upchurch Scientific Inc) between the
valve and the injection point, in order to maintain the necessary pressure gradient between the
isocratic pump and the low pressure CVD system. The small diameter also acts to minimize
the time lag downstream from the valve. The capillary is inserted into the carrier gas line (see
Fig.3-1) using a stainless steel “Tee” with capillary fitting. The injection point and the carrier
gas tubing leading downstream to the reactor are heat-traced to ensure complete evaporation
of both i-PrOH and Cu(hfac)$_2$.

- Pedestal Reactor. The Cu(hfac)$_2$, i-PrOH and H$_2$ gas mixture reaches the pedestal
reactor through heat-traced tubing. Figure 3-2 shows a schematic assembly of the pedestal
reactor, which includes a four-way stainless steel cross as the reactor body and a pedestal
substrate holder.

- Reactor body. The body is a Varian NW 40 1-1/2" stainless steel cross. The top arm
of the cross is connected to the gas tubing through intermediate 1/4" tubing. One side arm is
connected to the quadruple mass spectrometer (QMS) interface. The QMS can be decoupled
from the system by a blind flange. The other side arm is connected to the vacuum pump
through the trap. The bottom arm is used to mount the pedestal substrate holder. The wall of
the body is heat-traced to about 120°C. Temperature on each arm of the cross is measured by
thermocouple wire. The thermocouple wire is connected to a 12 point selector switch, which
displays the selected temperature on a temperature indicator. The temperature locations are
indicated in Fig. 3-1.

- Pedestal substrate holder. The pedestal substrate holder is shown in Fig. 3-2. It holds
and heats the substrate. The main body of the holder is a hollow stainless steel tube with
diameter of 1" and length of 2.5". The top end is fitted with a tapered copper plug. The Cu plug serves as the platform on which the substrate is fixed by four cross-position screws. The bottom end of the tube is welded to a 1 ½" coupling flange. The flange fits over the bottom arm of the 4-way reactor cross, and the reactor is sealed from the outside with a quick-connect clamp.

Two cavities are opened in the narrow end of the copper plug on the atmospheric side. One hole is drilled for a cartridge heater (Watlow) that is connected to a variable voltage transformer. The cartridge is 1/4" diameter, 1" long, and maximum rated power of 150 watts. The second hole is a 1/16" thermo-well for housing a thermocouple to measure the temperature of the pedestal base.

The substrate is clamped down on to the base of the pedestal using four screws and is heated by the cartridge heater under the copper plug to about 300°C. The temperature of the substrate is measured by the type K thermocouple placed in the thermo-well, and indicated by a digital readout (Omega, 115KC). The walls of the reactor cross and connecting tubing are heat traced to about 120°C. This gives the ability to maintain a high temperature on the substrate, while keeping the walls of the reactor at a relatively lower temperature.

The Cu(hfac)_2/i-PrOH/H\textsubscript{2} mixture flows downward over the substrate before being pumped out of the system. This flow arrangement makes it a warm wall reactor with downward impinging flow arrangement. The unconsumed copper precursor is collected in a glass wool trap, which is a stainless steel pipe with a diameter of 1.1" and 8" long. One end of the tubing is connected to the reactor by a 1 ½" stainless steel bend, which is heat traced to prevent condensation of the unconsumed Cu(hfac)_2. The other end of the trap is connected to a vacuum pump.
Fig. 3-2 Schematic of Pedestal Reactor
• **Vacuum pump.** The gas flowing out from the trap is pumped by a rotary vane vacuum pump (Varian SD 300, rated free air displacement = 15.7 m³-h⁻¹). System pressure is controlled by a Nupro needle valve placed after the trap. The pump can be quickly isolated from the rest of the system by a Varian block valve placed after the needle valve. Before going to the gas hood, gas flow rates can be calibrated at ambient conditions by the displayed volume apparatus (DVA) located at the discharge of the vacuum pump.

### 3.1.2 Operating Procedure

The experimental procedure is described in two sections: cleaning steps, such as substrate and pedestal cleaning, and copper CVD procedure.

- **Cleaning Steps.**  - **Substrate Cleaning.** The substrate used in this study is a circular glass disk with a diameter of 15 mm (Ted Pella Inc.), which matches the pedestal diameter.

  Substrate surface condition has a very important effect on the quality of the deposited film. We tried several cleaning methods, including ultrasonic bath using acetone or isopropanol, and the RCA method using a diluted SC-1 solution. A good quality copper film can be obtained only using the substrate cleaned by diluted SC-1 solution. The composition of the diluted SC-1 mixture is H₂O(200):37% H₂O₂(4):29% NH₄OH(1) by volume (Wolf, 2000).

  The substrate is submerged in the fresh diluted SC-1 solution for 10 minutes with the temperature being maintained at 70°C. This step dissolves organic film and most metal complexes on the substrate surface. The substrate is then rinsed by deionized water for 1 minute, and dried by a Kim wipe. After immersing in 30% HNO₃ solution for 5 minutes, the substrate is etched to be smoother. This is confirmed by the AFM micrographs, which show surface RMS of 1.0 nm using SC-1 only vs. 0.5 nm using HNO₃ after SC-1 cleaning.
Pedestal Cleaning. Because the top surface of the pedestal has the same temperature as the substrate, copper is deposited on the copper block and approximately 0.5 cm length down the side of the stainless steel wall. So we initially attempted to remove the deposited copper before the pedestal is mounted into the system in every experiment. The deposited copper can be removed by concentrated HNO₃ with cotton applicators.

However, a reproducibility problem occurs if we clean the pedestal surface before every experiment. The deposited copper film sometimes is visually bad or non-uniform. Sometimes, even no deposition is on the substrate. The possible reason is that the pedestal cleaning procedure is not repeatable. We decided not to clean pedestal before every experiment until a thick copper film has deposited on the surface. Good reproducibility is obtained after this policy.

However the copper growth rate will decrease gradually with the increase of copper thickness on the pedestal. Usually, the pedestal will be cleaned one time in about six to eight weeks (about 30 to 40 experiments). We then observe that at least two recovery experiments are needed to be done before uniform and continuous copper film can be achieved on the glass substrate after the pedestal is cleaned.

- CVD Procedure. After the substrate is cleaned, weighed, and mounted on the pedestal, the pedestal is sealed in the system. Then the system is pumped down with no gas flow until the zero offset on the digital readout of manometer is reached. Ultra high purity hydrogen then flows from the cylinder through the Omega® MFC with a desired flow rate. The desired system pressure is obtained by adjusting the needle valve on the exhaust gas line. The system is heat-traced to the desired temperature, and the substrate is heated by the cartridge heater to the desired temperature.
After the desired flow rate, pressure, and temperature setting are reached, a suitable amount of fresh Cu(hfac)$_2$ : i-PrOH solution is transferred from a storage container to the precursor reservoir. The HP isocratic pump is started after immersing the filter head of pump inlet pipe into the solution. The desired liquid flow rate is set up by using the software provided by the pump itself. Before transporting the liquid precursor into the system, the pump delivery tubing, which includes the filter head and the plastic tubing before the four-way valve, needs to be filled with the precursor by directing the four-way valve to the waste copper solution reservoir. This step serves to prevent a lag in the precursor transport into the system at the beginning of the experiment.

The copper CVD experiment is started by switching the four-way valve to the system inlet tubing. During the experiment, the system pressure is increased significantly because of the evaporation of i-PrOH. The pressure is recorded every 30 seconds. The difference between the pressures before and after the transportation of solution into the system, together with the molar flow rates of the solution and the carrier gas, is used to calculate the partial pressures of Cu(hfac)$_2$ and i-PrOH according to ideal gas law.

After the experiment is carried out for the desired time, the four-way valve is switched back to the direction of the waste container. The last step of the CVD experiment is to clean each component of the system, in order to prevent the condensed Cu(hfac)$_2$ from clogging the system. The pump is flushed using i-PrOH until no copper solution remains in the inlet delivery plastic tubing, i.e., the solution color is changed from green to completely colorless. The same operation is used to clean the capillary tubing with i-PrOH for about 2 minutes by switching the four-way valve to the system, while keeping the system heat-traced.
The system is cooled to room temperature with the hydrogen gas and pump on. After the substrate has reached room temperature, the vacuum pump is stopped, hydrogen flow is cut off, and the pedestal is removed from the system. The substrate is then dismounted from the pedestal and weighed by the microbalance.

- **Operating Conditions.** The range of operating conditions for copper CVD are shown in Table 3-1. Low pressure and high volumetric gas flow rates are used. Low pressure leads to high diffusion coefficients of reactants, which enhances the mass transport of the reactants. Operating at high volumetric flow rate assures short residence time (average about 6s), which combined with relatively low deposition rate (using moderate deposition temperature) ensures differential conversion of the reactants. Differential conversion means that the concentration of the reactants is nearly unchanged in the reactor. Thus the concentration of reactants near the substrate can be approximated to be the same as those at the reactor inlet.

### Table 3-1 Operating Conditions for Copper CVD

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Glass, 15mm diameter</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>2 – 15 min</td>
</tr>
<tr>
<td>H$_2$ Flow Rate</td>
<td>400sccm</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Solution Flow Rate</td>
<td>0.005 – 0.04 ml/min</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Solution Concentration</td>
<td>0.05 – 0.4 g Cu(hfac)$_2$/ml i-PrOH</td>
</tr>
<tr>
<td>H$_2$ Partial Pressure</td>
<td>40 – 160 Torr</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Partial Pressure</td>
<td>0.0125 – 0.05 Torr</td>
</tr>
<tr>
<td>i-PrOH Partial Pressure</td>
<td>0.8 – 3.2 Torr</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>300°C</td>
</tr>
<tr>
<td>Conversion</td>
<td>$\leq$ 10%</td>
</tr>
</tbody>
</table>
3.2 Tantalum CVD

This section describes the pedestal reactor system built in-house to study tantalum CVD using TaF$_5$ and SiH$_4$ as reactants. Section 3.2.1 describes the main features of the warm wall low pressure pedestal reactor system. Section 3.2.2 presents the experimental operating procedure.

3.2.1 Tantalum CVD System

This subsection presents the reactor system built in-house to study tantalum CVD. The overall system is shown in Fig. 3-3. The system can be divided into three main parts: the reactant gases delivery section (the flow system before the reactor), the pedestal reactor, and exhaust section (flow system after the reactor).

- **Reactant Delivery Section.**
  - **SiH$_4$ Delivery.** A 5% SiH$_4$:H$_2$ mixture (Matheson Tri-Gas) is used as the reducing agent. One MFC (MKS Instrument, 1159-B, 50 sccm capacity) meters the flow of SiH$_4$/He from the cylinder into the system. A Pirani pressure gauge (MKS, series 315) with measuring range between $10^{-4}$ to 100 Torr is mounted on the SiH$_4$/He gas line to monitor the system pressure.

  - **TaF$_5$ Delivery.** Powdered TaF$_5$ precursor is bought from Strem Chemical Inc. with a stated purity of 99.5%. Purification of TaF$_5$ is reported to be an essential step for the production of good quality tantalum films (Ogolini, 1991). Two precursor evaporators are included in this CVD system, one for as-received TaF$_5$ sublimation and the other for purified precursor sublimation. Ultra high purity He gas is used as the carrier gas for TaF$_5$. A second MFC (MKS Instruments, 1159-B, 100 sccm capacity) meters the flow of He to the stainless steel evaporator. An iso-temperature oil bath (Fisher Scientific, Model 8000) is used to heat the TaF$_5$ powder in the evaporator. Each evaporator has a by-pass loop, which is used when
Fig. 3-3 Schematic of Warm Wall Low Pressure Tantalum CVD System
the CVD or TaF$_5$ purification is not in progress.

- **TaF$_5$ Evaporator Assembly.** Both of the TaF$_5$ evaporators consist of two Nupro bellows sealed valves and a stainless steel evaporator. They are connected to the system using Cajon VCR fittings. The valves (one at each end of the evaporator assembly) isolate the flow of helium in and out of the evaporator. Both evaporators consist of a lid and a stainless steel body. The lid of the as-received TaF$_5$ evaporator is made of a Varian NW40 blank-off flange with 90° elbow inlet and outlet tubing welded on the flange. The body of the evaporator is made of a Varian NW40 nipple with a base plate welded at the bottom. The TaF$_5$ precursor evaporator uses a Varian NW16 lid and body. The lid and the body of both evaporators are connected using a quick connect clamp with a Viton® O-ring vacuum seal.

- **Heat Tracing.** The evaporator assemblies and the tubing downstream of the evaporator to the reactor are wrapped with heating tapes to keep the temperature high enough (70°C) to prevent TaF$_5$ from condensing. Several variable voltage transformers are used to control the heating tape voltages and thus the tubing temperature. The tubing temperature is monitored at 12 locations using thermocouple wires, which are attached to the tubing using heat-resistant fiberglass tape (TimeMed Inc.) along the heat-traced path. A digital readout (Omega®, Model 115KC) is used to record the temperatures. The thermocouple locations are indicated in Fig. 3-3.

- **Pedestal Reactor.** SiH$_4$/He and TaF$_5$/He reach the pedestal reactor through separate inlet tubing and then mix and react in the pedestal reactor. Fig. 3-4 shows a schematic assembly of the pedestal reactor. The reactor consists of a stainless steel 3-way tee and a pedestal substrate holder.
° Reactor Shell. The shell is a Varian NW40 1½ inch stainless steel tee. The top arm of the tee is connected to the gas tubing through an intermediate ¼ inch tubing. The right side arm is connected to the vacuum pump through a trap. The bottom is used to introduce the pedestal substrate holder.

° Pedestal Substrate Holder. The pedestal substrate holder is shown in Fig. 3-4. The structure of this holder is the same as the holder used in the Cu CVD experiment. The detail of the substrate holder is presented in section 3.1.2.

° Exhaust Section. This section includes the parts from the reactor to the hood. A Varian NW40 tee is used to connect this section and the pedestal reactor. A second pressure gauge (Varian, Model 6543-25-045) is connected on the upside of the tee. A Nupro needle valve is placed on the third side of the tee. After the needle valve, a 90° Varian NW40 elbow is placed. A 12½ inch Varian NW40 nipple is connected to the other side of elbow using a quick clamp and a Viton® O-ring. A straight reducer (Varian NW40 to NW25) connects the nipple and a Varian high vacuum block valve, which prevents the back entry of absorbed gases from the sieve trap into the system, and also changes the flow path from vertical direction to horizontal. The sieve trap is obtained from MDC (Model KMST-100-2); the molecular sieves in the trap are designed to remove water vapor and unconsumed TaF\textsubscript{5} from the exhaust gas before entering the vacuum pump (Alcatel, Model 2004A). A second block valve (HEY High Vacuum Products, Model BA-112) between the trap and pump connects the pump to the rest of the system and also prevents the back-diffusion of pump oil into the trap when the pump is shut down. The pump discharge is exhausted to the hood through a water bath.
Fig. 3-4 Schematic of Pedestal Reactor
3.2.2 Operating Procedure

The experiment is performed in three main steps: TaF$_5$ purification, substrate cleaning, and tantalum CVD. The following subsections will describe them in more detailed.

- **TaF$_5$ Purification.** The TaF$_5$ is obtained from Strem Chemical Inc. with a 99.5% purity. It is necessary to purify the TaF$_5$ before it is used as tantalum precursor. Because of its sensitivity to water vapor, the as-received TaF$_5$ is loaded into the TaF$_5$ evaporator in an Ar atmosphere glove box, which is located in the laboratory of Dr. Maverick, Chemistry Department. The weight of evaporator assembly and TaF$_5$ in it is weighed by a balance (American Scientific Products, resolution 0.1 g) before it is mounted on the system. Then pure TaF$_5$ is produced by sublimating the crude material at 50°C using He as carrier gas, collecting the product in the TaF$_5$ precursor evaporator cooled with ice water. The system is kept at about 4 Torr with the He flow rate of 5 sccm during the whole sublimation procedure. After the sublimation process, the inlet and outlet valves of the as-received TaF$_5$ evaporator are always closed until the next purification and the valve on the by-pass loop is opened to let the He carrier gas go to the TaF$_5$ precursor evaporator assembly from the gas cylinder.

The weight of evaporator assembly is weighed again after the sublimation. The molar transport rate of TaF$_5$ can be calculated from the weight loss. Then the concentration of TaF$_5$ in the reactor can be calculated using the TaF$_5$ molar flow rate, the carrier gas flow rate from MFC, and the total pressure in the evaporator. Using the ideal gas law, we can get the partial pressure of TaF$_5$ leaving the evaporator. The observed partial pressure is only about 30% compared to the reported equilibrium vapor pressure of TaF$_5$ under the evaporating temperature. This indicates that the sublimation of TaF$_5$ is not fully equilibrated. We suspect
that a mass transport limitation may result from the small volume of the TaF$_5$ powder at the bottom of the evaporator.

- **Substrate Cleaning.** The substrates used in this study are Cu foils and round glass slides. The copper foil (Alfa Aesar, 99.999%, size = $12 \times 12 \times 0.025$ mm thickness) was cleaned by acetone. The glass slides (Ted Pella, D = 15 mm) were cleaned in the same way as those in Cu CVD which was described in section 3.1.2.

- **CVD Procedure.** After the pedestal is sealed into the system using a wing nut clamp with a Viton® O-ring, the system is pumped down to $10^{-2}$ Torr in order to remove the air and water vapor. Helium carrier gas then flows from the cylinder through the MFC on the TaF$_5$ gas line with a desired rate. The two evaporator by-pass loops are opened to let the He gas go through the TaF$_5$ gas line. Helium gas also flows into SiH$_4$ gas line by opening the by-pass valve, which is located on the line between the He gas cylinder and the SiH$_4$ MFC. The tubing after TaF$_5$ evaporator is heat-traced to $70 \pm 5^\circ$C and the oil bath for heating the TaF$_5$ evaporator is heated to $50^\circ$C. Simultaneously, the substrate is heated to $300^\circ$C using a cartridge heater.

After the desired temperature setting is obtained, the precursor evaporator is equilibrated by dipping in the oil bath for about 4 minutes. This ensures that the precursor is at the desired evaporating temperature and serves to prevent a lag in the precursor transport at the beginning of the experiments. TaF$_5$ precursor is delivered to the reactor after opening the valves of the evaporator and closing the by-pass valve.

The deposition experiment is started by flowing SiH$_4$/He mixture through the SiH$_4$ MFC with a desired flow rate after closing the by-pass valve for the He gas. After the desired
 deposition time, the SiH₄/He cylinder valve is closed, and then the valve on the cylinder regulator and the valve after the SiH₄ MFC. The flow of TaF₅ is stopped by closing the inlet and outlet valves. The TaF₅ evaporator by-pass loop valve is reopened for the He gas flow through. The system remains heating for 10 minutes to prevent condensing of TaF₅ before it is completely purged out the system. After the system is cooled down to the room temperature, the vacuum pump is shut down. The flow of He gas is stopped until the system pressure goes up to the atmospheric pressure, and then the pedestal is removed from the system. The substrate is taken off from the pedestal surface and weighed using the Cahn microbalance. The typical operating conditions of tantalum CVD are listed in Table 6-1.

3.3 Palladium CVD

In this section we describe the experimental apparatus and operating procedures for depositing Pd films either as seed layers for electroless copper deposition or as continuous films. We will first present the details about the CVD reactor and carrier gas flow system. We then discuss the operating procedure for Pd deposition, either using batch CVD activation, or using continuous CVD for Pd films.

3.3.1 Pd CVD Apparatus

This subsection describes the reactor system built to study Pd CVD using the horizontal APCVD reactor. Figure 3-5 gives a schematic view of the apparatus. The system consists of four main sections: the gas delivery section, the precursor evaporator, the APCVD reactor, and the vacuum pump. The delivery section sends mixed H₂/N₂ and N₂ gases from their individual cylinders to the system. The reducing gas H₂/N₂ is delivered directly into the reactor. The carrier gas N₂ flows through precursor evaporator, where it picks up a fixed amount of precursor, and then flows into the reactor through the heated tubing. In the reactor,
Pd is deposited primarily onto the substrates that are heated by a flat strip heater, while some Pd will also deposit on the reactor wall. The remaining gases either flow to the vacuum pump and then to the lab hood, or else directly to the hood. Further details are described below.

- **Gas Delivery System.** Ultra high purity N\textsubscript{2} gas is used as carrier gas. One mass flow controller (MKS Instruments, 1159-B, 100 sccm capacity) meters the flow of N\textsubscript{2} into a glass evaporator, where the precursor is loaded. A bypass line is engaged for N\textsubscript{2} flow when the CVD reaction is not in progress. A pre-blended mixture of 10% H\textsubscript{2} in N\textsubscript{2} is used as reducing gas. Another MFC (MKS Instruments, 1159-B, 50 sccm capacity) meters the flow of reducing gas into the reactor. The precursor mixture and reducing gas are kept separate until entering the reactor to prevent the premature deposition of Pd on the delivery tubing wall. The system pressure is measured using a capacitance manometer (Varian, Model 6543-25-045), which is connected to a digital readout (Varian DV1500).

The tubing in the flow system from the evaporator up to the reactor is heat-traced using a heating tape (VWR) to keep the temperature high enough (70 – 80°C) to prevent the Pd(hfac)\textsubscript{2} precursor from condensing and plugging the lines. The tubing is made of glass instead of stainless steel to avoid the premature decomposition of Pd(hfac)\textsubscript{2} on the metal surface. This change was made after we had some trouble using stainless steel tubing with the evaporator. Several variable voltage transformers are used to control the temperatures. Temperatures at four locations on the heat-traced line are measured using thermocouple wires, as indicated in Fig. 3-5. The thermocouple wires are connected to a type K thermocouple display unit (Cole-parmer, A-95001-00) using a plug type connector.
Fig. 3-5 Schematic of Cold Wall Pd CVD System
• **Precursor Evaporator.** The evaporator consists of two parts, both of which are made of glass. The bottom part, which holds the solid precursor, is a glass tube having 1” diameter and 9” length and a ground glass female connector. The top is a dome-shaped piece that connects to the reservoir by a male ground glass connector. Dow Corning® high vacuum grease is used to seal the connectors. The top connector has two arms. The inlet arm connects to a metal bellows valve using a rubber O-ring sealed Swagelok Ultra Torr fitting. The inlet arm extends ¼” glass tubing into the bottom reservoir. It ends about 1” above the surface of precursor. The outlet arm connects to a high vacuum glass valve (Chemglass, CG-527) using a rubber O-ring sealed Teflon hand-tight fitting. A bypass line across the evaporator is used to isolate the evaporator from the carrier gas. The evaporator is wrapped with a heating tape. The temperature of the evaporator is measured by a thermocouple wire taped on the outside of the reservoir bottom.

Preliminary evaporation experiments were performed to obtain a mass flow rate of Pd(hfac)$_2$ at 70°C evaporation temperature. The other experimental conditions were: volumetric flow rate of carrier gas = 80 sccm, and system operating pressure = 400 Torr. The measured evaporation rate of Pd(hfac)$_2$ under above conditions is about 0.31 mg/min, which corresponds to a partial pressure of 0.062 Torr for Pd(hfac)$_2$ at the inlet of the reactor.

• **APCVD Reactor.** Figure 3-6 shows a schematic assembly of the reactor. The reactor body is a Pyrex glass tube with 1” outside diameter and 12” length, which is mounted horizontally on two support stands. A stainless steel strip heater is used to support and heat the substrates.
Fig. 3-6 Schematic of Pd APCVD Reactor
Inlet Configuration. The inlet end of the reactor is connected to an end piece using a 1” Ultra-Torr union. The end piece is a 1×2” (diameter × length) stainless steel tube with one end sealed by a round stainless steel plate. A ¼” hole is drilled at the upper center of the plate, and a ¼” Ultra-Torr union adapter is welded to cover the hole. The delivery glass tubing from the evaporator passes through the union adapter and directly reaches into the reactor.

Gas Mixing Region. The end of the glass tubing in the reactor holds a ceramic-made reducing gas distributor through a ¼” hole drilled on its upper center. The reducing gas from a stainless steel tubing, which is welded on the inlet end tube, flows evenly through six 5/32” small holes, which are drilled on the edge of the upper half gas distributor. In such an arrangement, the reducing gas and precursor will mix only within the upper half region of the reactor.

Strip Heater. A 5/8 × ¼” (L × W) strip heater (30 W/in², Tempco Electronic Heater Corporation) is used to provide the thermal energy for the CVD Pd. Three half cylindrical-shaped ceramic blocks are evenly glued using a high thermally conductive alumina based adhesive (Duralco 132, Contronics Corp.) on the bottom surface of the heater. The ceramic cylinders sit on the reactor wall in order to reduce the heat conduction to the wall. The temperature of the heater surface is measured by a thermocouple wire glued using the same adhesive on the edge of the heater. Both the thermocouple wire and the heater power wire are connected to an electrical vacuum feedthrough (Kurt J. Lesker, Model #: TFT1KY2C158).

Outlet Configuration. The outlet end of the reactor body is connected to the feedthrough using a KF to compression adapter and a NW40 to NW16 reducer. The adapter is connected to the reducer using a rubber O-ring and a hand-tight quick clamp. The NW16 end
of the reducer is connected to the feed through. A ¼” stainless steel tubing as an exhaust line is welded on one side of the adapter.

- **Exhaust Section.** The unreacted components and by-products can be either directly discharged to the hood under atmospheric pressure, or pumped to the hood using a vacuum pump under low pressure. The following describes the vacuum exhaust configuration.

  After the remaining gases flow out of the reactor, first they meet a pressure gauge (Varian, Model 6543-25-045). The pressure gauge is connected vertically on a NW40 KF tee. The system pressure is adjusted by a Nupro needle valve right after the pressure gauge. After the needle valve, a Varian high vacuum block valve is connected to a sieve trap (MDC, Model KMST-100-2), which is designed to remove water vapor and unconsumed Pd(hfac)$_2$ from the exhaust gas before entering the vacuum pump (Alcatel, Model 2004A). A second block valve (HEY High Vacuum Products, Model BA-112) between the trap and pump connects the pump to the rest of the system and also prevents the back-diffusion of pump oil into the trap when the pump is shut down.

### 3.3.2 Operating Procedure

The substrates used in this study are square glass slides with size of 18 × 18 mm (Ted Pella). Seven substrates are used in each experiment. The cleaning procedure is the same as that in the Cu CVD, presented in the section 3.1.2. Some of the substrates are weighed using the Cahn microbalance, which has a resolution of 0.027 mg. The Pd CVD is then performed using either the batch activation process or the continuous CVD process.

- **Batch Pd Activation.** The batch activation step is used to deposit a very thin non-visible Pd seed layer for subsequent continuous CVD Pd or ELD Cu. The Pd activation
process is a batch CVD after the precursor and H$_2$ are delivered into the reactor. The following is the detailed description about the operating procedure.

After the substrates and strip heater are sealed inside the reactor shell, the system is pumped down to a hard vacuum and kept about 5 minutes in order to eliminate the air and water vapor inside the reactor system, including the precursor evaporator by opening the outlet valve of the evaporator. The vacuum pump is shut down and the valves on the exhaust line are closed. After the system is filled up to about 800 Torr with N$_2$ flowing through the evaporator by-pass line, the valve on the exhaust line which points directly to the hood is opened, and the system is kept under atmospheric pressure. Then the evaporator and the precursor delivery line are heat-traced to the desired temperature.

The evaporator is equilibrated by staying at the desired evaporation temperature for about 5 minutes. This ensures that the precursor is at the desired evaporating temperature and serves to prevent a lag in the precursor transport at the beginning of the experiment. The Pd(hfac)$_2$ precursor is transferred to the reactor by opening the inlet valve of the evaporator and closing its by-pass valve. After Pd(hfac)$_2$ is delivered into the reactor, it will re-condense on the upper surface of the reactor wall because the reactor is at room temperature. This is verified by the appearance of the small yellow particles on the inlet of the reactor wall. Hydrogen flows through the reactor during the precursor pulse period.

The reactor system is then isolated from the rest of the system by closing all the valves connected to it after a desired Pd(hfac)$_2$ pulse time. The batch Pd activation CVD is started by heating the substrates to a desired temperature which requires about 7 to 8 minutes. The substrates are held at the desired temperature for a specified additional period in order to study the effect of activation time on the following ELD of Cu or continuous CVD of Pd. The
system is cooled to room temperature with N\textsubscript{2} gas flowing through the system. At this point, either continuous Pd CVD can be carried out next, or the substrates can be removed from the reactor, weighed using the Cahn microbalance, and used for Cu ELD.

The ranges of operating conditions used for the batch Pd activation in these experiments are listed in Table 3-2.

Table 3-2 Operating Conditions for Batch Pd Activation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2} Flow Rate</td>
<td>80 sccm</td>
</tr>
<tr>
<td>H\textsubscript{2} Flow Rate</td>
<td>2.5 sccm</td>
</tr>
<tr>
<td>Evaporation Temperature</td>
<td>70°C</td>
</tr>
<tr>
<td>Pd(hfac)\textsubscript{2} Evaporation Time</td>
<td>0, 15, 30 s</td>
</tr>
<tr>
<td>Activation Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Heater Ramping Time</td>
<td>7 to 8 min</td>
</tr>
<tr>
<td>Batch Temperature</td>
<td>110, 150, 180, 210°C</td>
</tr>
<tr>
<td>Batch Time</td>
<td>0, 5, 7.5, 15, 30 min</td>
</tr>
</tbody>
</table>

• **Continuous Pd CVD.** After the substrates are sealed in the reactor, the reactor and the evaporator are pumped down to hard vacuum. Nitrogen with a desired volumetric rate flows from its cylinder through the evaporator by-pass line to the reactor. The system is adjusted to a desired pressure using the needle valve in the exhaust line. Substrates are pretreated at 150°C about 30 minutes. As the substrates are cooling, the evaporator is heated to the desired evaporation temperature, and the delivery tubing after the evaporator is heat-traced to about 5 to 10°C higher than the evaporator.
After heating the evaporator about 5 minutes under the evaporation temperature, the deposition experiment is started. The precursor is delivered to the reactor by opening the evaporator inlet valve and closing the by-pass valve, and the H₂/N₂ co-reactant is fed to the reactor through the H₂ MFC with a desired rate. After the desired deposition time, the flow of Pd(hfac)₂ is stopped by closing the inlet and outlet valves of the precursor evaporator, and the H₂/N₂ cylinder valve is also closed. The evaporator by-pass valve is reopened for the N₂ gas flowing through. The system remains heated for several minutes to prevent condensing of Pd(hfac)₂ before it is completely purged out of the system. After the system is cooled to room temperature, the vacuum pump is shut down. The flow of N₂ gas is stopped until the system pressure goes up to atmospheric pressure. The substrates are removed from the reactor by disassembling the strip heater from the system, and the substrates with visible Pd films are weighed using the Cahn microbalance.

The operating conditions for continuous Pd CVD are summarized in the Table 3-3.

**Table 3-3 Operating Conditions for Continuous Pd CVD without Activation**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ Flow Rate</td>
<td>80 sccm</td>
</tr>
<tr>
<td>H₂ Flow Rate</td>
<td>2.5 sccm</td>
</tr>
<tr>
<td>Substrate Preheating Temp</td>
<td>150°C</td>
</tr>
<tr>
<td>Preheating Time</td>
<td>30 min</td>
</tr>
<tr>
<td>Evaporator Temperature</td>
<td>60, 65, 70°C</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>65, 80, 95, and 110°C</td>
</tr>
<tr>
<td>System Pressure</td>
<td>200, 400, and 600 Torr</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>30 min</td>
</tr>
</tbody>
</table>
- **Pd CVD with Batch Pd Activation.** In a few experiments, the substrates are kept in the reactor after the batch Pd activation instead of being removed. This will be done to test the effects of Pd seed layers on the properties of Pd films continuously deposited by CVD. The system is re-pumped down to hard vacuum state, and then the continuous CVD process is performed as described above, after the substrates have cooled to room temperature.

### 3.4 Film Characterization

The characterization of thin film properties is needed to complement our kinetic efforts in film modeling, device designing and optimization. The accurate determination of deposited thin film parameters, such as surface structure, chemical composition, and crystal structure is the key to verify and improve experimental conditions. In this section, the techniques used to examine the quality of CVD deposited films are described. The film weight gain is measured by a microbalance. The equivalent film thickness is calculated from the weight change of the substrate after the deposition, by assuming that the film is uniform and has the same density as the bulk metal. Surface topography is characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). A 4-point resistivity probe is used to measure the resistance of blank films. X-ray photoelectron spectroscopy (XPS) is used to determine the film compositions.

- **Substrate Weight Measurement** A Cahn CN2000 microbalance is used to measure the weight of the substrate before and after an experiment. The resolution of microbalance is 0.027 mg. This resolution is the standard deviation of a sample weight which was measured by the microbalance 12 times.

- **Equivalent Film Thickness** The equivalent film thickness is used for calculating film resistivity. This thickness is calculated by dividing the substrate weight gain in mass per
unit area by the bulk metal density. This is a valid approximation as long as the obtained thin films are non-porous and deposited uniformly on the whole substrate surface. The film also needs to be pure, at least with very low concentration of impurity. The calculation formula is:

\[ t_{eq} = \frac{\Delta m}{\rho_{Bulk} \times A} \quad \text{(Eq. 3-1)} \]

where:  
\( t_{eq} \): equivalent thickness of the material in cm,
\( \Delta m \): weight change of substrate, in g;
\( \rho_{Bulk} \): bulk metal density, \( \text{Cu} = 8.96; \text{Ta} = 16.6; \text{Pd} = 12.02 \text{ g/cm}^3 \);
\( A \): substrate area in cm²;

- **Image by SEM** Scanning electron microscopy is a traditional technique for observing topography on the micro scale. SEM provides a high magnification image of a material surface and can have resolutions approaching a few nm. The SEM machine (Jeol 840A) is located in the department of Geology and Geophysics of LSU. Typical magnification and electron beam voltage are 10,000× and 20kV. Secondary electrons, which are emitted from the film surface within a depth about 10 nm because of electron beam’s bombardment, are collected by an Everhart-Thornley detector to be used to construct the image of CVD copper film’s surface. Several samples were viewed by SEM in the present study.

- **Roughness by AFM** Atomic force microscopy is a high-spatial-resolution instrument capable of real space electronic and spectroscopic imaging of surfaces and interfaces on a scale that extends to atomic dimensions. The facility (Digital Instrument, MMAFM-2) is located at the department of Chemistry of LSU, courtesy of Dr. McCarley.
The surface roughness of CVD copper film is obtained with a unit of nanometer root mean square (RMS) by this technique.

- **Film Composition by XPS.** X-ray photoelectron spectroscopy is the most broadly general surface analysis technique today, because of its surface sensitivity, combined with quantitative and chemical state analysis capabilities. The XPS machine (Kratos, AXIS 165) is located in the material characterization center of LSU. Depth profiling about Ta films on Cu foils and the composition of Pd seed layers on glass slides in this study were examined by XPS.

- **Resistivity by 4-Point Probe** Resistivity is the one of the most important properties for interconnect application, and it is also an important index to reflect the uniformity and purity of the deposited copper film. A 4-point probe (FPP) resistivity device is used to measure the resistivity of copper film. The instrument we use is a model FPP-100 by Veeco instrument Inc., the use of which is made accessible by Dr. Ajmera, in the processing and lithography lab, in the Department of Electrical and Computer Engineering of LSU.

  Figure 3-7 is a schematic of FFP configuration. The sheet resistance is measured by lowering the probe array to contact the central symmetric axis of the sample. By passing direct current travels through the sample between the outer probes and measuring the potential drop between the inner probes, the sheet resistance will be displayed on the front panel of the instrument. To ensure the correct measurement, three different positions of each sample are measured.

  The measured resistance needs to be calibrated by two factors, named sample geometric correction factor, $f_G$, and instrument calibration factor, $f_C$: 

73
Fig. 3-7 Schematic of four point probe

\[ R_s = R_m \times f_G \times f_C \]  \hspace{1cm} (Eq. 3-2)

where:  \( R_s \): sheet resistance, mΩ/sq;

\( R_m \): measured sheet resistance, mΩ/sq;

The sample geometric correction factor, \( f_G \), is to correct the substrate edge effects. The correction is generally related to the ratio of the size (diameter for circle or length for square) of wafer (D) divided by the probe spacing (S). The correction factor can be found from the FPP-100 operating manual (Veeco). For our Cu CVD experiment, the probe spacing (S) of FPP-100 is 1.27 mm, and the diameter of the substrate is 15 mm, so the ratio of D/S is about 12, which leads to a geometric factor, \( f_G \), equal to 0.94.

The instrument calibration factor for Cu CVD experiments, \( f_C \), is to correct the instrument disturbance, which is found by measuring the sheet resistance of a standard copper (Alfa Products, 99.999%) with an area of 2×2 cm². The calibration factor is obtained by dividing the bulk resistivity of copper by the copper foil’s sheet resistance and thickness:
\[ f_c = \frac{\rho_{Cu}(m\Omega\cdot cm)}{t_{foil}(cm) \times R_{m,foil}(m\Omega) \times f_{G,foil}} \]  
(Eq. 3-3)

where:  \( \rho_{Cu} \): resistivity of bulk copper, \( 1.67 \times 10^{-3} \) m\(\Omega\)-cm;

\( t_{foil} \): copper foil thickness, \( 2.5 \times 10^{-3} \) cm;

\( R_{m,foil} \): measured copper foil sheet resistance, m\(\Omega\)/sq;

\( f_{G,foil} \): geometric correction factor of copper foil, 0.96;

The measured copper foil sheet resistance is \( 1.51 \pm 0.07 \) m\(\Omega\)/sq, which leads the \( f_c \) of 0.461. The resistance of copper foil is measured before and after the each set of copper film resistance measurement.

Finally, the resistivity of a sheet is given:

\[ \rho = R_s \times t_{eq} \]  
(Eq. 3-4)

where:  \( \rho \): resistivity of material in \( \mu\Omega\)-cm;

\( t_{eq} \): equivalent thickness of the material in cm.
CHAPTER 4 RESULTS AND DISCUSSION ABOUT COPPER CVD

This chapter describes growth rates and film properties of copper CVD using Cu(hfac)$_2$ dissolved in isopropanol as the liquid precursor delivery method. Section 4.1 presents the baseline experimental results with partial pressures of 0.025, 1.6, and 80 Torr, respectively, for Cu(hfac)$_2$, isopropanol and hydrogen. The deposition temperature is 300°C and deposition time is 2 to 15 minutes. Section 4.2 focuses on the effects of Cu(hfac)$_2$, isopropanol and H$_2$ partial pressure on the growth rates (i.e., reaction order), and film properties.

4.1 Baseline Results

These experiments are the first systematic kinetic studies of copper CVD using Cu(hfac)$_2$ dissolved in isopropanol as the liquid precursor delivery method. This approach provides the advantages of easily controlling the precursor flow rate with precise partial pressure, while avoiding the requirement to handle the precursor at its high melting point. The baseline experimental results presented here establish a reference for the remaining experiments. Two sets of baseline experiments were performed during the periods of 07/31/01 to 08/24/01 and 12/06/01 to 01/09/02, in order to ascertain the reproducibility of experimental equipment and operating conditions. We found the film appearance, weight change, and resistivity are all similar for both sets of experiments. The combined results are presented here.

- **Operating Conditions.** The operating conditions of all the baseline experiments are summarized in Table 4-1.
Table 4-1 Operating Conditions for Baseline Copper CVD

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Time</td>
<td>2, 4, 7.5 and 15 minutes</td>
</tr>
<tr>
<td>H₂ Flow Rate</td>
<td>400 sccm</td>
</tr>
<tr>
<td>Cu(hfac)₂ Solution Flow Rate</td>
<td>0.02 ml/min</td>
</tr>
<tr>
<td>Cu(hfac)₂ Solution Concentration</td>
<td>0.1g/ml i-PrOH</td>
</tr>
<tr>
<td>Initial Pressure</td>
<td>79.3 ± 0.5 Torr</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>82.8 ± 0.7 Torr</td>
</tr>
<tr>
<td>Cu(hfac)₂ Partial Pressure</td>
<td>0.025 Torr</td>
</tr>
<tr>
<td>i-PrOH Partial Pressure</td>
<td>1.61 ± 0.01 Torr</td>
</tr>
<tr>
<td>H₂ Partial Pressure</td>
<td>81 ± 0.5 Torr</td>
</tr>
<tr>
<td>Wall Temperature</td>
<td>120°C</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>300°C</td>
</tr>
</tbody>
</table>

- **Detailed Observed Results.** Table 4-2 gives a summary of the detailed experimental results. The first column lists the deposition time. Column 2 gives the experiment number which is related to the experiment date and sequence number. Column 3 and 4 give the substrate weight gain and the associated film equivalent thickness. Column 5 lists the film resistivity that is calculated from the film sheet resistance and film equivalent thickness (see Eq.(3-4)). The last column is a simple description of film visual quality. A total of sixteen runs were carried out with the baseline conditions, and each deposition time was repeated 2 to 5 times. The experimental sequence was 4, 7.5, 15, 7.5 and 2 minutes, and the experiments were continued until the 95% confidence level of growth rate fell below ± 3 nm/min.
Table 4-2 Baseline Results of Cu CVD on Glass

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ·cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>07/26/01-1</td>
<td>0.381</td>
<td>0.2631</td>
<td>1.607 ± 0.131</td>
<td>uniform, golden</td>
</tr>
<tr>
<td></td>
<td>07/26/01-2</td>
<td>0.406</td>
<td>0.2804</td>
<td>1.578 ± 0.076</td>
<td>uniform, golden</td>
</tr>
<tr>
<td></td>
<td>08/23/01-2</td>
<td>0.420</td>
<td>0.2900</td>
<td>1.499 ± 0.084</td>
<td>uniform, golden</td>
</tr>
<tr>
<td></td>
<td>01/03/02</td>
<td>0.366</td>
<td>0.2527</td>
<td>1.515 ± 0.196</td>
<td>uniform, golden</td>
</tr>
<tr>
<td>7.5</td>
<td>07/23/01-1</td>
<td>0.227</td>
<td>0.1568</td>
<td>1.492 ± 0.077</td>
<td>uniform, red golden</td>
</tr>
<tr>
<td></td>
<td>08/24/01-1</td>
<td>0.226</td>
<td>0.1561</td>
<td>1.798 ± 0.067</td>
<td>uniform, golden</td>
</tr>
<tr>
<td></td>
<td>08/24/01-2</td>
<td>0.205</td>
<td>0.1416</td>
<td>1.588 ± 0.062</td>
<td>uniform, golden</td>
</tr>
<tr>
<td></td>
<td>01/04/02</td>
<td>0.193</td>
<td>0.1333</td>
<td>2.096 ± 0.081</td>
<td>uniform, golden</td>
</tr>
<tr>
<td></td>
<td>01/08/02</td>
<td>0.229</td>
<td>0.1581</td>
<td>1.764 ± 0.135</td>
<td>uniform, golden</td>
</tr>
<tr>
<td>4</td>
<td>07/24/01-1</td>
<td>0.100</td>
<td>0.0691</td>
<td>6.812 ± 0.395</td>
<td>uniform, dark golden</td>
</tr>
<tr>
<td></td>
<td>07/24/01-2</td>
<td>0.097</td>
<td>0.0670</td>
<td>2.433 ± 0.116</td>
<td>uniform, dark golden</td>
</tr>
<tr>
<td></td>
<td>12/06/01</td>
<td>0.112</td>
<td>0.0773</td>
<td>4.309 ± 0.474</td>
<td>uniform, dark golden</td>
</tr>
<tr>
<td></td>
<td>01/07/02</td>
<td>0.077</td>
<td>0.0532</td>
<td>5.115 ± 0.604</td>
<td>uniform, dark golden</td>
</tr>
<tr>
<td></td>
<td>01/09/02</td>
<td>0.098</td>
<td>0.0677</td>
<td>3.783 ± 1.097</td>
<td>uniform, dark golden</td>
</tr>
<tr>
<td>2</td>
<td>07/25/01-1</td>
<td>0.052</td>
<td>0.0359</td>
<td>26.38 ± 4.034</td>
<td>uniform, dark golden</td>
</tr>
<tr>
<td></td>
<td>07/25/01-2</td>
<td>0.046</td>
<td>0.0318</td>
<td>50.19 ± 11.25</td>
<td>uniform, dark golden</td>
</tr>
</tbody>
</table>
**Growth Rate.** The deposition times for the baseline experiments are 2, 4, 7.5 and 15 minutes. Figure 4-1 is a plot of mass loading (mg/cm²) vs. growth time. All the data are fitted to a straight line with the form of y=bx+a to estimate the steady state deposition rate and induction time. The slope with units of mg/(cm²\cdot min) represents the film growth rate and the x-axis intercept represents the induction time. From Fig. 4-1, we find all the data are distributed around the straight line, which suggests that the experiments are demonstrating a steady state growth rate.

Table 4-3 presents the steady state kinetic results. From the table, the growth rate is 0.0159 ± 0.0013 mg/(cm²\cdot min). It is widely accepted in the literature to use thickness per time instead of weight change per time for the growth rate. The conversion factor for converting the deposition rate is 1 nm/min = 1,116 mg/(cm²\cdot min). Thus the growth rate for the baseline conditions is 17.7 ± 1.5 nm/min. The induction time is 0.0 ± 0.8 min. The zero induction time indicates that a steady state growth rate has been established with no nucleation resistance. This is consistent with an earlier report that the alcohol co-reactant can significantly enhance the deposition on SiO₂ substrates (Chiang, 1993).

**Comparison with Previous Growth Rate Measurements.** This 17.7 ± 1.5 nm/min growth rate is about one-half of the growth rate observed by Boey et al (1999) in our lab. It is significant that although Boey’s experiments were performed using a Cu(hfac)₂ partial pressure of 2.5 Torr (i.e., 100-fold higher than in the present study) and a two times higher isopropanol partial pressure with all the other conditions almost the same as the present study, the growth rate of his study is only two times higher.
A similar growth rate was also reported by Cho (1992) using higher Cu(hfac)$_2$ partial pressure. This suggests that the reaction rate has become saturated with respect to the concentration of precursor. We will discuss more about this in the next section. Furthermore, it also tells us that the presence of isopropanol is able to establish similar growth rates using much lower values of Cu(hfac)$_2$ partial pressure.

Fig. 4-1 Steady State Growth Rate using Baseline Deposition Conditions

<table>
<thead>
<tr>
<th>Slope [mg/(cm$^2$-min)]</th>
<th>Growth Rate [nm/min]</th>
<th>Y-intercept [mg/cm$^2$]</th>
<th>Induction Time [min]</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0159 ± 0.0013</td>
<td>17.7 ± 1.5</td>
<td>-0.0004 ± 0.0121</td>
<td>0.0 ± 0.8</td>
<td>0.9785</td>
</tr>
</tbody>
</table>
The enhancement of growth rate is clear due to isopropanol. Our rate is higher than Borgharkar (1999a), who reported a 9.2 nm/min copper growth rate. The reaction conditions of Borgharkar (1999a) were Cu(hfac)$_2$ partial pressure of 1.8 Torr, H$_2$ partial pressure of 40 Torr, 300°C substrate temperature and without isopropanol.

The growth rate in this study about six times higher than the value of 3 nm/min reported by Awaya and Arita (1992) at a partial pressure of 0.9 Torr Cu(hfac)$_2$ reduced by 14 Torr H$_2$. The deposition temperature was 350°C.

This growth rate is about 50 times greater than that reported by Chen et al (1995) using a partial pressure of 0.0028 Torr for Cu(hfac)$_2$ with Ar/H$_2$ at 295°C deposition temperature. In this comparison, isopropanol increases the growth rate 50 times with only a 10 times increase in Cu(hfac)$_2$ partial pressure.

- **Visual Appearance.** All of the deposited films were uniform and had copper color. The 7.5 and 15 minute samples had a golden copper color, while the 2 and 4 minute films were dark gold with some degree of transparency. The backside of all the samples were reflective and shiny. All the samples have four small half circle areas with no deposition due to shadowing by the screws used to mount the substrate on the pedestal surface.

- **Film Morphology by SEM.** The plan view SEM secondary electron images of the films deposited for 4, 7.5 and 15 minute are shown in Fig. 4-2. Fig. 4-2 (a) is a SEM image of 4 minute film, which has equivalent thickness of 57 nm. The image is visually blurred. The film consists of isolated clusters which have not grown large enough to contact each other. Since the film is very thin, the SEM image shows some difficulty to distinguish the boundary between copper cluster and the void, which is uncovered glass substrate surface. We
attempted to analyze the image using software available in the SEM laboratory (NIH Image). However, the software could not distinguish the cluster boundaries clearly, and could not provide a quantitative grain size distribution.

Fig. 4-2 (b) shows the film produced after 7.5 minutes deposition. The clusters have grown larger, and they now cover almost all the substrate surface. The clusters have an average diameter of 0.23 ± 0.10 µm, which is determined using NIH Image. This cluster radius (i.e. 115 nm) is comparable to the equivalent thickness of the film (i.e. 108 nm). The SEM image at 7.5 minute shows that the film is uniform and the clusters have a narrow size distribution.

Fig. 4-2 (c) shows the film produced after 15 minutes. The copper cluster size is much larger than the 7.5 minute film, and the grain size (diameter) is 0.45 ± 0.35 µm calculated by NIH Image. The average cluster growth rate is comparable to the overall film growth rate (i.e., the equivalent thickness of this film is 272 nm). The big uncertainty of grain size means the clusters have wide size distribution. There also appears to be some “stacking” of clusters on top of others, thus leading to some voids between clusters.

- **Surface Roughness by AFM.** Surface roughness is analyzed using atomic force microscopy (AFM), and reported as root mean square (RMS) values. The normalized roughness is RMS roughness divided by film thickness. Fig. 4-3 shows the surface morphologies of 4, 7.5 and 15 minute samples using baseline conditions. According to the AFM analysis over the 10 × 10 µm² area shown in each figure, the RMS roughness values are 10, 22, and 41 nm for 4, 7.5 and 15 minutes film with associated thicknesses of 53, 133 and 253, respectively. From Fig. 4-3, we find that the shorter the deposition time, the smoother the film. This is represented by the color contrast in the micrographs. The color difference of the
Fig. 4-2 SEM Images of Copper Films with Deposition Time: (a) 4 (B) 7.5 (c) 15 min
Fig. 4-3 AFM Images of Copper Films with Deposition Time: (a) 4 (b) 7.5 (c) 15 min
15 minute micrograph is sharper than the 7.5 minute film, which is sharper than 4 minute film.

Fig. 4-4 represents the relationship between RMS and film equivalent thickness. The RMS varies linearly with increasing deposition time. The normalized roughness of all the three films is about 16%, which is similar to the normalized roughness of copper films deposited from Cu(hfac)(TMVS) using water vapor as co-reactant (Yang, 2002).

![Fig. 4-4 RMS Roughness vs. Film Thickness](image)

- Resistivity. Fig. 4-5 is a plot of resistivity as a function of equivalent thickness for the baseline samples. From the figure, we find that the resistivity approaches the bulk value of copper for film thicknesses greater than 0.1 µm. For thinner films, the resistivity is 2 to 3 times higher than the bulk value, and the standard deviations are large. This behavior will be seen again in all the operating conditions in section 4.2, (i.e., it will not vary significantly when either Cu(hfac)₂ or isopropanol partial pressure is changed). This critical thickness value
is lower than the value of 0.3 μm reported by Lecohier (1992) and the value of 0.5 μm reported by Kim et al (1992). Both of these studies did not add isopropanol as co-reactant. The lower critical thickness value in this study indicates that isopropanol improves the copper nucleation on the glass substrate.

This resistivity behavior of the films is consistent with their microstructure evolution. For the films described in Fig. 4-2 (a) (4 minute deposition), the resistivity values lie between 3 to 6 μΩ-cm, which is 2 to 4 times higher than the bulk Cu resistivity of 1.67 μΩ-cm. The presence of the uncovered voids between clusters produces this high resistivity with large deviation. When the film thickness achieves more than 0.1 μm, the substrate is almost totally covered by copper (Fig. 4-2 (b)). So the resistivity reaches the bulk value.

Fig. 4-5 Resistivity vs. Equivalent Thickness for Baseline Films
4.2 Reaction Order Experiments

This section presents the results from reaction order experiments. The effects of partial pressures of Cu(hfac)$_2$, isopropanol and H$_2$ on the steady state copper growth rate are studied systematically.

4.2.1 Cu(hfac)$_2$ Effect

- **Operating Conditions.** In order to determine the reaction order of copper CVD with respect to Cu(hfac)$_2$, the partial pressure of Cu(hfac)$_2$ is varied by changing the concentration of Cu(hfac)$_2$ liquid precursor, while keeping other parameters, like isopropanol and H$_2$ partial pressures, deposition temperature, and gas volumetric flow rate unchanged. The detailed operating conditions are summarized in Table 4-4. The baseline Cu(hfac)$_2$ partial pressure is 0.025 Torr. The partial pressure of Cu(hfac)$_2$ is varied from 0.0063 to 0.05 Torr. The precursor solution flow rate is 0.02 ml/min. The partial pressure of i-PrOH is about 1.6 Torr. The H$_2$ pressure is around 80 Torr with flow rate of 400 sccm. The deposition temperature is 300°C.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)$_2$ Partial Pressure (Torr)</td>
<td>0.0063</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Flow Rate (ml/min)</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Concentration (g/ml·i-PrOH)</td>
<td>0.025</td>
</tr>
<tr>
<td>Initial Pressure (Torr)</td>
<td>79.8 ± 0.4</td>
</tr>
<tr>
<td>Operating Pressure (Torr)</td>
<td>82.6 ± 0.6</td>
</tr>
<tr>
<td>H$_2$ Flow Rate (sccm)</td>
<td>400</td>
</tr>
<tr>
<td>i-PrOH Partial Pressure (Torr)</td>
<td>1.61 ± 0.01</td>
</tr>
<tr>
<td>H$_2$ Partial Pressure (Torr)</td>
<td>81.0 ± 0.5</td>
</tr>
<tr>
<td>Wall Temperature (°C)</td>
<td>120</td>
</tr>
<tr>
<td>Substrate Temperature (°C)</td>
<td>300</td>
</tr>
</tbody>
</table>
• **Observed Results.** The detailed experimental results using 0.025 Torr Cu(hfac)$_2$ as the baseline case were shown in Table 4-2. Table 4-5 summarizes the new experimental results with 0.0063, 0.0128, and 0.05 Torr Cu(hfac)$_2$ partial pressure.

### Table 4-5 Experimental Results with Different Cu(hfac)$_2$ Partial Pressure

**$P_{\text{Cu(hfac)}_2}=0.0063$ Torr**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ-cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>11/06/02</td>
<td>0.105</td>
<td>0.0725</td>
<td>3.220 ± 0.330</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>11/13/02</td>
<td>0.121</td>
<td>0.0836</td>
<td>2.920 ± 0.199</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>7.5</td>
<td>11/05/02</td>
<td>0.060</td>
<td>0.0414</td>
<td>–</td>
<td>uniform, blue shiny</td>
</tr>
<tr>
<td></td>
<td>11/14/02</td>
<td>0.056</td>
<td>0.0387</td>
<td>–</td>
<td>uniform, blue shiny</td>
</tr>
<tr>
<td>4</td>
<td>11/04/02</td>
<td>0.029</td>
<td>0.0200</td>
<td>–</td>
<td>uniform, blue shiny</td>
</tr>
<tr>
<td></td>
<td>11/12/02</td>
<td>0.031</td>
<td>0.0214</td>
<td>–</td>
<td>uniform, blue shiny</td>
</tr>
</tbody>
</table>

**$P_{\text{Cu(hfac)}_2}=0.0128$ Torr**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ-cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>12/06/02</td>
<td>0.252</td>
<td>0.1740</td>
<td>1.146 ± 0.079</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>12/11/02</td>
<td>0.251</td>
<td>0.1733</td>
<td>1.294 ± 0.031</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>7.5</td>
<td>12/03/02</td>
<td>0.120</td>
<td>0.0829</td>
<td>1.513 ± 0.068</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>12/13/02</td>
<td>0.132</td>
<td>0.0912</td>
<td>1.203 ± 0.059</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>4</td>
<td>12/09/02</td>
<td>0.061</td>
<td>0.0421</td>
<td>4.988 ± 0.217</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>12/12/02</td>
<td>0.072</td>
<td>0.0497</td>
<td>3.447 ± 0.377</td>
<td>uniform, shiny</td>
</tr>
</tbody>
</table>

**$P_{\text{Cu(hfac)}_2}=0.05$ Torr**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ-cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>02/06/02</td>
<td>0.437</td>
<td>0.3018</td>
<td>1.388 ± 0.077</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>02/14/02</td>
<td>0.389</td>
<td>0.2686</td>
<td>1.513 ± 0.081</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>7.5</td>
<td>02/04/02</td>
<td>0.204</td>
<td>0.1409</td>
<td>1.990 ± 0.110</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>02/13/02</td>
<td>0.194</td>
<td>0.1340</td>
<td>1.658 ± 0.147</td>
<td>uniform, haze</td>
</tr>
<tr>
<td>4</td>
<td>02/01/02</td>
<td>0.115</td>
<td>0.0794</td>
<td>1.781 ± 0.047</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>02/08/02</td>
<td>0.081</td>
<td>0.0559</td>
<td>1.849 ± 0.089</td>
<td>uniform, shiny</td>
</tr>
</tbody>
</table>

Note: “–” indicates the film resistance is over the 4 point probe measurement range.
• **Growth Rate.** The deposition times for these experiments are 4, 7.5 and 15 minutes, except for the 0.025 Torr Cu(hfac)$_2$ group, which included 2 minutes deposition. Fig. 4-6 is a plot of mass loading (mg/cm$^2$) vs. growth times using data from different groups with individual Cu(hfac)$_2$ partial pressures. The data are fitted to straight lines to determine the steady state growth rates using the slopes and to find the induction times using the intercepts. The regression results are tabulated in Table 4-6. The absolute growth rates for 0.0063, 0.0128, 0.025 and 0.05 Torr Cu(hfac)$_2$ pressures are in the ratio of 0.28 : 0.63 : 1 : 1.04.

![Fig. 4-6 Mass Loading vs. Deposition Time under Different Cu(hfac)$_2$ Partial Pressure](image)

Fig. 4-6 Mass Loading vs. Deposition Time under Different Cu(hfac)$_2$ Partial Pressure

• **Reaction Order.** Described in Chapter 5.

• **Visual Appearance.** The films look similar in all cases. Generally, the 7.5 and 15 minutes samples have golden copper color, while the 2 and 4 minutes samples are dark golden. The backside of all the films are shiny and show a reflective copper color.
Table 4-6 Steady State Kinetic Results with Different Cu(hfac)$_2$ Partial Pressure

<table>
<thead>
<tr>
<th>Cu(hfac)$_2$ Partial Pressure (Torr)</th>
<th>Slope [mg/(cm$^2$-min)]</th>
<th>Growth Rate [nm/min]</th>
<th>Y-intercept [mg/cm$^2$]</th>
<th>Induction Time [min]</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0063</td>
<td>0.0045 ± 0.0009</td>
<td>5.0 ± 0.9</td>
<td>0.0004 ± 0.0087</td>
<td>-0.1 ± 1.9</td>
<td>0.9806</td>
</tr>
<tr>
<td>0.0128</td>
<td>0.0100 ± 0.0009</td>
<td>11.2 ± 0.9</td>
<td>-0.0003 ± 0.0085</td>
<td>0.0 ± 0.9</td>
<td>0.9963</td>
</tr>
<tr>
<td>0.025</td>
<td>0.0159 ± 0.0013</td>
<td>17.7 ± 1.5</td>
<td>-0.0004 ± 0.0121</td>
<td>0.0 ± 0.8</td>
<td>0.9785</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0171 ± 0.0031</td>
<td>19.0 ± 3.5</td>
<td>-0.0096 ± 0.0309</td>
<td>0.6 ± 1.8</td>
<td>0.9831</td>
</tr>
</tbody>
</table>

- Resistivity. Fig. 4-7 is a plot of resistivity vs. equivalent thickness of the samples with different Cu(hfac)$_2$ partial pressures. From the figure, we find that the resistivities are similar if the thicknesses of films are close, and they are independent of the Cu(hfac)$_2$ partial pressure. This indicates that the Cu(hfac)$_2$ partial pressure has no effects on film properties. We also find the resistivity approaches to the bulk copper value for film thickness greater than 0.1 µm (the same phenomena as in Fig. 4-5). The films with higher resistivity usually have higher deviation value.

![Resistivity vs. Equivalent Thickness for Cu(hfac)$_2$ Reaction Order Experiments](image-url)
4.2.2 Isopropanol Effect

This section describes the reaction order of isopropanol. The partial pressure of isopropanol is varied from 0.8 to 3.2 Torr. The Cu(hfac)$_2$ partial pressure is 0.025 Torr, and the H$_2$ partial pressure is 80 Torr with a flow rate of 400 sccm. The deposition temperature is the same as the baseline of 300°C. Three groups of experiments were carried out with isopropanol partial pressures of 0.8, 1.6 and 3.2 Torr. The following sub-sections present the detailed results.

- Operating Conditions. The detailed operating conditions are shown in Table 4-7. The baseline isopropanol partial pressure is 1.6 Torr. The partial pressure of isopropanol is varied by changing the precursor solution flow rate. The partial pressure of Cu(hfac)$_2$ is kept the same as the baseline pressure by changing the concentration of precursor solution in the opposite direction, (i.e., doubling the solution flow rate while halving the solution concentration, vice versa).

Table 4-7 Operating Conditions for isopropanol Reaction Order Experiments

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-PrOH Partial Pressure (Torr)</td>
<td>0.81 ± 0.01</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Flow Rate (ml/min)</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Concentration (g/ml-i-PrOH)</td>
<td>0.2</td>
</tr>
<tr>
<td>Initial Pressure (Torr)</td>
<td>79.6 ± 0.5</td>
</tr>
<tr>
<td>Operating Pressure (Torr)</td>
<td>82.2 ± 1.0</td>
</tr>
<tr>
<td>H$_2$ Flow Rate (sccm)</td>
<td>400</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Partial Pressure (Torr)</td>
<td>0.025</td>
</tr>
<tr>
<td>H$_2$ Partial Pressure (Torr)</td>
<td>81.3 ± 1.0</td>
</tr>
<tr>
<td>Wall Temperature (°C)</td>
<td>120</td>
</tr>
<tr>
<td>Substrate Temperature (°C)</td>
<td>300</td>
</tr>
</tbody>
</table>
• **Observed Results.** The detailed experimental results using 1.6 Torr isopropanol as the base case were shown in Table 4-2. Table 4-8 summarizes the additional results using 0.8 and 3.2 Torr isopropanol partial pressures.

Table 4-8 Summary of Experimental Results with different i-PrOH Partial Pressure

<table>
<thead>
<tr>
<th>$P_{i-PrOH}$=0.8 Torr</th>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ-cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>01/24/02</td>
<td>0.404</td>
<td>0.2790</td>
<td>1.540 ± 0.134</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>01/23/02</td>
<td>0.191</td>
<td>0.1319</td>
<td>1.389 ± 0.069</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td></td>
<td>01/29/02</td>
<td>0.189</td>
<td>0.1305</td>
<td>1.955 ± 0.112</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>01/22/02</td>
<td>0.093</td>
<td>0.0642</td>
<td>1.827 ± 0.094</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td></td>
<td>01/28/02</td>
<td>0.100</td>
<td>0.0691</td>
<td>9.057 ± 0.771</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>01/25/02</td>
<td>0.054</td>
<td>0.0373</td>
<td>2.553 ± 0.323</td>
<td>uniform, shiny</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$P_{i-PrOH}$=3.2 Torr</th>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ-cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>03/01/02</td>
<td>0.394</td>
<td>0.2721</td>
<td>1.415 ± 0.082</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>03/04/02</td>
<td>0.205</td>
<td>0.1416</td>
<td>3.210 ± 0.195</td>
<td>small hole @ center</td>
</tr>
<tr>
<td></td>
<td></td>
<td>03/07/02</td>
<td>0.202</td>
<td>0.1395</td>
<td>3.014 ± 0.114</td>
<td>some spots</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>02/27/02</td>
<td>0.089</td>
<td>0.0615</td>
<td>4.128 ± 0.262</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td></td>
<td>03/05/02</td>
<td>0.101</td>
<td>0.0697</td>
<td>3.052 ± 0.092</td>
<td>uniform, cloudy shade</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>03/06/02</td>
<td>0.078</td>
<td>0.0338</td>
<td>-</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td></td>
<td>03/08/02</td>
<td>0.049</td>
<td>0.0539</td>
<td>-</td>
<td>uniform, blue</td>
</tr>
</tbody>
</table>

**Note:** “–” indicates the film resistance is over the 4 point probe measurement range.
Fig. 4-8 Mass Loading vs. Deposition Time under Different isopropanol Pressures

- **Growth Rate.** The deposition times for these experiments are 2, 4, 7.5 and 15 minutes. Fig. 4-8 is a plot of mass loading (mg/cm²) vs. growth time using the data from experiments with different isopropanol partial pressure. The data are regressed linearly to find the steady state growth rates via the slopes and to determine the induction time through intercepts. The fitting results are tabulated in Table 4-9.

### Table 4-9 Steady State Kinetic Results with Different i-PrOH Pressures

<table>
<thead>
<tr>
<th>Isopropanol Partial Pressure (Torr)</th>
<th>Slope [mg/(cm²-min)]</th>
<th>Growth Rate [nm/min]</th>
<th>Y-intercept [mg/cm²]</th>
<th>Induction Time [min]</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.0163 ± 0.0011</td>
<td>18.1 ± 1.2</td>
<td>-0.0061 ± 0.0088</td>
<td>0.4 ± 0.5</td>
<td>0.9976</td>
</tr>
<tr>
<td>1.6</td>
<td>0.0159 ± 0.0013</td>
<td>17.7 ± 1.5</td>
<td>-0.0004 ± 0.0121</td>
<td>0.0 ± 0.8</td>
<td>0.9785</td>
</tr>
<tr>
<td>3.2</td>
<td>0.0161 ± 0.0014</td>
<td>18.0 ± 1.5</td>
<td>-0.0041 ± 0.0109</td>
<td>0.3 ± 0.7</td>
<td>0.9962</td>
</tr>
</tbody>
</table>

- **Reaction Order.** Described in Chapter 5.
- **Visual Appearance.** The films look similar in all cases. Generally, the 7.5 and 15 minutes samples have golden copper color, while the 2 and 4 minutes samples are dark golden. The backside of all the films are shiny and show a reflective copper color.

- **Resistivity.** Fig. 4-9 is a plot of resistivity and equivalent thickness of the samples with different isopropanol partial pressures. From the figure, we find that the values of resistivities of samples with different partial pressures of isopropanol are similar if their thicknesses are close. There is a possible exception of 7.5 minute samples with 1.6 Torr isopropanol partial pressure, whose resistivities are higher than those samples with different isopropanol pressures. Again, the film thickness needs to be greater than 0.1 µm for the film resistivity to approach the bulk copper resistivity value of 1.67 µΩ-cm. Based upon these observations, the isopropanol partial pressure appears to have no significant effect on the properties of deposited copper films.

![Fig. 4-9 Resistivity vs. Equivalent Thickness for isopropanol Order Experiments](image)

Fig. 4-9 Resistivity vs. Equivalent Thickness for isopropanol Order Experiments
4.2.3 H₂ Effect

- **Operating Conditions.** The effect of H₂ on copper CVD is studied by varying the H₂ partial pressure while keeping other parameters like partial pressures of Cu(hfac)$_2$ and isopropanol, deposition temperature, and volumetric flow rate unchanged. The system pressure is controlled by adjusting the needle valve before the vacuum pump. At the same time, the solution delivery rate is adjusted to maintain the baseline values for the partial pressures of Cu(hfac)$_2$ and isopropanol.

The operating conditions are summarized in Table 4-10. The baseline partial pressure of H₂ is 80 Torr. The range of H₂ pressure is over 40 to 160 Torr with flow rate of 400 sccm. The partial pressure of Cu(hfac)$_2$ is about 0.025 Torr, and isopropanol is about 1.6 Torr. The deposition temperature is 300°C.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Partial Pressure (Torr)</td>
<td>42.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>81.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>161.5 ± 1.3</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Flow Rate (ml/min)</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Concentration (g/ml·i-PrOH)</td>
<td>0.1</td>
</tr>
<tr>
<td>Initial Pressure (Torr)</td>
<td>39.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>79.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>159.8 ± 0.2</td>
</tr>
<tr>
<td>Operating Pressure (Torr)</td>
<td>44.0 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>82.8 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>163.1 ± 1.4</td>
</tr>
<tr>
<td>H₂ Flow Rate (sccm)</td>
<td>400</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ Partial Pressure (Torr)</td>
<td>0.025</td>
</tr>
<tr>
<td>i-PrOH Partial Pressure (Torr)</td>
<td>1.61 ± 0.01</td>
</tr>
<tr>
<td>Wall Temperature (°C)</td>
<td>120</td>
</tr>
<tr>
<td>Substrate Temperature (°C)</td>
<td>300</td>
</tr>
</tbody>
</table>
• **Observed Results.** The detailed experimental results for baseline H$_2$ partial pressure were shown in Table 4-2. Table 4-11 presents the results with 40 Torr and 160 Torr H$_2$ partial pressures.

Table 4-11 Summary of Experimental Results with different H$_2$ Partial Pressure

$P_{H2} = 40$ Torr

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ-cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>10/02/01</td>
<td>0.340</td>
<td>0.2348</td>
<td>1.687 ± 0.099</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>10/04/01</td>
<td>0.333</td>
<td>0.2299</td>
<td>1.722 ± 0.055</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>7.5</td>
<td>09/27/01</td>
<td>0.169</td>
<td>0.1167</td>
<td>1.649 ± 0.040</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>10/05/01</td>
<td>0.167</td>
<td>0.1153</td>
<td>1.882 ± 0.075</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>4</td>
<td>09/28/01</td>
<td>0.044</td>
<td>0.0304</td>
<td>1.913 ± 0.068</td>
<td>uniform, shiny</td>
</tr>
</tbody>
</table>

$P_{H2} = 160$ Torr

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ-cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>03/13/02</td>
<td>0.254</td>
<td>0.1754</td>
<td>0.985 ± 0.038</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>03/14/02</td>
<td>0.275</td>
<td>0.1899</td>
<td>0.965 ± 0.055</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>7.5</td>
<td>03/12/02</td>
<td>0.162</td>
<td>0.1119</td>
<td>1.123 ± 0.119</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>03/15/02</td>
<td>0.155</td>
<td>0.1070</td>
<td>1.597 ± 0.182</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>12/10/01</td>
<td>0.186</td>
<td>0.1284</td>
<td>1.048 ± 0.036</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>4</td>
<td>12/07/01</td>
<td>0.096</td>
<td>0.0663</td>
<td>1.625 ± 0.188</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>12/12/01</td>
<td>0.104</td>
<td>0.0718</td>
<td>1.182 ± 0.020</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td></td>
<td>03/11/02</td>
<td>0.083</td>
<td>0.0573</td>
<td>8.080 ± 0.230</td>
<td>uniform, shiny</td>
</tr>
<tr>
<td>2</td>
<td>12/11/01</td>
<td>0.073</td>
<td>0.0504</td>
<td>3.626 ± 0.153</td>
<td>thin edge, shiny</td>
</tr>
</tbody>
</table>
• **Growth Rates.** The experiments are performed using deposition times of 2, 4, 7.5 and 15 minutes for each set except for 40 Torr H\textsubscript{2}, where no 2 minute experiment was performed. Fig. 4-10 is a plot of mass loading (mg/cm\textsuperscript{2}) vs. growth time using data with respect to different H\textsubscript{2} partial pressure. The data of each set of experiments are fitted to straight lines to determine the steady state growth rates from the associated slopes and to obtain the induction time from intercepts. The fitting results are tabulated in Table 4-12.

![Graph showing mass loading vs. deposition time under different H\textsubscript{2} partial pressure](image)

**Fig. 4-10 Mass Loading vs. Deposition Time under Different H\textsubscript{2} Partial Pressure**

An exception is noted for the 160 Torr experiments. From Table 4-11, we can find that the weight gain for 15 minutes is too low compared to 40 and 80 Torr data (see Table 4-2). The 2 minute experiment of 160 Torr H\textsubscript{2} was performed only one time, and it was higher than both 40 and 80 Torr weight changes. Therefore, we analyzed the 160 Torr results by using the 4 and 7.5 minute experiments. Because only two times were used, we also constrain the straight line fit to pass through the origin.
Table 4-12 Steady State Kinetic Results with Different H\textsubscript{2} Partial Pressures

<table>
<thead>
<tr>
<th>H\textsubscript{2} Partial Pressure (Torr)</th>
<th>Slope [mg/(cm\textsuperscript{2}⋅min)]</th>
<th>Growth Rate [nm/min]</th>
<th>Y-intercept [mg/cm\textsuperscript{2}]</th>
<th>Induction Time [min]</th>
<th>R\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.0133 ± 0.0012</td>
<td>14.9 ± 1.4</td>
<td>-0.0100 ± 0.0653</td>
<td>0.8 ± 5.0</td>
<td>0.9402</td>
</tr>
<tr>
<td>80</td>
<td>0.0159 ± 0.0013</td>
<td>17.8 ± 1.5</td>
<td>-0.0004 ± 0.0121</td>
<td>0.0 ± 0.8</td>
<td>0.9785</td>
</tr>
<tr>
<td>160</td>
<td>0.0135 ± 0.0013</td>
<td>15.0 ± 1.5</td>
<td>0.0000 ± 0.0000</td>
<td>0.0 ± 0.0</td>
<td>0.9082</td>
</tr>
</tbody>
</table>

- **Reaction Order.** Figure 4-11 is a plot of growth rates against H\textsubscript{2} partial pressures. The growth rate increases about 15% from 40 Torr to 80 Torr, then decreases about the same percent from 80 Torr to 160 Torr. Comparing 15% growth rate change with four-fold change of H\textsubscript{2} partial pressures between 40 Torr to 160 Torr, we conclude that the H\textsubscript{2} partial pressure has no effects on the copper growth rate between this pressure range. Thus the reaction order of H\textsubscript{2} is zero.

![Fig. 4-11 Influence of H\textsubscript{2} Partial Pressure on Growth Rate](image_url)
This observation is consistent with the results provided by Thiruvenkatachari (2000) in our lab, in which the H\textsubscript{2} reaction order experiments were carried out using various H\textsubscript{2} partial pressure from 40 Torr to 160 Torr and keeping Cu(hfac)\textsubscript{2} partial pressure at 1.6 Torr and isopropanol partial pressure at 8.0 Torr. He observed that the growth rate increased only about 20\% with increasing H\textsubscript{2} partial pressure from 40 Torr to 80 Torr, and the same percent of decrease with increasing H\textsubscript{2} from 80 Torr to 160 Torr.

- **Visual Appearance.** The films look similar in all cases. Generally, the 7.5 and 15 minutes samples have golden copper color, while the 2 and 4 minutes samples are dark golden. The backside of all the films are shiny and show a reflective copper color.

- **Resistivity.** Fig. 4-12 is a plot of resistivity and equivalent thickness of the samples with different H\textsubscript{2} partial pressures. From the figure, we find that the values of resistivity with 160 Torr H\textsubscript{2} partial pressure are slightly less than the bulk copper resistivity value, and they are also a bit lower than those in the other two groups. All the samples were measured by the same 4-point probe resistivity device, so the systematic error can be ignored. High H\textsubscript{2} partial pressure might help to desorb the precursor ligand quickly to prevent them decomposing to impurities, like carbon and oxygen, which are one of the most important reasons for the higher resistivity of deposited films from metal-organic CVD.

### 4.2.4 Baseline Results Using N\textsubscript{2} as Carrier Gas

In the above sections of this chapter, Cu CVD experiments are performed by using H\textsubscript{2} as carrier gas. Uniform copper films with bulk copper resistivity values can be deposited on glass substrate using this method. In this section, we will use N\textsubscript{2} as carrier gas to see if uniform Cu film with bulk copper resistivity can be obtained by using Cu(hfac)\textsubscript{2} dissolved in isopropanol as the liquid precursor.
Fig. 4-12 Resistivity vs. Equivalent Thickness for H\textsubscript{2} Reaction Order Experiments

- **Operating Conditions.** The operating conditions of all the experiments using N\textsubscript{2} as carrier gas are summarized in Table 4-13.

Table 4-13 Operating Conditions for Copper CVD using N\textsubscript{2} as Carrier Gas

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Time</td>
<td>4, 7.5 and 15 minutes</td>
</tr>
<tr>
<td>N\textsubscript{2} Flow Rate</td>
<td>400 sccm</td>
</tr>
<tr>
<td>Cu(hfac)\textsubscript{2} Solution Flow Rate</td>
<td>0.02 ml/min</td>
</tr>
<tr>
<td>Cu(hfac)\textsubscript{2} Solution Concentration</td>
<td>0.1g/ml i-PrOH</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>79.9 ± 0.6 Torr</td>
</tr>
<tr>
<td>Cu(hfac)\textsubscript{2} Partial Pressure</td>
<td>0.029 Torr</td>
</tr>
<tr>
<td>i-PrOH Partial Pressure</td>
<td>1.85 ± 0.61 Torr</td>
</tr>
<tr>
<td>N\textsubscript{2} Partial Pressure</td>
<td>78.1 ± 0.6 Torr</td>
</tr>
<tr>
<td>Wall Temperature</td>
<td>120°C</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>300°C</td>
</tr>
</tbody>
</table>
Detailed Observed Results. Table 4-14 gives a summary of the detailed experimental results using N₂ as carrier gas.

Table 4-14 Cu CVD Results using N₂ as carrier gas

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Number</th>
<th>Weight Change (mg)</th>
<th>Equivalent Thickness (µm)</th>
<th>Resistivity (µΩ-cm)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>05/10/02</td>
<td>0.424</td>
<td>0.2928</td>
<td>1.100 ± 0.127</td>
<td>uniform, 2 patches</td>
</tr>
<tr>
<td></td>
<td>05/23/02</td>
<td>0.231</td>
<td>0.1595</td>
<td>1.207 ± 0.178</td>
<td>shiny, 3 patches</td>
</tr>
<tr>
<td></td>
<td>05/24/02</td>
<td>0.351</td>
<td>0.2424</td>
<td>0.902 ± 0.046</td>
<td>uniform, no Cu @ edge</td>
</tr>
<tr>
<td>7.5</td>
<td>05/06/02</td>
<td>0.110</td>
<td>0.0760</td>
<td>1.969 ± 0.089</td>
<td>thin @ center</td>
</tr>
<tr>
<td></td>
<td>05/07/02</td>
<td>0.170</td>
<td>0.1174</td>
<td>1.886 ± 0.071</td>
<td>rough, many holes</td>
</tr>
<tr>
<td></td>
<td>05/16/02</td>
<td>0.134</td>
<td>0.0925</td>
<td>1.449 ± 0.117</td>
<td>uniform</td>
</tr>
<tr>
<td></td>
<td>05/22/02</td>
<td>0.154</td>
<td>0.1063</td>
<td>0.972 ± 0.036</td>
<td>uniform</td>
</tr>
<tr>
<td>4</td>
<td>05/08/02</td>
<td>0.092</td>
<td>0.0635</td>
<td>1.957 ± 0.099</td>
<td>green patches</td>
</tr>
<tr>
<td></td>
<td>05/09/02</td>
<td>0.076</td>
<td>0.0525</td>
<td>–</td>
<td>rough, holes</td>
</tr>
<tr>
<td></td>
<td>05/20/02</td>
<td>0.068</td>
<td>0.0470</td>
<td>–</td>
<td>uniform</td>
</tr>
<tr>
<td></td>
<td>05/21/02</td>
<td>0.067</td>
<td>0.0463</td>
<td>–</td>
<td>thin, many holes</td>
</tr>
</tbody>
</table>

“−”: The resistance value is out of the measurement range of the 4-point probe.

Growth Rate. The deposition times for the experiments are 4, 7.5 and 15 minutes. Figure 4-13 is a plot of mass loading (mg/cm²) vs. growth time. All the data are fitted to a straight line with the form of y=bx+a to estimate the steady state deposition rate and induction time. The slope with units of mg/(cm²-min) represents the film growth rate and the x-axis intercept represents the induction time. From Fig. 4-13, we find all the data are scattered widely around the straight line, especially for 15 minute samples, which suggests that the
experiments have weaker reproducibility compared to the baseline results using H₂ as carrier gas (see Fig. 4-1).

![Graph showing steady state growth rate using N₂ as carrier gas](image)

**Fig. 4-13 Steady State Growth Rate using N₂ as Carrier Gas**

Table 4-15 presents the regressed kinetic results. From the table, the growth rate is $0.0142 \pm 0.0046 \text{ mg/(cm}^2\cdot\text{min})$, (ca. $15.9 \pm 5.2\text{ nm/min}$). The growth rate with relatively large uncertainty is mostly the result of the bad repeatability of 15 minutes samples. The growth rate is similar to the baseline rate using H₂ as carrier gas with the same partial pressures of Cu(hfac)₂ and i-PrOH. This indicates that H₂ might only play the role as carrier gas, and the main reducing agent for steady state growth is i-PrOH.

The induction time is $1.1 \pm 3.0 \text{ min}$. This induction time is higher than the induction time of baseline results using H₂ as carrier gas, which is $0.0 \pm 0.8 \text{ min}$. This indicates that there is some nucleation resistance of copper deposition using N₂ as the carrier gas. As noted
above, the standard deviation of the growth rate data using N\(_2\) as the carrier gas is also weaker. Both results suggest that using H\(_2\) as the carrier gas improves the nucleation behavior of the copper growth process.

Table 4.15 Steady State Growth Rate and Induction Time

<table>
<thead>
<tr>
<th>Slope [mg/(cm(^2)-min)]</th>
<th>Growth Rate [nm/min]</th>
<th>Y-intercept [mg/cm(^2)]</th>
<th>Induction Time [min]</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0142 ± 0.0046</td>
<td>15.9 ± 5.2</td>
<td>-0.0158 ± 0.0430</td>
<td>1.1 ± 3.0</td>
<td>0.8446</td>
</tr>
</tbody>
</table>

- **Visual Appearance.** The visual appearance of this set of films is much worse than the baseline films using H\(_2\) as carrier gas. Most of the deposited films do not have copper color. They are not uniform and have some transparent holes in the film. Some samples have different patches with different color and thickness. The backside of all the samples is reflective and shiny. All the samples have four small half-circle areas with no deposition due to shadowing by the screws used to mount the substrate on the pedestal surface.

- **Resistivity.** Figure 4-14 is a plot of resistivity as a function of equivalent thickness. The solid circle data are the resistivities of this set of films, and the open circle ones are the baseline samples using H\(_2\) as carrier gas. From Fig. 4-13, the resistivities of this set are found to be lower than baseline films using H\(_2\) as the carrier gas with similar thicknesses. Some films even have resistivity values lower than the bulk Cu resistivity value. This suggests that the resistivity values for the N\(_2\) films are unreliable. This may reflect the larger standard deviation in growth rate and poor visual appearance.
Fig. 4-14 Resistivity vs. Equivalent Thickness using N\textsubscript{2} as Carrier Gas
CHAPTER 5 REACTION MECHANISM FOR COPPER CVD

This chapter describes a series reaction mechanism for Cu CVD using isopropyl alcohol reduction of Cu(hfac)$_2$. The kinetic results with low partial pressure ratios of Cu(hfac)$_2$ to isopropanol are presented in Chapter 4 of this dissertation. The earlier kinetics using high partial pressure ratios of the precursor and isopropanol were investigated by the former graduate student of our group (Borgharkar et al, 1998b). We summarize the kinetic behaviors with respect to precursor and isopropanol in section 5.1. We then propose a series reaction mechanism to explain the observed kinetics.

5.1 Observed Reaction Orders

This section summarizes the observed reaction orders with respect to the precursor and the reducing agent. First we list the results from this study using low precursor partial pressure. Next, we present the reaction order with respect to isopropanol using a high precursor partial pressure.

- **Cu(hfac)$_2$ Order.** The dependence of film growth rates as a function of Cu(hfac)$_2$ partial pressure is shown in Fig. 5-1. The measured growth rates are indicated by the solid symbols. Qualitatively, the observed growth rates initially increase linearly with partial pressure of Cu(hfac)$_2$ below 0.02 Torr. Then the growth rate begins to deviate below linearity. This deviation is consistent with the fact that reported growth rates using much higher precursor partial pressure (ca. 2 Torr) are not greatly different than the present results (Borgharkar et al, 1998b).

- **Isopropanol Order under low Cu(hfac)$_2$ pressure.** Fig. 5-2 is a plot of growth rate against isopropanol partial pressure using a Cu(hfac)$_2$ partial pressure of 0.025 Torr. The measured growth rates are indicated by the solid symbols. The deposition rate shows no signi-
significant deviation from a mean value of 18 nm/min over the full four-fold range of isopropanol partial pressures between 0.8 – 3.2 Torr. This means the reaction order of isopropanol is zero.

![Graph of Copper Deposition Rate vs. Cu(hfac)$_2$ Pressure](image)

**Fig. 5-1 Copper Deposition Rate as a Function of Cu(hfac)$_2$ Partial Pressure**

- **Isopropanol Order under high Cu(hfac)$_2$ pressure.** We re-plot the growth rates from a previous study (Borgharkar et al, 1998b) as a function of isopropanol partial pressure in Fig. 5-3. The remaining operating conditions were fixed as 1.7 Torr for Cu(hfac)$_2$ partial pressure, 40 Torr for H$_2$ partial pressure, and 300°C for deposition temperature. The two reactants were introduced to the reactor separately using H$_2$ as the carrier gas from their individual evaporator. The solid symbols show the measured rates.

The growth rate is seen to increase significantly as the isopropanol partial pressure is made larger. The increase is roughly linear up to isopropanol partial pressure up to 5 Torr, where the growth rate reaches about 60 nm/min. This linear dependence of isopropanol partial
pressure appears to be in conflict with our current study, which is independent of isopropanol partial pressure. However the experiments reported by Borgharkar et al (1998b) were performed using a much higher ratio of precursor and alcohol partial pressures. As we will discuss below, the reactant ratio can affect the kinetic regime of the reaction mechanism.

Fig. 5-2 Copper Deposition Rate as a Function of i-PrOH Partial Pressure (low Cu(hfac)$_2$ partial pressure)

5.2 Series Reaction Mechanism

In this section we discuss a proposed series reaction mechanism to explain the observed kinetic behavior with respect to each reactant. We first present the assumptions for series reaction mechanism, and then we discuss the mechanisms with single and two surface intermediates in sequence.

• **Series Assumptions.** The main goal of the proposed reaction mechanism is to examine the kinetics of the alcohol-assisted reaction in the operating regime of low precursor
partial pressure that is encountered using a solution-based liquid delivery system. The proposed reaction mechanism should account for the presently observed first-order behavior with respect to precursor and zero-order behavior with respect to isopropanol. The mechanism should also be able to show zero order in precursor and positive order in isopropanol for earlier works at high precursor pressure. Finally the proposed mechanism should allow us to deduce that the reaction order in isopropanol will become positive at very low alcohol partial pressure.

A series reaction mechanism can fulfill the mentioned tasks. The reaction process begins with a precursor molecule reacting at the clean surface to produce an adsorbed intermediate. Isopropanol then reacts with the intermediate to remove precursor ligands from the surface and leave clean metal. If both reactants are present simultaneously (as in a
conventional CVD process), reaction orders are determined by the relative partial pressure of precursor and alcohol.

- **Series Mechanism with Single Intermediate.** It is possible to fit present growth rates at low precursor partial pressure using a minimal-parameter model for a series mechanism that includes a single intermediate and two elementary steps:

\[
\text{Cu(hfac)₂(g)} + \frac{k_1}{\eta_1} \rightarrow \text{I(a)} \quad \quad \text{(Eq. 5-1)}
\]

\[
i\text{-PrOH(g)} + \text{I(a)} + \frac{k_2}{\eta_2} \rightarrow \text{Cu(s)} + \text{Co-Product(g)} + \square \quad \quad \text{(Eq. 5-2)}
\]

We assume that the individual molecular steps obey elementary kinetics:

\[
\text{Cu adsorption:} \quad r_1 = k_1 P_{\text{Cu(hfac)₂}} \theta_v \quad \quad \text{(Eq. 5-3)}
\]

\[
\text{Alcohol reduction:} \quad r_2 = k_2 P_{\text{ROH}} \theta_i \quad \quad \text{(Eq. 5-4)}
\]

Here \(\theta_i\) is the fraction of surface covered by adsorbed intermediate, \(k_1\) is rate constant for adsorption of precursor, and \(k_2\) is rate constant for removal of precursor ligands by alcohol.

Assuming the same rates between two elementary steps and the conservation of surface sites, we can calculate the coverage of the intermediate and then the Cu deposition rate by solving the following equations:

\[
r_{\text{overall}} = r_1 = r_2 \quad \quad \text{(Eq. 5-5)}
\]

\[
\theta_v + \theta_i = 1 \quad \quad \text{(Eq. 5-6)}
\]

Fitting the above model to the growth rates shown in Fig. 5-1 gives a value of \(10^{17}\) molecule-cm\(^{-2}\)-s\(^{-1}\)-Torr\(^{-1}\) for precursor adsorption rate constant (\(k_1\)). This value corresponds to an estimated sticking coefficient for adsorption of Cu(hfac)₂ to be \(S = 10^{-3}\). This value is
consistent with those based on exposures required to achieve saturation adsorption of Cu(II) acetamidinate precursor for atomic layer Cu deposition (Lim et al, 2003). The current S value also agrees with the value (10^{-2}) reported by Girolami et al (1993) for adsorption kinetics of Cu(hfac)_2 on metal surfaces. The obtained S value is much larger (ca. 10^3 times) than value reported by Farkas et al (1994) for adsorption of Cu(hfac)_2 on SiO_2, which further confirms that we are measuring the growth kinetics on the copper surface.

Fitting the single intermediate model to the growth rates shown in Fig. 5-2 gives a lower limit value of 10^{17} molecule-cm^{-2}-s^{-1}-Torr^{-1} for the alcohol reduction rate constant (k_2). This is the lowest value that can remove the surface intermediate fast enough to maintain zero-order kinetics with respect to isopropanol using a low precursor partial pressure (see Fig. 5-2). However, this value leads to calculated rates that at least 10 times too large when applied to conditions of high precursor partial pressure (see Fig. 5-3). This is an inherent shortcoming of the single intermediate series mechanism, and it occurs because the calculated coverage of the single proposed surface intermediate (θ_i) does not reach a high enough value to reduce the rate of precursor adsorption (r_1) into agreement with the observed rates. The same shortcoming is still observed if we apply different reaction orders and vacant site requirements in Eq. 5-3.

- **Series Mechanism with Two Intermediates.** Because of the inability of the single intermediate series mechanism to describe kinetics using high precursor partial pressure, we consider a series mechanism involving more than one surface intermediate. There are three possible intermediates: molecular Cu(hfac)_2, dissociated (hfac) ligands, and singly dissociated Cu(hfac) moieties. The latter species is the primary intermediate for disproportionation of
Cu(I) precursors. The disproportionation reaction is much faster than Cu(II) reduction, thus Cu(hfac) is unlikely to be the coverage determining intermediate in the present study.

This leaves molecular Cu(hfac)$_2$ and dissociated (hfac) ligands as the two surface intermediates likely to be present in kinetically significant amounts. The reaction mechanism will require three kinetically significant elementary steps to determine the coverage of these intermediates. The proposed dual intermediate series mechanism is summarized in Table 5-1. The three kinetically significant elementary steps are discussed below:

- **Cu(hfac)$_2$ adsorption.** The molecular adsorption of Cu(hfac)$_2$ is assumed to occur rapidly and reversibly. The same assumption has been applied previously to derive the Hougen-Watson expression for H$_2$ reduction of Cu(hfac)$_2$. The desorption of Cu(hfac)$_2$ is a requisite elementary step in the disproportionation of Cu(I) precursor, which occurs at much higher rates than Cu(II) reduction. With the rapid adsorption and desorption of Cu(hfac)$_2$, the coverage of molecular Cu(hfac)$_2$ can be calculated using the quasi-equilibrium approximation.

- **Ligand dissociation.** The second step is the dissociation of one of the (hfac) ligands from adsorbed Cu(hfac)$_2$ molecule onto the Cu surface. The remaining Cu(hfac) species is assumed to react rapidly via disproportionation, as noted in Table 5-1. The ligand dissociation step is relatively slow, which implies a modest activation energy barrier for the dissociation step. This would be consistent with the fact that an analog of the reverse reaction (i.e., ligand association) is also a requisite elementary step in the faster Cu(I) disproportionation mechanism. Ligand dissociation will be the rate determining step in the series mechanism at low ratios of Cu(hfac)$_2$ to isopropanol partial pressures, as in the present work. Thus the kinetics will be near first-order with respect to Cu(hfac)$_2$ partial pressure and zero-order to isopropanol.
Table 5-1 Proposed Reaction Mechanism for $i$-propanol-assisted Reduction of Cu(hfac)$_2$

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Reaction Order</th>
<th>Optimized Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)$<em>2$(g) $\xrightarrow{k</em>{2a}}$ + 2□ $\rightarrow$ Cu(hfac)$_2$(a)</td>
<td>$\theta_{\text{Cu(hfac)}<em>2} = K_a P</em>{\text{Cu(hfac)}_2} \theta_V^2$</td>
<td>$K_a = 2.8 \text{ Torr}^{-1}$</td>
</tr>
<tr>
<td>Cu(hfac)$<em>2$(a) $\xrightarrow{k</em>{2s}}$ + □ $\rightarrow$ Cu(hfac)(a) + (hfac)(a)</td>
<td>$r_2 = k_2 \theta_{\text{Cu(hfac)}_2} \theta_V$</td>
<td>$k_2 = 5.6 \times 10^{16} \text{ cm}^{-2} \text{s}^{-1}$</td>
</tr>
<tr>
<td>i-PrOH(g) + (hfac)(a) $\xrightarrow{k_{3s}}$ + □ $\rightarrow$ H(hfac)(g) + i-PrO(a)</td>
<td>$r_3 = k_3 P_{\text{i-PrOH}} \theta_{\text{(hfac)}} \theta_V$</td>
<td>$k_3 = 1.8 \times 10^{16} \text{ cm}^{-2} \text{s}^{-1} \cdot \text{Torr}^{-1}$</td>
</tr>
<tr>
<td>2Cu(hfac)(a) $\rightarrow$ Cu(hfac)$_2$(g) + Cu(s) + 2□</td>
<td>very fast</td>
<td>----</td>
</tr>
<tr>
<td>i-PrO(a) $\rightarrow$ $\frac{1}{2}$H$_2$(g) + Me$_2$CO(g) + □</td>
<td>very fast</td>
<td>----</td>
</tr>
</tbody>
</table>

□: vacant site on Cu surface.
Ligand Desorption. The final kinetically significant step is the removal of (hfac) ligands from the Cu surface. This occurs via proton transfer between isopropanol and adsorbed (hfac), which allows the ligand to desorb as H(hfac). The residual isoproproxide group is known to decompose rapidly to acetone and H$_2$ on Cu surface at this temperature, as indicated in Table 5-1. The ligand desorption step becomes rate determining at high ratios of Cu(hfac)$_2$ to isopropanol partial pressures, as in Borgharkar et al (1998b). In this case, the combined coverage of adsorbed Cu(hfac)$_2$ and (hfac) dominates the Cu surface. Thus the kinetics become first-order with respect to isopropanol and zero-order with respect to Cu(hfac)$_2$.

Parameter Fitting. We have optimized the three kinetic constants to the observed growth rates (Fig. 5-1 to 5-3) by solving the following equations with assumed reaction orders:

\begin{align*}
\theta_{\text{Cu(hfac)}_2} + \theta_{\text{(hfac)}} + \theta_V &= 1 \quad \text{(Eq. 5-7)} \\
\theta_{\text{Cu(hfac)}_2} &= K_a P_{\text{Cu(hfac)}_2} \theta_V^2 \quad \text{(Eq. 5-8)} \\
k_2 \theta_{\text{Cu(hfac)}_2} \theta_V &= k_3 P_{1\text{-PrOH}} \theta_{\text{(hfac)}} \theta_V \quad \text{(Eq. 5-9)}
\end{align*}

Here $\theta_{\text{Cu(hfac)}_2}$ and $\theta_{\text{(hfac)}}$ are the fraction of surface covered by Cu(hfac)$_2$ molecule and the (hfac) ligand, $K_a$ is the equilibrium constant for the adsorption of Cu(hfac)$_2$, $k_2$ is the rate constant for the ligand dissociation, and $k_3$ is the rate constant for the ligand desorption.

The optimized rate constants for three kinetically significant steps are listed in the third column of Table 5-1. The calculated rate expressions are shown by solid curves in Fig. 5-1 to 5-3. In Fig. 5-1, the curve shows a nearly first-order with respect to Cu(hfac)$_2$ partial pressure in the range of experimental values. The proposed mechanism provides reasonable
predictions compared to the experimental observations. In Fig. 5-2, the rate expression shows a first-order reaction at very low isopropanol pressure, and then quickly saturates when the isopropanol partial pressure is higher than 0.6 Torr. This is consistent with the zero-order behavior with respect to isopropanol partial pressure seen in the present solution-delivery study using low partial pressure of Cu(hfac)$_2$. In Fig. 5-3, the rate expression shows a positive-order dependence on the isopropanol partial pressure, which was observed in our group’s previous co-evaporation study using higher Cu(hfac)$_2$ partial pressure.
CHAPTER 6 DEPOSITION OF TANTALUM USING \text{TaF}_5

This chapter describes the efforts to deposit thin CVD Ta films using silane (SiH\textsubscript{4}) reduction of tantalum pentafluoride (\text{TaF}_5). Section 6.1 describes the reasons to choose these reactants. Section 6.2 discusses the thermodynamic calculations for the effect of the inlet reactant composition on the products of the reaction between \text{TaF}_5 and SiH\textsubscript{4}. Section 6.3 presents some preliminary experimental results about the CVD tantalum films that were obtained.

6.1 Choice of the Reactants

In this study, we used \text{TaF}_5 and SiH\textsubscript{4} as the reactants for the tantalum CVD process. The choice of \text{TaF}_5 as the tantalum source is based primarily on thermodynamic considerations. Similar to other tantalum halides, \text{TaF}_5 has adequate volatility to act as a CVD precursor, and will produce volatile reaction products. As one of the inorganic tantalum precursors, \text{TaF}_5 is less susceptible to impurity incorporation compared to the metal organic tantalum precursors, which may suffer from ligand decomposition as a side reaction. Furthermore, \text{TaF}_5 is the only halide for which tantalum metal is the thermodynamically favored reduction product when using SiH\textsubscript{4} as the reducing agent.

Our literature survey revealed no publication about tantalum metal deposition using \text{TaF}_5 as the precursor in a continuous flow CVD system. Ugolino et al (1991) reported depositing tantalum onto clean silicon substrates using \text{TaF}_5 alone. In this case, the Si substrate itself served as the reducing agent for \text{TaF}_5. Because of its transient and self-limiting nature, this process is not suitable to deposit tantalum barrier films on the dielectric materials in silicon devices.
The choice of SiH₄ as reducing agent is based on the difficulty of reducing tantalum, which has a high electropositive potential. For example, reduction of TaF₅ using H₂ is thermodynamically unfavorable at temperatures suitable for microelectronic device fabrication. In contrast, reduction using SiH₄ is thermodynamically favorable:

\[ \text{TaF}_5 + 1.25\text{SiH}_4(g) = \text{Ta} + 1.25\text{SiF}_4(g) + 2.5\text{H}_2(g) \]  
(Eq. 6-1)

This reaction is favorable because of the large Gibbs free energy change (−313.6 kJ/mol Ta) and the relative stability of the SiF₄ reaction product.

### 6.2 Thermodynamic Calculations

A potential concern using SiH₄ as the reducing agent is the formation of Ta silicides. This is known to occur for the WF₆ + SiH₄ reaction at high SiH₄/WF₆ ratio (Wolf et al, 2000). To examine this possibility in the present system, we used a commercial chemical thermo-dynamic package (HSC Chemistry, Roine 1999) to perform yield calculations for the TaF₅ + SiH₄ reaction system before we decided on the SiH₄/TaF₅ inlet composition ratios.

Figure 6-1 shows the calculated product yields as a function of the inlet composition of the reactants. The other applied conditions are: system pressure = 10 Torr and deposition temperature = 350°C. From the figure, three regions of products are observed. When the inlet ratio of SiH₄/TaF₅ is less than 1.25 (region I), Ta metal is predicted to be essentially the only product. When the inlet ratio of SiH₄/TaF₅ is between 1.25 and 3.25 (region II), the yield of the Ta goes down, and the tantalum silicide phase begins to form. Finally, when the ratio of SiH₄/TaF₅ is greater 3.25 (region III), the thermodynamic calculations predict that no metal Ta will be included in the products, but instead only some silicon and silicides.
6.3 Experimental Results of CVD Ta Films

From the last section, we know that the formation of Ta metal is favorable on the thermodynamic grounds given that a suitable inlet reactant composition ratio is used. In this section, we will test whether Ta metal is the kinetically favored reaction product as well. We report the deposition rate of the Ta films, and the elemental composition of the films using X-ray photoelectron spectroscopy (XPS).

- Operating Conditions. The experiments were performed using an impinging pedestal reactor assembled in-house, which was described in section 3.2.1. The precursor (TaF$_5$) with He carrier gas and the reducing agent (SiH$_4$/He mixture) were delivered separately into the reactor. The entire system was heat-traced to 90°C to prevent condensation...
of TaF$_5$ onto walls of the reactor and the delivery tubing. Copper foils and glass slides were used as substrates. The typical deposition conditions are listed in Table 6-1.

Table 6-1 Operating Conditions for Tantalum CVD

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVD Time</td>
<td>15 min</td>
</tr>
<tr>
<td>He Carrier Flow Rate</td>
<td>5 sccm</td>
</tr>
<tr>
<td>SiH$_4$/He Flow Rate</td>
<td>5 sccm</td>
</tr>
<tr>
<td>Evaporator Temperature</td>
<td>85°C</td>
</tr>
<tr>
<td>System Pressure</td>
<td>13 Torr</td>
</tr>
<tr>
<td>TaF$_5$ Partial Pressure</td>
<td>0.2 Torr</td>
</tr>
<tr>
<td>SiH$_4$ Partial Pressure</td>
<td>0.3 Torr</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>350°C</td>
</tr>
<tr>
<td>Substrate</td>
<td>Cu foil or Glass Slide</td>
</tr>
</tbody>
</table>

- **Deposition Rate.** The growth rate is determined by the weight difference of samples before and after the experiment. All measured rates are reported in units of mass deposition; a rate of 1 mg cm$^{-2}$ h$^{-1}$ corresponds to a thickness growth rate of 10 nm min$^{-1}$ for a pure fully dense Ta film. Most of the deposited Ta films on Cu foil were continuous, metallic, and silver bright, while some films presented yellow color. The mass deposition rate at the above conditions was $0.215 \pm 0.168$ mg cm$^{-2}$ h$^{-1}$. This corresponds to a thickness growth rate of $2.2 \pm 1.7$ nm min$^{-1}$ for a fully dense film. This growth rate is much greater than the rate obtained by Kim et al (2002 and 2003), who deposited Ta films with a rate about $0.5$ Å min$^{-1}$ using plasma assisted ALD from TaCl$_5$ and H atom.
We also tried to deposit Ta films on glass substrates. The appearance of deposited films on glass substrates was white and uniform. The substrates lost weight after the deposition experiments, so we cannot determine the growth rate on glass using weight increase measurement. Thermodynamic equilibrium composition calculations using commercial software (HSC chemistry, Roine 1999) revealed that SiO$_2$ can be etched by gaseous TaF$_5$ at 350 °C.

- **Elemental Composition of the Films.** X-ray photoelectron spectroscopy (XPS) depth profiling was used to determine the elemental composition of the film. Only the films deposited on Cu foil substrates were examined by XPS, since interpreting the XPS depth profiling results would be complicated by the main elements of glass substrate, Si and O. The depth profile was performed using Ar$^+$-ion sputtering and under ultra high vacuum (10$^{-9}$ to 10$^{-8}$ Torr).

Figure 6-2 shows the measured composition (mass concentration) by XPS depth profile. The profile indicates that tantalum is the main atomic constituent throughout the depth of the film. The film contained a small level of F impurity (< 5%). There is no Si detected anywhere in the film. This is consistent with the thermodynamic predictions, which indicate that Ta metal will be the main product if the inlet composition ratio of SiH$_4$ and TaF$_5$ is less than 1.25. The molar ratio of SiH$_4$ and TaF$_5$ in our experiment is about 1.5. However, if we consider the possible error from the calculated TaF$_5$ vapor pressure, we conclude that the CVD process for depositing metal tantalum film is kinetically feasible.

The major impurity of the Ta film is O, which is present at about 10% throughout the film. One main cause for the observed film impurity could be that the reactor used in the present study was adapted from the previous copper CVD study (Borgharkar et al, 1999). The
Cu CVD system was originally designed to operate at a relatively high pressure (ca. 80 Torr), compared to the likely optimal pressure for Ta CVD. Operation at high pressure may lead to excessive gas phase reactions, which can decrease surface reaction rates, degrade film properties, and hinder experimental reproducibility. In addition, the residual background gases, including water vapor, might cause the observed impurities in the Ta CVD films. Tantalum precursor (TaF$_5$) is very sensitive to air and water vapor. The presence of water vapor in the reactor can result the deposition of Ta oxide, and this reaction is actually applied for the deposition of Ta$_2$O$_5$ (Kukli et al, 1995).

Fig. 6-2 XPS Depth Profile of a CVD Ta Film
CHAPTER 7 DEPOSITION OF PALLADIUM SEED LAYERS

This chapter describes efforts to deposit thin CVD Pd films to use as seed layers for electroless copper deposition. Section 7.1 describes an attempt to use a continuous flow CVD process. This failed to give reproducible results, apparently because of the nucleation barrier for continuous Pd CVD on glass substrates.

We then developed a new batch CVD activation process for depositing the Pd seed layer. In section 7.2, we describe the results using the batch CVD step followed by continuous CVD to provide a two-step process for depositing the desired Pd layer. The batch CVD step succeeds in reducing the nucleation barrier and improves the local uniformity of the final films. However, the subsequent continuous CVD process deposits Pd films under mass transport limited conditions, which leads to globally non-uniform deposition profiles.

We next investigated the batch CVD activation step by itself for depositing the Pd seed layers. This succeeds in producing seed layers that give smooth, shiny, and continuous electroless copper films. In sections 7.3 to 7.5, we describe the effects of holding time, activation temperature, and precursor evaporation time on the properties of the electroless copper films. Based on the visual quality of deposited copper films and the deposition rate, we conclude that the batch activation process with a holding time of 5 min, an activation temperature of 180°C, and a precursor evaporation time of 15 s provides the best performance as a baseline procedure for further study.

In section 7.6 we examined the atomic composition and morphology of the Pd seed layer using XPS, SEM and AFM. The samples were prepared using the baseline activation temperature and holding time, but with 4, 7.5 and 15 seconds precursor evaporation times. XPS analysis shows that the amount of Pd seeds on the substrate increase linearly as a
function of the amount of the precursor delivered into the reactor (i.e., the precursor evaporation time). SEM and AFM results suggest that the precursor evaporation times have no significant effects on the grain size and height of Pd seeds. However, the nucleus densities of Pd seeds increase from about 1 cluster/µm² to 14 clusters/µm² when the evaporation time is increased from 4 to 15 s.

In the last section of this chapter, we tested the addition of H₂O or i-PrOH into the reactor during the batch CVD activation process in order to improve the quality of Pd seed layers and obtain crack-free electroless copper films. After comparing the visual qualities and the growth rates of electroless copper films, we found that neither of the additives has a significant effect on the Pd seed layers.

7.1 Palladium CVD without Activation Step

This section presents the experimental results of Pd CVD without using an activation step. These experiments were performed before we applied the activation step for the Pd CVD. Initially we hoped to deposit the Pd seed layer using a single CVD step, but the poor quality of the results motivated us to use the activation step. These results also provide a comparison to those obtained using the activation step.

- **Operating Conditions.** The experiments were performed using the horizontal flow APCVD reactor described in section 3.3.1. Seven glass substrates were used in each experiment in order to determine the axial deposition profile. The substrates were numbered according to their distance from the reactor inlet. We tested several combinations of evaporation temperature, reactor total pressure, and substrate temperature. The range of operating conditions is summarized in Table 7-1.
Table 7-1 Operating Conditions for Pd CVD without activation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ Flow Rate</td>
<td>80 sccm</td>
</tr>
<tr>
<td>H₂ (10%) Flow Rate</td>
<td>2.5 sccm</td>
</tr>
<tr>
<td>Evaporator Temperature</td>
<td>60, 65, and 70 °C</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>200, 400, 600 Torr</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>65, 80, 95 and 110 °C</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>30 min</td>
</tr>
<tr>
<td>ELD Temperature</td>
<td>50 °C</td>
</tr>
</tbody>
</table>

- **Results.** As shown in Table 7-1, we tested many combinations of operating conditions in an effort to obtain uniform, high quality Pd films. However, the results were generally not satisfactory. The following features are representative of the overall behavior:

  - **Experimental Reproducibility.** A total of 32 experiments were completed. Of these, 24 experiments (75%) had visual Pd profiles as described below, while 8 experiments (25%) had no visual Pd on any substrate.

  - **Induction Time.** The first visually observable region of the Pd film usually appeared at the boundary between the slides 1 and 2 about 15 minutes after starting delivery of the precursor. Thus the minimum induction time for the Pd CVD on the bare glass substrates without using the activation step is about 15 minutes.

  - **Visual Appearance.** The observed Pd films showed a significant axial profile. Although details for each set of experiments varied, the general visual features were observed:
◊ **Slide 1:** The Pd film usually is very thick, and grey shiny. Many visual voids exist. The first half of the substrate is usually blank because of the re-entrant configuration of the precursor inlet tubing.

◊ **Slide 2:** The Pd film is the best among all the 7 substrates. The substrate is completely covered by a shiny and very thick film. Some holes exist in a few of the films.

◊ **Slide 3:** The film is continuous, but much thinner than slides 1 and 2. The film is mostly translucent.

◊ **Slide 4:** The films are very faint and not reproducible.

◊ **Slides 5 to 7:** These slides usually do not show visible films.

Overall the visual appearance of the CVD Pd films without activation showed an exponential decay from slide 1 to slide 4. The non-continuous films might result from a spatially variable Pd nucleation resistance on the bare glass substrate.

- **Weight Gain.** Only slide 1 showed consistently measurable weight change after Pd deposition. We have a total of 14 recorded weight gains for slide 1. If we assume the Pd film has bulk Pd density, we can calculate the thickness of the film. The average film thickness is $16 \pm 10$ nm. The average value is much smaller than the thickness observed when the activation step is used (see section 7.2). The large standard deviation indicates that the growth rate without using the activation step is not very reproducible.

- **Copper ELD.** Because slides 5 – 7 usually did not show a visible Pd film, we also decided to test the presence of Pd using Cu electroless deposition (ELD). The following results were observed:
Some Cu patches are deposited on part of its surface.

No continuous Cu films are deposited on these slides. Small Cu patches or spots sometimes appear on them.

The ELD Cu results indicate that there might be some Pd clusters on slides 5 to 7, but the density of clusters is not big enough to initiate the autocatalytic reduction reaction to form a continuous Cu film.

7.2 Palladium CVD with Activation Step

In this section we describe the experimental results about Pd CVD using the activation step. The Pd film properties, such as visual appearance, thickness, and resistivity, are included. The Pd films from this group of experiments are much better than those without activation, which were described in section 7.1. These improvements are believed to result from the seed layer formed by the activation step.

- **Operating Conditions.** The experiments were performed using the same horizontal flow APCVD reactor that was used in the continuous CVD experiment described in the previous section. The batch activation step was carried out before the continuous CVD step. The detailed procedure for the activation is described in section 3.3.2. Seven glass substrates were used in each experiment in order to determine the axial deposition profile.

The operating conditions for the batch activation step are summarized in Table 7-2. The Pd(hfac)$_2$ pulse time is the length of time that carrier gas is sent through the evaporator and into the unheated reactor, in order to deposit a fixed amount of precursor onto the reactor wall. The reactor is next purged with H$_2$ and then isolated from the rest of the system. The
substrate heater is raised to the desired activation temperature, where it is held constant for the indicated holding time.

The operating conditions for the continuous CVD step are summarized in Table 7-3. The reactor is pumped to the desired pressure after the substrates were cooled to room temperature. The evaporator and substrate heater are next raised to the indicated temperatures. The Pd deposition begins after the precursor and H\(_2\) are transferred continuously into the reactor.

Table 7-2 Operating Conditions for Activation Step

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporator Temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Pd(hfac)(_2) Pulse Time</td>
<td>30 s</td>
</tr>
<tr>
<td>Activation Temperature</td>
<td>110°C</td>
</tr>
<tr>
<td>Holding Time</td>
<td>30 min</td>
</tr>
<tr>
<td>System Pressure</td>
<td>760 Torr</td>
</tr>
</tbody>
</table>

Table 7-3 Operating Conditions for Continuous CVD Step

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2) Flow Rate</td>
<td>80 sccm</td>
</tr>
<tr>
<td>H(_2) (10%) Flow Rate</td>
<td>2.5 sccm</td>
</tr>
<tr>
<td>Evaporator Temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>110°C</td>
</tr>
<tr>
<td>System Pressure</td>
<td>200 Torr</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>5 min</td>
</tr>
</tbody>
</table>
• **Results.** Adding the activation step improved the quality of the subsequent continuous CVD step. Films began to appear almost immediately after the precursor reached the substrate. The Pd films present much higher quality and uniformity compared to films without using activation step. Results for specific film properties are described below:

  - **Experimental Reproducibility.** A total of seven experiments were performed. Only one set of experiments was not successful. Thus the reproducibility of Pd CVD using the activation step is better than without activation (75%).

  - **Induction Time.** The Pd film appeared as soon as the Pd(hfac)$_2$ was delivered into the reactor, i.e., there was no induction time for the Pd CVD using the activation step. Compared to an induction time of 15 min for the CVD without activation, we can conclude the Pd seed layer from the activation step eliminated the nucleation resistance of CVD Pd on the glass substrate.

  - **Visual Appearance.** The observed Pd films also showed a significant axial profile, but the profile extended farther along the length of the reactor than without activation. The details for each set of experiments varied somewhat, but the following general features were observed:

    ◊ **Slide 1:** The Pd film usually is very thick, and grey shiny. Fewer voids exist compared to those from without activation. The first half of the substrate is usually blank because of the configuration of the precursor inlet tubing.

    ◊ **Slide 2:** The Pd film is the best among all the 7 substrates. The substrate is wholly covered by a shiny, uniform and very thick film, which generally does not have voids. The visual quality is better than the slide at the same axial position without activation.
Slide 3: The film is uniform. Although it is much thinner than slide 1 and slide 2 from the same experiment, it is much thicker than the slide 3 without activation.

Slide 4: The film is visually translucent and uniform. The visual thickness is much smaller than slide 3.

Slide 5: The film is very faint, but still visible

Slides 6 and 7: These slides usually do not show visible films.

Overall, the film visual appearance is much better than that without activation. Most of the films do not show voids, or show fewer voids compared to the films without activation. However, film thickness still showed a significant axial profile from slide 1 to slide 5. Batch activation removed the nucleation barrier, but the rapid reactant depletion due to mass transport limited deposition resulted in the quick decrease of deposition rate from slide 1 to slide 5 in the continuous CVD step.

Weight Gain. Larger weight gains were observed after the continuous CVD step using the batch activation step. We were able to measure the weight change on slide 1 and slide 2 in all of the two-step experiments that gave visual films (i.e., 6 out of 7 experiments). In contrast, only slide 1 gave measurable weight gain when the activation step was omitted (section 7.1).

The weight change results are summarized in Table 7-4. The results are reported in terms of equivalent thickness, calculated using bulk Pd density and the area of the slide covered by palladium. All six experiments gave consistent results for both slides. The average thickness for slide 1 is $44 \pm 4$ nm. This is three times thicker than the films on slide 1 obtained without using the batch activation step. The average thickness for slide 2 is $16 \pm 3$ nm. This decrease provides a quantitative indication of the magnitude of the axial deposition profile.
The small value of the standard deviation for these experiments also gives an indication of the improved reproducibility of film growth using the two-step CVD process.

**Table 7-4 Measured Film Thickness of Slide 1 and 2**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Slide 1 (nm)</th>
<th>Slide 2 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>07/19/04</td>
<td>40</td>
<td>11</td>
</tr>
<tr>
<td>07/20/04</td>
<td>46</td>
<td>13.6</td>
</tr>
<tr>
<td>07/21/04</td>
<td>N/A (substrate chipped)</td>
<td>18.5</td>
</tr>
<tr>
<td>07/22/04</td>
<td>40</td>
<td>17</td>
</tr>
<tr>
<td>08/03/04</td>
<td>48</td>
<td>18</td>
</tr>
<tr>
<td>08/05/04</td>
<td>48</td>
<td>18</td>
</tr>
<tr>
<td>Average</td>
<td>44 ± 4</td>
<td>16 ± 3</td>
</tr>
</tbody>
</table>

Table 7-4 shows that the average thickness of slide 2 is about three times lower than slide 1. Slide 3 does not have enough Pd deposition to be measured by the microbalance. These results indicate that there is a large decrease in thickness along the reactor even after the nucleation barrier is removed by the batch activation step. A possible explanation could be that the deposition rate of the continuous CVD step in the absence of the nucleation barrier is so fast that the reaction becomes mass transfer limited. The steep axial thickness profile then develops because of the fast depletion of precursor along the reactor.

We developed a simple reactor transport model to test this hypothesis. Details about the model and the calculation are given in the Appendix. The primary assumptions are: 1) the carrier gas obeys laminar flow along horizontal streamlines; 2) the flux of Pd(hfac)$_2$ at the top surface is zero because there is no reaction on the reactor wall; 3) the concentration of precursor is zero along the bottom surface because of the fast reaction on the heated substrates;
4) the precursor is introduced at the reactor inlet along the centerline of the carrier gas. The mass transfer limited model is solved by integrating the precursor concentration along the carrier gas flow streamline (horizontal direction) using the Runge-Kutta method and applying a finite-difference discretization on the diffusion term in the vertical direction.

Figure 7-1 shows the calculated film thickness vs. slide position after 5 minutes deposition. The maximum near the inlet is caused by the entrance length required for the inlet precursor to distribute across the whole reactor cross section. The simulated results not only predict the observed rapid axial decay profile along the reactor, but also give a reasonable quantitative agreement with observed results for the activated deposition process. This agreement is achieved without any adjustable parameters. The most important parameter in the model is the diffusion coefficient of Pd(hfac)$_2$ in N$_2$, which is estimated using the Chapman-Enskog formulas.

Fig. 7-1 Thickness Profile of Pd Film using Mass-Transfer Limited Model
Resistivity. Because we obtained a measurable thickness of Pd on slides 1 and 2 using the two-step process, it was also possible to obtain resistance measurements for these films. In Figure 7-2 we show the resistivity for all of the continuous Pd films on these slides. From the figure, we find that the film resistivity is always larger than bulk value of palladium (11 µΩ-cm). The average resistivity value for Pd films on slide 1 is 25 ± 9 µΩ-cm, which is smaller than the average value for films on slide 2 (36 ± 11 µΩ-cm). Film thickness is known to affect the apparent resistivity of thin films as the thickness of the film approaches the mean free path of electrons in the material. The same phenomenon occurred for CVD Cu films (section 4.1).

Fig. 7-2 Resistivity of Pd Films with Activation Step
Electroless deposition of Cu was applied to slides 6 and 7 in order to test the existence of Pd on these two visually empty substrates. Uniform and shiny Cu films were deposited on their entire surfaces. The ELD Cu results indicate that there is a very thin Pd film on slides 6 and 7.

To determine whether this Pd was deposited during the batch activation step or the continuous CVD step, we also tested some substrates which were treated using only the activation step with an activation temperature of 110°C. None of these slides produced a Cu film from ELD. Thus we conclude that the Pd came from the continuous CVD step. Batch activation performed by itself at 110°C did not produce enough Pd for Cu ELD.

### 7.3 Palladium Seed Layers for Copper ELD – Holding Time Effects

In the last section we showed that the batch activation step was able to improve the film quality of a subsequent continuous CVD step by eliminating the initial nucleation barrier for film growth. However, the transport-limited growth rate of the continuous CVD step resulted in a globally non-uniform Pd profile. The Pd films on the first several slides were too thick to be suitable as seed layers for ELD Cu. Since the Pd seed layer produced by the batch activation step was able to eliminate the nucleation barrier for the continuous CVD step, we decided to investigate using the activation step to deposit seed layers for ELD Cu.

In this section we examine whether the batch CVD activation step by itself (i.e., without a subsequent continuous CVD step) is able to produce a Pd seed layer for Cu electroless deposition. Experiments in the previous section showed that the batch activation step using 110°C was not sufficient to produce enough Pd seed for ELD Cu. Here we use 180°C as the activation temperature. By varying the length of holding time at this activation...
temperature, we find that it is possible to produce a suitable Pd seed layer for Cu ELD using only the batch CVD process.

• **Experimental.** The activation step was performed using the horizontal flow APCVD reactor (see section 3.3.1). The detailed procedure for the activation is described in section 3.3.2. Seven glass substrates were used in each experiment in order to determine the average value of the Cu deposition rate and the general film visual appearance.

The operating conditions for the batch activation step are listed in Table 7-5. The precursor evaporation time is fixed to 30 seconds to deposit the same amount of precursor onto the reactor wall for all the tested conditions. We fixed the activation temperature at 180°C, and we used three holding times, ranging from 0 to 15 minutes, after the substrate reached its activation temperature (i.e., about 7.5 minutes).

The electroless Cu deposition was performed at 50°C in a plating bath which contained 0.5g copper sulfate (CuSO₄), 3.0g ethylenediaminetetraacetic acid (EDTA), 23ml tetramethylamonium hydroxide (TMAH, 25% in H₂O) and 77 ml deionized (DI) water. The reducing agent, formaldehyde (37%), was mixed with the plating solution using a volumetric ratio of 1:60 before the plating.

We recorded two parameters, i.e., appearance time and weight gain, for each Cu ELD experiment in order to determine the effectiveness of the Pd seed layer. The film appearance time was determined by the disappearance of the black marks on the substrate holder. The Cu weight gain was obtained by weighing the slide before and after the ELD using a microbalance. The equivalent Cu thickness was calculated using the bulk Cu density and the
slide area covered by Cu. A third parameter, Cu film growth rate, was calculated from the film thickness and the related appearance time.

Table 7-5 Operating Conditions of Activation Step for ELD Cu

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporator Temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Pd(hfac)$_2$ Evaporation Time</td>
<td>30 s</td>
</tr>
<tr>
<td>Activation Temperature</td>
<td>180°C</td>
</tr>
<tr>
<td>Holding Time</td>
<td>0, 5, 15min</td>
</tr>
<tr>
<td>System Pressure</td>
<td>760 Torr</td>
</tr>
</tbody>
</table>

- **Results.** The following results summarize the influence of the Pd activation step holding time on the properties of the subsequent Cu ELD films. About 7.5 minutes were required to heat the substrates to the desired deposition temperature during the batch activation step. Then a period of holding time, ranging from 0 to 15 minutes, was applied to keep the substrates at this temperature. Finally the substrates were cooled to the room temperature to perform the electroless deposition step. The main results discussed here include Cu film visual appearance, appearance time, thickness, and deposition rate. We also concluded an optimum holding time at the end of this section.

  - **Visual Appearance.** Metallic and highly reflective Cu ELD films were obtained on all seven slides except the leading edge of slide 1. One possible reason is that the strip heater might have a lower temperature at its front end during the Pd activation step, and thus less Pd seeds might be deposited at this location. The general appearance of the Cu films produced during the ELD treatment using different activation holding times is summarized below:
◊ **Holding Time = 0 min.** The first Cu spots appeared on the substrate surface after about 10 to 20 seconds. It took about 50 to 60 seconds before the Cu spots grew to patches and connected with each other to cover the entire substrate surface. Some gas bubbles were formed during the plating. The final Cu films were not cracked or delaminated, but they did exhibit numerous voids.

◊ **Holding Time = 5 min.** A very faint gray film appeared right after the substrate was immersed into the plating solution. Then the Cu film quickly grew thicker and developed a mirror-like reflective appearance. A large number of gas bubbles formed on the Cu surface, which we tried to get rid of by stirring the substrate holder. The Cu films were continuous when they were removed from the plating solution and rinsed by DI water. No voids were observed on the Cu films. However, these Cu films became cracked or delaminated after they were exposed to air for several minutes.

◊ **Holding Time = 15 min.** Sparsely distributed Cu spots were formed right after the substrate was placed in the Cu plating solution. These spots coalesced to form a continuous film in about 10 to 20 seconds. Fewer gas bubbles formed on the film surface during the developing period compared to the substrates with 5 minutes holding time. The final Cu films were continuous with a mirror-like reflective appearance before they were removed from the Cu plating solution and rinsed by DI water. The films also began cracking or delaminating when they were dried in the air.

◊ **Growth Kinetics.** Two parameters, including film appearance time and film thickness, were recorded during the ELD Cu experiments. We calculated the film growth rate by dividing the film thickness to appearance time. The detailed results are described as below:
◊ **Appearance time.** Figure 7-3 shows the appearance time for ELD Cu films. The solid symbols in the figure represent the individual experimental results, and the open larger symbols are the average appearance time for each group. The average times are $100 \pm 22$, $65 \pm 27$, and $81 \pm 21$ seconds for 0, 5 and 15 minutes holding time, respectively. The scatter in the data is relatively large. This may be at least partially because operator judgment is required to determine when the Cu film completely covers the marks on the substrate holder.

![Fig. 7-3 Effects of Batch Holding Time on Cu ELD Time](image)

One-way analysis of variance (ANOVA) was applied to test the significance of difference among the three mean appearance times. The obtained $F$-value was 8.15, which corresponds to a p value of 0.0009. This is much smaller than $\alpha = 0.05$, which means a significant difference exists among the three means at the 95% confidence level. Because the means are not all the same, we further compared all the pairs using the Tukey-Kramer
honestly significant difference (HSD) method (Freund 1996). The results suggested that the shortest appearance time for the films using holding time of 5 minutes is statistically significant. However, the difference in appearance times for Cu films on the substrates using 0 or 15 minutes holding times is not significant.

◊ **Film Thickness.** Figure 7-4 shows the equivalent thickness of the Cu ELD films deposited on glass substrates prepared using different activation holding times. As in Fig. 7-4, the solid symbols are the individual film thickness, and the three open symbols present the average thickness for each group. The average values are 120 ± 44, 155 ± 47, and 149 ± 41 nm using 0, 5, and 15 minutes activation holding time, respectively.

![Fig. 7-4 Effects of Batch Holding Time on ELD Cu Film Thickness](image)

Fig. 7-4 Effects of Batch Holding Time on ELD Cu Film Thickness
An F-value of 2.61 with a non-significant p value of 0.085 was obtained from ANOVA. We conclude that there is no significant difference between the three mean film thicknesses with an α level of 0.05. This quantitatively suggests that we obtain Cu films with similar thickness by monitoring the disappearance time of the marks underneath the substrate.

\[\text{Deposition Rate.}\] Finally, we calculated the average growth rate for each film. The growth rate is calculated using the measured equivalent film thickness divided by the film appearance time. Figure 7-5 shows the growth rates for each substrate as a function of activation step holding time. The three mean values are 1.26 ± 0.51, 2.79 ± 1.43, and 1.94 ± 0.64 nm/s for 0, 5 and 15 minutes holding time, respectively.

![Graph showing Cu Film Growth Rate vs. Holding Time](image)

Fig. 7-5 Effects of Batch Holding Time on ELD Cu Film Growth Rate
An F-value of 10.6 with a significant p value of 0.0002 was obtained using ANOVA. This suggests that not all the growth rates are the same with an \( \alpha \) level of 0.05. Tukey-Cramer HSD showed that the deposition rate using 5 minutes as holding time is significantly greater than the other two rates, which in turn are not significantly different. Combined with the analysis of figures 7-2 and 7-3, this indicates that there is a statistical basis for selecting 5 minutes as the optimum holding time for the batch activation step.

**Optimum Holding Time.** Based on the above visual observations during the ELD Cu process and the quantitative statistical results of the obtained Cu films, we believe that the best Pd seed layers were deposited on the substrates that were batch activated using 5 min holding time. At this holding time, the ELD Cu film at its initial stage was continuous. At both shorter and longer holding time, the initial Cu films were discontinuous. To account for this, we propose that the quality of the Cu ELD nucleation behavior is affected by the morphology of the Pd seed layer. For example, Chang et al (2003, 2004) reported that the quality of ELD Cu films depends on the morphology of Pd seed layer. They observed that small and uniformly distributed Pd nanoparticles with size about 10 nm required short initial coalescence time to deposit smooth and conformal Cu films, while large Pd clusters with size of 20 to 200 nm resulted in the discontinuity and rough surfaces of ELD Cu films.

In our case, we propose that the continuity and particle size of CVD Pd seed layer may vary with the activation step holding time. During the initial period of batch activation step, the concentration of Pd(hfac)\(_2\) precursor in the reactor is near its maximum. This generates a high flux of Pd(hfac)\(_2\) onto the substrate, and thus the precursor is reduced to Pd atoms at a high rate. These Pd monomers in turn diffuse and coalescence to form isolated Pd clusters. Concentration of the seed clusters increases with the holding time, and the substrates with 5
minutes holding time will obtain more continuous seed clusters than those using 0 minute holding time.

If longer holding time than 5 minutes is applied, almost all of the precursor in the reactor has been consumed to form Pd atoms. Thus the generation rate of Pd monomers along with the formation rate of new Pd clusters both decrease. Instead the existing Pd clusters continue to evolve by diffusion and agglomeration. This leads to larger and more isolated Pd clusters compared to those formed by shorter holding time, so the continuity of initial Cu ELD films deceases on these Pd seed layers.

### 7.4 Activation Temperature Effects

In the last section, we tested the effects of holding time on the properties of the CVD Pd seed layer. The activation temperature was fixed at 180°C. Based on the properties of the obtained ELD Cu films deposited on these Pd seed layers, we concluded that 5 minutes is the best holding time at 180°C.

In this section, we discuss the effects of the batch CVD activation temperature on the properties of the Pd seed layers. The seed layers in turn decide the properties of the subsequent ELD Cu films. Thus we will still use the performance of the ELD Cu to decide the effects of the temperature on the formation of the Pd seed layers. We also use several holding times at each tested activation temperatures. The goal of the experiments in this section is to obtain an optimum combination of the activation temperature and the holding time for the further study on the CVD activation step.

- **Experimental.** The activation step was performed using the same horizontal flow APCVD as in the last section. The operating conditions for the batch activation step are listed
in Table 7-6. Two more activation temperatures, i.e., 150 and 210°C, were used to find the effects of activation temperature on the deposited Pd seed layers for ELD Cu films. The electroless Cu deposition was performed in the same way as described in the last section.

Table 7-6 Operating Conditions of Activation Step for Temperature Effects

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporator Temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Pd(hfac)₂ Pulse Time</td>
<td>30 s</td>
</tr>
<tr>
<td>Activation Temperature</td>
<td>150, 210°C</td>
</tr>
<tr>
<td>Holding Time</td>
<td>0, 4, 5, 7.5, 30 min</td>
</tr>
<tr>
<td>System Pressure</td>
<td>760 Torr</td>
</tr>
</tbody>
</table>

- **Results.** The following results describe the influence of the batch CVD activation temperature on the properties the subsequent Cu ELD films. We will first present the ELD Cu film results deposited on the glass substrates using activation temperatures of 150°C and 210°C. Then we will combine these with the results using 180°C activation temperature from the last section to determine the best combination of the activation temperature and holding time after comparing all the results.

  - **Activation Temperature = 150°C** We investigated 5 different holding times with this temperature. The holding times were 0, 4, 7.5, 15 and 30 minutes. We were able to deposit acceptable Cu films on these CVD Pd activated glass substrates using all the holding times except the 0 minute holding time. We will first present the Cu films visual appearance, and then we will discuss the Cu film appearance time, thickness, and deposition rate.
◊ **Visual Appearance.** The visual appearance of Cu film varied between substrates using different holding times. If the slides were activated using holding time longer than 7.5 minutes (including 7.5), all the slides except slide 1 were entirely covered by Cu films. If the holding time was decreased to 4 minutes, only slides 3 to 5 had several Cu patches deposited on them. No Cu appeared on the substrates with holding time of 0 minutes except a very thin gray Cu film on the slide 2. Most of the Cu films had lots of voids. The obtained Cu films appear much worse than those formed on the substrates activated using 180°C.

◊ **Appearance time** Figure 7-6 shows the appearance time for Cu ELD films using 150°C as activation temperature. We did not include the data from the experiments using 0 minute holding time, because only slide 2 had some film. The four mean appearance times are 173 ± 61, 102 ± 13, 113 ± 25, and 122 ± 32 s for 4, 7.5, 15 and 30 minutes holding time. These appearance times are larger than those using 180°C as the activation temperature.

![Fig. 7-6 ELD Cu Film Appearance Time using 150°C as Activation Temperature](image-url)
One-way ANOVA provides an F-value of 4.25, which corresponds to a p value of 0.0114. This suggests that there exists significant difference in these four average appearance times at the 95% confidence level. Tukey-Cramer HSD shows that the longest appearance time is belonged to the ELD films using 4 minutes holding time, while the other three are not significantly different.

◊ Film Thickness. Figure 7-7 shows the equivalent Cu thicknesses using 150°C as the activation temperature. The four mean thicknesses are 160 ± 37, 150 ± 36, 114 ± 40, and 131 ± 45 nm for 4, 7.5, 15 and 30 minutes holding time. The overall values are very similar to those from ELD films using activation temperature of 180°C. Since we obtained an F-value of 1.9 with a non-significant p value of 0.14, we conclude that there is no significant difference in these four mean thicknesses at the 95% confidence level.

Fig. 7-7 ELD Cu Film Thickness using 150°C as Activation Temperature
◊ **Growth Rate.** Figure 7-8 shows the electroless Cu growth rate using 150°C as activation temperature. The four average growth rates are \(0.96 \pm 0.17\), \(1.48 \pm 0.37\), \(1.03 \pm 0.36\), and \(1.10 \pm 0.33\) nm/s for 4, 7.5, 15 and 30 minutes holding time, respectively. The overall growth rate is about two times lower than that from the ELD Cu film on substrate activated using 180°C activation temperature. One-way ANOVA produces an F value of 2.4 with a non-significant p value of 0.084 in the \(\alpha\)-level of 0.05. It indicates that there is no significant difference between all these four growth rates, i.e., holding time has no effect on Cu deposition rate when Cu was electrolessly deposited on the substrates using 150°C as the activation temperature.

![Fig. 7-8 ELD Cu Film Growth Rate using 150°C as Activation Temperature](image-url)
Activation Temperature = 210°C. Three holding times, i.e., 0, 5 and 15 minutes, were tested using this activation temperature. The following summarizes the properties of ELD Cu films, including film visual appearance, film appearance time, thickness, and growth rate, on the substrates activated using temperature of 210°C.

◊ Visual Appearance. We were able to deposit highly reflective Cu films on all seven slides except slide 1 regardless of the length of the applied holding time. Like in the electroless Cu deposition on the substrates using 180°C as activation temperature, we also observed lots of gas bubbles on the substrate during the Cu developing. The Cu films were similar in appearance to those using 180°C activation temperature. The films were also cracked when they were dried in air.

◊ Appearance Time. Figure 7-9 presents the appearance time for Cu ELD films using 210°C as activation temperature. The three average appearance times are 86 ± 24, 83 ± 18, and 74 ± 37 s for 0, 5, and 15 minutes holding time. The appearance times in these experiments are quite similar to those from the experiments using 180°C as activation temperature. A small F-value of 0.32 with a highly non-significant p value of 0.73 was obtained from one-way ANOVA. This means there is no significant difference between these three mean appearance times with an α level of 0.05.

◊ Film Thickness. Figure 7-10 shows the equivalent Cu thicknesses using 210°C as activation temperature. The three average values are 77 ± 33, 166 ± 23, and 111 ± 12 for 0, 5, and 15 minutes holding time, respectively. One-way ANOVA provides an F-value of 21 with a significant p value less than 0.0001. Thus there is significant difference in these three mean thicknesses at 95% significant level. Tukey-Kramer HSD comparison of all pairs tells us that
the average film thickness with 5 minutes holding time is significantly greater than the other two, which in turn are not significantly different.

![Graph showing ELD Cu Film Appearance Time](image)

**Fig. 7-9 ELD Cu Film Appearance Time using 210°C as Activation Temperature**

◊ **Film Growth Rate.** Figure 7-11 shows the electroless Cu growth rate using 210°C as activation temperature. The three average growth rates are 0.90 ± 0.22, 2.06 ± 0.48, and 1.88 ± 0.96 nm/s for 0, 5 and 15 minutes holding time, respectively. The individual growth rate with different holding times is very similar to the rate from the ELD films on Pd seed layers with the same holding time using 180°C as activation temperature.

With an F value of 7.85 and a significant p value of 0.004, we conclude that not all of these three rates are equal. Tukey-Kramer HSD comparison of all pairs suggests that the growth rate from zero holding time is the lowest rate among all the three. The other two rates
do not have significant difference. This suggests that several minutes holding time is necessary to produce enough Pd seed sites for the electroless Cu deposition when we use 210°C as the CVD activation temperature.

Fig. 7-10 ELD Cu Film Thickness using 210°C as Activation Temperature

- **Comparison of All Results** We were able to electrolessly deposit Cu films on the glass substrates activated by Pd using a batch CVD step with 0 to 30 minutes as holding time after the substrates reached their constant activation temperatures (i.e., 150, 180, and 210°C). However, there are several differences, including Cu film appearance and deposition rate, that still exist due to the various combinations of operating conditions in the batch CVD activation step. This permits us to choose an optimum combination of the activation temperature and holding time for further experiments using the batch CVD activation step.
The Cu films presented very similar appearance on the substrates using either 180 or 210°C activation temperatures in the batch CVD step. However, films deposited on substrates using 150°C were generally much worse than those using 180 and 210°C. We think that low activation temperature can not produce enough Pd seed sites for the subsequent ELD Cu. Holding time also had significant effects on the appearance of the Cu Films. Those deposited on the substrates activated using 180 or 210°C with 5 min holding time showed the best Cu appearance.

The electroless Cu deposition rates on the substrates using different combinations of batch CVD conditions are shown in Figure 7-12. This figure suggests that the Cu deposition rate with 150°C activation temperature is about two times lower than the other two rates. The two growth rates with 180 and 210°C as activation temperatures are similar if the activation
holding times are the same. From further comparison, we find that the growth rates on the substrates using 5 min as holding time show the highest among the three rates using either 180 or 210°C as the activation temperature.

![Fig. 7-12 Cu Deposition Rates with Different Pd Activation Temperature](image)

Based on the above comparisons, we select 180°C as the activation temperature and 5 min as the holding time for the further experiments using the batch CVD step. The main reason is that we can obtain ELD Cu films with good visual appearance and the highest deposition rate using this combination of operating conditions. The choice of 180°C as the activation temperature is also experimentally convenient, because the Viton® O-ring seal for the reactor connector is rated for a maximum temperature of 200°C.
7.5 Precursor Evaporation Time Effect

In the last two sections we found that the ELD Cu films with the best appearance and highest growth rate are deposited on the glass substrates that were activated using 180°C activation temperature and 5 minutes holding time. All of these experiments were performed using 30 seconds as the precursor evaporation time.

In this section we examine the effects of precursor evaporation time. In principle, this should determine the amount of the Pd(hfac)$_2$ delivered into the reactor for the batch CVD step. In particular, we test evaporation times shorter than 30 seconds to see if it is possible to obtain ELD Cu films with similar visual quality and growth rate as those obtained in the previous section, but using smaller Pd loadings.

- **Experimental.** The activation step was performed using the same horizontal flow APCVD reactor as in the last section. The operating conditions for the batch activation step are listed in Table 7-7. Four precursor evaporation times, ranging from 4 to 30 seconds, were used to find the effects of evaporation time on the deposited Pd seed layers for ELD Cu films. The electroless Cu deposition was performed in the same way as described in the last section.

Table 7-7 Operating Conditions of Activation Step for Evaporation Time Effect

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporator Temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Pd(hfac)$_2$ Pulse Time</td>
<td>4, 7.5, 15 and 30 s</td>
</tr>
<tr>
<td>Activation Temperature</td>
<td>180°C</td>
</tr>
<tr>
<td>Holding Time</td>
<td>5min</td>
</tr>
<tr>
<td>System Pressure</td>
<td>760 Torr</td>
</tr>
</tbody>
</table>
• **Results.** As shown in Table 7-7, we have investigated four different evaporation times for the batch activation step. For each evaporation time we fixed the activation temperature and holding time as 180°C and 5 minutes. We will first discuss the effect of precursor evaporation time on the visual appearance of the ELD Cu films. Then we will present the kinetic results, i.e., film appearance time, thickness, and growth rate using different evaporation times. We also measured film resistance and present the resistivity results in this section. We conclude by comparing all the results to obtain a best evaporation time for the further experiments on the batch CVD activation.

- **Visual Appearance.** We were able to deposit metallic shiny ELD Cu films on the glass substrates activated using different precursor evaporation times. This suggests that Pd seed layers could be deposited using evaporation times shorter than 30 seconds. However, the visual appearance of Cu films varied between different evaporation time experiments. The general appearance of the Cu films is summarized below:

  ◊ **Evaporation Time = 4 s.** Slides 2 to 5 had shiny Cu films covering their whole surface, and the other three slides (1, 6, and 7) usually did not have continuous Cu films but some Cu spots or patches on them. The general appearance of the Cu films is worse than that using longer evaporation time (see below). Most of the Cu films had lots of voids. This suggests that there is not enough precursor in the reactor for the formation of a uniform Pd seed layer during the batch CVD step.

  ◊ **Evaporation Time = 7.5 s.** The Cu films obtained in this group were much better than those using evaporation time of 4 seconds. All seven slides except the leading edge of slide 1 were covered by good Cu films. Fig. 7-13 (a) shows a picture of the typical Cu films using evaporation time of 7.5 seconds. The picture suggests that the Cu films on slides 2 to 5
are locally continuous, but all of them are cracked. However these films are much better than those on slides 1, 6 and 7, which have numerous voids. It suggests that the amount of Pd(hfac)$_2$ in the reactor was still not enough to produce Pd seed layers that continuously cover all the seven slides.

◊ Evaporation Time = 15 s. Fig. 7-13 (b) shows the picture of films using 15 s evaporation time. All the slides were covered by highly reflective Cu films. Most of the Cu films are continuous without cracking and peeling off. Some differences in appearance exist in the same slide, such as slides 2 and 3. The general appearance of films in this group is very close to that of films using 30 s evaporation time, but the films appear to have a lower amount of cracking.

◊ Evaporation Time = 30 s. Films in this group are deposited under the conditions that were chosen for the baseline conditions for the further batch CVD study in the last section. We also present a picture of typical films in Fig. 7-13 (c). As described in the last section, the films are uniform but have a great deal of cracking.

According to the above observation, we believe that 15 s evaporation time is the shortest time to deliver enough precursor into the reactor for producing continuous Pd seed layers for the subsequent ELD Cu films. At shorter evaporation time, the amount of delivered precursor is not enough to deposit continuous Pd seed layers to produce continuous ELD Cu films. At this evaporation time the Cu films show less cracking than the films using longer evaporation time.
(a) Evaporation Time = 7.5s

(b) Evaporation Time = 15s

(c) Evaporation Time = 30s

Fig. 7-13 Effects of Precursor Evaporation Time on ELD Cu Film Appearance

◊ **Growth Kinetics.** Two parameters, including film appearance time and film thickness, were recorded during the ELD Cu experiments. We calculated the film growth rate by dividing the film thickness to appearance time. The detailed results are described as below:

◊ **Appearance time.** Figure 7-14 shows the appearance time for ELD Cu films. The solid symbols in the figure represent the individual experimental results, and the open larger symbols are the average appearance time for each group. The average times are 54 ± 9, 54 ± 13, 53 ± 18, and 65 ± 27 seconds for 4, 7.5, 15, and 30 seconds precursor evaporation time, respectively. An F-value of 1.98 with a non-significant p value of 0.123 was obtained from
ANOVA. We conclude that there is no significant difference between the four mean appearance times with an $\alpha$ level of 0.05.

![Graph showing effects of precursor evaporation time on Cu ELD time.](image)

Fig. 7-14 Effects of Precursor Evaporation Time on Cu ELD Time

◊ **Film Thickness.** Figure 7-15 presents the measured thickness of the Cu ELD films deposited on glass substrates prepared using different precursor evaporation times. The four average thicknesses are $120 \pm 24$, $146 \pm 36$, $164 \pm 47$, and $155 \pm 47$ nm for 4, 7.5, 15, and 30 seconds precursor evaporation time, respectively.

One-way ANOVA gives us an F-value of 3.2, which corresponds to a p value of 0.03. This suggests that some difference exists between these four mean film thicknesses at 95% significant level. Tukey-Kramer HSD shows that the average thicknesses of films using 4 and 15 seconds evaporation times are significantly different. All the other pairs have no significant difference. From Fig. 7-15 we notice that the average film thickness goes through
a maximum as a function of precursor evaporation time, and the largest average thickness is from the group of 15 seconds evaporation time.

![Graph showing the effects of precursor evaporation time on Cu film thickness.](image)

Fig. 7-15 Effects of Precursor Evaporation Time on Cu Film Thickness

◊ **Film Growth Rate.** Figure 7-16 shows the calculated film growth rates of Cu ELD films deposited on glass substrates prepared using different precursor evaporation times. The four average growth rates are $2.34 \pm 0.79$, $2.96 \pm 1.25$, $3.38 \pm 1.43$, and $2.79 \pm 1.43$ nm/s for 4, 7.5, 15, and 30 seconds precursor evaporation time, respectively. After combining the effects of Fig. 7-14 and Fig. 7-15, we find that the growth rate has a more scattered distribution. Thus one-way ANOVA gives an F-value of 2.13, which corresponds to a non-significant p value of 0.10. We conclude that there is no significant difference in these four average growth rates. Similar to the film thickness, we notice that the largest average film growth rate is the group using 15 seconds as the evaporation time.
Fig. 7-16 Effects of Precursor Evaporation Time on Cu Film Growth Rate

- **Resistivity.** Figure 7-17 shows the measured film resistivities of Cu ELD films deposited on glass substrates prepared using different precursor evaporation times. The ELD Cu films on the substrates activated using 4 seconds evaporation time contain too many voids to be measured by 4-point probe. The other three mean film resistivities are $16.1 \pm 3.9$, $3.58 \pm 1.38$, and $12.2 \pm 5.5 \, \mu\Omega\text{-cm}$ for 7.5, 15, and 30 seconds precursor evaporation time, respectively.

From Fig. 7-17, we find that all the average resistivities are larger than the bulk Cu resistivity value. However, the Cu films deposited on the substrates using 15 seconds as precursor evaporation time have the lowest resistivity value. This is statistically confirmed using Tukey-Kramer HSD method. The resistivities of the films on substrates using 7.5 or 30 seconds as evaporation time are not significantly different.
The lowest resistivity with 15 seconds evaporation time is still about 2 times higher than bulk Cu value. As shown in Fig. 7-13 (b), most of the Cu films in this group are visually continuous, and some are cracked but still locally continuous in the measuring range of the 4-point probe. We speculate that the increase of resistivity is due to non-visible micro-crevices in the films. For the films using 7.5 and 30 seconds precursor evaporation time, as shown in Fig. 7-13 (a) and (c), the films have a great deal of cracking and delaminating. We believe this is the reason for the high increase of the resistivity value for these Cu films.

Optimum Evaporation Time. After we compared the visual appearance of the obtained ELD Cu films, we believe that the Pd seed layers using 15 seconds precursor evaporation time generate Cu films with the best visual appearance and the least film cracking and delaminating. Although we can not claim that the effects of evaporation time on the film
deposition rate are statistically significant because of the scattering of the data distribution, we find that the average growth rate with 15 seconds evaporation time is the largest among the four mean values. Furthermore the Cu films with 15 seconds evaporation time have the lowest resistivity, and the resistivity value is relatively close to the bulk Cu resistivity. Thus we decide to choose 15 seconds as the new baseline precursor evaporation time for the further study on the batch CVD activation step.

7.6 Characterization of Palladium Seed Layers

In this section we discuss the characterization results of Pd seed layers. The samples were deposited by the batch Pd CVD step using different precursor evaporation times, in order to deliver different amounts of Pd(hfac)$_2$ into the reactor to form the Pd seed layer. We used X-ray photoelectron spectroscopy (XPS) to find the elemental composition and the equivalent thickness of Pd seed layer on the glass substrate. We also used scanning electron microscopy (SEM) and atomic force microscopy (AFM) to examine the surface morphology.

• **Experimental.** The Pd seed layers were deposited using the same apparatus and operating conditions as in the previous section. The details about the operating conditions are listed in Table 7-7. These operating conditions are applied as the baseline conditions for the further experiments on the batch Pd CVD step.

The XPS experiments were performed using an AXIS 165 XPS instrument from Kratos Analytical, which is equipped with a monochromatic Al kα x-ray source and a spherical mirror analyzer. The XPS machine is located in the Material Characterization Center of LSU. All XPS measurements were made at a takeoff angle of 90° in order to obtain
maximum signal intensities. Operating pressure of the system during the sample measurement was about $10^{-8} – 10^{-9}$ Torr.

The plan-view SEM images for the same samples were taken using a Hitachi 3600 SEM equipment, which is located in the Material Characterization Center of LSU. Since the samples are glass substrates, low vacuum (50 – 60 Pa) and environmental secondary electron detector (ESED) were applied during the sample measurement. All the SEM images were obtained using a working distance of 10 mm and a magnification factor of 8000.

The same samples were also analyzed using AFM, which was performed using a Nanoscope III multimode instrument from Digital Instruments. The AFM instrument is located in the Chemistry Department of LSU. A scan size of $10 \times 10 \mu m$ was obtained with the vendor’s software and a J-type piezoelectric scanner. All the analysis was performed in contact mode using a silicon cantilever (NSC15/3, MikroMasch), which has a radius of curvature of 10 nm. After capturing the AFM images, a flattening procedure was performed, and the dimensions of the aggregates were determined using the manufacturer’s software.

• **Results.** We analyzed Pd seed layers activated using three different precursor evaporation times, i.e., 4, 7.5 and 15 seconds. We will first discuss the XPS results, which include elemental composition and Pd atomic coverage. Then we will show the plan-view SEM images and some qualitative results from these images. At last we will present the AFM results about surface roughness, Pd particle grain size, and Pd coverage on the substrate.

• **XPS Analysis.** Figure 7-18 shows the XPS spectrum of Pd seed layers deposited using different precursor evaporation times. The peaks have been labeled, indicating the presence of O, Pd, Si, and C. The major elements are Si and O, which are the main
components of the glass substrate. The signal intensities of Si and O do not change with the variation of the precursor evaporation time, which suggests that the substrate surface is not heavily covered by the Pd seed atoms. Carbon is also present in significant amounts. This C does not appear to be due to the decomposition of the precursor, since we did not observe the F 1s peak at binding energy of 686 eV. Instead we propose that C occurs because the substrate was exposed to the air for several days before it was analyzed by XPS.

The Pd 3d peak region is shown in the inset of Fig. 7-18. We find that the binding energy of Pd 3d_{5/2} peak (336 eV) has shifted about 1eV compared to the peak position from the metal palladium 3d_{5/2} peak (334.9 eV). The binding energy of Pd 3d_{3/2} peak (341.8 eV) has also shifted from its metal state position (340.1eV). This suggests that some of the Pd atoms may have been oxidized to palladium oxide (Pd 3d_{5/2} = 336.3 ± 0.5 eV for PdO), or the Pd atoms are in direct contact with the O atoms of the SiO_2 substrate.

![Fig. 7-18 XPS of CVD Pd Activated Glass Substrates](image-url)
The inset of Fig. 7-18 also shows that the intensity of the Pd 3d peak increases when the precursor evaporation time increases. This confirmed quantitatively by the atomic composition information listed in columns two through four of Table 7-8. The atomic fraction of each element, \(X_i\), is calculated as the ratio of the integrated peak intensity, \(I_i^{\text{obs}}\), divided by the reference intensity of the pure element, \(I_i^{\infty}\):

\[
X_i = \frac{I_i^{\text{obs}}}{I_i^{\infty}}
\]  

(Eq. 7-1)

Equation (7-1), i.e., the atomic fraction, is evaluated for each element using the software package in the XPS operating system.

As seen in the second column of Table 7-8, the Pd atomic concentration increases from 0.57 to 2.76\% when the precursor evaporation time is increased from 4 to 15 seconds. These listed values are based on 2 samples each for 4 s and 7.5 s evaporation times, and 4 samples using 15 s evaporation time.

<table>
<thead>
<tr>
<th>Evaporation Time (s)</th>
<th>Atomic Percent</th>
<th>Pd Equivalent Thickness (nm)</th>
<th>Equivalent Pd Monolayer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd</td>
<td>Si</td>
<td>O</td>
</tr>
<tr>
<td>4</td>
<td>0.57 ± 0.29</td>
<td>32.0 ± 0.6</td>
<td>67.4 ± 0.3</td>
</tr>
<tr>
<td>7.5</td>
<td>0.81 ± 0.03</td>
<td>31.7 ± 1.2</td>
<td>67.5 ± 0.2</td>
</tr>
<tr>
<td>15</td>
<td>2.76 ± 1.31</td>
<td>30.4 ± 1.9</td>
<td>66.8 ± 0.9</td>
</tr>
</tbody>
</table>

We also plotted the Pd atomic percent as a function of precursor evaporation time in Fig. 7-19. We fitted the data as a linear function of the evaporation time, and the results
suggest that the amount of Pd seeds on the substrate increase linearly as a function of the amount of the precursor delivered into the reactor.

Because the Pd atoms are deposited on the surface of the SiO$_2$ substrate, it is more useful to present the Pd loading results in terms of equivalent layer thickness. This can be done assuming the Pd atoms are distributed as a uniform layer of thickness, $t_{\text{Pd}}$. The thickness is then given by (Hill, 1976):

$$t_{\text{Pd}} = \lambda_{\text{Pd}} \sin \theta \ln \left( \frac{X_{\text{Pd}}}{X_{\text{Si}}} + 1 \right) \text{ (nm)}$$  

(Eq. 7-2)

Here $\theta$ is the angle between the sample surface plane and the electron analyzer ($\theta = 90^\circ$ for our instrument), and $X_i$ is the atomic fraction of Pd and Si described above. The remaining parameter, $\lambda_{\text{Pd}}$, is the mean free path of photoelectrons traveling through the Pd surface layer. We have calculated a value of $\lambda_{\text{Pd}} = 1.509 \text{ nm}$ using the correlation reported by Seah and Dench (1979).

The calculated equivalent thicknesses of Pd seed layers using different precursor evaporation times are listed in the fifth column of Table 7-8. We see that all the equivalent thickness values are much smaller than the Pd monolayer thickness, which is about 0.245 nm. This means that not all the substrate surface can be covered by Pd atoms. Therefore in the final column of Table 7-8 we also present the Pd coverage in terms of the fraction of an equivalent monolayer. This is calculated by dividing the Pd equivalent thickness by the Pd monolayer thickness. The equivalent Pd monolayer increased significantly from 0.109 to 0.542 when the precursor evaporation time is increased from 4 to 15 seconds.
SEM Results. The plan-view SEM images of the Pd seed layers deposited using different precursor evaporation times are shown in Fig. 7-20. The images show mainly isolated Pd clusters that are distributed randomly over the glass substrate. We have some difficulties in obtaining quantified results about cluster size distributions using some analysis software, such as ImageJ from NIH, because of the quality of the SEM images. Qualitatively the sizes of Pd clusters using different precursor evaporation time are very close. The nuclei densities using 4 and 7.5 s evaporation times are very close, and they are much lower than that from 15 s evaporation time. These qualitative results are consistent with the results from the AFM analysis (see below), which provided quantified cluster size distributions and nuclei densities.
AFM Results. Figure 7-21 shows the topographical images of Pd seed layers deposited using different precursor evaporation times. The Pd deposits are clearly identified as small particles adhered on the substrate surface. We speculate the big islanded particles in Fig. 7-21(a) were contaminates. Although similar surface morphologies of the activated substrates were obtained by the batch CVD process with different precursor evaporation times, the nucleus densities of Pd particles were increased from about 1 to 14/µm² when the evaporation times increased from 4 s to 15 s. The Pd nucleus densities for Fig. 7-21 (a) to (c) are listed in the column 2 of Table 7-9.
The mean diameters of the Pd particles in Fig. 7-21 (a) to (c) were analyzed using a program named ImagJ from NIH. Figure 7-22 shows the statistical results of Pd seeds under different evaporation times, i.e., using different batch precursor concentrations. The three mean diameters are also presented in the column 3 of Table 7-9. All the three diameters are close to 80 nm, and they are not significantly different. Thus it indicates that the precursor evaporation time has no significant effects on the size of the Pd seeds, given that they were activated using the same activation temperature and holding time.

Fig. 7-21 AFM Images of Pd Seed Layers using Different Evaporation Time
(a) 4 s; (b) 7.5 s; (c) 15 s
Table 7-9 Surface Morphology Analyses of Pd Seed Layers using AFM

<table>
<thead>
<tr>
<th>Evaporation Time (s)</th>
<th>Particles in 100 µm²</th>
<th>Pd Grain Size (nm)</th>
<th>RMS (nm)</th>
<th>Coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Diameter</td>
<td>Height</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>82</td>
<td>88 ± 28</td>
<td>5.69 ± 3.45</td>
<td>9.5</td>
</tr>
<tr>
<td>7.5</td>
<td>215</td>
<td>79 ± 40</td>
<td>5.72 ± 2.38</td>
<td>2.5</td>
</tr>
<tr>
<td>15</td>
<td>1375</td>
<td>74 ± 22</td>
<td>6.10 ± 2.86</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Fig. 7-22 Effects of Precursor Evaporation Time on Pd Particle Size

The mean size of Pd particles in this study is about the same as the Pd seeds activated using Sn/Pd sensitization activation method on TaN surface (AFM analysis, Hsu et al 2002) and the Pd seeds using displacement activation method on Ta surface (SEM analysis, Hsu et al, 2001) or TaN surface (SEM analysis, Hong et al 2002). However, Chang et al (2004) reported that they could prepare Pd seeds on TaN with size about 10 nm using sensitization
activation method, and the Pd nucleus density was about $10^3/\mu m^2$. Compared to this study, the much lower activation temperature in their experiments (65°C) might reduce the agglomeration of Pd clusters, and then produce Pd seeds with higher nucleus density and smaller grain size.

The surface roughness is obtained as root mean square (RMS) value using the vendor’s software. The three RMS roughnesses are listed in the column 5 of Table 7-9. We speculate that the two large islands at the center of the scanning area dramatically increased the RMS value for 4 s evaporation time sample. This is verified by the mean heights of the Pd particles (column 4 of Table 7-9). These mean heights were obtained using the software provided by the AFM vendor, and all these three mean grain heights are close to 6 nm.

The Pd coverage on the substrate is the fraction of the scanning area covered by Pd grains (obtained by ImageJ). The three mean values are listed in the column 6 of Table 7-9. We also plotted them in Fig. 7-23 as the function of the precursor evaporation time, and fitted the data as a linear function of the evaporation time. The fitted results indicate that the superficial coverage of Pd seeds on the substrate will increase linearly as a function of the amount of the precursor delivered into the reactor.

It is also possible to reconcile the AFM results with the XPS signal intensities given above. We can calculate the expected XPS intensity ratio for Pd and Si if we know the coverage of each component and the thickness of the Pd seed layer using the following equations (Seah, 1983):

$$\frac{I_{obs}^{Pd}}{I_{Pd}^\infty} = \theta_{Pd}\left[1 - \exp\left(-\frac{h_{Pd}}{\lambda_{Pd}}\right)\right] \quad (Eq. 7-3a)$$
Fig. 7-23 Effects of Precursor Evaporation Time on Pd Coverage

\[
\frac{I_{\text{Si}}^{\text{obs}}}{I_{\text{Si}}^{\infty}} = (1 - \theta_{\text{Pd}}) + \theta_{\text{Pd}} \exp \left( -\frac{h_{\text{Pd}}}{\lambda_{\text{Pd}}} \right)
\]  
(Eq. 7-3b)

Here \(I_{\text{Si}}^{\text{obs}}\) and \(I_{\text{Si}}^{\infty}\) are the observed peak intensity and reference intensity for Pd or Si, \(\theta_{\text{Pd}}\) is the coverage of Pd clusters on the substrate surface, \(h_{\text{Pd}}\) is the Pd grain height, and \(\lambda_{\text{Pd}}\) is the meaning free path of photoelectrons traveling through the Pd surface layer.

We present the results about intensity ratios of Pd and Si in Fig. 7-24, from which we find that the calculated mean values from AFM are all smaller than the XPS results and the differences are all very close regardless of the precursor evaporation times. From AFM analysis (Fig. 7-21), we know that only a small percent of substrate surface is covered by Pd clusters. We speculate that some very small Pd clusters or Pd atoms are adsorbed separately on these open areas, because the nucleus density is not high enough to let them coalesce and form big Pd clusters. AFM technique can not detect these clusters and atoms because of the
resolution of its contact tip. However XPS is a bulk surface analysis technique to allow it to
detect all the Pd on the substrate. This also can explain the peak shift of the binding energy of
Pd 3d$_{5/2}$ since these Pd are in direct contact with the O atoms of the SiO$_2$ substrate.

![Graph showing intensity ratio of Pd and Si from XPS and AFM analysis]

**Fig. 7-24 Comparison of Intensity Ratio of Pd and Si from XPS and AFM**

### 7.7 Water Vapor and Isopropanol Effects

In section 7.5, we determined the baseline conditions for depositing Pd seed layers on
glass substrates using the batch CVD process. We were able to electrolessly deposit uniform
Cu films on these Pd seed layers in the electrolyte solution. However the ELD Cu films still
have some cracking after they were dried in the air.

The Pd seed layer can determine the quality of the subsequent ELD Cu film, so one of
the methods to improve the properties of the ELD Cu films might be to improve the quality of
the Pd seed layer. Water and alcohols are widely accepted as co-reactants to improve the film
nucleation quality and growth rate for Cu CVD process using the reduction of Cu(hfac)$_2$ (Lecohier et al, 1991; Cho, 1992; Borgharkar et al, 1999). In this section, we will test both water vapor and isopropanol as an additive during the batch Pd CVD process to find their effects on the Pd seed layer.

- **Experimental.** The activation step was performed using the same horizontal flow APCVD reactor as in section 7.5. The operating conditions for the batch activation step are listed in Table 7-10. Two evaporation temperatures were used for H$_2$O or i-PrOH evaporator: room temperature and 35°C. The latter temperature is low enough that heat tracing of the line between the evaporator and reactor was not necessary.

Table 7-10 Operating Conditions of Activation Step for Additive Effect

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(hfac)$_2$ Evaporation Temperature</td>
<td>70°C</td>
</tr>
<tr>
<td>Pd(hfac)$_2$ Pulse Time</td>
<td>15 s</td>
</tr>
<tr>
<td>Activation Temperature</td>
<td>180°C</td>
</tr>
<tr>
<td>Holding Time</td>
<td>5min</td>
</tr>
<tr>
<td>System Pressure</td>
<td>760 Torr</td>
</tr>
<tr>
<td>Additive Evaporation Temperature</td>
<td>25 or 35°C</td>
</tr>
</tbody>
</table>

- **Results.** As shown in Table 7-10, we have examined two different evaporation rates for H$_2$O or i-PrOH using two different evaporation temperatures. We will first discuss the visual appearance of ELD Cu films on the Pd seed layers. Then we will present the kinetic results, i.e., film appearance time, thickness, and growth rate. All the results are compared to
the baseline results without using H₂O or i-PrOH as additive, in order to determine if H₂O vapor or i-PrOH has positive effect on the quality of the Pd seed layer.

- **Visual Appearance.** We were able to deposit metallic shiny Cu films on the Pd seed layers using both evaporation temperatures for either H₂O or i-PrOH. The general appearance of the Cu films produced during the ELD treatment and after drying using different additive evaporation temperatures is similar. The Cu films were continuous and uniform when they were still in the electrolyte Cu solution. The Cu films began to crack after they were removed from the solution and rinsed by DI water. All of the finally dried Cu films have a similar amount of cracking compared to the Cu films on the Pd seed layers using baseline conditions (i.e., without H₂O vapor or i-PrOH).

- **Growth Kinetics.** We recorded two parameters: film appearance time and thickness, during the ELD experiments. We calculated the film growth rate by dividing the film thickness by the appearance time. The detailed results are described as below:

  - **H₂O as additive.** ◇ **Appearance time.** Figure 7-25 shows the appearance time for ELD Cu films. The horizontal axis of Fig. 7-25 is a categorical data set. The values 1, 2, and 3 represent the baseline condition without H₂O, the baseline with H₂O vapor using 25°C evaporation temperature, and the baseline with H₂O vapor using 35°C evaporation temperature, respectively. The average times are 53 ± 18, 44 ± 12, and 42 ± 12 seconds for without H₂O, 25°C H₂O, and 35°C H₂O, respectively. From the figure, we notice the longest appearance time is for the ELD Cu films deposited on the substrate using baseline condition without H₂O vapor additive. This is confirmed statistically using Tukey-Kramer HSD method.
Fig. 7-25 Effects of H₂O Vapor on Cu ELD Time

◊ **Film Thickness.** Figure 7-26 shows the measured thickness of the Cu ELD films. The horizontal axis has the same meaning as in the Fig. 7-25. The three average thicknesses are 164 ± 47, 154 ± 48, and 134 ± 35 nm for without H₂O, 25°C H₂O, and 35°C H₂O, respectively. These three mean thicknesses are not significantly different at 95% confidence level with a p-value of 0.08.

◊ **Film Growth Rate.** Figure 7-27 shows the calculated film growth rates of Cu ELD films deposited on Pd seed layers with or without H₂O additive. The three average growth rates are 3.38 ± 1.43, 3.71 ± 1.49, and 3.26 ± 1.00 nm/s for without H₂O, 25°C H₂O, and 35°C H₂O, respectively. One-way ANOVA gives a small F-value of 0.38, which corresponds to a highly non-significant p value of 0.69. We conclude that there is no significant difference in these three average growth rates.
Fig. 7-26 Effects of H₂O Vapor on Cu Film Thickness

Fig. 7-27 Effects of H₂O Vapor on Cu Film Growth Rate
i-PrOH as additive. ♦ Appearance time. Figure 7-28 shows the appearance time for ELD Cu films. The values 1, 2, and 3 of the horizontal axis represent the baseline condition without i-PrOH, the baseline with i-PrOH using 25°C evaporation temperature, and the baseline with i-PrOH using 35°C, respectively. The average times are 53 ± 18, 53 ± 9, and 42 ± 7 seconds for without i-PrOH, 25°C i-PrOH, and 35°C i-PrOH, respectively. From the figure, we find the shortest mean appearance time is from the ELD Cu films deposited on the substrate using baseline condition with 35°C i-PrOH vapor. This is confirmed statistically using Tukey-Kramer HSD method.

◊ Film Thickness. Figure 7-29 shows the measured thickness of the Cu ELD films. The horizontal axis has the same meaning as in the Fig. 7-28. The three average thicknesses are 164 ± 47, 163 ± 24, and 145 ± 32 nm for without i-PrOH, 25°C i-PrOH, and 35°C i-PrOH,
respectively. These three mean thicknesses are not significantly different at 95% confidence level with a p-value of 0.21.

![Graph showing Cu Film Thickness vs Additive](image)

**Fig. 7-29 Effects of i-PrOH Vapor on Cu Film Thickness**

◊ **Film Growth Rate.** Figure 7-30 shows the calculated film growth rates of Cu ELD films deposited on Pd seed layers with or without i-PrOH additive. The three average growth rates are $3.38 \pm 1.43$, $3.18 \pm 0.61$, and $3.53 \pm 0.98$ nm/s for without i-PrOH, $25^\circ C$ i-PrOH, and $35^\circ C$ i-PrOH, respectively. One-way ANOVA gives a small F-value of 0.32, which corresponds to a highly non-significant p value of 0.73. We conclude that there is no significant difference in these three average growth rates.

◊ **Comments on the Effect of Additives.** After we compared the visual appearance of Cu films on Pd seed layers activated using H$_2$O vapor or i-PrOH as additive during the batch CVD process, we conclude that H$_2$O vapor or i-PrOH does not have significant effect on the
quality of the obtained Pd seed layers. This is also reflected by the results from ELD Cu film growth kinetics. The Cu film growth rates on Pd seed layers using either 25°C or 35°C additive’s evaporation temperature are not statistically different. Both the growth rates using H₂O or i-PrOH vapor are also not statistically significant from the Cu growth rate without using additive. Thus we conclude that H₂O or i-PrOH did not improve the quality of Pd seed layer.

Fig. 7-30 Effects of i-PrOH Vapor on Cu Film Growth Rate
CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes the studies done in this dissertation and presents the conclusions based on these studies. We also give some recommendations for future work.

8.1 Conclusions

- **Alcohol-Assisted Copper CVD.** We have investigated the CVD copper films deposited on the glass substrate using Cu(hfac)$_2$ dissolved in isopropanol solution as liquid precursor. The solution delivery system was built around a high pressure liquid chromatography pump. For base case conditions with partial pressures of 0.025 Torr Cu(hfac)$_2$, 1.6 Torr isopropanol and 80 Torr H$_2$ and a deposition temperature of 300°C, we observe a growth rate of 17.7 ± 1.5 nm/min. This growth rate is similar to those observed using conventional precursor delivery method, like solid sublimation, with the additional benefits of easy and precise precursor transport. Moreover this growth rate is achieved by using a much lower partial pressure of precursor in the reactor compared to those solid sublimation methods.

We also studied the kinetics of Cu CVD using different reactant partial pressures. The partial pressure of Cu(hfac)$_2$ is varied from 0.0063 to 0.05 Torr. The observed growth rates (5 to 19 nm/min) initially increase linearly with partial pressure of Cu(hfac)$_2$, then begin to saturate when the pressure of Cu(hfac)$_2$ is higher than 0.025 Torr. The growth rate is nearly independent of the partial pressures of isopropanol and H$_2$ over the range of operating conditions examined (0.8 to 3.2 Torr for isopropanol, and 40 to 160 Torr for H$_2$). Copper CVD experiments are also performed using N$_2$ as carrier gas with baseline conditions for other reactants. Similar growth rate is obtained compared to the rate with H$_2$ gas, but the visual appearance of films is much worse than those using H$_2$ as carrier gas.
The measured film resistivity is close to copper bulk value of 1.67 $\mu\Omega\cdot$cm when the film thickness is greater than about 100 nm. This critical thickness value is much lower than those from the research with H$_2$ alone; this suggests the presence of isopropanol can improve the deposited film quality. The film resistivity is largely unaffected by the deposition conditions, with some evidence that higher H$_2$ partial pressure might improve copper film properties.

- **Mechanistic Model for Copper CVD.** We proposed a series mechanism model with two surface intermediates to explain the observed kinetic results. The two intermediates are adsorbed Cu(hfac)$_2$ molecule and (hfac) ligand. The series mechanism includes three kinetically significant elementary steps: the adsorption of Cu(hfac)$_2$ molecule on clean surface from bulk gas phase, the dissociation of adsorbed Cu(hfac)$_2$ to Cu(hfac) and (hfac), and the desorption of (hfac) in the form of H(hfac) via the proton transfer between isopropanol and (hfac) ligand. Optimized rate constants were determined by fitting the mechanism to the observed Cu growth rates. We concluded that the proposed series mechanism can represent the first-order behavior with respect to Cu(hfac)$_2$ and zero-order behavior with respect to isopropanol as seen in the present study using low ratios of Cu(hfac)$_2$ to isopropanol partial pressure. The series mechanism also shows a positive-order behavior with respect to isopropanol as seen in a previous study using higher ratios of Cu(hfac)$_2$ to isopropanol partial pressures (Borgharkar et al, 1998b).

- **Tantalum CVD.** We have examined a low temperature CVD process for the growth of tantalum thin film using silane (SiH$_4$) reduction of tantalum pentafluoride (TaF$_5$). A pedestal reactor system was built in house for this purpose. We also applied a commercial chemical thermodynamic package to perform yield calculations for the TaF$_5$ + SiH$_4$ reaction
system to determine the SiH$_4$/TaF$_5$ inlet composition ratios needed to produce silicide free Ta film. The calculated SiH$_4$/TaF$_5$ inlet composition ratios are less than 1.25. Using a temperature of 350°C and reactant partial pressures of 200 mTorr TaF$_5$, and 300 mTorr SiH$_4$, we obtained a growth rate of $0.215 \pm 0.168$ mg cm$^{-2}$ h$^{-1}$ (ca. $2.2 \pm 1.7$ nm min$^{-1}$). The x-ray photoelectron spectroscopy analysis results showed that the Ta film was Si free, but contained relatively high oxygen concentration, probably because of residual gas contamination.

- **CVD Palladium Seed Layer for ELD Copper.** Finally, we developed a batch CVD process to deposit nano-sized Pd particles to use as seed layers for continuous CVD Pd films or electroless copper deposition. An APCVD reactor with a flat strip heater was assembled in house for this purpose. The continuous CVD Pd experiments on batch activated glass substrates were performed under a 200 Torr system pressure, a 110°C deposition temperature, and a 70°C precursor evaporation temperature. Because the deposition was under mass transport limited conditions, a rapid decay of film thickness along the axial reactor was observed even after the nucleation barrier was removed by the batch activation step. We developed a simple reactor transport model to simulate the thickness profile along the reactor. The model is able to predict the observed rapid axial decay profile, and also provide a reasonable quantitative agreement with observed results for the activated deposition process.

We also investigated the Pd seed layers for electroless Cu deposition. Based on the visual quality of deposited copper films and the deposition rate, we have found an optimized combination of operating conditions as baseline procedure for the future study: holding time = 5 min, activation temperature = 180°C, precursor evaporation time = 15 s, and evaporation temperature = 70°C. The visual appearance of the ELD Cu films obtained using baseline
conditions was smooth, shiny, and continuous in the electrolyte solution, but with some cracking after the drying. The electroless deposition rate was $3.38 \pm 1.43 \text{ nm/s}$.

The atomic composition and morphology of the Pd seed layer were examined using XPS and AFM, respectively. The samples were prepared using the baseline activation temperature and holding time, but with 4, 7.5 and 15 seconds precursor evaporation times. XPS analysis shows that the amount of Pd seeds on the substrate increase linearly as a function of the amount of the precursor delivered into the reactor (i.e., the precursor evaporation time). AFM results suggest that the precursor evaporation time has no significant effects on the grain size and height of Pd seeds. However, the nucleus densities of Pd seeds increase from about 1 cluster/µm$^2$ to 14 clusters/µm$^2$ when the evaporation time is increased from 4 to 15 s.

Finally, we tested the addition of H$_2$O or i-PrOH into the reactor during the batch CVD activation process in order to improve the quality of Pd seed layers and obtain crack-free electroless copper films. After comparing the visual qualities and the growth rates of electroless copper films, we found that neither of the additives has a significant effect on the Pd seed layers.

8.2 Recommendations

The recommendations for the future work apply to the continued study on the Pd seed layer for electroless Cu deposition. Improving the quality of Pd seed layers and the adhesion and resistivity of ELD Cu films will be the main studies in the future.

- **Pd Seed Layers.** Pd seeds determine properties of the subsequently electroless deposited Cu film because Cu nucleates on these seeds and then grows. Thus the preparation
of small and dense Pd decides the quality of electroless Cu films. From the AFM analysis results in section 7.6, we know that the Pd nuclei density from batch process CVD is much lower than that prepared by wet chemistry (Change et al, 2004), and the cluster size is much larger than that reported by the same authors. We speculate that the agglomeration of Pd seeds under high temperature in CVD preparation causes the large size of Pd seeds with low nuclei density. Based on the above facts, we recommend decreasing the activation temperature as low as possible but still high enough to reduce precursor to metal Pd.

- **Electroless Cu Deposition.** Adhesion and high electrical resistivity are the two main concerns for the current ELD Cu films. Improving the quality of Pd seed layer is the primary step to obtain better ELD Cu film. We also suggest lowering the deposition rate and adopting a post heat-treatment for as-deposited films.

Introducing additives to the Cu plating solution is able to decrease the Cu deposition rate, thus reducing the formation rate of H$_2$, one of the by-products of the electroless Cu using formaldehyde reduction of CuSO$_4$. It is believed that H$_2$ trapped between Cu and the substrate surface weakens the adhesion of the Cu film. The accumulation of H$_2$ on the Cu surface will also increase the possibility of blister formation, and it will increase the roughness of Cu films (Nakahara et al, 1983). We suggest adding 2-2’-dipyridyl, a widely used stabilizer, into the current Cu solution to reduce the effect of H$_2$ gas release. We also propose to study the concentration effects of 2-2’-dipyridyl on the quality of Cu film in future.

Annealing as-deposited ELD Cu film is another method to improve the adhesion and decrease the Cu resistivity. Hsu et al (2001) reported that the resistivity of as-deposited ELD Cu film on Cu$_{seed}$/Ta/SiO$_2$/Si substrate was lowered from 4.8 to 1.8 $\mu\Omega$-cm after it was annealed 60 min at 400°C in N$_2$/H$_2$. So we suggest that after we obtain crack-free Cu films
dried atmospherically, an annealing step should be adopted to test if this step could decrease the ELD Cu resistivity. If we obtain positive result, we should continue to find an optimized combination of annealing conditions.
REFERENCES


Chin, B.L.; Yao, G.; Ding, P.; “Barrier and Seed Technologies for Sub-0.10 µm Copper Chips”, *Semiconductor International*, May, 107-113 (2001).


JCPDS Standard Diffraction File No. 4-0838.


Veeco Instrument Inc, “Model FPP-100 Four Point Probe Operation and Maintenance”.


APPENDIX: MASS TRANSFER LIMITED MODEL FOR PD CVD

In this section, we describe the mass transfer limited model for simulating the thickness profile of CVD Pd films presented in Chapter 7.2. These films were deposited under transport-limited conditions on glass substrates that were pre-activated using the batch Pd CVD step. We will present the model and its assumptions first, and then we will describe the numerical discretization of the model. The estimation of the gas velocity and the precursor diffusivity will be discussed next. Finally we will present the calculated precursor concentration profile and the film thickness profile.

- **Description of Model.** The reactor used for Pd CVD is a horizontal glass tube with an inside diameter \( d \) of 2.3 cm. The strip heater that serves as the substrate holder is located at horizontal diameter of the tube. Thus the carrier gas flows through the upper half of the reactor with a height \( H \) of 1.15 cm. Seven substrates were placed on the strip heater. Each substrate is a square with a size of 1.8×1.8 cm, so the deposition length \( L \) along the main gas flow direction is 12.6 cm.

   The primary assumptions are: 1) the carrier gas obeys laminar flow along horizontal streamlines; 2) the concentration of precursor is zero along the bottom surface because of the fast reaction on the heated substrates; 3) the flux of Pd(hfac)_2 at the top surface is zero because there is no reaction on the reactor wall; 4) the precursor is introduced at the reactor inlet along the centerline of the carrier gas.

   The model is based on the precursor conservation equation, and includes transport terms for convection along the carrier gas streamlines \( (x \) direction) and diffusion along the perpendicular to the streamlines \( (y \) direction):
\[
\frac{\partial C_{Pd(hfac)_2}}{\partial t} = D_{AN} \frac{\partial^2 C_{Pd(hfac)_2}}{\partial y^2}
\]  

(A-1)

where \(v_x(y)\) is the parabolic velocity of the carrier gas and \(D_{AN}\) is the diffusivity of Pd(hfac)\(_2\).

The boundary conditions and the inlet condition are:

\begin{align*}
\text{B.C.1} & \quad \text{at } y = 0 & C_{Pd(hfac)_2} &= 0 \quad \text{(A-2a)} \\
\text{B.C.2} & \quad \text{at } y = H & \frac{\partial C_{Pd(hfac)_2}}{\partial y} &= 0 \quad \text{(A-2b)} \\
\text{I.C.} & \quad \text{at } x = 0 & C_{Pd(hfac)_2} &= C_{Pd(hfac)_2,0} \quad \text{if } y = H/2 \\
& & C_{Pd(hfac)_2} &= 0 \quad \text{elsewhere} \quad \text{(A-2c)}
\end{align*}

Equation (A-2a) and (A-2b) are two boundary conditions. Equation (A-2a) accounts for the assumption of fast deposition on the substrate surface, and equation (A-2b) accounts for the condition of no reactant flux through the reactor wall. Equation (A-2c) is the inlet condition, which reflects the assumption that the precursor is introduced at the reactor inlet centerline.

- **Computational Method.** The mass transfer limited model (Eq. A-1) is set up by applying a finite-difference discretization on the diffusion term in the vertical direction, and integrating the precursor concentration along the horizontal direction using the Runge-Kutta method. In the following, we will first form the finite difference equations by numerically differentiating the diffusion term in Eq. A-1, and then we will integrate the difference equations along the \(x\) direction.

- **Finite Difference Equations.** A maximum of 9 equally spaced grid points are used to define the concentration profile in the \(y\) direction, with numbering started at the substrate surface.

Applying the first boundary condition (Eq. A-2a), we obtain the equation for the precursor concentration at the substrate surface \((y = 0)\):
For streamlines numbered from 2 to 8, we model the diffusion term in Eq. A-1 using centered finite-divided-difference formulas (Chapra and Canale, 2002):

\[
v(y, i) \frac{dC_i}{dx} = D \frac{C_{i+1} - 2C_i + C_{i-1}}{h^2} \quad i = 2 \cdots 8 \tag{A-3b}
\]

For the flux at the reactor wall, we difference the second boundary condition (Eq. A-2b) using backward finite-divided-difference formulas (Chapra and Canale, 2002):

\[
\frac{dC_9}{dy} = 0 = 3C_9 - 4C_8 + C_7 \tag{A-4}
\]

Differentiating Eq. A-4 on \(x\), we obtain the model equation for the precursor concentration at the reactor surface:

\[
\frac{dC_9}{dx} = \frac{4}{3} \frac{dC_8}{dx} - \frac{1}{3} \frac{dC_7}{dx} \tag{A-3c}
\]

where \(\frac{dC_8}{dx}\) and \(\frac{dC_7}{dx}\) are from Eq. A-3b.

**Inlet Condition.** The initial conditions for integrating Eq. A-3 are based on the inlet condition (Eq. A-2c) which specifies that the precursor is introduced at the reactor inlet along the centerline of the carrier gas. Thus all the initial concentrations are zero except the center one. In order to satisfy the continuity equation, we substitute an artificial value for the inlet concentration of precursor at centerline:

\[
C_{s0} = \sum_i \frac{V_{xi}}{V_{s5}} C_{i0} \tag{A-5}
\]
Here $V_{sl}$ is the parabolic gas velocity at different streamlines, and $C_{A0}$ is the actual inlet concentration of the precursor. $C_{A0}$ is determined using the ideal gas law with the mean temperature of the substrate and the reactor wall and together with the evaporation partial pressure of Pd(hfac)$_2$ under 70°C (0.062 Torr, see Chapter 3.3.1). The obtained value is: $C_{A0} = 1.758 \times 10^{15}$ molecular/cm$^3$.

▫ **Parabolic Velocity Profile.** The laminar velocity formula in the rectangular system is:

$$v_x(y) = \frac{3}{2} u_{ave} \left( 1 - \left( \frac{y}{H} \right)^2 \right)$$

(A-6)

where $u_{ave}$ is the average velocity of carrier gas and $y$ is the distance to the centerline of the carrier gas in the $y$ direction.

Since the reaction is operated at low pressure, we can apply ideal gas law to relate the average velocity of carrier gas with the substrate temperature and the system pressure:

$$u_{ave} = \frac{Q}{A_c} \left( \frac{T}{273.15} \right) \left( \frac{760}{P} \right)$$

(A-7)

Here $Q$ is the total flow rate in sccm, $A_c$ is cross-section area (2.08 cm$^2$), $T$ is the temperature and $P$ is the pressure.

▫ **Binary Diffusion Coefficient of Pd(hfac)$_2$ in N$_2$.** The diffusivity of Pd(hfac)$_2$ (= A) in N$_2$, $D_{AN}$, is assumed to follow the Chapman-Enskog formulas (Bird et al, 2002):

$$D_{AN} = 0.0018583 \frac{T^2 \left( \frac{1}{M_A} + \frac{1}{M_N} \right)}{P \sigma_{AN}^2 \Omega_{D,AN}} \left( \frac{cm^2}{s} \right)$$

(A-8)
where $\Omega_{D,AN}$ is a dimensionless function of $\kappa T/\epsilon_{AN}$ given in Table E-2 in Bird et al (2002). Both $\sigma_{AN}$ and $\epsilon_{AN}$ are Lennard-Jones parameters that can be expressed by combining the Lennard-Jones parameters of $N_2$ and Pd(hfac)$_2$:

$$\sigma_{AN} = \frac{1}{2}(\sigma_A + \sigma_N) \quad \epsilon_{AN} = \sqrt{\epsilon_A \epsilon_N}$$ \hspace{1cm} (A-9)

For $N_2$, the parameters can be obtained from Table-E1 in Bird et al. As follows:

Molecular weight, $M_N = 28.01$ g/mole
Lennard-Jones parameter $\sigma_N = 3.667$ Å
Lennard-Jones parameter, $\epsilon_N/\kappa = 99.8$ K

For Pd(hfac)$_2$, some parameters can only be estimated using Equation 1-4-13 in Bird et al (2002) as follows:

Molecular weight, $M_A = 520.51$ g/mole
Lennard-Jones parameter $\sigma_A = 1.222V_{m,sol}^{1/3}$ Å
Lennard-Jones parameter, $\epsilon_A/\kappa = 1.92T_m$ K
molar density at melting point, $V_{m,sol} = \rho/M_A$ mole/cm$^3$
mass density at melting point, $\rho = 2.250$ g/cm$^3$
melting point, $T_m = 328$ K

Among the above parameters for Pd(hfac)$_2$, we have used the sublimation temperature as the melting point temperature, and the mass density at the melting point is adopted by using the bulk density at room temperature (Siedle et al 1983) because of the absence of the literature data for both the melting point and the melting density.
Based on the above information, the values for $\sigma_{AN}$ and $e_{AN}/\kappa$ are 5.584 Å and 250.7, respectively. From Table E2-2 in Bird et al., $\Omega_{D,AN} = 1.19$ at $T = 383$ K. Therefore, the estimation is $D_{AN} = 0.277$ cm$^2$/s.

• Results. We used the built-in integration function *rkfixed* from MathCAD 2001 to integrate Eq. A-3 along the $x$-direction. The followings are the results about the precursor concentration profile along the $x$-direction. We also present the method to estimate the film thickness profile in the second part of this subsection.

▫ Pd(hfac)$_2$ Concentration Profile. Figure A-1 shows the concentration profile of the precursor along the carrier gas flow direction. Two regions of concentration behavior are observed. An entrance region exists along the first 1 – 2 cm of the reactor. In this region, the precursor diffuses away from the inlet centerline and redistributes along the vertical cross-section of the reactor. For distance greater than 2 cm, the precursor concentration profile becomes semi-parabolic in shape and decays quasi-exponentially along the length of the reactor as precursor is consumed at the substrate surface ($y=0$).

▫ Film Thickness. The film deposition rate is equal to the diffusion rate of precursor at $y = 0$. The film thickness with molecule units is the product of the deposition rate and the deposition time ($t$):

$$n = -D_{AN} \left( \frac{\partial C_{Pd(hfac)_2}}{\partial y} \bigg|_{y=0} \right) t \quad (A-10)$$

The forward finite difference formula for the first derivative is:
Fig. A-1 Precursor Concentration Profile using Mass-Transfer Limited Model

\[ \frac{\partial C_{Pd(hfac)_2}}{\partial y} = -\frac{C_3 + 4C_2 - 3C_1}{2h} \]  

where \( C_1 \), \( C_2 \) and \( C_3 \) are the precursor concentration on the substrate surface, the concentration of one step above the surface, and the concentration of two steps above the surface, respectively.

We convert the results into length units using molecular weight \( (M_{Pd} = 106.42 \text{ g/mole}) \) and mass density \( (\rho_{Pd} = 12.02 \text{ g/cm}^3) \). The calculated film thickness profile is shown previously in Fig. 7-1. The maximum film thickness near the inlet is caused by the maximum in the precursor concentration profiles near the inlet for redistributing the inlet precursor across the whole cross section.
VITA

Lidong Wang was born in Ningbo city of Zhejiang Province, People’s Republic of China. He received his Bachelor of Science and Master of Science degrees from Tianjin University in July 1994 and February 1997, both in chemical engineering. In August 2000, he flew over the Pacific Ocean and joined the Department of Chemical Engineering at Louisiana State University. His dissertation research was focused on chemical vapor deposition of thin films (copper, tantalum, and palladium) for ULSI interconnect application under the guidance of Dr. Gregory L. Griffin. Lidong will receive the degree of Doctor of Philosophy at the May 2005 Commencement.