2000

Chemical Vapor Deposition of Copper Metal Using Copper(hexafluoroacetylacetonate)(2) Alcohol Adducts.

Hui Fan
Louisiana State University and Agricultural & Mechanical College

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CHEMICAL VAPOR DEPOSITION OF COPPER METAL
USING CU(HFAC)₂ ALCOHOL ADDUCTS

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 Department of Chemistry

by

Hui Fan
B.E. East China University of Chemical Technology, 1992
August, 2000
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ABSTRACT

A series of alcohol adducts of Cu(hfac)$_2$ (Cu(hfac)$_2$-ROH, where hfac$^-$ = hexafluoroacetylacetonate and ROH = C1, C2, C3, C4 alcohols) were synthesized as precursors for CVD of Cu metal. The low melting points of some Cu(hfac)$_2$-ROH adducts allowed 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 compounds as precursors under either H$_2$ or N$_2$ mixed with the corresponding alcohol vapor. The details of each CVD reaction were studied by IR analysis of byproducts and electrical and thickness measurements on the resulting films. A reaction scheme is proposed in which the alcohol acts as a reducing agent in the deposition of the Cu film.

Cu(hfac)$_2$-i-PrOH was identified as the most effective precursor for Cu CVD. An average growth rate of 1.3 ± 0.5 μm/hr was obtained for the films deposited using Cu(hfac)$_2$-i-PrOH + i-PrOH(g) + N$_2$. This growth rate is almost three times greater than that using Cu(hfac)$_2$ + H$_2$ (the best Cu(II) precursor previously known), under similar deposition conditions.

CVD experiments were also performed using Cu(hfac)$_2$-i-PrOH + i-PrOH(g) + (N$_2$ or H$_2$) on TiN or Pd-treated TiN surfaces. No continuous Cu films were deposited on either of these surfaces under N$_2$, but films were obtained under H$_2$. The Cu films showed faster and more uniform growth on PVD TiN than on CVD TiN substrates. The addition of i-PrOH increased the growth rate of Cu films on PVD TiN surfaces under H$_2$ (from 0.26 ± 0.04 μm/hr to 0.8 ± 0.3 μm/hr). The films deposited with i-PrOH also showed improved adhesion to the PVD TiN surface, as compared with those obtained in
the absence of the alcohol. Pre-treatment of TiN surface using Pd also led to somewhat improved film adhesion. However, the films deposited on such pre-treated substrates showed a higher resistivity than those deposited on clean TiN. Appropriate cleaning of the substrate was also critical for the deposition of good Cu films using Cu(hfac)$_2$·$i$-PrOH + $i$-PrOH(g) + H$_2$ on PVD TiN substrates.
CHAPTER 1 INTRODUCTION

Copper is a versatile metal. During the Chalcolithic Age, six millennia ago, Middle Eastern craftsmen used it for tools and ritual objects. And among the old alchemists (early chemists) it was the symbol of Venus.

Nowadays, when microelectronic devices have become an integral part of modern society, copper once again comes under the spotlight. It is because of the important role that it will play in the next revolution of microelectronics technology. Silicon-based integrated circuits (ICs) have come to the point where their performance cannot be further improved without replacing aluminum (Al), (now used as a conductor in ICs), with a superior one. Copper is the choice of materials for metallization in the new ICs due to its better physical properties.

As a result, research regarding the issues of copper metallization is intensively underway in both industrial and academic sectors. The deposition of copper using chemical vapor deposition (CVD) is one of the areas that has received much attention. In the past few years, I have been lucky enough to be involved in the work of developing new precursors for Cu CVD. The current writing covers my study on the subject.

Background information concerning Cu CVD is introduced in this chapter. First, chemical vapor deposition (CVD) is described in general. It is followed by discussion of Cu metallization and the damascene process, which is an IC fabrication process specially tailored for Cu metallization. Finally, the precursors for CVD processes in general and for Cu CVD in specific are reviewed.
1.1 Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition (CVD) is a technique for producing a solid film on a surface by chemical reactions of precursors from the vapor phase. But unlike traditional chemistry, in which the reactions happen in homogeneous solution or gas, CVD reactions happen on a two-dimensional solid surface, usually called the substrate. The chemical reactions can be initiated and maintained by heat (thermal CVD), photons (photo CVD), electrons, ions or in a plasma (plasma-enhanced CVD/PECVD). CVD is mainly used to produce thin films, whose thickness is on the order of 1 μm. Thin film materials find applications in a wide range of fields, such as optical coatings, wear-resistant surfaces, computer microchips and solar cells.

CVD is not the only available method for preparing thin films. The other common techniques include Physical Vapor Deposition (PVD) and electroplating. PVD is an atomistic deposition process in which atoms vaporized from source materials are transported to the substrate where they condense and film growth takes place. Unlike CVD, no chemical reactions are involved in the PVD process. High temperature and vacuum are usually required to generate the atoms of the precursor. Compared with other methods, chemical vapor deposition process holds some intrinsic advantages. The two most important advantages of CVD process are its abilities of conformal coverage and selective deposition, which make CVD a very attractive alternative for obtaining thin films.

Conformal coverage refers to the uniform coating of complex surface features. The conformality of the CVD process can be primarily attributed to the gaseous nature of the precursor (vapor). The diffusing ability of the precursor on the surface allows the
precursor to reach all areas of the substrate prior to the deposition reaction. Figure 1-1 illustrates schematically the films grown by PVD and CVD techniques on the same underlying topography. The CVD film more precisely reflects the underlying topography and more uniformly covers the wall and bottom of the trench.

![Figure 1-1. Illustration of Conformality of CVD and PVD Films on the Substrate](image)

Selective CVD refers to the preferential deposition of a film on one surface in the presence of another. Selectivity is closely related to the chemical properties of the precursor and is controlled by its tendency to interact with different surfaces. For example, in the case of copper CVD, copper metal often more easily deposits on conductive surfaces than on the dielectric ones. Selective deposition can be achieved by chemical treatment of the substrate, judicious choice of ligands on the precursor, and introduction of additional reactants into the system.

A CVD process can generally be divided into various sequential steps based on the physical and chemical status of the precursor. It involves the generation, transport and finally reaction of the precursor vapor. A more detailed sequence is depicted in Figure 1-2.
Figure 1-2. Flow Chart of CVD Process
The study of chemical vapor deposition is a multi-disciplinary area, which involves the understanding of mass and heat transfer (chemical engineering), molecular interactions (chemistry and surface physics), and film structure and properties (materials science). It also means studying the impact of various process parameters (substrate temperature, source temperature, carrier gas flow and reactor pressure) on key film properties, such as resistivity, step coverage, film purity, growth rate, structure and morphology.

1.2 Copper and Integrated Circuits

Modern integrated circuits (ICs) are built from three categories of materials: conductors (Al, Cu, W), semiconductors (Si) and dielectrics (e.g. SiO₂). Each of them plays an equally important role to make the ICs function properly. The conductors are used as interconnects linking the electronic devices inside the circuits. Aluminum (Al) metal is used as interconnect material in nearly all current ICs. In order to further improve the performance of integrated circuits, the IC’s feature size needs to be further scaled down. Based on this consideration, the semiconductor industry is developing the next generation of ICs, the ultra-large-scale integrated circuits (ULSI), with feature sizes of 0.18 μm or below. As the size of ICs continues to go down, the relatively high RC delay (i.e. the product of the interconnect resistance and the dielectric capacitance) limits their performance. Meanwhile, the deteriorating resistance to electromigration (movement of metal atoms during current flow) in smaller devices will also begin to compromise the performance and reliability of aluminum as interconnect. These limitations can be overcome at the same time by replacing aluminum with copper in the IC as interconnect. Compared with aluminum, copper has a lower resistivity (1.67
μΩ-cm for Cu vs. 2.66 μΩ-cm for Al) and greater resistance to electromigration. The use of copper interconnects will enable lower RC delay, and therefore higher device speed and reduced power consumption, and enhanced electromigration reliability. The transition from aluminum to copper interconnects in semiconductor manufacturing is rapidly accelerating: major microprocessor companies such as IBM, Motorola and NEC have recently implemented Cu interconnect in their new products. As a matter of fact, Intel has just released the latest version of its Pentium III processor ("Coppermine") with a feature size of 0.18 μm, in which Cu partially replaces Al as the interconnect.

Although the advantage of copper as interconnect material has long been known, its implementation has been withheld until recently. This is primarily because of the manufacturability of copper and the cost associated with the development of new processes. One of the concerns is copper's compatibility with other materials present in ICs. Specifically, copper exhibits a high tendency to diffuse into Si and SiO₂, two of the most common materials in ICs. The diffusion of Cu will alter the properties of such materials, leading to shorter lifetime and malfunction of microelectronics devices. Therefore, diffusion barriers must be used to prevent the diffusion of copper into Si and SiO₂. Materials such as TaN, TaₓSiᵧNₓ,¹,² and WNₓ,³ are being closely examined as diffusion barriers for copper. Another problem of copper metallization is that copper is difficult to etch. In the traditional metallization process, plasma etching is used to remove excess Al resulting from blanket deposition. Cu is too hard to etch at a reasonable rate using this method. Fortunately, a new metallization scheme has been developed to circumvent this problem. The new scheme is coded "damascene" after the
popular steel swords in the ancient Middle East. The damascene process is elaborated in the next section.

1.3 Damascene Process

As mentioned previously, copper is difficult to etch. Accordingly, a new metallization strategy, called the damascene process, has been developed for copper interconnects. The advantage of the new process is that it eliminates the etching steps for the metal interconnect. Two variations of the damascene process are proposed. One is the single damascene process, and the other is the dual damascene process. Single damascene processing etches lines into a blanket oxide, and then fills them with metal. Dual damascene is similar, but fills a via layer and a trench layer simultaneously. Both single and dual damascene processes then use the Chemical Mechanical Planarization/Polishing (CMP) technique to polish away excess metal, exposing the oxide for deposition of the next layer.

Mainstream copper metallization is based on the dual-damascene process, as depicted in Figure 1-3. The inlaid copper via plugs and metal lines are formed in three steps:

a) diffusion barrier layer (typically TaN, deposited by PVD);

b) thin Cu seed layer (deposited by PVD at present);

c) Cu fill (deposited electrochemically).

Although CVD is not involved in the current dual-damascene process, it may be especially suitable for the deposition of seed layers of Cu before the vias are filled by more copper (Step 7), since it requires the conformal coverage of the underlying
structure. As the feature size decreases further (and therefore the vias and trenches become smaller), the conformal coverage of CVD will become more desirable.

1.4 Precursors for CVD

The precursor is vital to the success of a CVD process. Because of the chemical nature of the process, chemical vapor deposition can be only as good as the precursor is. The chemical properties of a precursor will have a direct impact on the growth rate and quality of the deposited film. Thus, a fundamental challenge to any CVD process is to identify a suitable precursor.

1.4.1 General Considerations for CVD Precursors

An ideal CVD precursor should meet most of the following requirements: volatility, stability, reactivity, and safety. Sufficient volatility of precursor is necessary to generate a uniform and high concentration of precursor in the gas flow, which makes rapid film growth possible. The volatility of a precursor is reflected by its equilibrium vapor pressure. The molecular weight and inter-molecular forces usually will influence a precursor’s volatility, as a result of structure and bonding of the species. Stability is required for the easy management and storage of a precursor. Additionally, a precursor that tends to prematurely decompose or reacts with unrelated species will usually lead to unpredictable deposition results and high manufacturing cost. Reactivity means that a precursor should be able to undergo the desired pathway efficiently and predominantly on the substrate. It is required to ensure high growth rate and high purity of the film. Safety means that the precursor and especially the byproducts of the CVD process should be safe to the environment and human health.
Step 1. Silicon device ready for damascene process

Step 2. Dielectric deposition

Step 3. Via Patterning

Step 4. Partial via etch

Step 5. Trench patterning

Step 6. Trench & via etch

Step 7. Barrier Layer and Copper Fill

Step 8. Copper CMP

Figure 1-3. Schematic Illustration of Dual-damascene Copper Process⁴

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Simple metal compounds are rarely used as precursors because of their normally low vapor pressure. Instead, most successful precursors are complexes of the intended elements. On one hand, this type of precursor complicates the chemistry of the process and brings in possible impurities. On the other hand, it provides the opportunity to fine-tune the properties of the precursor by modifying its structure and ligands. The bond strength and ligand structure of the precursor species all could have an effect on the process temperature, film growth rate and film composition (purity). There are several classes of compounds that are commonly used as precursors, such as carbonyls, halides and diketonates. Some representative precursors in each class are listed in Table 1-1.

Table 1-1. Some Common Precursors for CVD

<table>
<thead>
<tr>
<th>Precursor Type</th>
<th>Examples</th>
<th>Films Deposited</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrides</td>
<td>SiH₄, GeH₄, AlH₃·NMe₃, NH₃</td>
<td>Si, Ge, Al, Si₃N₄</td>
</tr>
<tr>
<td>halides</td>
<td>TiCl₄, MoF₆, WF₆</td>
<td>TiSi₂/TiN, MoSi₂, W/WSi₂</td>
</tr>
<tr>
<td>alkyls</td>
<td>AlMe₃, Al(i-Bu)₃, Ti(CH₂-t-Bu)₄</td>
<td>Al/GaAlAs, TiC</td>
</tr>
<tr>
<td>alkoxides</td>
<td>Ti(O-t-Pr)₄, [Cu(O-t-Bu)]₄</td>
<td>TiO₂, Cu</td>
</tr>
<tr>
<td>dialkylamides</td>
<td>Ti(NMe₂)₄, Cr(NEt₂)₄</td>
<td>TiN</td>
</tr>
<tr>
<td>diketonates</td>
<td>Cu(acac)₂, Pt(hfac)₂, Cu(hfac)₂, Ag(hfac)</td>
<td>Cu, Pt, Ag</td>
</tr>
<tr>
<td>carbonyls</td>
<td>Fe(CO)₅, Ni(CO)₄</td>
<td>Fe, Ni</td>
</tr>
</tbody>
</table>

1.4.2 Precursors for CVD of Copper Metal

The precursors for Cu CVD are almost exclusively complexes with organic ligands. This is partly because of the relatively high vapor pressures and low melting points of the organometallic copper compounds and partly because of the lack of other...
volatile Cu compounds. Cu was known to form very few stable and volatile alkyls, carbonyls, hydrides or halides, which eliminated several major classes of compound used in most existing processes for CVD of metals.⁵

Precursors for copper CVD can be divided into two groups, based on the Cu oxidation states: Cu(I) precursors and Cu(II) precursors. The most studied precursors in both groups are all β-diketonate compounds. The Cu(I) β-diketonates contain one β-diketonate ligand and one or more neutral ligands.⁶ Cu(II) β-diketonates, on the other hand, usually contain two β-diketonate ligands. Both groups of compounds have their own strengths and weaknesses as precursors. Cu(I) precursors, as represented by Cu(hfac)(VTMS) (VTMS = vinyltrimethylsilane), usually show high Cu deposition rates, although they tend to be thermally unstable, sometimes decomposing prematurely. In contrast, Cu(II) precursors, such as Cu(hfac)₂, show high thermal stability, but they suffer from relatively low deposition rates. The general structure of Cu(II) β-diketone compounds is shown in Figure 1-4. With different groups R and R' in the ligands, many derivatives can be obtained. When both R and R' are CF₃, the compound is called copper(II) bis(hexafluoroacetylacetonate) (Cu(hfac)₂).

The two groups of precursors undergo different reactions to produce copper thin films. Cu(II) precursors are usually reduced by additional reactant such as H₂ (Reaction 1-1), while Cu(I) precursors undergo disproportionation (Reaction 1-2).

\[
\begin{align*}
\text{Cu}^{n}(\text{hfac})_{2} + \text{H}_2 &= \text{Cu}^{0} + 2\text{H(hfac)} & \text{Reaction 1-1} \\
2\text{Cu}^{n}(\text{hfac})L &= \text{Cu}^{0} + \text{Cu}^{n}(\text{hfac})_{2} + 2L & \text{Reaction 1-2}
\end{align*}
\]

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Group Identities | Ligand Names
---|---
R = R' = CH₃ | acac
R = CH₃, R' = CF₃ | tfac
R = R' = CF₃ | hfac
R = C(CH₃)₃, R' = n-C₃F₇ | fod

**Figure 1-4. General Structure of Cu(II) bis(β-diketonates)**
CHAPTER 2  CVD USING ALCOHOL ADDUCTS OF Cu(hfac)$_2$

Copper(II) bis(hexafluoroacetylacetonate), denoted as Cu(hfac)$_2$, is the Cu(II) β-diketonate that shows the most promise as a Cu CVD precursor. The present study of the Cu(II) precursors is concentrated on this compound. The major shortcoming of Cu(hfac)$_2$ as a precursor for Cu CVD is its lower deposition rate compared with related Cu(I) complexes. Previous studies have shown that certain additives such as MeOH or H$_2$O improve the deposition rate using Cu(hfac)$_2$ (see the literature review below for details). With this in mind, we synthesized a series of Cu(hfac)$_2$ alcohol adducts. They were then tested in thermal CVD experiments as precursors for CVD of Cu metal. Their performances as CVD precursors were evaluated, particularly against that of Cu(hfac)$_2$. The chemistry of the alcohols in the new system was also studied.

In the following, major papers related to the study of Cu(hfac)$_2$ both as a purely metal-organic compound and as a precursor for Cu CVD are first reviewed. Then, the results of the present study, using Cu(hfac)$_2$ alcohol adducts as precursors for CVD, are examined.

2.1 Literature Review on CVD using Cu(hfac)$_2$

2.1.1 Chemistry of Cu(hfac)$_2$

Cu(hfac)$_2$ (see Figure 1-4) was first prepared during the synthesis of the H(hfac) ligand by Henne et al. in the 1940’s. Cu(hfac)$_2$ exhibits high Lewis acidity at the Cu atom, readily binding water and other electron donating molecules. This binding is further facilitated by the planar orientation of the ligands, which provides space for extra molecules in the perpendicular direction. As a result, Cu(hfac)$_2$ usually exists in the blue-green hydrated form (Cu(hfac)$_2$·H$_2$O) in the open air. Although the hydrate is

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stable enough to sublime intact, it can be converted to anhydrous Cu(hfac)₂ by dehydration over sulfuric acid or P₂O₅ in vacuum.

(a) Spectroscopic Studies of Cu(hfac)₂

The early studies on Cu(hfac)₂ were purely out of academic interest. The focus was on understanding the compound’s bonding and structural information through various spectroscopic measurements. Retrospectively, these fundamental studies of the compound do help to reveal the properties that make it a good precursor for CVD.

The finding that is of importance for CVD in the previous studies is the substitution effect on the physical and chemical properties of general copper bis(β-diketonate) compounds. In particular, the fluorine-substituted groups on Cu(hfac)₂ have a measurable effect on the thermal stability and the volatility of the compound. As a result, copper metal can be deposited at relatively low temperature. The fluorinated ligand makes Cu(hfac)₂ more volatile than other copper(II) β-diketonate. This is because C-F bonds weaken van der Waals interactions between the molecules. The volatilities of the metal β-diketonates are in the order hfac ≫ tfac > fod > acac.

(b) Cu(hfac)₂ in Alcohol Solutions

Gafney and Lintvedt studied the photochemical reactions of Cu(hfac)₂ in alcohol solutions. The alcohols studied included methanol, ethanol and 1-propanol. The authors reported the formation of metallic copper after irradiation (254 nm) of alcoholic solutions containing Cu(hfac)₂. The proposed mechanism involved two steps (see Figure 2-1). The first step was the photochemical process, which involved the reduction of Cu(II) to Cu(I) through free-radical dissociation of the ligand from Cu(hfac)₂,
followed by hydrogen atom transfer from alcohol to the ligand. The second step was the thermal reduction of Cu(I) to Cu metal by a disproportionation reaction.

2.1.2 Cu(hfac)$_2$ as Precursor for Cu CVD

This discussion of Cu(hfac)$_2$ as CVD precursor is organized into three areas, roughly based on the timeline. The first area involves the recognition of the necessity for a reducing co-reactant to produce high quality Cu films at relatively low temperature. Hydrogen was identified for that purpose. Only after this discovery did Cu(hfac)$_2$ become a strong candidate as a Cu CVD precursor. The second area involves the mechanistic study of the deposition process using Cu(hfac)$_2$ in H$_2$. In an effort to deduce the reaction mechanism of Cu(hfac)$_2$ in H$_2$, various groups studied the surface behavior of Cu(hfac)$_2$ on substrates and the kinetics of the process. The third area mainly focuses on the further enhancement of film growth rates using Cu(hfac)$_2$. This was achieved by the addition of co-reactants to the Cu(hfac)$_2$/H$_2$ system. Water is the most famous co-reactant for that purpose.

(a) Effects of Reducing Agent/Carrier Gas

The carrier gas has a significant effect on the film purity, growth rate and deposition temperature. Copper deposition using Cu(hfac)$_2$ was carried out by Moshier et al.$^{16}$ initially and by Temple et al.$^{17}$ later using pure argon gas as carrier gas. They obtained moderate purity copper films with resistivities of 3-7 $\mu$Ω·cm in the temperature range of 340-390 °C. Above 390 °C, the films were contaminated with both oxygen and carbon, due to fragmentation of the hfac ligand. Armitage et al.$^{18}$ compared the CVD performance of Cu(hfac)$_2$ under dry air and argon at atmospheric pressure. At a temperature of 478 °C under argon, metallic copper was obtained with small amounts of
Figure 2-1. Photochemical Reaction Scheme of Cu(hfac)$_2$ in Ethanol Solution (Adapted from reference 15)
copper(I) oxide and ligand decomposition products. Under dry air at the same
temperature, the main product was copper(II) oxide. The proportion of ligand
incorporated into the film was greatly reduced under air. At higher temperature (800
°C), the film deposited under air comprised mainly copper(I) oxide with small amounts
of metallic copper. Again, contamination was reduced at these conditions, compared
with the ones deposited under Ar.

All these studies indicate that Cu(hfac)$_2$ undergoes decomposition at elevated
temperature under chemically inert carrier gas. Not only is this temperature too high,
but also the deposited films contain too many impurities to be suitable for IC
fabrication. The addition of H$_2$ in the Ar stream would improve the deposition rate of
Cu(hfac)$_2$. But the films still contained large concentrations of carbon, fluorine and
oxygen.

Higher quality copper films could be obtained at lower temperatures in the
presence of only hydrogen gas. Van Hemert et al.$^{19}$ first demonstrated the deposition of
Cu films with Cu(hfac)$_2$ under H$_2$ in 1965. Their experiments were performed at
atmospheric pressure and at temperatures as low as 250 °C. More recently, this process
was “rediscovered” in the effort to prepare device-quality Cu films for the new
generation of ICs.$^{20}$ The resistivities of these films were reported to be as low as 2
μΩ·cm,$^{21}$ which is very close to that of bulk copper. Film growth rates under H$_2$ were in
the range of 40-1,800 Å/min, depending upon the deposition conditions and the reactor
design.

By now, it has been widely accepted that an additional reducing agent like H$_2$ is
required for Cu(hfac)$_2$ to deposit device-quality films at relatively low processing
temperatures. In the presence of H\textsubscript{2}, Cu(hfac\textsubscript{2}) undergoes reduction instead of thermal decomposition on the substrate. The mechanism of Cu(hfac\textsubscript{2})/H\textsubscript{2} CVD in an atmospheric pressure hot wall reactor was proposed by Lai et al.,\textsuperscript{22} as shown below. Reaction 2-3 was believed to be the deposition-rate-limiting step. It involved the combination of the adsorbed hfac groups and H atoms to permit the dissociation of H(hfac) from the substrate.

\begin{align*}
\text{Cu(hfac)}\textsubscript{2}(g) & \leftrightarrow \text{Cu(hfac)}(\text{ads}) + \text{hfac(ads)} \quad \text{Reaction 2-1} \\
\text{H}_2(g) & \leftrightarrow 2\text{H(ads)} \quad \text{Reaction 2-2} \\
\text{hfac(ads)} + \text{H(ads)} & \leftrightarrow \text{H(hfac)}(g) \quad \text{Reaction 2-3} \\
\text{Cu(hfac)}(\text{ads}) & \rightarrow \text{hfac(ads)} + \text{Cu(s)} \quad \text{Reaction 2-4}
\end{align*}

(b) Surface Chemistry of Cu(hfac\textsubscript{2}) and Related Species

The behavior of Cu(hfac\textsubscript{2}) and H(hfac) have been studied on various surfaces. They are usually observed in the form of a monolayer absorbed on a specific surface under ultrahigh vacuum conditions (UHV). Various kinds of surface analysis methods are used for this purpose, including Auger spectroscopy, X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS) and surface-reflectance infrared spectroscopy. The studies of surface chemistry of reactants involved in the CVD process provided valuable information concerning the reaction mechanism and optimum processing conditions.
Cohen et al.\textsuperscript{23} studied the adsorption of Cu(hfac)\textsubscript{2} on Ag. At room temperature (300 K), no complete Cu(hfac)\textsubscript{2} was found on the surface. Instead, Cu(hfac)\textsubscript{2} decomposed in two loosely connected parts: Cu(hfac) and hfac. The Cu(hfac) species was stabilized by reduction to an oxidation state close to Cu(I) by the Ag substrate below. And one hfac ligand was directly bound to the Ag surface; it may be partially associated with the Cu(I)-hfac species.

Girolami et al.\textsuperscript{24} observed similar dissociation of Cu(hfac)\textsubscript{2} on Cu surfaces. Meanwhile they also presented a more complete picture of the interaction between Cu(hfac)\textsubscript{2} and metal substrates at various temperatures. They observed that the dissociation of one hfac ligand from Cu(hfac)\textsubscript{2} (ads) occurred at temperatures as low as 125 K on the metal surface. The detached hfac group was believed to be oriented perpendicular to the substrate, based on interpretation of the infrared signals. The species remained stable until \textasciitilde{}375 K, when they began to decompose to CO and CO\textsubscript{2} (which desorbed promptly) and trifluoromethyl (CF\textsubscript{3} (ads)) and ketenylidene (CCO(ads)) (which remained adsorbed). The trifluoromethyl groups started to desorb from the surface at \textasciitilde{}525 K. Finally, the ketenylidene groups decarbonylated above 550 K and left behind a carbon residue. Some of the carbon-containing residues in CVD Cu films may arise by this type of process.

The same authors also studied the behavior of H(hfac). While H(hfac)(ads) stayed intact on the Cu surface at 125 K, it underwent dissociation into H(ads) and hfac(ads) at temperatures of 150 K or higher. To leave the surface, the hfac presumably needs to recombine with H to form the volatile species H(hfac).
It should be cautioned that the pressures (especially) and temperatures commonly used in the surface study are often much lower than those under which CVD is conducted. As a result, reactions that occur under ultrahigh vacuum (UHV) conditions do not always follow the same pathways under CVD conditions. Nevertheless, these studies do identify several adsorbed species related to Cu(hfac)₂, and thus help to establish their plausibility as intermediates that may be involved in the CVD process.

(c) Chemical Additives for CVD with Cu(hfac)₂

Water (H₂O) It is the most well-known and well-studied additive for CVD of copper metal. Water vapor increases the Cu deposition rates when either Cu(I)²⁵, ²⁶ or Cu(II) precursors are used. A tenfold increase in deposition rate with Cu(hfac)₂ under H₂ was reported in the presence of water vapor. ²⁷ The film morphology is also improved by H₂O. The films were more smooth and reflective, indicating a finer grain size. Detrimental effects of water were observed when its concentration exceeded a critical level. Such effects included a loss of deposition selectivity on metallic versus nonmetallic surfaces and the formation of copper oxide rather than metallic copper.

Lecohier et al. ²⁸, ²⁹ investigated the effect of water on copper film growth rates using Cu(hfac)₂ as precursor. The experiments were performed at 400 °C in a low pressure CVD reactor. Hydrogen or helium was used as carrier gas. The deposition occurred on bare SiO₂ or platinum seeded SiO₂ substrates. They found that the effect of water varied in the two gases and on the two different substrates. On the platinum seeded SiO₂ surface, the film growth rates were identical under H₂ and He and increased almost linearly with the amount of water vapor. This observation suggested that water was involved in the rate-limiting step of the overall process. On bare SiO₂,
however, no copper film was observed with helium as carrier gas, while a continuous copper film was obtained with hydrogen for water flow rates larger than 5 sccm.

Lecohier et al. further explored the effect of water on selective CVD using Cu(hfac)$_2$. Copper was deposited preferentially on metal surfaces as compared with SiO$_2$. They reported that the selectivity of the copper deposition was significantly enhanced on the metal (platinum) when using He rather than H$_2$ as carrier gas, especially at high water vapor concentrations where rapid film growth can be obtained. Selectivity of deposition was lost when the concentration of water vapor reached a critical level.

Pinkas et al. studied the mechanistic role of H$_2$O in the CVD of Cu from Cu(hfac)$_2$. The deposition temperature was 280 °C or 400 °C, and the pressure in the reactor was maintained at ~ 10 mTorr. Glass or silicon, instead of metal, was used as substrate. Their study was focused on the reaction of Cu(hfac)$_2$ with H$_2$O under argon gas. Powder X-ray analysis of the films revealed that the major component of the film obtained in argon was Cu$_2$O with a small amount of CuO at 280 °C, while the amount of metallic copper dramatically increased at 400 °C. When H$_2$ was used as carrier gas, similar results were obtained at 280 °C but complete reduction to metallic copper occurred at 400 °C. Unfortunately, no film growth rate data was provided. They proposed a reaction scheme of Cu(hfac)$_2$ with H$_2$O, as shown in Figure 2-2, based on the byproduct analysis and comparative experiments. The initial proton transfer from H$_2$O to hfac resulted in Cu$^{II}$O. The resultant H(hfac) was mainly responsible for the reduction of Cu$^{II}$O to Cu$_2$O. The reduction process became more complete at high
temperature (400 °C), resulting in Cu° metal. A labeling experiment using H$_2^{18}$O confirmed that oxygen in the CuO film came from H$_2$O rather than the ligands.

In the presence of water, Cu(hfac)$_2$ seems to adopt different reaction pathways on conductive and insulating surfaces, leading to metallic copper on the metal surface, but copper oxide on the insulating surfaces. Water enhancement of deposition rates using Cu(hfac)$_2$ is mostly observed on metal surfaces. The surfaces of metals are electron-rich, and are capable of partially reducing Cu(hfac)$_2$ as observed by different groups.\textsuperscript{23,24} The improved selectivity of deposition in water vapor is the direct result of preferential deposition rate enhancement on the metal substrate. It is also worth mentioning that most CVD experiments with Cu(hfac)$_2$ and water are performed at the temperature of ~400 °C, at which Cu(hfac)$_2$ readily decomposes even in chemically inert gas. At high temperatures, decomposition may be favored over any other pathways.

![Reaction Scheme of Cu(hfac)$_2$ and H$_2$O Proposed by Pinkas and coworkers](reproduced_with_permission_of_the_copyight_owner_further_reproduction_prohibited_without_permission)

Figure 2-2. Reaction Scheme of Cu(hfac)$_2$ and H$_2$O Proposed by Pinkas and coworkers

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Alcohols

Having structures similar to water, some alcohols also seem to be able to participate in Cu CVD using Cu(hfac)$_2$.

Houle et al.$^{32}$ reported the successful deposition of Cu film from Cu(hfac)$_2$ ethanolate (Cu(hfac)$_2$·(EtOH)$_x$) gas in a sealed quartz cell using a laser. A laser with a wavelength of ~275 nm was used, which was similar to that used to obtain copper metal from Cu(hfac)$_2$ in alcohol solutions.$^{15}$ The pressure inside the cell was ~3 mTorr. They found that the principal contamination in the deposited film was carbon. However, when ethanolates were used as precursors, the amount of carbon in the films decreased rapidly with increasing amounts of ethanol (i.e. Cu(hfac)$_2$·xEtOH, x=0, 2).

Cho$^{33}$ showed that the incorporation of isopropyl alcohol, methanol or isobutyl alcohol as a co-reactant with Cu(hfac)$_2$ and H$_2$ led to a significant reduction in the processing temperature and an improvement in the growth rate and quality of copper grown on Si and SiO$_2$. On the other hand, no enhancement was observed when acetone, toluene or tert-butyl alcohol was employed.

Chiang et al.$^{34}$ investigated the vapor-phase, solution and surface chemistry of Cu(hfac)$_2$ dissolved in alcohols (methanol, ethanol, isopropyl alcohol), acetone, and water by molecular beam/mass spectrometry, nuclear magnetic resonance (NMR) and reflection-absorption infrared spectroscopies. The authors believed that Cu(hfac)$_2$ evaporated from alcohol solutions in the form of a molecular complex. In the case of ethanol solution, it would be Cu(hfac)$_2$·xEtOH, where x could be 1 or 2. In the gas phase, Cu(hfac)$_2$·2EtOH was less thermally stable than Cu(hfac)$_2$·EtOH. They reported that, while Cu(hfac)$_2$ did not react with the alcohol solution at room temperature, it reacted directly with water, leading to the partial reduction of Cu(II). The authors

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postulated that the roles of the solvent in the Cu(hfac)$_2$ CVD process were two-fold. First, they proposed that the coordination of alcohol molecules to Cu(hfac)$_2$ improved the precursor’s evaporation rate, though this effect was later called into question. Second, the alcohol lowered the reaction barrier of Cu(hfac)$_2$ and H$_2$ to produce Cu metal.

Zheng et al.$^{35}$ studied evaporation patterns of Cu(hfac)$_2$-ROH (where ROH = MeOH, EtOH and i-PrOH), using in-situ quadrupole mass spectroscopy (QMS). The study showed that the alcohols and water always evaporated first discretely at relatively low temperatures (<50 °C), indicating the weak coordination between Cu(hfac)$_2$ and these species. Thus, all of these adducts should essentially be dissociated in practical precursor delivery temperatures at ~80 °C (at least in the absence of excess H$_2$O/ROH). The strength of the coordination (judging from the dissociation temperature) appeared to be inversely proportional to the size of the substituent attached to the hydroxyl group in the solvent molecule. The authors further pointed out that i-PrOH should be a good additive for CVD of Cu because it can readily decouple from the precursor in the gas phase.

Kaloyeros et al.$^{36}$ reported in-situ mass spectral and IR observations of alcohols (EtOH, i-PrOH and s-BuOH) in a plasma CVD setting. Despite the fact that the study only included the alcohols in the absence of any precursor, it bore clear implications for the role of alcohols in real plasma CVD reactions. It was observed via QMS that hydrogen was released from i-PrOH under argon (Ar) plasma. The hydrogen concentration increased linearly with the plasma power. The byproducts from the alcohol oxidation (ketones and aldehydes) were also observed via in-situ infrared.
spectroscopy. \textit{i-PrOH} was found to be more efficient in releasing hydrogen than the other studied alcohols. The authors proposed that the alcohols contributed atomic hydrogen, which assisted the Cu(hfac)$_2$ reduction process and led to a higher probability of hydrogen-precursor interaction and therefore a higher copper growth rate.

Borghini et al.\textsuperscript{37} from this project group have studied the influence of small alcohols (ethanol, methanol and isopropyl alcohol) on the mass transport behavior and reaction kinetics of Cu(hfac)$_2$. The authors measured the evaporation rates of alcohol adducts by thermogravimetric analysis (TGA). The evaporation rate of Cu(hfac)$_2$ was not increased by the adduction of alcohols under N\textsubscript{2}. However, the authors did report that the Cu deposition rate from Cu(hfac)$_2$ under H\textsubscript{2} increases with increasing partial pressure of alcohols. Among the alcohols studied, the film growth rate increased most significantly on addition of isopropyl alcohol, followed by that of ethanol and methanol. It was proposed that, in the alcohol-assisted CVD process, the rate-limiting step was H$^+$ transfer between the OH group of the adsorbed alcohol and the first dissociated (hfac) ligand of the adsorbed Cu(hfac)$_2$ molecule.

\textit{H(hfac)} The only other well-known chemical additive for Cu(hfac)$_2$ CVD process is hexafluoroacetylaceton (H(hfac)). Awaya et al.\textsuperscript{38} found that the addition of H(hfac) in the Cu(hfac)$_2$ + H\textsubscript{2} system could inhibit copper deposition on SiO$_2$. They proposed the H(hfac)$_{ad}$ would lower the concentration of the adsorbed H atoms, which was required for the copper nucleation on the insulator. The reactions were:

\begin{align*}
H(hfac)(ads) & \rightarrow H(ads) + \text{hfac}(ads) \quad \text{Reaction 2-5} \\
2H(ads) + H(ads) + \text{hfac}(ads) & \rightarrow H_2(g) + \text{H(hfac)}(g) \quad \text{Reaction 2-6}
\end{align*}
On the other hand, the addition of H(hfac) did not affect copper film growth on metal surfaces under the same conditions. As a result, H(hfac) was considered to be an effective additive for enhancing the selective deposition of Cu from Cu(hfac)$_2$.

In summary, three kinds of additives have been studied for the CVD using Cu(hfac)$_2$ for the purposes of enhancing film growth rate and selectivity of the deposition. Depending on the reaction conditions, water can enhance film growth rates, improve film morphology and influence the selectivity of the copper film deposition. H(hfac) can be used to enhance selectivity. A small number of alcohols are also reported to enhance the deposition rate, while their effects on selectivity are unknown.

2.2 The Goal of Our Study

The reports on the use of alcohols to increase the Cu film growth rate using Cu(hfac)$_2$ are limited to a small number of alcohols, i.e. EtOH, MeOH and i-PrOH. Furthermore, these studies were performed by different groups under different conditions, making the results difficult to compare. Many other alcohols have not been investigated as candidates for deposition enhancement. As a result, the best alcohol for the purpose has not been identified and the mechanism of their reaction is not clear. Meanwhile, the previous studies on alcohols were largely focused on the in-situ observation of ROH and its interaction with Cu(hfac)$_2$ in the gas phase or on surfaces. Few real CVD experiments have been performed using alcohol adducts. Additionally, the deposition rate enhancements by alcohols are usually cited in H$_2$. Their performance in N$_2$ seems to get less attention and is less well known.

With these observations in mind, we chose to study the alcohol-Cu(hfac)$_2$ CVD system in a more systematic fashion. Methanol, ethanol, and all of the C$_3$ and C$_4$
alcohols are included in our study. First of all, we investigated Cu(hfac)$_2$-alcohol adducts as discrete precursors, as opposed to introduction of Cu(hfac)$_2$ and alcohol separately, as in the other studies. Their properties pertinent to CVD, such as evaporation rates and thermal stability, were also studied. Furthermore, we carried out thermal CVD experiments using these precursors under similar conditions. The results were compared so as to identify the best alcohol for the system. Such comparisons also shed light on the mechanistic role of the alcohol in the CVD process in the respects of complex formation, proton transfer and solvent effects.

2.3 Experimental Details

This section includes information on all the parameters for the CVD experiments and descriptions of methods used in the measurements and analysis.

2.3.1 Synthesis of Alcohol Adducts

The synthesis of Cu(hfac)$_2$-ROH started with copper(II) bis(hexafluoroacetylacetonate) hydrate (Cu(hfac)$_2$.xH$_2$O). It was either purchased from Strem Chemicals, or synthesized in this lab according to the method in the literature.$^{11}$

The Cu(hfac)$_2$.xH$_2$O, which had a color of light green, was first dehydrated in a vacuum desiccator over concentrated H$_2$SO$_4$ or P$_2$O$_5$, for an extended period of time. The degree of dehydration could be judged by the color of the solid. The process was complete when the solid turned to dark blue. The Cu(hfac)$_2$.ROH adducts were prepared by mixing the resultant Cu(hfac)$_2$ with a stoichiometric amount of alcohol (ROH) in excess dichloromethane (CH$_2$Cl$_2$). The alcohols were anhydrous materials from Aldrich and were used without further purification. The dark blue Cu(hfac)$_2$ complex dissolved in the alcohol solution immediately to form a green solution. After thorough agitation,
the excess alcohol was removed under vacuum and the green solid Cu(hfac)$_2$-ROH adducts were obtained.

2.3.2 CVD Equipment

The CVD reactions were carried out in a vertical warm wall reactor. A schematic diagram of the CVD setup is shown in Figure 2-4. The precursor was placed in the evaporator, which was immersed in a thermostated oil bath. In a typical experiment, the carrier gas was passed first through a bubbler that contained the proper alcohol reagent, then through the evaporator and finally to the CVD reactor. High purity gases (grade 5; BOC) were used for the experiments. The gas volume flow rate was determined by a flowmeter, which had been calibrated beforehand (see the calibration procedure for details). The substrate was attached to an electrically heated metal susceptor in the CVD reactor using silver paint purchased from SPI Supplies. Either borosilicate glass cover slips or small pieces of silicon wafers were used as the substrates. The substrates were cleaned with acetone in an ultrasonic bath and blown dry before mounting. The temperature of the substrate was monitored by a thermocouple (Omega, iron-constantan J type). The delivery line between the evaporator and reactor, and the wall of the reactor, were wrapped with heating tape to prevent condensation of precursor.

2.3.3 CVD Experiment Parameters

The conditions listed in Table 2-1 were used for all the CVD experiments unless otherwise noted.

2.3.4 Film Characterization

The films deposited were characterized in the respects of thickness, electrical resistivity, morphology and chemical composition.
<table>
<thead>
<tr>
<th>Table 2-1. Standard Parameters for CVD Experiments</th>
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<tbody>
<tr>
<td>Precursor evaporation temperature</td>
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<tr>
<td>Precursor delivery line temperature</td>
</tr>
<tr>
<td>Deposition temperature</td>
</tr>
<tr>
<td>CVD reactor pressure</td>
</tr>
<tr>
<td>Gas flow rate</td>
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<tr>
<td>Length of deposition</td>
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<tr>
<td>Substrate</td>
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</tbody>
</table>

The thicknesses of the films were measured using a stylus profilometer (Alpha-Step 200, Tencor Instruments). On each sample, the thickness was measured in the center and in one position on each side, as illustrated in Figure 2-3. The average of the five measurements was used to represent the thickness of the film.

![Figure 2-3. Illustration of Thickness and Resistivity Measurements of a CVD Film](image)

The resistivities of the films were measured using a four-point probe (model FPP-100, Veeco Instrument Inc.). They were done at approximately the same positions on each sample where the thicknesses were measured. The resistances (R) were the direct readings from the instrument. They were then converted to bulk resistivity values ($\rho_{\text{raw}}$).
by multiplying by the corresponding film thickness value (T) and a correction factor (C.F.) as described by Equation 2-1. The correction factor was determined from the calibration chart based on the geometry and size of the sample (see Appendix A and B).

\[
\rho_{\text{raw}} = C.F. \times T \times R
\]  

Equation 2-1

The resistivity values calculated for many of the CVD Cu films from the four-point probe data were consistently less than the literature value for the bulk resistivity of pure copper (1.67 \( \mu \Omega \cdot \text{cm} \)). A reference sample for high-purity copper foil (0.0125 mm thick, 99.9% pure) also gave anomalously low resistivity. These low apparent resistivities may have been caused by a systematic error in the four-point probe. As a result, the raw resistivity values of the sample (\( \rho_{\text{raw}} \)) were subsequently corrected using the experimental value for pure Cu (\( \rho_{\text{Cu}} = 1.16 \mu \Omega \cdot \text{cm} \)) obtained from the same instrument, according to Equation 2-2.

\[
\rho_{\text{film}} = \frac{(1.67 \mu \Omega \cdot \text{cm} \times \rho_{\text{raw}})}{\rho_{\text{Cu}}}
\]  

Equation 2-2

The chemical composition of some of the films was determined by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). AES measurements were performed in the Mechanical Engineering Department at LSU while XPS measurements were performed in Dr Koplitz's lab at Tulane University.

2.3.5 Titration of Cu in Cu(hfac)\(_2\)-ROHs

A titration method was developed to analysis the Cu contents in Cu(hfac)\(_2\)-ROH in our lab,\(^{39}\) based on the principle of iodometric titration.\(^{40}\) The freshly prepared Cu(hfac)\(_2\)-ROH complex was first dissolved in a concentrated solution of HNO\(_3\) and
H₂SO₄ (1:2). The solution was then diluted with distilled water and boiled to eliminate NO₂. Then, excess KI (aq) was added to form CuI and I₂. The pH was subsequently adjusted through the addition of concentrated ammonia and H₃PO₄ (85%). The liberated iodine was then titrated by standard Na₂S₂O₃ (0.02064 M, Aldrich). Starch and KSCN were used as the first and the second titration indicator respectively. Three titrations were conducted on each adduct. The mass percentage of Cu in Cu(hfac)₂-ROH was calculated from the titration of iodine in such prepared solution. It was deemed acceptable if it was within ± 0.4% of the theoretical one. All the C3 and C4 adduct precursors gave acceptable Cu analyses.

2.3.6 Precursor Evaporation Rate Measurements

The setup for the measurement of evaporation rates of Cu(hfac)₂ alcohol adducts was the same as that used for actual CVD experiments except that the CVD reactor was replaced by a vertical glass column filled with glass wool. Glass wool was uniformly packed in the glass column. It was packed in three layers. 5-mL i-PrOH was injected into the glass wool at the inlet end, and about 0.5 g of Cu(hfac)₂ alcohol adduct was placed in the evaporator before each measurement. The glass wool and the i-PrOH liquid would trap the Cu(hfac)₂ alcohol adduct vapor which was indicated by a green deposit on the glass wool after each measurement. The green color usually only reached to ¼ of the length of the glass wool column, indicating that all of the vapor was effectively trapped, i.e. that the glass wool column was long enough. The vapor collection was conducted under the same conditions used for CVD experiments in terms of evaporation temp (80 °C), flow rate and excess alcohol (if indicated). Every a flask with i-PrOH. More i-PrOH was added if necessary to make the overall volume of

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solution 50 mL. The collected solution was then analyzed using UV/vis spectroscopy. Each evaporation rate was measured in triplicate, with a fresh precursor sample used each time. The absorbance at 743 nm was chosen for comparison of the concentration of Cu(hfac)$_2$ in $i$-PrOH solution. Usually there was a small amount of green color on the glass wool that could not be removed by rinsing. This tinted portion was replaced with fresh glass wool for each experiment. Usually only the lowest layer of glass wool needed to be changed after each measurement. The total weight of glass column and glass wool was kept at around 35 g for each measurement.

![Graph](image_url)

Figure 2-4. Visible Spectrum Standard Curve for Cu(hfac)$_2$-$i$-PrOH in $i$-PrOH Solution

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Figure 2-5. Schematic Drawing of CVD Experiment Setup
A linear regression equation was derived from a series of standard UV/vis spectra for various concentrations of \( \text{Cu(hfac)}_2 \cdot i\text{-PrOH} \) in \( i\text{-PrOH} \) solution, as shown in Figure 2-4. The real evaporation rates of the precursors were determined according to the equations shown below (where "EvapRate" represents the weight of \( \text{Cu(hfac)}_2 \cdot i\text{-PrOH} \)):

\[
\text{concentration (g / mL)} = 0.0198 \times \text{absorbance (743 nm)} \quad \text{Equation 2-3}
\]

\[
\text{EvapRate (g / hr)} = \text{concentration (g / mL)} \times 50 \text{ (mL)} / 0.5 \text{ (hr)} \quad \text{Equation 2-4}
\]

2.3.7 Calibration of Flowmeter

The flowmeter (Linde) was calibrated under \( \text{H}_2 \) and \( \text{N}_2 \). A 1-liter flask filled with water was connected to the appropriate gas cylinder through the flowmeter. The pressure was maintained at 30 Psi at the gas source. The gas flow rate was derived from the time that it took to expel all the water from a 1-liter flask inverted in a water bath. The flowmeter readings were correlated with corresponding gas flow rates. The calibration curves between the flowmeter and gas flow rates are included in Figure 2-6.

2.3.8 Measurements of Alcohol Evaporation Rates

The evaporation rates of the alcohols in the CVD experiments were measured at intervals of 20 minutes or 10 minutes for a total of 60 minutes. The purpose of the measurements was to determine whether the evaporation rate of \( i\text{-PrOH} \) was constant during the period. (60 minutes was the duration of a typical CVD experiment.)

The experiments started with the bubbler full of alcohol. \( \text{H}_2 \) or \( \text{N}_2 \) was used as carrier gas, at the same flow rate at which the CVD experiments were conducted. The gas was bubbled through the alcohol as in the CVD experiment. The bubbler was
weighed every 10 minutes for the first 30 minutes. The amount of alcohol evaporated between the intervals was determined by the difference in weight. The measurements for 30 minutes were repeated at least twice for each carrier gas/alcohol combination.

Figure 2-6. Calibration Curve for H₂ and N₂ Gas Flow Rates

2.3.9 Collection and Analysis of CVD Byproducts

The byproducts of CVD using Cu(hfac)₂·ROH + ROH + H₂/N₂ were analyzed during typical CVD experiments using FTIR spectroscopy. The byproducts comprised the alcohol (ROH), unreacted Cu(hfac)₂, H(hfac) and the product of alcohol oxidation (ketones or aldehydes). Among them, ROH was the majority. The collection process was repeated twice for each condition. The reaction parameters are listed below.
All the byproducts exited the reactor in the gaseous state. They were trapped at the outlet using liquid $N_2$. After the CVD experiments, the cold trap was left at room temperature for about 10 min to allow any low-boiling materials to evaporate. Then, samples for IR analysis were prepared from the resultant condensate. The amount collected was determined by weight difference before and after the CVD experiment. Meanwhile the amount of ROH evaporated was also tracked in the same fashion. Two methods were used to prepare the samples for IR analysis. Both methods gave similar results, in the terms of determining the amount of the byproducts in the cold trap. (Acetone, the oxidation product of $\textit{i}$-PrOH, is used here as example)

**Method 1-no dilution method:** The condensate was directly transferred to the IR cell for measurement. For the sample prepared in this way, the acetone peak intensity on IR spectrum indicates the acetone concentration in the overall condensate. Since the total mass of condensate was also measured, the acetone concentration could also be converted to the total amount of acetone collected.

**Method 2- dilution method:** The condensate was first diluted in $\textit{i}$-PrOH to achieve a total volume of 25 mL in a volumetric flask. And then, the sample taken from this solution was measured using IR. For the sample prepared in this way, the acetone peak intensity in the IR spectrum indicates the acetone concentration in the 25 mL of $\textit{i}$-PrOH solution.

2.4 Results and Discussion

2.4.1 Cu(hfac)$_2$-ROH Preparations

Dichloromethane was used as the solvent in the preparation of alcohol adducts, in which Cu(hfac)$_2$ readily dissolved. The subsequent addition of most of the alcohols did
not cause any visible color change in the solution, except for \( n\text{-BuOH} \). When \( n\text{-BuOH} \) was added into the solution, a cloudy precipitate was immediately formed. But it disappeared quickly after agitation. Most of the alcohol adducts were easily isolated as solids, except for the \( t\text{-BuOH} \) adduct, which took a longer time and required moderate heat.

**Water** This has been a concern for the synthesis of \( \text{Cu(hfac)}_2\cdot\text{ROH} \) due to the extreme sensitivity of \( \text{Cu(hfac)}_2 \) to water. Care was taken to protect the \( \text{Cu(hfac)}_2 \) compound from contacting with any trace of water. Preparations of adducts were conducted in the glove box and anhydrous alcohol reagents were used. The preparation by the same procedure in the open air resulted in a product with notably different color and lower melting point, as listed in Table 2-2. The “open-air” products were more likely a mixture of \( \text{Cu(hfac)}_2\cdot\text{ROH} \) and \( \text{Cu(hfac)}_2\cdot\text{xH}_2\text{O} \). Similar melting points were found for methanol and ethanol adducts prepared in both environments, which suggests that these precursors are relatively inert to water. For the rest, the open-air products all show lower melting points, which we attribute to contamination with \( \text{H}_2\text{O} \).

<table>
<thead>
<tr>
<th>Adducts</th>
<th>Glove Box M.P. (°C)</th>
<th>Color</th>
<th>Open Air M.P. (°C)</th>
<th>Literature M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu(hfac)}_2 )</td>
<td>95-98</td>
<td>Blue</td>
<td>N/A</td>
<td>95-98 (^6)</td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{H}_2\text{O} )</td>
<td>N/A</td>
<td>Pale green</td>
<td>135-140</td>
<td>133-136 (^8)</td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{MeOH} )</td>
<td>134-138</td>
<td>Green</td>
<td>135-140</td>
<td>134-138 (^{41})</td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{EtOH} )</td>
<td>103-104</td>
<td>Green</td>
<td>103-105</td>
<td>103-104 (^{41})</td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{n-PrOH} )</td>
<td>57-60</td>
<td>Pale green</td>
<td>40-45</td>
<td></td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{t-PrOH} )</td>
<td>50-53</td>
<td>Green</td>
<td>35-40</td>
<td>53-55 (^{41})</td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{n-BuOH} )</td>
<td>65-70</td>
<td>Pale green</td>
<td>37-43</td>
<td></td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{s-BuOH} )</td>
<td>40-42</td>
<td>Green</td>
<td>35-40</td>
<td></td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{t-BuOH} )</td>
<td>40-45</td>
<td>Pale green</td>
<td>37-40</td>
<td></td>
</tr>
<tr>
<td>( \text{Cu(hfac)}_2\cdot\text{t-BuOH} )</td>
<td>38-40</td>
<td>Dark green</td>
<td>30-35</td>
<td></td>
</tr>
</tbody>
</table>

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Stoichiometric Synthesis  Another question concerning the identity of the adduct compound is the number of alcohol molecules that attach to each Cu(hfac)\textsubscript{2} complex. It has been reported that one or two water molecules can coordinate to each Cu(hfac)\textsubscript{2} to form mono- or di-hydrates.\textsuperscript{11} There are also similar reports about the di-ethanol adduct of Cu(hfac)\textsubscript{2}.\textsuperscript{32} A series of syntheses were performed for each adduct using different amounts of alcohol. The mole ratio between the Cu(hfac)\textsubscript{2} and alcohol was controlled at 1:0.5, 1:1, 1:1.5 and 1:2. The physical properties of the resulting products are included in Table 2-3.

**Table 2-3. Cu(hfac)\textsubscript{2} Alcohol Adducts Prepared with Different Amounts of Alcohols in the Glove Box**

(a) Cu(hfac)\textsubscript{2}-\textit{n-PrOH}

<table>
<thead>
<tr>
<th>Cu(hfac)\textsubscript{2} (mol)</th>
<th>\textit{n-PrOH} (mol)</th>
<th>Product Melting Point (°C)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>64-70</td>
<td>Green+lime green</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>67-70</td>
<td>Green</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>55-60</td>
<td>Lighter green</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>55-60</td>
<td>Lime green</td>
</tr>
</tbody>
</table>

(b) Cu(hfac)\textsubscript{2}-\textit{i-PrOH}

<table>
<thead>
<tr>
<th>Cu(hfac)\textsubscript{2} (mol)</th>
<th>\textit{i-PrOH} (mol)</th>
<th>Product Melting Point (°C)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>60-75</td>
<td>Blue + green</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>50-53</td>
<td>Green</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>50-52</td>
<td>Green</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>50-52</td>
<td>Green</td>
</tr>
</tbody>
</table>

(c) Cu(hfac)\textsubscript{2}-\textit{n-BuOH}

<table>
<thead>
<tr>
<th>Cu(hfac)\textsubscript{2} (mol)</th>
<th>\textit{n-BuOH} (mol)</th>
<th>Product Melting Point (°C)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>70-72</td>
<td>Dark green</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>66-75</td>
<td>Forest green</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>45-51</td>
<td>Lime green</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>45-46</td>
<td>Yellow green</td>
</tr>
</tbody>
</table>

(table continued)
<table>
<thead>
<tr>
<th>Cu(hfac)$_2$ (mol)</th>
<th>s-BuOH (mol)</th>
<th>Product Melting Point ($^\circ$C)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>47-65</td>
<td>Dark green</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>38-41</td>
<td>Green</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>40-42</td>
<td>Green</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>40-42</td>
<td>Green</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu(hfac)$_2$ (mol)</th>
<th>n-BuOH (mol)</th>
<th>Product Melting Point ($^\circ$C)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>57-63</td>
<td>Dark green</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>49-55</td>
<td>Green</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>45-50</td>
<td>Green</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>45-50</td>
<td>Lime green</td>
</tr>
</tbody>
</table>

Most of the (1:0.5) products of the alcohols show a mixed color of pure Cu(hfac)$_2$ and alcohol adducts (except that of n-PrOH) and melt over a wide temperature range (except that of n-BuOH), which are indicative of a mixture. The adducts of primary alcohols (n-PrOH, n-BuOH and i-BuOH) show a similar trend: the melting points of the product decreased with increasing amounts of alcohol added, until the ratio reached 1:1.5. The (1:2) products had similar melting points to (1:1.5) ones. The colors of the products were generally in the green region, but shifted toward yellow with increasing amounts of alcohol. The correlation between the physical properties and the amount of alcohol added suggests that either one or two alcohol molecules may be incorporated in the final products for primary alcohols. For the secondary alcohols, i-PrOH and s-BuOH, all the products prepared with the alcohol to Cu(hfac)$_2$ ratio larger than or equal to 1 had similar melting points and colors. This suggests that only one secondary alcohol molecule is attached to Cu(hfac)$_2$, regardless of the amount of alcohol used.
The possibility of Cu(hfac)$_2$·$2$ROH is supported by the crystal structure of the $n$-PrOH adduct. As shown in Figure 2-7, one $n$-PrOH molecule is attached at each side of the Cu(hfac)$_2$ plane. The crystal structure of Cu(hfac)$_2$·$n$-BuOH is shown in Figure 2-8, in which only one $n$-BuOH molecule is attached to the Cu(hfac)$_2$ host.

In CVD experiments, only adducts prepared with 1:1 ratio were used as precursors. The CVD performance of the alcohol adducts with different stoichiometries were not studied comparatively. But it may not be practically important in our study because an excess of alcohol vapor is always present in our CVD experiments and the attached alcohol molecules dissociate readily from the Cu center in the gas phase.

**Elemental Analysis**  
Elemental analysis of the synthesized alcohol adducts was also attempted to prove the identity of the products. C-H analyses were performed by an external laboratory (M-H-W Laboratories, Phoenix, AZ 85060). The results of elemental analysis on some the products mentioned above are listed in Table 2-4. The results do not check very well with the expected theoretical values. However, the melting points of the alcohol adducts are reproducible by repeated preparation and fall in a narrow range. These indicate that the products are relatively pure and consistent. The errors in analysis were probably caused by the loss of solvent during transit.

**Table 2-4. Elemental Analysis Results of Some Cu(hfac)$_2$ Alcohol Adducts**

<table>
<thead>
<tr>
<th>Adducts</th>
<th>Elements</th>
<th>Theory %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)$_2$·n-PrOH (1:1)</td>
<td>C</td>
<td>29.03</td>
<td>24.44/25.99</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>1.87</td>
<td>0.60/0.70</td>
</tr>
<tr>
<td>Cu(hfac)$_2$·n-BuOH (1:1)</td>
<td>C</td>
<td>31.88</td>
<td>29.19</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>2.28</td>
<td>1.41</td>
</tr>
<tr>
<td>Cu(hfac)$_2$·s-BuOH (1:1)</td>
<td>C</td>
<td>31.88</td>
<td>29.16</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>2.28</td>
<td>3.41</td>
</tr>
</tbody>
</table>
We also carried out titrations on freshly prepared alcohol adducts in our own lab in order to measure the percentage of Cu in each adducts. Since the percentage of Cu differs in different alcohol adducts due to the incorporation of a specific alcohol, such a value reflects the amount of alcohol adducted to Cu(hfac)$_2$. The results are listed in Table 2-5. The experimental values match the theoretical ones well (within ± 0.4%), suggesting that each Cu(hfac)$_2$ adduct contains one molecule of the appropriate alcohol. The results also support our belief that the poor results of the C-H micro-analysis are likely caused by the solvent loss during transit.

Table 2-5. Cu Amount (%) in Cu(hfac)$_2$-ROH (1:1) Obtained by Cu Titration

<table>
<thead>
<tr>
<th>Adducted Alcohol</th>
<th>Theory (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$-PrOH</td>
<td>11.82</td>
<td>11.70</td>
</tr>
<tr>
<td>$n$-PrOH</td>
<td>11.82</td>
<td>11.48</td>
</tr>
<tr>
<td>$n$-BuOH</td>
<td>11.52</td>
<td>11.52</td>
</tr>
<tr>
<td>s'-BuOH</td>
<td>11.52</td>
<td>11.76</td>
</tr>
<tr>
<td>i'-BuOH</td>
<td>11.52</td>
<td>11.47</td>
</tr>
</tbody>
</table>

2.4.2 The Effect of Alcohol on the Melting Points of Cu(hfac)$_2$ Adducts

For practical CVD processes, liquid precursors are favored over solids because handling is easier and their evaporation rates are often more reproducible. Cu(hfac)$_2$ is a solid under normal CVD evaporation temperature (~80 °C). Suitable Cu(II) liquid precursors have not been previously identified. The Cu(hfac)$_2$-ROHs show a wide range of melting points that are displayed in Table 2-2. For methanol, the smallest of the alcohol molecules, its Cu(hfac)$_2$ adduct has the highest melting point, which is close to that of the hydrate. As the sizes of alcohols increase, the melting points of the corresponding adducts generally decrease. Additionally, the adducts with branched alcohols have lower melting points than those with linear alcohols.
Figure 2-7. Crystal Structure of Cu(hfac)$_2$-2π-PrOH
Figure 2-8. Crystal Structure of Cu(hfac)$_2$·$n$-BuOH
This phenomenon can be taken advantage of to produce liquid Cu(II) precursors. The Cu(hfac)$_2$ adducts of several propanol and butanol isomers show melting points that are much lower than the commonly used evaporation temperature. Thus, they can be practically used as liquid precursors.

### 2.4.3 The Dissociation of ROH from Cu(hfac)$_2$ and Its Implications for CVD

In the gas phase, the water or alcohol molecules dissociate readily from the Cu(hfac)$_2$ complex. This phenomenon has been observed by several authors.\textsuperscript{13,15,16} Our study of Cu(hfac)$_2$·$i$-PrOH also suggested this. We found that IR spectra of the vapor phase above Cu(hfac)$_2$·$i$-PrOH at 40 °C were very similar to that of $i$-PrOH (g) and different from that of solid Cu(hfac)$_2$·$i$-PrOH.

We also studied the alcohol adducts' evaporation behavior by the means of TGA. The focus was on physical and chemical change at the stage when a precursor transits to the gas phase from the liquid/solid phase. The sample was heated in the temperature-programmed furnace under a steady flow of N$_2$ gas. The weight change of the precursor was recorded against temperature. A typical TGA curve of an alcohol adduct showed two peaks, indicating two weight changes of the sample during the heating process. The peaks are denoted “A” and “B” for the ease of discussion. Peak “A” was characteristic for the individual alcohol adducts. It appeared at different temperatures depending on the alcohol attached to the Cu(hfac)$_2$. Peak “B” appeared at ~100 °C on the curves of all the alcohol adducts. Peak “A” is attributed to the dissociation of alcohol from the Cu(hfac)$_2$ host. The resultant Cu(hfac)$_2$ would always start to evaporate at approximately 100 °C, as shown by the peak “B” on all of the TGA curves of alcohol.
adducts. The temperatures for the dissociation of the alcohols and water from their Cu(hfac)$_2$ adducts are listed in Table 2-6.

The results suggest that all the adducted molecules decouple from the Cu complex well below the typical evaporation temperature for Cu CVD, namely, 80 °C. Therefore, to keep the alcohol precursor from dissociating during CVD, alcohol vapor was introduced into the evaporator via a bubbler. The excess alcohol vapor over the Cu(hfac)$_2$·ROH precursor effectively prevented the early dissociation of ROH from Cu(hfac)$_2$. This is evidenced by the fact that the residual precursor remained liquid during and after each CVD run in the 80 °C oil bath, and retained its original melting point after the run. If the precursor had been converted to Cu(hfac)$_2$ as a result of alcohol dissociation, a solid substance would be observed at the temperature of 80 °C (since the melting point of Cu(hfac)$_2$ is close to 100 °C). Additionally, the excess alcohol vapor also increases the chance of reaction between the Cu(hfac)$_2$ and the alcohol molecules at the stage of film deposition.

Table 2-6. The Approximate Dissociation Temperatures of Some Molecules from Their Cu(hfac)$_2$ Adducts

<table>
<thead>
<tr>
<th>Adducts</th>
<th>Dissociation Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)$_2$·H$_2$O</td>
<td>59</td>
</tr>
<tr>
<td>Cu(hfac)$_2$·MeOH</td>
<td>48</td>
</tr>
<tr>
<td>Cu(hfac)$_2$·EtOH</td>
<td>38</td>
</tr>
<tr>
<td>Cu(hfac)$_2$·n-PrOH</td>
<td>73</td>
</tr>
<tr>
<td>Cu(hfac)$_2$·i-PrOH</td>
<td>56</td>
</tr>
<tr>
<td>Cu(hfac)$_2$·n-BuOH</td>
<td>76</td>
</tr>
<tr>
<td>Cu(hfac)$_2$·s-BuOH</td>
<td>56</td>
</tr>
</tbody>
</table>
The dissociation of adducted alcohol or water molecules from the Cu(hfac)₂ at low temperature can be taken advantage of. Because of that, the solvent impurity in the precursor may not be important to the quality of the final films, as shown in the following comparison experiments. Two batches of Cu(hfac)₂·i-PrOH prepared in the open air and in the moisture-free glove box respectively were tried as precursors for CVD under the same conditions. As mentioned before, the precursor synthesized in the air has a lower melting point than that in glove box, probably due to partial reaction with water vapor in air. The results, however, did not show significant difference in thickness and resistivity of films obtained from these two compounds (see Table 2-7).

Table 2-7. Properties of Films Deposited Using Different Batches of Cu(hfac)₂·i-PrOH (200 °C, 60 min, N₂)

<table>
<thead>
<tr>
<th>Melting Point (°C)</th>
<th>Film Thickness (µm)</th>
<th>Resistivity (µΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35-40</td>
<td>1.3±0.3</td>
<td>2.8±1.1</td>
</tr>
<tr>
<td>50-53</td>
<td>1.4±0.3</td>
<td>2.8±1.5</td>
</tr>
</tbody>
</table>

Additionally, the ready departure of H₂O molecule from Cu(hfac)₂·xH₂O prompted us to investigate the possibility of preparing the Cu(hfac)₂ alcohol adducts during the course of the CVD process. We reasoned that, because water molecules dissociate easily from the parent Cu(hfac)₂ at the typical evaporation temperature, the application of excess alcohol vapor might facilitate the formation of more volatile alcohol adducts. The successful in-situ conversion of Cu(hfac)₂·H₂O to Cu(hfac)₂·ROH could possibly eliminate the difficulty and cost of precursor pre-preparation and purification. Accordingly we performed preliminary CVD experiments with Cu(hfac)₂·H₂O under the excess isopropyl alcohol vapor and N₂. Cu films were obtained.
from three such experiments (average thickness: 1.3 ± 0.4 μm; resistivity: 4.0 ± 3.2 μΩ\cdot cm). After the experiment, the melting point of the remaining precursor dropped to 50 °C, indicating that the hydrate had been converted to the 2-propanol adduct.

2.4.4 Evaporation Rates of Cu(hfac)$_2$-ROH

High volatility, and thus high evaporation rate, is always desired for a CVD precursor. Low evaporation rate is often one of the reasons for low film growth rate in CVD.

The vapor pressure of Cu(hfac)$_2$ was measured before by Temple et al.\textsuperscript{17} using a transpiration technique. An equation was obtained that describes the vapor pressure of Cu(hfac)$_2$ at various temperatures, as shown in equation 2-5. It was derived from evaporation rates of Cu(hfac)$_2$ at a limited number of temperatures.

$$\log_{10}(P_{vap}(\text{torr})) = 9.40-3113 / T (K)$$ \textbf{Equation 2-5}

There are also some reports concerning the evaporation rate of alcohol adducts of Cu(hfac)$_2$. They are mainly limited to the methanol and ethanol adducts. Chiang et al.\textsuperscript{34} observed increased evaporation rates of Cu(hfac)$_2$ dissolved in MeOH or EtOH compared with Cu(hfac)$_2$ using QMS, while Borgharkar et al.\textsuperscript{37} reported no enhancement of evaporation rates for either methanol or ethanol adducts via TGA analysis.

The goal of our measurement on the evaporation rates of the alcohol adducts is to study the effect of the alcohol adduction on the volatility of the Cu(hfac)$_2$ and eventually on growth rate of the deposited film. The focus of the measurements is mainly on the larger alcohol adducts, i.e. C$_3$ and C$_4$ alcohol adducts of Cu(hfac)$_2$, which

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have not been reported before. Furthermore, the measurements were conducted under
the same conditions and in the same apparatus as that used for our CVD experiments.
The details of the measurement were described in the experimental section. The
evaporation rates of all the studied precursors are listed in Table 2-8, in which the
“g/hr” represents the amounts of individual alcohol adduct evaporated per hour.

The data shows that, whether using N\textsubscript{2} or H\textsubscript{2} as carrier gas, there is little
difference in evaporation rates for the same precursor under our CVD experimental
conditions. However, there is a difference in the evaporation rates for different
precursors. Cu(hfac)\textsubscript{2}-i-PrOH exhibits the highest evaporation rate, which is close to
that of Cu(hfac)\textsubscript{2}. Contrary to the previous report of ref 34, and in agreement with ref
37, we find that alcohol adducts do not show higher evaporation rates. As a matter of
fact, the adductions decrease the evaporation rates for most of the precursors we
studied. Despite this, alcohol adducts do show lower melting points. This should allow
them to be used as liquid precursors under conventional CVD conditions.

The evaporation rates of the alcohol adducts approximately fall in the reverse
order as that of the boiling points of their corresponding alcohol, but not that of the
adducts’ melting points. As shown in the following sequence, the adduct with n-BuOH
shows the lowest evaporation rate while n-BuOH has the highest boiling point (117.7
\textdegree C) among the compared alcohols.

\[\text{Adduct evaporation rates increase}\]
\[
\begin{array}{cccccc}
\text{Cu(hfac)\textsubscript{2}-i-PrOH} & \text{Cu(hfac)\textsubscript{2}-s-BuOH} & \text{Cu(hfac)\textsubscript{2}-n-PrOH} & \text{Cu(hfac)\textsubscript{2}-i-BuOH} & \text{Cu(hfac)\textsubscript{2}-n-BuOH} \\
\text{(82.3 \textdegree C)} & \text{(98.0 \textdegree C)} & \text{(97.0 \textdegree C)} & \text{(108 \textdegree C)} & \text{(117.7 \textdegree C)}
\end{array}
\]

\[
\text{Alcohol boiling points increase}\rightarrow
\]
Table 2-8. Evaporation Rates of Cu(hfac)$_2$:ROH Under Practical CVD Conditions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Evaporation Rate (g/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)$_2$</td>
<td>0.55 ± 0.11*</td>
</tr>
<tr>
<td>H$_2$</td>
<td></td>
</tr>
<tr>
<td>Cu(hfac)$_2$-n-PrOH</td>
<td>0.35 ± 0.02</td>
</tr>
<tr>
<td>n-PrOH (g) + N$_2$ (g)</td>
<td></td>
</tr>
<tr>
<td>n-PrOH (g) + H$_2$ (g)</td>
<td>0.32 ± 0.02</td>
</tr>
<tr>
<td>Cu(hfac)$_2$-i-PrOH</td>
<td>0.53 ± 0.04</td>
</tr>
<tr>
<td>i-PrOH (g) + N$_2$ (g)</td>
<td></td>
</tr>
<tr>
<td>i-PrOH (g) + H$_2$ (g)</td>
<td>0.57 ± 0.12</td>
</tr>
<tr>
<td>Cu(hfac)$_2$-n-BuOH</td>
<td>0.20 ± 0.06</td>
</tr>
<tr>
<td>n-BuOH (g) + N$_2$ (g)</td>
<td></td>
</tr>
<tr>
<td>n-BuOH (g) + H$_2$ (g)</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>Cu(hfac)$_2$-s-BuOH</td>
<td>0.42 ± 0.06</td>
</tr>
<tr>
<td>s-BuOH (g) + N$_2$ (g)</td>
<td></td>
</tr>
<tr>
<td>s-BuOH (g) + H$_2$ (g)</td>
<td>0.49 ± 0.05</td>
</tr>
<tr>
<td>Cu(hfac)$_2$-i-BuOH</td>
<td>0.29 ± 0.04</td>
</tr>
<tr>
<td>i-BuOH (g) + N$_2$ (g)</td>
<td></td>
</tr>
<tr>
<td>i-BuOH (g) + H$_2$ (g)</td>
<td>0.31 ± 0.04</td>
</tr>
</tbody>
</table>

The gas flow rates were 15 mL/sec for H$_2$ and 13 mL/sec for N$_2$, unless specified otherwise.

We also notice that the Cu deposition rate of a precursor is not necessarily directly related to its evaporation rate: The n-BuOH adduct has the lowest evaporation rate. However, its Cu deposition rates under both N$_2$ and H$_2$ are higher than those of the s-BuOH adduct, which has the second highest evaporation rate.

2.4.5 The Analysis of CVD Exhausts

The purpose of the IR analysis of the exhausts is to identify the major byproducts of the CVD reaction and, eventually to provide information for the understanding of the mechanism of the process.

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The exhausts from the CVD experiments were collected using a liquid N\textsubscript{2} cold trap and analyzed using FTIR spectroscopy. The components of the cold trap include the excess alcohol, Cu(hfac\textsubscript{2}) and H(hfac). But we were particularly interested in such components as ketones and aldehydes as evidence of oxidation of the corresponding alcohols. Table 2-9 lists the products of alcohol oxidation and the IR wavenumbers used to detect them. The particular wavenumber was characteristic of C=O stretching in corresponding ketones or aldehydes. These compounds have been qualitatively identified in the collected byproducts by both literature spectra and the actual measurement of authentic samples of the ketones or aldehydes.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Major Byproducts</th>
<th>IR Wavenumber (C=O stretch) (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac\textsubscript{2})\textperiodcentered i-PrOH</td>
<td>CH\textsubscript{3}COCH\textsubscript{3}</td>
<td>1712</td>
</tr>
<tr>
<td>Cu(hfac\textsubscript{2})\textperiodcentered n-BuOH</td>
<td>CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CHO</td>
<td>1724</td>
</tr>
<tr>
<td>Cu(hfac\textsubscript{2})\textperiodcentered s-BuOH</td>
<td>CH\textsubscript{3}CH\textsubscript{2}COCH\textsubscript{3}</td>
<td>1724</td>
</tr>
<tr>
<td>Cu(hfac\textsubscript{2})\textperiodcentered i-BuOH</td>
<td>(CH\textsubscript{3})\textsubscript{2}CHCOH</td>
<td>1724</td>
</tr>
</tbody>
</table>

Furthermore, a calculation was carried out of the quantity of acetone collected during Cu CVD using Cu(hfac\textsubscript{2})\textperiodcentered i-PrOH + i-PrOH(g) + H\textsubscript{2}/N\textsubscript{2}. It was found that more acetone was present in the collected condensate when N\textsubscript{2} was used as carrier gas than with H\textsubscript{2}.

2.4.6 The Properties of Films Deposited Using Cu(hfac\textsubscript{2})\textperiodcentered ROH

Thermal CVD experiments were conducted using each adduct as precursor. The properties of the deposited films were used as the criteria to assess the CVD
performance of each alcohol adduct. The film properties that we are interested in are the thickness and resistivity, two of the most important concerns for Cu CVD. It will be shown in the following discussions that both carrier gas and alcohol have an effect on properties of the deposited film and its growth rate. During the process, the best combination of alcohol precursor and carrier gas will be identified. The results using individual adducts are summarized in Table 2-10.

(a) Cu(hfac)$_2$·MeOH and Cu(hfac)$_2$·EtOH

No good films were obtained using methanol or ethanol adducts under either H$_2$ or N$_2$ in our CVD experiments. The precursors remained solid during the experiments. The films were usually thin and transparent, but with a yellow color, similar to that of copper metal. They were too thin for reliable thickness or resistivity measurements.

(b) Cu(hfac)$_2$·n-PrOH

Films were routinely obtained using Cu(hfac)$_2$·n-PrOH under H$_2$ and n-PrOH vapor. This set of conditions is denoted “Cu(hfac)$_2$·n-PrOH + n-PrOH + H$_2$”. In contrast, Cu deposition occurred only irreproducibly under N$_2$ and n-PrOH vapor on glass substrates. Even when deposition occurred, the films were patchy and discontinuous. However, a thickness close to 1 μm (for 1 hr) was observed for two such films. It is suspected that the poor deposition of Cu(hfac)$_2$·n-PrOH under N$_2$ is due to the difficulty of nucleation of Cu from the reactants on the glass substrate. This claim is supported by five CVD experiments performed on Pd-coated Si substrates. Continuous films were repeatedly obtained under N$_2$ and n-PrOH on the palladium surface at the same temperature. Films near 2 μm in thickness were observed after one hour.
<table>
<thead>
<tr>
<th>ROH</th>
<th>( \text{H}_2 + \text{ROH}(\text{g}) )</th>
<th>( \text{N}_2 + \text{ROH}(\text{g}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Deposition rate (( \mu \text{m/h} ))</td>
<td>Resistivity (( \mu \Omega \cdot \text{cm} ))</td>
</tr>
<tr>
<td>Cu(hfac)$_2$ only</td>
<td>0.38 ± 0.05</td>
<td>2.4 ± 0.3</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>thin</td>
<td>thin</td>
</tr>
<tr>
<td>MeOH</td>
<td>thin</td>
<td>thin</td>
</tr>
<tr>
<td>( \text{t-PrOH} )</td>
<td>0.49 ± 0.11</td>
<td>2.3 ± 0.4</td>
</tr>
<tr>
<td>t-PrOH</td>
<td>0.54 ± 0.15</td>
<td>2.3 ± 0.8</td>
</tr>
<tr>
<td>( \text{i-PrOH} )</td>
<td>0.43 ± 0.12</td>
<td>3.6 ± 2.6</td>
</tr>
<tr>
<td>( \text{t-BuOH} )</td>
<td>0.35 ± 0.06</td>
<td>2.2 ± 0.8</td>
</tr>
<tr>
<td>( \text{i-BuOH} )</td>
<td>0.27 ± 0.08</td>
<td>2.2 ± 0.8</td>
</tr>
<tr>
<td>( \text{t-BuOH} )</td>
<td>0.27 ± 0.08</td>
<td>2.2 ± 0.8</td>
</tr>
</tbody>
</table>
(c) Cu(hfac)$_2$·i-PrOH

Copper films were readily deposited using Cu(hfac)$_2$·i-PrOH. The deposition rates varied depending on the carrier gases and whether excess i-PrOH vapor was present. The average film growth rate was about 0.54 ± 0.15 μm/hr under H$_2$ and about 1.30 ± 0.50 μm/hr under N$_2$ both with the presence of excess i-PrOH vapor. Under excess i-PrOH vapor and N$_2$, copper films were obtained at temperatures as low as 160 °C. At 200 °C, a few films as thick as 3 μm were observed after 60 minutes. On average, Cu(hfac)$_2$·i-PrOH gives more than twice the deposition rate in N$_2$ as in H$_2$ on glass substrates under comparable flow rates. The resistivities of films deposited under H$_2$ were somewhat lower than those under N$_2$.

We further investigated the CVD performance of Cu(hfac)$_2$·i-PrOH by varying the gas flow rate and composition. The changes in carrier gas flow rate do not affect the film thickness significantly whether under N$_2$ or H$_2$ (see Table 2-11).

This result can be attributed to two reasons: 1) the changes of gas flow rates did not cause dramatic change in the partial pressures of precursor and alcohol when compared with the total pressure in the system. The evaporation rates of each component of the system are shown in Table 2-12. They are calculated based on the evaporation rate of the alcohol, Cu(hfac)$_2$·i-PrOH, and the gas flow rate. 2) the Cu deposition rate may be limited by the surface reaction rate under our conditions.

The change of composition of the carrier gas, however, did have an impact on the film growth rate and resistivity. When a mixture of H$_2$ (10 %) and N$_2$ (90 %) was used as carrier gas, the deposited films had an average of thickness of 1.51 ± 0.32 μm and resistivity of 2.11 ± 0.49 μΩ·cm. The growth rate of the films under such
conditions is similar to that under pure N\textsubscript{2}, while the resistivity is lowered with the addition of H\textsubscript{2} in the stream. Such trend may have very significant implication on the practical CVD processing, where the right combination of H\textsubscript{2} and N\textsubscript{2} can be identified to produce the best results (high film growth rate and low resistivity).

Table 2-11. CVD Results vs. Carrier Gas Flow Rates

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Flow Rate (mL/s)</th>
<th>Thickness (µm)</th>
<th>Resistivity (µΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2} + i-PrOH</td>
<td>43</td>
<td>0.50 ± 0.11</td>
<td>1.99 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.66 ± 0.21</td>
<td>3.01 ± 1.48</td>
</tr>
<tr>
<td>N\textsubscript{2} + i-PrOH</td>
<td>26</td>
<td>1.16 ± 1.10</td>
<td>2.51 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.05 ± 0.17</td>
<td>2.44 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.35 ± 0.35</td>
<td>2.95 ± 0.98</td>
</tr>
</tbody>
</table>

Prescursor: Cu(hfac)\textsubscript{2}·i-PrOH; Substrate: glass; Deposition time: 60 minutes

Table 2-12. Calculated Evaporation Rates for the Reactants of CVD Using Cu(hfac)\textsubscript{2}·i-PrOH + i-PrOH + H\textsubscript{2}/N\textsubscript{2} @ 80 °C

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>H\textsubscript{2} (x 10\textsuperscript{-4} g/s)</th>
<th>N\textsubscript{2} (x 10\textsuperscript{-4} g/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (mL/s)</td>
<td>15</td>
<td>43</td>
</tr>
<tr>
<td>Cu(hfac)\textsubscript{2}·i-PrOH</td>
<td>1.6 ± 0.3</td>
<td>4.3 ± 0.7</td>
</tr>
<tr>
<td>i-PrOH (x 10\textsuperscript{-4} g/s)</td>
<td>12.2 ± 0.1</td>
<td>29.3 ± 2.2</td>
</tr>
</tbody>
</table>

The presence of sufficient i-PrOH vapor in the carrier gas is important to obtain high deposition rate for Cu(hfac)\textsubscript{2}. The growth rate of Cu films deposited using Cu(hfac)\textsubscript{2}·i-PrOH under H\textsubscript{2} without excess i-PrOH is 0.17 ± 0.06 µm/hr, only one third of those deposited with excess i-PrOH. Under N\textsubscript{2} without the additional i-PrOH vapor,
films deposited for 60 min are thin and transparent. The low deposition rate can be attributed to two possible reasons: 1) stoichiometric \textit{i}-PrOH (1:1) is not enough for the reaction between Cu(hfac)$_2$ and the alcohol; 2) \textit{i}-PrOH is lost preferentially from the original precursor, so that most of the Cu(hfac)$_2$ evaporates without any reductant. The residual precursor was found solid with a dark green color in 80 °C oil bath after the CVD process, indicating the premature departure of \textit{i}-PrOH from Cu(hfac)$_2$-\textit{i}-PrOH. Therefore, the extra \textit{i}-PrOH vapor is necessary in order to stabilize the \textit{i}-PrOH adducts and achieve good deposition rate using Cu(hfac)$_2$-\textit{i}-PrOH.

The CVD experiments were also performed using Cu(hfac)$_2$-\textit{i}-PrOH for various lengths of time in order to better understand the effect of alcohol and carrier gas on the film growth rate. The thickness of the resulting films is plotted against deposition time in Figure 2-9. Under all conditions, film thickness increases approximately linearly with deposition time. The results from Cu(hfac)$_2$ under H$_2$ serve as the baseline. The addition of \textit{i}-PrOH clearly increases film thickness at all the stages. The presence of \textit{i}-PrOH seems to shorten the induction time for the film formation regardless of carrier gas, as the film thicknesses are similar for \textit{i}-PrOH + N$_2$ and \textit{i}-PrOH + H$_2$, but higher than that of H$_2$ at the early stages of deposition (20 minutes). With prolonged deposition time, \textit{i}-PrOH + N$_2$ becomes more effective in enhancing film growth than \textit{i}-PrOH + H$_2$.

\textbf{On Silicon Substrates}

All the films mentioned above were deposited on glass substrates. CVD experiments under similar conditions using Cu(hfac)$_2$-\textit{i}-PrOH + \textit{i}-PrOH on silicon ((100), native oxide) substrates did not generate comparable results. The deposited films showed much lower thickness (0.46 ± 0.25 μm) and much higher resistivity (12.3 ± 3.9
\( \mu \Omega \cdot \text{cm} \) on Si surface under \( \text{N}_2 \). The silicon substrates were not specially treated, except for ultrasonical cleaning in acetone. Considering the notorious reactivity of copper with silicon materials, the silicon may have to do with the high resistivities of the copper films that deposited on it. The CVD reactions may be different on the silicon surface than on the glass.

![Graph](image)

**Figure 2-9. Thicknesses of Films vs. Deposition Time with Cu(hfac)\(_2\)-i-PrOH + H\(_2\) + H\(_2\)O + i-PrOH**

Auger analysis showed that the primary impurity in the Cu film deposited on glass substrate using Cu(hfac)\(_2\)-i-PrOH was carbon along with a smaller amount of
oxygen. Fluorine (F), which was part of the hfac ligand and was considered most
detrimental to the functions of ICs, was not detected within the instrument’s sensitivity.
Furthermore, no significant difference was found in impurity level between the films
deposited under $i$-PrOH + H$_2$, $i$-PrOH + N$_2$ or straight H$_2$. The details of the Auger data
are listed in the appendix. Films deposited using Cu(hfac)$_2$·$i$-PrOH show good
conformality on the complicated surface, as revealed by SEM analysis. Figure 2-9
shows good step coverage of Cu(hfac)$_2$·$i$-PrOH deposited film on a patterned Si/SiO$_2$
wafer.

(d) Cu(hfac)$_2$·$n$-BuOH

Films were also obtained using Cu(hfac)$_2$·$n$-BuOH with $n$-BuOH vapor. The
deposition rates were very similar under H$_2$ or N$_2$, and approximately linear with
deposition time, as shown in Figure 2-10.

(e) Cu(hfac)$_2$·$s$-BuOH

Copper films were deposited using Cu(hfac)$_2$·$s$-BuOH under either H$_2$ or N$_2$ with
excess s-BuOH vapor. As with Cu(hfac)$_2$·$n$-BuOH, the Cu deposition rates with
Cu(hfac)$_2$·$s$-BuOH were similar under H$_2$ and N$_2$, as shown in Figure 2-12. However,
the deposition rates with Cu(hfac)$_2$·$s$-BuOH under either carrier gas were slightly lower
than with Cu(hfac)$_2$·$n$-BuOH (see Table 2-7).

(f) Cu(hfac)$_2$·$i$-BuOH

Copper films were obtained using Cu(hfac)$_2$·$i$-BuOH under both H$_2$ and N$_2$. The
deposition rates were marginally higher under N$_2$ (0.36 ± 0.09 µm/hr) than under H$_2$
(0.27 ± 0.08 µm/hr). The deposition rate with Cu(hfac)$_2$·$i$-BuOH under N$_2$ increased to
0.62 ± 0.11 µm/hr when the deposition temperature was raised to 250 °C.
Figure 2-10. SEM Cross Section of a Trenched Wafer Covered by Cu Film
(Deposited Using Cu(hfac)$_2$·i-PrOH + i-PrOH + N$_2$)
Figure 2-11. Thicknesses of Films vs. Deposition Time with Cu(hfac)$_2$-$n$-BuOH + $n$-BuOH + H$_2$/N$_2$

Figure 2-12. Thicknesses of Films vs. Deposition Time with Cu(hfac)$_2$-$s$-BuOH + $s$-BuOH + H$_2$/N$_2$
(g) Cu(hfac)$_2$-$t$-BuOH

No films were obtained using Cu(hfac)$_2$-$t$-BuOH under N$_2$ and $t$-BuOH vapor. Because of its relatively high melting point (25 °C), $t$-BuOH alcohol in the bubbler tends to solidify. Therefore, it was warmed to ca. 40 °C to ensure proper operation. The poor CVD results under N$_2$ show that $t$-BuOH is not an effective reactant in the CVD using Cu(hfac)$_2$-$t$-BuOH. Also, the adduct is unstable and difficult to handle. Therefore, we did not test the performance of Cu(hfac)$_2$-$t$-BuOH under H$_2$.

(h) Anhydrous Cu(hfac)$_2$

Control experiments using anhydrous Cu(hfac)$_2$ under H$_2$ were also conducted under similar conditions. Films deposited for one hour have a thickness of 380 ± 50 nm. No film was obtained under N$_2$.

(i) Summary

Copper films were deposited using most of the studied alcohol adducts of Cu(hfac)$_2$. Not only were the films deposited with the alcohol adducts under H$_2$ as expected because of its reducing property, but also films were obtained in chemically inert N$_2$ in the presence of all of the alcohols studied except $t$-BuOH.

Most of the alcohol adducts outperform Cu(hfac)$_2$ in Cu deposition rate. The specific growth rates of the adducts vary depending on the alcohols and carrier gases used for the process.

Under H$_2$, most of the alcohol adducts yielded films at higher deposition rates compared with the parent Cu(hfac)$_2$. Besides i-PrOH, which has been known to enhance deposition rates of Cu(hfac)$_2$ under H$_2$, other alcohols including n-PrOH, n-BuOH, s-BuOH, i-BuOH all have similar effects. The degrees of enhancement are all
comparable to that of \(i\)-PrOH. The deposition rates of the adducts under \(H_2\) are all close to 0.40 \(\mu m/hr\). Although there are small increases in deposition rates in the order \(i\)-BuOH \(<\) \(s\)-BuOH \(<\) \(n\)-BuOH \(<\) \(i\)-PrOH \(<\) \(n\)-PrOH, the differences are within the margins of statistical errors of film thickness measurement and thus can not be overemphasized. On the other hand, the addition of MeOH and EtOH appears to inhibit the Cu deposition rate using Cu(hfac)\(_2\) under \(H_2\).

Under \(N_2\), the deposition rate using Cu(hfac)\(_2\)-\(i\)-PrOH under \(N_2 + i\)-PrOH(g) was most noticeable: it was almost four times as great as that using Cu(hfac)\(_2\) under \(H_2\) and almost three times that using Cu(hfac)\(_2\)-\(i\)-PrOH under \(H_2 + i\)-PrOH(g). MeOH and EtOH adducts again only produced very thin and transparent films. Continuous films could not be deposited reproducibly using the \(n\)-PrOH adduct under \(N_2\). Also no films were obtained using the \(t\)-BuOH adduct under \(N_2\). Films were readily obtained using the other alcohol adducts. The deposition rates are in the range of 0.40 \(\mu m/hr\) for \(n\)-PrOH, \(n\)-BuOH, \(s\)-BuOH and \(i\)-BuOH adducts under \(N_2\), which is similar to results with the same alcohol adducts under \(H_2\).

(j) Uniformity in Thickness and Resistivity Measurements

The uniformity of a single film varied depends on its thickness. When deposited under similar conditions, a thick film generally shows more roughness than a thin one. As depicted in Figure 2-3, five positions on a film were measured for thickness and sheet resistance. The uniformity of a film is reflected by the standard deviation of the average value of the five measurements. A rough film usually had a high value of standard deviation for the measurements of thickness. Two samples of such measurements are shown in Table 2-13. The sub-table (a) includes the thickness and
sheet resistance measurement data for a film deposited using Cu(hfac)$_2$·i-PrOH + i-PrOH + N$_2$ and the sub-table (b) for a one deposited using Cu(hfac)$_2$·i-PrOH + i-PrOH + H$_2$. The average of the measurements at five positions and its standard deviations are shown at bottom of each table. The absolute value of the standard deviation is normally 15% of the value of average for a single film.

### Table 2-13. Samples of Measurements of Film Thickness and Resistivity

<table>
<thead>
<tr>
<th>Position</th>
<th>Thickness (µm)</th>
<th>Sheet Resistance* (mΩ/sq)</th>
<th>Bulk Resistivity# (µΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Cu(hfac)$_2$·i-PrOH + i-PrOH + N$_2$ (No. 106)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.155</td>
<td>7.22</td>
<td>1.56</td>
</tr>
<tr>
<td>2</td>
<td>1.665</td>
<td>13.88</td>
<td>1.48</td>
</tr>
<tr>
<td>3</td>
<td>2.040</td>
<td>10.88</td>
<td>2.24</td>
</tr>
<tr>
<td>4</td>
<td>2.560</td>
<td>7.89</td>
<td>2.03</td>
</tr>
<tr>
<td>5</td>
<td>2.008</td>
<td>10.9</td>
<td>1.48</td>
</tr>
<tr>
<td>Average</td>
<td>2.09 ± 0.32</td>
<td>10.0 ± 2.7</td>
<td>2.1 ± 0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Position</th>
<th>Thickness (µm)</th>
<th>Sheet Resistance (mΩ/sq)</th>
<th>Bulk Resistivity (µΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b) Cu(hfac)$_2$·i-PrOH + i-PrOH + H$_2$ (No. 213)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.475</td>
<td>28.1</td>
<td>1.33</td>
</tr>
<tr>
<td>2</td>
<td>0.500</td>
<td>22.6</td>
<td>1.13</td>
</tr>
<tr>
<td>3</td>
<td>0.485</td>
<td>23.1</td>
<td>1.12</td>
</tr>
<tr>
<td>4</td>
<td>0.505</td>
<td>24.4</td>
<td>1.23</td>
</tr>
<tr>
<td>5</td>
<td>0.480</td>
<td>22.8</td>
<td>1.09</td>
</tr>
<tr>
<td>Average</td>
<td>0.49 ± 0.01</td>
<td>24 ± 2.3</td>
<td>1.2 ± 0.1</td>
</tr>
</tbody>
</table>

Both films were deposited at 200 °C for 60 minutes. *The correction factor (C.F. = 4.22) was included in the measurement of sheet resistance. #Bulk resistivity data was corrected with the measurement value of the high purity Cu foil.

As for the film resistivity, the films deposited under H$_2$ have a lower resistivity compared with those under N$_2$. Take the films deposited using Cu(hfac)$_2$·i-PrOH as example. The value of resistivity of films deposited under H$_2$ is about 20% less than under N$_2$ in Table 2-7. There is not much difference in the level of impurities for the

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films deposited under the two gases, as indicated by Auger and XPS analysis. However, films deposited under H\textsubscript{2} are generally thinner than those deposited under N\textsubscript{2}. It has been reported that the resistivities of CVD deposited Cu films increase, to some extent, with increasing thicknesses.\textsuperscript{42} The same trend was indeed observed in our data on film thickness and resistivity. As revealed in Figure 2-11, the resistivities of films deposited using Cu(hfac)\textsubscript{2}-i-PrOH +i-PrOH + N\textsubscript{2} generally increase with increasing film thickness. Meanwhile, films with similar thickness (e.g. near 500 nm) have similar resistivities, whether N\textsubscript{2} or H\textsubscript{2} is used. The higher resistivity observed for thicker films can be related to the morphologies of the films. It was noticed that films deposited under H\textsubscript{2} (which were thinner) were generally smoother and had finer grain size than those under N\textsubscript{2}, as observed under SEM (see Figure 2-14 and Figure 2-15).

![Figure 2-13. Resistivities vs. Thicknesses of Films Deposited Using Cu(hfac)\textsubscript{2}-i-PrOH +i-PrOH + H\textsubscript{2}/N\textsubscript{2}](image)

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Figure 2-14. SEM Image of a Film Deposited Using Cu(hfac)$_2$·i-PrOH + i-PrOH + N$_2$ (at 200 °C for 60 min, thickness ca. 3800 nm, resistivity 2.9 $\mu$Ω·cm, x 4000)

Figure 2-15. SEM Image of a Film Deposited Using Cu(hfac)$_2$·i-PrOH + i-PrOH + H$_2$ (at 200 °C for 60 min, thickness ca. 720 nm, resistivity ca. 1.9 $\mu$Ω·cm, x 4000)
2.5 Roles of Alcohols in CVD Using Cu(hfac)$_2$ Alcohol Adducts

In this section, the roles of the alcohols in CVD with Cu(hfac)$_2$ will be discussed based on the results presented above. We believe that the alcohols have two positive impacts on the CVD process with Cu(hfac)$_2$.

First, the binding of the C$_3$ and C$_4$ alcohols to the Cu(hfac)$_2$ results in a complex with a lower melting point, which allows some of them to be used as liquid precursors at a typical CVD evaporation temperature (80 °C). The liquid precursors are expected to produce more uniform and controllable vapor flow, even if they do not lead to a higher precursor vapor pressure. They can also be used in direct-liquid-injection CVD sources.

Second, the alcohols facilitate the film growth process by chemically promoting Cu formation. This becomes very obvious when considering the facts that 1) the deposition rate of Cu(hfac)$_2$ is increased when alcohols are added and 2) there is no deposition of copper film from Cu(hfac)$_2$ under N$_2$ under our conditions unless alcohols are introduced.

The most interesting finding in our study is that alcohols can replace H$_2$ as reducing agent in the CVD process. In particular, $i$-PrOH is more effective than H$_2$ as a reductant for Cu(hfac)$_2$. This function of alcohols has not been clearly identified previously in Cu CVD.

Overall, our study shows that combination of Cu(hfac)$_2$-$i$-PrOH, $i$-PrOH(g) and N$_2$ produces the best results: The film growth rate is much higher than for Cu(hfac)$_2$ + H$_2$ or any combinations involved with other alcohols, while the resistivities of the deposited films remain low. Because of this, Cu(hfac)$_2$-$i$-PrOH is used below as an example to illustrate the role of alcohols in CVD using Cu(hfac)$_2$ based precursors.
We have studied Cu(hfac)$_2$-i-PrOH closely from two aspects: evaporation rate and possible reaction pathways. The evaporation rate of Cu(hfac)$_2$-i-PrOH indeed is higher than other alcohol adducts from our measurements in the real settings. However, the high evaporation rate may not be the major reason for the enhanced deposition rate. It is believed that, under our experimental conditions, the CVD reaction on the substrate is reaction-rate-limited instead of mass-transfer-limited. This is likely because, for example, the evaporation rate of Cu(hfac)$_2$-i-PrOH + i-PrOH(g) + N$_2$ is almost identical to that of Cu(hfac)$_2$ + H$_2$ while its deposition rate is much higher in the i-PrOH system. Therefore, we believe that the different reaction pathways involved with i-PrOH likely play a major role in determining the deposition rate of copper film.

Accordingly, we propose a reaction mechanism for Cu CVD in the Cu(hfac)$_2$-ROH system. The mechanism is built on the following two assumptions.

First, we assume that interactions between i-PrOH and Cu(hfac)$_2$ occur mainly on the substrate surface. In other words, the alcohol and Cu(hfac)$_2$ should land on the substrate largely independently. Thus, the addition of i-PrOH most likely affects the deposition process on the substrate surface, rather than in the gas phase. Even if excess i-PrOH(g) converts a lot of Cu(hfac)$_2$(g) into Cu(hfac)$_2$·i-PrOH(g), this adduct is unlikely to react at 80 °C (i.e. before it gets to the substrate).

Second, it is also recognized that the surface reactions occur largely on the freshly formed copper surface except at the beginning when they do on the bare glass substrate. The copper films are usually visible to the naked eye within 1 minute after a CVD experiment starts.
As a result, our proposed reaction steps are mainly concerning the activity of alcohol on the Cu surface. The proposed mechanism is described in the following set of reactions and summarized schematically in Figure 2-15.

At the beginning, Cu(hfac)\(_2\) and \(i\)-PrOH will land on the Cu surface separately. It is believed that the adsorbed Cu(hfac)\(_2\) dissociates rapidly into Cu(hfac)(ads) and hfac(ads) (refer to reaction 2-7).\(^{22}\) As described by reaction 2-8, an \(i\)-PrOH molecule will split into a hydrogen atom and an isopropoxy species (CH\(_3\)CHOCH\(_3\)),\(^{23, 24}\) which adsorbs on the surface through the bonding between the oxygen on the alkoxy group and the copper atoms underneath. The isopropoxy intermediate could further transform to other more stable species depending on the carrier gas used. When H\(_2\) is used, the concentration of adsorbed H atoms will be higher than otherwise because of the occurrence of H\(_2\) adsorption (reaction 2-10). As a result, the adsorbed isopropoxy group is favored to recombine with adsorbed hydrogen to form alcohol, which leads to desorption of a complete \(i\)-PrOH molecule (reaction 2-8). When N\(_2\) is used as carrier gas, the adsorbed alkoxy species can adopt another pathway: releasing one more hydrogen from its \(\alpha\) carbon and leaving the surface in the form of acetone (reaction 2-9). The H atoms generated by \(i\)-PrOH adsorption on the substrate surface can reduce the Cu(hfac)\(_2\) to Cu (reaction 2-11, reaction 2-12). Under H\(_2\), the \(i\)-PrOH can act like a catalyst in the sense that it enhances the deposition rate of Cu(hfac)\(_2\) while desorbing intact at the end of the cycle. On the other hand, \(i\)-PrOH acts as the sole reducing agent under N\(_2\).

We have found several pieces of evidence that are consistent with the proposed reactions. From the IR analysis of the trapped exhausted gas, we are able to identify the
products of alcohol oxidation (i.e. ketones or aldehydes) when alcohols were used in CVD. More acetone is generated from CVD using Cu(hfac)$_2$·i-PrOH + N$_2$ + i-PrOH than under H$_2$ (see below) for the growth of films with identical thickness. This is because i-PrOH must be the reducing agent (source of H atoms) when H$_2$ is not used.

\[
\text{Cu(hfac)$_2$(g) } \leftrightarrow \text{Cu(hfac)(ads) + hfac(ads)} \quad \text{Reaction 2-7}
\]

\[
\text{CH}_3\text{CH(OH)CH}_3(g) \leftrightarrow \text{CH}_3\text{CHOCH}_3(ads) + \text{H(ads)} \quad \text{Reaction 2-8}
\]

\[
\text{CH}_3\text{CHOCH}_3(ads) \leftrightarrow \text{CH}_3\text{COCH}_3(g) + \text{H(ads)} \quad \text{Reaction 2-9}
\]

\[
\text{H}_2(g) \leftrightarrow 2\text{H(ads)} \quad \text{Reaction 2-10}
\]

\[
\text{hfac(ads) + H(ads) } \leftrightarrow \text{H(hfac)(g)} \quad \text{Reaction 2-11}
\]

\[
\text{Cu(hfac)(ads) + H(ads)} \rightarrow \text{H(hfac)(g) + Cu(s)} \quad \text{Reaction 2-12}
\]

Since this scheme is only feasible for primary and secondary alcohols, a tertiary alcohol is not expected to be a good reducing agent under N$_2$ due to its lack of α-H atoms. To desorb from the surface, it can only recombine with a dissociated hydrogen atom from the hydroxy group. Thus, under N$_2$, there will be no additional hydrogens available to reduce Cu(hfac)$_2$. This observation is consistent with our finding that Cu(hfac)$_2$·t-BuOH is not able to deposit Cu films under N$_2$.

The chemistry we propose for i-PrOH in the CVD reaction is similar to the dissociative adsorption process of a monolayer of methanol observed on a clean copper surface under vacuum.$^{43,44}$ It will not be surprising that other alcohols also have similar behavior on the copper surface, since the reactions are mainly involved with the hydroxy group. Actually, copper has long been known as an effective catalyst for
oxidizing alcohols to ketones or aldehydes. In fact, in our control experiment, when we passed i-PrOH vapor over a hot copper surface (200 °C), acetone was detected in the trapped effluent, as expected for i-PrOH oxidation on Cu surface. Again, the amount of acetone detected in CVD experiments varied depending on the carrier gas used. More acetone in the effluent was found when N\textsubscript{2} was used as carrier gas than H\textsubscript{2}.

It is also very interesting to compare water and alcohols in their effects on CVD with Cu(hfac\textsubscript{2}). Water is also believed to enhance the Cu deposition rate using Cu(hfac\textsubscript{2}) + H\textsubscript{2} by providing one of its hydrogen atoms to increase the concentration of H(ads), required for H(hfac) desorption. Water and alcohols usually give different results under chemically inert gases (such as Ar and N\textsubscript{2}) for CVD with Cu(hfac\textsubscript{2}). Copper oxide films are usually obtained under such inert gases when water is used, while metallic copper films are deposited with alcohols.\textsuperscript{31} The oxygen in the copper oxide film can be traced back to water. This can be attributed to the fact that water is unable to form a volatile and stable species after the first atom transfer. The adsorbed oxygen atoms are more likely incorporated into the film growth process, leading to CuO films when no extra hydrogens are available. In contrast, many alcohols can release a second hydrogen atom, forming ketones or aldehydes, which can then desorb from the surface. As a result, water is only effective for depositing Cu films under H\textsubscript{2}, while under N\textsubscript{2}, CuO rather than pure Cu is deposited using Cu(hfac\textsubscript{2}).

If dissociative adsorption of alcohols on the substrate surface is important in the CVD process under N\textsubscript{2}, the ease of oxidation of an alcohol should be useful to explain effectiveness of alcohols as reducing agents. Thermodynamic data for oxidation of alcohols is listed in Table 2-14. The enthalpy for oxidation of i-PrOH is significantly
more favorable than that of any other studied alcohols, (except for s-BuOH). Therefore, it is not surprising to find that Cu(hfac)$_2$:i-PrOH exhibits a much higher deposition rate under N$_2$ than any other alcohol adducts (except s-BuOH).

The considerations of bond dissociation enthalpies also favor the i-PrOH as a better reducing agent than the other alcohols. Table 2-15 lists the data available for bond dissociation enthalpies of the studied alcohols. It has been shown that the rate-determining step in methanol oxidation is the bond breaking between $\alpha$-carbon and hydrogen$^{44}$ If that is the case for all the other alcohols, then i-PrOH should be oxidized faster than the others, because the energy required to cleave the $\alpha$-C-H bond in i-PrOH is substantially lower than the rest listed in the table. Thus it should be the most efficient reducing agent in the CVD using Cu(hfac)$_2$ under N$_2$, as shown in our experiment. Under H$_2$, our scheme proposes that O-H bond breaking is the major step involved in the CVD process. The energies for O-H dissociation are almost identical for all the alcohols, suggesting they should be equally efficient in the reduction of Cu(hfac)$_2$ under H$_2$. This may explain why the deposition rates of Cu(hfac)$_2$ alcohol adducts are all similar under H$_2$.

H$_2$ and N$_2$ have very different adsorption behaviors on Cu. It has been reported that hydrogen shows strong affinity for copper. In contrast, adsorption of N$_2$ on copper is believed to be minimal.$^{45}$ Therefore, in the CVD process, the strong adsorption of H$_2$ gas onto Cu (e.g. under 1 atm H$_2$) may block the adsorption sites for the precursor molecules, resulting in a lower deposition rate. If alcohols can provide a ready source of hydrogen atoms for the reduction process of Cu(hfac)$_2$, then it is not surprising that the addition of alcohols would increase the deposition rate.
Table 2-14. Thermodynamics of Alcohol Oxidation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_f$ (alcohol, g)</th>
<th>$\Delta H_f$ (aldehyde/ketone, g)</th>
<th>$\Delta H_{rxn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{OH}(g) \rightarrow \text{CH}_2\text{O}(g) + \text{H}_2(g)$</td>
<td>-201.0</td>
<td>-115.9</td>
<td>85.1</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{OH}(g) \rightarrow \text{CH}_3\text{CHO}(g) + \text{H}_2(g)$</td>
<td>-235.3</td>
<td>-170.7</td>
<td>64.6</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(g) \rightarrow \text{CH}_3\text{CH}_2\text{CHO}(g) + \text{H}_2(g)$</td>
<td>-255.6</td>
<td>-188.7</td>
<td>66.9</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{CHOH}(g) \rightarrow (\text{CH}_3)_2\text{CO}(g) + \text{H}_2(g)$</td>
<td>-272.8</td>
<td>-218.5</td>
<td>54.3</td>
</tr>
<tr>
<td>$\text{CH}_3(\text{CH}_2)_2\text{OH}(g) \rightarrow \text{CH}_3(\text{CH}_2)_2\text{CHO}(g) + \text{H}_2(g)$</td>
<td>-275.3</td>
<td>-211.8</td>
<td>63.5</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{CHOHCH}_3(g) \rightarrow \text{CH}_3\text{CH}_2(\text{CO})\text{CH}_3(g) + \text{H}_2(g)$</td>
<td>-293.0</td>
<td>-238.1</td>
<td>54.9</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{CHCH}_2\text{OH}(g) \rightarrow (\text{CH}_3)_2\text{CHCH}(\text{CO})\text{CH}_3(g) + \text{H}_2(g)$</td>
<td>-283.8</td>
<td>-215.8</td>
<td>68.0</td>
</tr>
</tbody>
</table>

All values in kJ/mol

Table 2-15. Bond Dissociation Enthalpies ($D^\circ_{298}$) for Some Alcohols

<table>
<thead>
<tr>
<th>Alcohols</th>
<th>O-H</th>
<th>$\alpha$-C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>498</td>
<td>428$^{47}$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH}$</td>
<td>436</td>
<td>410</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{OH}$</td>
<td>438</td>
<td>389</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$</td>
<td>432</td>
<td>387</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{CHOH}$</td>
<td>438</td>
<td>381</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$</td>
<td>431</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$</td>
<td>441</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{COH}$</td>
<td>440</td>
<td></td>
</tr>
</tbody>
</table>

All values in kJ/mol

Additionally, the steric properties of the alcohols seem to have little effect on the deposition rate. The deposition rates of Cu(hfac)$_2$ with the C$_3$ and C$_4$ alcohols are very similar (especially under H$_2$) despite the fact that the alcohols are different in size and orientation.
Figure 2-16. Proposed Mechanism of CVD from Alcohol adducts of Cu(hfac)$_2$
2.6 Conclusions

We synthesized and studied systematically a series of Cu(hfac)$_2$ alcohol adducts as the first class of self-reducing Cu(II) precursors for Cu CVD. The thermal CVD experiments show that the new precursors formed high-quality Cu films without H$_2$ as the external reducing agent. We propose that alcohol molecules bearing $\alpha$-H atoms provide the H source for Cu(hfac)$_2$ reduction. Cu(hfac)$_2$·$i$-PrOH was identified as the best in the series based on the results from CVD experiments. It shows several significant improvements over Cu(hfac)$_2$, the best Cu(II) precursor previously recognized. 1) It is the first Cu(II) precursor that is a liquid at typical evaporation temperatures. 2) It can form high quality Cu films at much higher deposition rates than Cu(hfac)$_2$, especially under N$_2$. 3) As mentioned above, H$_2$ is not required as a reducing agent.
In the previous chapter, CVD using Cu(hfac)$_2$ alcohol adducts mostly on borosilicate glass substrates is discussed. Cu(hfac)$_2$·i-PrOH under N$_2$ is identified as the best precursor. Cu metallization also requires a suitable diffusion barrier, to prevent its migration into Si and SiO$_2$. TiN is a promising material for use as a diffusion barrier. But there have been few studies of Cu CVD on TiN surfaces. In this chapter, results from CVD experiments using Cu(hfac)$_2$·i-PrOH on TiN-coated substrates will be presented.

3.1 Introduction

3.1.1 Diffusion Barriers for Cu Metallization

In Cu-based Si circuits, a suitable diffusion barrier is required between Cu and Si/SiO$_2$. Direct contact between Cu and Si/SiO$_2$ will lead to the fast diffusion of Cu into Si and through SiO$_2$. Copper is regarded as the fastest interstitially diffusing element in Si, with a diffusion coefficient of $\sim$10$^{-8}$ cm$^2$/s at room temperature; even small amounts of Cu can jeopardize the function of Si devices. The material used as a Cu diffusion barrier should, first of all, have a good resistance to Cu migration, especially at circuit processing temperatures. Second, it should have relatively low resistivity and low contact resistance. Last but not least, it should have good adhesion to both the Cu metallization and the underlying materials.

Various materials have been studied as diffusion barriers between Cu and Si/SiO$_2$: the most common are the high-melting transition metals and their nitrides. These
materials include elements like Cr, Ti, W, Ta, Pt, Ni and Pd,\textsuperscript{50, 51, 52} and TiN, WN\textsubscript{x} and TaN\textsubscript{x}. Among these materials, TiN is a leading candidate as a diffusion barrier for Cu.

3.1.2 TiN as Diffusion Barrier for Cu

TiN is a material already used as diffusion barrier for Al and W in Al-based Si devices. Besides its low resistivity and high chemical stability,\textsuperscript{53} its maturity in fabrication also makes it a very attractive candidate for Cu diffusion barrier. The physical properties of TiN are listed in Table 3-1.

<table>
<thead>
<tr>
<th>Table 3-1. Physical Properties of TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cc)</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
</tr>
<tr>
<td>Resistivity (μΩ·cm)</td>
</tr>
<tr>
<td>Heat of formation (kJ/mol) at 25 °C</td>
</tr>
</tbody>
</table>

Data adapted from reference 56

The diffusion barrier effectiveness of TiN thin films against Cu has been widely studied. These properties are measured largely through depth-profiling analysis of Cu/TiN bilayer thin films, after annealing at high temperatures (500 °C, for example). Such studies revealed that TiN is an effective diffusion barrier. It was reported that a 20 nm thick TiN film prevented the migration of Cu during 500 °C annealing for 60 minutes.\textsuperscript{54} The maximum temperature at which TiN remains as an effective diffusion barrier depends on its microstructure,\textsuperscript{49, 50, 54} which is closely related to the deposition methods, processing conditions, and oxygen content within the grain boundaries of the surface region.\textsuperscript{55} For example, it has been reported that PVD TiN is more effective as a
diffusion barrier than LPCVD TiN at temperatures as high as 450 °C. This difference was attributed to the higher density and smaller grain size in PVD TiN.

3.1.3 Adhesion of Cu Thin Films to TiN

An important issue concerning TiN as diffusion barrier for Cu metallization is the adhesion between the two materials. In electronic packaging, good contact between the Cu and the diffusion barrier is a necessity for both mechanical strength and electrical conduction.

The adhesion between two adjacent solid substances is the result of the chemical or physical interactions at the interface. Such interactions include 1) van der Waals forces, 2) diffusion of the film and substrate into each other to form a transition region, or 3) formation of chemical bonding by inter-surface reactions. Any of these interactions can be taken advantage of to achieve good adhesion.

If TiN is to be used as diffusion barrier for Cu, it should have good adhesion with both SiO₂ and Cu, since it is sandwiched in-between. On the TiN/SiO₂ side, strong contact is established by the formation of chemical bonds. Ti, which is more electronegative than Si, can reduce the native oxygen in the SiO₂. The adhesion between Cu and TiN, however, is often poor.

It is believed that oxygen is always present in the TiN films, particularly on the surface, because Ti is extremely reactive to oxygen. As a result, the composition of such films is often denoted as TiN(O). Actually, oxygen, incorporated on surface region of TiN, is essential to prevent Cu diffusion into TiN (and ultimately into Si). It is reported that most barrier breakdowns occur along grain boundaries. However, this thin layer of oxide may pose problems for Cu adhesion. Cu is known not to adhere
well on a variety of metal oxide surfaces. The generally accepted criterion for adhesion between a metal film and an oxide substrate is that the deposited metal must have a high oxygen affinity to react chemically with the oxide surface. This oxygen affinity is related to the heat of formation of the oxide: metals whose oxides have a very negative heat of formation (e.g. Al, Ti, Cr, Mo; see examples in Table 3-2) make direct contact with the oxide layer and display good adhesion. Noble metals (Cu, Ag, Au) have a low oxygen affinity and therefore often show poor adhesion. This explains why TiN works well both as diffusion barrier and adhesion promoter in the Al metallization system (Al/TiN/SiO₂), while it has adhesion problems in the Cu system (Cu/TiN/SiO₂).

Table 3-2. Heats of Formation for Some Ti, Al and Cu oxides

<table>
<thead>
<tr>
<th>Bond</th>
<th>Phases</th>
<th>ΔH° at 298 K (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-O</td>
<td>TiO₂</td>
<td>-944.0</td>
</tr>
<tr>
<td>Al-O</td>
<td>Al₂O₃</td>
<td>-1675.7</td>
</tr>
<tr>
<td>Cu-O</td>
<td>CuO</td>
<td>-157.3</td>
</tr>
</tbody>
</table>

3.1.4 Approaches to Improving the Adhesion

The approaches to improving the adhesion of Cu to some oxide surfaces are discussed in this section. Although they do not address directly the problem of Cu with TiN(O), these methods can certainly serve as a guide to tackle the current problem.

(a) Surface Roughening

Improved adhesion can be achieved by surface roughening of the substrate using a chemical or mechanical etching process. Such process increases the effective area on the substrate upon which the van der Waals force can act. It has been used successfully in applications such as printing Cu lines on circuit boards, in which the introduced
surface roughness (a few micrometers) is much smaller than the size of the deposited Cu lines.\textsuperscript{62} However, due to the difficulties of controlling the etching conditions and reproducible surface roughness,\textsuperscript{63} this process may not be feasible for more sophisticated applications such as the production of submicron Cu conductor patterns.

(b) "Metal Glue"

A layer of a metal thin film can be inserted between Cu and the oxide, serving as adhesion promoter. Two new interfaces are created in this process. If each of the new interfaces is stronger than the one being replaced, the selected metal layer will glue Cu and metal oxide together. The method has been demonstrated to improve the adhesion of Cu to SiO\textsubscript{2}. The common materials used for this purpose are Cr,\textsuperscript{64} Ti\textsuperscript{65} and Nb.\textsuperscript{66} It would be ideal if the interposing layer can serve simultaneously as an adhesion promoter and a diffusion barrier.

(c) Ion Beam Assisted Deposition

Another effective approach is ion beam assisted deposition (IBAD), in which the film is bombarded by an ion beam during the growth process. Metallic films on a variety of substrates formed by IBAD show dramatic enhancement in interface adhesion,\textsuperscript{67} including Cu to SiO\textsubscript{2}, Cu to Al\textsubscript{2}O\textsubscript{3} and Cu to Ti.\textsuperscript{68,70} It is believed that ion bombardment reduces the stress state of the deposited Cu films.

(d) Substrate Surface Modification

The modification, or chemical treatment, of a substrate surface may also improve its adhesion to Cu. It has been reported that depositing a monolayer of Pd nuclei on the surface of Si or TiW will greatly improve the adhesion between each of them and Cu.\textsuperscript{62,69}
3.1.5 Adhesion Measurement Techniques

There are four most common techniques for assessing thin film adhesion: tape peeling, scratch, peel and pull tests. Among them, the Scotch tape peeling test is a qualitative and less reliable method. But the simplicity and the wide availability of testing materials make it a popular option and it is often used in a preliminary test. The other three testing methods require more complicated equipment. The strengths of the adhesion are normally expressed in grams, grams per mm of width and grams per mm$^2$ for scratch, peel and pull tests, respectively. In the test, a stylus is drawn over the sample surface. The load is increased until the film detaches from the substrate. The force at that point is essentially the adhesion of the film with respect to the applied load.

3.2 Previous Studies of Cu CVD on TiN

Kim at el. studied the CVD performance of Cu(hfac)$_2$ under H$_2$ on TiN substrates. The deposition temperatures were from 310-385 °C, total pressures were from 2-10 Torr, and evaporation temperatures were from 60-80 °C. They reported that copper formed only small crystalline aggregates, not continuous films on the TiN substrates, regardless of processing conditions. Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) analysis revealed that a thin layer of oxide was formed on the top of the TiN substrate, which was due to the exposure of substrates to air before the CVD experiment.

Riedel et al. studied the adhesion of CVD Cu on TiN surfaces. They reported that a thin interlayer containing C and F impurities was a reason for the poor adhesion of CVD Cu on TiN. This problem of interfacial contamination is due to the fact that
substrate materials are often more reactive than Cu towards C-O bonds. Such interfacial contamination can also result in high contact resistance even when high bulk purity of the Cu film yields low sheet resistance.\textsuperscript{73}

If the interfacial impurities were the reason for poor adhesion and high contact resistance between Cu and TiN, then an effective way to remove such impurities would help to solve the problems. It has been reported that atomic deuterium, generated by flowing deuterium gas (D\textsubscript{2}) over a heated tungsten filament, can effectively clean hydrocarbon and carbide species on the TiN surface by reduction.\textsuperscript{74} Meanwhile, the atomic deuterium can also reduce Cu(hfac\textsubscript{2}) to Cu on TiN, as indicated by surface analysis using XPS.\textsuperscript{73} Also, the interaction of a TiN surface with hydrogen plasma in the course of chemical vapor deposition of Al has previously been studied.\textsuperscript{75} Ti (2p) XPS indicated the reduction of some Ti(IV) to a metallic state, suggesting oxygen removal. This is a potential problem, since diffusion studies have shown that oxygen within the surface region is important for good diffusion barrier performance. However, the atomic deuterium, when applied as a cleaning and reducing agent, will not change significantly either N or O composition within the surface region.

The addition of atomic deuterium during the Cu CVD process may also enhance the adhesion of the resulting films to TiN, since the contamination of the interface is also believed to be one of the reasons for poor adhesion between the two materials.

Our study in CVD using Cu(hfac\textsubscript{2}) alcohol adducts indicates that alcohols can also serve as a source for atomic hydrogen. The hydrogen atoms released from alcohols during the CVD process may work in a similar way as the atomic deuterium to reduce Cu(hfac\textsubscript{2}) to Cu. They may also have the ability to clean impurities on the surface.
Therefore, we explored the possibility of using alcohols to improve the adhesion and resistivity of CVD Cu on TiN surface. The real thermal depositions of Cu film on TiN were conducted using Cu(hfac)$_2$ alcohol adducts. In contrast, previous studies on atomic deuterium were focused on the XPS analysis of pre-treated TiN surfaces under UHV. Cu(hfac)$_2$-$i$-PrOH was chosen as the precursor for our experiments, because $i$-PrOH was the most effective reducing agent, as indicated by our previous study.

### 3.3 Experimental Details

Two kinds of TiN thin film were used as substrates in our study. One is chemical vapor deposited; the other is physical vapor deposited. Both types of TiN film were deposited on 100 mm silicon wafers. The details of the substrates are listed in Table 3-3.

<table>
<thead>
<tr>
<th>Table 3-3. Information on the TiN Substrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVD TiN</td>
</tr>
<tr>
<td><strong>Vendor</strong></td>
</tr>
<tr>
<td><strong>Film Thickness (nm)</strong></td>
</tr>
<tr>
<td><strong>Sheet Resistance (Ω/sq)</strong></td>
</tr>
<tr>
<td><strong>Deposition Details</strong></td>
</tr>
</tbody>
</table>

The experimental setup shown in Figure 2-5 was used for the CVD experiments. The processing conditions were the same as included in Table 2-1.

Besides the measurements of film thickness and sheet resistance (which are described in 2.3.4), the adhesion of the film to the substrate was also tested by scotch tape. If a film did not come off or only less than 1/4 of it came off during the tape test, it was assessed as “pass”. Otherwise it was “fail”.

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Two methods were used to clean TiN substrates. Method one was the same as the one used for glass substrates, i.e. the substrates were immersed in acetone in an ultrasonic bath for 15 minutes. Method two was to first place the substrates in boiling trichloroethylene for 10 minutes, followed by washing in deionized water. They were then boiled in acetone for 10 minutes and rinsed again with deionized water. They were finally dried by flowing N\textsubscript{2} gas.

The PdCl\textsubscript{2} solution, which was used to treat the TiN substrate, was prepared by adding the desired amount of PdCl\textsubscript{2} (Alfa) into water. The brown solid PdCl\textsubscript{2} would not dissolve initially until a few drops of concentrated HCl were added.

To treat the TiN surface with PdCl\textsubscript{2}, the PdCl\textsubscript{2} solution was placed on the top of the clean TiN. It required approximately 9 drops of PdCl\textsubscript{2} to cover a substrate with an area of 2.25 cm\textsuperscript{2} (1.5 cm x 1.5 cm). The PdCl\textsubscript{2} covered substrate was subsequently heated at 120 °C for 30 or 60 minutes under flowing H\textsubscript{2} (5 ml/sec). Higher flow rates would risk blowing away the solution from the surface.

3.4 Results and Discussion

We investigated CVD using Cu(hfac)\textsubscript{2}·i-PrOH on TiN-coated substrates mainly from two aspects: 1) The CVD performance of Cu(hfac)\textsubscript{2}·i-PrOH on TiN surface, particularly the effects of i-PrOH on the qualities of the resultant films (i.e. growth rate, resistivity and adhesion to the substrate); 2) Whether the CVD performance of Cu(hfac)\textsubscript{2}·i-PrOH can be improved by the pre-treatment of TiN substrate with Pd nuclei.

To address these two questions, CVD experiments were conducted using Cu(hfac)\textsubscript{2}·i-PrOH + i-PrOH. They were carried out under different carrier gases (H\textsubscript{2} or N\textsubscript{2}) and on different types of substrates (CVD-deposited TiN, PVD-deposited TiN or Pd
treated PVD TiN, all on Si wafers). For control experiments, CVD was also conducted using Cu(hfac)$_2$ under H$_2$. The properties of the resultant films will be discussed below based on the film growth rate, resistivity and adhesion to substrate.

3.4.1 CVD on Clean TiN

(a) PVD and CVD TiN

Our study showed that the type of TiN substrate (i.e. deposited by CVD or PVD) has an effect on the properties of films deposited on them using Cu(hfac)$_2$ or Cu(hfac)$_2$·i-PrOH. The results are summarized in Table 3-4.

Cu(hfac)$_2$ did not produce any continuous films under H$_2$ on the CVD TiN surfaces. The experiments were carried out for either 60 or 30 minutes. Small amounts of isolated deposits were found on the substrate after each experiment. These deposits were probably copper, because they have a golden metallic color similar to that of Cu. This observation is consistent with that reported by Kim, et al. They reported that only small amounts of isolated deposits were obtained when using Cu(hfac)$_2$ + H$_2$ on TiN surface. However, the method to prepare the TiN films was not explained (i.e. CVD or PVD).

We obtained continuous films, however, using Cu(hfac)$_2$ + H$_2$ under similar processing conditions on the PVD TiN substrates.

No continuous films were obtained using Cu(hfac)$_2$·i-PrOH + i-PrOH + N$_2$ on either PVD or CVD TiN substrates. The experiments lasted as long as 60 minutes and were repeated several times. Small amounts of discontinuous deposits appeared on the substrate surface, which were very similar to those obtained using Cu(hfac)$_2$ + H$_2$. Increasing the N$_2$ flow rate from 13 mL/sec to 20 mL/sec to 27 mL/sec increased the
amount of this substance, but did not produce any continuous Cu metal. The deposit
was very soft and easily scratched by a coin.

Cu(hfac)$_2$-$i$-PrOH produced continuous films under $i$-PrOH and $H_2$, on both PVD
and CVD TiN substrates.

Table 3-4. Comparison of Film Properties Deposited on PVD and CVD
TiN Substrates

<table>
<thead>
<tr>
<th>Reactants</th>
<th>TiN</th>
<th>Deposition Time (min)*</th>
<th>Thickness (nm)</th>
<th>Resistivity ($\mu\Omega$-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)$_2$ + $H_2$</td>
<td>PVD</td>
<td>30 (6)</td>
<td>141 ± 59</td>
<td>8.0 ± 8.4</td>
</tr>
<tr>
<td></td>
<td>PVD</td>
<td>60 (1)</td>
<td>138 ± 12</td>
<td>14.5 ± 6.8</td>
</tr>
<tr>
<td></td>
<td>CVD</td>
<td>30/60</td>
<td>no continuous film</td>
<td></td>
</tr>
<tr>
<td>Cu(hfac)$_2$-$i$-PrOH + $i$-PrOH + $H_2$</td>
<td>PVD</td>
<td>15 (3)</td>
<td>75 ± 3</td>
<td>5.4 ± 1.8</td>
</tr>
<tr>
<td></td>
<td>PVD</td>
<td>15 (6)</td>
<td>300 ± 150</td>
<td>13 ± 12</td>
</tr>
<tr>
<td></td>
<td>CVD</td>
<td>30 (4)</td>
<td>100 ± 50</td>
<td>46 ± 27</td>
</tr>
<tr>
<td></td>
<td>CVD</td>
<td>30 (2)</td>
<td>130 ± 10</td>
<td>6.4 ± 6.0</td>
</tr>
<tr>
<td>Cu(hfac)$_2$-$i$-PrOH + $i$-PrOH + $N_2$</td>
<td>PVD</td>
<td>30/60</td>
<td>no continuous film</td>
<td></td>
</tr>
</tbody>
</table>

*The number of films deposited is included in the parentheses. All the substrates were
cleaned by acetone in ultrasonic bath only.

In general, the films grew faster on PVD TiN than on CVD TiN under similar
conditions. It has been known that the levels of chemical impurity and microstructures
vary for TiN film prepared by CVD and PVD.\textsuperscript{76, 77} The TiN films prepared by PVD are
generally more pure. These differences in the TiN substrates could have some influence
on the Cu films deposited on them. After becoming aware of the difference among the
TiN substrates, we used PVD TiN substrates in the remaining CVD experiments.
(b) Cleaning Procedures for TiN

The cleaning methods of the TiN substrates also affected the qualities of the film deposited on them. As mentioned in section 3.3, we tried two cleaning procedures for TiN substrate. The first one was ultrasonic cleaning with acetone; the second one involved boiling trichloroethylene followed by acetone. We found that films deposited on the substrates cleaned by the second method were much more shining and smooth. The smoothness of the films was shown by the much lower standard deviation for the thickness of individual films. The films also had lower resistivities. Although still larger than that of pure copper, they were reduced by as much as six times, compared to those deposited on TiN cleaned by the first method. This improvement in the resistivity could be attributed to the effective removal of impurities from the substrate surface by the second cleaning method, which results in less impurity incorporated into the films. On the other hand, the film growth rates were similar under the same processing conditions, regardless of the cleaning procedures. It suggested that, if the impurities did contribute to the high resistivity of the deposited films, they might do so by simply becoming incorporated into the film, rather than take part in the reaction with Cu(hfac)$_2$ and alcohol.

(c) CVD Performance of Cu(hfac)$_2$-i-PrOH and Cu(hfac)$_2$ on TiN

Films with a metallic golden color were obtained using either Cu(hfac)$_2$ + H$_2$ or Cu(hfac)$_2$-i-PrOH + i-PrOH + H$_2$ for various lengths of time. CVD experiments were conducted for as long as 60 minutes using Cu(hfac)$_2$ + H$_2$, in order to achieve a film thickness comparable to that with i-PrOH for 30 minutes. No film was obtained under N$_2$ and i-PrOH at the deposition temperature of 200 °C.
The experiments discussed in this section were all performed on PVD TiN substrates which were cleaned using boiling trichloroethylene and acetone. The results are listed in Table 3-5. A few trends are observed on the properties of films deposited on TiN substrates, as compared to those on borosilicate glass. Under similar conditions, the film growth rates are lower on TiN surfaces on TiN, while the bulk resistivities are higher than the counterpart. The film growth rate and resistivity are less reproducible on the TiN, as indicated by the large standard deviations. The thicknesses and bulk resistivities also vary greatly from one position to another on one film. This could be a result of the difficulty of Cu growth on the TiN surface. Another group has reported the difficulty of growing continuous Cu films on TiN using Cu(hfac)$_2$ + H$_2$ at low pressure.\textsuperscript{71} They attributed this difficulty to the high oxygen content on the top of the TiN. The TiN substrates used in our experiments also probably contained some amount of oxygen due to their long exposure to air.

As shown clearly in Table 3-5, the addition of $i$-PrOH increases the deposition rate of Cu using Cu(hfac)$_2$ under H$_2$. Under N$_2$, however, no continuous films were obtained by the addition of $i$-PrOH, whether on PVD or CVD substrates. This could be the case if $i$-PrOH does not adsorb and dissociate extensively on TiN surface. Then, there would not be a pathway available to reduce Cu(hfac)$_2$ to Cu under N$_2$. Under H$_2$, in the contrast, H$_2$ could act initially as the only reducing agent. Once the first layer of Cu film was formed, $i$-PrOH could participate in the process, since it was known to adsorb on the Cu surface.

Although the effects of $i$-PrOH on the film adhesion are less clear, the introduction of $i$-PrOH under H$_2$ does seem to improve the film adhesion to TiN.
substrates to some extent. We noticed that thinner films deposited under similar
conditions generally had better adhesion to the substrates than the thicker ones,
regardless of the precursor. As shown in Table 3-5 under both Cu(hfac)$_2$ + H$_2$ and
Cu(hfac)$_2$-i-PrOH + i-PrOH + H$_2$ categories, the number of the films that failed the
adhesion test increased with the increased deposition time (and therefore thicker films).
Therefore, when considering the effects of i-PrOH on the film adhesion, it is important
to compare the films with similar thicknesses, deposited with and without i-PrOH. The
films deposited for 15 minutes with Cu(hfac)$_2$-i-PrOH + i-PrOH + H$_2$ all passed the tape
test, while two of three films deposited for 30 minutes with Cu(hfac)$_2$ + H$_2$ (which had
comparable thicknesses) failed. Although two films deposited for 30 minutes with
Cu(hfac)$_2$-i-PrOH + i-PrOH + H$_2$ also failed the tape test, they had very high thickness
values (384 ± 47 nm; 506 ±147 nm). The other film with a thickness of 233 ± 20 nm
passed. In contrast, all three films with similar thicknesses (~255 nm) that were
deposited with Cu(hfac)$_2$ + H$_2$ failed the test.

Table 3-5. The Properties of Films Deposited on PVD TiN
Substrates

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Deposition Time (min)</th>
<th>Thickness (nm)</th>
<th>Resistivity (μΩ·cm)</th>
<th>Films # Passed Adhesion Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)$_2$ + H$_2$</td>
<td>15 (2)</td>
<td>50 ± 8</td>
<td>8.3 ± 3.3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>30 (3)</td>
<td>130 ± 30</td>
<td>3.6 ± 1.7</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>60 (3)</td>
<td>255 ± 40</td>
<td>3.3 ± 1.4</td>
<td>0</td>
</tr>
<tr>
<td>Cu(hfac)$_2$-i-PrOH + i-PrOH + H$_2$</td>
<td>15 (3)</td>
<td>140 ± 40</td>
<td>3.9 ± 0.3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>30 (3)</td>
<td>400 ± 140</td>
<td>2.6 ± 1.4</td>
<td>1</td>
</tr>
<tr>
<td>Cu(hfac)$_2$-i-PrOH + i-PrOH + N$_2$</td>
<td>30/60</td>
<td>no continuous film</td>
<td>blue color</td>
<td></td>
</tr>
</tbody>
</table>

All substrates were cleaned by boiling C$_2$HCl$_3$ and acetone.
3.4.2 CVD on Pd-treated TiN

Palladium (Pd) has been widely used to activate dielectric, semiconductor, or metal surfaces for electroless metal deposition. Pd crystals with sizes from 50 to 150 nm were observed on the surface of Si under SEM, after the silicon substrate was treated with a solution containing Pd$^{2+}$.  

Because of the relatively poor CVD performance of Cu(hfac)$_2$·i-PrOH on bare TiN, our attention turned to the possibility of utilizing Pd crystals as nuclei on a TiN surface to promote Cu deposition from Cu(hfac)$_2$·i-PrOH, and to promote adhesion of the film to the substrates. 

(a) Deposition of Pd on TiN

Since a successful method of depositing Pd on TiN surfaces has not been reported, we started by searching for an effective method to treat TiN surface with Pd. PdCl$_2$ solution was used as the source of Pd. It was assumed that the following reaction (reaction 3-1) would occur when H$_2$ gas was flowed through with heating, resulting in the formation of metallic Pd nuclei.

\[
PdCl_2(aq) + H_2(g) = Pd(s) + 2HCl(g)
\]

First, we tried just dipping the clean TiN substrate in the PdCl$_2$ solution for 60 minutes before the CVD experiments under H$_2$. But the films deposited on such substrates were similar in growth rate and resistivity to those on the un-dipped ones. Furthermore, we found no change in the sheet resistances of the samples with and without Pd treatment. This suggested that this method might not be effective for coating TiN with Pd. This technique works well with Si substrates following etching in HF: the
H-terminated surface reacts readily with PdCl₂. However, there is no comparable etching method available for TiN.

We modified the procedure by placing PdCl₂ solution directly on the TiN surface and then baking it under H₂ at 120 °C.

The amounts of Pd deposited were controlled by the concentrations of the PdCl₂ solutions that were placed on the TiN surface. Two concentrations of PdCl₂ were used. One contained approximately 5 mg of PdCl₂ in 50 mL of H₂O, which should produce approximately 600 layers of Pd on the substrate. The other one contained approximately 0.8 mg of PdCl₂ in 1000 mL of H₂O, which would just produce half of a monolayer of Pd. Such estimates were based on the calculation on basis of the size of a Pd atom.

In fact, a condensed thin film with silver metallic color (which is the characteristic color of Pd metal) was routinely observed on TiN substrate after it was treated with high concentration PdCl₂ solution (5 mg PdCl₂ in 50 mL H₂O) under H₂. Two such films were measured, which produced an average thickness of 130 ± 30 nm and a resistivity of 29 ± 5 μΩ-cm. In contrast, no Pd film was visible on the TiN surface after the Pd treatment using the low concentration PdCl₂ (0.8 mg PdCl₂ in 1000 mL H₂O).

(b) CVD on Pd-treated TiN

CVD experiments were tried on the Pd-treated TiN substrates. The results are shown in Table 3-6. Unlike the Cu films obtained on clean TiN (listed in Table 3-5), which were shining, all the films on PdCl₂-baked TiN appeared dark and dull, with a silver/gray color. The growth rates of the films were actually slower, as compared with those deposited on clean TiN substrates under similar conditions.
The addition of i-PrOH in the Cu(hfac)$_2$ + H$_2$ increased the deposition rate, as observed on clean TiN surface. But still no film was obtained using Cu(hfac)$_2$ + N$_2$ even when i-PrOH was added.

The resistivities of the films obtained under the listed conditions were all very high. The higher resistivities may be caused by the chemical species introduced by PdCl$_2$ solution. The reaction of PdCl$_2$ with H$_2$ on the TiN is not well understood.

Most of the deposited films passed the adhesion test. For the films that failed, the back of the film always had a color of Pd (silver), instead of yellow. This suggests that the adhesion between the Cu and Pd was stronger than that between Pd and TiN. As a result, Cu and Pd films came off together during such test.

The film growth rates are similar between the films grown on the substrates treated by PdCl$_2$ solution with high concentration and that with low one, when factoring in the thickness of Pd film (~130 nm for the high concentration PdCl$_2$ and negligible for the low one).

3.5 Conclusions

We explored the effectiveness of Cu(hfac)$_2$-i-PrOH as a precursor for Cu CVD on TiN-coated surfaces. Continuous Cu films were obtained under H$_2$, but not under N$_2$. Faster film growth rates were observed on PVD TiN than on CVD TiN under H$_2$. The addition of i-PrOH in the Cu(hfac)$_2$ + H$_2$ system increases the Cu deposition rate. However, it does not improve the resistivities of the films. The bulk resistivities of all the films are much higher than that of pure copper. The effect of i-PrOH on the adhesion of Cu film to TiN is less definite in our preliminary study. But the films with
similar thickness are more likely to pass the adhesion test if they are deposited using

\[ \text{Cu(hfac)}_2 \cdot \text{i-PrOH + i-PrOH + H}_2 \] than using \[ \text{Cu(hfac)}_2 + \text{H}_2 \].

### Table 3-6. Results of CVD on Pd-Treated PVD TiN Substrates

<table>
<thead>
<tr>
<th>Reactants</th>
<th>PdCl\textsubscript{2} Concent.</th>
<th>Deposit. Time (min)</th>
<th>Thickness (nm)</th>
<th>Resistivity ((\mu\Omega\cdot\text{cm}))</th>
<th>Films # Passed Adhesion Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Cu(hfac)}_2 \cdot \text{i-PrOH + i-PrOH + H}_2</td>
<td>5 mg in 50mL H\textsubscript{2}O</td>
<td>30 (3)</td>
<td>322 ± 41</td>
<td>30.5 ± 5.3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 (1)</td>
<td>501 ± 34</td>
<td>17.7 ± 2.9</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.8 mg in 1000 mL H\textsubscript{2}O</td>
<td>15 (3)</td>
<td>134 ± 11</td>
<td>7.0 ± 1.3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 (3)</td>
<td>175 ± 12</td>
<td>5.6 ± 2.3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 (3)</td>
<td>386 ± 82</td>
<td>21.5 ± 2.9</td>
<td>2</td>
</tr>
<tr>
<td>\text{Cu(hfac)}_2 \cdot \text{i-PrOH + i-PrOH + N}_2</td>
<td>5 mg in 50mL H\textsubscript{2}O</td>
<td>30/60</td>
<td>no film</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8 mg in 1000 mL H\textsubscript{2}O</td>
<td>30/60</td>
<td>no film</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The treatment of TiN surface with PdCl\textsubscript{2} does not seem to promote the film growth on it using \[ \text{Cu(hfac)}_2 \cdot \text{i-PrOH + i-PrOH + H}_2 \]. The films deposited on such substrates show higher resistivity than those on the clean TiN.

It should be noted that our work on the subject is preliminary and exploratory by nature. The CVD reactions on the TiN surface seem to be very surface sensitive. Therefore, more work needs to be done, preferably under vacuum conditions, before more concrete conclusions can be drawn.
CHAPTER 4 CONCLUSIONS AND FUTURE WORK

We synthesized and studied several alcohol adducts of Cu(hfac)$_2$ (Cu(hfac)$_2$-ROH) as the precursors for Cu CVD. Thermal CVD experiments were carried out systematically to test the effectiveness of these compounds as the precursors. Meanwhile, other aspects of the CVD process related the new precursors were also examined. These include the evaporation rates and the stabilities of the compounds at the processing conditions, and the byproducts of the reactions. We proposed a scheme of the CVD reaction involving Cu(hfac)$_2$ with the studied alcohols. These are the first class of Cu(II) precursors that can be used in the liquid state under the normal processing conditions. Our results show that some of the alcohols can improve the Cu deposition rate in the Cu(hfac)$_2$-based CVD system. Particularly, $i$-PrOH is most effective in deposition using Cu(hfac)$_2$. The resistivities of the films were not compromised by the addition of $i$-PrOH. Not only are the Cu(hfac)$_2$-ROH technically important as improved precursors for Cu CVD, but they are also chemically interesting. We reported for the first time that alcohols can act as the reducing agents to reduce Cu(hfac)$_2$ to Cu metal in CVD under N$_2$.

Most of the studies mentioned above were conducted on borosilicate glass substrates. We also particularly explored the CVD performance of Cu(hfac)$_2$-$i$-PrOH on TiN-coated surfaces under various conditions. Contrary to what we observed on glass substrates, continuous Cu films were not obtained on TiN substrates using Cu(hfac)$_2$-$i$-PrOH under N$_2$, even with the addition of extra $i$-PrOH vapor. But Cu deposition occurred under H$_2$, whether or not the alcohol was introduced. And faster film growth rates were achieved on PVD TiN surfaces than on CVD TiN under H$_2$. The Cu(hfac)$_2$-$i$-
PrOH + i-PrOH + H₂ system produced higher Cu deposition rate than Cu(hfac)₂·i-PrOH + i-PrOH + N₂ under similar conditions. It appeared to be caused by the addition of i-PrOH vapor. The bulk resistivities of all the films deposited on TiN are much higher than that of pure copper. The effect of i-PrOH on the adhesion of Cu films to TiN is less definite in our preliminary study. But films with similar thickness are more likely to pass the adhesion test if they are deposited using Cu(hfac)₂·i-PrOH + i-PrOH + H₂ than using Cu(hfac)₂ + H₂. Treatment of the TiN surface with Pd (from PdCl₂(aq) followed by reduction under H₂) does not seem to promote Cu film growth using Cu(hfac)₂·i-PrOH + i-PrOH + H₂. The films deposited on Pd-treated TiN substrates show higher resistivity than those on the clean TiN.

CVD in general is a surface-sensitive process. Most of the commercial CVD processes are conducted under vacuum to ensure the high quality of the deposited films. We are also in the process of building a new CVD reactor, which can be operated under low-pressure conditions. It will also be equipped with two mass flowmeters to give better control on flow rates of the precursors and carrier gas. A study of these precursors under such conditions may be more practically significant. Compared with the old reactor, the new one will also be useful in the kinetic study of CVD reactions due to its more accurate control and measurement of the reactant flows and temperatures.

More studies of Cu(hfac)₂ and alcohols could be conducted on fresh TiN surfaces. Our results in the subject are inconclusive, particularly in the areas of resistivity of the deposited Cu films and adhesion to TiN. This may be because these properties are very dependent on the conditions of the substrate surface. The substrate surface should be free of particles, oxygen and other chemical impurities. The new reactor will provide
the opportunity to investigate these areas because cleaner substrate surfaces can be achieved and repeated under vacuum conditions. It is also necessary to look into further the interaction of \(i\)-PrOH with TiN surface, i.e. whether the alcohol reacts with the surface; and if so, how this may affect the Cu film resistivity and the adhesion to the underlying TiN surface.

We also could study the performance of \(\text{Cu(hfac)}_2\cdot i\text{-PrOH} + i\text{-PrOH} + \text{H}_2/\text{N}_2\) on other potential barrier surfaces, such as Ta based materials.
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4. The diagram was originally adapted from the Novellus website in January 1999: http://www.novellus.com/damascus/tsd/tsd.htm.

5. Griffin, G. L.; Maverick, A. W., “CVD of Copper from Cu(II) Precursors” in Kodas, T. T.; Hampden-Smith, M. J., Eds. The Chemistry of Metal CVD; VCH, 1994; Chapter 4, 177-235


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39. Hatfield, B; Klauctter, F, unpublished results


46. CRC Handbook of Chemistry & Physics; 77th Ed., CRC Press: Boca Raton, FL, 1997; and references therein


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APPENDIX A. ILLUSTRATION OF FOUR-POINT PROBE

Probe tip copper film

Substrate

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APPENDIX B. CORRECTION FACTOR (C.F.) FOR SHEET RESISTANCE OF COPPER FILMS WITH FOUR-POINT PROBE

<table>
<thead>
<tr>
<th>d/s</th>
<th>Circle</th>
<th>Square a/d = 1</th>
<th>a/d = 2</th>
<th>Rectangle a/d = 3</th>
<th>a/d ≥ 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
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<td>1.25</td>
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<td>3.00</td>
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<td>2.7000</td>
<td>2.7005</td>
</tr>
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<td>4.00</td>
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<td>2.9289</td>
<td>3.1127</td>
<td>3.2246</td>
<td>3.2248</td>
</tr>
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<td>5.00</td>
<td></td>
<td>3.3625</td>
<td>3.5098</td>
<td>3.5749</td>
<td>3.5750</td>
</tr>
<tr>
<td>7.50</td>
<td></td>
<td>3.9273</td>
<td>4.0095</td>
<td>4.0361</td>
<td>4.0362</td>
</tr>
<tr>
<td>10.0</td>
<td></td>
<td>4.1716</td>
<td>4.2209</td>
<td>4.2357</td>
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<tr>
<td>15.0</td>
<td></td>
<td>4.3646</td>
<td>4.3882</td>
<td>4.3947</td>
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<tr>
<td>20.0</td>
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<td>4.4364</td>
<td>4.4516</td>
<td>4.4553</td>
<td>4.4553</td>
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<td>4.5076</td>
<td>4.5120</td>
<td>4.5129</td>
<td>4.5129</td>
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<td>4.5324</td>
<td>4.5324</td>
<td>4.5325</td>
<td>4.5324</td>
</tr>
</tbody>
</table>

Example (the settings I usually used):

Spacing between two probes: s = 0.0625 in

Square substrate: \( a = d = 0.625 \) in

\( d/s = 10 \)

Correction Factor: \( C. F. = 4.2209 \)
### APPENDIX C. AUGER ANALYSIS OF SOME FILMS DEPOSITED USING Cu(hfac)$_2$

#### Sample No: Pure Cu

<table>
<thead>
<tr>
<th>Sputtering T (min)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Cu (%)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>81.5</td>
<td>3</td>
<td>15.5</td>
<td>12/7/95</td>
</tr>
<tr>
<td>10</td>
<td>17.7</td>
<td>0</td>
<td>82.3</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>11.8</td>
<td>0</td>
<td>88.2</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>11.4</td>
<td>0</td>
<td>88.6</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>9.2</td>
<td>0</td>
<td>90.8</td>
<td></td>
</tr>
</tbody>
</table>

#### Sample No: 101, Cu(hfac)$_2$-i-PrOH+N$_2$+i-PrOH

<table>
<thead>
<tr>
<th>Sputtering T (min)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Cu (%)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>57</td>
<td>7</td>
<td>36</td>
<td>10/25/95</td>
</tr>
<tr>
<td>15</td>
<td>23</td>
<td>1</td>
<td>76</td>
<td>1.70 ± 0.58 μm</td>
</tr>
<tr>
<td>30</td>
<td>17</td>
<td>0</td>
<td>83</td>
<td>2.82 ± 1.65 μΩ·cm</td>
</tr>
<tr>
<td>45</td>
<td>11</td>
<td>0</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>7</td>
<td>0</td>
<td>93</td>
<td></td>
</tr>
</tbody>
</table>

#### Sample No: 100, Cu(hfac)$_2$-i-PrOH+N$_2$+i-PrOH

<table>
<thead>
<tr>
<th>Sputtering T (min)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Cu (%)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>89</td>
<td>2</td>
<td>8</td>
<td>10/25/95</td>
</tr>
<tr>
<td>2</td>
<td>46</td>
<td>1</td>
<td>53</td>
<td>1.60 ± 0.64 μm</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>2</td>
<td>77</td>
<td>2.30 ± 0.30 μΩ·cm</td>
</tr>
<tr>
<td>10</td>
<td>17</td>
<td>2</td>
<td>81</td>
<td></td>
</tr>
</tbody>
</table>

#### Sample No: 164, Cu(hfac)$_2$-i-PrOH+H$_2$+i-PrOH

<table>
<thead>
<tr>
<th>Sputtering T (min)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Cu (%)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>92.0</td>
<td>1</td>
<td>7.0</td>
<td>11/13/95</td>
</tr>
<tr>
<td>5</td>
<td>84.7</td>
<td>1</td>
<td>14.5</td>
<td>720 ± 70 nm</td>
</tr>
<tr>
<td>10</td>
<td>85.3</td>
<td>0</td>
<td>14.7</td>
<td>1.34 ± 0.27 μΩ·cm</td>
</tr>
<tr>
<td>20</td>
<td>74.7</td>
<td>0</td>
<td>25.3</td>
<td></td>
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<tr>
<td>35</td>
<td>46.0</td>
<td>3.5</td>
<td>50.5</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>43.0</td>
<td>0</td>
<td>57.0</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>42.1</td>
<td>0</td>
<td>57.9</td>
<td></td>
</tr>
</tbody>
</table>

(table continued)

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Sample No: 144, Cu(hfac)$_2$·i-PrOH+H$_2$+i-PrOH

<table>
<thead>
<tr>
<th>Sputtering T (min)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Cu (%)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84</td>
<td>3</td>
<td>12</td>
<td>12/7/95</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>0</td>
<td>85</td>
<td>440 ± 48 nm</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>0</td>
<td>90</td>
<td>1.60 ± 0.39 μΩ·cm</td>
</tr>
<tr>
<td>30</td>
<td>15</td>
<td>0</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>7</td>
<td>9</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>54</td>
<td>46</td>
<td></td>
</tr>
</tbody>
</table>

Sample No: 142, Cu(hfac)$_2$·i-PrOH+H$_2$

<table>
<thead>
<tr>
<th>Sputtering T (min)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Cu (%)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.9</td>
<td>4.6</td>
<td>28.1</td>
<td>11/13/95</td>
</tr>
<tr>
<td>10</td>
<td>31.3</td>
<td>1.3</td>
<td>67.4</td>
<td>360 ± 30 nm</td>
</tr>
<tr>
<td>20</td>
<td>25.9</td>
<td>1.4</td>
<td>72.7</td>
<td>2.33 ± 0.39 μΩ·cm</td>
</tr>
<tr>
<td>35</td>
<td>25.9</td>
<td>0.8</td>
<td>73.3</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>22.4</td>
<td>0.2</td>
<td>77.5</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>19.3</td>
<td>0.2</td>
<td>80.6</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>18.8</td>
<td>0</td>
<td>81.2</td>
<td></td>
</tr>
</tbody>
</table>
# APPENDIX D. TABLE OF ACRONYMS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(acac)</td>
<td>2,4-pentanedione</td>
</tr>
<tr>
<td>H(tfac)</td>
<td>1,1,1-trifluoro-2,4-pentanedione</td>
</tr>
<tr>
<td>H(hfac)</td>
<td>1,1,1,5,5,5-hexafluoro-2,4-pentanedione</td>
</tr>
<tr>
<td>H(dpm)</td>
<td>2,2,6,6-tetramethyl-3,5-heptanedione</td>
</tr>
<tr>
<td>H(fod)</td>
<td>6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanodione</td>
</tr>
<tr>
<td>H(tdf)</td>
<td>1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanodione</td>
</tr>
<tr>
<td>H(ppm)</td>
<td>6,6,7,7,7-pentafluoro-2,2-dimethyl-3,5-heptanodione</td>
</tr>
<tr>
<td>H(acim)</td>
<td>4-imino-2-pentanone</td>
</tr>
<tr>
<td>H₂(acen)</td>
<td>4,4'-(1, 2-ethanediylidinitriolo)bis(2-pentanone)</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>VTMS</td>
<td>vinyltrimethylsilane</td>
</tr>
<tr>
<td>CMP</td>
<td>Chemical Mechanical Planarization / Polishing</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>ULSI</td>
<td>Ultra-large-scale Integrated (Circuits)</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetry Analysis</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
VITA

Hui Fan, the son of Zhisheng Fan and Lijun Cheng, was born on March 14, 1969, in Beijing, People’s Republic of China. He received his bachelor of engineering (B.E.) degree in inorganic materials science and engineering from East China University of Chemical Technology in 1992. In 1993, he started his graduate study in chemistry under the guidance of Dr. Andrew W. Maverick at Louisiana State University. He is currently a candidate for the degree of Doctor of Philosophy (Ph.D.) in the Department of Chemistry.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate:       Hui Fan

Major Field:     Chemistry

Title of Dissertation:  Chemical Vapor Deposition of Copper Metal Using Cu(hfac)$_2$ Alcohol Adducts

Approved:

[Signatures]

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:  May 17, 2000