Copper metal is an important conductive material, particularly in microelectronics. It was introduced by IBM in 1997, and has been used as the interconnect material in computer microprocessors since that time. The electrochemical deposition of copper metal for this application took nearly ten years to develop, and continued effort in electroplating has extended the utility of this method to today. Copper metal has a bulk resistivity of 1.7241 μΩ cm, which should be used as a reference for reported resistivities in this review.

According to the international road map of semiconductors, manufacturing is reaching the point whereby electrochemical deposition methods such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). Here we review the deposition processes and in particular surface chemistry for depositing copper metal by CVD and ALD. A summary of known processes is given, and new trends in copper film deposition research are discussed. As well, process parameters and properties of copper films deposited from precursors using key ligand systems such as aminoketoximes, amidoximes, guanidinates, betaketoiminates are presented. Surface chemistry is examined from the point of view of the similarities of CVD and ALD, considering precursors that can be used in both types of processes. This serves to highlight trends in decomposition mechanisms and illuminates some interesting similarities in process temperature and other parameters.

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thickness after one cycle vary significantly, but typically are below one Å ngström for metals; indicating that growth does not occur in ideal monolayer-by-monolayer fashion, but by sub-monolayer growth. An excellent summary of known ALD processes was written by Puurunnen, and many copper processes are reported there.\textsuperscript{7}

The stability of the chemisorbed precursor monolayer is the defining factor for growth rate per cycle (GPC). Deposition processes can range from strictly ALD growth where the monolayer is completely, thermodynamically stable to processes that exhibit ALD growth at shorter cycle times, but show a continual growth CVD component at higher cycle times. This indicates the decomposition or autoconversion of the chemisorbed monolayer. This nuance, where the cycle time can differentiate whether a process is ALD or CVD, is a common concept in copper metal deposition. It is notable that having a “CVD” component of growth in a step-wise ALD process does not render it useless, and such processes can show excellent conformity of the deposited film.

Copper Reduction

Copper metal is easily reduced compared to many metals on the periodic table, a discussion that was central to an excellent review of transition metal precursors by Winter.\textsuperscript{5} As discussed by this review, copper (in its +2 state) has a standard reduction potential of 0.3419 V, making it the most easily reduced metal in the first row of the transition metals. In contrast, Ti\textsuperscript{3+} has a standard reduction potential of –1.630 V. Although this means that copper films are easily produced, it also means that copper precursors need to be designed with stability in mind so that the compounds only undergo self-reduction in desired conditions. It is even easier to reduce Cu\textsuperscript{+} to copper metal, which has a standard reduction potential of 0.521 V. Therefore, the thermal stability of copper precursors is an often-discussed characteristic when designing precursor compounds.

Typically, hydrogen gas is used as a reductant for copper precursors. Dihydrogen gas can homolytically dissociate to hydrogen adatoms on clean metal surfaces, greatly increasing the rate of reduction. However, there have recently been some interesting attempts to use a variety of other reducing agents, and novel techniques to do so. Table I outlines many key CVD and ALD processes for copper deposition, and gives several typical process parameters and conditions. This table highlights the predominance of dihydrogen gas as a reducing agent.

It should be noted that the substrate influences the effectiveness of hydrogen gas. Metal substrates can help cleave dihydrogen into hydrogen adatoms, which are at a higher chemical potential and so more effective at reduction. This has made noble metals a favored substrate for copper deposition.\textsuperscript{7} However, these metals (with some exceptions) are less useful for microelectronics applications. Ruthenium is a notable exception: copper has a low (i.e., preferable) wetting angle when deposited on a ruthenium substrate. This allows for better conductivity due to less crystallization and better connectivity of the copper.

Diethyl Zinc

An interesting reducing agent was introduced in 2009 from Hanyang University (Figure 2).\textsuperscript{10} Using [Cu(dmap)]\textsubscript{2} volatilized at 70°C (where “dmap” = dimethylamino-2-propoxide), copper metal films were deposited between 100°C–120°C using diethylzinc as the second reactant. Here, the copper and zinc undergo a ligand exchange, and the resulting copper alkyl surface species spontaneously reductively eliminates to produce copper metal. The film was found to incorporate significant zinc, oxygen, and carbon impurities above a deposition temperature of 120°C. Diethylzinc was used in a similar manner with Cu(pyrim)\textsubscript{2} (where “pyrim” = N-ethyl-2-pyrrolylaldiminate) at an evaporation temperature of 120°C, and a deposition temperature of 130°C.\textsuperscript{11} In this study, SiO\textsubscript{2}, Ta, and Ru substrates were used, and relatively smooth copper (120 nm) with a resistivity of 89 μΩ·cm was found on SiO\textsubscript{2} as well as Ta. There was significant incorporation of impurities, with the metallic film containing roughly 10% zinc and significant oxygen contamination in the bulk film. In both cases where diethyl zinc was used, reductive elimination of butane from diethyl zinc is the likely contributor to the metallic impurity, as discussed at length in a computational model from Tyndall.\textsuperscript{12}

It should be noted that the computational study modeled all species as gas phase molecules, while this review uses surface species notation (for consistency with subsequent chemical equations and schemes). In general, the elimination of ZnX\textsubscript{2} where X is an anionic ligand, is more likely when ZnX\textsubscript{2} is a more volatile species, and this was modeled in two steps in this paper (Figure 3). It is interesting to note that this study finds that the reduction of the surface species is more likely if the surface species is copper(I). If the precursor is Cu\textsuperscript{2+} and remains in this oxidation state when chemisorbed, then a “double” ligand exchange will result in a surface bound CuEt\textsubscript{2} species, which will not easily reductively eliminate to form metallic copper. However, two chemisorbed CuEt moieties will undergo reductive elimination to form metallic copper and butane:

\[
\|\text{CuEt}_2 \rightarrow \text{unfavorable reaction}
\]

\[
2\|\text{CuEt} \rightarrow 2\|\text{Cu}_0 + \text{C}_4\text{H}_{10}(g)
\]

The reductive elimination of two ethyl groups to form butane is always more favorable than any other reductive elimination with respect to the ligands modeled in this study. It was also noticeable that the “pyrim” ligands had a greater propensity to drive the deposition of zinc metal through favorable disproportionation from a chemisorbed zinc(I) species:

\[
2\|\text{ZnX} \rightarrow \|\text{Zn}_0 + \text{ZnX}_2(g)
\]

Iodine Catalyzed Copper Deposition

In 2000, Seoul National University published a study showing that copper-adsorbed iodine could greatly enhance copper metal...
Table I. Summary of copper metal deposition processes by chemical vapor deposition or atomic layer deposition.

| Process Type | Precursor A/ Temperature (°C) | Precursor B | Process Temp (°C) | Substrate | Growth rate | Resistivity (μΩ·cm)/ thickness (μm) | Year, Ref. |
|--------------|-------------------------------|-------------|-------------------|-----------|-------------|-------------------------------------|-----------|
| CVD          | CuCl/300–350                  | H₂          | 350–500           | Si, SiO₂  | 8 Å/min     | 3.3/1.5                             | 1992, 22  |
| ALD          | CuCl/350                      | H₂          | 360–410           | Ta        | 0.8–1.25 Å/cycle | NR                                   | 1997, 23  |
| ALD          | CuCl/340                      | H₂O, H₂     | 375–475           | Al₂O₃, SiO₂ | 1.6 Å/cycle | NR                                  | 2004, 25  |
| ALD          | CuCl/390                      | Zn/435      | 500 (Cu:Zn alloy) | Al₂O₃     | 1–5.5 Å/cycle | NR                                  | 1997, 24  |
| CVD          | Cu(dmae)/90–98                |            | 200–210           | SrTiO₃    |             | 200/NR                              | 1993, 26  |
| CVD          | Cu(OCR₂CH₂NH₃⁺)₂, R: CH₃, CF₃ R': tBu, CH₃CH₂OCH₂/155 |            |                   |           |             |                                     |           |
| ALD          | CuCl/350                      | H₂          | 360–410           | Si        | 19.0 Å/min  | 3.44/0.15                           | 2001, 27  |
| ALD          | Cu(dmae)₂/90                  | H₂          | 230–350           | Al₂O₃, SiO₂ | 1.6 Å/cycle | NR                                  | 2004, 25  |
| CVD          | CuCl/340                      | H₂          | 375–475           | Al₂O₃     | 1–5.5 Å/cycle | NR                                  | 1997, 24  |
| CVD          | Cu(dmae)₂/70                  | H₂ plasma   | 150               | Ta        | 0.65 Å/cycle | 5.2/0.010                           | 2011, 29  |
| ALD          | Cu(dmamb)₂/100                | H₂          | 130–160           | Ru        | 0.13 Å/cycle | 68/0.017, 1250/0.025                 | 2014, 32  |
| ALD          | Cu(dmamb)₂/100                | H₂          | 155–165           | Pt, Pd    | 0.20 Å/cycle | 6.4–21.4/0.020 (Pd), 15.6–21.4/0.020 (Pt) | 2014, 32  |
| ALD          | Cu(dmamb)₂/100                | H₂          | 150               | glass     | -           | 2.9/0.080                           | 2003, 34  |
| CVD          | Cu(iPr-guan)/125              | H₂          | 200–300           | steel, Si | 2.0–4.2 Å/min | 4/0.270                           | 2009, 35  |
| ALD          | Cu(iPr-amd)₂/100              | H₂          | 280               | Si, glass | 0.5 Å/cycle | NR                                  | 2003, 33  |
| CVD          | Cu(iPr-guan)/125              | H₂          | 200               | optical fibre | 18 Å/min | NR                                  | 2011, 39  |
| CVD          | Cu(acac)₂, Cu(tfac)₂, Cu(hfac)₂/60–200 | H₂          | 225–390           | -         | 4.0 Å/min  | 3–6/NR                              | 1991–002, 42, 43, 45 |
| CVD          | Cu(hfac)·vtms/50              | H₂          | 75–240            | -         | >140 Å/minute | NR                                  | 1996, 34  |
| ALD          | Cu(acac)₂/130                 | H₂          | 250               | Al, Ti, glass | -         | -                                   | 2000, 40  |
| ALD          | Cu(acac)₂/125                 | H₂          | 140               | Si, glass | 0.18 Å/minute | 15/0.025                           | 2007, 47, 48 |
| ALD          | Cu(thd)₂/120                  | H₂          | 150–350           | Pt/Pd     | 0.36 Å/minute | 8/0.060                           | 1998–2007, 49–51 |
| ALD          | Cu(thd)₂/120                  | H₂          | 235               | Ti/Pt     | 0.7 Å/minute | NR                                  | 2009, 52  |
| ALD          | Cu(thd)₂/123.5                | H₂          | 180               | Si, Pd    | 0.12 Å/minute | NR                                  | 2005, 53  |
| ALD          | Cu(hfac)₂(H₂O)/75             | H₂          | 300               | Si        | 1.78/0.120 | -                                   | 2000, 54  |
| ALD          | Cu(hfac)₂/60                  | H₂          | 250               | RT-100    | 0.185 Å/minute | 19/0.015                           | 2010, 55  |
| ALD          | Cu(hfac)·vtmos/60             | H₂          | 200–300           | TiN       | 0.5 Å/minute | 2/0.040                           | 2009, 56  |
| ALD          | Cu(dmae)₂/70                  | H₂          | 100–120           | Si, Pd    | 0.2 Å/minute | 2.78/0.050                        | 2009, 58  |
| ALD          | Cu(pyrim)₂/120                | H₂          | 130               | SiO₂, Ta, Ru | -         | 89/0.120                           | 2010, 11  |
| ALD          | Cu(dki)·vtms/60               | H₂          | 120               | Si        | 0.2 Å/minute | 11.23/0.035                        | 2013, 60  |
| ALD          | Cu(nhc)(hmds)/90              | H₂          | 225               | Si        | 0.2 Å/minute | -                                   | 1998, 61  |

*“NR” herein means that the film thicknesses were not reported with the resistivity data.

Deposition. Using Cu(hfac)·vtms where hfac is hexafluoroacetylacetone and vtms is vinyltrimethylsilane, copper was shown to deposit with an enhanced rate of 155 Å/min at 150 °C without hydrogen. Ethyl iodide was used to catalyze the reaction, and was found to cover the surface with about 1/10th of a monolayer. The enhancement was so successful that copper even deposited with a growth rate of 25 Å/min at 50 °C, well below the common deposition temperature required for such a system. Interestingly, the authors found that the hfac desorbed from the surface as a dimer. This discovery led to a flurry of research with a variety of precursors, surface treatments and substrates. Molecular iodine has also been used to catalyze copper metal deposition. The substrate was pretreated with I₂ plasma and, using the same copper precursor, growth was enhanced from 10 Å/min to 20 Å/min at 170 °C. Catalyzed surface growth also showed the excellent characteristic of allowing bottom-up pore filling by deposited copper metal. This was shown be the result of a concentration of the iodine adatoms at the bottom of the feature compared to on the side-walls, thus accelerating bottom-up growth.
Solution Testing of Second Precursors

One burgeoning method of testing secondary “co-reagents” for copper metal deposition is solution testing. An excellent example of this was published in 2010 from a collaboration between McMaster University and Intel. In this publication, AlMe₃, BeCl₂, and ZnEt₂ were tested with a variety of copper(II) precursors to ascertain whether copper metal would precipitate from the solution reaction. These three compounds were of interest because they are all hard and borderline Lewis acids and can alkylate copper reagents easily. Also, their tolerance for oxygen and nitrogen-containing ligands makes them more chemically compatible as reducing agents. The copper compounds used in this study can be found in Figure 4, which has structural diagrams for all precursors mentioned in this review.

The reactions were carried out in a 1:1 or 2:1 stoichiometric mixture of coreagent:copper precursor in toluene. These were kept for 24 hours at each of the following temperatures: 25 °C, 50 °C, 75 °C, 100 °C, and 120 °C while being observed for copper metal formation. Any suspected copper metal depositions were verified by PXRD and XPS. Successful reactions were repeated in the presence of a variety of substrates to get copper films for imaging by SEM. In general, AlMe₃ and ZnEt₂ were found to be better co-reactants than BeCl₂. Interestingly, in the case of copper(II) N-isopropyl-2-salicylaldiminate, the precipitate was seen to be a mixture of amorphous zinc and brass (β-CuZn).

This straightforward technique can be quite easily adapted to any synthetic lab, and is likely in our opinion to become a common screening technique for precursors and co-reactants alike. Caution should be taken in its employment, however: it is possible that solvent polarity could influence both the stability and reactivity of given precursor/co-reactant pairs by either stabilizing the copper compound through coordinative bonding, or enhancing reactivity by solvent cage or similar effects. This is certainly an excellent technique to use in conjunction with other reactivity studies to enhance reactivity studies prior to committing to full-scale deposition process development.

Comparison of CVD and ALD of Copper

In a field as diverse and widely researched as copper deposition, it is impossible to assess the chemistry and deposition characteristics of every process. However, since the driving force behind the deposition of copper metal by CVD and ALD is undeniably the surface chemistry that is involved, it is useful to investigate this aspect more deeply. It is particularly instructive to compare CVD and ALD processes that exist for the same chemical precursors. This will highlight the necessary surface chemistry involved in physisorption, chemisorption, and chemical reaction to produce a target film.

From the outset, copper(II) (d⁹) centers and copper(I) (d¹⁰) centers need to be differentiated. Cu²⁺ prefers a square planar arrangement due to its favorable electronic configuration, but distortion from this geometry by steric effects is not uncommon. This generally means that CuX₂ species undergo cleavage upon chemisorption to a surface. In general, one can consider the growing film to consist of copper metal atoms, and so one ligand can adsorb to the surface, while the copper center in the precursor becomes a ligand-supported surface adatom. A simple formalism is the comproportionation to Cu⁺ of the surface Cu₀ state and the Cu²⁺ precursor state:

\[ \text{Cu}^{2+} \text{X}_2(g) + ||\text{Cu}^0 \rightarrow 2||\text{Cu}^+ \text{X} \]

This is in contrast to Cu⁺. The d¹⁰ electronic configuration favours a linear geometry, and by only supporting one anionic ligand, the precursor compound needs to satisfy its coordination sphere somehow. Thus, there are generally two forms of volatile copper(I) compounds. If there is an attendant coordinative ligand, the linear geometry will be satisfied through a coordinative bond to form CuX·L (L being a neutral ligand). In this case, loss of the coordinative ligand is the most straightforward method of chemisorption:

\[ ||\text{Cu}^+ \text{X} \cdot \text{L}_{\text{ad}} + || \rightarrow ||\text{Cu}^+ \text{X} + \text{L}_{\text{ad}} \]

In the absence of a coordinating ligand, the compound can oligomerize, typically to a dimer (i.e. [CuX₂]₂). Thus chemisorption can be a simple matter of cleaving the dimer into surface-supported monomers:

\[ [\text{CuX}]_{2(g)} + 2|| \rightarrow 2||\text{Cu}^+ \text{X} \]

It should be noted that CVD and ALD growth rates cannot necessarily be compared directly: CVD growth rates are reported in Å/min, while ALD growth rates are reported in Å/cycle. The cycle time for different ALD processes can vary significantly, and are not necessarily optimized to be the shortest possible cycle. Thus, while ALD growth rates are typically lower than CVD growth rates, the reader should keep in mind that CVD is reported with respect to time, and ALD is reported with respect to “cycle”.

Copper Chloride

Cuprous chloride (CuCl) was first reported as a deposition precursor in 1992 at Uppsala University. Here, CVD deposition of copper metal was seen at temperatures between 350 °C–500 °C in a quartz tube furnace with a growth rate of 5–8 Å/min. This precursor required an extremely high temperature to volatilize (300 °C–350 °C), limiting its practicality. However, conductive films of copper metal (1.5 μm, with a resistivity of 3.3 μΩ·cm) were deposited on silica using hydrogen as a reducing agent. There was no further exploration of the surface chemistry of this deposition in this paper, but the authors suppose the copper is formed by elimination of hydrogen chloride gas.
The Uppsala group were also able to undertake deposition of copper metal by ALD using copper(1) chloride. In this case, the copper metal was deposited on tantalum metal foils, using an evaporation temperature of 350°C and a deposition temperature range of 360°C–410°C. The growth per cycle (GPC) was limited at 0.8 Å/cycle with respect to a pulse of CuCl of less than 10s, but increased at higher deposition times. This led the authors to speculate that the chloride disproportionated to Cu0 and Cu(II) at higher temperatures. The growth rate of deposited copper increased as the hydrogen pulse increased, from 0.8–1.25 Å/cycle at 410°C. This also showed a 1/T relationship with respect to the deposition temperature. The authors speculate that the surface maintains a saturated copper chloride monolayer, but the hydrogen inserts itself into the adsorbed CuCl bond, and eliminates HCl while leaving a surface hydride (Figure 5). We speculate that this surface hydride can react with the next pulse of CuCl and eliminate HCl to form a clean copper metal surface. This surface is then able to uptake another equivalent of CuCl, thus showing the increased deposition rate.

ALD of copper metal on alumina-covered silica using CuCl was reported in 1997 from the University of Helsinki. In this case, the CuCl was held at 390°C and zinc vapor was used as the reducing agent, held at 435°C. CuZn alloyed films were deposited on alumina at 500°C. Saturation was not observed in this case, and very large growth rates (1.0–5.5 Å/cycle) were seen. The authors speculate that self-limiting growth initially occurs, but once copper was formed, the zinc metal started to dissolve in it, as well as acting as a reducing agent. This report showed no reaction using hydrogen for a reducing agent at these temperatures.

The Uppsala group also deposited copper metal by ALD using hydrogen and water as second precursors in the deposition process. Here, the evaporation temperature was 340°C, and deposition occurred on alumina and silica between 375°C–475°C, which was very similar conditions to the deposition on tantalum. Herein, the authors added water to the deposition process between the copper and hydrogen pulses (i.e., CuCl/H2O/H2). As reported, this generally had the effect of significantly increasing the rate of copper metal deposition on.

**Figure 4.** Chemical structures for the variety of copper precursors discussed in this review.

**Figure 5.** Insertion of dihydrogen gas into the existing copper-chloride bond of a copper chloride surface species, with subsequent elimination of hydrogen chloride gas.
alumina, but not on silica. The authors reported that this enhancement was caused by forming an intermediate copper oxide:

\[ 2\text{[CuCl + H}_2\text{O}(g) \rightarrow \text{Cu}_2\text{O + 2HCl}(g)} \]

With alumina as the substrate, water greatly improved the growth rate, giving a saturation “plateau” at 1.6 Å/cycle, but the “saturation curve” with respect to hydrogen pulse length showed a significantly decreasing plateau. We suggest that this could be the desorption of the copper species. In the process without water (i.e., CuCl/H₂), this report showed some growth, which contrasts the results from the Helsinki group. There was no saturation curve for this process, and the difference in deposition might be attributed to reactor design.

The effect of water in the growth process on silica did not change the deposition rate. The rate topped out at 1.1 Å/cycle, again showing a decreasing plateau. With both substrates, saturation started somewhere between pulse times of 10s and 15s, showing a slower reaction to hydrogen than when tantalum was used as the substrate. This supports the idea that the metal substrate participates in fixing hydrogen for the reaction.

Our interpretation of using CuCl as a precursor is that the CVD process is limited by the kinetics of decomposition of cuprous chloride by hydrogen, a process estimated to have an activation energy of 80 kJ/mol. With CuCl pulse lengths lower than 10s, the kinetic stability of the adsorbed layer is sufficient to allow layer-by-layer ALD growth, but CVD deposition occurs at higher exposures. Thus, kinetic stability of the monolayer can be sufficient to allow an ALD process to occur. The process is obviously quite sensitive to substrate, and this highlights an important aspect of CVD and ALD: the process is often more dependent on the substrate than on the kinetic parameters of the system, and thus is an important chemical partner in the process.

There are no known CVD or ALD processes using copper(II) chloride. Presumably this is due to the low volatility of this species compared to the copper(I) compound.

### Aminoalkoxides

Copper aminoalkoxides were first used for copper metal deposition in 1993 at Virginia Tech. Copper films were deposited between 200–210 °C with the precursor held between 90–98 °C. The resulting films had resistivities on the order of 200 μΩ·cm with low levels of oxygen, and no detectable levels of nitrogen. Careful thermal decomposition studies showed metal formation by the oxidation of a ligand through β-hydrogen abstraction, coupled with reductive elimination to produce one equivalent of the parent ligand (Figure 6). It should be noted that the mechanism given in Figure 6 incorporates the chemisorption modeled at the Tyndall Institute, and so is our reinterpretation of the (similar) original mechanism. In this model, the simple chemisorption of a variety of copper(II) precursors (CuX₂) was shown to undergo a ligand shift of one ligand to a growing copper surface while the chemisorbed species maintained its second ligand:

\[ \text{[Cu + CuX}_2\text{]} \rightarrow \text{2[CuX]} \]

This comproportionation has been discussed earlier in this review, but seems to be a common surface adsorption mechanism.

Similar compounds were used to deposit copper at the National Research Council Canada in 2001. Here, the ligands were of the general formula O-CR₂-CH₂-NHR, where R was CH₃ or CF₃, and R' was tert-Bu or CH₂CH₂OH. The best deposition had a precursor evaporation temperature of 155 °C and a deposition temperature of 250 °C. The deposition rate was 19 Å/min and the films (150 nm) had a sheet resistance of 3.44 μΩ·cm. These deposition showed minimal impurities of oxygen and nitrogen.

Copper(II) dimethylamino-2-propoxide (Cu(dmap)²) was used as a CVD precursor in 2003 at Ruhr-University Bochum along with the ethyl analogue copper(II) diethylamino-2-propoxide (Cu(deap)²).
saturated growth with a growth rate of 0.13 Å/cycle on both Pd and Pt substrates with a 3s pulse of Cu(dmap)$_2$. At $\sim$170°C, the growth rate increased dramatically, showing that the substrate might activate Cu(dmap)$_2$ to undergo CVD at lower temperatures than on silica. The resistivity was similar to the Ru substrate, suggesting that the films were not very conductive. Interestingly, this process required a 50 cycle nucleation initiation step on ruthenium before growth started.

The aminoborane could also be used with formic acid to convert the copper-containing monolayer to formate. In this case, the growth rate was 0.20 Å/cycle on Pt and Pd with an ALD window of 135°C–165°C without the necessity of nucleation cycles. It should be noted that the resistivities reported for this process in Table I might be misleading, since the deposited copper formed alloys with the Pt and Pd in this process. Here, as in the previous use of formic acid, the growth rate dropped when the temperature was higher than 160°C. This paper suggests that dimethylaminoborane is acting as a reducing agent: we speculate this occurs by producing dihydrogen at the process temperature. The dihydrogen could then react with the monolayer to eliminate the parent ligand, and generate copper metal (Figure 9).

Copper(II) dimethylamino-2-propoxide and related compounds all show similar, and very promising behavior. With low volatilization temperatures, these compounds undergo CVD at relatively low temperatures ($\sim$225°C), and can be activated by plasma hydrogen or novel thermal processes to produce copper thin films. In general, the surface chemisorbed precursors are stable up to about 160°C–170°C, where they typically undergo $\beta$-hydrogen abstraction and act as “single-source” precursors for copper metal.

**Amidinates**

Amidinates are relatively new precursors for CVD and ALD, with the first report of a copper(I) amidine in 2005 from Harvard.33 In this case, the compound was [Cu(iPr-amd)$_2$, where iPr-amd is N,N-diisopropyl-acetamidinate. The virtue of amidinates and guanidinates are their flexibility with respect to replacing alkyl groups, and the Harvard group ultimately published a paper reporting the use of the secondary butyl version of this precursor for copper metal deposition.34 This precursor was used with hydrogen as a reducing agent. It was evaporated at 100°C, and deposition occurred at 185°C. The copper film (80 nm) was granular, but on alumina it had a resistivity of 2.9 $\mu$Ω·cm. The authors speculate that the mechanism of the deposition is protonation of the amidine by dihydrogen, thus reducing the Cu(I).

Interestingly, [Cu(iPr-amd)$_2$]$_2$ was used for CVD deposition of copper metal in 2009.35 Here, the precursor was heated to 95°C, and the deposition was carried out between 200°C–300°C with hydrogen as a reducing agent. At 280°C, the films (270 nm) had a resistivity of 4 $\mu$Ω·cm, and the process had a growth rate in the mass-transport limited regime of 2.0–4.2 Å/min. This same group found that this precursor would decompose at 140°C without hydrogen.36 This corroborated decomposition work that was under taken at UC-Riverside.37 These works highlight the fact that the copper aminate compounds undergo very slow decomposition at 140°C that accelerates when temperatures reach $\sim$200°C. The ligand undergoes complex fragmentation at these high temperatures (Figure 10).

This thermal profile is mirrored by copper guanidinates, although the thermolysis follows a different path.38 Here, copper metal was found to deposit without a reducing gas at 225°C. Further exploration of the decomposition showed that Cu(I) guanidinates decompose by $\beta$-hydrogen elimination (Figure 11). This copper guanidinate [Cu(iPr-guan)$_2$], where iPr-guan is N,N’-diisopropyl-N”,N”-dimethylguanidinate was later shown to deposit copper metal as low as 200°C using pulsed CVD at Carleton University.39 The precursor was evaporated at 125°C and was used without a reducing agent. The copper film was deposited on an optical fibre, and the growth rate was 18 Å/min, based on the pulse length of the deposition.

**Figure 8.** The surface reaction of hydrazine and subsequent reaction to produce copper metal from surface-bound copper formate.

**Figure 9.** Dimethylaminoborane forming dihydrogen in the gas phase, and the subsequent reaction of dihydrogen to reduce surface-bound copper “dmap” to metallic copper.

**Figure 10.** Thermal fragmentation of copper(I) amidine at a nickel surface with increasing temperatures.
Typically, copper(I) precursors have a tendency to disproportionate at a surface. However, very careful investigation of the surface chemistry of [Cu(guan)]₂ was undertaken by matrix-isolated IR and TOF-MS analysis, and no evidence of this disproportionation was found. This is striking, considering the strong evidence for this disproportionation as a major thermal decomposition pathway for surface species containing β-diketonates. Amidinates and guanidinates do not show significant improvement in their range of thermal deposition, and the switch-over between ALD to CVD growth occurs around 225°C. This is in line with other precursor families.

Thermolysis can be tuned in these systems by redesigning the amidinate so that it lacks the ability to undergo β-hydrogen elimination. By using iminopyrrolidinates with judiciously placed methyl groups, the temperature of the onset of thermolysis can be raised by over 200°C (Figure 12). Although the ligand undergoes some decomposition at 275°C, there is still an intact, chemisorbed monolayer at 350°C, and copper metal formation is not seen until above 400°C. Although high temperature copper deposition by CVD is not particularly sought after, this thermally stable precursor may show promise for ALD applications.

Beta-diketonates and Betaketoiminates

Copper β-diketonates exist for both oxidation states: Cu⁺ β-diketonates are typically monomers, while Cu²⁺ β-diketonates typically have an attendant ligand to saturate their coordination sphere. The CVD of copper β-diketonates has previously been excellently reviewed, and so a summary of these precursors are presented in the following paragraph.

Copper(II) diacetylacetonate (Cu(acac)₂) evaporates between 180°C–200°C and deposits copper metal between 225°C–250°C with hydrogen as a coreactant. Generally, fluorination improves the volatility of this compound while increasing the deposition temperature, with copper(II) bistri fluorooctylacetonate (Cu(tfac)₂) evaporating between 135°C–160°C and depositing between 250°C–300°C and copper(II) hexafluoroacetetylacetonate (Cu(hfac)₂) evaporating at 120°C and depositing metal between 340°C–390°C. This hexafluoro precursor also can be used in its monohydrate form (Cu(hfac)₂·H₂O), which drastically lowers the evaporation temperature to between 30°C–60°C and the deposition temperature to 250°C–350°C. Interestingly, this precursor also produces a lower resistivity copper film (1.9–2.8 μΩ·cm) compared to the water-free precursor (3–6 μΩ·cm). Thus, it appears that the fact that an equivalent of water might produce some copper oxide is ungrounded. Other β-diketonate ligands on copper(II) fall into these ranges for evaporation, deposition, and resistivity.

Copper(II) β-diketonates overshadow the Cu(II) precursors by having much lower volatilization temperatures as well as lower deposition temperatures. In this oxidation state, the copper precursor is supported by a coordinative ligand. There are many examples of this precursor family listed in the very thorough review by Rickerby and Steinke, and these show a range of volatilization temperatures from 35°C–77°C and deposition temperatures from 30°C–420°C. As an example, Cu(hfac)·vtms where vtms is vinyltrimethylsilane (known by the trade name “Cupraselact”) has an evaporation temperature of 50°C and a deposition range of 75°C–420°C. This large range for both evaporation and deposition makes this family of CVD precursors very useful in many different applications.

The surface chemistry of the β-diketonates (bdk) changes depending on copper’s oxidation state. In the case of Cu(bdk)₂, the surface decomposition chemistry has been shown to follow the typical CuL₂ decomposition of loss of one ligand to the growing surface, followed by combination of the ligand with an adsorbed hydrogen atom to produce the protonated ligand. This same study showed that Cu(bdk)₂·vtms has a growth temperature of 4.0–10 Å/min, depending on substrate while Cu(hfac)·vtms has a growth rate of greater than 140 Å/min at 200°C.

It is reasonable to expect that this surface etching limits the growth rate of the copper(I) precursors compared to the copper(II) precursors. However, this is not the case, and the Cu(I)(bdk)·L precursors have higher growth rates than their Cu(II) cousins because of the kinetics of growth. In fact, Cu(hfac)₂ has a growth rate at 350°C of 4.0–10 Å/min, depending on substrate while Cu(hfac)·vtms has a growth rate of greater than 140 Å/min at 200°C.

The atomic layer deposition of copper metal from β-diketonates is dominated by Cu²⁺. Initially, the thermal deposition of copper metal using Cu(acac)₂ and H₂ was reported by the Technical University of Helsinki (now Aalto University). The Cu(acac)₂ was volatilized at 130°C and deposition occurred at 250°C. Copper metal was deposited on glass, Si, Al, and Ti substrates, but the report gave no other deposition data. Plasma-assisted ALD of copper metal using...
dihydrogen was demonstrated at the University of Helsinki in 2005. Here, the precursor was evaporated at 125°C and the substrate was kept at 140°C. The growth saturated at around 5s pulse time of Cu(acac)₂. The process had a growth rate of 0.18 Å/cycle and the copper films showed a resistivity of 15 μΩ·cm (25 nm) on a variety of silicon, glass, and conductive substrates. These results were corroborated by a similar study carried out at SUNY. A related Cu(bdk)₂ was reported to undergo ALD deposition of copper in 1998 from Uppsala. In this case Cu(bdk)₂ was used, where thd is 2,2,6,6-tetramethylheptane-3,5-dionate: the tert-butyl analogue of acac. A Pt/Pd seed layer was used to nucleate the copper film, and substrate temperature was varied between 150°C–350°C. The precursor was evaporated 120°C. Growth saturated at about 3s and the film (60 nm) had a growth rate of 0.36 Å/cycle and a resistivity of 8 μΩ·cm. These values were corroborated by other studies, and a higher growth rate of 0.7 Å/cycle was found in one instance. Cu(thd)₃ was also used to deposit copper metal using plasma assisted ALD at Rensselaer Polytechnic Institute in 2005. The process used an evaporation temperature of 123.5°C with the Pt and silica substrates held 180°C. In the absence of hydrogen plasma, no copper growth was seen before 400°C, which agrees with the previously reported CVD studies. The growth rate of copper metal was found to be 0.12 Å/cycle, and varied with substrate. Interestingly, this study found that the growth had a CVD component at 250°C, which suggests that the plasma left an active surface species that permitted some CVD growth.

Cu(hfac)₂·H₂O was also used as a thermal ALD precursor. Here, the precursor was heated at 75°C. Several reducing agents were used, including methanol, ethanol and formaldehyde. The best film was grown at 300°C using formaldehyde as the reducing agent on a silica substrate. The resistivity was 1.78 μΩ·cm (120 nm), but no saturation curve or growth rate were reported. Interestingly, fluorine was not found as an impurity, and less than 2% of oxygen and a trace of carbon were found. The authors proposed a mechanism for alcohol reduction at the surface, but since it is not chemically balanced and involves some unsubstantiated side-products, the surface chemistry of this interesting process needs further study.

Another interesting thermal ALD process using Cu(hfac)₂ and H₂ was shown with pyridine as a catalyst. The copper was deposited on TiN with the pyridine added during the dihydrogen pulse. The precursor was evaporated at 60°C and depositions were performed from room temperature to 100°C. The growth rate was 0.185 Å/cycle and the resistivity was 19 μΩ·cm (15 nm). The films showed higher than normal impurities, with carbon ranging from 5%-16% and oxygen from 4%-5% over the deposition range. The role of pyridine was clarified by computational analysis: the pyridine stabilized the copper center as a coordinative ligand, but also weakened the Cu–O bond in the surface species by interacting with the bridgehead proton in the hfac ligand. This allowed the surface species to react with adsorbed hydrocarbon adatoms at lower the typical temperatures (Figure 13).

The only example of a copper(I) precursor employing a β-diketonate comes from Hanyang University. This group reports plasma-assisted ALD of copper metal from the precursor Cu(hfac)₂·vtmos where vtmos is vinyltrimethoxysilane. The precursor was evaporated at 60°C, and deposition was seen between 200°C–300°C on TiN using hydrogen plasma. The growth rate was 0.5 Å/cycle and the resistivity was 2 μΩ·cm (40 nm).

### Conclusions

In general, the deposition of copper metal by thermal atomic layer deposition can be accomplished using a wide variety of precursors exhibiting a wide variety of evaporation rates and decomposition mechanisms. However, it stands out that ALD of copper, in general, starts to show CVD behavior around 200°C–230°C. This is a surprisingly small range, considering significant differences in the ligands described above. This highlights the fact that chemisorption, and the lower thermal limit of that process, is a very important factor in designing ALD processes, and the second precursor that is used can activate copper metal deposition at surprisingly low temperatures. With respect to CVD, the picture is also clear: given the success of the copper(I) β-diketonate family, any new copper precursor of metallization would have to be remarkable and remarkably versatile to compete as a process. However, there is significant opportunity in process design, and given the ranges of CVD process temperatures, CVD can still compete with ALD to deposit low temperature copper metal films.

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