Fluorinated aminoalkoxide CuII complexes: new CVD precursors for deposition of copper metal

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Volatile low-melting CuII metal complexes of formula Cu[OC(CF3)R1CH2NHR2]2 (R1 = CF3 or CH3; R2 = CH3CH2OMe, Bu’ or Bu’) and Cu[OC(CF3)R1CH2NMe2]2 (R1 = CF3 or CH3) have been synthesized and characterized by spectroscopic methods. A single-crystal X-ray diffraction study on Cu[OC(CF3)2CH2NHCH2CH2OMe]2 shows that one methoxyethyl group of the aminoalkoxide ligand forms an intramolecular dative bond to the Cu atom to produce a square-pyramidal geometry at the metal center, while the second is linked to the Cu atom of the adjacent molecule, giving an N2O4 octahedral coordination arrangement. For the second Bu’-substituted complex, Cu[OC(CF3)2CH2NHBu’]2, the X-ray structural analysis demonstrated an N2O4 square-planar geometry, with one alkoxide oxygen atom forming strong H-bonding to an adjacent water molecule. Metal CVD experiments were carried out, showing that the source reagents Cu[OC(CF3)2CH2NHBu’]2, Cu[OC(CF3)2CH2NHBu’]2, and Cu[OCMe(CF3)CH2NHBu’]2, which possess a secondary amino group, are capable of depositing copper metal at temperatures of 250–300 °C under inert Ar carrier gas, while Cu[OCMe(CF3)CH2NMe2], with a tertiary amine group, requires the use of reductive H2 carrier gas to induce metal deposition at lower temperatures.

Copper metal thin films have great potential for fabricating metal interconnections as well as for filling contacts and via holes designed for next-generation ultra large scale integrated (ULSI) circuit technology. The advantages of copper over other conducting metals, such as aluminum, include lower resistivity, enhanced electromigration resistance, and increased resistance to stress-induced formation of voids due to a higher melting point. In addition, copper metal also provides improvements related to device performances, such as greater operation speed, reduced cross-talk and RC delay, etc.

The copper(n) hexafluoroacetylacetonate complex Cu(hfac)2 has been used as a CVD source reagent to deposit copper metal.2 Precursors of this type also include the related β-acetoacetate and β-ketoiminate CuII complexes.3 The strategy of changing the coordination ligand is aimed at trying to increase the volatility and thermal stability of the complex, while also being able to induce the selective deposition of copper metal on patterned substrate surfaces and to lower the deposition temperature. For the parent complex Cu(hfac)2, it was reported that pure copper thin film can be obtained in the presence of H2 as a reducing agent.4

\[
Cu(hfac)2 + H2 \rightarrow Cu(s) + 2 hfacH
\]

Upon removal of the external reducing reagent, CuII diketonate source reagents leave an excess of carbon and other contaminants on the thin film due to unwanted heat-induced ligand fragmentation.5 In addition, lower temperatures must be used in order to ensure clean conversion to the metallic state.

On the other hand, a second type of CuII CVD source reagent has been developed, for which the best known reagent is the complex (hfac)Cu(tmvs) (tmvs = trimethylvinylsilane), which has been used as an industry standard to deposit copper by the CVD method. Other established CuI CVD source reagents include (hfac)CuL, where L = phosphine ligands such as PMe3, and PEt3,6 alkylene ligands such as 2-butyne, and olefins such as butadiene, 1,5-cyclooctadiene,7 and 2-methyl-1-hexene-3-yne.8 Using the parent complex (hfac)Cu(tmvs) as an example,9 the deposition of copper is represented by the thermally-induced disproportionation reaction:

\[
2 (hfac)Cu(tmvs) \rightarrow Cu + 2 tmvs + Cu(hfac)2
\]

However, the complex (hfac)Cu(tmvs) is thermally unstable and begins to decompose at temperatures above 55–60 °C. Thus, this metal complex must be stored in a refrigerator and the addition of a chemical stabilizer, such as free tmvs ligand, is needed to improve the stability.10 Moreover, the conversion from the liquid to the vapor phase requires excessive heating, thus, the aging and decomposition of (hfac)Cu(tmvs) at higher temperatures causes many difficulties, such as extensive maintenance of the CVD apparatus due to premature precursor decomposition. In order to prevent decomposition, lower temperatures have to be used for vapor transport. As a result, this reduces the precursor vapor pressure, giving a low deposition rate, and eventually leads to the formation of rough metal surfaces and large variations in surface resistivity.

Accordingly, there is a demand for new CVD source reagents, which should possess the combined advantages of both CuII and CuI compounds mentioned above, namely higher thermal and oxidative stability in air during storage, higher vapor pressure under the designated CVD conditions,
and the capacity to induce copper deposition in the absence of a reducing carrier gas such as H2.11 In this paper, we will report our achievement in synthesizing copper source reagents that fulfill these essential requirements. Part of this investigation has already been published as a Communication.12

Experimental

General information and materials

Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) mode. The thermogravimetric analyses (TGA) were recorded on a Seiko TG/DTA 300 instrument under an atmospheric pressure of N2 with a flow rate of 100 cm3 min−1 and with a heating rate of 10 °C min−1. Elemental analyses were carried out at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan. All aminoalkoxide ligands, HOC(CF3)2CH2NHR, R = CH3,CH2OMe, Bu' and Bu', HOC(CF3)2CH2NMe2, HOMe(CF3)2CH2NHBu', and HOCMe(CF3)2CH2NMMe2, were prepared according to the method reported in the literature.13 All reactions were performed under N2 using anhydrous solvents or solvents treated with an appropriate drying reagent.

The Cu metal thin films were studied using an X-ray diffractometer (XRD) with Cu-Kα radiation. Scanning electron microscopies (SEM) images were recorded on a Hitachi S-4000 system to study the surface morphology. The resistivities were measured using the four-point probe method at room temperature, for which the instrument was assembled using a Keithley 2182 nanovoltmeter and a Keithley 2400 constant current source. The composition of the thin film was determined by X-ray photoelectron spectroscopy (XPS) utilizing a Physical Electronics PHI 1600 system with an Al/Mg dual anode X-ray source. The surface composition in atom percent was measured from XPS spectra collected after 1–2 min sputtering with argon at 4 keV until a constant composition was obtained.

Synthesis of complex 1. Sodium hydride (0.15 g, 6 mmol) was suspended in 25 mL of THF. To this was added dropwise 1.26 g of aminoalcohol HOC(CF3)2CH2NHC6H4CH2OMe (5 mmol) in THF (25 mL). The mixture was further stirred for 2 h until evolution of gas had ceased. The solution was filtered to remove the unreacted NaH. The filtrate was then transferred into a 100 mL reaction flask containing a 1.0 mmol of hydride (6 mmol), 0.85 g of the aminoalcohol ligand HOC(CF3)2CH2NMe2 (5 mmol) and 0.37 g of CuCl2 (2.8 mmol). After removal of THF solvent, vacuum sublimation (20 mTorr, 72 °C) gave the purple solid Cu[(OCMe(CF3)2)CH2NMe2]2 (1, 0.73 g, 1.6 mmol) in 64% yield.

Synthesis of complex 2. Procedures identical to those employed to prepare 1 were followed, using 0.15 g of sodium hydride (6 mmol), 1.26 g of the aminoalcohol ligand HOC(CF3)2CH2NHBu' (5 mmol) and 0.37 g of CuCl2 (2.8 mmol). After removal of THF solvent, vacuum sublimation (20 mTorr, 68 °C) gave the purple solid Cu[OC(CF3)2CH2NHBu]2 (2, 1.12 g, 2.0 mmol) in 79% yield. Single crystals suitable for an X-ray diffraction study were grown from a mixture of CH2Cl2 and hexane at room temperature.

Spectral data for 2: MS (EI, 70 eV, m/e), L = C3H6F2NO, observed (actual) [assignment] [relative intensity]: 567 (567) [CuL2] (14.69), 401 (401) [CuL2 – C6F6O] (43.83), 316 (315) [CuL2 – L] (48.70), 252 (252) [L] (29.22), 148 (149) [CuL2 – C6F6O] (50.32), 86 (86) [L – C6F6O] (100.00), 69 (69) [CuF3] (9.901), 57 (57) [CH4] (12.66). Anal. calcd for Cu3H4F12N2O2Cu: C, 33.84; H, 4.26; N, 4.93; found: C, 32.92; H, 4.37; N, 4.96%.

Synthesis of complex 3. Procedures identical to those employed to prepare 1 were followed, using 0.15 g of sodium hydride (6 mmol), 1.26 g of the aminoalcohol ligand HOC(CF3)2CH2NMe2 (5 mmol) and 0.37 g of CuCl2 (2.8 mmol). After removal of THF solvent, vacuum sublimation (184 mTorr, 60 °C) gave the purple solid Cu[(OC(CF3)2)CH2NMe2]2 (3, 1.25 g, 2.2 mmol) in 88% yield.

Spectral data for 3: MS (EI, 70 eV, m/e), L = C3H6F2NO, observed (actual) [assignment] [relative intensity]: 567 (567) [CuL2] (0.67), 498 (498) [CuL2 – CF3] (1.31), 401 (401) [CuL2 – C6F6O] (47.18), 385 (386) [CuL2 – C6F6O]-CH3 (13.59), 316 (315) [CuL] (50.77), 300 (300) [CuL – CH2] (18.08), 260 (258) [CuL – Cu4H6 (11.79), 238 (238) [L – Cu4H6] (100.00), 148 (149) [CuL – C6F6O] (76.41), 86 (86) [L – C6F6O] (96.41), 69 (69) [CuF3] (9.90), 57 (57) [CH4] (12.66). Anal. calcd for Cu3H6F12N2O2Cu: C, 33.84; H, 4.26; N, 4.93; found: C, 34.07; H, 4.32; N, 4.65%.

Synthesis of complex 4. Procedures identical to those employed to prepare 1 were followed, using 0.15 g of sodium hydride (6 mmol), 1.12 g of the aminoalcohol ligand HOC(CF3)2CH2NMe2 (5 mmol) and 0.37 g of CuCl2 (2.8 mmol). After removal of THF solvent, vacuum sublimation (228 mTorr, 65 °C) gave the purple solid Cu[(OC(CF3)2)CH2NMe2]2 (4, 0.92 g, 1.8 mmol) in 72% yield.

Spectral data for 4: MS (EI, 70 eV, m/e), L = C3H6F2NO, observed (actual) [assignment] [relative intensity]: 511 (511) [CuL2] (0.33), 442 (442) [CuL2 – CF3] (0.27), 345 (345) [CuL2 – C6F6O] (0.20), 288 (287) [CuL] (0.25), 224 (224) [L] (1.87), 154 (154) [L – CF3] (2.37), 58 (58) [L – C6F6O] (100.00). Anal. calcd for Cu3H6F12N2O2Cu: C, 33.84; H, 4.26; N, 4.93; found: C, 32.87; H, 3.50; N, 5.20%.

Synthesis of complex 5. Procedures identical to those employed to prepare 1 were followed, using 0.15 g of sodium hydride (6 mmol), 1.0 g of the aminoalcohol ligand HOCMe(CF3)2CH2NHBu' (5 mmol) and 0.37 g of CuCl2 (2.8 mmol). After removal of THF solvent, vacuum sublimation (350 mTorr, 90 °C) gave the purple solid Cu[OCMe(CF3)2CH2NHBu]2 (5, 0.73 g, 1.6 mmol) in 64% yield.

Spectral data for 5: MS (EI, 70 eV, m/e), L = C3H12F2NO, observed (actual) [assignment] [relative intensity]: 459 (459) [CuL2] (7.81), 347 (347) [CuL2 – C6F6O] (6.50), 262 (261) [CuL] (90.79), 198 (198) [L] (100.00), 148 (149) [CuL – C6F6O] (40.79), 128 (129) [L – CF3] (15.71), 106 (106) [CuL – CF2CH2NBu] (17.27), 86 (86) [L – C6F6O] (98.68), 57 (57) [Cu4H6] (41.12). Anal. calcd for Cu3H6Cu2F4N2O2Cu: C, 41.78; H, 6.57; N, 6.69; found: C, 41.78; H, 6.70; N, 6.24%.

Synthesis of complex 6. Procedures identical to those employed to prepare 1 were followed, using 0.15 g of sodium hydride (6 mmol), 0.85 g of the aminoalcohol ligand HOCMe(CF3)2CH2NMe2 (5 mmol) and 0.37 g of CuCl2 (2.8 mmol). After removal of THF solvent, vacuum sublimation (350 mTorr, 90 °C) gave the purple solid Cu[OCMe(CF3)2CH2NMe2]2 (6, 0.75 g, 1.85 mmol) in 74% yield.
Spectral data for 6: MS (EI, 70 eV, m/e +, L = C6H12F3N2O) observed (actual) [assignment] [relative intensity]: 403 (403) [CuL2] 0.46, 334 334) [CuL2 - CF3] 0.10, 291 291) [CuL2 - C6H12F3O] 2.91, 120 120) [CuL2 - C6H12F3O] 5.82, 58 58) [L - C6H12F3O] 100.0. Anal. calcd for C14H20CuF12N2O4: C, 35.69; H, 5.49; N, 6.94%.

X-Ray crystallography

Single-crystal X-ray diffraction data were measured on a Bruker SMART CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The data collection was executed using the SMART program. Cell refinement and data reduction were performed using the SAINT program. The structure was solved using the SHELXTL/PC program and refined using full-matrix least squares procedures. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at calculated positions and included at the final stage of refinements with fixed parameters. The crystallographic refinement parameters of complexes 1 and 2 are summarized in Table 1, and selected bond distances and angles are listed in Tables 2 and 3, respectively.

CCDC reference numbers 187010 and 187011.

http://www.rsc.org/suppdata/jm/b2/b205419a/ for crystallographic data in CIF or other electronic format.

CVD procedures

Deposition of copper was carried out using a home-made vertical cold-wall reactor, consisting of a substrate holder placed at the center of a 20 × 20 × 20 cm³ stainless steel CVD chamber (Fig. 1). The substrate holder was heated by a 600 W quartz lamp and controlled electronically. Working pressure during deposition was maintained at 0.2–0.35 Torr, with a typical background pressure of 1 × 10⁻³ Torr. Carrier gas was introduced through the sidearm of the sample reservoir, which was loaded with 50–75 mg of the source reagent during each CVD experiment. The flow rate of carrier gas was adjusted to 10–20 cm³ min⁻¹. The deposition time was adjusted to 10–15 min. Before each experiment, the Si wafers were cleaned using a dilute HF solution, followed by washing with de-ionized water and acetone in sequence, and dried under nitrogen.

For experiments involving analysis of the organic co-products, the aminoalkoxide source reagent was passed through a long Pyrex tube of i.d. 25 mm under reduced pressure. The tubing was then placed within an electric temperature-controlled tube furnace, the heating block of which is about 30 cm long. The organic volatiles were then trapped at 77 K and dissolved into CDCl₃ or acetone solution for both NMR analysis and GC-MS studies.

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**Table 1** X-Ray structural data for complexes 1 and 2

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**Table 2** Selected bond distances (Å) and angles (°) for complex 1 (esds in parentheses)

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**Table 3** Selected bond distances (Å) and angles (°) for complex 2 (esds in parentheses)

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<tr>
<td>Cu(1)-N(2)</td>
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**Fig. 1** Schematic diagram of the set-up of the cold-wall CVD apparatus.
Results and discussion

Synthesis and characterization

The copper CVD source reagents synthesized in this study consisted of a CuII metal center encapsulated by two chelating fluorinated β-aminoalcohol ligands. The latter were prepared in good yields by mixing an amine with a fluorinated oxirane, (CF3)2COCH2 or (CF3)MeCOCH2, in diethyl ether solution at room temperature, which was in situ-generated from hexafluoroacetone or trifluoroacetone and diazomethane etherate.16 Subsequently, the copper complexes were prepared using a method related to that designed for the analogous metal complex Cu[OC(CF3)2CH2NH2]2, involving prior treatment of the aminoalcohol ligand with excess NaH to generate the anionic ligand fragment, followed by addition of the aminoalcoholate into a THF suspension of CuCl2. Finally, the products were purified by vacuum sublimation and recrystallization from a mixture of CH2Cl2 and hexane (Scheme 1). Notably, all these metal complexes are soluble in organic solvents such as CH2Cl2 or acetone, and their excellent stability in air is comparable to those of the fluoroalkoxide complexes Cu(en)2(ORF)2 and Cu(py)2(ORF)2, where ORF = hexafluoro-isopropoxy or hexafluoro-tert-butoxy groups.17

For structural identification, a single-crystal X-ray diffraction study on the complex Cu[OC(CF3)2CH2NHCH2CH2OMe]2 (1) has been carried out to confirm the exact structure in the solid state. As indicated in Fig. 2, two crystallographically and structurally different molecules are observed within the unit cell, with one metal complex located at a special position, the inversion center. The relevant bond lengths and angles are listed in Table 2. The average Cu–N distance is 2.020 Å, which is longer than the average value of the Cu–O distances (1.907 Å) and is comparable to that observed in the dimer complex [Cu(hfac)(OCH2CH2NMe2)]2 [2.020(5) Å].18 However, the structures of these two molecules differ greatly from one another. This is evident from the fact that the methoxyethyl group of the first molecule resides on the same side of the N2O2 square-planar arrangement. The first methoxyethyl group forms an intramolecular dative bond to the central Cu atom, showing a short Cu(1)–O(3) intramolecular bond distance of 2.628 Å, which completes a distorted square-pyramidal coordination geometry for this molecule. Moreover, the second methoxyethyl group is found to coordinate to the Cu(2) atom of the adjacent molecule, which is indicated by a dashed line connecting these atoms in Fig. 2, with a longer Cu(2)–O(1) bonding interaction of 3.874 Å. As the Cu(2) atom of this molecule is located on the crystallographic center of inversion, it automatically generates a second, intermolecular O−Cu dative interaction located at the trans-position to the Cu(2)−O(1) bond. Consequently, the copper metal atom of the second complex is surrounded by a distorted octahedral arrangement involving two oxygen atoms derived from the methoxyethyl group, two alkoxide oxygen atoms, and two amino nitrogen atoms located at mutually trans-positions. This observed structure is very similar to that observed in the six-coordinate complex Cu(hfac)2(pyrazine)2, in which the two pyrazine donor ligands adopt a trans-geometry, while two hfac chelating ligands reside in the square plane.19

For the purposes of comparison, an X-ray diffraction study of a second CuII aminoalkoxide complex, Cu[OC(CF3)2CH2NBu·i]2 (2), was also conducted to reveal the consequences of removal of the methoxyethyl substituent from the ligands. As shown in Fig. 3, this complex shows two essentially identical molecules in the asymmetric unit, each have their Cu atom located on an inversion center. Moreover, these two independent
molecules are linked to each other through a pair of intermolecular H-bonds to a water solvate [O(1)⋯H⋯O(3) = 2.02(2) Å and O(2)⋯H⋯O(3) = 2.01(2) Å], which is presumably incorporated into the crystal lattice during recrystallization. These results are in contrast to those reported for the related Cu(II) metal complex Cu(hfac)$_2$H$_2$O, for which the strongly bonded water solvate is located at the axial site with a much shorter Cu–O(H$_2$O) distance of 2.204(3) Å. Moreover, the molecular structure of 2 adopts a trans-disposition for the N$_2$O$_2$ square framework, as well as for the iso-butyl substituent of the amino fragments. The average Cu–O distance of 1.886 Å and Cu–N distance of 2.023 Å are similar to those of the previously discussed methoxyethyl complex 1. The chelating nature of the aminooxalolate ligand leads to the formation of a five-membered ring structure, causing the corresponding O–Cu–N angle of ~86.2° to deviate slightly from the ideal value of 90° for a perfect square-planar arrangement.

After understanding their molecular structures, we then proceeded to investigate the physical data relevant to chemical vapor deposition. We observed that these copper complexes are fairly volatile and can be readily sublimed below 90 °C under a vacuum of 350 mTorr. Thermogravimetric analyses (TGA) were carried out at atmospheric pressure under N$_2$ and the data are plotted as the relative weight loss in wt% as a function of temperature. The derivative of the thermograph for each compound is shown in Fig. 4 Thermogravimetric analysis data: all experiments were carried out at atmospheric pressure with N$_2$ as carrier (100 cm$^3$ min$^{-1}$) and a heating rate of 10 °C min$^{-1}$.

Thermogravimetric analysis showed that all the Cu$^{II}$ aminoalkoxide complexes prepared in this study can be volatilized below 150 °C under atmospheric pressure with almost no decomposition. Hence, these complexes should be potentially suitable for CVD use and, for complexes 2, 3, and 5, deposition of copper metal has been achieved using an inert carrier gas (Ar) at temperatures of 250–325 °C in a standard cold-wall reactor. The run conditions selected for the CVD experiments and basic properties of the thin films are listed in Table 4. In general, growth of smooth copper metal thin films was realized under all conditions, and the as-deposited thin films were found to be reflective and have good adhesion.

Deposition of copper metal

Thermogravimetric analysis showed that all the Cu$^{II}$ aminoalkoxide complexes prepared in this study can be volatilized below 150 °C under atmospheric pressure with almost no decomposition. Hence, these complexes should be potentially suitable for CVD use and, for complexes 2, 3, and 5, deposition of copper metal has been achieved using an inert carrier gas (Ar) at temperatures of 250–325 °C in a standard cold-wall reactor. The run conditions selected for the CVD experiments and basic properties of the thin films are listed in Table 4. In general, growth of smooth copper metal thin films was realized under all conditions, and the as-deposited thin films were found to be reflective and have good adhesion.

The first Cu thin film was deposited using complex 2 as the source reagent and argon as the carrier gas (film 1). The SEM photo of this film [Fig. 5(a)] shows formation of a dense microstructure with grain sizes in the range 100–300 nm. Preliminary XPS analysis revealed a composition of >98% copper metal, along with approximately 2% carbon, while other impurities, such as oxygen and fluorine, were not observed.

Table 4 Physical properties of the Cu$^{II}$ source reagents

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<th>Compound</th>
<th>Formula</th>
<th>M. p./°C</th>
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<th>Residue$^*$/wt%</th>
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<td>Cu[OC(CF$_3$)$_2$CH$_2$NHC$_2$H$_2$OMe]$_2$</td>
<td>87–88</td>
<td>170</td>
<td>190</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>Cu[OC(CF$_3$)$_2$CH$_2$NHBu$_2$]$_2$</td>
<td>121–122</td>
<td>159</td>
<td>176</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>Cu[OC(CF$_3$)$_2$CH$_2$NHBu$_2$]$_2$</td>
<td>167–168</td>
<td>202</td>
<td>178</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>Cu[OC(CF$_3$)$_2$CH$_2$NMe$_2$]$_2$</td>
<td>177–178</td>
<td>232</td>
<td>166</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td>Cu[OCMe(CF$_3$)$_2$CH$_2$NHBu$_2$]$_2$</td>
<td>130–131</td>
<td>160</td>
<td>162</td>
<td>12.0</td>
</tr>
<tr>
<td>6</td>
<td>Cu[OCMe(CF$_3$)$_2$CH$_2$NMe$_2$]$_2$</td>
<td>145–146</td>
<td>194</td>
<td>154</td>
<td>0.9</td>
</tr>
</tbody>
</table>

$^*$The temperature at which 50 wt% of the sample has been lost during TGA analysis (N$_2$ flow rate = 100 cm$^3$ min$^{-1}$). $^*$Total wt% of the sample observed at 500 °C during TGA analysis.
Table 5 Data obtained from CVD experiments using the CuII source reagents 2, 3, 5, and 6

<table>
<thead>
<tr>
<th>Film no.</th>
<th>Gas (flow rate/cm³ min⁻¹)</th>
<th>Tₛ/°C</th>
<th>Tₖ/°C</th>
<th>Pₛ/Torr</th>
<th>Film thickness/Å</th>
<th>Deposition rate/Å min⁻¹</th>
<th>Film resistivity, ρ/μΩ cm</th>
<th>Film contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (2)</td>
<td>Ar (35)</td>
<td>150</td>
<td>250</td>
<td>0.2</td>
<td>800</td>
<td>133</td>
<td>4.9</td>
<td>Cu, &gt;98%; C, &lt;2%</td>
</tr>
<tr>
<td>2 (2)</td>
<td>H₂ (25)</td>
<td>150</td>
<td>250</td>
<td>0.2</td>
<td>600</td>
<td>140</td>
<td>7.2</td>
<td>Cu, &gt;98%; C, &lt;2%</td>
</tr>
<tr>
<td>3 (2)</td>
<td>H₂ (25)</td>
<td>150</td>
<td>275</td>
<td>0.2</td>
<td>1600</td>
<td>133</td>
<td>3.7</td>
<td>Cu, &gt;99%; C, &lt;1%</td>
</tr>
<tr>
<td>4 (2)</td>
<td>H₂ (25)</td>
<td>150</td>
<td>300</td>
<td>0.2</td>
<td>2200</td>
<td>73</td>
<td>19.8</td>
<td>Cu, &gt;98%; C, ~1%; O, F, &lt;1%</td>
</tr>
<tr>
<td>5 (2)</td>
<td>H₂ (25)</td>
<td>150</td>
<td>325</td>
<td>0.2</td>
<td>2300</td>
<td>140</td>
<td>22.2</td>
<td>Cu, &gt;95%; C &lt;4%; O, F, &lt;1%</td>
</tr>
<tr>
<td>6 (3)</td>
<td>Ar (10)</td>
<td>110</td>
<td>300</td>
<td>1</td>
<td>2400</td>
<td>60</td>
<td>16.4</td>
<td>Cu, &gt;97%; C, O, F, &lt;3%</td>
</tr>
<tr>
<td>7 (5)</td>
<td>Ar (35)</td>
<td>130</td>
<td>250</td>
<td>0.2</td>
<td>2640</td>
<td>176</td>
<td>2.9</td>
<td>Cu, &gt;99%; C, O, F, &lt;1%</td>
</tr>
<tr>
<td>8 (6)</td>
<td>Ar (15)</td>
<td>70</td>
<td>325</td>
<td>1</td>
<td>N. A.</td>
<td>N. A.</td>
<td>N. A.</td>
<td>Cu, &lt;53%; C, &gt;27%</td>
</tr>
<tr>
<td>9 (6)</td>
<td>H₂ (15)</td>
<td>70</td>
<td>325</td>
<td>1</td>
<td>2500</td>
<td>167</td>
<td>5.7</td>
<td>Cu, &gt;98%; C, &lt;1%; O, F, &lt;1%</td>
</tr>
</tbody>
</table>

*a*: Tₛ: source temperature; Tₖ: deposition temperature; Pₛ: system pressure.

Fig. 5 SEM micrographs of the Cu films deposited using complex 2 as the source reagent: (1a and 1b) under Ar at 250 °C; (2a and 2b) under H₂ at 250 °C; (3a and 3b) under H₂ at 275 °C; (4a and 4b) under H₂ at 300 °C.

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Four-point probe measurements gave a resistivity of 4.9 μΩ cm (800 Ω), which is slightly higher than that of bulk copper (1.7 μΩ cm). The observed physical characteristics of the thin film suggest that the aminoaalkoxide complex 2 should possess the capacity to deposit copper metal in the absence of an external reducing reagent, which is not the case for CuI source reagents such as Cu(bf3)- or even Cu(acac). The deposition reactions were next carried out using H2 carrier gas to investigate the possible effect of an external reductant (film 2). A copper thin film with a slightly smoother morphology is obtained under these conditions [Fig. 5(2a)], for which the purity and the electrical resistivity show no further improvement compared with the sample prepared under Ar carrier gas. Upon increasing the temperature to 275°C, the thickness of the thin film nearly doubled, showing a much faster rate of deposition, as expected for a temperature-dependent process [Fig. 5(3a)]. The thin film consists of well-defined microcrystalline grains, and several small voids are also visible at the grain boundaries. It appears that the physical characteristics of this thin film sample are optimal for the source reagent 2; the resistivity is close to 3.7 μΩ cm and the metal purity is approaching 99%. On further increasing the deposition temperature to 300°C, the thickness and the morphology of the thin film remain about the same [Fig. 5(4a)], but the resistivity and the purity dropped slightly with respect to the film obtained at 275°C. This result is consistent with the occurrence of a slightly contaminated metal thin film at the higher temperature. We therefore assume that both Ar and H2 can be used as the carrier gas and that the optimum temperature for copper deposition is about 275°C, as used in this series of investigations. Moreover, the purity, as well as the resistivity, of the as-deposited copper thin films shows a continuous degradation upon further increasing the deposition temperature to 325°C (see the analytical data for film 5 in Table 5).

In order to determine the conformal deposition on substrate surfaces, we chose a patterned wafer containing via holes with a diameter of 0.4 μm and an aspect of ~2, and repeated thin film depositions under the conditions described for films 1–4. A thin layer of TiN was applied to these patterned wafers to serve as a diffusion barrier and to improve the copper metal adhesion. Fig. 5(1b) and (2b) show SEM pictures of the films resulting from deposition at the lowest temperature (250°C) under Ar and H2 carrier gas, respectively. It is clear that the via hole has been covered with a thin layer of copper metal in both experiments. Although the surface of the resulting copper film is rather rough, we estimate that the thickness of the copper film within the via hole is about two times thinner than that of the copper deposited on the more exposed top layer, an indication of lower step coverage.

Upon raising the temperature to 275°C, the faster reaction on the substrate surface causes a substantial increase in copper deposition at all positions, giving a better conformal coverage, which is shown in Fig. 5(3b). We believe that this will provide the optimum conditions for completely filling the via holes with copper metal if the deposition time is increased and a sufficient amount of CVD source reagent is provided. Finally, on further increasing the temperature to 300°C, it can be seen that both the copper deposition and the grain growth reaction becomes much faster on the top surface [Fig. 5(4b)], and the formation of larger copper crystallites severely blocks the entrance to the via hole and prevents the source reagent from diffusing into the bottom layer. Accordingly, a very small amount of copper is deposited into the via hole, showing the deleterious effect of excessively high temperatures.

Fig. 6 shows the X-ray diffraction patterns (XRD) of the as-deposited copper thin films: the labeling of each diffraction pattern is identical to those listed in Table 5.

The CVD experiments have also been executed using other source reagents, complexes 3, 5, and 6, to determine the effect of the different substituents on the aminoaalkoxide chelate ligands. The first experiment involved the use of the t-butyl derivative, complex 3, conducted under Ar carrier gas at a temperature of 300°C (film 6). Although the basic properties of the thin film look only slightly inferior to those of the previously discussed films prepared using source reagent 2, the SEM photo shown in Fig. 7(a) shows the formation of large voids and cracks at the grain boundaries on the substrate surface. This change in surface morphology would appear to result from the different alkyl substituents of the ligand in 6, but this cannot be stated with any certainty at present.

For deposition experiment using complex 5 as the source reagent, a light red and adherent thin film of thickness 2640 Å, containing over 99% Cu metal, was obtained under Ar at 250°C (film 7). The electrical resistivity of this film (ρ = 2.9 μΩ cm) is very close to the physical limit of the resistivity of bulk copper (1.7 μΩ cm). In good agreement with these physical data, the SEM photo shows the formation of closely packed microcrystalline grains [Fig. 7(b)], suggesting that source reagent 5 has equally good potential for depositing Cu film as complex 2.

We speculate that the excellent behavior of compound 5 is caused by replacement of one CF3 group with a less electron-withdrawing methyl substituent, which reduces the thermal stability of the copper complex and, in turn, allows the deposition of metal to occur at a lower temperature, resulting in the inclusion of less impurities. This fine tuning of the structure means that complex 5 (with one CF3 and one Me group at the alkoxide α-position) has a stability intermediate between those of complex 2 (with two CF3 groups) and their non-fluorinated aminoaalkoxide analogues, such as Cu[OCH2-CH2-NMe2]2 and Cu[OCHMeCH2-NMe2]2,24 thus giving the observed CVD results.

Finally, the CVD experiments were performed using the source reagent 6, which contains a tertiary amino functional group at the chelating alkoxide ligands. As indicated in
suggests that a reducing agent such as H₂ is capable of inducing
aminoethanol observed.
quent hydride transfer to the second dimethylaminoethoxide
ation, giving a transient copper hydride intermediate. Subse-
cular chemistry should be somewhat related to that of the previously reported
copper metal is of interest, and we speculate that the chemistry
Delineation of the exact mechanism that afforded the pure
Possible reaction mechanism
Fig. 7 SEM micrographs of the Cu films deposited using copper complexes 3, 5, and 6 (a) using 3 as source reagent under Ar at 300 °C; (b) using 5 as
source reagent under Ar at 250 °C; (c) using 6 as source reagent under Ar at 325 °C; (d) using 6 as source reagent under H₂ at 325 °C.
Fig. 7(c), there is no formation of a continuous thin film for
a deposition experiment conducted under Ar carrier gas at a
temperature of 325 °C (film 8). Under these conditions, only a
couple copper metal droplets spreading over the substrate surface are
observed, which shows a typical situation for the nucleation and growth of copper nanoparticles during the initial stage of
deposition.25 This observation unambiguously confirms that the source reagent 6 is unsuitable for the deposition of thin
films under these conditions, for which the selected deposition temperature is at least 50 °C higher than that utilized for the
CVD experiments using source reagents 2, 3, and 5. However,
by changing the carrier gas from Ar to H₂, formation of good
quality, copper thin film was clearly evidenced (film 9). The
SEM photo of the resulting thin film is shown in Fig. 7(d),
revealing a surface morphology consisting of granular, densely
packed microcrystallites with diameters of ~300 nm. This
suggests that a reducing agent such as H₂ is capable of inducing
a clean conversion to copper metal.
accessible β-hydrogen atom within the coordinated ligand. On
the other, hand, as complexes 2, 3, and 5 possess secondary
amino functional groups, this unique molecular architecture
would allow formation of an imino fragment via a dehydro-
genation reaction. The hydrogen atom(s) released would then
transfer to the oxygen atom of the second alcoholate, leading to
the formation of copper metal and an equal amount of
iminoalcohol and aminooalcohol:

\[
\text{Cu[OC(CF}_3\text{R}_1\text{CH}_2\text{NHR}_2]}_2 \rightarrow \text{Cu}(\alpha) + \\
\text{HO[C(CF}_3\text{R}_1\text{CH}_2\text{NHR}_2]} + \text{HO[C(CF}_3\text{R}_1\text{CH}_2\text{NHR}_2]} (R = \text{CF}_3 \text{or Me; } R^2 = \text{Bu}^t \text{or Bu}^\prime)\]

This postulated decomposition pathway is partially supported
by a literature report involving facile oxidation of a secondary
amine with a Cu^{II} oxidant in THF at room temperature, in
which the Cu^{II} oxidant is generated in situ from mixing equal
amounts of CuBr₂ and LiOBu₂.27

Alternatively, we propose a second pathway that involves the
formation of a fluorinated ketone molecule, CF₃(R')C=O and
an imine fragment, H₃C=NR₂, as well as the corresponding
aminooalcohol, according to the transformation below.

\[
\text{Cu[OC(CF}_3\text{R'}\text{CH}_2\text{NHR}_2]}_2 \rightarrow \text{Cu}(\alpha) + \text{CF}_3(R')C=O + \\
\text{H}_2\text{C}=\text{NR}_2 + \text{HO[C(CF}_3\text{R'}\text{CH}_2\text{NHR}_2]} \]

The ketone and the imine could possibly be produced via a
C(α)–C(β) bond fission reaction and a co-operative hydrogen
transfer from the nitrogen atom of one aminooalcoholate to
the oxygen atom of the second ligand while, concurrently, the
central Cu^{II} ion is reduced to the Cu^{I} state. According to the
literature, the oxidation of a β-aminooalcohol in solution by
electrochemical methods would afford the related imine
intermediate and the ketone product by cleavage of the
carbon–carbon bond between the hydroxyl and the amine
functional groups.28

In order to shed light on the reaction mechanism of the metal
deposition process, we collected the volatile organic co-
products and analyzed the constituents. We decided to select
the source reagent 3 as the target for this study, since the t-butyl
substituent of the amino alkoxide ligand would simplify the
NMR spectra and assist the interpretation of spectral data.
The organic volatiles were dissolved in d$_6$-acetone solution and this solution was then subjected to NMR analysis. The $^1$H NMR spectrum shows seven signals at $\delta$ 4.68 (~4), 4.09 (100), 3.29 (~4), 3.02 (~4), 1.29 (~12), 1.11 (~15), and 1.10 (~15), with approximate integration ratios for the peaks included in parentheses. The strongest signal at $\delta$ 4.09 is identified as due to the hydroxyl group of hexafluoroacetone hydrate, since the observed chemical shift is identical to that of a commercial sample and the water was probably inadvertently identified as due to the hydroxyl group of hexafluoroacetone ($\delta$ 4.681 and 3.293, and one Bu' signal at $\delta$ 1.107 unidentified. The identity of the CH$_3$ resonance signals was confirmed using a 2D DEPT NMR experiment.

The $^{19}$F NMR spectrum confirmed the presence of the dissociated free aminooalcohol ligand and the hexafluoroacetone hydrate by showing two sharp signals at $\delta$ ~83.12 (100) and ~78.75 (99%), respectively, while the third signal at $\delta$ ~77.53 (92%) is assigned to the third compound observed in the $^1$H NMR spectrum. Based on these $^1$H and $^{19}$F NMR data and the subsequent GC-MS analysis, which shows a weak parent ion at $m/z$ = 265 and a base peak at $m/z$ = 250 due to the $M^{+}$–Me ion, we can identify this unknown compound as a CF$_3$-substituted 1,3-oxazolidine (7).

If the assignment of this organic compound is correct, we can then postulate that its formation may involve a thermally-induced, bimolecular condensation between the dissociated imine H$_2$C=C=NR$_2$ and free aminooalcohol ligand, according to a similar reaction reported in the literature. 59

\begin{equation}
\text{H}_2\text{C}=\text{CNBu' + HOC(CF}_3\text{)_2CH}_2\text{NHBu' \rightarrow CF}_3\text{N=CHBu' + H}_2\text{Bu' + H}_2\text{NBu' (7)}}
\end{equation}

Moreover, the CH$_2$ signals at $\delta$ 4.68 and 3.29 are also observed in the $^1$H NMR spectrum of the mixture of products obtained from a control reaction using the $\beta$-aminooalcohol reagent HOC(CF$_3$)$_2$CH$_2$NHBu' and iodobenzene. This reaction has been utilized to prepare both aromatic and aliphatic imines from secondary amines. 30 As a result, although we cannot rule out the first possibility, we currently favor the second reaction pathway involving the cleavage of the C(\(\alpha\))-C(\(\beta\)) bond during the deposition of copper. Of course, more detailed studies are required to fully establish and confirm this reaction mechanism.

Finally, the CVD experiments conducted at 325 °C using Ar carrier gas show that complexes 4 and 6 do not afford the anticipated copper metal, but yield only a few droplets of Cu-containing particulates on the substrate. The reduced activity for complex 6 may be the result of the lack of such a low energy pathway for copper deposition. Therefore, the aminooxaloid chelate complexes involving the tertiary amino group are probably unsuitable as CVD source reagents. However, upon changing the carrier gas from Ar to H$_2$, deposition of copper metal proceeded rapidly at this temperature, and the volatile co-product collected during the CVD runs showed exclusive formation of free HOCMe(CF$_3$)CH$_2$NMe$_2$. Thus, the deposition of copper from complex 6 is best understood as shown in the equation below,

\[
\text{Cu(OH)(OCMe(CF}_3\text{)_2CH}_2\text{NMe}_2})_2 + \text{H}_2 \rightarrow \text{Cu}_{60} + 2 \text{HOCMe(CF}_3\text{)_2CH}_2\text{NMe}_2
\]

in which the hydrogen serves as the stoichiometric reagent to reduce the copper complex during deposition.

**Conclusion**

Several new Cu$^{II}$ complexes with chelating aminoalkoxide ligands have been reported in this study. Although they are all very stable at room temperature, deposition of copper metal can be achieved at a substrate temperature between 250 and 325 °C. However, as revealed by CVD experiments, the complexes with chelating alkoxide ligands bearing secondary amino groups, CH$_3$NH$_2$, R = CH$_2$CH$_2$OMe, Bu', and Bu'' showed a greater tendency to deposit copper metal at lower temperature, even in absence of an external reducing reagent. The deposition of copper probably proceeds via a self-catalyzed reduction of Cu$^{II}$, for which the driving force is provided by the concomitant conversion of amine to imine or the direct cleavage of the C(\(\alpha\))-C(\(\beta\)) bond. This observation is reminiscent of a recent report that addition of alcohol co-reactant in the process gas stream accelerates the reaction rate of copper deposition in an experiment using Cu(hfac)$_2$ as the source reagent. 31 It was proposed that, when N$_2$ is used as the carrier gas, the alcohol served as the reducing reagent. In a similar fashion, the secondary amine fragment, supplies here the hydrogen atoms that are formally required for the reduction of Cu$^{II}$. A preliminary CVD experiment showed that filling of a vial hole with a diameter of 0.4 μm is possible using 2 as the source reagent at a temperature of 275 °C.

Finally, the Cu$^{II}$ fluoroalkoxide complexes 4 and 6, containing a tertiary amino group, showed an even greater volatility and thermal stability. These physical properties were demonstrated by the TGA experiments, where rapid loss of weight was observed at a lower temperature, as well as in the actual CVD experiments, for which no deposition of copper was observed at typical deposition temperatures of 250–325 °C under an inert atmosphere. It appears that the lack of the NH functional group completely blocks the lower energy deposition pathway observed for the previous complexes possessing the secondary amine coordination group. Nevertheless, the deposition of copper metal was successfully achieved at the same temperature by changing the carrier gas from Ar to H$_2$, which suggests that the deposition of copper is facilitated by the hydrogenation, rather than the self-catalyzed, intramolecular disproportionation reaction involving the coordinated amine fragments.

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**References**