Comparative Study of Cu-Precursors for 3D Focused Electron Beam Induced Deposition

A. Lusier, I. Utke, T. Bret, F. Cicoira, R. Hauter, S.-W. Rhee, P. Doppelt, and P. Hoffmann

*Institute of Imaging and Applied Optics, School of Engineering, Swiss Federal Institute of Technology, CH-1015 Lausanne-EPFL, Switzerland
b EMPA Dübendorf, CH-8600 Dübendorf, Germany
Laboratory for Advanced Powder Materials, Department of Chemical Engineering, Pohang University of Science and Technology, San 31 Hyoja-dong, Nam-gu, Pohang, Kyungbuk 790-784, Korea

c Ecole Supérieure de Physique et Chimie Industrielles-CNRS, 75231 Paris Cedex 05, France.

The copper precursors bis-hexafluoroacetylactonato-copper Cu(hfac)$_2$, vinyl-trimethyl-silane-copper(I) hexafluoroacetylacetonate (hfac/Cu/VTMS), 2-methyl-1-hexen-3-yne-copper hexafluoroacetylacetonate (hfac/Cu/MHY), and dimethylbutene-copper(I) hexafluoroacetylacetonate (hfac/Cu/DMB) are compared with respect to deposition rates and metal content obtained by focused electron beam induced deposition. Exposure was performed with 25 keV electrons in a Cambridge S100 scanning electron microscope equipped with a lithography system. Tip deposition rates increase with increasing precursor vapor pressure and range between 2 - 4 nm/s for Cu(hfac)$_2$. A decay of deposition rates with time, i.e., tip length, is observed. Electric four-point measurements indicate an insulating behavior of deposited lines for all precursors. In contrast, Cu contents of up to 45-60 atom% were found by Auger electron spectroscopy in thin rectangular deposits using (hfac/Cu/DMB) and (hfac/Cu/VTMS) as precursors. A discussion in terms of monolayer coverage, completeness of precursor molecule dissociation, and precursor stability is presented.

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Due to its superior electrical conductivity over Al or W, Cu is being implemented as standard in high performance integrated circuits in microelectronics. Scanning electron microscopy (SEM) failure analysis combined with focused electron beam induced writing would offer a powerful important tool for in situ reworking of circuit defects. FEB induced writing is essentially a local chemical vapor deposition (CVD) process. Deposition is achieved by interaction of electrons with surface adsorbed molecules and results in three-dimensional (3D) growth. Controlling the electron beam with a lithography program allows writing almost all kind of nanostuctures from dots, lines, tips, and periodic patterns to sophisticated structures by high precision and resolution. According to the precursors used deposition properties can be tuned to different applications like thermal nanoprobes, nanotweezers, field-emitters, magnetic force microscopy tips, atomic force microscopy tips, circuit reparation, mask repair, etch masks, and nanoantennae on scanning near field optical fiber probes.

In this study we compare different copper precursors, shown in Fig. 1, for their suitability in FEB induced writing with respect to their deposition rates and the deposit metal content: Cu(I)(hfac)$_2$, Cu(I)(MHY): 2-methyl-1-hexen-3-yne, (hfac/Cu/VTMS), (hfac/Cu/I)(MHY): vinyltrimethylsilane, and (hfac/Cu/DMB): dimethylbutene.

In Fig. 3 shows that the initial deposition rate increases with increasing precursor vapor pressure, i.e., increasing precursor flux. The differing initial deposition rates can be related to the initial surface monolayer coverage θ using Langmuir’s isotherm, according to which

\[ \theta = bP/(1 + bP) \]

The thermodynamic parameter b describes the surface adsorption/desorption behavior and P is the local pressure above the sample being proportional to the precursor flux reported in Table I. From their similar molecular structures, the Cu(I) precursors can be supposed to have similar thermodynamic behavior, i.e., b$_{VTMS}$ ≈ b$_{DMB}$ ≈ b$_{MHY}$ · and electron dissociation cross sections. In other words, the initial growth rates R$_0$ would depend only on the amount of precursor adsorbed at the surface. The ratios R$_{DMB}$/R$_{VTMS}$ = 47:20 (see Fig. 2A) and P$_{DMB}$/P$_{VTMS}$ = 30 (from Table I) lead to monolayer coverages of $\varphi_{VTMS}$ = 40.6% and $\varphi_{DMB}$ = 95.3%. The value for (hfac/Cu/VTMS) agrees well with the value of 2 × 10$^{14}$ molecules/cm$^2$ reported in Ref. 14. Agreement is also accomplished within a glove box under dry nitrogen atmosphere. FEB exposure was performed with 25 keV electrons in a Cambridge S100 scanning electron microscope (SEM). Deposition rates were determined from vertical tip series produced with the SEM spot mode at 500 pA corresponding to a measured electron beam diameter (1/e$^2$) of 132 nm. The deposits were analyzed ex situ with respect to their geometry in a SEM (FEG XL30). The deposition rate was taken as length interval divided by exposure time interval. Composition analysis was performed on 5 × 7 μm$^2$ large and about 1 μm thick rectangles deposited at 1 nA using the SEM scan mode. Sputter profiling Auger electron spectroscopy (AES) was performed with two different conditions of probe current I$_p$ and probe energy E$_p$. (a) I$_p$ = 75 nA and E$_p$ = 5 kV (PHI 4300) and (b) I$_p$ = 5 nA and E$_p$ = 3 kV (PHI 660-EPFL). Line deposits of about 60 μm length were written with a Nabiity lithography system on SiO$_2$ (150 nm)/Si substrates with lift-off gold electrodes for four-point electrical resistivity measurements (HP 4156A precision semiconductor parameter analyzer).
Figure 1. Chemical formulas of Cu precursors used in our comparative study.

Figure 2. Schematics of the experimental setup.

Table I. Summarized precursor properties: vapor pressure ($P_{vap}$), estimated flux at nozzle exit, ligand dissociation temperature ($T_{diss}$), and minimum CVD temperature ($T_{min}$) to obtain films with electrical resistivity $<2.5 \mu \Omega \text{cm}$.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>$P_{vap}$ at 25°C (mbar)</th>
<th>Precursor flux (no./cm² s)</th>
<th>$T_{diss}$ (°C)</th>
<th>$T_{min}$ CVD (°C)</th>
<th>Cu:C ratio</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)₂</td>
<td>0.004</td>
<td>$3.5 \times 10^{-6}$</td>
<td>—</td>
<td>250</td>
<td>1:10</td>
<td>19</td>
</tr>
<tr>
<td>(hfac)Cu(MHY)</td>
<td>0.1</td>
<td>$1 \times 10^{-8}$</td>
<td>63</td>
<td>100</td>
<td>1:10</td>
<td>20</td>
</tr>
<tr>
<td>(hfac)Cu(VTMS)</td>
<td>0.2</td>
<td>$2 \times 10^{-9}$</td>
<td>207</td>
<td>180</td>
<td>1:11</td>
<td>20</td>
</tr>
<tr>
<td>(hfac)Cu(DBM)</td>
<td>1.3</td>
<td>$3 \times 10^{-9}$</td>
<td>88</td>
<td>125</td>
<td>1:12</td>
<td>20</td>
</tr>
</tbody>
</table>
vertical deposition rate superposed with the constant lateral scan speed evolves into a horizontal rod shape. When the focused electron beam partially advances in front of the deposit or gets transmitted through the horizontal rod end volume it hits again the substrate and a new deposit starts. This mechanism produces “free-standing” lines with a periodic pattern as shown in Fig. 4B, which can be tuned by the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed. Line resistivity measurements indicate an insulating behavior independent of the precursor used. Improved conductivity may be obtained by variation of the scan speed.

It remains the question why AES gives much higher Cu-content values for (hfac)Cu(DMB) and (hfac)Cu(VTMS). The largely fluctuating value of both precursors leads us to the assumption that the electron/ion exposure during sputter cycle Auger measurements probably alters these deposits. Moreover, the etching rate of incompletely reticulated carbonaceous species could be larger during sputtering than that of copper and dense carbon polymers, leading to an increase in the Cu proportion. The minimum value of the AES measured Cu content should thus be closer to the original FEB decomposition whereas the maximum value should correspond to the postdecomposition/etching induced from the inspection itself. No measurable postdecomposition/etching takes place for the more stable precursors Cu(hfac)$_2$ and (hfac)CuMHY for which the Cu/C ratio of 1:5 to 1:6 is maintained throughout the measurement/sputter cycles. Hence decomposition of these precursors and reticulation of the remaining carbonaceous species seems to be complete which goes along with the estimated high electron/precursor flux ratios of 55-1500 for these precursors.

In this context it should be noted that XPS measurements show considerable lower Cu contents in (hfac)CuVTMS deposits by FEB than AES. This was discussed as a result of weaker interaction of electrons to get fragmented into Cu and organic species, the FEB deposit metal content should thus increase Cu(hfac)$_2$ $<$ (hfac)CuMHY $<$ (hfac)Cu(DMB) $<$ (hfac)Cu(VTMS). This precursor stability-based order is obtained by AES except for the last two precursors, the composition of which however largely fluctuates during depth profiling. As noted above, at large precursor fluxes, i.e., small electron/precursor flux ratios, the fragmentation is incomplete and a nonvolatile carbon-rich matrix grows from polymerization of remaining ligands. The electron/precursor flux ratio (primary electrons/molecule) reported in Table II hence suggests an inverse order of metal content of deposits than that obtained by the precursor stability. Because both mechanisms counteract, they could approximately outbalance and result in about the same low Cu-contents for all deposits. This is at least supported by the electrical measurements, which resulted in insulating behavior for all deposits.

Figure 3. (a) Comparison of deposition rates of different Cu precursors. (b) Scanning electron micrograph of Cu tips grown at 25 kV and 500 pA with (hfac)Cu(VTMS) on Si substrate with varying exposure time. The inset shows Monte Carlo simulated electron trajectories for one tip deposit (same scale as image): electron energy 25 keV, tip composition and density set to Cu$_x$C$_y$ and 4.2 g/cm$^2$ on Si substrate.

Figure 4. Tilt SEMs of FEB 125 kV, 500 pA, single scan with scan speed of 35 nm/s) deposits for four-point electrical measurements on lift-off gold electrodes on SiO$_2$/Si substrate. Distance between the two outermost electrodes is 55 µm. (a) Line deposited with (hfac)CuVTMS. (b) 3D freestanding line grown by a single scan with (hfac)Cu(DMB).
Table II. Chemical composition measured by AES of FEB deposits at room temperature from different Cu precursors and estimation of the electron/precursor flux ratio (electron flux 5.5 × 10^17 cm^-2 s^-1 at 500 pA and 25 kV). The fluorine signal was not significantly above the noise level of the AES measurements.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Cu</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Flux-Ratio e^-/molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(hfac)</td>
<td>14</td>
<td>75</td>
<td>5</td>
<td>—</td>
<td>1500</td>
</tr>
<tr>
<td>Cu(hfac)CuMHY</td>
<td>13</td>
<td>82</td>
<td>3</td>
<td>—</td>
<td>55</td>
</tr>
<tr>
<td>Cu(hfac)CuVTMS</td>
<td>20-45</td>
<td>35-70</td>
<td>8-14</td>
<td>2-10</td>
<td>28</td>
</tr>
<tr>
<td>Cu(hfac)CuDMB</td>
<td>25-60</td>
<td>15-60</td>
<td>5-25</td>
<td>—</td>
<td>2</td>
</tr>
</tbody>
</table>

X-rays\textsuperscript{23} and supports the mechanism of a postdecomposition/etching process of a polymerized matrix induced by AES as discussed above.

Conclusions

We presented a comparative study of Cu precursors for FEB induced deposition. The initial deposition rate could be related to the monolayer coverage according to Langmuir’s adsorption isotherm. Deposit compositions in this study were not dependent on the Cu/C-ratio of the precursor. The deposit Cu content was experimentally shown to decrease with increasing precursor stability. With electron/precursor flux ratios <55, being below the electron decomposition efficiency complete dissociation seems not to be achieved as indicated by AES values fluctuating within 15-70 atom % for Cu. The maximum value also indicates that the low-stability precursors (hfac)Cu(DMB) and (hfac)Cu(VTMS) have a great potential for high conductivity deposits useful for local in situ microcircuit repair, when deposited by FEB under high electron/precursor flux-ratio conditions.

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References