Mechanisms of copper chemical vapor deposition

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The mechanism of copper chemical vapor deposition from Cu(II)bis-hexafluoroacetylacetonate \([\text{Cu(hfac)}_2]\) and 1,5-cyclooctadiene-Cu(1)-hexafluoroacetylacetonate (COD-Cu-hfac) has been determined. The results explain the different processing conditions required for deposition from the precursors. Both molecules react at room temperature on Ag to form a similar Cu(I)-hfac surface intermediate. Subsequent reaction of the COD-Cu-hfac fragment can lead to loss of the organic ligands leaving clean Cu. In contrast, for Cu(hfac)_2, the presence of one extra surface hfac requires the addition of an external reductant to produce a ligand-free Cu film.

Cu is a material that, compared to Al, has favorably low resistivity and electromigration properties.\(^1\) Thus there is much interest in developing a process for copper chemical vapor deposition (CVD) from organometallic precursors.\(^2,3\) Two related classes of Cu precursors have been shown to provide low-resistivity Cu films by thermal decomposition, however, the optimum processing conditions used in these depositions are significantly different. Cu(II) bis-hexafluoroacetylacetonate \([\text{Cu(hfac)}_2]\) must be reduced to Cu metal in the presence of H\(_2\) and at temperatures above 250–300 °C.\(^1,4\) In the absence of H\(_2\), the Cu films contain significant amounts of impurities,\(^1,5\) while interestingly, addition of alcohols or H\(_2\)O to the H\(_2\) leads to increased Cu deposition rates.\(^5\) In contrast, 1,5-cyclooctadiene-Cu(I)-hexafluoroacetylacetonate (COD-Cu-hfac) and other related precursors have recently been shown to provide high-quality Cu deposition at temperatures below 200 °C and in the absence of any added reducing agent.\(^2,6-10\) Interestingly, Cu(hfac)_2 is known to be a reaction product of COD-Cu-hfac decomposition,\(^7,8\) thus the chemistry of these two precursors must be intimately related.

We provide in this letter an explanation for the quite different processing conditions required for CVD from these two precursors by determining their mechanisms of adsorption and decomposition. Our findings indicate that in both cases the molecules are activated for reaction by the metallic surface giving a similar surface intermediate, but the major difference in reactivity is due to the subsequent mechanism for removal of the organic ligands.

Experiments were performed in an ultraclean integrated processing laboratory with both analysis and processing capability.\(^11\) Ag was used as a model metallic surface instead of Cu so as to avoid overlap of spectroscopic features from the substrate and the precursors. Clean Ag surfaces were prepared either by in situ evaporation or by heating air exposed Ag/Si(111) substrates at 300 °C. Both precursors were prepared according to published methods.\(^12,13\) The room-temperature Ag substrates were exposed to \(1 \times 10^{-3}\) Torr of the precursor for 5 min during which time the pressure was monitored only by a baratron gauge so as to avoid ion-gauge-induced dissociation.

The chemical identity of the surface precursor fragments were determined using both x-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS). The XPS core-level spectra for adsorbed COD-Cu-hfac and Cu(hfac)_2 are shown in Fig. 1. The spectra are almost identical for the two different precursors. The three-peaked C 1s spectrum is characteristic of the hfac ligand. The peaks at 291.6, 286.4, and 283.8 eV correspond to the C—F, C—O, and C—H moieties, respectively, and the relative intensities of 2.0, 1.6, and 1.1 are close to that expected from the intact ligand stoichiometry (2,2,1). A strong C 1s signal at 284–285 eV would be expected as a signature of the eight-member carbon ring COD ligand if it were present in the adsorbed fragment. This feature is clearly absent, indicating that the Cu—COD bond has broken as part of the adsorption process. Measurement of the C 1s, O 1s, and Cu 2p XPS intensity shows a 65% ± 10% greater hfac ligand signal after exposure to Cu(hfac)_2 as compared to COD-Cu-hfac. This corresponds to 1.2 and 2.0 hfac ligands per Cu atom after COD-Cu-hfac and Cu(hfac)_2 adsorption, respectively, using atomic sensitivity factors from Wagner et al.\(^14,15\)

The HREELS spectra of the Ag surface after dosing with Cu(hfac)_2 and COD-Cu-hfac are shown in Fig. 2, and the vibrational assignments are made by analogy to IR data.\(^7,16\) Once again the most striking feature of the spectra is their similarity. The major peaks at 1200, 1625, and 3111 cm\(^{-1}\) are due to the C—F, C—O, and C—H stretching vibrations of the intact hfac molecule. The COD —C—H stretching modes are expected to give a signal at a lower frequency of 2820–2950 cm\(^{-1}\) with an intensity significantly greater than that of the single —C—H stretching vibration of the hfac ligand,\(^7\) and much larger than the small peak at 7850 cm\(^{-1}\). This peak is attributed to residual hydrocarbon contamination since it is also observed in the Cu(hfac)_2 data where no COD is present during dosing. Thus, as with XPS, no evidence for the COD ligand is found with HREELS.

For COD-Cu-hfac, initial loss of the COD relative to the hfac ligand is reasonable. The COD is a neutral ligand, thus there is little ionic character to the Cu—C bond. Ad-

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Additionally, the crystal structure of COD-Cu-hfac\textsuperscript{17} indicates that the bond lengths between the Cu and the two double bonds of the COD ligand are inequivalent, suggesting a fluctuating structure or a weakened bonding arrangement.

To determine the oxidation state of the adsorbed precursor species we have analyzed the Cu 2\(p\) and Cu LMM Auger lines. The Cu 2\(p\) lines are not sensitive to the differences between Cu(0) and Cu(I) [and no Cu(II) was observed]\textsuperscript{18,19} however, the kinetic energy of the Cu LMM Auger line does shift significantly upon oxidation, as illustrated for Cu metal and Cu\(_2\text{O}\) in Fig. 3. This change in kinetic energy is due to differences in electronic screening of the Auger two-hole final state. For the Cu adsorbates, screening by ligand valence electrons or from electron density in the substrate will contribute to this shift and is thus useful for indicating the degree of electron transfer between the Cu atom and its surrounding environment.\textsuperscript{20,21} For the Cu(hfac)\(_2\) and COD-Cu-hfac, the Cu LMM Auger lines fall at approximately 919.0 and 919.5 eV, indicating that the Cu atoms are screened more effectively in the adsorbed precursors than in Cu\(_2\text{O}\) (918 eV), but not as well as in metallic Cu (920.1 eV). Thus while the Cu fragment is formally assigned as a Cu(I) atom due to the presence of the attached hfac ligand, the shift toward higher kinetic energy indicates that the Cu atom is activated with respect to reduction to Cu metal, through interaction with the electron-rich Ag surface.

For COD-Cu-hfac adsorption, the presence of a Cu(I)-hfac surface intermediate is strong evidence that Cu deposition occurs through a bimolecular disproportionation reaction [common in solution chemistry of Cu(I) complexes\textsuperscript{22}]. As shown in Fig. 4, two Cu(I)-hfac fragments react to give Cu(0) and volatile Cu(hfac)\(_2\) consistent with the observation of Cu(hfac)\(_2\) in reaction pumping lines.\textsuperscript{7,8} By removing the ligands from the surface as part of an intact Cu(hfac)\(_2\) molecule, growth of clean Cu films is assured. It is likely that other Cu(I)-\(\beta\)-diketonate complexes react similarly by initial liberation of the neutral ligand and subsequent disproportionation of two Cu(I)-hfac species.\textsuperscript{23}

For Cu(hfac)\(_2\) adsorption, the Cu(II) atom is reduced by the Ag surface to form a similar Cu(I)-hfac intermediate to that found for COD-Cu-hfac except that there is one additional hfac per Cu on the surface (Fig. 4). This second hfac ligand should be directly bound to the Ag surface and may be partially associated with the Cu(I)-hfac species. Since the hfac ligand had lost a proton upon formation of Cu(hfac)\(_2\), it can only be removed from the surface as part of an intact Cu(hfac)\(_2\) molecule or by protonation to form
the volatile hfac-H neutral molecule. No Cu deposition will occur if the Cu(hfac)$_2$ desorbs intact. Disproportionation of two Cu(I)-hfac units (as for COD-Cu-hfac in Fig. 4) would leave one extra hfac ligand per Cu on the surface, leading to carbon incorporation in the growing film. Thus an external reducing agent such as H$_2$ or alcohols is required to act as a proton source so that the hfac ligands can be removed from the surface.

Comparison of these two reaction mechanisms provides a straightforward explanation why Cu deposition from COD-Cu-hfac has been found to be more reliable than that of Cu(hfac)$_2$. While the initial adsorption and activation of both complexes is facile even at room temperature, it is removal of the ligands that determines the quality of the Cu films. Since no external reductant is needed in the bimolecular disproportionation of COD-Cu-hfac, this is the simpler, lower-temperature process.

In light of our findings, it is likely that protonation of the excess surface ligand is the rate-determining step in Cu deposition from Cu(hfac)$_2$. This would explain why the deposition rate increases significantly with increasing H$_2$O concentration; H$_2$O could either protonate the adsorbed hfac (leaving surface OH which would be subsequently removed by reaction with H$_2$) or H$_2$O could complex with the adsorbed hfac ligand forming another volatile product. This also explains why Cu deposition from Cu(2,2,6,6-tetramethyl-3,5-heptanedione)$_2$ (where both CF$_3$ groups are replaced by t-butyl groups) occurs at a lower temperature than from the Cu(hfac)$_2$ precursor as more facile protonation is expected for this ligand.

The initial surface activation process is critical in the subsequent reactivity of these two molecules and the presence of an electron rich metallic substrate appears to be extremely important. For Cu(hfac)$_2$ the initial reduction of the molecule on Ag is likely due to the ease of electron transfer from the Ag into the partially filled Cu(II) d orbitals. For both precursors, the Ag provides stabilization of the Cu(I)-hfac intermediate after loss of the other ligands.

This substrate precursor electronic coupling must therefore be a critical factor in the selective nucleation of these precursors on metallic-versus-insulating surfaces.$^{1,3,8}$

In summary, our adsorption studies on COD-Cu-hfac and Cu(hfac)$_2$ have provided mechanistic data that explains why COD-Cu-hfac produces clean Cu films without the addition of an external reductant. In both cases, the metallic substrate plays an important role in activating the precursor toward subsequent reaction. Studies such as these on related precursor systems and hopefully in conjunction with molecular orbital calculations are critical as they aid the synthetic chemistry community in the design of better and more specific metalorganic precursors.

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15. The absolute concentration can vary by 30% depending upon the choice of cross section and transmission function, however, the measured intensity difference between the surfaces is accurate within 10%.
19. No evidence for Cu(II) was found even after Cu(hfac)$_2$ adsorption and no effects due to x-ray-induced reduction were observed.