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Role of the Deposition Precursor Molecules in Defining Oxidation State of Deposited Copper in Surface Reduction Reactions on H-Terminated Si(111) Surface

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Abstract

Surface-limited deposition reactions leading to the formation of copper nanoparticles on H-terminated Si(111) surface can serve as a model for understanding the role of structure of the deposition precursor molecules in determining the oxidation state of the metal deposited. This study compares three different precursor molecules: $\text{Cu}(\text{acac})_2$ (Cu(II) acetylacetonate), $\text{Cu}(\text{hfac})_2$, and $\text{Cu}(\text{hfac})\text{VTMS}$ (Cu(I)-(hexafluoroacetylacetonato)-vinyltrimethylsilane) as copper deposition sources in a process with a controlled oxidation state of copper. X-ray photoelectron spectroscopy suggests that single-electron reduction governs the deposition of Cu(I) from the first two precursor molecules and that the last of the precursors studied yields predominantly metallic copper. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and infrared spectroscopy are utilized to interrogate surface species produced. Atomic force microscopy is used to quantify the deposition process and to follow the size distribution of the deposited copper containing nanoparticles. A plausible explanation supported by density functional theory calculations is offered on the basis of the difference in the reaction pathways for Cu(I) and Cu(II) precursors.

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b08287. Summary of infrared investigations of $\text{Cu}(\text{acac})_2$ reaction with the H-terminated Si(111); proposed ball-and-stick illustration of the reaction pathways and DFT calculations reflecting the corresponding energies of each state for $\text{Cu}(\text{acac})_2$, $\text{Cu}(\text{hfac})_2$, and $\text{Cu}(\text{hfac})\text{VTMS}$; and complete ref 31 (PDF)

1. INTRODUCTION

Copper is a very versatile material with properties that are highly desirable in a wide range of applications. Many of these applications require the use of copper as a component of thin films or nanoparticles. For example, exceptional electronic and thermal properties make copper a popular metal for interconnect applications,¹⁻⁴ where the purity of the metal affects these properties tremendously. At the same time, supported copper serves as an outstanding catalyst for hydrogenation processes,^{5,6} methanol dehydrogenation,^{7,8} steam reforming,^{9,10} and many others. In the catalytic applications, the oxidation state of copper in a heterogeneous catalyst is obviously very important as well as in applications such as gas sensing or solar energy conversion.^{11,12} Among the methods that provide a high degree of control over the properties of copper deposited in the form of films or nanoparticles are low-pressure chemical vapor deposition (LP-CVD) and atomic layer deposition (ALD).

$\text{Cu}(\text{acac})_2$ (Cu(II)acetylacetonate) and $\text{Cu}(\text{hfac})_2$ (Cu(II)-hexafluoroacetylacetonate) are common deposition precursors for the formation of copper or copper oxide thin films on a variety of substrate surfaces by ALD or CVD processes.¹³⁻¹⁹ Their structures are illustrated schematically in Figure 1. Both precursors have planar structure and have Cu(II) at the center of the molecule. However, compared to $\text{Cu}(\text{acac})_2$, all 12 methyl hydrogens in $\text{Cu}(\text{hfac})_2$ are replaced with electron-withdrawing fluorine atoms, making electronic properties (and thus possibly the reactivity in deposition processes) of these two molecules very different. On the other hand, in $\text{Cu}(\text{hfac})\text{VTMS}$ (Cu(I)-(hexafluoroacetylacetonato)-vinyltrimethylsilane), six methyl hydrogen atoms are replaced by fluorine atoms, and the oxidation state of copper atom is (I). Thus, the reactivity and possibly even the end product of copper deposition from this precursor could be very different from those of $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{hfac})_2$. Hence, by comparing the deposition processes for these three precursor molecules on a well-characterized H-terminated Si(111) surface, the effect of different oxidation states of copper, as well as that of the structures of the precursor molecules, on the formation of surface copper-containing structures can be explored.

In this work, the deposition of copper-containing nanoparticles was explored on H-terminated Si(111) surface in high vacuum. X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), and infrared spectroscopy were used to elucidate the mechanism of the deposition process and to examine the oxidation state of copper. Atomic force microscopy (AFM) was conducted to reveal the surface morphology. Density functional theory (DFT) calculations were performed to supplement and explain the experimental observables and to propose feasible initial reaction steps of the deposition mechanism for each precursor.

2. EXPERIMENTAL SECTION

2.1. Materials

P-type double-side polished Si(111) wafers (Virginia Semiconductor, >0.1 ohm-cm resistivity, 500 μm thickness) were used as substrates. All chemicals were reagent grade or better: copper(II) acetylacetonate, $\text{Cu}(\text{acac})_2$ (Acros, 98%); copper(II) hexafluoroacetylacetonate, $\text{Cu}(\text{hfac})_2$ (Strem Chemicals, Inc., 99.99%); Cu(I)-

(hexafluoroacetylacetonate)-vinyltrimethylsilane, Cu(hfac)VTMS (CupraSelect, Air Products); Ar (Matheson, research purity); hydrogen peroxide (Fisher, 30% certified ACS grade); ammonium hydroxide (Fisher, 29% certified ACS plus grade); hydrochloric acid (Fisher, 37.3% certified ACS grade); buffer-HF improved (Transene Company, Inc.). The deionized water used to rinse the surfaces and containers was from a first-generation Milli-Q water system (Millipore) with 18 M Ω ·cm resistivity.

2.2. Procedures

2.2.1. Preparation of Hydrogen-Terminated Si(111) Surface—The hydrogen-terminated Si(111) surface was freshly prepared by a modified RCA cleaning procedure.²⁰⁻²² The Teflon beakers were cleaned with SC-1 solution freshly prepared from Milli-Q water, hydrogen peroxide, and ammonium hydroxide (volume ratio 4:1:1) for 30 min on an 80 °C water bath. Following this precleaning step, Si(111) wafers were cleaned by the same procedure for 10 min. After rinsing with Milli-Q water, the clean wafers were etched in HF buffer solution for 2 min and were rinsed again with Milli-Q water. Then, the wafers were placed in SC-2 solution, which was freshly prepared from Milli-Q water, hydrogen peroxide, and hydrochloric acid (volume ratio 4:1:1), for 10 min to grow a silicon oxide layer. After that, the rinsed silicon wafers were etched in HF buffer solution again for 1 min, followed by a 6 min etching process in ammonium fluoride solution to form a well-ordered hydrogen-terminated Si(111) surface, as confirmed by a sharp 2083 cm⁻¹ peak corresponding to monohydride Si–H in the infrared spectra²²⁻²⁴ described in detail later.

2.2.2. Precursor Molecules—Cu(acac)₂ and Cu(hfac)₂ were used as received in these experiments. Both compounds are solid powders at room temperature. Following the copper deposition, these diketonates are expected to release corresponding diketones, acacH (pentane-2,4-dione) for Cu(acac)₂ and hfacH (hexafluoroacetylacetone) for Cu(hfac)₂, into the gas phase. The third precursor, Cu(hfac)VTMS, is liquid at room temperature. VTMS (vinyltrimethylsilane) used to stabilize Cu(hfac) is found to desorb from the solid substrates immediately during the deposition process and does not pose contamination threat.²⁵⁻³⁰ The molecular structures of all the precursors and key desorption products are shown in Figure 1.

2.2.3. The Organo-Metallic Precursor Doser—Organometallic precursor doser (McAllister Technical Services) was used for depositing Cu(acac)₂ and Cu(hfac)₂. The doser was connected directly to a high-vacuum chamber that had a base pressure of 1.0×10^{-6} Torr. The solid-state precursors were dosed using sublimation into the gas phase. A differentially pumped (by Adixen Drytel 1025C pump) section of the doser was connected in such a way that the precursor could be reloaded without breaking the high vacuum. The precursor was loaded into the dosing section of the doser and was heated to 373 ± 5 K. Porous frits placed on both sides of the precursor section prevented the solid precursor from leaking out while allowing the vapor to flow into the reaction chamber during the deposition. A resistive heater was used to heat the precursor volume during the deposition process. A thermocouple was connected directly to the heater, so that the heating temperature could be monitored. To stabilize the heater temperature at 373 ± 5 K, 3 ± 0.2 V of AC was applied. Once the temperature reached this range, the deposition was started by turning the doser to deposit position and by opening access to the chamber. Cu(acac)₂ and Cu(hfac)₂ precursors

were dosed for 60 min at 2.0×10^{-5} Torr, which was determined to be sufficient to complete the deposition on the basis of XPS and AFM experiments described later, as no noticeable changes were observed for higher exposure times. Because high pressure can potentially cause contaminations of the reaction system, 2.0×10^{-5} Torr was chosen as the dosing pressure. After the deposition, the doser was turned again back to lock position to ensure that no additional precursor could enter the chamber. Cu(hfac)VTMS was dosed directly via a standard leak valve following at least three cycles of freeze–pump–thaw procedure. The purity of the compounds dosed was confirmed in situ by mass spectrometry (Stanford Research Systems).

2.2.4. Computational Details—Density functional theory (DFT) calculations were performed using Gaussian 09 suite of programs³¹ and GaussView 5 interface with B3LYP^{32,33} functional and LANL2DZ basis set.^{34–37} A Si₁₇H₂₄ cluster was used to represent the unreconstructed H-terminated Si(111) surface with two neighboring topmost surface sites. All the subsurface silicon atoms in the cluster were saturated with hydrogen atoms to maintain appropriate silicon coordination. This computational approach has been previously used successfully to evaluate surface reactions and spectroscopic observables for surface processes on silicon.^{23,24} Synchronous transit-guided quasi-newton (STQN) method was used to predict transition states, and a single negative eigenvector (frequency) was observed for every transition state reported. The energy baseline of a reaction pathway was calculated as a sum of the energy of the silicon cluster and the energy of the precursor molecule separately.

2.2.5. Characterization Methods—The K-Alpha⁺ X-ray photoelectron spectrometer (XPS) system from Thermo Scientific was used for all the XPS studies. The Al K α X-ray source ($h\nu = 1486.6$ eV) at a 35° takeoff angle with a resolution of 0.1 eV was used for all the XPS experiments. All the raw data were then analyzed by CasaXPS software, version 2.3.17. The carbon peak at 284.6 eV^{38–41} was used to calibrate all the other peaks and components of the spectra.

Atomic force microscopy (AFM) images were collected in tapping mode on a J-scanner scanning probe microscope (Multimode, NanoScope V). AFM probes (Budget Sensor) with a resonant frequency of 300 kHz and a force constant of 40 N/m were utilized. The images were processed using Gwyddion software.

Fourier transform infrared spectroscopy (FTIR) was used to investigate functional groups available on a surface at different modification steps. Nicolet Magna-IR 560 spectrometer with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector was used to collect all the infrared spectra. The incident angle of the beam was set to 60°. All spectra were collected at a resolution of 8 cm^{−1} with 512 scans averaged per spectrum. The native oxide-covered and hydrogen-terminated Si(111) wafers were used as background, as indicated.

Time-of-flight secondary ion mass spectroscopy in static mode was used with a ToF-SIMS V spectrometer (ION-TOF, Munster, Germany). The samples were analyzed in high-current bunched mode with 25 keV Bi³⁺ primary ions with a target current of 0.27 pA and a beam

dosage of 10^{12} ions/cm². The mass resolution was $m/m = 6000$ for SiH⁺. The data was collected within the range of m/z 0–350. There are at least three different samples analyzed for each set of experiments with a single spot analyzed in each sample. The calibration masses were H⁺, H₂⁺, CH₃⁺, C₂H₃⁺, C₃H₅⁺, C₄H₇⁺, C₅H₅⁺, C₆H₅⁺, and C₇H₇⁺ for the positive mode and H⁻, H₂⁻, CH₃⁻, C₂H⁻, C₃⁻, C₄⁻, C₅⁻, C₆⁻, and C₇⁻ for the negative mode.

For the ex situ characterization methods, the freshly prepared samples were transported under nitrogen to the experimental setups with minimal exposure to ambient conditions.

3. RESULTS AND DISCUSSION

3.1. Spectroscopic Identification of Surface Species Formed following the Reaction of Cu(hfac)₂ and Cu(acac)₂ with the H-Terminated Si(111)

Because oxidation states of the copper atom in the three precursors used are different, this may affect the surface reaction leading to copper deposition and the oxidation state of the deposited metal. Specifically, Cu(hfac)₂ and Cu(acac)₂ have similar structures and the same oxidation state for copper, Cu(II). Thus, it may be expected that the reactions leading to copper deposition for both precursors are similar and that the chemical environment of the copper deposited is similar for these two precursors. On the other hand, because the oxidation state of copper in Cu(hfac)VTMS is Cu(I), the corresponding deposition reactions may differ from those for Cu(II) precursors, and the final products can be affected by this difference. A detailed XPS investigation of Cu(hfac)VTMS reaction with H–Si(111) surface has been reported previously,^{28–30} and so the following spectroscopic characterization will pertain mostly to the Cu(hfac)₂ and Cu(acac)₂ molecules.

To test the hypothesis outlined above, the deposition procedures were performed, and XPS was used to investigate the resulting surface species. As shown in Figure 2, Cu 2p_{3/2} peaks for both Cu(acac)₂ and Cu(hfac)₂ are observed at 932.8 eV following deposition. The corresponding Cu 2p_{1/2} peaks are observed corresponding to the expected spin–orbit coupling energy, at 952.7 eV. More importantly, no peaks are observed between those two, around 940 eV, where the shakeup peak is expected as a signature of Cu(II) presence.⁴² In other words, only Cu(I) or metallic copper are present on the surface at this point. To differentiate these two possibilities, the Cu LMM Auger spectral region was inspected, as summarized in the bottom panel of Figure 2. The presence of metallic copper within the XPS sampling depth is expected to be indicated by the kinetic energy of 918.6 eV,^{29,43} which is shown by a vertical black line in Figure 2. However, the corresponding signal is observed at 916.5 eV for the samples exposed to both Cu(acac)₂ and Cu(hfac)₂, which is fully consistent with the peak position for Cu₂O reported at 916.4 eV.⁴³ This observation suggests that for both precursors, Cu(II) is reduced to Cu(I) during the deposition process.

Similar oxidation states for the products of deposition processes for both precursor molecules suggest that similar reduction pathways may be followed. For example, when Cu(acac)₂ or Cu(hfac)₂ is introduced into the reaction chamber, a hydrogen atom from the silicon surface can combine with a ligand of a copper deposition precursor to form acacH or hfacH, respectively, as a byproduct. At the same time, the central copper atom of the

remaining metalorganic entity is expected to interact with an available surface silicon atom to form a new copper–silicon bond. Thus, Cu(II) is reduced to Cu(I). Following this step, the remaining ligand is expected to be nearly perpendicular to the silicon surface, making it difficult for copper to undergo further reduction. The reaction of Cu(hfac)VTMS with a H–Si(111) surface investigated in detail by XPS previously^{28,30} showed that the majority of copper deposited corresponded to a metallic state, which is also consistent with a one-electron reduction process observed here for Cu(II) precursor molecules.

The integrity of the ligands remaining on a surface following the deposition process can also be investigated spectroscopically. For hfac ligand, XPS can be used especially successfully, since this technique is highly sensitive to fluorine-containing features present in the spectrum. For Cu(hfac)₂, the results of this technique will be further elaborated by ToF-SIMS. For Cu(acac)₂, infrared spectroscopy combined with ToF-SIMS will be used, as described in detail below.

To verify if the hfac ligands of the precursor molecule remain intact following deposition, XPS studies of F 1s were conducted for a sample prepared by Cu(hfac)₂ dose. As shown in Figure 3a, there is a single main feature observed in the spectrum at 689.3 eV. The position of this feature is fully consistent with the presence of –CF₃ entity reported previously for hfac on the surface of silicon, ZnO, or TiO₂.^{28,29,44} The density functional theory (DFT) calculations based on Koopmans' theorem⁴⁵ were performed and applied to predict the binding energy of F 1s. The calibration procedures for N 1s⁴⁵ and C 1s⁴⁶ features on the basis of comparisons with multiple experimental studies and multiple corresponding computational investigations have been reported previously. Despite the fact that similar calibration procedures have not yet been reported for F 1s, the relative differences (core level shifts) between fluorine atoms in different chemical environments can still be used to examine the chemical environment of fluorine atoms observed in this study and to rule out the presence of Cu–F and Si–F bonds that could potentially result from decomposition of –CF₃ groups during the deposition.^{28,29} Thus, all the binding energies of fluorine atoms in Figure 3b–d are calibrated by setting the average binding energy predicted by DFT for the structure in Figure 3b to the corresponding experimental energy in Figure 3a, which is at 689.3 eV. Specifically, from Figure 3b–d, the binding energy difference between C–F and Si–F is predicted to be 2.4 eV while the binding energy difference between C–F and Cu–F is expected to be 3.9 eV on the basis of the computational investigation. These large differences would be easily observed in experimental XPS studies; however, this is not the case. Thus, on the basis of this comparison, the computational results further support the statement that the major fluorine-containing chemical groups present on a surface following copper precursor reactions at room temperature are –CF₃ groups. Although a small shoulder around 686 eV suggests a possible decomposition process, this peak is very minor compared to the dominant peak at 689.3 eV. This assessment is also consistent with previously reported experimental binding energies for Cu–F or Si–F around 684 or 685 eV, respectively.^{29,47}

To confirm this assessment and to evaluate the distribution and binding of other surface species, additional studies utilized ToF-SIMS. Figure 4 summarizes the most informative spectral regions of this work for Cu(hfac)₂ reaction with the H-terminated Si(111) surface.

Positive ion ToF-SIMS spectra are used for Figure 4a and c; negative ion spectra are used for Figure 4b and d. For easy comparison, the fragments discussed later are shown with the corresponding m/z values rounded to the second decimal. Although the spectral region corresponding to copper species is complicated by the presence of many other fragments including SiH_3O_2^+ (m/z 62.99), C_5H_3^+ (m/z 63.02), C_5H_4^+ (m/z 64.03), SiC_3H^+ (m/z 64.98), and C_5H_5^+ (m/z 65.04), the peaks at m/z 62.93 and 64.93 (Figure 4a) clearly prove the presence of surface copper, and m/z 90.90 and 92.90 (Figure 4c, where the slight shift can be explained by the overlapping peaks) reveal that the Cu–Si bond is present (partially obscured by the presence of C_7H_7^+ at m/z 91.05, Si_2C_3^+ at m/z 91.95, C_7H_8^+ at m/z 92.06, C_3F_3^+ at m/z 92.99, and C_7H_9^+ at m/z 93.07). These studies are fully consistent with the XPS investigations and also confirm the formation of the Cu–Si interface, suggested indirectly by the XPS studies of the oxidation process shown later. Additionally, the peaks at m/z 206.99 (Figure 4b) and 234.97 (Figure 4d) reveal the presence of the intact hexafluoroacetylacetonate anion (less hydrogen compared to the intact hexafluoroacetylacetone molecule, labeled in Figure 4b at m/z 207.99) and Sihexafluoroacetylacetone anion species, respectively. Figure S1 also shows the peak at m/z 235.97 that reflects the contribution of other isotopes. Because of the calibration limitations, the assignment of the peaks at high m/z region such as the one at m/z 234.97 in Figure 4d might not be as accurate as that at low m/z region. These observations suggest that the hfac ligand is intact following deposition and that the process results in the formation of Si-hfac[−] species following the reaction of the H-terminated silicon with Cu(II) precursors. Although ToF-SIMS results can only be treated as semiquantitative, no Cu-hfac cation fragments (as a signature of Cu(hfac) surface species) were observed in these studies (Figure S1), suggesting that the formation of Cu–Si interface is related to the reaction leading to hfacH elimination upon copper deposition.

As shown in Figure 5, ToF-SIMS for $\text{Cu}(\text{acac})_2$ was also used to investigate the species formed on the surface following the deposition process. Positive ion ToF-SIMS spectra are used for Figure 5a, b, and d; negative ion spectra are used for Figure 5c. The peaks at m/z 62.93 and 64.93 in Figure 5a clearly prove the presence of copper, although additional minor peaks indicate the existence of other features at similar m/z , likely from background, since they are also recorded for H–Si(111) surface. Figure 5b shows Cu–Si⁺ species at m/z 90.90 and 92.90 (also complicated by the presence of several peaks within a similar spectral range on the background spectra). Figure 5c illustrates acac anion and molecular acacH[−] ion at m/z 99.04 and 100.05, respectively. The minor species present on the background include Si_3NH^- at m/z 98.93, $\text{C}_4\text{H}_3\text{O}_3^-$ at 99.01, and Si_3O^- . Cu-acac⁺ species are shown in Figure 5d at m/z 161.97 and 163.97. All these results suggest similarities with the ToF-SIMS investigation of $\text{Cu}(\text{hfac})_2$ and confirm the formation of the Cu–Si bond on the surface. Second, they prove the intactness of the acetylacetonate ligand on the surface. Along with the results of infrared investigation presented in Figure S2, they indicate that the $\text{Cu}(\text{acac})_2$ precursor did not undergo a surface-induced decomposition process for the acac ligand upon copper deposition.

3.2. Formation, Stability, and Oxidation of Copper–Silicon Interface following Reactions of Cu(hfac)₂ and Cu(acac)₂ with the H-Terminated Si(111) Surface

During the deposition process, one important question concerns the formation and stability of the interface between copper and silicon. The ToF-SIMS studies indicate that Si–Cu species are indeed present on the resulting surface. Figure 6 compares the XPS investigations of the Si 2p spectral region for (a) freshly prepared H-terminated silicon, (b) the same surface as in (a) followed by the deposition of Cu(hfac)₂, and (c) the same surface as in (a) followed by the deposition of Cu(acac)₂. Surface oxidation manifests itself as a broad SiO_x peak in the 101–104 eV range.^{23,24} Interestingly, both for Cu(acac)₂ and for Cu(hfac)₂, the oxidation is minimal, most likely resulting from defect site oxidation in ambient during transferring the sample from the reaction chamber to the XPS instrument. The general reaction pathway suggested earlier for copper reduction may lead to the formation of Cu–Si interface; however, the binding energy for copper silicide at 99.6 eV⁴⁸ makes it difficult to directly distinguish the silicide formation from the signal of bulk silicon within the Si 2p spectral region, especially for such a complex system.

However, additional information can be obtained about the stability of this interface with respect to oxidation on the basis of the Cu 2p and Cu LMM spectral regions. XPS investigation for Cu(acac)₂ deposited onto silicon surface was performed following exposure of the sample prepared by copper deposition to ambient conditions for extended periods of time, as summarized in Figure 7. Upon oxidation, the Cu–Si interface could be expected to produce species of the general formula of CuSi_xO_y. The freshly deposited sample in Figure 7c is compared to those exposed to air for 2 days (Figure 7b) and 1 week (Figure 7a). In addition to the satellite peaks indicative of the formation of Cu(II) following oxidation, a new peak for Cu 2p_{3/2} is observed at 934.9 eV, with a corresponding spin–orbit coupling peak at 954.8 eV. These features are indicative of the formation of CuSi_xO_y species, possibly CuSiO₃.⁴⁹ It also seems that on the basis of the Cu LMM Auger spectral region (Figure 7d–f), the majority of copper present on the surface is still in Cu(I) oxidation state, as confirmed by the peak around 915 eV. This observation will be important later for comparing the morphology of the surface produced by copper precursor reactions on H-terminated Si(111).

3.3. Surface Morphology following Copper Deposition: Formation of Nanoparticles

It is expected that the reaction chemistry for Cu(acac)₂ and Cu(hfac)₂ on a H-terminated Si(111) surface would be similar; however, it is also obvious that the electronic properties of these deposition precursor molecules may be affected substantially by the electron-withdrawing fluorine atoms in Cu(hfac)₂ compared to the electron-donating substituents in Cu(acac)₂. Thus, it is important to investigate if these differences will manifest themselves in different morphologies of the resulting surfaces. Since in both cases surface termination is the only source of hydrogen that can reduce the oxidation state of copper and form the corresponding product diketone, the overall deposition reaction is expected to proceed only until surface hydrogen is consumed and then to stop in a self-limiting fashion. Similar processes have been reported on differently functionalized silicon surfaces^{28,30,50} and on other semiconductors.²⁹ The Cu(II) precursors will be further compared to Cu(hfac)VTMS whose reactions with the H–Si(111) have been studied in detail spectroscopically earlier.^{28–30}

Figure 8 shows the AFM images of the nanoparticles deposited onto H-terminated Si(111) surface using $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{hfac})_2$ and compares them to the surface resulting from $\text{Cu}(\text{hfac})\text{VTMS}$ deposition. The figure also shows the corresponding nanoparticle height distribution diagrams. $\text{Cu}(\text{hfac})\text{VTMS}$ is an important addition to this comparison since, unlike the other two precursors, the oxidation state of the central copper atom in $\text{Cu}(\text{hfac})\text{VTMS}$ is Cu(I). While the different substituents ($-\text{CH}_3$ or $-\text{CF}_3$) of the first two precursors may affect the deposition process and thus surface morphology, different oxidation states of the central copper atom and different molecular structures may influence the morphology even more. From this comparison, it is clear that overall, the morphologies of the surfaces produced are very similar. The surface exposed to $\text{Cu}(\text{hfac})_2$ has a slightly higher particle density than the one following the deposition of $\text{Cu}(\text{acac})_2$; the height distribution for the nanoparticles formed by $\text{Cu}(\text{hfac})_2$ deposition is slightly wider than that derived from $\text{Cu}(\text{acac})_2$ deposition. However, overall, both processes lead to very similar results. As for $\text{Cu}(\text{hfac})\text{VTMS}$, it has a very similar particle height distribution as $\text{Cu}(\text{acac})_2$ does, but it is different from that of $\text{Cu}(\text{hfac})_2$. In particular, the height of most of the surface particles for $\text{Cu}(\text{hfac})\text{VTMS}$ and $\text{Cu}(\text{acac})_2$ is below 2 nm while the height of the particles resulting from $\text{Cu}(\text{hfac})_2$ deposition mainly ranges from 2 to 4 nm.

3.4. Computational Investigation of Possible Surface Reaction Mechanisms

Despite the similarities of spectroscopic and microscopic descriptions of nanoparticles deposited from the three copper precursors, can anything be distinguished on the basis of the computational analysis of the initial deposition steps? This question is especially important given that the oxidation state of copper in the majority species in the nanoparticles deposited is different for Cu(I) and Cu(II) precursors.

To prove the validity of the reaction mechanism proposed for one-electron reduction, DFT calculations (Figure 9 and ball-and-stick illustration in Figure S3) are performed to further investigate the reaction process. In this figure, four reaction states for the reaction between H-terminated Si(111) surface and $\text{Cu}(\text{acac})_2$ are listed. From left to right, they are weak interaction state, transition state for ligand elimination/ hydrogen removal, result of ligand elimination with the byproduct weakly bound to the surface, and the final product after the ligand leaves the surface (desorption). Overall, the processes for all three precursors considered are slightly endothermic; however, similarly to the previously described deposition of $\text{Cu}(\text{hfac})\text{VTMS}$ onto different functionalized silicon surfaces,^{28,30,51} it is important to realize that the actual deposition processes can be substantially more complex and possibly self-catalyzed by the copper that is deposited in the preceding steps. In other words, it is more important to compare the three processes rather than invoke quantitative information about the energy landscape for each one.

The oxidation state of copper in $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{hfac})_2$ is Cu(II). However, XPS only shows the existence of Cu(I) on the surface following the deposition process. The mechanisms suggested in Figure 9 explain this reduction process. For example, as the $\text{Cu}(\text{acac})_2$ precursor approaches the H-terminated Si(111) surface, it abstracts one hydrogen atom from the surface to form acacH as a byproduct, leading to the formation of a Si dangling bond. At the same time, the central copper atom is reduced during the formation of

the Si–Cu bond that results from the interaction between the central copper and the silicon dangling bond. Following this reduction, acacH leaves the surface and the copper remains in its Cu(I) state. A similar reaction is shown for Cu(hfac)₂. However, the analogous process for Cu(hfac)VTMS involves only the Cu(hfac) fragment, as it has been shown that upon adsorption, VTMS is immediately released into the gas phase.^{27,51} Then, for this Cu(I) precursor molecule, it is clear that the reduction reaction produces a formally Cu(0) deposit, which is completely consistent with the previously reported observations.^{28,30}

Again, it is important to realize that these processes are only the initial steps in the formation of copper-based nanoparticles described in the previous section.

An important difference between Cu(I) and Cu(II) precursors interacting with the H-terminated Si(111) illustrated in Figure 9 is the formation of a weakly bound initial state that is substantially more stable for Cu(hfac)VTMS, as compared to any other precursor studied. This difference is likely caused both by the different electronic structure of the precursor molecules and also by their different geometries. Namely, the Cu(II) precursors are both planar, which makes weak interaction between the surface and the copper atom of a precursor in this relatively open configuration possible. However, this stable structure would also have to be distorted substantially to make this interaction strong. The exact numbers obtained by this simple calculation are possibly misleading; however, it is clear that it is a very weak interaction. On the other hand, the open and unsaturated structure of the Cu(hfac) species resulting from Cu(hfac)VTMS reaction with the same surface results in a much more stable intermediate, with 70.1 kJ/mol stabilization energy. This comparison also infers that the structures formed following elimination of a single ligand of the Cu(II) precursors could serve as a protective layer to prevent any further reduction reactions for copper, which is also consistent with the XPS results that show only Cu(I) following the deposition based on Cu(II) precursors. The exact mechanisms of surface ligand migration and confirmation of surface Cu(hfac) species thermochemistry could be the target of further investigations.

4. CONCLUSIONS

By depositing Cu(acac)₂, Cu(hfac)₂, and Cu(hfac)VTMS onto the H-terminated Si(111) surface under high vacuum conditions, a one-electron reduction reaction was observed by XPS for copper atom. The Cu–Si interface formed during the deposition of Cu(II) precursors can be further oxidized to form CuSiO₃ if the freshly prepared sample is left in ambient conditions for an extended period of time.

One possible explanation for such behavior would be that the outmost layers of the copper-based nanoparticles serve as protective layers to prevent additional oxidation of copper, and instead, the interface between copper-based nanoparticles and silicon is the main target of oxidation processes. A plausible initial reaction pathway was proposed and evaluated by DFT calculations and showed initial endothermic reaction for all of the precursors, with Cu(I) precursor clearly forming a much more stable surface adsorbate compared to the Cu(II) precursor molecules. These differences likely result in the differences observed for the final product, the deposited nanoparticles, for Cu(I) and Cu(II) precursors.

In other words, Cu(I) is reduced to metallic copper for Cu(hfac)VTMS^{28,30} while Cu(II) is reduced to Cu(I) for Cu(acac)₂ and Cu(hfac)₂; on the basis of the AFM images, the morphologies of the surfaces are slightly different as discussed earlier in detail; the reaction mechanism described by the DFT calculation shows a weakly bound initial state for Cu(hfac)-VTMS, which is the most likely reason for such differences between Cu(I) and Cu(II) precursor reactions with the H-terminated Si(111) surface.

This set of studies allows for controlling the oxidation state of copper on functionalized surfaces by varying the oxidation state of this metal in the starting precursor and also outlines approaches for further evaluation of the interface oxidation processes for the Cu–Si interface.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Molecular structures of (a) $\text{Cu}(\text{acac})_2$, (b) $\text{Cu}(\text{hfac})_2$, (c) $\text{Cu}(\text{hfac})\text{VTMS}$, (d) acacH , and (e) hfacH .

Figure 2.

XPS investigation of the reactions between Cu(hfac)₂ or Cu(acac)₂ and H-terminated Si(111) surface. Cu 2p region is shown at the top and Cu LMM Auger region is shown at the bottom. (a, c) The spectra of Cu 2p and Cu LMM Auger region for Cu(hfac)₂, respectively; (b, d) the spectra of Cu 2p and Cu LMM Auger region for Cu(acac)₂, respectively. The kinetic energy expected for metallic copper is labeled in the bottom figure as Cu(0) line.

Figure 3.

XPS studies of the F 1s region following reaction of $\text{Cu}(\text{hfac})_2$ with H-terminated Si(111) surface. The main peak at 689.3 eV in (a) indicates the intactness of $-\text{CF}_3$. The black bars in (b) show the predicted binding energy of $-\text{CF}_3$ using DFT calculations and its corresponding computational structure. All the six fluorine atoms have very similar binding energy with a spread of 0.1 eV. The average binding energy is calibrated to be 689.3 eV. Plot (c) illustrates the predicted binding energy of the Si-F bond by DFT calculation at 686.9 eV and the corresponding computational structure. Plot (d) illustrates the predicted binding energy of the Cu-F bond by DFT calculation at 685.4 eV and the corresponding computational structure. All the energies are calibrated by setting the average energy predicted by DFT for the structure in (b) to the corresponding experimental energy in spectrum (a).

Figure 4.

ToF-SIMS taken immediately after the deposition of Cu(hfac)_2 showing (a) Cu, (b) hfac species, (c) Cu–Si species, and (d) Si-hfac species. Each figure presents the signal recorded for the sample following deposition on the top and the signal from the background (freshly prepared H-terminated Si(111) surface) at the bottom. Positive ion ToF-SIMS spectra are used for plots in a and c; negative ion spectra are used for the results presented in b and d. The intensity scale is shown in counts per second.

Figure 5.

ToF-SIMS taken immediately following the deposition of $\text{Cu}(\text{acac})_2$ showing (a) Cu, (b) Cu-Si species, (c) acac anion and acacH molecule, and (d) Cu-acac species. Each figure shows the signal recorded for the sample following deposition on the top and the signal from the background (freshly prepared H-terminated Si(111) surface) at the bottom. Positive ion ToF-SIMS spectra are used for Figure 5a, 5b, and 5d; negative ion spectra are used for Figure 5c. The intensity scale is shown in counts per second.

Figure 6.

Comparison of the XPS spectra within the Si 2p region for (a) freshly prepared H-terminated Si(111) surface, (b) freshly prepared H-terminated Si(111) surface followed by the deposition of Cu(hfac)_2 , and (c) freshly prepared H-terminated Si(111) surface followed by the deposition of Cu(acac)_2 . A vertical line is drawn around 103 eV to indicate the position of SiO_x .

Figure 7.

Comparison of Cu 2p peaks (top) and Cu LMM Auger peaks (bottom) over time for Cu(acac)₂. (a, d) Spectra taken after 1 week of exposure to ambient; (b, e) spectra taken after 2 days of exposure to ambient; (c, f) spectra taken immediately following the deposition. The kinetic energy for metallic copper is labeled in the figure as Cu(0) line. From this comparison, it is clear that at least some copper is oxidized from Cu(I) to Cu(II) following long-time exposure to ambient, which is indicated by the satellite peaks between 940 and 945 eV. Furthermore, the new peak at 934.9 eV implies the formation of a silicate-like compound.

Figure 8.

(a, b) AFM image and the corresponding surface nanoparticle size distribution following the reaction of $\text{Cu}(\text{acac})_2$ with the H-Si(111) surface. (c, d) AFM image and the corresponding surface nanoparticle size distribution following the reaction of $\text{Cu}(\text{hfac})_2$ with the H-Si(111) surface. (e, f) AFM image and the corresponding surface nanoparticle size distribution following the reaction of $\text{Cu}(\text{hfac})\text{VTMS}$ with the H-Si(111) surface. All the AFM images were recorded immediately following the deposition. The particle density of c is higher than that of a, and the average height of the particles of d is larger than that of b. In addition, sample d has a wider height distribution compared to both b and f. As for d and f, d not only has a wider size distribution but also has a larger average height of the nanoparticles.

Figure 9.

Proposed reaction pathways and DFT calculations reflecting the corresponding energies of each state for Cu(acac)₂ (top), Cu(hfac)₂ (middle), and Cu(hfac)VTMS (bottom). From left to right, the structures shown correspond to weak interaction, transition state for corresponding hydrogenated ligand removal, product before the ligand leaves the surface, and product after the ligand leaves. The baseline is set as 0 kJ/mol for the sum of the energy of the silicon substrate (represented by a cluster model) and the energy of the corresponding precursor molecule calculated separately.