# X-ray photoelectron spectroscopy (XPS) studies of initial stages of copper deposition from bis(hexafluoroacetylacetonato)copper(II) (Cu(hfac)$_2$) on Si(111)-7×7 at room temperature. Part B

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Organometallic chemical vapourdepostion (OMCVD) of copper compounds is the preferred method for metallization of semiconductors over physical vapour deposition. The advantages of CVD are selectivity and ambient conditions for deposition (low vacuum and room temperature). UPS and XPS spectra of Cu deposited from Cu(hfac)$_2$ via chemical vapour deposition onto Si(111)-7x7 were studied for apparent exposures of 0.02, 0.04, 0.06, 0.08, 0.1 L at room temperature. Cu(hfac)$_2$ adsorption on Si(111)-7x7 at RT follows a ligand dissociative pathway with ligand fragmentation. At low exposures (i.e. 0.04 L) the precursor adsorbs onto Si surface in the reduced form, probably as Cu(I). This is supported by the absence of the shake-up features in the Cu XPS spectrum. Also Cu(II) was accounted for 5% of the total amount of Cu. The driving force for the reduction (Cu(II) → Cu(I)) is the Si(111) surface in its 7x7 reconstructed form. The process takes place at electron states on adatoms in Takayanagi's model.

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## 1. Introduction

Chemical vapour deposition (CVD) is a method of growing thin films in which volatile metal-organic, organometallic or inorganic components are transported in the vapour phase towards a substrate on which these chemicals react resulting in the formation of a thin solid film [1]. Chemical vapour deposition is preferred over physical vapour deposition since the latter process requires more rigorous vacuum conditions and higher temperatures; in addition CVD is conformal and selective. Since 1965 [2] many investigations of Cu CVD have been reported [3, 4, 5].

Organometallic chemical vapour deposition (OMCVD) of copper compounds was explored for metallization of semiconductors in microelectronics via the deposition of (hexafluoroacetylacetonato)copper(II) (Cu(hfac)$_2$), hfac$^-$ = [CF$_3$OCHCOCF$_3$$^-$], a bidentate ligand and the related Cu(I) compound hexafluoroactetylactonato (1,5 octadiene) copper(I) ((hfac)Cu(COD)) [6, 7].

In a previous article we presented a room temperature ultraviolet photoelectron spectroscopy (UPS)) study of the Cu(hfac)$_2$ interaction with Si (111)-7×7 Part A (Fig. 1 and Fig. 2) [20].

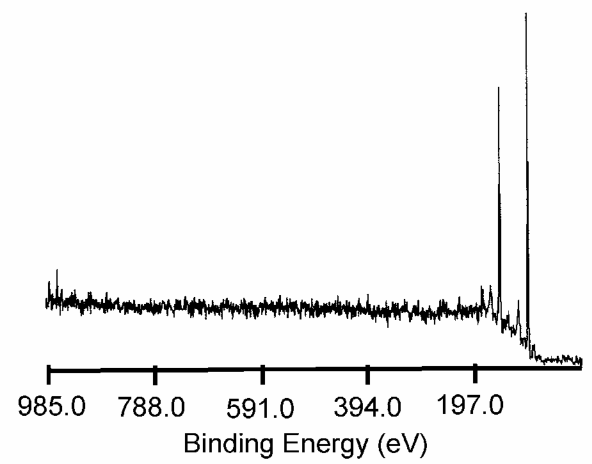

*Fig. 1. XPS spectrum of clean Si(111)-7×7 on which the Cu(hfac)$_2$ deposition was performed. It shows a surface free of C and O as contaminants. Peaks centered around 150.96 eV and 98.7 eV correspond to Si 2s and Si 2p respectively. UPS spectra proved that the clean surface was reconstructed 7×7.*

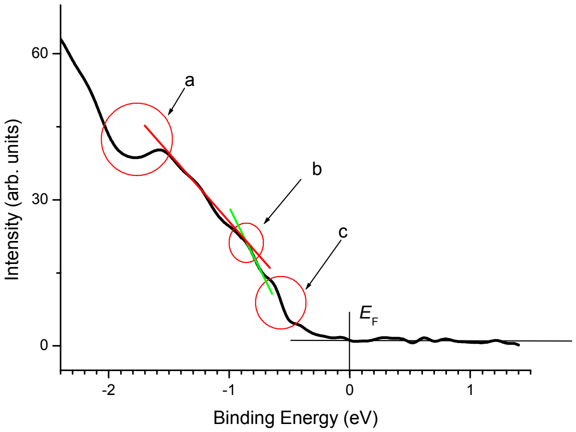

*Fig. 2. The UPS spectrum for the bare Si(111) surface shows three surface states [8]: 1. the surface state (a) at 1.8 - 2 eV related to the backbonds between the Si adatoms and the three Si atoms directly beneath them, 2. the surface state (b) at ~1 eV related to the filled dangling bond states situated on the rest atoms, and near the Fermi level $E_F$ (0 eV), and 3. the surface state (c) at 0.4 - 0.6 eV related to a half-filled dangling bond state located at the adatom that forms part of the 7×7 reconstruction. The intensity of the state at 0.4 - 0.6 eV is a good indication of the quality of the 7×7 surface reconstruction*

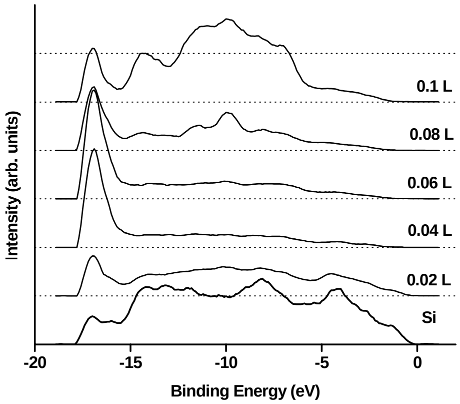

*Fig. 3. Wide scan UPS spectra taken after each deposition show a difference in the valence features for Si (2.5 - 15 eV), suggesting that a transformation occurred from one deposition to another. UPS spectra following the first deposition at 0.02 L revealed that the Si peaks due to emission from bulk states (-4 eV and -8 eV) are attenuated as a result of the adsorption of Cu(hfac)$_2$ on the surface. The peak at -17 eV is the secondary electron peak and its variation with the exposure reflects changes in the secondary electron emission caused by the presence of Cu (I) and fluorinated moities.*

We concluded that the enhanced emission in the broad structure centered around -10 eV for the 0.08 L exposure probably arises from deposited metal species, most likely Cu(I). At the same time, emission from Si bulk states is highly reduced for the 0.08 L spectrum. Similar behaviour was observed by Tadayyon (9) for metals. The difference in the intensity of the spectra between 0.08 L and 0.1 L suggested that the local density of states around Si is affected by a continuous increase in the number of Cu atoms with the exposure. The shoulder that appears at around 3.6 eV in the 0.1 L spectrum is double the intensity of the shoulder that appears at the same value of the binding energy in the 0.08 L spectra. It corresponds to the Cu *3d* band and it is probably produced by Cu clusters of very small size. The rapid disappearance of the Si features around 3.6 eV for exposures of 0.04 L and higher is given by the higher cross-section of Cu *d* band emission as suggested by Ringeisen *et al*. (10) for the Cu-Si room temperature interface at submonolayer coverages (Fig. 3).

A previous study performed at various temperatures (6) (below the Cu dissolution temperature) has shown that the Cu(hfac)$_2$ deposits on the Si(111)-7×7 showing a physical separation between the Cu (which forms clusters of 8-10 atoms) and the ligands which also appear to be aggregated. The structure and hence the quality of the metallic film is controlled by nucleation and growth processes at the initial stages of growth. Our goal was to understand the mechanism of initial stages of the Cu(hfac)$_2$ deposition at room temperature (RT). A number of questions are addressed in the present study:

- In the case of a dissociative adsorption will the ligand adsorb intact or it will adsorb as smaller molecular fragments?
- In the case of a dissociative adsorption will the growth of clusters terminate via saturation of Cu clusters with ligands or fragments of ligands? In other words which is the key to the formation of the so-called magic number clusters reported by Horton *et al*. (6).

## 2. Experimental details

The experiments were carried out in a home built ultra high vacuum (UHV) chamber which contains a differentially pumped He-discharge lamp, XPS capabilities and other standard surface science tools. The XPS facility uses a Combined Lens and Analyser Module (CLAM 2) system (VG Microtech-Fisons Instruments, East Sussex, UK). The electron energy analyser is a 100 mm mean radius hemispherical electron/ion analyser and it is equipped with an integral dual element transfer lens and channel electron multiplier (Channeltron). The chamber operated at a base pressure of $2\times10^{-10}$ Torr. The UPS spectra were acquired by using the He(I) line (21.2 eV) and an analyzer pass energy of 15 eV. The overall resolution was < 100 meV. The XPS analyses were performed at 10 kV anode voltage and 14 mA emission current, using an Al $K_\alpha$ - X-ray source (1486.6 eV), collecting data at 50 eV pass energy. The overall resolution was ~ 1.2 eV. Wide scans (500-1580 eV) were obtained in a single sweep with a step size of 1 eV at 655 ms/step dwell time. Narrow scans were recorded for each element with a step size of 0.1eV at 655 ms/ step dwell time. All data were recorded at RT. The binding energy scale of the spectrometer was calibrated to the Au $4f_{7/2}$ line of a polycrystal Au plate (83.95 eV) after ion sputter cleaning. The Au plate used for calibration had the same dimensions as the Si sample used in this measurement and was mounted on a similar sample holder. The Si 2s peak (at 150.8 eV) was used as the internal reference for the binding energy.

A sample of p-Si (boron as dopant - Virginia Semiconductor Inc.) double side polished, ($5\times21$ mm$^2$) thickness 300 μm ± 25 μm, orientation <111> ± 0.5º, 0.7-1.2 Ohm-cm resistivity was cut from the Si wafer and wiped with methanol using a Q-tip then degreased by sonication in MeOH for 5 min. then in acetone for 3 min. and again in MeOH for 5 min. and finally rinsed with deionized water (ρ = 18 MΩcm). Then, the oxide was grown (($H_2O$-$NH_4OH$(30%)-$H_2O_2$(30%) 4:1:1 at 80 ºC for 5 min.), then $H_2O$-$H_2O_2$(30%)-HCl (37%) 1:1:3 as long as reaction continued (~20 min.)) then rinsed repeatedly in deionized water and dried by using pre-purified $N_2$.

The sample was mounted on a pod by using two Ta shims ($5\times5\times0.5$ mm$^3$) in order to avoid hot spots which are always responsible for the sample melting at elevated temperatures. The sample was manipulated by using only teflon tweezers. Outgassing via resistive heating lasted for 12 hours at 700 ºC until the pressure was in the low $10^{-10}$Torr range. Oxide and carbide removal was done by repeatedly flashing in the 1147-1177 ºC range for a total time of ~2 minutes. During flashing the pressure never increased above $1\times10^{-9}$ Torr. The cooling process was rapid from the highest flashing temperature to 850 ºC (this was done by decreasing the current in 0.2 amps increments until the temperature reached 850 °C) and then more slowly from 850 °C to room temperature (the current was constantly decreased in 0.1 amps increments). During the entire process a close inspection for hot spots was carried out and a satisfactory temperature gradient was observed between the middle and the ends of the sample [11]. The pressure recovered from < $1\times10^{-9}$ Torr to < $10^{-10}$Torr within 25 seconds of cooling.

The XPS/UPS chamber did not have LEED capabilities, but since the cleaning recipe was identical to that used in previous STM experiments [11], we are confident the samples would exhibit excellent 7×7 reconstruction. The UPS spectrum of the "as-prepared" sample was used as a proof for the 7×7 reconstruction.

For dosing the Cu(hfac)$_2$ we used a home built doser, an UHV compatible device designed to maximize the volatilization of low-pressure compounds used in chemical vapour deposition (CVD) with minimal dissociation. A full description of this device has appeared previously [12]. Briefly, it is a differentially pumped system in which the precursor is located close to the sample, minimizing its dissociation during the transport process. It has 2 positions: extended (i.e. dosing position) and retracted, and the precursor can be loaded without breaking the vacuum. This CVD doser wassuccessfully used for Cu(hfac)$_2$ deposition without using a carrier gas (the Cu(hfac)$_2$ the vapour pressure of 60 mTorr is high enough for it to reach the sample). A variable leak valve controls both the flow rate and the pressure in the UHV chamber. Previous infrared (IR) measurements have shown no contamination of the sample when the doser was in its retracted position [12].

Prior to deposition the precursor purchased from Sigma-Aldrich as a green hydrated compound was dehydrated over concentrated $H_2SO_4$ in a vacuum dessicator. The colour changed from grass-green to greenish-blue over a period of few days. Then the dehydrated compound was loaded into the doser and kept there 24 hours prior to deposition.

The apparent exposures for Cu(hfac)$_2$ deposition are given in langmuir (L) (1L = $1\times10^{-6}$ Torrs).

The Si sample faced the doser at a distance of ~5 cm (similar to the one used for the previous Cu(hfac)$_2$ deposition studied by UHV-STM) (11) and the dosing was performed at room temperature in 21 sec. (i.e. 0.02 L) increments, until the compound in the reservoir evaporated totally. The amount deposited each time was approximately the same since the increase in the pressure during deposition was the same for each of the 5 depositions. The deposition time for each subsequent exposure to Cu(hfac)$_2$ was 21 sec. each time, and the sample was not flashed in between depositions; thus the coverage after the second deposition corresponded to an exposure time of 42 sec. (i.e. 0.04 L), the third of 63 sec. (i.e. 0.06 L), the fourth of 84 sec. (i.e. 0.08 L), and the fifth of 105 sec. (i.e. 0.1 L) respectively.

## 3. Results and discussion

After flashing the sample, the XPS spectra (Fig. 1) showed no C1s peak which would appear at 284.15 eV suggesting a surface free of C as contaminant. XPS also confirmed the absence of $SiO_2$.

### XPS experiments (Part B)

Wide scans were taken, followed by narrow scans looking for an increase in the area under the Cu $2p_{3/2}$XPS binding energy signal with the deposition time. Then the same procedure was done for C 1s, F 1s and O 1s. The signal for C 1s was weak throughout the entire experiment (the C 1s XPS spectra are not presented here) due to its small cross-section but enough to give semi-quantitative information that was correlated to UPS data.

The signal for Cu $2p_{3/2}$ after the first deposition time was also weak so we started our investigation from the second deposition time (i.e. the 42 sec. deposition time or 0.04 L) and those data are presented here.

The overall deposition time was 105 sec. which corresponds to an exposure of 0.1 L.

The data for Cu, O and F as a function of exposure are shown in Figs. 4-7 respectively. The deconvoluted data for each exposure appear in Figs. 8-19.

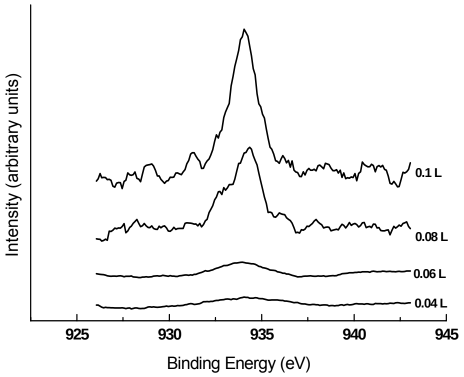

*Fig. 4. XPS spectra of copper deposited on Si(111)-7×7 from Cu(hfac)$_2$ at RT.*

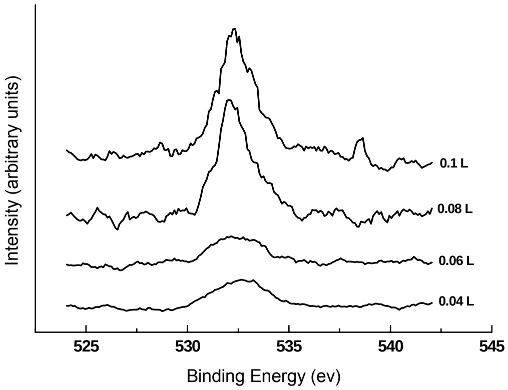

*Fig. 5. XPS spectra of oxygen deposited on Si(111)-7×7. from Cu(hfac)$_2$ at RT.*

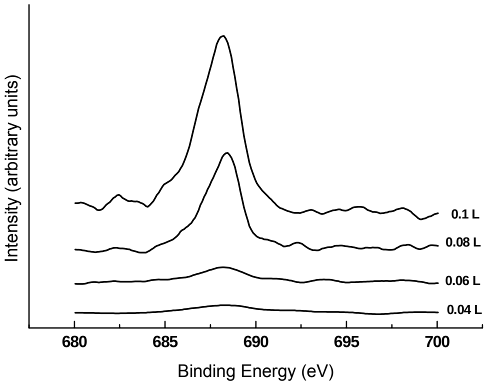

*Fig. 6. XPS spectra of fluorine deposited on Si(111)-7×7 from Cu(hfac)$_2$ at RT.*

The area under each XPS signal for Cu $2p_{3/2}$, O 1s, and F 1s, relative to Si $2p_{3/2}$XPS signal (i.e.the relative area) (A $Cu2p_{3/2}{}^{t\,(sec.)}$ / ASi $2p_{3/2}{}^{t\,(sec.)}$, A O 1s $^{t\,(sec.)}$ / A Si $2p_{3/2}{}^{t\,(sec.)}$, and A F $1s^{t\,(sec.)}$ / A Si $2p_{3/2}{}^{t\,(sec.)}$ respectively - where *t* is the deposition time in seconds)) was calculated in all cases around the same values for the binding energies of Cu $2p_{3/2}$, O 1s, and F 1s. The relative area for Cu $2p_{3/2}$, O 1s, and F 1s increases with time; this is shown in Table 1 and corroborates the UPS data. The non-linearity of the fluorine data will be discussed later.

*Table 1. Relative XPS areas for Cu, O, and F as a function of deposition time.*

| Deposition time/ Exposure time(s) /(L) | Relative area A $Cu2p_{3/2}{}^{t\,(sec.)}$ / ASi $2p_{3/2}{}^{t\,(sec.)}$ | Relative area A O $1s^{t\,(sec.)}$ / A Si $2p_{3/2}{}^{t\,(sec.)}$ | Relative area A F $1s^{t\,(sec.)}$ / A Si $2p_{3/2}{}^{t\,(sec.)}$ |
|---|---|---|---|
| 42 / 0.04 | 0.0737 | 0.1118 | 0.0575 |
| 63 / 0.06 | 0.1061 | 0.1218 | 0.0754 |
| 84 / 0.08 | 0.1563 | 0.1345 | 0.1742 |
| 105 / 0.01 | 0.2026 | 0.1477 | 0.4139 |

A "quantitative" view of the deposition process is given in Fig. 7. It shows a plot of corrected relative intensities (corrected for cross-section and spectrometer sensitivity effects) *vs.* apparent exposures (in Langmuir) for each of the Cu, O, and F (A Cu $2p_{3/2}{}^{t\,(sec.)}$ / A Si $2p_{3/2}{}^{t\,(sec.)}$, A $O1s^{t\,(sec.)}$ / A $Si2p_{3/2}{}^{t\,(sec.)}$, and A F $1s^{t\,(sec.)}$ / A

Si $2p_{3/2}{}^{t\,(sec.)}$ respectively - where *t* is the deposition time in seconds).

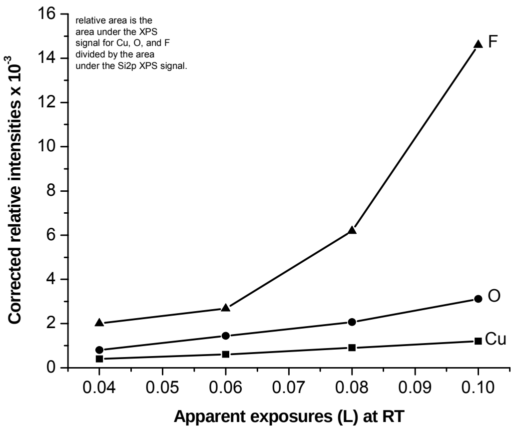

*Fig. 7. Corrected relative intensities for apparent exposures for the Cu(hfac)$_2$ deposition on Si(111)-7x7. Most dissociation of Cu(hfac)$_2$ and ligand fragmentation occurs at the beginning of deposition. At the end of the deposition, fluorine is quantitatively retained; i.e. the ratio F:Cu is close to that in the intact ligand. These observations support the proposed dissociative pathway with ligand fragmentation proposed for the Cu(hfac)$_2$ deposition on Si(111)-7×7 at room temperature.*

Fig. 4 and Fig. 7 show the exposure dependence of the XPS spectra of copper deposited on Si(111)-7×7 from Cu(hfac)$_2$ at room temperature. The intensities for the 0.04 L exposure and 0.06 L exposure reveal a clear increase in the amount of deposited copper. Increasing the exposure to 0.08 L and 0.1 L results in further increases in the amount of copper deposited. Copper deposition does not show a plateau, suggesting that the entire amount of Cu deposits on the Si(111)-7x7 surface. This is again consistent with the UPS data (Fig. 3); for an exposure of of 0.08 - 0.1 L a higher electron intensity is observed in the valence band.

Figs. 5 and 7 show the XPS spectra of oxygen deposited on Si(111)-7×7 from Cu(hfac)$_2$ at room temperature. The intensities for the 0.04 L exposure and 0.06 L exposure reveal a small increase in the amount of deposited oxygen. Increasing the exposure to 0.08 L, increases the oxygen intensity, and further increase to 0.1 L shows a small increase the deposited quantity. Fig. 5 shows a larger than expected O1s signal at 0.04 L exposure. There are two possible explanations: i) the exposure is larger than calculated (it is difficult to quantitatively estimate exposures for a high molecular weight species in a clean UHV system). However this should affect all elements studied equally for a given exposure; ii) impurity oxygen or water was present in the initial dose of precursor. Water might be present as water of hydration of the Cu(hfac)$_2$ because of the incomplete dehydration or by rehydration when the doser is loaded with precursor. The intensity data for the O1s signal shown in Fig. 7 have been corrected by an estimate for this impurity signal. At higher exposures, the data indicate that the XPS signal is dominated by O in Cu(hfac)$_2$, and the ratio of O:Cu is close to that expected in the precursor, consistent with the F:Cu ratio.

Figs. 6 and 7 show the XPS spectra of fluorine deposited on Si (111)-7×7 from Cu(hfac)$_2$ at room temperature. The intensities for the 0.04 L exposure and 0.06 L exposure reveal an increase in the amount of deposited fluorine. Increasing the exposure to 0.08 L and 0.1 L results in further increases in the amount of deposited fluorine.

## 4. Conclusions

One conclusion is immediate: at the end of the deposition, fluorine is quantitatively deposited; i.e. the ratio F:Cu is close to that in the intact ligand.

The above observation regarding F 1s is also consistent with previous work of Cheng *et al.* [7]. At T < 233 K their O 1s XPS data indicate that the ligand remains intact; F 1s XPS data for the same temperature indicates only slight changes in the binding energy. Above 288 K, the temperature at which we performed our experiments, ligand fragmentation occurs, C-F bonds in $CF_3$ groups are being broken and the $CF_x$groups are generated, and hence F bonds to Si. Cohen *et al.* (13) reported ligand fragmentation via X-ray decomposition of the ligand. Ligand fragmentation was also reported by Donnely *et al.* (14) and Parmeter [15].

The fact that F "sticks" more than oxygen on Si is thermodynamically consistent: the standard bond formation energy $\Delta H^0_f$ for the Si-F bond is -135 kcal/mol (or -564.84 kJ/mol) while that of Si-O is -108 kcal/mol (or - 451.87 kJ/mol) [16, 17, 18, 19].

The intensities for the 0.04 L exposure and 0.06 L exposure reveal a clear increase in the amount of deposited copper. Increasing the exposure to 0.08 L and 0.1 L results in further increases in the amount of copper deposited. Copper deposition does not show a plateau, suggesting that the entire amount of Cu deposits on the Si(111)-7×7 surface. This is again consistent with the UPS data (Fig. 3); for an exposure of of 0.08 - 0.1 L a higher electron intensity is observed in the valence band.

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