

Trial to implement transmission infrared (IR) spectrometry for studying initial stages of copper deposition from bis(hexafluoroacetylacetonato) copper(II) ($\text{Cu}(\text{hfac})_2$) on $\text{Si}(111)\text{-}7\times 7$

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IR experiments were performed in order to get spectra in the monolayer regime after CVD of $\text{Cu}(\text{hfac})_2$ on clean $\text{Si}(111)\text{-}7\times 7$. They originated from the need to understand the chemistry of Cu cluster termination via saturation with ligands the mechanism which we proposed after performing the UPS /XPS experiments (6) (7). The acquired spectra in the monolayer regime showed only noise. When a freshly prepared Si-H terminated surface (also 1 ML) was analyzed, the Si-H stretch which appears at 2084 cm^{-1} was not observed, and this confirmed that the experiment cannot be performed in transmission mode. These experiments were unsuccessful because of the limited sensitivity on this experimental geometry. Multiple internal reflection infrared spectrometry (MIR) should be used instead in order to get information regarding the orientation of the hfac ligand in the monolayer regime.

(Received December 8, 2011; accepted February 20, 2012)

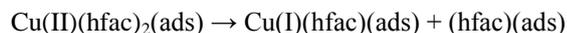
Keywords: IR spectroscopy, Cu deposition

1. Introduction

There are no published reports regarding transmission UHV-IR of initial stages of $\text{Cu}(\text{hfac})_2$ deposited at very low coverage on $\text{Si}(111)\text{-}7\times 7$ at room temperature.

The work of Girolami *et al.* (1) Cohen *et al.*(2), and Parmeter (3) focussed on $\text{Cu}(\text{hfac})_2$ adsorption on Cu, Ag, and Pt(111) at various temperatures. Lin *et al.* (4) studied the $\text{Pd}(\text{hfac})_2$ adsorption on a Cu surface at various temperatures. Most of the above experiments were performed at high coverages (Girolami *et al.* (1), Cohen *et al.* (2), and Lin *et al.* (4) while Parmeter (3) also investigated the behavior at low coverages.

Donnelly (5) showed that when deposited, the $\text{Cu}(\text{II})(\text{hfac})_2$ complex splits via adsorption into:



Parmeter (3) showed that at high coverages of $\text{Cu}(\text{hfac})_2$ on Pt(111), after the molecule splits, the hfac adopts a “standing-up” geometry with the OCCCCO skeleton perpendicular to the surface. Girolami *et al.* (1) and Lin *et al.*(4) made a similar observation.

At lower coverages of $\text{Cu}(\text{hfac})_2$, Parmeter reported that the hfac adopts a “lying-down” geometry with the OCCCCO skeleton parallel to the surface. He also reported that the hfac species begin to decompose below 300 K similar to what we observed by UPS/XPS (6) (7).

The idea of performing UHV-IR experiments in transmission mode originated from the need to understand

the chemistry of cluster termination via saturation with ligands that we proposed after performing the UPS/XPS experiments (6) (7). It was an attempt to determine the exact geometry of the hfac ligands or hfac fragments deposited via CVD on the reconstructed and atomically clean $\text{Si}(111)$ surface. Because all the above experiments were performed at low coverage (6) (7), the UHV-IR experiments had to be performed at low coverage as well (monolayer or sub-monolayer regime).

2. Experimental details

Experiments were carried out in a differentially pumped UHV chamber (home built) at a base pressure of 3×10^{-10} Torr. A new sample receiver was designed to accommodate the UHV-IR experiment in transmission mode.

The spectrometer used was the FTS 7000 series (DIGILAB-Randolph, MA 02368 -U.S.A.) with a He-Ne laser operating in the visible region at 632.8 nm.

The detector used was a broad-band MCT (Cryogenic Mercury Cadmium Telluride) detector (Graseby Infrared - Model MI-0465-0008-00) for mid-IR.

UHV-IR data was acquired using the Win-IR Pro software (DIGILAB-Randolph, MA 02368 - U.S.A.).

The p-Si (111) samples (Boron as dopant - Virginia Semiconductor Inc.) were processed in a similar manner as those used for the STM, HIBS, and UPS/XPS

experiments. This procedure is described in our previous articles (6) (7).

For the previous experiments, we thoroughly checked each time by LEED the extent of the 7×7 reconstruction, always observing sharp spots indicative of a 7×7 reconstructed surface. The UPS spectrum of the Si(111)- 7×7 surface (6) (7) proved that we were able to reproduce this recipe in other chambers operating at a similar base pressure.

The Si (111) samples had the same dimensions and were mounted on an identical pod used for the STM, UPS, and XPS experiments (6) (7).

The doser used to deliver the liquid hfacH on the Si(111)- 7×7 substrate is a glass tube attached to the UHV system.

The doser used to deliver the $\text{Cu}(\text{hfac})_2$ is identical to that used for CVD in the UHV chambers where the STM, UPS, and XPS experiments were performed and it is described in the article of Serghini-Monim *et al.* (8).

The hfacH (1,1,1,5,5,5-Hexafluoro-2,4-pentane-dione) was purchased from Alfa Aesar and kept under dry N_2 for a few hours until it was attached to the UHV-IR chamber for dosing. The same procedure was applied to the isopropanol and to the $\text{Cu}(\text{hfac})_2$.

Prior to deposition the precursor purchased from Sigma-Aldrich as a green hydrated compound was dehydrated over concentrated H_2SO_4 in a vacuum desiccator. 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 (6) (7).

Polystyrene film (Mattson Instruments, Inc., Madison, WI, USA) was used for checking the so called "minimum position". This position corresponds to the output voltage detector signal given by the laser beam that is passing through the sample.

Data were acquired in the rapid scan mode in which the interferograms (1000 in our experiments) are co-added for a period of time and a single spectrum is produced.

Prior to each deposition, IR spectra at atmospheric pressure for hfacH, and $\text{Cu}(\text{hfac})_2$ were performed on a Vector 33 FT-IR spectrometer (Bruker, MA 01821, USA).

For isopropanol we referred to the IR spectrum from the NIST Standard Reference Data Program (9).

The first problem to be solved was that of laser alignment to ensure that the beam passes through the sample. The manipulator was moved between three positions: two maxima and one minimum located in between the two maxima. Each maximum corresponds to the output voltage signal of the detector when the laser beam does not hit the sample. The minimum position was defined above.

The temperature during cooling using liquid N_2 was read with an alumel-chromel thermocouple that was attached not to the sample but to the manipulator shaft. This was so because we could not attach a thermocouple to the sample. It would have obstructed the laser beam that would have passed through the Si sample. The thermocouple was mandatory in order to monitor the substrate temperature when depositing the isopropanol and

$\text{Cu}(\text{hfac})_2$ in the multilayer regime. Even though we did not measure the sample temperature the fact that we deposited multilayers of isopropanol and $\text{Cu}(\text{hfac})_2$ was a clear evidence that the sample temperature was less than -80°C . The temperature read at the manipulator shaft when obtaining multilayers of isopropanol was -164°C . The Si H-terminated surface was prepared by immersing the Si wafer (Si(111) - Boron doped (identical to those used in previous experiments)) in a solution of 40% NH_4F and holding it there for 6 minutes (10) Then the Si wafer was thoroughly rinsed with deionized water. A new Si (111) - Boron doped wafer (identical to those used in previous experiments) was used to acquire the background scan prior to inserting the H-terminated Si wafer into the FT-IR spectrometer. These spectra were acquired using the internal detector.

3. Results and discussion

After flashing the Si sample, a background scan was acquired at room temperature on the clean (as-flashed) Si (111)- 7×7 sample. Then the hfacH was dosed on the Si sample at room temperature. By keeping the same resolution, sensitivity and speed we moved the manipulator up and down and two maxima (detector voltage reading) were identified corresponding to 0 absorbance or 100% transmittance; therefore those positions were both off-sample. In between them a minimum was recorded (detector voltage reading) corresponding to the laser beam that passed through the sample.

The acquired room temperature UHV-IR hfacH spectrum in the rapid scan mode showed no IR fingerprint when compared to that of the hfacH obtained at atmospheric pressure using the Vector 33 FT-IR spectrometer (Bruker).

Three possible reasons for not seeing the IR spectrum of the deposited hfacH were considered:

1. After flashing the sample and acquiring the background spectrum we had to orient the sample in the front of the doser, deposit the hfacH then rotate the sample back so that it faced the laser beam in the same position (judged as the minimum - detector voltage reading) as that used for acquiring the background spectra on the bare (as- flashed) Si sample. As a result of this procedure the position at which we obtained the background scan (on bare Si) might have changed.
2. After the exposure hfacH might not have been deposited on the sample, or might have desorbed.
3. The small IR signal might be due to a small deposited quantity of hfacH.

To rule out possibility no. 1 we decided to first deposit the hfacH (after the sample was flashed and cooled down to room temperature) and record the spectrum the UHV-IR spectrum as the background scan. Then without moving the sample, the as-deposited sample was flashed and the UHV-IR spectrum was recorded at the same position where the background spectrum was taken. The

result was again no IR signal. At this point we suspected that the minimum that we claimed as the output voltage corresponding to the laser beam passing through the sample is not a real minimum. In order to rule this out a foil of polystyrene film (with the same dimensions as the Si sample) was inserted onto the same pod used for the hfacH UHV-IR measurement. The IR spectrum of the polystyrene (Fig. 1) proved that our minimum was defined correctly.

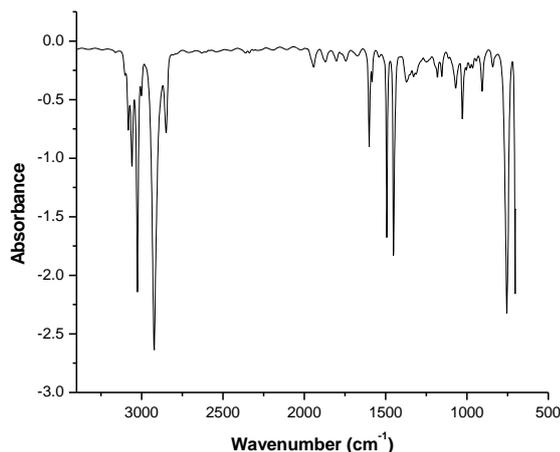


Fig. 1. The UHV-IR spectrum of the polystyrene used for checking our sample position. The standard peak at 1601 cm^{-1} is clearly visible.

In order to ensure that the hfacH indeed adsorbs on Si(111)- 7×7 sample we performed a simple mass spectrometry experiment (MS); the as-deposited sample was located close to the MS entrance slit. The CF_3^+ fragment with $m/Z = 69$ was identified and its peak increased upon resistive DC heating, suggesting that we got material onto the sample surface. At this point we suspected that too little material was deposited at room temperature. The next step involved the cooling of the Si(111)- 7×7 substrate to as low a temperature as possible by monitoring the decrease in the temperature at the manipulator shaft. The compound to be dosed was isopropanol.

Before depositing the isopropanol, the sample was flashed and the manipulator shaft cooled to liquid N_2 temperature. Then the isopropanol was condensed on the cold Si(111)- 7×7 surface forming one monolayer (ML) via chemisorption then a multilayer via physisorption. The UHV-IR spectrum of the isopropanol during deposition at $-164\text{ }^\circ\text{C}$ (multilayer coverage) is shown in Fig. 2a. Again the temperature refers to the reading at the manipulator shaft.

The acquired isopropanol spectrum matched perfectly with the isopropanol spectrum from NIST Standard Reference Data Program / NIST Chemistry WebBook (9) (Fig. 2b).

Now having checked both the sample position and the way of depositing the compound to be studied, we switched to $\text{Cu}(\text{hfac})_2$.

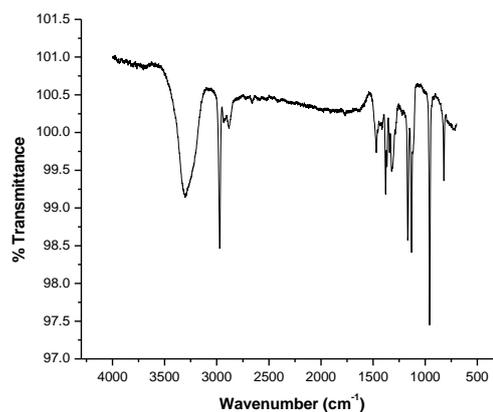


Fig. 2a. The UHV-IR spectrum of the isopropanol during deposition at $-164\text{ }^\circ\text{C}$ (multilayer coverage). The temperature was read with an alumel-chromel thermocouple that was attached to the manipulator shaft.

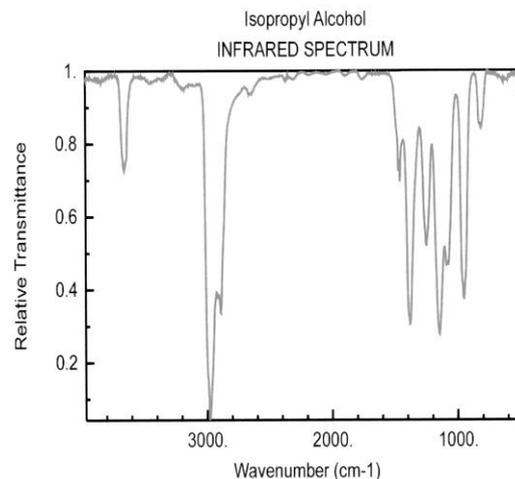


Fig. 2b. The IR spectrum of isopropanol (from NIST Chemistry WebBook) (9).

The goal of our IR experiments was to obtain the spectra from $\text{Cu}(\text{hfac})_2$ in the monolayer and possible sub-monolayer regime. Because the spectrum of $\text{Cu}(\text{hfac})_2$ at room temperature was nothing but noise we adopted the following strategy:

1. We deposited the $\text{Cu}(\text{hfac})_2$ on a liquid N_2 cooled and atomically clean Si (111)- 7×7 substrate, forming 1 ML via chemisorption then a multilayer via physisorption.
2. Then the background multilayer spectrum was recorded at $-161\text{ }^\circ\text{C}$ (temperature at manipulator shaft).
3. Immediately after acquiring this spectrum we stopped cooling the sample.
4. As the sample warmed up we took spectra corresponding to the $\text{Cu}(\text{hfac})_2$ deposited in the multilayer regime (Fig. 3 and Table 1).
5. When the sample reached room temperature (corresponding to a complete desorption of the

- multilayer - the sample was cooled down again and the background "monolayer" spectrum was recorded.
6. Then we resistively heated the sample by first passing a DC current of 0.3 A then increasing to 2 A in order to desorb the monolayer.
 7. Subsequently the sample was cooled again to liquid N₂ temperature and the recorded UHV-IR spectra contained nothing but noise (Fig. 4).
 8. The spectrum of hfacH was also obtained in the multilayer regime.

The spectrum of multilayer for a 2 L dose is similar to that of polycrystalline Cu(hfac)₂. Showing a multilayer of randomly oriented precursor. Peak assignments are summarized in Table 1. Two possible reasons for the differences in our reported values for 1460, 1260, and 1150 cm⁻¹ when compared to corresponding data from literature (1): our IR measurement was done in transmission mode and the multilayer was grown in our experiment via a single exposure using a different exposure.

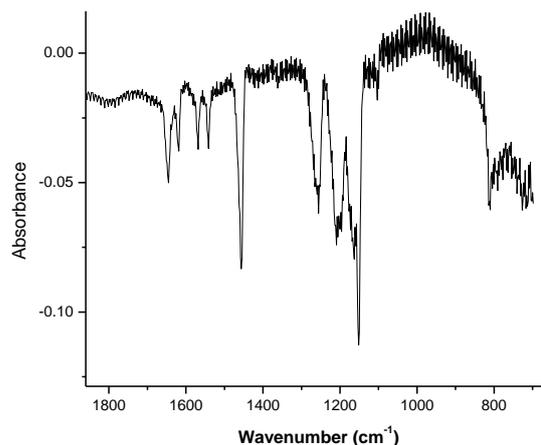


Fig. 3. The UHV-IR spectra of 2 L Cu(hfac)₂ deposited in the multilayer regime during sample warming. A comparative view of peak assignments is given in Table 1.

Table 1. Comparative vibrational frequencies ^{a, b} and mode assignments for 2 L of Cu(hfac)₂ deposited in multilayer regime on Si(111)-7×7 during sample warming up. ^a refers to the measurement performed on a Vector 33 FT-IR Spectrometer (Bruker, MA 01821, USA). ^b refers to the data from Girolami et al.(1).

Cu(hfac) ₂ Multilayer ν (cm ⁻¹)	Cu(hfac) ₂ Cryst alline ν (cm ⁻¹) ^a	Values reported in literature ν (cm ⁻¹) ^b	Assignment
1648	1638.34	1648	C=C stretch
1620	1613.48	1619	C=O stretch
1567	1564.49	1567	C=O stretch + CH bend
1540	1537.21	1540	CH bend
1460	1466.82	1482	C=C stretch + CCF ₃ stretch
1260	1259.85	1275	CF ₃ stretch
1150	1152.53	1176	CH bend

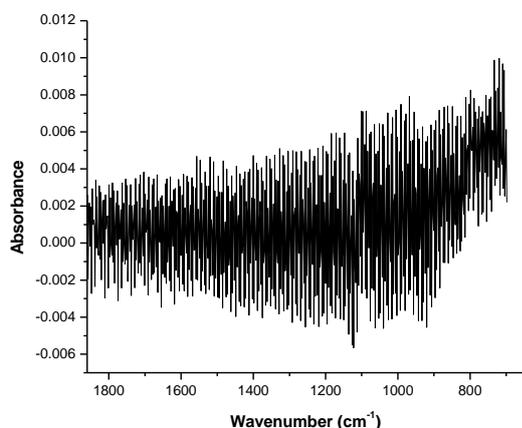


Fig. 4. After the sample reached the room temperature corresponding to a complete desorption of the multilayer it was cooled down then DC resistively heated in order to desorb the monolayer. Subsequently the sample was cooled down again to liquid N_2 temperature and the recorded UHV-IR spectrum is nothing but noise.

The fact that we cannot obtain information at the monolayer and sub-monolayer regime prevents any discussion of the orientation of the hfac ligand on the surface.

An additional experiment was performed in air using the internal detector of the IR spectrometer on a Si (111) wafer recorded as a background scan followed by a sample scan on the H-terminated Si (111) surface. The experiment was repeated taking a background scan on the H-terminated Si (111) surface followed by a sample scan on a Si (111) wafer. In both cases the Si-H stretch (11) at 2084 cm^{-1} was not observed and identical noise spectra were obtained showing that the experiment cannot be performed in transmission mode. Multiple internal reflection infrared spectroscopy (MIR) should be used instead.

4. Conclusion

Transmission mode IR spectrometry was employed in order to get information in the monolayer regime after CVD of $\text{Cu}(\text{hfac})_2$ on clean $\text{Si}(111)\text{-}7\times 7$. The acquired spectra in the monolayer regime showed only noise. Then a freshly prepared Si-H terminated surface (also 1 ML) was analyzed. The Si-H stretch (11) which appears at 2084 cm^{-1} was not observed, and this confirmed that the experiment cannot be performed in transmission mode. These experiments were unsuccessful because of the limited sensitivity on this experimental geometry.

Future work will try using multiple internal reflection infrared spectroscopy (MIR) to get information regarding the orientation of the hfac ligand in the monolayer regime. An answer to whether or not the cluster growth terminates by being covered with ligands or fragments of ligands will be the milestone of future work.

Acknowledgements

We are grateful to Professor Keith Griffiths (The University of Western Ontario, London, Canada) for setting-up the experimental geometry and to Dr. Milan Kovar for valuable discussions regarding the experiment.

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