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Cu clusters onto Si(111)-7×7 after sample annealing at 1170°-1190°C

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Cu CVD from Cu(hfac)$_2$ onto Si(111)-7x7 has been studied with STM, XPS, UPS, and HIBS. Here we confirm that features described by STM as clusters on the Si(111)-7x7surface after flashing it at a temperature range 1170°-1190°C were indeed made of Cu as seen by XPS via the “loss-structure”.

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1. Introduction

The Cu/Si(111)-7×7 system has been studied mostly by using physical vapour deposition [1-3]. Our study is motivated by important applications and by the advantages of chemical vapor deposition (CVD) of copper from Cu(hfac)$_2$ onto Si(111)-7×7. UPS, XPS, STM and HIBS were used for sample characterization after Cu deposition. After flashing the as-deposited sample at temperature range 1170°-1190°C Cu was still present on the surface as CuO as revealed by the “loss-structure” in the XPS spectrum.

2. Experimental details

Experiment set-up

Experiments were performed in two separate home built UHV chambers. The UHV-STM and the LEED are housed in one UHV chamber; the XPS and UPS are located in another UHV chamber both operating at the same base pressure. For this experiment we used four samples as follows: three of them for the STM experiment (sample#1-the 5sec., sample #2-the 45 sec. and sample#3-the 105 sec. deposition sample) and one (sample#4) for the UPS / XPS experiment. Of the three samples only one has been flashed namely the 105 sec. sample (sample#3). On the XPS / UPS chamber we did successive Cu(hfac)$_2$ depositions on the same Si(111)-7x7 sample (sample#4) namely: 0.02L, 0.04L, 0.06 L, 0.08L and 0.1L [6,7]. Sample#4 on which we deposited Cu(hfac)$_2$ in the UHV-XPS / UPS chamber for 105 sec. has a coverage of 0.1L.

Samples were all from the same stock (p-Si / Boron as dopant), had the same dimensions and were mounted on identical pods in the two UHV chambers. We used for both chambers the same CVD doser. [4]. In its retracted postion experiments have shown no sample contamination.

STM experiments were carried out in an ion-pumped UHV chamber at a base pressure of 3×10^{-11} Torr. The three samples of p-Si (Boron as dopant-Virginia Semiconductor Inc.), double side polished, (5×21 mm^2), thickness 300 μm ± 25 μm, orientation <111> ± 0,5°, 0,7- 1,2 Ohm-cm resistivity were cleaned as described in a previous article [5].

The sample was mounted on a pod by using two Ta shims (5×5×0,5 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. The Pulsar II IR pyrometer model 7000 (E^{2}Technology Corp., 4475 DuPont CT, Ventura CA 93003) was used for temperature readings of the Si sample during annealing and flashing. It is a single unit, compact, electro-optical non-contact thermometer with sight through aiming. Outgassing via resistive heating lasted for 12 hours at 700°C until the pressure was in the low 10^{-10} Torr range. Oxide and carbide removal was done by repeatedly flashing the sample in the 1147°-1177°C range for a total time of ~ 2 min. During flashing the pressure never increased above 1×10^{-9} Torr. The cooling process was rapid from the highest flashing temperature to 850°C (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. The fact that during the heating process the colour of the Si sample showed an increasing intensity from sides to the middle suggested a correct way of mounting and hence of heating it. The pressure recovered from < 1×10^{-9} Torr to < 10^{-10} Torr within 25 seconds of cooling. Surface reconstruction was checked using Reverse View LEED-RVL 900 (Fisions Instruments) with a beam voltage of 84V. Sharp spots revealed an excellent 7×7 pattern - Fig. 1[5].

The fourth sample (sample #4) of the same stock was cleaned, flashed and reconstructed 7×7 in the UHV-XPS/UPS chamber as described previously [5-7]. An XPS spectrum performed on sample#4 showed a surface free of C and O as contaminants - Fig. 3 [6]. Surface reconstruction was further revealed on sample #4 by UPS - Fig. 3 [6].

XPS and UPS

Sample #4 was from the same stock (p-Si / Boron as dopant – Virginia Semiconductor Inc.) double side polished, (5×21 mm^2), thickness 300 µm ± 25 µm, orientation <111> ± 0,5°, 0,7- 1,2 Ohm-cm resistivity) as that used in the UHV-STM / LEED chamber in the UHV-XPS / UPS chamber. That UHV chamber 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 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_α - 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 room temperature (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 (sample#4) 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 [6].

STM

UHV-STM experiments were performed in the home-built UHV chamber with base pressure of 5x10^{-11} Torr. After reconstruction and STM imaging, each sample was transferred to the preparation chamber and Cu(hfac)$_2$ was dosed from the home made CVD doser. The doser provides delivery of the intact precursor to the substrate without breaking vacuum at room temperature [4].

The green compound of copper(II)hexafluoroacetyacetonate hydrate (Aldrich Chemicals) was dried over concentrated H_2SO_4 in a vacuum desiccator and kept in the doser in vacuum conditions for 24 hours prior to deposition. The three samples were exposed to the vapor of Cu(hfac)$_2$ at a temperature of 28°C for 5s (sample#1), 45s (sample#2), and 105s (sample#3). After the deposition, each sample was transferred back to the STM stage for imaging. The precursor from the 105 sec. sample the was then removed from by heating at 850°C for 2 hours followed by repeated flashing for 30 seconds with total time of 6 minutes at temperatures ranging from 1170°C to 1190°C. The surface was studied again with UHV-STM to determine the size and location of clusters formed due to decomposition of the precursor (results of this experiment will be subject to a future article). Samples were transferred into the XPS / UPS chamber to confirm that the clusters on Si(111)-7x7 observed with STM after heating at 1170°-1190°C contain Cu atoms. HIBS was used to determine the total Cu content [8]. These samples were transferred between STM, XPS, and HIBS chambers through the atmosphere; this assumes that the amount of Cu deposited onto the surface remained unchanged.

HIBS

Heavy Ion Backscattering Spectrometry (HIBS) with C^{3+} ions was used in order to obtain the total Cu coverage (Cu atoms/cm^2) on each sample. This method was chosen because we suspected that we are depositing Cu(hfac)$_2$ in small amounts (i.e. microanalysis regime) and the signal will be hardly distinguishable from background using standard Rutherford Backscattering (RBS) methods which utilize the backscattering of light ions such as $^4He^+$.

The samples were removed from UHV, transported through air, and loaded onto an RBS precision goniometer (Model 941 - High Voltage Engineering Europa). The fact that the samples were transported through air clearly produced the oxidation of the Cu but the amount of Cu deposited onto the surface should remain unchanged. Since HIBS is not a surface sensitive technique and insensitive to the oxidation state, any oxidized Cu atoms can still be detected.

The terminal voltage of the accelerator was 1.48 MV and the injected energy was 80 keV; the resulting energy of the C^{3+} ions was 6 MeV. The beam current on the target was 300 nA within a beam spot of ~1mm^2. Ions backscattered to 170° from the incident direction were detected by a TU-012-050-100 ORTEC detector (active area: 50 mm^2, minimum depletion depth: 100µm, FWHM: 12 KeV for 5.486 MeV α particles). The target angle was 7°[8].

3. Results and discussion

Sample processing

After flashing, the extent of the 7x7 reconstruction on the three samples (sample#1,2 and 3) (processed in the UHV chamber having the LEED and STM facility) were studied by low energy electron diffraction (LEED) using with a beam voltage of 84V. Sharp spots revealed an excellent 7x7 pattern (Fig. 1) on each sample.

On sample#4 XPS spectra following flashing showed no C1s peak that would appear at 284.15 eV suggesting a surface free of C as contaminant. XPS also confirmed the absence of SiO_2 (Fig. 2).

UPS spectra provide information on the valence electrons and hence on chemical bonds. These data provide a connection to STM, data that give information on the same electrons but with 3-D resolution (Fig. 3).

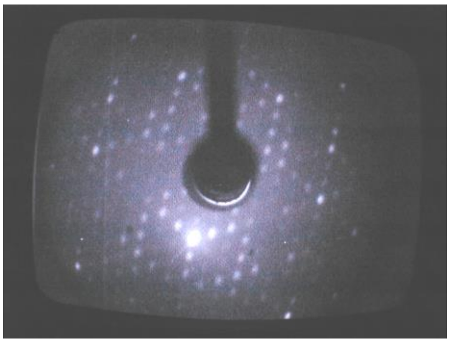


Fig. 1. The 7×7 pattern showing the correct reconstruction for the Si(111) surface.

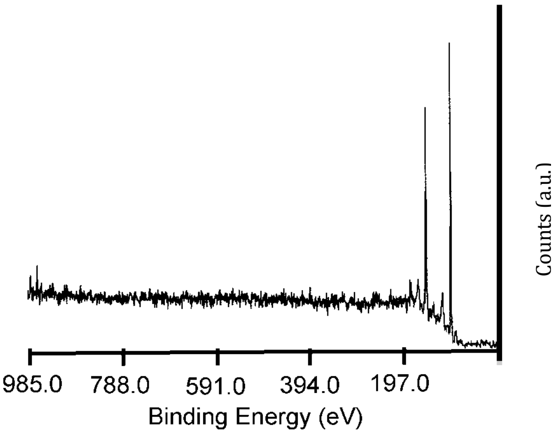


Fig. 2. XPS spectrum of clean Si(111)-7x7. It shows a surface free of C and O as contaminants. Peaks centered around 150.96 eV and 98.7 eV correspond to Si 2s and Si 2p respectively. UPS spectra proved that the clean surface was reconstructed 7x7.

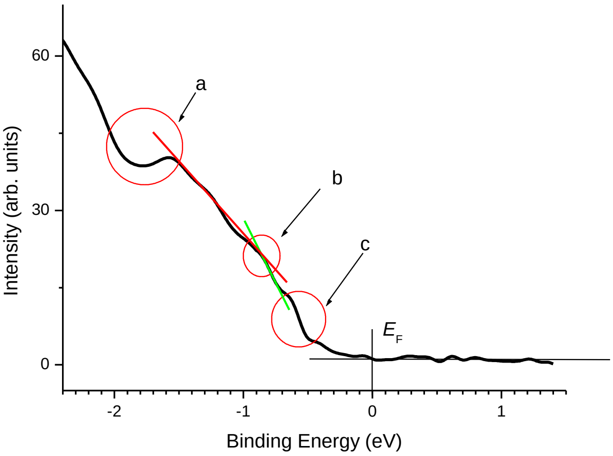


Fig. 3. The UPS spectrum for the bare Si(111) surface shows three surface states (14): the surface state (a) at 1.8 - 2 eV related to the backbonds between the Si adatoms and the three Si atoms directly beneath them; the surface state (b) at ~1 eV related to the filled dangling bond states situated on the rest atoms, and near the Fermi level E_F (0 eV), and 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 7x7 reconstruction. The intensity of the state at 0.4 - 0.6 eV is a good indication of the quality of the 7x7 surface reconstruction.

The wide scan UPS spectrum of clean Si - same sample (sample#4) on which we performed the XPS spectrum - shows the Si valence band (Fig. 4). For binding energies between 0 and -2 eV the UPS spectra of clean Si(111)-7x7 consist of electron emission from surface states already discussed in Fig. 4. For energies higher than 2 eV the emission comes from bulk states (peaks at -4 eV and -8 eV). The data are consistent with those reported in the literature by Martenson et al. [14] and Uhrberg et al. [15].

UPS and XPS

Wide scans UPS spectra were performed after depositing 0.02L, 0.04L, 0.06L, 0.08L and 0.1 L. 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 behavior was observed by Tadayyon [16] 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 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. [17] for the Cu-Si room temperature interface at submonolayercoverages (Fig. 4) [6].

XPS 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. Fig. 5 and Fig. 6 show the exposure dependence of the XPS spectra of copper deposited on Si(111)-7x7 from $Cu(hfac)_2$ at room temperature. Fig. 6 shows a "quantitative view of the deposition process. The relative intensities were corrected for cross-section and spectrometer sensitivity effects.

The signal for Cu $2p_{3/2}$ after the first deposition time was also weak - Fig. 5 - so we started our investigation from the second deposition time (0.04 L). The overall deposition time was 105 sec. that corresponds to an exposure of 0.1 L – here we present only this data. The same deposition time was used to obtain a similar Cu coverage (whether metallic free or bonded as Cu(I) as reported in our HIBS work [8].

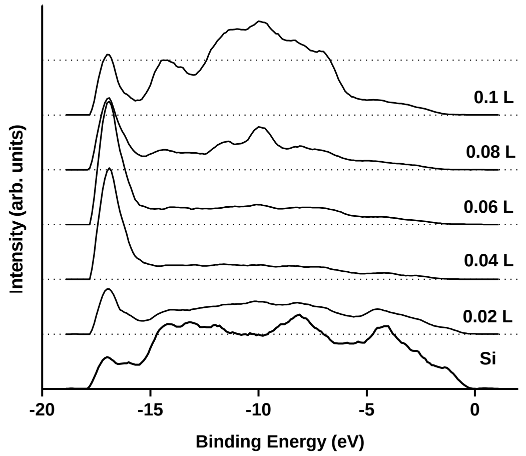


Fig. 4. Wide scan UPS spectra taken after each deposition show a difference in the valence features for Si (2.5 - 15 eV), suggesting that a transformation occurred from one deposition to another. UPS spectra following the first deposition at 0.02 L revealed that the Si peaks due to emission from bulk 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.

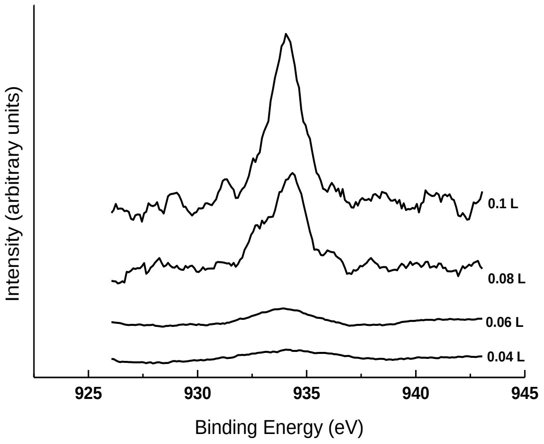


Fig. 5. XPS spectra of Cu deposited onto Si(111)-7x7 at room temperature.

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 [5][7]. The relative area for Cu $2p_{3/2}$, O 1s, and F 1s increases with time and corroborates the UPS data. The non-linearity of the fluorine data was discussed elsewhere [5][7].

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. The deconvoluted data appear in Fig. 7.

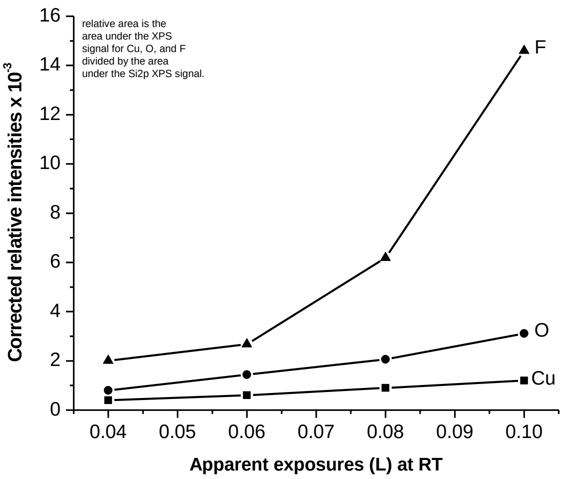


Fig. 6. Corrected relative intensities for apparent exposures for the Cu(hfac)$_2$ deposition on Si(111)-7x7. Most dissociation of Cu(hfac)$_2$ and ligand fragmentation occurs at the beginning of deposition. At the end of the deposition, fluorine is quantitatively retained; i.e. the ratio F:Cu is close 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)-7x7 at room temperature.

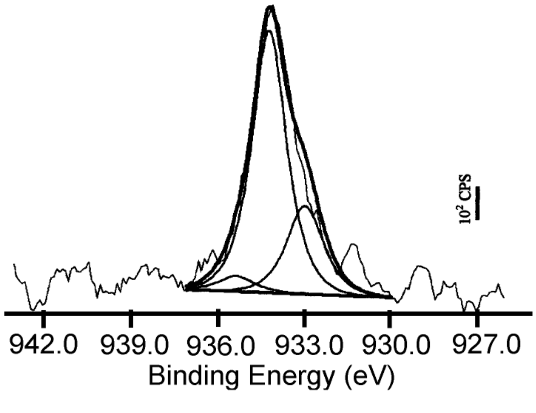


Fig. 7. Cu $2p_{3/2}$ XPS spectrum for a 0.1 L exposure of Cu(hfac)$_2$ on Si(111)- 7x7 at room temperature.

The XPS spectra for Cu $2p_{3/2}$ (Fig. 7), O 1s, and F 1s (presented elsewhere [5][7]) were deconvoluted using mixed Gaussian-Lorentzian functions with a linear background approach as provided by the XPS Peak Fitting Program Version 4.1.We present here the 0 0.1 L data for Cu $2p_{3/2}$. Data for 0,04 0,06 0.08L are presented elsewhere [5][7].

The Cu $2p_{3/2}$ XPS spectrum for the 0.1 L exposure (Fig. 7) shows after deconvolution three peaks:

- 932.9 eV associated with the Cu metal [18] [19] [20]; it shows an increase in the intensity compared to the corresponding peak for the 0.08 L exposure;
- 934.2 eV - the main peak which corresponds to Cu(I) adsorbed on Si as Cu(I)(hfac) [21][22][23] and which is triple the corresponding peak in the 0.08 L spectrum; and
- 935. 3 eV - the Cu(II) peak [21][24]; it shows almost no increase compared to the corresponding peak for the 0.08 L exposure (Table 1).

Table 1. Height of Cu(I) and Cu(II) peaks in counts/second as retrieved from the corresponding Cu $2p_{3/2}$ XPS spectra.

Exposure(L)	**Cu(I)** (CPS)	**Cu(II)** (CPS)
0.04	25.9	18.0
0.06	42.0	20.4
0.08	249.0	30.0
0.1	783.0	42.0

The question arises as to why the Si surface reduces Cu(II) to Cu(I). Semiconductors have an energy gap around the Fermi level. In the case of the 7x7 reconstructed surface, electronic states of Si are within this gap and this is why the Si(111)-7x7 surface exhibits a metallic character [15] [25] [26]. The metallic character is manifested in terms of a continuum of electron states near the Fermi level - energy levels that are close to each other. We believe that it is this metallic character that is the driving force for the reduction Cu(II) → Cu(I). The origin of "precursor splitting" into Cu and the hfac ligand, followed by (hfac) bonding to Si as smaller molecular fragments or to Cu clusters and Cu deposition onto the Si surface, might reside in the electron states on adatoms in Takayanagi's model. Our future STM work will present Cu clusters of specific size sitting in the faulted halves of the Si (111)-7x7 unit cell (Semenov et al.[27] similar to the size of clusters reported by Horton et al. [21].

HIBS

The HIBS signal was calibrated against P3 standard (Bi-implanted Si) (4.86×10^{15} atoms/cm^2). The Bi cross-section and Cu cross-sections, σ_{Bi} and σ_{Cu}, were calculated by using the RELKIN program [28] and found to be 8.9054 barn/str for Bi and 1.02407 barn/str for Cu. The yield for the Bi-implanted Si standard, 5 sec. sample, 45 sec. sample, and 105 sec. sample (Fig. 8) were calculated from HIBS spectra by using the SPAN program [29] (SPECTRUM ANalysis). The results are summarized in Table 2.

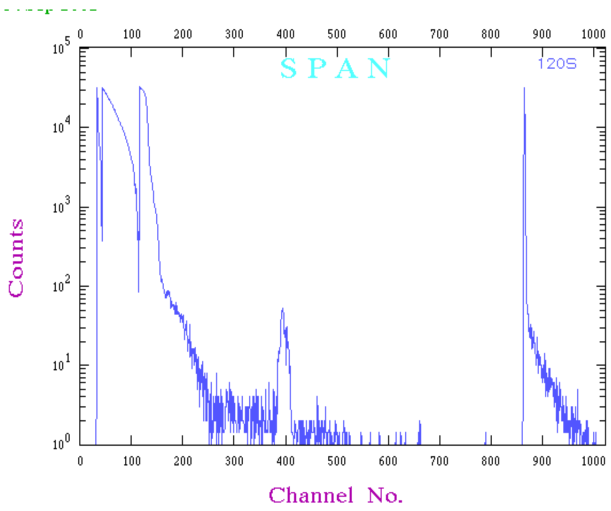


Fig. 8. The HIBS spectrum for 105 sec. sample.

The nonlinear behavior of the measured Cu coverage *vs.* deposition time is consistent with the behavior of the pressure in the UHV chamber when the doser was in the deposition position. The pressure in the chamber increased by a factor of 1000 from 10^{-11} Torr to 10^{-8} Torr (measured using the ion pump current) and lasted for 1 minute. Next the pressure in the chamber decreased by a factor of 10 in the second minute of the deposition. The image of a step on Si(111)-7x7 exhibiting Cu clusters after 105 sec. deposition time (Fig. 9) will be discussed in the next paragraph. The HIBS confirmed that the imaged clusters by STM where indeed made of Cu atoms, but the coverages are not linearly related to the apparent exposure.

Table 2. Results for the HIBS measurement with 6 MeV $^{12}C^{3+}$, detector angle 170°, and target angle 7°.

Ion charge (Q) (μC)	**Yield**	**Sample**	**Results (atoms/cm^2)**	**Error (%)**
5	5919.18	P3 (Bi)	4.82×10^{15}	
200	411.5	5 sec.	7.35×10^{13}	5.6
197.94	447	45 sec.	8.06×10^{13}	6.2
200	570	105 sec	1.02×10^{14}	4.4

STM before and after annealing

After dosing and STM imaging, the precursor (Fig. 9) was removed by annealing the Si substrate at 850°C and a short flash at 1170º-1190°C as described earlier. STM revealed magic clusters of 7.2±0.9Å and 13.8 ±2.3Å in diameter in specific locations on Si(111)-7x7 – Fig. 10[27].

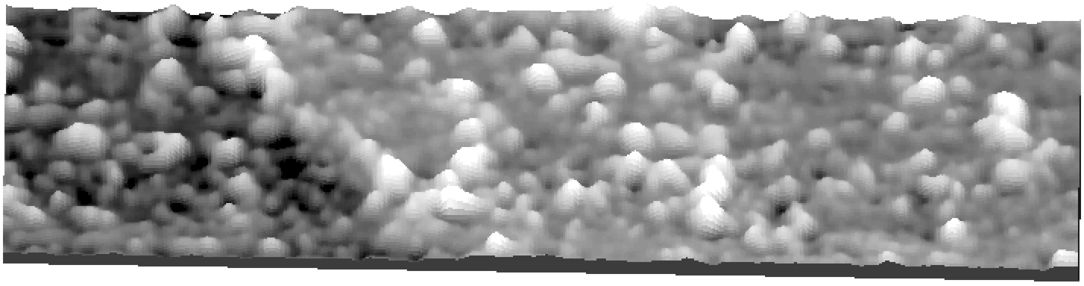


Fig. 9. STM image reveals homogeneous coverage of clusters on a mono-atomic step of Si(111) for exposure time of 105s. Size 210.0nm x 49.0nm. V $_{sample}$ =+3V, I = 200pA.

Fig. 10 shows the STM topography on Si annealed and flashed after deposition of $Cu(hfac)_2$ for 105s (exposure of ~0.1L). The STM image demonstrates a reconstructed Si(111)-7x7 surface covered with clusters, which are visible as bright spots.

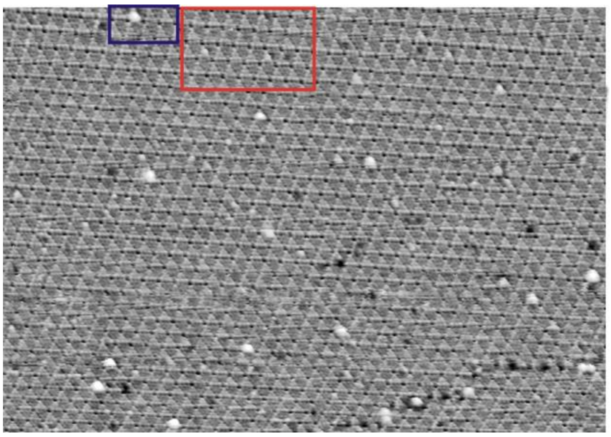
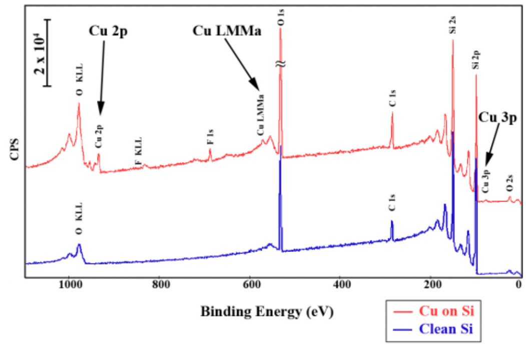


Fig. 10. STM topography 1010Å x 720Å, Usample = +3.3 V.

Samples were transferred through the atmosphere from the STM to the XPS chamber. We assume that the amount of Cu deposited onto the surface remained unchanged by this transfer through air. We believe this is a reasonable assumption as the copper is firmly bonded. We recognize that the Si surface undergoes some oxidation during transfer that could alter the chemistry and the exact location of the Cu.

The XPS survey scan after sample flashing is presented in Fig. 11.



Name	Pos.	FWHM	Area	%
Cu 2p3/2	935.00	3.92	1744.5	1.4
F 1s	688.60	2.96	557.4	1.6
O 1s	532.50	2.71	9113.1	32.5
C 1s	285.40	2.81	1782.4	17.8
Si 2p	99.20	2.50	5503.2	46.7

Name	Pos.	FWHM	Area	At%
O 1s	532.50	2.85	4784.7	25.9
C 1s	285.40	2.93	921.8	14.0
Si 2p	99.90	2.42	4659.9	60.1

Fig. 11. The XPS survey scan shows Cu on Si (111)-7x7 sample on which $Cu(hfac)_2$ was dosed for 105 sec. then the sample was annealed and subsequently flashed in 1170-1190 ºC range.

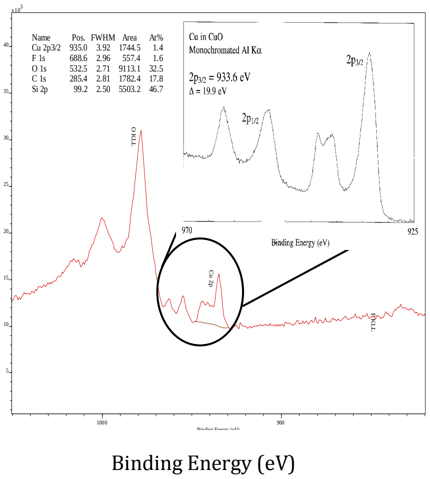


Fig. 12. Shows a zoomed area around the Cu $2p_{3/2}$ XPS signal for the flashed sample presented in Fig. 9. In this zoomed area the position of the "loss-structure" coincides with the position for the "loss-structure" reported in the Handbook of X-ray Photoelectron Spectroscopy for the XPS spectra for Cu in CuO) [30].

Fig. 12 shows a zoomed area around the Cu $2p_{3/2}$ XPS signal for the flashed sample presented in Fig. 10. In this zoomed area the position of the “loss-structure” coincides with the position for the “loss-structure” reported in the *Handbook of X-ray Photoelectron Spectroscopy* for the XPS spectra for Cu in CuO (Fig. 7) [30]. The “loss-structure” is observed when plasmon excitation is created due to the outgoing photo- or Auger electrons that modifies the equilibrium potential in a solid [31]. The same position for the “loss-structure” was reported by Ghijsen et al. [32][33].

Three reasons why the assigment was attributed to CuO:

1. The position of the main peak is very sensitive to the ligand as reported by Ghijsen et al. [33] and van der Laan et al. [34].
2. The satellite peak found at about 9 eV higher than the Cu 2p peak (binding energy units) suggests that the “loss-structure” cannot be attributed to Cu_2O.
3. At room temperature, Cu from Cu(hfac)$_2$ binds to the substrate mostly as Cu(I), a fact demonstrated by the absence of shake up features in the XPS spectra [5][7].

The fact that CuO was identified via the “loss-structure” confirms the presence of Cu on the surface, which is presumably oxidized during transportation in air. The Si(111)-7x7 sample flashed without deposition shows no Cu content.

4. Conclusion

The initial stages of nucleation of copper deposition via chemical vapor deposition (CVD) from bis(hexafluoroacetylacetonato)copper(II) (Cu(hfac)$_2$) on a clean Si (111)-7x7 surface were studied by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS) and heavy ion backscattering spectrometry (HIBS). After flashing the sample at 1170°-1190°C Cu was XPS identified as CuO via the “loss-structure”.

This study is motivated by important applications and by the advantages of chemical vapor deposition of copper on Si(111)-7x7: Cu clusters could be used in nano-electronics for metallization, for interconnection of active elements, and as active elements themselves. Self-assembly of Cu on Si(111)-7x7 template could provide higher stability of size and location of clusters compared to methods of lithography.

This work is dedicated to the memory of Dr. Eugen Segal from The University of Bucharest who we wish were here.

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