Total Cu coverage from $Cu(hfac)_2$ deposition on Si(111)-7×7 at room temperature using HIBS

C. IONESCU*, M. A. IONESCU, I. CIUCA
Faculty of Science and Materials Engineering, Politechnical University of Bucharest, Romania, UE

UPS, STM, XPS, and HIBS were performed to study initial stages of nucleation of Cu deposited from $Cu(hfac)_2$ via chemical vapor deposition (CVD) on clean Si(111)-7x7 surface. At room temperature Cu binds to the substrate mostly by Cu(I) as demonstrated by the absence of shake-up features in the XPS spectra. HIBS using $^{12}C^{3+}$ was performed in order to obtain the total Cu coverage (Cu atoms/cm^2). The coverages are not linearly related to the apparent exposures.

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

Keywords: Cu/Si(111), HIBS

1. Introduction

This study is motivated by important applications and advantages of Cu CVD on Si(111)-7×7: Cu clusters could be used in nano-electronics for metallization, for interconnections of active elements, and as active elements itself; self-assembly of Cu on Si(111)-7×7 template could provide higher stability of size and location of clusters compared to methods of lithography.

CVD of Cu on Si is compatible with modern Si technology. This compatibility could reduce the cost of practical devices. Ultraviolet Photoelectron Spectroscopy (UPS), Scanning Tunnelling Microscopy (STM), X-ray Photoelectron Spectroscopy (XPS), and Heavy Ion Backscattering Spectrometry (HIBS) were employed to study initial stages of nucleation of Cu deposited from $Cu(hfac)_2$ via chemical vapor deposition (CVD) on clean Si (111)-7×7 surface.

2. Experimental

The experiments were carried out in ultra high vacuum (UHV) chamber that contains a differentially pumped He-discharge lamp, XPS capabilities and other standard surface science tools. After flashing the Si(111) sample via resistive heating, low energy electron diffraction (LEED) using Reverse View LEED-RVL 900 (Fisions Instruments) with a beam voltage of 84V was performed. Sharp spots revealed an excellent 7×7 pattern.

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.

LEED and UPS have shown that the Si(111) surface was reconstructed 7×7. The data obtained are similar to those obtained by Tadayyon [1] for clean Si(111)-7×7 and consistent with those reported in literature by Martenson et al. [2].

STM experiments were performed in a UHV-STM system with base pressure of 5×10^{-11} Torr [3]. After STM imaging each sample was transferred to the preparation chamber and $Cu(hfac)_2$ was dosed. The doser [4] provides delivery of the intact precursor to the substrate at room temperature without breaking of vacuum. The green compound of $Cu(hfac)_2$ 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 samples were exposed to the $Cu(hfac)_2$ at 28°C for 0.02L (5s) (not reliable as discussed in HIBS section), 0.22L (45s), 0.25L (60s), and 0.3L (105s). These samples were transferred between STM, XPS, and HIBS chambers through the atmosphere presuming that the amount of Cu deposited onto the surface remained unchanged.

The XPS analysis was performed a UHV system operated at a base pressure of 2×10^{-10} Torr and room temperature. The X-ray source was an Al cathode using K_α (1486.6 eV) line, data were collected at 50 eV pass energy and 14 mA emission current. The XPS facility uses a Combined Lens and Analyser Module (CLAM 2) system (VG Microtech-Fisons Instruments, 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) [6].

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 ~1 mm^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: 100 μm, FWHM: 12 KeV for 5.486 MeV α particles). The target angle was 7°.

3. Results and discussion

LEED, UPS spectra, and STM images demonstrated reconstruction Si(111)-7×7 each time before deposition of the precursor $Cu(hfac)_2$ [5][6] [7]. No reconstruction was observed with STM after the deposition at room temperature at coverages in the range from 0.02L to 0.3L. The STM image for the sample with coverage of 0.3L is presented in Fig. 1. The image reveals steps on Si and clusters on the steps. The smallest clusters have diameter of 20Å and height of 5Å, largest cluster is of 100Å in diameter and 20Å in height. At this deposition time, clusters cover all surface area and are distributed homogeneously including the top and bottom of the Si steps [3].

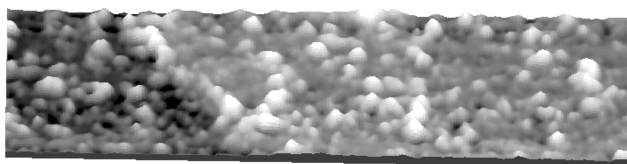

Fig. 1. The monoatomic step on Si(111)-7x7 is visible under the layer of precursor deposited. This image was taken on the sample with maximum deposition time in our experiments. The step visible demonstrates that the surface is covered with nearly one monolayer and all others our experiments are done in monolayer and sub-monolayer regime [3].

To determine the mechanism of $Cu(hfac)_2$ decomposition at room temperature, an independent XPS and UPS measurements were also performed in a separate chamber without breaking the vacuum.

In the UPS spectra the peak at -17eV is the secondary electron peak and its increase with exposures reflects changes in the secondary electron emission caused by the presence of Cu(I) and fluorinated moieties. The fact that the precursor adsorbs as Cu(I) is supported by the XPS data and the difficulty to obtain good STM images for exposures of 0.04-0.1L as reported by Horton et al. [8].

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 (RELativistic KINematics - Yale University) and found to be 8.9054 barn/str for Bi and 1.02407 barn/str for Cu. The yield for Bi-implanted Si standard (Fig. 2), 5 sec. sample (Fig. 3), 45 sec. sample (Fig. 4), and 105 sec. sample (Fig. 5) were calculated from HIBS spectra by using the SPAN program (SPECTRUM ANalysis).

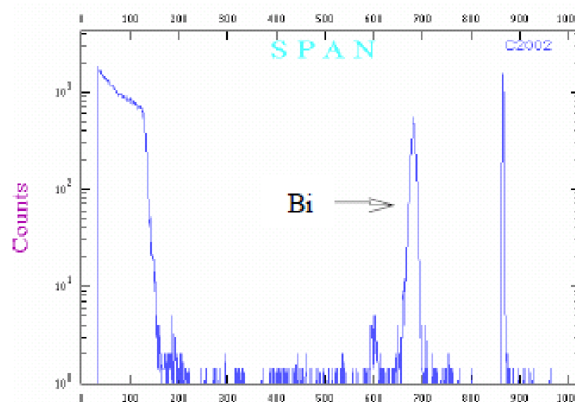

Fig. 2. The HIBS spectrum for the P3 standard (Bi-implanted Si standard).

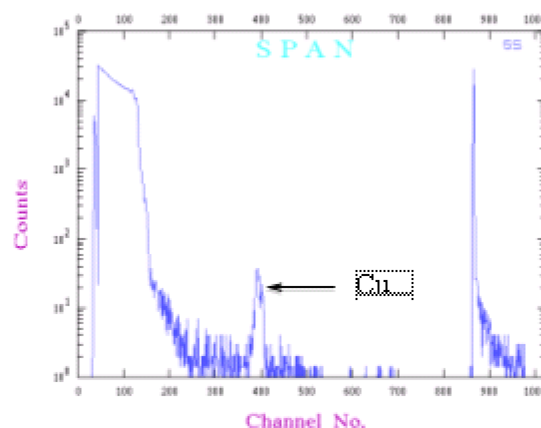

Fig. 3. The HIBS spectrum for the 5 sec. sample.

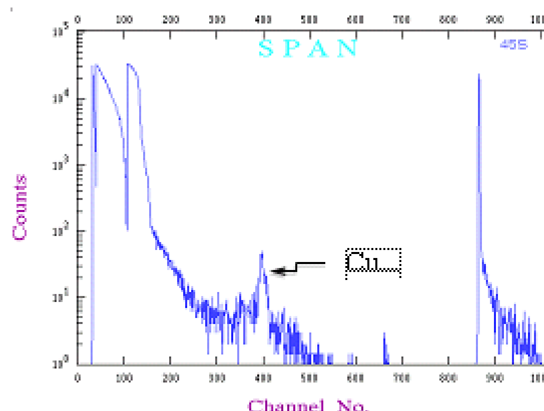

Fig. 4. The HIBS spectrum for the 45 sec. sample.

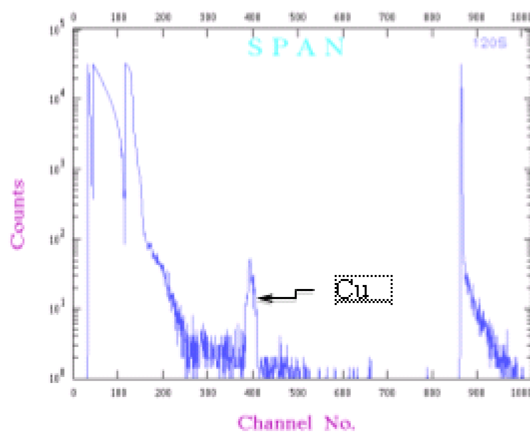

Fig. 5. The HIBS spectrum for the 105 sec. sample.

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. HIBS confirmed that the imaged clusters by STM were indeed made of Cu atoms, but the coverages are not linearly related to the apparent exposure. The results are summarized in Table 1:

Table 1. Results for the HIBS measurement with 6 MeV $^{12}C^{3}$, detector angle 170° and target angle 7°.

Ion Charge (Q) (μC)	Yield	Sample	Atoms/cm^2	Error(%)
5	5919,180697	P3(Bi)	$4{,}82\times10^{15}$	
200	411,5	5 sec.	$7{,}35\times10^{13}$	5,6
197,946	447	45sec.	$8{,}06\times10^{13}$	6,2
200	570	105 sec.	$1{,}02\times10^{14}$	4,4

4. Conclusion

HIBS 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 the background in RBS. HIBS is able to detect metallic levels significantly below those that can be detected by medium-energy ion backscattering or RBS both of which have a limit of ~ 1×10^{13} for near surface impurity. HIBS confirmed that the imaged clusters by STM were indeed made of Cu atoms, but the coverages are not linearly related to the apparent exposure.

References

[1] S. M. Tadayyon, Unpublished paper.
[2] P. Martenson, W.-X. Ni, G. V. Hansson, Phys. Rev. B **36,** 5974 (1987).
[3] A. Semenov, C. Ionescu, Unpublished paper.
[4] S. Serghini-Monim, L. L. Coatsworth, P. R. Norton, R. J. Puddephatt, Rev. Sci. Instrum., **67**(10), (1996).
[5] C. Ionescu, M. A. Ionescu, I. Ciuca, Optoelectron. Adv. Mater. - Rapid Commun. **5**(7), 722 (2011).
[6] C. Ionescu, M. A. Ionescu, I. Ciuca, Optoelectron. Adv. Mater. - Rapid Commun. **5**(8), 883 (2011).
[7] C. Ionescu, M. Ionescu, I. Ciuca, Optoelectron. Adv. Mater. - Rapid Commun. **5**(11), 1146 (2011).
[8] J. H. Horton, J. G. Shapter, T. Cheng, W. N. Lennard, P. R. Norton, Surf. Sci **375**, 171 (1997).

*Corresponding author: cionescuphd@gmail.com