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Ultraviolet photoelectron spectroscopy (UPS) studies of initial stages of copper deposition from bis(hexafluoroacetylacetonato)copper(II) (Cu(hfac)$_2$) on Si(111)-7x7 at room temperature. Part A

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Organometallic chemical vapour depostion (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 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. The UPS spectra after each deposition showed a difference in the valence features for the Si in the range -2.5 to -15 eV, suggesting that a transformation occurred from one deposition to another. The reduction in the peak intensity for Si(111)-7x7 bulk states (-4 eV and -8 eV) as the deposition proceeds (exposures of 0.04 and 0.06 L), is accompanied by a concomitant increase in the secondary electron peak (~ -17 eV) for the same exposures, suggesting that the sample is receiving an increased amount of Cu (I) and fluorinated moities. Data are similar to those obtained by Tadayyon [11] for organics. 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.

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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).

Here, we present a room temperature ultraviolet photoelectron spectroscopy (UPS) study of the Cu(hfac)$_2$ interaction with Si (111)-7x7. 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)-7x7 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)? In order to answer the above questions XPS studies along with RBS will be performed after the UPS experiment. We present here only the UPS experiment. The XPS experiment will be presented in a future article.

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 2×10^{-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.

A sample of p-Si (boron as dopant - Virginia Semiconductor Inc.) double side polished, (5x21 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 (5x5x0.5 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 $1x10^{-9}$ 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 (8) The pressure recovered from < $1x10^{-9}$ 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 (8), we are confident the samples would exhibit excellent 7x7 reconstruction. The UPS spectrum of the "as-prepared" sample was used as a proof for the 7x7 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 (9). 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 was successfully 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 (9).

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 = $1x10^{-6}$ 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) (8) 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

UPS spectra (Part A)

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.

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

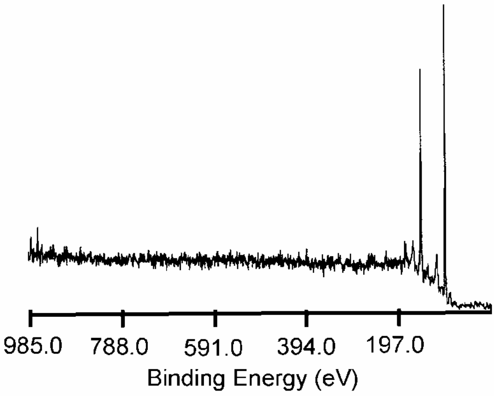

Fig. 1. XPS spectrum of clean Si(111)-7x7 on which the Cu(hfac)$_2$ deposition was performed. It shows a surface free of C and O as contaminants. Peaks centered around 150.96 eV and 98.7 eV correspond to Si 2s and Si 2p respectively. UPS spectra proved that the clean surface was reconstructed 7x7.

The UPS spectrum for the bare Si(111) surface shows three surface states (Fig. 2) similar to those reported by Martenson *et al.* (10).

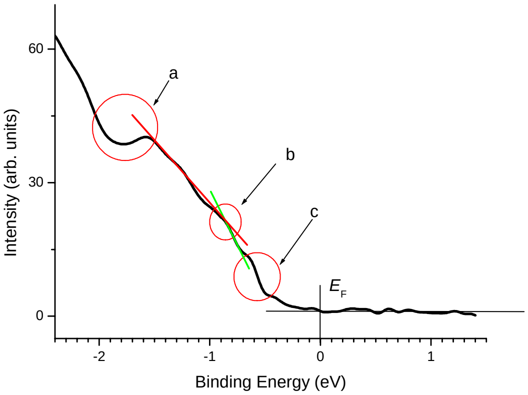

Fig. 2. The UPS spectrum for the bare Si(111) surface shows three surface states [10]: 1. the surface state (a) at 1.8 - 2 eV related to the backbonds between the Si adatoms and the three Si atoms directly beneath them, 2. the surface state (b) at ~1 eV related to the filled dangling bond states situated 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 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.*

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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 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 (10).

The wide scan UPS spectrum of clean Si shows the Si valence band (Fig. 3).

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. 2. For energies higher than 2 eV the emission comes from bulk states (peaks at -4 eV and -8 eV). The data are similar to those obtained by Tadayyon (11) for clean Si(111)-7x7 and are consistent with those reported in the literature by Martenson *et al.* (10) and Uhrberg *et al.* (12).

The UPS spectra after each deposition showed a difference in the valence features for the Si in the range -2.5 to -15 eV, suggesting that a transformation occurred from one deposition to another (Fig. 3).

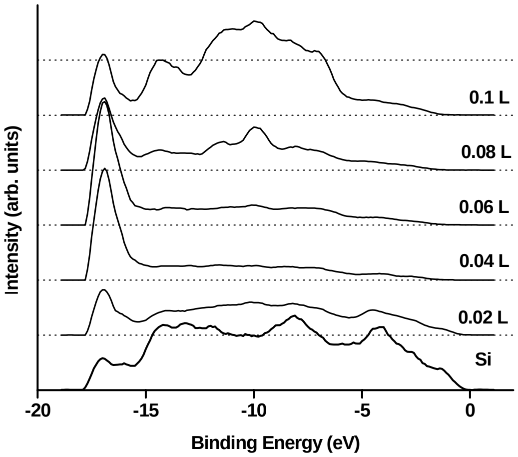

Fig. 3. Wide scan UPS spectra taken after each deposition show a difference in the valence features for Si (2.5 - 15 eV), suggesting that a transformation occurred from one deposition to another. UPS spectra following the first deposition at 0.02 L revealed that the Si peaks due to emission from bulk 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.*

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The reduction in the peak intensity for Si(111)-7x7 bulk states (-4 eV and -8 eV) as the deposition proceeds (exposures of 0.04 and 0.06 L), is accompanied by a concomitant increase in the secondary electron peak (~ -17 eV) for the same exposures, suggesting that the sample is receiving an increased amount of Cu (I) and fluorinated moities. Data are similar to those obtained by Tadayyon *(*11) for organics.

The features in the spectrum for 0.06 L are very weak and therefore hard to interpret.

The peak at -8 eV (i.e.bulk emission) - in the UPS spectrum of bare Si due to the sp^3 hybrid, shifts more than 1 eV toward a higher binding energy (~ -10 eV) for an exposure of 0.08 L suggesting that the tetrahedral symmetry was broken due to an electron density increase. 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 (11) 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. (13)* for the Cu-Si room temperature interface at submonolayer coverages.

Further studies using our XPS facility will follow after this experiment.

4. Conclusion

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.

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