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Abstract
The adsorption and decomposition of methylsilane gas onto Cu(111) has been investigated by reflection–absorption infrared spectroscopy (RAIRS). The initial adsorption of methylsilane at 15 K results in the formation of an initially ordered physisorbed monolayer, adsorbed with a small tilt angle from the plane of the surface. Further increase in exposure results in the formation of a more dense monolayer, with methylsilane lying nearly parallel to the surface of the crystal, before the growth of the disordered multilayer. Adsorption at 78 K appears to result in the formation of an SiH–CH$_3$ species for which there is some evidence of further Si–Si coupling. At 295 K, methylsilane is observed to adsorb with the Si–C axis perpendicular to the surface. Adsorption at 395 K results in the decomposition of methylsilane, with both Si–H and Si–C bond scission. Adsorbing CO at 15 K on the Cu/Si surface structure thus formed indicates that CO adsorbs mostly in atop positions on Si atoms, suggesting that any metal atom sites are blocked by either adsorbed C or Si atoms.

1. Introduction

The deposition of metals on silicon surfaces has been attracting the attention of the semiconductor industry for a number of years because of its pivotal role in the fabrication of microelectronic devices. Investigation of the formation of silicides has allowed a better understanding of the formation and the electronic properties of the silicide interface which can either result in the formation of Ohmic contacts or Schottky barriers. The epitaxial growth and the structure of copper layers on silicon substrates have been the main subject of investigation, mainly because of the known reactivity of copper atoms with silicon surfaces at low temperature. Copper/silicon surfaces are also of interest because of their role in some chemical syntheses: for example, the Rochow direct synthesis method [1, 2]. In this reaction, methyl chloride reacts with silicon present on the substrate containing a catalytic amount of copper to produce chloromethylsilanes, an essential precursor to silicones. The catalyst active in this reaction has been shown to be crystallites of Cu$_3$Si stoichiometry [3]. However, very little is known of the mechanism of this surface reaction and the active site from which chloromethylsilane is formed. The role of the copper is not yet fully understood and it is likely copper does not react as just a simple catalyst. In recent years, in an attempt to achieve a better understanding of the science behind the formation of the silicide interfaces, studies of the adsorption of silicon on single-crystal surfaces have been reported, predominantly involving the deposition of silicon, silane and disilane gases on copper surfaces [4–18]. In several of these studies, surface-sensitive infrared spectroscopy (RAIRS) was employed to exploit the sensitivity of this technique to the nature of adsorbed fragments, their orientation with respect to the surface and, in some cases, their local environment during the adsorption and decomposition of the adsorbed gas on the metal surfaces. In the adsorption and decomposition of silane gas on Cu(111), a variety of species are formed and an assignment of the characteristic spectral features of the individual silyl species has been proposed. However, some questions still remain over these proposed assignments, particularly in the identification of the adsorption sites and the structures formed.

The adsorption of methylsilane on copper surfaces has recently been examined using vibrational electron energy-loss spectroscopy (VEELS), angular-resolved ultraviolet photoelectron spectroscopy (ARUPS) and x-ray photoelectron spectroscopy (XPS) [19]. On Cu(111), it appears methylsilane partially dissociates upon adsorption at room temperature whilst at elevated temperatures, the gas completely dissociates,

leaving adsorbed Si atoms and CH_3 fragments on the surface. However, some fundamental questions remain unanswered. In particular, the preferential adsorption sites of chemisorbed methylsilane is highly uncertain.

In this paper, the presence of two spectrally distinct functional groups in methylsilane is used to identify the species formed during its adsorption and decomposition on a metal surface. This has two advantages. First, the functional groups have the same structure (the CH_3 and the SiH_3 groups both have local threefold symmetry) and therefore tend to show the same pattern of adsorption bands for the species which are the same shape. Second, they absorb in different regions of the infrared spectrum, so few overlaps between the CH and SiH modes are observed. Taken together, these two factors allow a much more definitive assignment for the adsorbate composition and geometry to be made than, for example, simple hydrocarbons.

The technique of reflection–absorption infrared spectroscopy has been described extensively in the literature, and is an excellent tool for the identification of adsorbate geometries on metal surfaces [20]. The optics of the experiment employ a single reflection from a metal surface at a highly grazing angle (typically 88° from the surface normal), under which conditions only vibrational modes with transition dipole moments perpendicular to the surface can be observed in the resulting RAIR spectrum. With accurate assignment of the individual vibrational modes, the presence or absence of individual modes can thus be used to deduce orientation with respect to the surface. For example, as seen in many of the spectra presented below, the symmetric C–H stretching mode of a methyl group attached to another moiety has its transition dipole oriented along the C_3 rotation axis, whilst the antisymmetric C–H stretch is polarized in a plane perpendicular to the axis. Simultaneous absence of the antisymmetric mode and presence of the symmetric mode in the RAIR spectrum would therefore imply that the C_3 axis for the methyl group is perpendicular to the plane of the surface. The opposite configuration, i.e. where the C_3 axis is parallel to the surface, would reverse the activity of the modes in the resulting RAIR spectrum. In this work, the relative intensities of vibrational modes from methyl and silyl groups (and related dehydrogenated moieties) are analysed in this manner.

2. Experimental details

The equipment used in this work has been described in detail elsewhere [21]. Briefly, the experiments were carried out in a UHV chamber operating at a base pressure of 1×10^{-10} Torr equipped with a sample mount capable of being cooled to 14 K using a closed-cycle cryostat. Upper temperatures of above 600 K were attained by e-beam heating for cleaning purposes. IR light from a Mattson RS1 FTIR spectrometer was focused onto the crystal at a grazing incidence, re-collimated and detected using an external mercury–cadmium–telluride detector in a custom-built housing.

A mechanically polished copper crystal (Metal Crystals and Oxides Ltd) cut and oriented to within ±0.5° of the (111) plane was used as a substrate. The sample was cleaned by
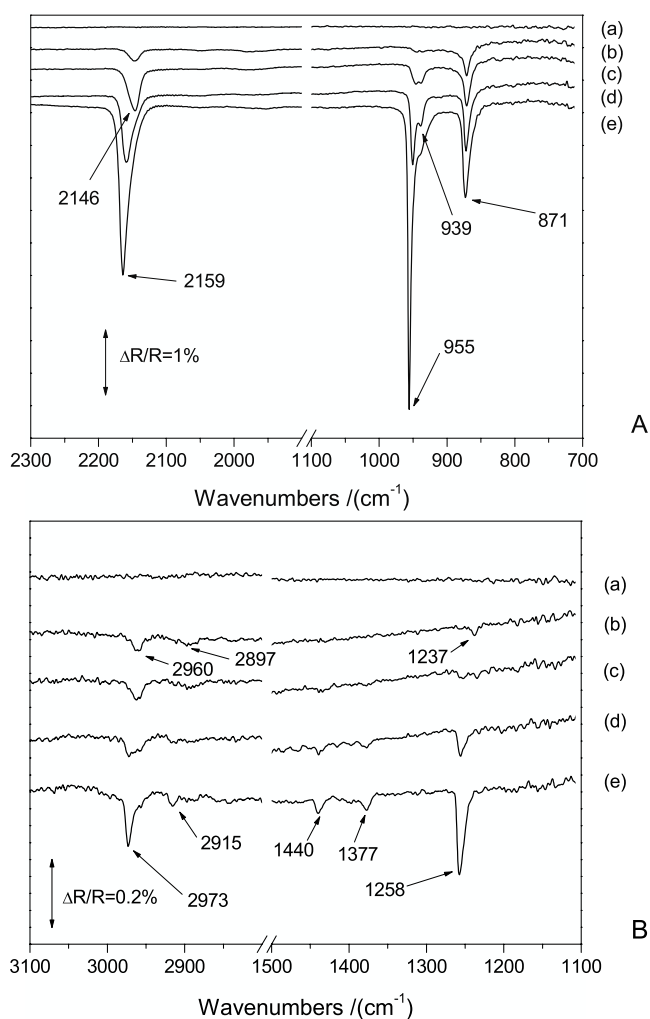

Figure 1. RAIR spectra of methylsilane adsorbed on Cu(111) at 15 K. (a) Clean copper surface, (b) 3 L, (c) 5 L, (d) 7 L, (e) 15 L.

successive cycles of argon-ion sputter at room temperature and annealing to 700 K. The methylsilane gas was supplied by ABCR as pure. No further purifications were carried out before dosing.

All the IR spectra shown here are the result of 750 co-added single-beam scans at 2 cm^{-1} resolution, ratioed to a background of 1025 co-added scans from the clean crystal. For clarity of view, the spectra are presented as [A] and [B] in each case, with [A] showing the Si–H vibrations and [B] showing the C–H vibrations, as far as is possible.

3. Results and discussion

Figures 1(A) and (B) show the results of sequential dosing of methylsilane at 15 K. The first features appear at 869, 2146 and 2960 cm^{-1} in the spectra labelled (b), which correspond to an exposure of 3 L. These are accompanied by weak features at 1237 and 2897 cm^{-1} at 3 L exposure, although these are lost as coverage increases to 5 L (traces labelled (c)), whilst a new band at 939 cm^{-1} is observed. Continuing to successively higher exposures, the peak at 869 cm^{-1} increases

Table 1. Vibrational frequencies (cm^{-1}) of SiH$_3$CH$_3$ in the gas and crystal phases and adsorbed on clean Cu(111). The vibrational frequencies reported for the multilayer were observed after dosing 100 L of methylsilane on the clean Cu(111) surface at 15 K.

Assignment	Gas phase [25]	Solid phase [22]	Monolayer[a]	Multilayer	C$_{3v}$	C$_s$
νCH$_3$ (ν_7)	2982	2970	2960	2973	E	A$'$ + A$''$
νCH$_3$ (ν_1)	2929	2910	(2897)	2915	A$_1$	A$'$
νSiH$_3$ (ν_2)	2169	2168	(2150)	2159	A$_1$	A$'$
νSiH$_3$ (ν_8)	2166	2168	2146	2150(sh)	E	A$'$ + A$''$
δCH$_3$ (ν_9)	1403	1436	—	1440	E	A$'$ + A$''$
δCH$_3$ (ν_3)	1264	1257, 1250	(1237)[b]	1258	A$_1$	A$'$
δSiH$_3$ (ν_{10})	946	941	939	955	E	A$'$ + A$''$
δSiH$_3$ (ν_4)	—	923, 914	—	945(sh)	A$_1$	A$'$
ρCH$_3$ (ν_{11})	871	853, 847	869	871	E	A$'$ + A$''$
νC–Si (ν_5)	701	705, 702(sh)	—	705	A$_1$	A$'$
ρSiH$_3$ (ν_{12})	545	533, 525	—	—	E	A$'$ + A$''$
τCH$_3$ (ν_6)	—		—	—	A$_2$	A$'$

[a] Values in parentheses are those modes seen weakly in the low-coverage monolayer only.

[b] May also be due to some adsorbed methyl fragments (see text).

in intensity (shifting slightly to 871 cm^{-1}) and new sharp features are observed at 2159 and 955 cm^{-1} in figure 1(A)(e) and 1440 and 1377 cm^{-1} in figure 1(B)(e). Bands also grow in at 1258 cm^{-1}, 2915 cm^{-1} and 2973 cm^{-1}, respectively. These higher wavenumber features at increased exposure are generally significantly greater in intensity than those seen initially at low exposure, and they continue to grow roughly linearly with continued exposure. As a result, the spectra show clear asymmetry in the majority of band shapes as a result of the presence of two species.

The relative intensities and the band positions reported above are in broad agreement with extensive vibrational investigations carried out on methylsilane gas and condensed crystal phases [22–25]. A full summary of these results along with band assignments are summarized in table 1. In previous crystalline and gas phase studies of SiH$_3$CH$_3$, some anomalies in the assignment of the vibrational frequencies are noticeable. The CH$_3$ deformation mode varies from 1403 cm^{-1} in the gas phase to 1436 cm^{-1} in the pure crystal phase. This discrepancy between previous studies was largely due to the ambiguity arising from the presence of overtone and combination bands in this region. A site-related shift is not expected as the deformation mode is, to a large degree, independent of its surroundings [24]. The CH$_3$ rocking mode showed, however, a shift downward from 870 to 853 cm^{-1}. This shift indicates a degree of interaction between the methyl group and its environment.

Utilizing the accepted band assignments and vibrational mode symmetries, analysis of the band positions and intensities in the low exposure spectra presented here can be used to determine the orientation of the molecules in the monolayer and the multilayer. In the gas phase, the molecule has C$_{3v}$ symmetry in both the eclipsed or staggered conformation and the majority of the modes have either A$_1$ or E symmetry. Upon condensation, the symmetry descends to C$_s$ due to the presence of the Cu surface. Although the degeneracy of the antisymmetric E modes is lifted to produce two separate modes with A$'$ and A$''$ symmetry, the two components are likely to still have the same vibrational frequency unless very close to the surface and are simply polarized in different (orthogonal) directions, in a plane perpendicular to the molecular axis. On

a surface, the symmetric A$_1$ modes become A$'$ and possess a transition dipole moment parallel to the molecular axis. The directionality of these modes with respect to the molecular axis in combination with the metal-surface selection rule (MSSR) can be used to identify molecular orientation with respect to the plane of the surface. For example, if individual methylsilane molecules were lying parallel to surface (i.e. with their molecular axes perpendicular to the surface normal) the vibrational modes which are formally antisymmetric (E) in the free molecule would have a component of their transition dipole moments (A$'$, A$''$ or a proportion of both) perpendicular to the surface for any rotation around the Si–C axis and would be RAIRS-active, whereas the symmetric vibrations would be completely suppressed by the MSSR. Consequently, by using the band assignments and mode symmetries in table 1, the following observations about relative orientation can be made.

At very low exposures as shown in figures 1(A)(b) and (B)(b), the features at 2960, 2146 and 869 cm^{-1}, due to the antisymmetric CH$_3$ and SiH$_3$ stretches and the CH$_3$ rocking mode, are clearly seen. However, figure 1(B)(b) also shows weak features at 2897 and 1237 cm^{-1}, which are due to the symmetric stretching and deformation modes of the CH$_3$ moiety. Their presence therefore indicates that the molecules are not exclusively parallel to the surface in the low-coverage monolayer. As coverage increases upon the adsorption of a further 2 L exposure (figure 1(B)(c)), these symmetric bands diminish whilst those assigned to antisymmetric modes increase in intensity slightly. It is therefore reasonable to assume that, as a result of an increase in methylsilane exposure up to 5 L, the axes of adsorbed methylsilane molecules tilt toward a position parallel to the copper surface. This is possibly due to the formation of a denser monolayer. The interpretation of the features at ca. 940 cm^{-1} is slightly more complicated, in that there is some uncertainty as to the exact assignment of the symmetric and antisymmetric modes, which are very close in frequency. Previous investigations have suggested that the dominant band at 940 cm^{-1} in the gas phase is the A$_1$ symmetric deformation of the silyl group [22, 24]. The antisymmetric silyl deformation was reported to be hidden under this band. In a thin film methylsilane investigation by Oxton [23], two sharp components and a markedly broad

feature were assigned to the silyl deformation in this region, with the highest frequency attributed to the ν_{10} mode and the two others to the ν_4 mode. In figure 1(A)(c), a doublet is observed. The lower frequency component of this is attributed here to the antisymmetric SiH$_3$ deformation mode ν_{10} on the basis that, at this stage, all of the symmetric CH$_3$ modes and the Si–C stretch ν_5, expected at ca. 705 cm^{-1}, are absent. The higher frequency component is assigned to the multilayer, discussed below. Taken together, these observations lead to the conclusion that the full monolayer consists of molecules aligned parallel to the surface.

Upon increasing exposure above 5 L, a multilayer forms. The majority of the new features seen as the coverage increases occur at higher frequencies of the monolayer values, concomitant with a stronger interaction between the molecules in the monolayer with the surface. The bands observed are due to a mixture of symmetric and antisymmetric modes (for example, both of the methyl stretches ν_1 and ν_7 at 2915 and 2973 cm^{-1}, respectively, are seen). Additionally, the Si–C stretch ν_5 becomes active (figure 1(A)(e), right on the 700 cm^{-1} detector cutoff). This suggests that the multilayer is either disordered or ordered in such a way that there is an array of molecular orientations with respect to the surface normal.

Figure 2 shows the result of annealing a multilayer of methylsilane on a Cu surface at 15 K to successively higher temperatures. Upon annealing to 52 K (figures 2(A) and (B)(a)), a number of significant changes in relative intensity are observed and a number of new features grow in. These changes result from increased ordering at 52 K compared to the amorphous multilayer at 15 K. The 2159 cm^{-1} band attributed to the antisymmetric SiH$_3$ stretching mode shifts up to 2162 cm^{-1}, with a shoulder to lower wavenumber. Similarly, the sharp features at 955 and 871 cm^{-1} become sharp doublets (952/946 and 872/862 cm^{-1}) of comparable intensity. The methyl-related features at 2973 and 1257 cm^{-1} also sharpen considerably. This provides strong evidence for an ordered multilayer with several arrangements of molecules with respect to the surface normal within the structure. Upon further annealing to 55 K (figures 2(A)(b) and (B)(b)), all of these multilayer features are attenuated and the lower wavenumber components of the ca. 950 and 870 cm^{-1} doublets are lost. At 72 K (figures 2(A)(c) and (B)(c)), the multilayer is completely gone and the remaining features are the same as those assigned to the ordered monolayer at 15 K, entirely dominated by antisymmetric (surface perpendicular) vibrational modes. The exception is the weak feature at 1237 cm^{-1}. Further heating to 97 K (figures 2(A)(d) and (B)(d)) results in the loss of all of the Si–H related features, leaving bands at 2956, 2885, 1237 and 870 cm^{-1}. These features can be assigned to the vibrational modes of adsorbed methyl groups and the presence of both antisymmetric and symmetric components suggests that the adsorbed fragment is tilted at some angle with respect to the surface normal. These features remain to at least 140 K.

These observations are consistent with the dehydrogenation of the methylsilane monolayer following the desorption of the multilayer above 55 K. The vibrational modes of the residual adsorbed methyl fragments are consistent with a tilted
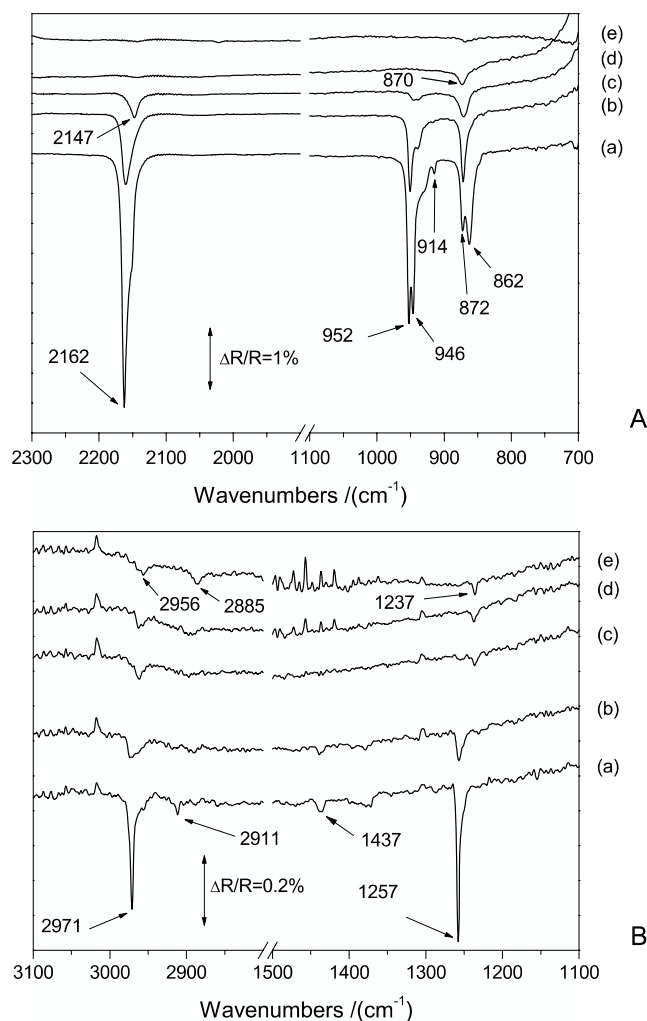

Figure 2. RAIR spectra of 15 L methylsilane adsorbed on Cu(111) at 15 K and heated. (a) 52 K, (b) 55 K, (c) 72 K, (d) 97 K, (e) 140 K. Each spectrum was recorded at the indicated temperature. The weak positive-going features at 3040 and 1290 cm^{-1} are due to gas-phase methane in the spectrometer purge.

structure. This is different to that observed by Nuzzo *et al* for the dissociative adsorption of methylsilane on Pt(111) at 108 K, also studied by RAIRS. In their experiments, direct adsorption at 108 K resulted in the formation of an adsorbed Me–Si fragment with the Si–C axis perpendicular to the surface, characterized by the presence of only symmetric methyl modes (ν_sCH$_3$ at 2949 cm^{-1} and δ_sCH$_3$ at 1231 cm^{-1}) and the Si–C stretch (at 760 cm^{-1}). Similarly, Spencer and Nyberg report the room temperature adsorption of methylsilane on Cu(111) studied by EELS, observing losses at 2890, 1400 and 745 cm^{-1} to which they made the same assignment [19].

3.1. Adsorption at 78 K

Figures 3(A) and (B) were obtained after subsequent dosing of methylsilane at 78 K. After a dose of 1 L, the most prominent feature is a moderately strong band at 2075 cm^{-1}, accompanied by a weak, sharp feature at 1237 cm^{-1}. Upon increasing exposure, the 2075 cm^{-1} band increases in intensity
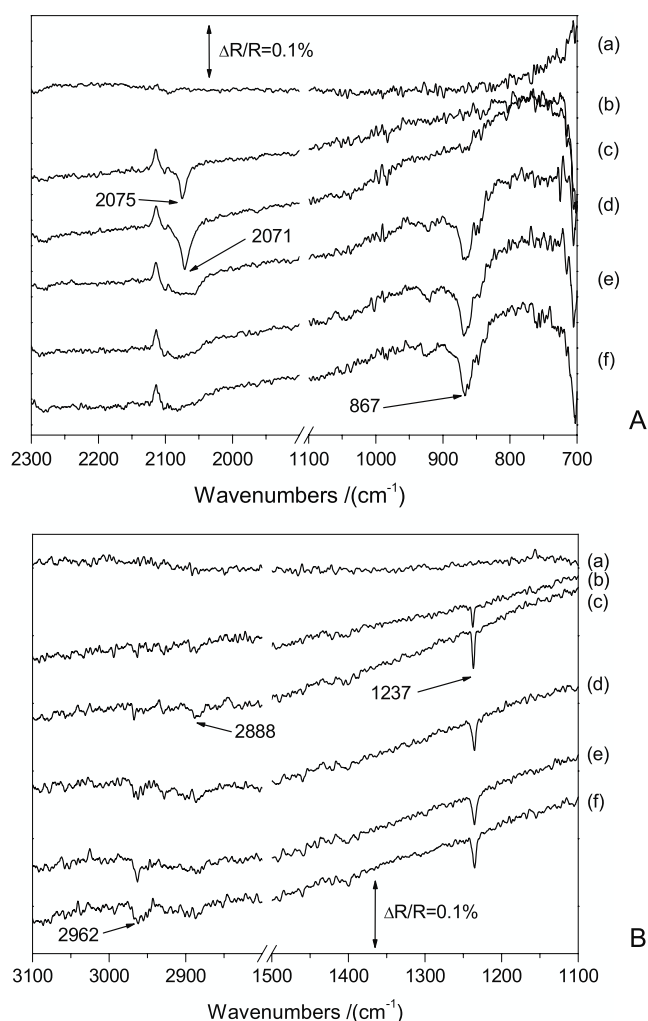
Figure 3. RAIR spectra of methylsilane adsorbed on Cu(111) at 78 K. (a) Clean copper surface, (b) 1 L, (c) 2 L, (d) 3 L, (e) 4 L, (f) 5 L, methylsilane adsorbed on Cu(111) at 78 K.

transformation is accompanied by the strengthening of the 1237 cm^{-1} band and the appearance of the ca. 867 cm^{-1} band. Given the previous assignments of these bands to the symmetric deformation and methyl rocking modes, this change is indicative of a change of orientation of the methyl group with respect to the surface.

On the basis of this evidence, it is proposed that a surface reaction is occurring in which the final Si atom dehydrogenation (as a result of either a slow surface reaction or due to increasing surface coverage) results in a change of orientation of the adsorbed Si–CH$_3$ moiety. Although such a transformation has not been directly observed for methyl-containing silane species, such behaviour has been identified for H-terminated silicon surfaces by Chabal *et al*, who observed temperature-and exposure-dependent transformation of an H-saturated 'dihydride monomer' Si(100)(1 × 1) surface (consisting of surface SiH$_2$ groups) to a 'monohydride dimer' Si(100)(2 × 1) surface (consisting of domains of HSi–SiH) species [27]. If such a process were to occur between two neighbouring SiH–CH$_3$ species, the resulting Si–Si bond would necessarily result in a tilting of the C$_3$ symmetry axis of the methyl group further towards the surface normal, with concomitant changes in vibrational mode intensity and activity as observed in figure 3. Theoretical studies of the adsorption of methylsilane on Si(100) also suggest that the main adsorption mechanism is via Si–H bond cleavage and that adsorbed fragments can readily undergo rearrangements [28].

3.2. CO adsorption on SiH$_3$CH$_3$-treated Cu(111)

The adsorption of CO on metal surfaces is regarded as an excellent probe of local environment and surface cleanliness because of the sensitivity of the CO stretching mode to the nature of its occupation site. On clean Cu(111), CO is observed to adsorb into atop and bridge sites. Figures 4(A) and (B) show the result of dosing 100 L of methylsilane at 295 K, cooling to 15 K and subsequent dosing of CO at 15 K. Upon initial methylsilane exposure, two bands are observed at 2883 and 1237 cm^{-1} (previously attributed to the symmetric methyl stretching and deformation modes), which sharpen upon cooling to 15 K. Additional weak features are observed, resulting from a small proportion of residual methylsilane and CO pickup at low temperature. After exposure to 0.1 L at 15 K, the spectrum is dominated by a relatively intense band at 2094 cm^{-1}, accompanied by weaker features at 2143 and 2080 cm^{-1}. Upon increased exposure (1 L), the 2094 cm^{-1} band increases markedly and a new weak band appears at 2137 cm^{-1} (the methylsilane pickup feature at ca. 2143 cm^{-1} does not change in intensity).

The results of a similar procedure but with methylsilane exposure at 395 K are shown in figures 5(A) and (B). The crystal was first exposed to 100 L of methylsilane at 395 K and cooled to 15 K. No spectral features are observed upon initial exposure although again some residual background methylsilane pickup occurs upon cooling. Exposure to 0.1 L CO results in the appearance of two new features at ca. 2110 and 2088 cm^{-1}. Upon increased CO exposure (0.5 L then 1.0 L), the main feature at 2110 cm^{-1} increases in intensity,

and shifts downwards by ca. 4 cm^{-1}, whilst the 1237 cm^{-1} band also increases and a new strong feature appears at 865 cm^{-1}. In the CH stretching region, weak features are discernible at ca. 2962 cm^{-1} and 2888 cm^{-1} with a signal to noise ratio of about 3.

The evolution of these features with increasing time and exposure can be explained in terms of a surface reaction. The data obtained from annealing experiments (as shown in figure 2) suggest that 78 K appears to be very close to the temperature at which the dehydrogenation of the Si functional group becomes favourable. Initial adsorption of methylsilane results in the formation of adsorbed SiH$_x$–CH$_3$ fragments, and the lack of a band in the 850 cm^{-1} in the presence of the 2075 cm^{-1} band indicates that the Si moiety is a monohydrate (Si–H) since a dihydrate would necessarily also possess a deformation mode of comparable relative intensity in this region (cf. disilane adsorption on Ru(001)) [26]. The increase in intensity and shift to lower frequency of the 2075 cm^{-1} band is indicative of increasing surface coverage. Upon increasing exposure (and time), this band is lost, indicating dehydrogenation of the remaining silicon monohydride: this
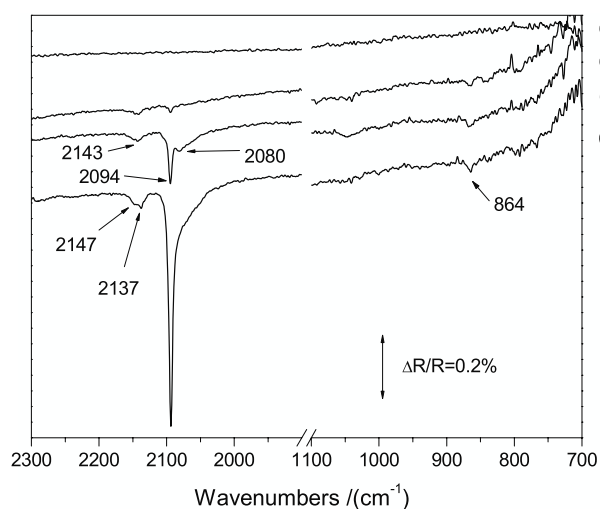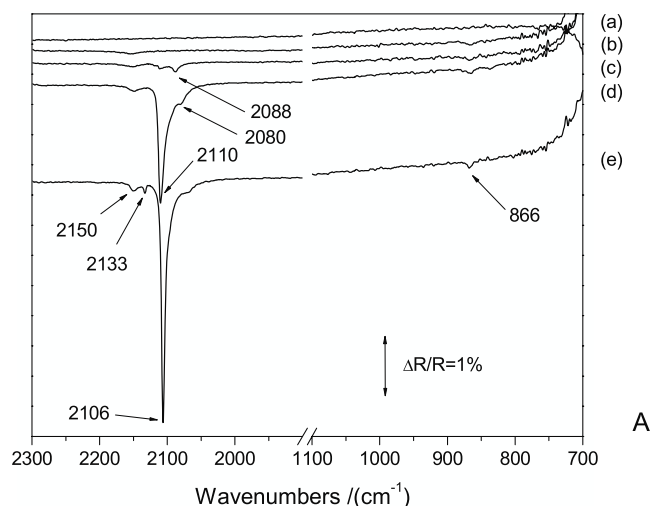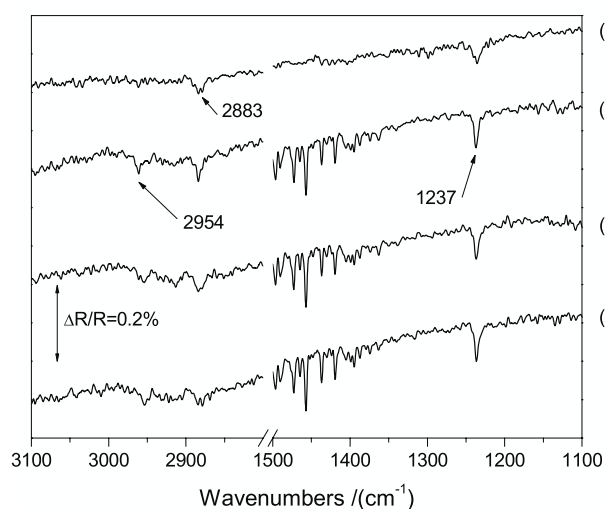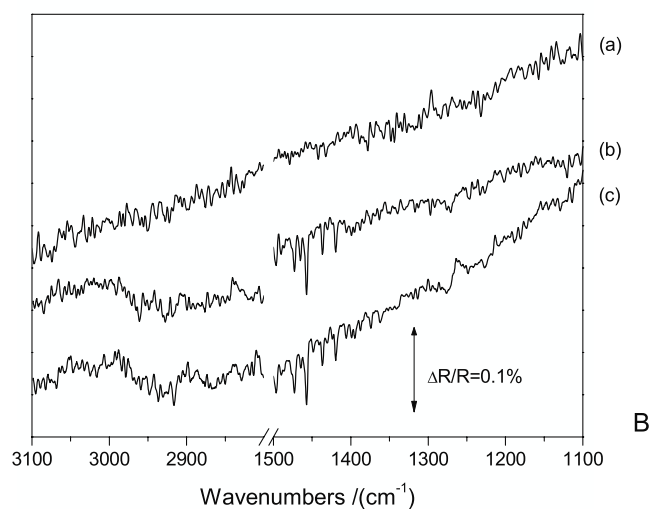
Figure 4. RAIR spectra of CO adsorbed on the CH₃SiH₃-modified Cu (111) surface. (a) 100 L methylsilane at 295 K, (b) after cooling to 15 K, (c) 0.1 L and (d) 1 L of co-added CO exposure at 15 K.

Figure 5. RAIR spectra of CO adsorbed on CH₃SiH₃-modified Cu(111) surface. (a) 100 L methylsilane at 395 K, (b) after cooling to 15 K, (c) 0.1 L, (d) 0.5 and (e) 1 L of co-added CO exposure at 15 K.

accompanied at the highest exposure by a weak feature at $2133\ \text{cm}^{-1}$.

These observations permit a number of conclusions to be drawn. Following the 295 K exposure, the presence of methyl symmetric stretch and deformation resonances indicates that all of the CH bonds remain intact and furthermore that the methyl fragment is oriented with its principal axis perpendicular to the surface. A comparison of the frequencies of these vibrational modes with those obtained in other studies for methyl moieties on a range of surfaces (metals and silicon) also suggests that the fragment is bonded to Si rather than to the metal surface. Table 2 summarizes the literature values for these modes, from which it can be seen that the symmetric deformation particularly is significantly higher in frequency when adsorbed on Si compared to Cu surfaces. The absence of any methyl features in the 395 K deposition is indicative of complete C–H bond scission (although it does not directly give any information about the eventual fate of the methyl fragment, i.e. decomposition or desorption).

The positions of the CO resonances on these two surfaces gives important information on the nature of the adsorption

Table 2. Vibrational frequencies (cm^{-1}) for methyl groups adsorbed on various surfaces.

	νCH_3	νCH_3	δCH_3	δCH_3	ρCH_3
SiH₃CH₃/Cu(111)	—	2883	—	1237	—
CH₃/Cu(111) [29, 30]	2940	2970	1371	1169	734
CH₃/Cu(111) [31]	2910	2781	1386	1185	854
CH₃Br/Cu(111) [31]	2990	—	1403	1374	935
CH₃I/Cu(111) [32]	2950	2820	1370	1180	—
CH₃Cl/Si(100) [33]	2967	—	1435	1266	709
CH₃I/Si(100) [34]	2955	2890	—	—	—
CH₃I/Si(100) [35]	3080	3000(sh)	1425	1250	900
CH₃/Si(100) [35]	2990	2930(sh)	1425	1260	710

sites available to CO on these two treated surface. Adsorption of CO on clean Cu(111) at temperatures below 20 K by Eve *et al* reveal the vibrational frequency of CO in a terminally bound state to be $2078\ \text{cm}^{-1}$ at a very low coverage, which shifts to lower frequency with increased coverage [36]. Eve *et al* also identified a physisorbed monolayer mode at $2132\ \text{cm}^{-1}$ and a thick physisorbed multilayer with a frequency of $2138\ \text{cm}^{-1}$. In comparison, there are few detailed studies of
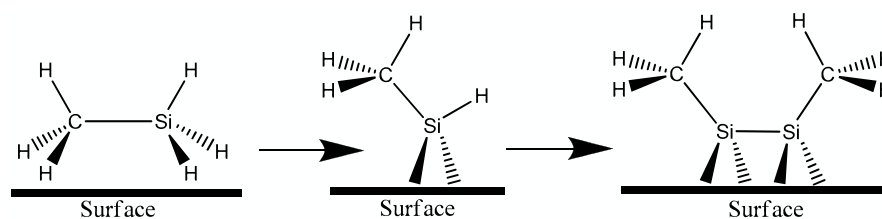
Figure 6. Schematic of the changes in orientation of methylsilane, showing from left to right the dense monolayer, the adsorbed (dehydrogenated) fragment and the Si–Si coupling product.

CO adsorbed on Si surfaces, and none below 100 K. It was, however, found that CO adsorption and desorption is strongly dependent upon surface morphology, adsorbing on Si(100) (2×1) at 100 K in an upright position and not at all on Si(111) (7×7) [37].

The study of CO adsorption onto silicon/metal surfaces is also quite limited, despite its obvious application in the CVD processes. In the study of silicide formation on Pd(110), the CO stretching frequency was observed to be strongly dependent upon the composition of the surface Pd/Si layer, typically exhibiting a frequency for CO on Si of 2104 cm^{-1}, very similar to that obtained for CO on amorphous silicon by Wälchli *et al* [38]. On the basis of these literature observations, the following assignments of the features in figures 4 and 5 can be made. In both cases, the features at 2137 cm^{-1} and ca. 2080 cm^{-1} are assigned to the physisorbed and chemisorbed monolayer, respectively. This is supported by the observation that the ca. 2080 cm^{-1} mode appears first, and that at 2137 cm^{-1} only appears at higher exposures. The relative weakness of these features (compared to the clean surface observations of Eve) is indicative of the scarcity of clean copper sites in these experiments and supports the assertion that the majority of the surface is covered with methylsilane fragments and/or decomposition products. The most intense features in figures 4(A) and 5(A) occur at 2094 and 2110 cm^{-1} and are assigned to chemisorbed CO adsorbed either near or onto surface silicon fragments. For the film deposited at 295 K, it would appear that there is partial dehydrogenation of the Si functional group, leading to adsorbed SiH$_x$–CH$_3$ species. Steric interactions between neighbouring adsorbates are likely to limit the coverage of methylsilane fragments such that fewer than 100% of the available copper sites are occupied. Consequently, upon cooling, there are likely to be free copper sites for CO adsorption, giving rise to the resonance at 2094 cm^{-1}. For the film deposited at 395 K, there appears to be complete dehydrogenation of both the Si-and C-containing functional groups. Although RAIRS does not give direct evidence for the presence of either Si or C adsorbed on the surface, an adsorbed CO frequency of 2104 cm^{-1} suggests that the CO is directly adsorbed on surface Si atoms, with few free Cu sites. On the basis of this evidence, it is suggested that the 395 K deposition results in the complete decomposition of methylsilane to produce adsorbed Si and C atoms, with CO adsorbing onto the Si atoms alone. This proposal is supported by low energy electron diffraction measurements, which reveal a $(\sqrt{3} \times \sqrt{3}R30°)$ pattern after deposition of methylsilane at 395 K [39–41].

4. Conclusion

The initial adsorption of methylsilane at 15 K results in the formation of an initially ordered physisorbed monolayer, adsorbed with a tilt angle. A further methylsilane exposure results in the formation of a denser monolayer, with methylsilane lying nearly parallel to the surface of the crystal. This monolayer is then followed by the adsorption of a disordered multilayer grown from the subsequent exposures. Heating the crystal surface to 52 K reveals a crystal reordering of the adsorbed methylsilane. Heating above 52 K indicates the decomposition or desorption of the physisorbed multilayer.

The chemisorption of methylsilane at 78 K shows some similarity with the adsorption of silane on Cu(111). At low coverage, the dissociative adsorption of methylsilane is observed by a partial silicon–hydrogen bond scission. As the surface coverage increases, the broadening of the silyl stretching frequency indicates a change of environment of the silicon present on the surface. At high methylsilane exposure, there is complete dissociation of the silicon–hydrogen bond whereas the Si–C and C–H bonds appear to be preserved. A Si–Si coupling mechanism is proposed to explain the changes in the spectral features. Figure 6 shows a schematic of these arrangements.

At 295 K, methylsilane undergoes silicon–hydrogen bond scission and adsorbs perpendicular to the surface, with local C$_{3v}$ point group symmetry, as only the symmetric CH$_3$ stretch and deformation modes, ν_1 and ν_3, are observed.

Adsorption of methylsilane at 395 K indicates, however, a complete decomposition of methylsilane, with Si–H and Si–C bond scission. The fate of the methyl fragments is uncertain, although they may desorb from the surface at 395 K by the formation of larger methylsilane gases such as trimethylsilane and tetramethylsilane. However, the presence of amorphous carbon remaining on the copper surface cannot be excluded using RAIRS. Adsorbing carbon monoxide at 15 K on the $(\sqrt{3} \times \sqrt{3}R30°)$ Si/Cu(111) surface structure indicates that CO adsorbs mostly on silicon at the atop position, suggesting that the majority of the surface Cu sites are blocked.

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