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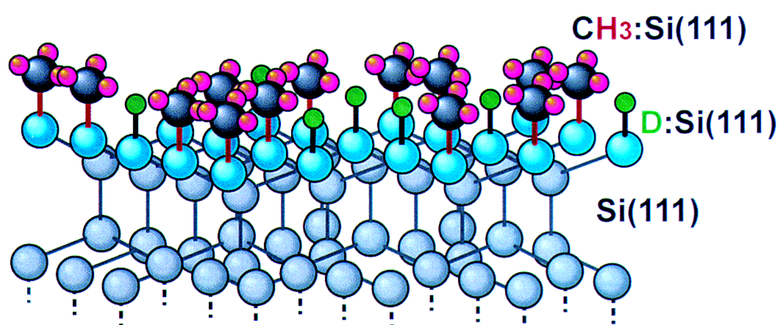

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Detection of C−Si Covalent Bond in CH_3 Adsorbate Formed by Chemical Reaction of CH_3MgBr and H:Si(111)

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Abstract: High-resolution electron energy loss spectroscopy (HREELS) yielded evidence for the formation of single covalent bonds between Si(111) surface atoms and CH_3 groups from the reaction of CH_3MgBr and hydrogen-terminated H:Si(111)(1 × 1). The vibration at 678 cm^{-1}, assigned to the C−Si bond, was isolated within the spectrum of CH_3 on deuterium-terminated D:Si(111)(1 × 1). The CH_3 groups were thermally stable at temperatures below 600 K. The C−Si bonds are essential for enhancing the usefulness of alkyl moieties, which will lead to a new prospective technology of nanoscale fabrication and biochemical application.

1. Introduction

Monolayers of organic adsorbates bonded on silicon wafer surfaces have prospective properties for applications in nanometer-scale industrial technology.[1,2] The covalent-bond linkage in organic adsorbates can mediate the connection of a variety of molecular groups with surface silicon atoms. Not only binding chemically functional groups but also grafting of biochemical polymers such as DNA and proteins can be realized by formation of covalent bonds.[3−5] The fixation of such biomolecules is one of the key issues in fabricating biochemical−silicon hybrid devices.[6,7] Within the diversity of organic species, alkyl (C_nH_{2n+1}-type hydrocarbon moieties) monolayers directly bonded on silicon surfaces are structurally simple and have useful properties for nanofabrication. Alkyl monolayers, having ultimate thinness and chemical robustness, can be applied as the surface passivating medium or as the high-resolution lithography materials of the next generation.[8]

Despite those beneficial properties for application, the formation of hydrocarbon moieties bonded on well-defined silicon surfaces has not been widely studied until recently. Hovis et al.[9] reported on an elegant reaction of hydrocarbons and the Si−Si dimer array of clean Si(100)(2 × 1), which resulted in the formation of well-ordered adlayers. This process involves the preparation of clean Si(100)(2 × 1) in ultrahigh vacuum (UHV), which is not routinely available in the industry. The hydrogen-terminated silicon surface, which can be prepared in aqueous solutions, is more practical as the starting material and hence attracts widespread interest in physics and chemistry in general. Linford et al.[10] surveyed methods of bonding alkyl groups directly on Si(111) by replacing H in H:Si(111) by those alkyl groups photochemically. De Villeneuve et al.[11] proposed a method of electrodepositing organic negative ions at an electrode of H:Si(111). The simplest method was presented by Boukherroub et al.,[12] in which Grignard reagent (alkylmagnesium halide, $C_nH_{2n+1}MgX$, X = Cl, Br, or I) was used to deposit the corresponding alkyl adsorbate on H:Si(111). Bansal et al.[13] used chlorine-terminated Si(111) to facilitate the deposition by alkylmetal reagents. H:Si(111) was preferred to H:Si(100) in those studies because Si(111) treated in appropriate fluoride solutions is covered homogeneously by well-ordered (1 × 1) monohydride silicon atoms.[14] The method to prepare ideal H-terminated Si(100) has not been established yet, and H:Si(100)

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prepared in aqueous solutions tends to be microscopically rough and inhomogeneous.[15]

We have studied methods of applying organic monolayers to nanometer-scale fabrication on silicon wafers suitable for mass production.[16,17] We examined the Grignard reaction of H:Si(111)[12] and found that the adlayers of alkyls between CH_3 and $C_{18}H_{37}$ are monolayers but not well ordered as observed by scanning tunneling microscopy (STM). Infrared vibrational spectroscopy showed that the reagent $C_nH_{2n+1}MgX$ used always resulted in the deposition of the same C_nH_{2n+1} group. The alkyl-covered surfaces are robust; they are storable in air and the Si substrate is blocked against an attack by O_2^- dissolved in water.[17] We further investigated the possibility of application to electron-beam nanolithography by alkyl monolayers.[16,17] Electron beam bombardment in the presence of ambient O_2 and successive treatment in an electrolytic solution containing Ni^{2+} or Cu^{2+} resulted in the deposition of corresponding metals only on the bombarded portions.[16] The alkyl monolayer was tolerant to the electrolytes containing F^-, even during the period of selective formation of an amount of Cu visible to the eyes (film thickness ca. 100 nm) on the bombarded spot.[17] In short, the alkyl adlayers have been shown to be useful for electron-beam nanolithography.

One important feature of the adsorption of alkyl moiety is that it involves the formation of a covalent bond between a C atom in the alkyl moiety and a Si atom at the surface. The C−Si single covalent bond, having a bonding energy of approximately 3 eV, is essential for strong fixation and low lateral mobility of the alkyl adsorbates. The macroscopic robustness is also considered to depend on the C−Si bond.

This report describes our results of vibrational analysis using high-resolution electron energy loss spectroscopy (HREELS) indicating the existence of C−Si bonds within the CH_3 adlayer formed by the Grignard reaction. Although much circumstantial evidence has been presented for the formation of a C−Si bond from H:Si(111) in previous reports, direct unambiguous detection of C−Si bonds has been rarely made.[8−13,16,17] Because of the processes for H:Si(111) in organic solvents and in air, the target alkyl adlayer may accompany contaminants, and it is naturally more difficult to discriminate them than in the cases under idealized conditions in UHV.[18−20] It is of course necessary to perform our entire procedure carefully to seize the amount of contaminants, and at the same time, we must monitor the contaminants and distinguish the target adsorbates from them by examining every available spectroscopic feature.

2. Experimental Section

Our experiment was performed in an UHV system equipped with a HREEL spectrometer (LK Technology, Inc., LK2000) and a two serially connected sample-introductory chambers (the ultimate pressure = 5×10^{-10} Torr). The first introductory chamber was pumped from the atmospheric pressure by using a liquid-nitrogen cooled sorption pump, by which we could perform oil-free evacuation and eliminate the chance of hydrocarbon contamination of the sample. The sorption pump could evacuate the first introductory chamber down to approximately 1×10^{-5} Torr and could be switched to a 50 L s^{-1} turbomolecular pump driven at the top speed. The evacuation procedure of this stage was completed in a few minutes and the sample was transferred to the succeeding UHV stages. The sample Si(111) chips diced from commercial *n*-Si(111) wafers (Shinetsu Handotai Co., Ltd., thickness 0.60 mm, 3∼8 Ω•cm) were washed in trichloroethylene and acetone and immersed in a SPM solution (4 parts concentrated H_2SO_4 + 1 part 30% H_2O_2 mixture at 120 °C) for 10 min to form a thin oxide and hydroxide protective layer on Si(111). The surface thus produced will be designated as O/Si(111). Just before use, the O/Si(111) was immersed in 40% NH_4F solution for 10 min to remove the surface oxide. This is the method employed to prepare H:Si(111)(1 × 1).[14] The alkyl adlayers were prepared by following the method reported by Boukherroub et al.[12] We used a commercial 1 M tetrahydrofuran (THF) solution of methylmagnesium bromide (CH_3MgBr, Kanto Chemical Co., Inc.). A specimen of H:Si(111) was placed in a glass tube connected with a reflux condenser purged with ultrapure Ar, and the Grignard reagent was poured in. The temperature was raised and kept at about 65 °C for 18 h to allow for this reaction to proceed. To stop the reaction, the specimen was transported into air and rinsed successively in THF containing 3% trifluoroacetic acid, water, and 1,1,2-trichloroethane. Then the specimen was promptly carried through air and subjected to HREELS measurement.

3. Results and Discussion

Figure 1 shows the HREEL spectra of H:Si(111), O/Si(111), and H:Si(111) after treatment in 1 M CH_3MgBr/THF. The spectrum of O/Si(111) (b) contains a characteristic vibration peak of SiO_2 at 1100 cm^{-1}. The same surface was subjected to Auger electron spectroscopy (AES) and the amount of SiO_2 deposit was estimated to be less than 0.4 monolayers. Hence we quantify SiO_2 appearing in all other spectra by multiplying 0.4 monolayers with the ratio of the SiO_2 loss peak area normalized by the elastic peak area to that of spectrum b, assuming that the loss peak intensity is proportional to the amount of O. The spectra of H:Si(111)(1 × 1) (a1, a2), measured by varying the electron exit angle from the specular direction, reproduce well the data reported by Dumas et al.[15,21] and Stuhlmann et al.[22] The Si−H stretching (2083 cm^{-1}) and bending (631 cm^{-1}) modes are prominent. The peak at 1100 cm^{-1} attributed to SiO_2 is estimated to be $<3 \times 10^{-3}$ monolayers.

The spectra of CH_3 (c), recorded immediately after the specimen was introduced from the air, exhibit peaks for the characteristic modes of CH_3. The CH_3-covered surface was then annealed at 573 K in UHV to eliminate volatile adsorbates, and it was subjected to HREELS again (d1, d2). Locations of all peaks were unchanged, indicating that the surface CH_3 moieties remained intact. The peak at 1080 cm^{-1} due to SiO_2 impurity was strengthened, corresponding to $<4 \times 10^{-3}$ monolayers. This enhancement might be due to crystallization of SiO_2 or adsorption of residual H_2O gas promoted by annealing. By Auger electron spectroscopy, no other contaminating elements, such as magnesium and halogens originated of the Grignard reagent, were found. The CH_3 asymmetric stretching (2989 cm^{-1}), symmetric stretching (2916 cm^{-1}), asymmetric bending (1424 cm^{-1}), and symmetric bending (1237 cm^{-1}) can be assigned by referring to the corresponding frequencies found

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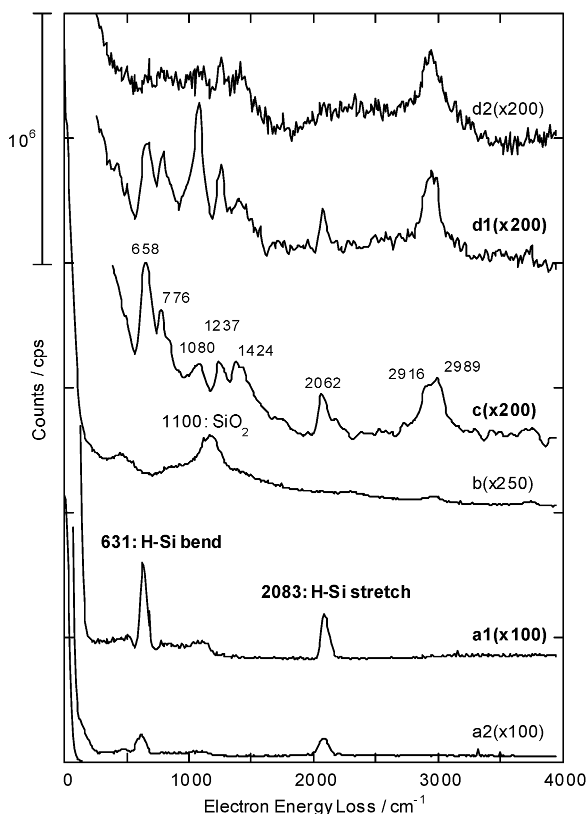

Figure 1. HREELS of H:Si(111), O/Si(111), CH_3:/H:Si(111) as deposited and after annealing in UHV at 573 K for 5 min. Hereafter all spectra were recorded with the incident electron energy = 5.000 eV, the incident angle = 65° from the surface normal, the increment of energy loss = 9.8 cm^{-1}/channel, and the accumulation time = 16 s/channel. The full width at half-maximum of the elastic peak was typically 70 cm^{-1}. (a1, a2) H:Si(111), (a1) exit angle = 65° (specular) and (a2) 70°. (b) O/Si(111), exit angle = 65°. (c) CH_3:/H:Si(111) as deposited, exit angle = 65°. (d1, d2) CH_3:/H:Si(111) after annealing at 573 K for 5 min in UHV, (d1) exit angle = 65° (specular) and (d2) 70°.

in the infrared spectra of methylsilanes.[23−26] Two more vibrations are expected for the CH_3−Si adspecies: the CH_3 rocking mode and the C−Si stretching mode. However, the peaks of these two modes are obscured by coexisting H−Si adsorbates as described below.

The single peak at 2062 cm^{-1} is apparently associated with the stretching mode of H−Si monohydride species, which remained unreplaced during the Grignard reaction. This peak should accompany the H−Si bending mode at about 630 cm^{-1}. Spectra c and d1 contain two peaks in the range of 600−900 cm^{-1}, in which the peaks for the CH_3 rocking mode and the C−Si stretching mode are expected. The intensity contribution of the H−Si mode to the peak at 658 cm^{-1} cannot be neglected, and the vibrations associated with CH_3 groups might be obscured.

The amount of residual H−Si is estimated to be about 30% of the H:Si(111)(1 × 1) surface by comparing the normalized intensities of H−Si peaks in spectra c and d1 with that of a1. The period of time for the Grignard reaction was varied to find the saturation level of carbon uptake by AES,[16] which showed that the carbon uptake could not be gained with the reaction time longer than 4 h. The present samples reached the upper limit of uptake of CH_3 groups. The red shift of H−Si stretching frequency from 2083 to 2062 cm^{-1} upon adsorption of CH_3 groups can be explained by the two-dimensional intermixing of H−Si and CH_3−Si. The STM images[16] showed that the islands of CH_3 were small and distributed randomly, indicating that H−Si adspecies are mostly neighbored by CH_3−Si adspecies, which strongly disturb the long-range ordering of H:Si(111)(1 × 1).

The presence of residual monohydride H−Si species within the CH_3 adlayer prepared by the Grignard reaction was once disproved by an FT-IR measurement in the internal multiple reflection mode, in which the H−Si signal was not detected.[16] As a reason for the depletion of infrared absorption at low H−Si contents, we can consider a dipole screening effect of CH_3 groups surrounding H−Si species.[27] In HREELS, the H−Si stretching signal is generated by the impact scattering mechanism,[15] and we could detect the residual H−Si without the influence of dipole screening.

To avoid the difficulty by obscuration of HREELS peaks by H−Si, we employed D:Si(111)(1 × 1) surfaces in place of H:Si(111)(1 × 1) to shift the H−Si bending mode away from the range of our interest. The D:Si(111) surface was prepared by dipping the O/Si(111) surface in a 30% solution of potassium fluoride (KF) in D_2O (isotope purity >99%) for 40 min at room temperature.

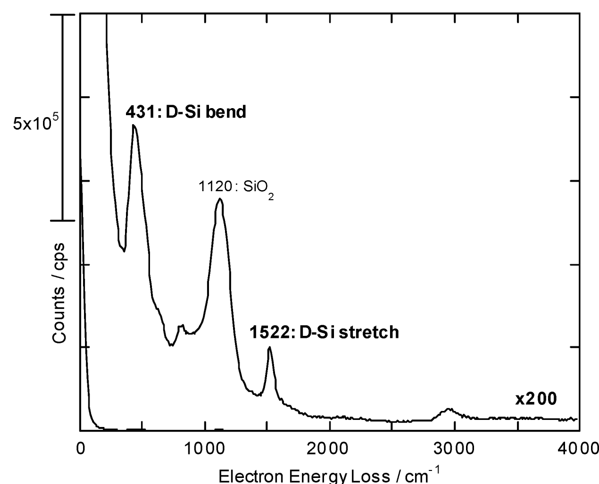

Figure 2. HREELS of D:Si(111) after annealing in UHV at 573 K for 5 min. Exit angle = 65°(specular).

Figure 2 shows HREEL spectra of the D:Si(111) surface after annealing at 573 K for 5 min in UHV. The spectra involve the D−Si stretching mode at 1522 cm^{-1} and the D−Si bending mode at 431 cm^{-1}, which are assigned by dividing the frequencies for H−Si by $\sqrt{2}$. No peaks associated with H−Si are seen, indicating a perfect isotopic purity. The SiO_2 is seen as a peak at 1120 cm^{-1}, corresponding to <0.01 monolayers of SiO_2. AES still did not detect adsorbed O. HREELS at this incident electron energy seems to be particularly sensitive to SiO_2 species. The C−H signals at about 800 and 3000 cm^{-1} are due to hydrocarbon contamination, which is not bonded on Si, as no C−Si signal is involved in this spectrum.

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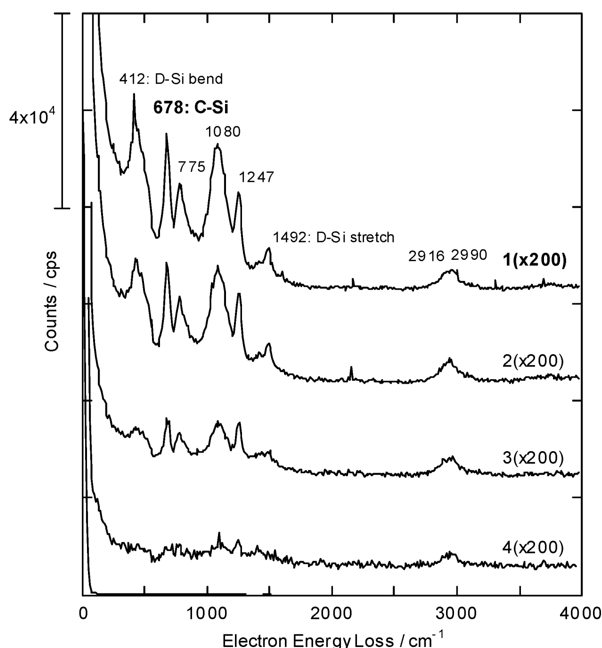

Figure 3. HREELS of CH_3 formed by Grignard reaction on D:Si(111) after annealing in UHV at 573 K for 5 min. (l) exit angle = 65° (specular), (2) = 66°, (3) = 68°, (4) = 70°.

This D:Si(111) surface was subjected to the Grignard reaction in 1 M CH_3MgBr/THF at 65 °C for 18 h and to HREELS measurement after annealing at 573 K in UHV for 5 min. Figure 3 shows the spectra. The peak at 1080 cm^{-1} corresponds to $<3 \times 10^{-3}$ monolayers of SiO_2. The H−Si bending peak seen in Figure 1 shifted to D−Si bending at 412 cm^{-1}, and the two peaks are still seen at 678 and 775 cm^{-1}. These peaks can be assigned to the C−Si stretching mode and CH_3 rocking mode, respectively, based on the comparison with the frequencies of 800−870 and 740−680 cm^{-1} for CH_3-replaced monosilane molecules.[23−26] Since the signals of other hydrocarbons involving $-CH_2-$ or $-CH{=}CH-$ are not visible in the C−H stretching region,[16] these two peaks are considered to be solely originated from the CH_3 adspecies. The frequency of 678 cm^{-1} is close to 669 cm^{-1} of a C−Si single bond in cyclic hydrocarbon adsorbed on Si(100).[20] This C−Si signal can be categorized as a dipole scattering peak as its intensity decreased sharply with deviation of the exit angle from the direction of specular reflection. According to the dipole selection rule, this is consistent with the configuration that the C−Si bond is in parallel to the axis of the robe of the Si sp^3 orbital that protrudes in the direction normal to the surface. The frequency 775 cm^{-1} is lower than the CH_3 rocking frequencies of isolated molecules, and this fact is also indicative of CH_3 groups being bonded on Si atoms embedded in the Si surface. The frequency of CH_3 rocking in a monosilane molecule drastically lowers as the number of non-carbon substituting groups on Si increases.[23−26] The D-Si peaks exhibit red shifts similar to those of CH_3 surface from H:Si(111). The residual amount of D-Si is estimated to be about 30% of the original D:Si(111).

It is now evident that the Grignard reaction on hydrogen-terminated Si(111) forms C−Si covalent bonds for CH_3 groups. The C−Si frequency 678 cm^{-1} found on Si(111) is close to those of CH_3-substituted silane molecules that are composed of genuine covalent bonds.[20] On Cu(111),[28] for example, all of the vibrational frequencies of CH_3 adspecies are lowered significantly, indicating an extended influence of the substrate electronic state. On Si(111), the frequencies are mostly close to those of free molecules, indicating that each bonding involved is localized as a covalent bond between two atoms. The C−Si bond on Si(111) should have a bonding energy similar to that of the free molecule, and therefore, the CH_3 adspecies should have a low lateral mobility and a high chemical stability. The spectrum of CH_3 was unchanged after annealing at a temperature higher than 573 K. We found the CH_3 stretching mode to disappear after annealing at 973 K, indicating decomposition of the CH_3 groups. As reported previously,[16,17] we can deposit longer hydrocarbon chains by using Grignard reagents. HREELS of these adlayers basically gave the same information concerning the residual H−Si species, the existence of C−Si bonds, and the maintenance of intramolecular structure as in the case of CH_3.

4. Conclusion

We observed the C−Si stretching vibration mode at 678 cm^{-1} on D:Si(111) surface treated in CH_3MgBr, unambiguously indicating the formation of C−Si covalent bonds replacing the terminating H by CH_3. A significant amount of H remained unreacted, which obscured the C−Si stretching peak. A D:Si(111) surface was utilized to avoid this spectroscopic obscuration. This deposition method is advantageous in practical processing because the starting surface H:Si(111) can be handled in air and the effects of contaminants can be fairly seized. The formation of C−Si covalent bonds in such a simple process will contribute to the development of novel physics and chemistry on semiconductor surfaces in general and will play an important role in industrial applications.

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