Temperature dependence of the electronic structure of C_{60} films adsorbed on Si(001)-(2×1) and Si(111)-(7×7) surfaces

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We report here the temperature-dependent measurements of the valence spectra, the C 1*s* and the Si 2*p* core level spectra of the one monolayer C_{60} film adsorbed on Si(001)-(2×1) and Si(111)-(7×7) surfaces, using photoelectron spectroscopy. At 300 K, most C_{60} molecules are physisorbed with the coexistence of minority chemisorbed species on both Si(001)-(2×1) and Si(111)-(7×7) surfaces. After annealing the samples at 670 K, C_{60} molecules change the bonding nature to a chemisorption that has both covalent and ionic characters. The covalent bonding orbital is observed at a binding energy of 2.10 eV on both Si surfaces. The amount of charge transfer is estimated to be 0.19 electrons per C_{60} molecule on the Si(001) surface, and to be 0.21 electrons per molecule on the Si(111) surface. We consider the origin of the change in bonding nature to the different distance between two dangling bonds that results from the rearrangement of the surface Si atoms. After annealing at 1070 K, C_{60} molecules decompose and the SiC formation takes progress at the interface. On the Si(001) surface, the molecular orbitals (MO's) disappear at 1120 K and the binding energies of peaks observed in the valence spectra indicate the formation of SiC islands at this temperature. On the Si(111) surface, the disappearance of MO's and the formation of SiC islands are verified at 1170 K. The difference in formation temperature is attributed to the different surface structure. [S0163-1829(99)00328-8]

I. INTRODUCTION

The interaction and the thermal reaction of C_{60} molecules with semiconductor surfaces play an important role in understanding the physical and chemical properties of fullerenes and in developing new material functions for C_{60} molecules. The recent observation of the epitaxial silicon carbide (SiC) formation by the thermal reaction of C_{60} molecules with Si(001)-(2×1) and Si(111)-(7×7) surfaces and the possibility of selective SiC growth,[1] have led to extensive experimental studies on the formation and growth mechanism. However, the temperature dependence of the electronic structures of the C_{60} molecules adsorbed on Si(001)-(2×1) and Si(111)-(7×7) surfaces is not investigated using photoelectron spectroscopy (PES) until now.

The thermal reactions of C_{60} molecules with the Si(001)-(2×1) and Si(111)-(7×7) surfaces are mainly studied by scanning tunneling microscopy (STM) and high-resolution electron-energy-loss spectroscopy (HREELS), though many techniques are used to study the interaction between C_{60} molecules and Si surfaces at 300 K. At 300 K, both chemisorption[2–4] and physisorption[5–7] of C_{60} molecules are reported on a Si(001)-(2×1) surface at a coverage lower than one quarter monolayer (ML), and the majority of the physisorbed species at 1.0-ML.[4,7] On a Si(111)-(7×7) surface, the chemisorption of approximately 30% of C_{60} molecules of a 1.0-ML film and the physisorption of the others molecules are confirmed by HREELS[7] and PES.[8] The majority of the physisorbed C_{60} molecules is also revealed by the observation of the ordered structure of the C_{60} film adsorbed on a Si(111)-(7×7) surface.[9,10] In order to investigate the interaction using HREELS, the assumption that the energies of the vibrational excitations shift linearly with the amount of charge transferred into the lowest unoccupied molecular orbital (LUMO) of a C_{60} molecule is used.[11–15] A coverage of 1.0 ML means the adsorption of two molecules in the 4×3 superlattice on a Si(001) surface,[5,16] and that of seven C_{60} molecules in the 7×7 unit cell on a Si(111) surface.[17] At a temperature of 670 K, the C_{60} islands grown by the layer-plus-island growth (Stranski-Krastanov) mode[2,16,18] desorb, and 1.0 ML films of C_{60} molecules are formed on both Si(001)-(2×1)[16] and Si(111)-(7×7) surfaces.[19] The C_{60} islands are determined to be C_{60} solid by STM,[20] in which the bonding nature is well established as weak as van der Waals interaction.[21] The desorption of the multilayer islands and the remainder of a 1.0-ML film indicate the strong interactions between C_{60} molecules and the Si surfaces at this temperature. These strong interactions are confirmed by the energy shifts of the vibrational excitations of C_{60} molecules using HREELS.[22,23] At 870 K, C_{60} molecules move from

their initial adsorption sites on both Si surfaces at low coverage.[17,24] At a temperature higher than 1070 K, the breaking of the C_{60} cages and the formation of SiC islands are observed by STM.[16,24] The formation temperatures of SiC are determined to be 1120 K on the Si(001) surface and 1170 K on the Si(111) surface by the observation of the Fuchs-Kliewer (FK) mode,[25] i.e., a long-wavelength surface optical phonon, using HREELS.[23] The reconstructed surface structure of the SiC islands grown on a Si(111)-(7×7) surface is cubic 3C-SiC(111)-(2×2) and (3×2) surfaces at 1170 K, and a 3C-SiC(111)-(3×3) surface at 1370 K.[26] Although several studies have been performed on the formation process of the SiC islands using C_{60} molecules as a precursor, little is known about the bonding nature of C_{60} molecules on Si surfaces at high temperature, and no information on the interface structure has been obtained up to now. These informations are important for a complete understanding of the SiC formation process on Si surfaces using C_{60} molecules as a precursor. PES is a very suitable technique for obtaining information to elucidate the bonding features and the interface structure.

PES measurements show the interactions of ionic[27–31] and covalent[8,32,33] characters from whether the electron-occupied LUMO of a C_{60} molecule is observed or not. Recently, a split of the highest occupied molecular orbital (HOMO), due to the symmetry-breaking interaction with the surface, is observed for the C_{60} molecules adsorbed covalently on Al(111) and Al(110) surfaces.[33] In our previous papers, we have reported that the split of the HOMO into two peaks is also observed for C_{60} molecules adsorbed on Si(001)-(2×1)[4] and Si(111)-(7×7)[8] surfaces at 300 K, with a coverage lower than 0.25 ML. The one peak is the HOMO that has shifted to a lower binding energy, and the another one is the bonding state between a C_{60} molecule and the Si substrate. Moreover, the Si 2*p* core-level measurement shows that the bonding state is localized at the interface.[8] For the 1.0-ML films, C_{60} molecules are mainly physisorbed on both Si surfaces.[4,8]

In this paper, we report on the temperature dependence of the valence spectra, the C 1*s* and Si 2*p* core level spectra of the 1.0-ML C_{60} films adsorbed on Si(001)-(2×1) and Si(111)-(7×7) surfaces, and the interface structure during the formation of the SiC islands on Si substrates using PES. The split of the HOMO indicates that the physisorbed C_{60} molecules change their bonding nature to a chemisorption at 670 K. The binding energies of the split peaks are 1.65 and 2.10 eV on the Si(001) surface, and 1.70 and 2.10 eV on the Si(111) surface. We assign the 1.65- and 1.70-eV peaks as the shifted HOMO and the 2.10-eV ones to the bonding state from the thermal dependence of their intensity and the Si 2*p* core level spectra. This bonding state is formed by the sp^3 hybridization of Si and C atoms, likewise the results obtained at 300 K.[4,8] We also observe the energy shifts of the molecular orbitals (MO's) and the C 1*s* core level that suggest the existence of charge transferred into the LUMO. These results indicate the strong interaction at 670 K to have both covalent and ionic characters. At 1070 K, the breaking of the cage of C_{60} molecules is verified by the disappearance of the MO's. The new C 1*s* component observed in the core level spectra indicates the progress of the SiC formation at the interface. The formation temperatures of SiC islands are 1120 and 1170 K on the Si(001)-(2×1) and Si(111)-(7×7) surfaces, respectively.

II. EXPERIMENTAL

PES measurements were performed on the beam line BL-18A at the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan. The experiment was carried out in a UHV system that consists of an analysis chamber and a preparation chamber. A spherical sector analyzer with a total energy resolution of 100 meV at a photon energy of 21.2 eV and angular acceptance of $\pm12°$, was used for all PES measurements. The analysis chamber was also equipped with a low-energy electron diffraction (LEED) system, an Auger-electron spectrometer, and a Mg/Al twin anode x-ray source for the x-ray photoelectron spectroscopy (XPS). The preparation chamber was used for the deposition of C_{60} molecules on the samples without contaminating the analysis chamber by C atoms. The base pressures were 2×10^{-11} Torr in the analysis chamber and below 1×10^{-9} Torr in the preparation one. A photon energy of 21.2 eV was used for the valence PES measurements, and a photon energy of 130 eV for the measurements of the Si 2*p* core level using the *p*-polarized synchrotron radiation (SR) light. For the measurement of the C 1*s* core level, we used the Mg Kα line whose photon energy is 1253.6 eV. The incidence angle of both the SR light and the Mg Kα line was 45° from the surface normal direction. The emission angle of the photoelectron was 0°.

The Si(001) and Si(111) samples were cut from B-doped (*p*-type) and P-doped (*n*-type) Si wafers, respectively. Both samples have the electrical resistivities of 1000 Ω cm and sizes of $7\times15\times0.5$ mm^3. We prepared the Si samples chemically following the Shiraki method[34] and then introduced them into the UHV chamber. The samples were annealed at 1150 K for 10 min, and then heated up to 1520 K for 5 sec by direct resistive heating in the UHV chamber to obtain the clean reconstructed Si(001)-(2×1) and Si(111)-(7×7) surfaces. The sample was spontaneously cooled for several minutes after heating up to 1520 K before the C_{60} deposition. We checked the qualities of the surfaces by the observation of clear (2×1) and (7×7) LEED patterns. The cleanliness of the surface was verified by Auger-electron spectroscopy and the lack of the O 1*s* and C 1*s* peaks in the XPS spectra. The sample temperature was measured by an infrared pyrometer with an emissivity setting of 0.64. All measurements were done at room temperature.

We prepared and purified the C_{60} powder carefully with the following procedure. First, the C_{60} powder was chromatographically separated from carbon soot. Second, the C_{60} was rinsed in tetrahydrofuran (THF) with ultrasonic cleaner in order to eliminate hydrocarbons and other impurities. Finally, C_{60} was distilled in vacuum. After these procedures, C_{60} powder was loaded in a quartz crucible and then introduced into the preparation chamber. The C_{60} powder was carefully outgassed below 600 K for over 24 hours prior to evaporation. The thickness was monitored by a quartz-crystal oscillator. The deposition rate was approximately 0.2 nm/min, and a thickness of 1.0 nm was estimated to be 1.0 ML of C_{60} by STM.[7] Using the deposition rate of 0.2 nm/min, no overlayer and no island formation were observed for a 1.0-ML C_{60} film in STM.[7] In the present experiment, we have used the same preparation chamber as that employed

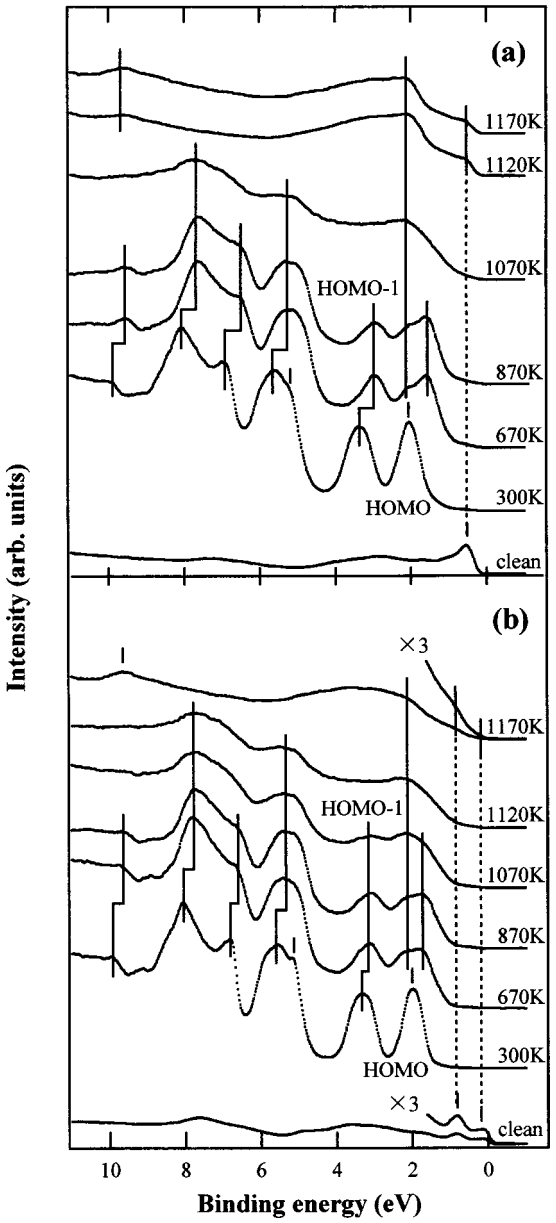

FIG. 1. Valence spectra of the clean surfaces, those after adsorbed a 1.0-ML C_{60} film on the Si surfaces, and after annealing the samples at 670, 870, 1070, 1120, and 1170 K. (a) and (b) show the results on the Si(001)-(2×1) and Si(111)-(7×7) surfaces, respectively. The samples were annealing for 300 sec, and then cooled down to room temperature before the measurements. All spectra were measured by the *p*-polarized synchrotron radiation light with a photon energy of 21.2 eV.

for the STM measurements to make the sample under the same condition.

III. RESULTS

A. Valence PES

Figure 1 shows the temperature-dependent valence spectra of C_{60} molecules adsorbed on Si surfaces. The valence spectrum of the Si(001)-(2×1) clean surface and those obtained after annealing the 1.0-ML C_{60} film adsorbed on a Si(001)-(2×1) surface at different temperatures are displayed in Fig. 1(a). The spectra of the C_{60}-adsorbed Si(111)-(7×7) surface are shown in Fig. 1(b). We annealed the sample for 300 sec at each temperature depicted in the figure and then cooled it down to room temperature before the measurement. The spectrum of the clean surface shows clearly the dangling bond state[35,36] of the Si(001)-(2×1) surface at 0.55 eV and the occupied surface states of the Si(111)-(7×7) surface at 0.20 and 0.90 eV. The surface states of the Si(111)-(7×7) surface are mainly localized at the adatom sites and the rest atoms sites of the dimer-adatom-stacking (DAS) fault structure.[37] After a 1.0-ML C_{60} film adsorption at 300 K, the surface states disappear and the MO's of a C_{60} molecule appear. The binding energies of the MO's are 2.05, 3.40, 5.15, 5.60, 7.00, 8.10, and 9.95 eV in Fig. 1(a), and 2.00, 3.30, 5.10, 5.60, 6.80, 8.10, and 9.90 eV in Fig. 1(b). Taking into account the binding energy reported previously, [8,27–33,38] we assign the 2.05- and 2.00-eV peaks to the HOMO, and the 3.40- and 3.30-eV peaks to the second highest occupied molecular orbital (HOMO-1). The HOMO is a fivefold degenerate MO's with h_u symmetry in the I_h point group, and the HOMO-1 is the overlap of a fourfold and fivefold degenerate MO's that have g_g and h_g symmetries, respectively.[39,40] Since the spectral features of the 1.0-ML films are the same as that of a C_{60} solid, where C_{60} molecules interact each other with van der Waals force, we consider that most of C_{60} molecules are physisorbed on both surfaces at 300 K. This consideration agrees well with the previous result of C_{60} molecules on the Si(001) surface[4] where the chemisorption is observed only at a coverage lower than 0.25 ML, and the previous studies on the Si(111) surface in which approximately 70% of C_{60} molecules of a 1.0-ML film is reported to be physisorbed and 30% to be chemisorbed.[7,8] On metal surfaces,[27–33,38] the substrate electronic states are observed even at a coverage of 1.0-ML. However, no substrate evidence is observed for the spectra of the 1.0-ML C_{60} film at 300 K in Figs. 1(a) and 1(b). This difference comes from the low cross section of the substrate states and the disappearance of the surface states that are located into the HOMO-LUMO gap of a C_{60} molecule. The disappearance of the Si surface states might result from the minority chemisorbed C_{60} molecules, because these molecules change the electronic states of the surface atoms and/or the density of surface states interacting with the dangling bonds. Moreover, the substrate states become invisible even at a coverage of approximately 0.5 ML on semiconductors like Si(001)-(2×1),[4] Si(111)-(7×7)[8], and GeS(001)[41] surfaces.

After annealing the 1.0-ML C_{60} film adsorbed samples at 670 K, we clearly observe the splits of the HOMO's into two peaks, the disappearances of the small shoulders around 5.1 eV, and the shifts of the other MO's to the lower binding energy side on both surfaces. The binding energies of the split peaks are 1.60 and 2.10 eV, and those of the shifted MO's are 3.00, 5.20, 6.60, 7.65, and 9.60 eV on the Si(001)-(2×1) surface. On the Si(111)-(7×7) surface, the split peaks are observed at binding energies of 1.75 and 2.10 eV, and the shifted peaks at 3.10, 5.40, 6.65, 7.75, and 9.70 eV. Furthermore, we observe the broadening in the full width at half maximum (FWHM) of all MO's in Figs. 1(a) and 1(b), e.g., the FWHM of the HOMO-1 at 670 K is 1.2 times larger than that at 300 K. The broadening in FWHM results from the removal of the degeneracy. This removal suggests the strong interaction between C_{60} molecules and the Si surfaces,

and, therefore, the change in the bonding nature of C_{60} molecules. That is, the physisorbed C_{60} molecules become a chemisorbed species and all molecules are chemisorbed at 670 K. The profiles of the spectra at 870 K are the same as those at 670 K in both Figs. 1(a) and 1(b), indicating that there is no change in interaction between C_{60} molecules and the surfaces within this temperature range.

After annealing the samples at a temperature higher than 1070 K, the valence spectra show different behavior on the Si(001) and Si(111) surfaces. On the Si(001) surface, the profiles of the spectrum change drastically after annealing the sample at 1070 K. The peaks indicating the MO's of C_{60} molecules disappear, except the 5.20- and 7.65-eV peaks. The FWHM's and the intensities of the 5.20- and 7.65-eV peaks become broad and small. These results indicate that the breakdown of the C_{60} cages occurs at 1070 K on the Si(001) surface. The breakdown of the cage is also reported by HREELS from the disappearance of the vibrational modes of a C_{60} molecule at the same temperature.[22] The profile of the spectrum is similar to that of an amorphous carbon film in which peaks are observed at binding energies of 3.5, 5.0, and 7.8 eV, and to that of an polycrystalline diamond film in which a broad peak is observed around 7.5 eV.[42,43] After annealing at 1120 K, the MO's of C_{60} molecules disappear completely. The peaks are observed at 0.55, 2.10, and 9.65 eV. In the valence spectrum of a Si-rich 3C-SiC(001)-(2×1) surface, a dominant peak is observed at a binding energy of 2.6 eV and a small peak at 10.4 eV with a photon energy of 21.2 eV,[44] and two peaks are observed at 3 eV and 12 eV with a photon energy of 151.4 eV.[45] The intensity ratio and the difference in binding energy of the two peaks observed previously[44,45] agree well with those of the 2.10- and 9.65-eV peaks observed in Fig. 1(a). Therefore, we consider that SiC islands are formed on the Si(001) substrate after annealing the 1.0-ML C_{60} film adsorbed sample at 1120 K. This consideration is consistent with the observation of the FK mode[25] of SiC by HREELS[23] at the same temperature. The spectrum obtained after annealing the sample at 1170 K has the same profile with that at 1120 K, indicating that there is no difference in the characteristics of SiC islands.

On the Si(111) surface, a dramatic change of the spectrum feature is also observed after annealing the sample at 1070 K. The 3.10-, 5.40-, and 7.75-eV peaks indicating the presence of C_{60} molecules become broad and small. This change indicates the large symmetry breaking of C_{60} molecules that results from the strong interaction between C_{60} molecules and the substrate, likewise the result on the Si(001) surface. The 5.40- and 7.75-eV peaks do not disappear even after annealing at 1120 K. After annealing the sample at 1170 K, the MO's of C_{60} molecules disappear completely and new peaks appear at binding energies of 0.20, 0.90, 3.50, and 9.65 eV. Since the profile of the spectrum is in good agreement with that of the 3C-SiC in which a broad peak is observed at 4 eV and a small feature around 10 eV,[46] we consider the spectrum obtained after annealing the 1.0-ML C_{60} film adsorbed sample at 1170 K to be that of the SiC islands grown on the Si(111) substrate. The observations of the FK mode[25] by HREELS,[22,23] and the 3C-SiC(111)-(2×2) and (3×2) reconstructed surfaces of islands by STM[26] support our consideration.

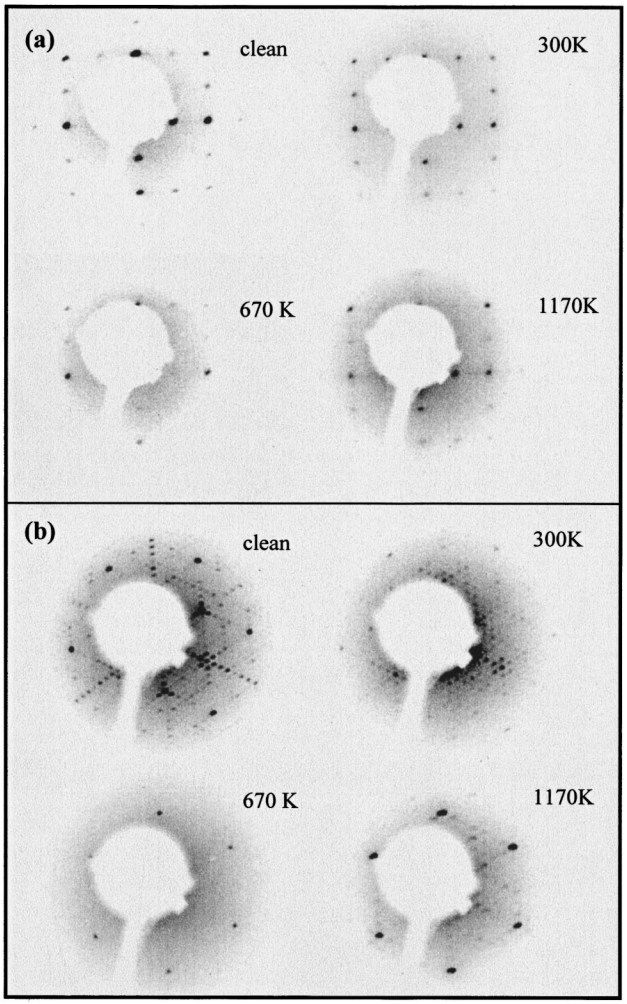

FIG. 2. LEED patterns of the clean and C_{60} molecules adsorbed on a Si(001)-(2×1) surface obtained at different annealing temperature in (a) and those of the C_{60} film adsorbed on a Si(111)-(7×7) surface in (b). The temperatures of the C_{60} adsorbed samples are 300, 670, and 1120 K in (a), and 300, 670, and 1170 K in (b). All patterns are obtained with a primary energy of 56 eV in (a). In (b), a primary electron energy of 108 eV is used for the clean surface, 77 eV is used for the C_{60} adsorbed surface at 300 K, and 46 eV after annealing the sample at 670 and 1170 K.

The change in profiles of the valence spectra indicates that the surface phase changes three times in the thermal reaction of C_{60} molecules with the Si surfaces, i.e., at 670, 1070, and 1120 K on the Si(001) surface, and at 670, 1070, and 1170 K on the Si(111) surface. Thus, four different surface phases exist on both Si surfaces within a temperature range from 300 to 1170 K. This number of surface phases is the same with that reported in the previous STM[19] and HREELS[22,23] studies.

B. LEED

Figure 2(a) shows the LEED pattern of the Si(001)-(2×1) clean surface and those of the 1.0-ML C_{60} film adsorbed Si(001)-(2×1) surface obtained after annealing the sample at different temperatures. The patterns for the 1.0-ML C_{60} film adsorbed on a Si(111)-(7×7) surface are displayed in Fig. 2(b). All patterns are obtained with a primary electron

energy of 56 eV in Fig. 2(a). In Fig. 2(b), we used a primary electron energy of 108 eV for the clean surface, 77 eV for the 1.0-ML C_{60} film adsorbed on a Si(111) surface at 300 K, and 46 eV after annealing the sample at 670 and 1170 K.

For the clean surfaces, the LEED spots originated from the (2×1) and the (7×7) structures are clearly observed in Figs. 2(a) and 2(b), respectively. The observations of the clear (2×1) and (7×7) spots suggest the high quality of the clean surfaces. These spots are still observed after the adsorption of the 1.0-ML C_{60} film at 300 K on both surfaces. The observations of the (2×1) and (7×7) spots for the 1.0-ML C_{60} film adsorbed on Si surfaces are also reported in the previous study where the coverage is confirmed by STM.[7] Since the Si surfaces are perfectly covered with a 1.0-ML C_{60} film, the observations of the (2×1) and (7×7) spots indicate that the surface structures hardly change upon the C_{60} adsorption, and, therefore, that most of the C_{60} molecules adsorbed weakly on both Si(001)-(2×1) and Si(111)-(7×7) surfaces at 300 K. After annealing the samples at 670 K, the (2×1) LEED spots become very weak on the Si(001) surface, and the (7×7) LEED spots disappear and only the (1×1) spots are observed on the Si(111) surface. On the Si(111) surface, weak (7×7) LEED spots reappear at 1170 K.

If C_{60} islands are formed and bare reconstructed Si surfaces remain after the initial adsorption, the (2×1) and (7×7) spots should be observed even after annealing at 670 K because the structures of the bare reconstructed Si surfaces do not change at this temperature. Moreover, the multilayers formation should weaken the intensity of these LEED spots. Therefore, the changes in the LEED spots also support the formation of a 1.0-ML C_{60} film on both Si surfaces at 300 K in the present experiment.

C. C 1*s* core level PES

Figure 3 shows the temperature-dependent C 1*s* core level spectra of the 1.0-ML C_{60} film adsorbed on a Si(001)-(2×1) surface in Fig. 3(a) and those of the C_{60} film adsorbed on a Si(111)-(7×7) surface in Fig. 3(b). The annealing temperatures are 300, 670, 870, 1070, 1120, and 1170 K. At 300 K, the C 1*s* core levels are observed at binding energies of 284.9 eV on the Si(001) surface and 284.8 eV on the Si(111) one. After annealing the samples at 670 K, the C 1*s* core level shifts to 284.5 eV on both surfaces, and no change is observed in the spectrum profile until 870 K. The symmetric 284.5-eV peaks suggest that no electron-hole pair is excited, and the C_{60} molecules are not metallic like the results of the 1.0-ML C_{60} films adsorbed on metal surfaces.[28–32] The insulating C_{60} molecule agrees well with the scarce density of occupied electrons at the Fermi level in the valence spectra.

After annealing the samples at 1070 K, the spectra become asymmetric with tails at the lower binding energy sides in both Figs. 3(a) and 3(b). The asymmetric peak is also observed at 1120 K on the Si(111) surface. In order to analyze these asymmetric spectra, we have deconvoluted them with Voigt line shapes, a convolution of a Gaussian and a Lorentzian. The results of the deconvolution are shown in Fig. 4. The open circles and the solid lines overlapped with the open circles are the experimental data points and the fitting curves, respectively. Each hatching indicates different

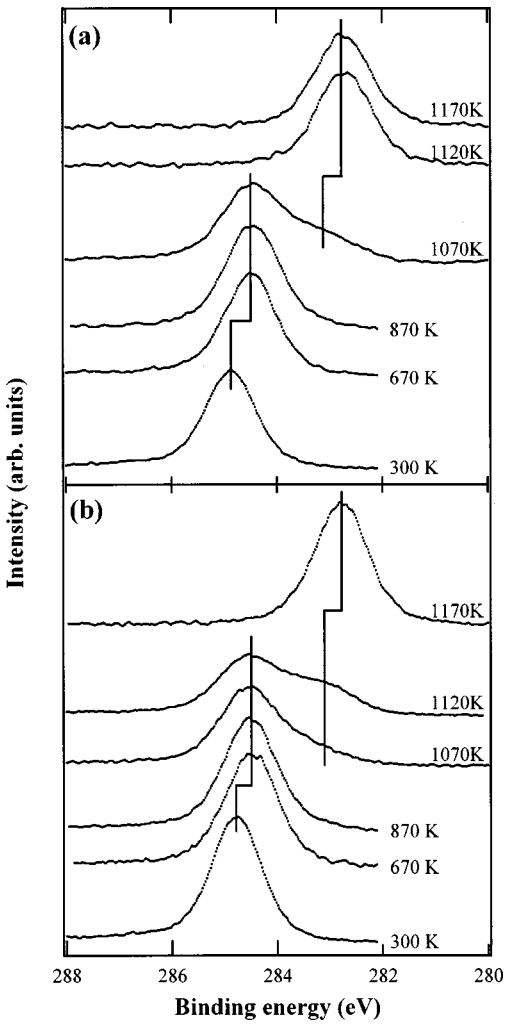

FIG. 3. Temperature-dependent C 1*s* spectra of the 1.0-ML C_{60} film adsorbed on Si(001)-(2×1) (a) and Si(111)-(7×7) (b) surfaces, observed by the Mg Kα line. The temperatures are 300, 670, 870, 1070, 1120, and 1170 K in both (a) and (b).

C 1*s* components. We obtain the best fit of each spectrum using two different components, C_1 and C_2, which binding energies are 284.5 and 283.1 eV, respectively. The intensities of the C_2 components relative to the C_1 ones are tabulated in Table I.

After annealing at a temperature above 1120 K, the asymmetric tail disappears and a symmetric peak is observed at 282.8 eV on the Si(001) surface. On the Si(111) surface, a symmetric peak is observed at a binding energy of 282.8 eV after annealing the sample at 1170 K. The binding energy of 282.8 eV agrees well with that of the C 1*s* core level of a SiC film reported previously.[45–47] The results on the C 1*s* core level also indicate the different formation temperature of SiC islands, and the presence of four different surface phases as suggested in the valence spectra.

D. Si 2*p* core level PES

The Si 2*p* core level spectra of the clean surfaces, those after adsorbed a 1.0-ML C_{60} film on the Si surfaces at 300 K, and after annealing the C_{60} adsorbed samples at 670, 1070, 1120, and 1170 K are displayed in Fig. 5. Figures 5(a) and 5(b) show the results on the Si(001)-(2×1) and Si(111)-(7

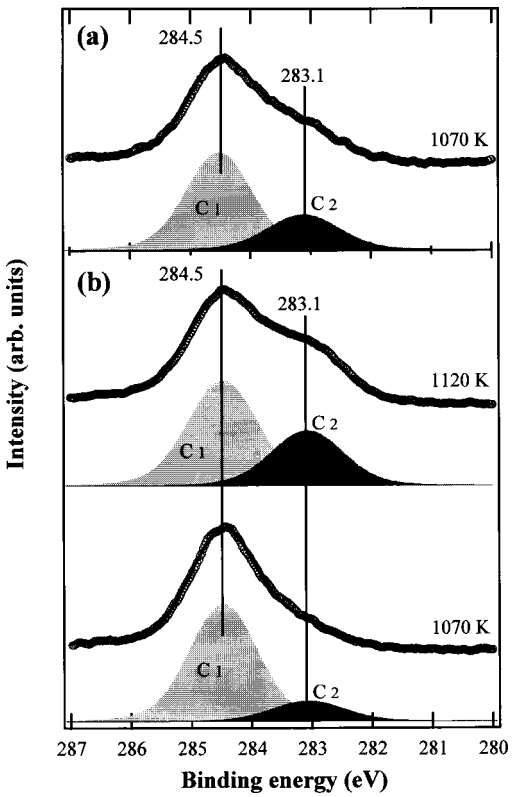

FIG. 4. C 1*s* core level spectrum measured after annealing the 1.0-ML film adsorbed on a Si(001)-(2×1) surface at 1070 K (a), and those after annealing the C_{60} film adsorbed on a Si(111)-(7×7) surface at 1070 and 1120 K (b). The open circles are the experimental data, and the solid lines overlapped with open circles are the fitting curves. Each hatching indicates a different C 1*s* component.

×7) surfaces, respectively. A photon energy of 130 eV is used for all spectra. In order to analyze the spectra by a standard least-squares-fitting method, we have used Voigt line shapes. Considering the previous report,[48] we use a parameter of 0.608 eV for the spin-orbit splitting. A polynomial background is subtracted before the decomposition of the spectrum. The open circles are the experimental data points and the solid lines overlapped with the open circles are the fitting curves. The solid lines indicate the bulk components, and each hatching different surface components.

For the Si(001)-(2×1) clean surface, we obtain the best fits of the spectrum using three different components, i.e., the bulk component *B*, and the surface components S_{a1} and S_{a2}. The binding energy shifts of the S_{a1} and S_{a2} components relative to the *B* one are 0.262 and −0.495 eV, respectively.

TABLE I. The binding energies and intensities of the C 1*s* components used for the line-shape analysis in Fig. 4. Underlines indicate the normalized components.

		C_1	C_2
Binding energy	(eV)	284.5	283.1
Si(001)	1070-K Intensity	<u>1.000</u>	0.390
Si(111)	1070-K Intensity	<u>1.000</u>	0.180
	1120-K Intensity	<u>1.000</u>	0.530

The positive value of the energy shift represents the shift to a higher binding energy. The intensity of the S_{a1} and S_{a2} components relative to the bulk ones are 0.309 and 0.179. Taking into account the previous results,[49–51] the S_{a1} and S_{a2} components are assigned to the second-layer atoms, and to the raised atoms of the asymmetric dimer,[52–54] respectively. In fact, the intensity ratio, $I(S_{a1})/I(S_{a2})=1.73$, agrees well with the ratio of surface atoms in the (2×1) unit cell, i.e., (second layer atoms)/(raised atoms of the dimer)=2/1=2. $I(S_{a1})$ and $I(S_{a2})$ indicate the relative intensities of the S_{a1} and S_{a2} components. Unfortunately, we are not able to resolve the component due to the down atoms of the asymmetric dimer, located at a higher binding energy of approximately 60 meV than the bulk component,[49,50] because of the poorer resolution of the experimental system.

For the Si(111)-(7×7) clean surface, the best fit of the spectrum is also obtained using three different components, i.e., the bulk component *B*, and the surface components S_{b1} and S_{b2}. The determined binding energy shifts and intensities relative to *B* are 0.314 eV and 0.310 for the S_{b1} component, and −0.716 eV and 0.038 for the S_{b2} component. Considering the energy shifts of the surface components reported previously,[55–57] we assign the S_{b1} and S_{b2} components to the adatoms and the atoms bonded with them, and to the rest atoms. The intensity ratio, $I(S_{b1})/I(S_{b2})=8.21$, is in good agreement with the ratio of surface atoms in the (7×7) unit cell, i.e., (adatoms+pedestal atoms)/(rest atoms)=(12+12×3)/6=8. $I(S_{b1})$ and $I(S_{b2})$ are the relative intensities of S_{b1} and S_{b2}. A pedestal atom is the atom bonded with an adatom in the DAS structure,[37] and, therefore, the number of pedestal atoms is three times larger than that of the adatom in the (7×7) unit cell.

After adsorbing a 1.0-ML C_{60} film on the Si(001)-(2×1) surface, the best fit of the Si 2*p* core level spectra are obtained using four different components at 300 and 670 K, three different components at 1070 K, and four different components at 1120 and 1170 K. For the results on the Si(111) surface, we used four different components at 300 and 670 K, three different components at 1070 and 1120 K, and four different components at 1170 K. The bulk components are labeled as *B*, and the surface ones as *S* with different subscripts as shown in each spectrum. Assuming that the charge states of the second-layer atoms and those of the atoms bonded with the outermost Si atoms hardly change upon both the C_{60} adsorption and the thermal reaction, the origins of the S_{a3}, S_{a6}, S_{a9}, S_{a11}, and S_{a14} might be the same as that of S_{a1}, and those of S_{b3}, S_{b6}, S_{b9}, S_{b11}, and S_{b13} components the same as S_{b1}, because the same binding energy suggests the same charge state. The term, the atoms bonded with the outermost Si atoms, is expressed especially because the pedestal atoms are the first layer atoms in the DAS structure[37] and does not belong to the second-layer atoms.

On the Si(001) surface, the surface component due to the raised atoms disappears and two new components, S_{a4} and S_{a5}, appear after the adsorption of C_{60} molecules at 300 K. On the Si(111) surface, two undetermined surface components, S_{b4}, and S_{b5} are observed at the same temperature. Taking into account the sign of the energy shift, the almost same intensity, and the unchanged surface structure confirmed by LEED, the S_{b4} component is considered to be due

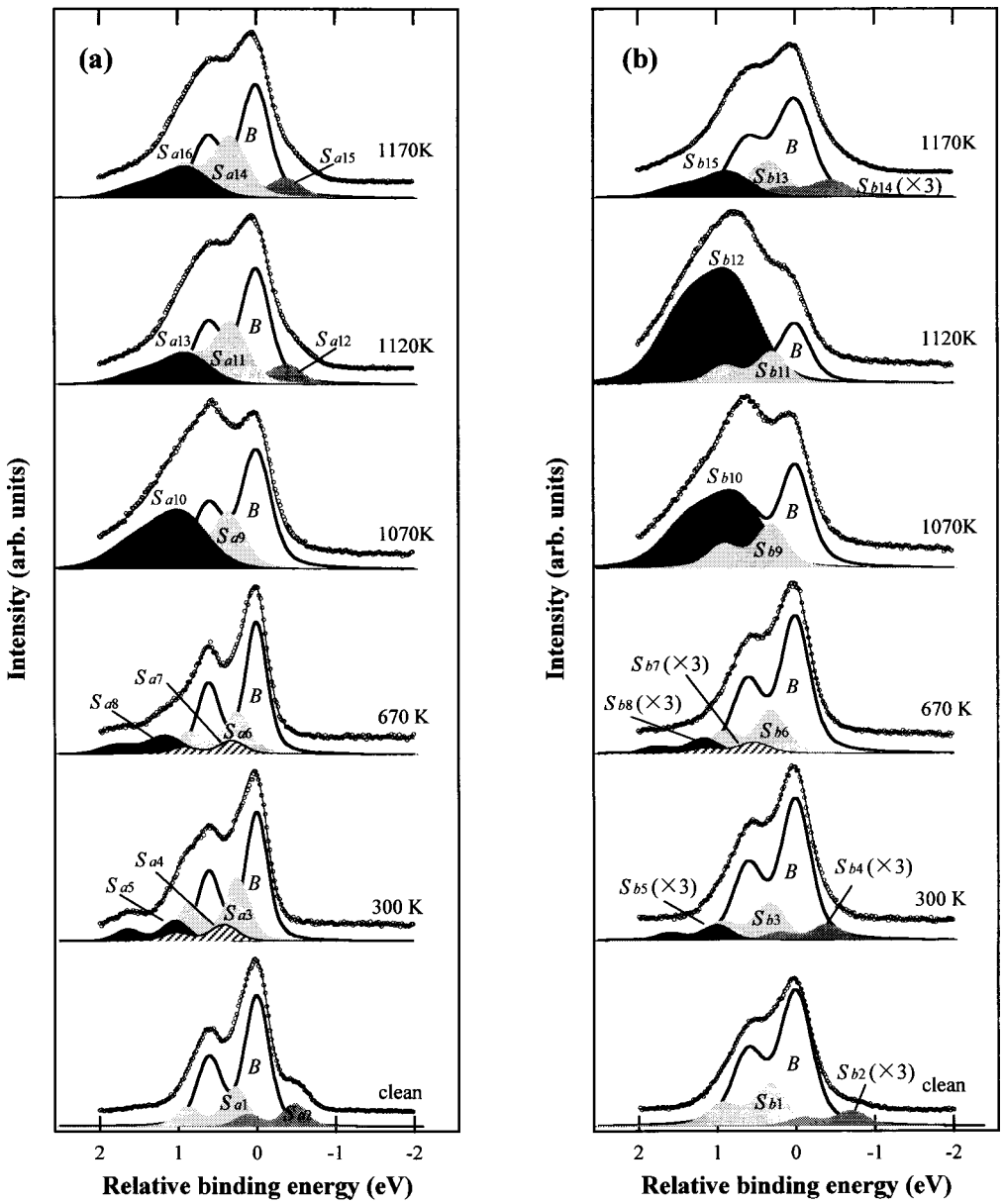

FIG. 5. Si 2*p* core level spectra of the clean surfaces, those after adsorbed a 1.0-ML C_{60} film on the Si surfaces, and after annealing the samples at 670, 1070, 1120, and 1170 K. (a) and (b) show the results of the Si(001)-(2×1) and Si(111)-(7×7) surfaces, respectively. The photon energy is 130 eV for all spectra. The open circles are the experimental data, and the solid lines overlapped with open circles are the fitting curves. The solid line labeled *B* is the bulk component. Each hatching indicates a different surface component. The same hatching pattern represents that the surface component has the same origin.

to the rest atoms. The difference in energy shift of S_{b2} and S_{b4} comes from the different charge states, and suggests the change in electronic structures of surface atoms. This change is consistent with the disappearances of the surface states in the valence spectra. The S_{b5} component observed on the Si(111) surface at 300 K is reported to be due to the surface Si atoms bonded covalently with a C_{60} molecule from the same energy shift with that of the Si 2*p* core level of SiC,[45–47] approximately 1 eV.[8] Since the energy shift is the same with that of S_{b5}, the S_{a5} component of the Si(001) surface might be also due to the surface Si atoms that make a covalent bond with a C_{60} molecule. The presence of the covalent bonded species at 300 K agrees well with the observation of the bonding state at a coverage lower than 0.25 ML in the valence spectra of C_{60} molecules adsorbed on a Si(001) surface.[4] Therefore, we consider that covalent bonded C_{60} molecules exist as minority species on both Si(001) and Si(111) surfaces at 300 K. The origin of S_{a4} is discussed below.

IV. DISCUSSION

A. Bonding nature of C_{60} molecules at 670 K

In order to determine the bonding nature at 670 K, we first consider the origin of the split HOMO's and then the origins of the energy shifts of the C 1*s* core level and MO's. The STM image obtained after annealing the C_{60} film adsorbed on a Si(111) surface at 670 K[19] does not show any dimerization and/or polymerization of C_{60} molecules, and the vibra-

tional modes of C_{60} are clearly observed and no mode originated by the dimerization of C_{60} is observed at 670 K in HREELS.[22,23] These results suggest that the split HOMO's observed in Fig. 1 are originated by the change in the bonding nature, namely, the change from a physisorption to a chemisorption. Since the 1.60- and 1.75-eV peaks observed at 670 K disappear at the temperatures where MO's of C_{60} molecules become invisible in Fig. 1, the origins of these peaks are MO's. We conclude that the 1.60- and 1.75-eV peaks are the HOMO's that have shifted to a lower binding energy, because the binding energies of 1.60 and 1.75 eV are rather higher than that of the electron-occupied LUMO of a C_{60} molecule.[58] In contrast, the 2.10-eV peaks are still observed at 1170 K on both Si surfaces. At this temperature, the cages of C_{60} molecules are perfectly broken and SiC islands are formed.

To resolve the origin of the 2.10-eV peaks, we consider the Si 2*p* core level spectra. The energy shifts of the S_{a8} and S_{b8} components observed at 670 K in Figs. 5(a) and 5(b) are almost the same with that of the Si 2*p* core level of SiC.[45–47] This equivalency in energy shift suggests the origins of the S_{a8} and S_{b8} components to be the Si atoms bonded covalently with C atoms, and indicates the existence of the covalent Si-C bond at 670 K on both surfaces. The covalent bond of C and Si atoms is formed by two sp^3 hybridizations and all C atoms of a C_{60} molecule have a sp^2-like hybridized character. Thus, the hybridization of a C atom should transform from a sp^2-like hybridized character into the sp^3 one to form a covalent bond. The sp^3 hybridization of a C atom is formed breaking a double bond of a C_{60} molecule.

The existence of a covalent bond indicates the reduction in symmetry of a C_{60} molecule as well as the formation of the bonding orbital. Since these two occurrences are inseparable, the origins of the 2.10-eV peaks are possible to be both the split HOMO originated by the reduced symmetry, and the bonding state. The split HOMO is observed for C_{60} dimers,[59–61] whose point symmetry is changed from I_h to D_{2h}. In the valence spectrum of the RbC_{60} dimer, which is obtained with a photon energy of 22 eV, only a small shoulder is observed at the lower binding energy side of the HOMO following the broadening of the other MO's.[60] For the photoinduced C_{60} dimer,[61] the split HOMO is observed with photon energies of 10.5, 40, and 65 eV, but no split is confirmed with a photon energy of 23 eV. These results suggest that the cross section of the split HOMO is small at a photon energy of approximately 20 eV, and, therefore, that the split HOMO is maybe hardly visible in the present experiment. In order to consider the bonding orbital, we regard the energy positions of the 2.10-eV peaks. The bonding states of C_{60} molecules adsorbed on Si surfaces at 300 K are observed at binding energies 0.8–1.0 eV lower than those of the HOMO-1's.[3,4,8] In Fig. 1, the differences in binding energies between the 2.10-eV peaks and the HOMO-1's are 0.90 eV on the Si(001) surface and 1.00 eV on the Si(111) one. The binding energy of 2.10 eV is also close to that of the bonding states between hydrocarbon molecules and Si surfaces, [62–68] whose C atoms rehybridize to a state near sp^3 and form covalent bonds with the dangling bonds of Si surfaces like the present result on C_{60} molecules. Furthermore, the small shift in the binding energy of the Si-C bond observed annealing the acetylene-adsorbed Si surface from 300 to 1200 K,[68] suggests that it is not strange to observe the Si-C bond at the same binding energy before and after the decomposition of C_{60} molecules. Taking into account these results, we consider that the bonding state might be the most appropriate origin for the 2.10-eV peaks.

In this case, the FWHM's of the 2.10-eV peaks at 670 K and those of the SiC are different. These differences in FWHM's are able to be explained by two origins. The first origin is the broadening of the 2.10-eV peak due to the dispersion, because the bonding at 670 K is localized at the interface between the Si surfaces and C_{60} molecules, and the Si-C bonding orbitals in a SiC island should have a correlation between them. The second origin is the variation of Si-C bonds. To determine the origin, we consider the Si 2*p* core level spectra obtained at 670 and 1170 K. The S_{a16} and S_{b15} components observed in Fig. 5 are considered to be due to the Si atoms of the SiC islands from their binding energies. The Gaussian widths of the S_{a16} and S_{b15} components, 0.511 and 0.475 eV, are larger than those of the S_{a8} and S_{b8} components, 0.345 and 0.291 eV. Since a larger Gaussian width suggests the larger variation of Si atoms that have a slightly different charge state, we consider that the SiC islands are amorphouslike SiC and the latter origin is more likely to explain the difference in FWHM's of the 2.10-eV peaks. The amorphouslike SiC island formation is also determined by HREELS.[22]

The annealing at 670 K induces energy shifts in the C 1*s* core level to the lower binding energy sides on both Si(001) and Si(111) surfaces as shown in Figs. 3(a) and 3(b). It is difficult to obtain quantitative information from the shift in the C 1*s* core level spectra, because it is referenced to the Fermi level and usually depends on the work function. On the contrary, the C_{60} film interacted by van der Waals force with the Si surface is insulating and its C 1 *s* level is, therefore, referenced to the vacuum level. We are only able to extract qualitative information. One origin for the energy shifts of the C 1*s* core level observed in Figs. 3(a) and 3(b) is the initial state effect, namely, the charge state. Another origin is the final-state effect, namely the screening effect. On metal surfaces,[28–32,69] where all C_{60} molecules of the 1.0-ML film are chemisorbed, the C 1*s* core level is always situated at a binding energy lower than that of a thick film. This result indicates that the shift does not depend on the work function and that the final-state screening is the more important effect.[31] Two origins contribute to the final-state effect, the image charge screening and the charge transfer screening. The former is a nonlocal effect, and the latter is a local effect due to the transferred charge. The change in bonding nature produces a different image plane for the C_{60} film adsorbed on an Si surface. However, no shift is observed within a coverage range of 0.25 to 5.0 ML in the C 1*s* core level measurement of C_{60} molecules adsorbed on a Si(111)-(7×7) surface in which C_{60} molecules interact covalently with the Si surface at low coverage.[8] Since the formation of covalent bonds hardly affects the energy shift, the shift observed in the C 1*s* core level at 670 K should be caused by charge transfer. Moreover, the shift observed on metal surfaces is usually accompanied with the charge transfer from occupied electronic state of surface metal atoms to C_{60} molecules.[28–32] Unfortunately, we are not able to determine which is the most important screening effect within the present results,

i.e., the local charge-transfer effect or the effect that results from the change of the image plane induced by charge transfer. Nevertheless, the energy shifts observed at 670 K on both Si(001) and Si(111) surfaces result from a small amount of charge transfer into the LUMO of C_{60} molecules in either case.

The shifts of MO's observed in the valence spectra are able to be explained by the hybridizations of the MO's with the substrate bands and the effect of the charge transfer from the substrate into the LUMO. Since no shift is observed for C_{60} molecules interacted covalently with surface Si atoms at 300 K,[8] the latter origin is the more plausible. In this case, the low intensity at the Fermi level in Figs. 1 is well explained by the low cross section of the partial filling LUMO,[32] e.g., the electron-occupied LUMO is scarcely visible on a Ag(111) surface[27] and on a Au(110) surface[32] where the interactions between the surfaces and C_{60} molecules are reported to have ionic characters. Moreover, the binding energies of 1.60 and 1.75 eV are consistent with the previous studies in which the small binding energy of the HOMO resulting from the charge transfer into the LUMO is observed at 1.85 eV on the Ag(111) surface[27], and at 1.7 eV on the Cu(111)[29] and Au(110)[32] surfaces. Therefore, we consider the origin of the energy shift of MO's as the charge transfer into the LUMO.

These evidences of charge transfer imply the existence of Si 2*p* components due to the surface Si atoms that transfer charge to C_{60} molecules. Since charges are transferred from the Si dangling bonds into the LUMO of C_{60} molecules, these surface atoms should be charged positively. A Si 2*p* component of a Si atom charged positively has a binding energy higher than that of the bulk one.[70,71] The Si 2*p* spectra measured after annealing the 1.0-ML C_{60} films adsorbed on Si(001) and Si(111) surfaces at 670 K show undetermined positively charged surface components, S_{a7} and S_{b7}. No component within this energy range is observed in the spectrum of C_{60} molecules adsorbed on a Si(111) surface at 300 K in Fig. 5, where the interaction has only a covalent character.[8] Therefore, the origins of the S_{a7} and S_{b7} components are considered to be the surface Si atoms whose dangling bonds hybridize with the LUMO of C_{60} molecules.

A semiquantitative correlation between the charge transfer and the adsorbate-induced core level shifts has been derived empirically for the Si 2*p* core level. Using this correlation, a relation between the charge transfer (δq) and the core-level shifts (δE) is derived as $\delta E/3.4\ \text{eV} = \delta q$.[72] Considering this relation and the energy shift of the S_{a7} and S_{b7} components, 0.414 and 0.531 eV, we obtain the transfer of 0.12 and 0.15 charges per surface Si atom that interact ionically with a C_{60} molecule on a Si(001) and Si(111) surface. To determine the number of ionically interacted Si atoms, we assume that only two covalent bonding orbitals are formed per one molecule by the breaking of one double bond, and, therefore, only two surface Si atoms contribute to the S_{a8} and S_{b8} components per a C_{60} molecule. This assumption is appropriate because the formation of four bonding orbitals should lead to the observation of a different C 1*s* component and/or an asymmetric peak in Fig. 3 considering the contribution of $(100\times4)/(60-4)\sim10\%$ of C atoms and the detection limit of the experimental setup, and because the formation of only one bonding orbital leads to the instability of the C_{60} cage by the presence of a lone pair. Since both surface Si atoms that interacted covalently and ionically are overlaid by C_{60} molecules, it is reasonable to consider that the cross section of S_{a7} and S_{a8}, and that of S_{b7} and S_{b8}, are the same. In this case, the intensity ratios $I(S_{a7})/I(S_{a8})$ and $I(S_{b7})/I(S_{b8})$ correspond to the number ratio of the contributed surface Si atoms. $I(S_{a7})$, $I(S_{a8})$, $I(S_{b7})$, and $I(S_{b8})$ are the intensities of the S_{a7}, S_{a8}, S_{b7}, and S_{b8}. The intensities of the S_{a7}, S_{a8}, S_{b7}, and S_{b8} components relative to the bulk ones are 0.190, 0.234, 0.062, and 0.089, respectively. These intensities and the contribution of two Si atoms per a C_{60} molecule for the S_{a8} and S_{b8} components lead the amount of 1.62 and 1.39 Si atoms for the contribution of S_{a7} and S_{b7} per a C_{60} molecule. Taking into account the amount of transferred charge and that of the ionically interacted Si atoms, the charge transfer is estimated to be 0.19 electrons per C_{60} molecule on the Si(001) surface, and to be 0.21 electrons per molecule on the Si(111) surface.

The observation of the bonding state and the evidence of charge transfer indicate that the chemisorption on the Si(001)-(2×1) and Si(111)-(7×7) surfaces at 670 K has both covalent and ionic characters. This bonding nature is different from that observed at 300 K, where C_{60} molecules interact mainly with van der Waals force at a coverage of 1.0 ML on both surfaces. In order to understand the change in bonding nature, we consider on the LEED patterns. The LEED spots observed at 670 K show different patterns comparing with that obtained at 300 K. At 300 K, clear (2×1) and (7×7) patterns are still observed after the growth of the 1.0-ML C_{60} film. At 670 K, the LEED spots originated from the (2×1) structure become weak on the Si(001) surface, and those from the (7×7) structure disappear and only (1×1) spots are observed on the Si(111) surface. These changes in LEED patterns indicate the rearrangement of surface Si atoms. On a Si(111) surface, there are only 19 dangling bonds in the (7×7) unit cell, and 49 dangling bonds in the same area of the (1×1) surface. Since the chemisorption is originated from the Si dangling bonds, it is appropriate to consider that the change in interaction results from the different number of dangling bonds, i.e., the larger number of dangling bonds permits the larger number of chemisorbed C_{60} molecules. Moreover, the difference in dangling bond's density makes a different distance between two dangling bonds. The shortest distance between two dangling bonds is 0.46 nm on a Si(111)-(7×7) surface, and that on a Si(111)-(1×1) surface is 0.38 nm. Comparing the radius of a C_{60} molecule, 0.36 nm, with the distance between two dangling bonds, we recognize that a free dangling bond is able to hybridize with the LUMO on a Si(111)-(1×1) surface. A free dangling bond means a dangling bond that does not form a covalent bond with a C_{60} molecule. Hence, we consider that the change in bonding nature comes from the high density of dangling bonds that are originated from the rearrangement of surface atoms on the Si(111) surface.

On the Si(001) surface, it is difficult to discuss the density of dangling bonds because the observation of the (2×1) LEED pattern suggests that the surface structure hardly changes. At a temperature lower than 900 K, C_{60} molecules are reported to adsorb just above the trough between the dimer rows of the (2×1) surface structure.[2,6,16] Taking into

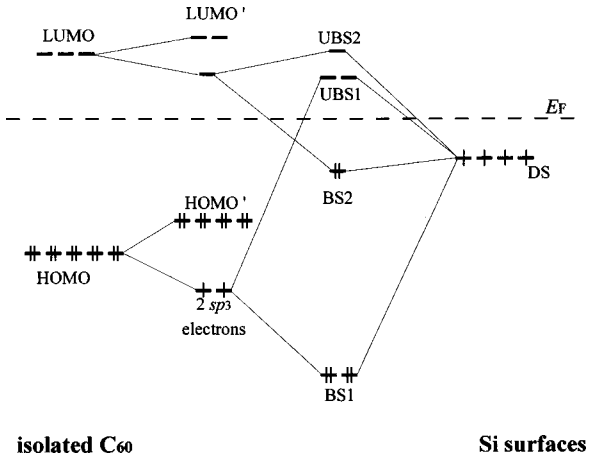

FIG. 6. A schematic diagram of the energy levels for the adsorption of a C_{60} molecule on the Si(001) and Si(111) surfaces at 670 K. Upon adsorption, the fivefold degenerated HOMO and the threefold degenerated LUMO split due to the C_{60}-surface interaction. These split MO's hybridize with the occupied dangling bond states of the Si surfaces and make two bonding states. HOMO' and LUMO' are the shifted HOMO and LUMO, BS1 and BS2 are the bonding states, UBS1 and UBS2 are the antibonding states, and DS is the occupied dangling bond state of the Si surfaces.

account the bond length of the dimer, approximately 0.24 nm,[53,54] and lattice constant of the Si(001)-(1×1) surface, 0.38 nm, the width of the trough is about 0.52 nm. This length is larger than the radius of a C_{60} molecule. Since the (2×1) LEED pattern is still observed, we propose that the Si atoms of the dimer located around a C_{60} molecule, move slightly making the width of the trough shorter at 670 K. Under this assumption, a free dangling bond becomes able to hybridize with the LUMO more easily compared to the adsorption on a Si(001)-(2×1) surface at 300 K. Therefore, we attribute the origin of the change in bonding nature to the shorter distance of dangling bonds that are originated from the rearrangement of surface Si atoms on the Si(001) surface.

In order to understand the bonding nature at 670 K, we propose an energy-level scheme presented in Fig. 6. The Blyholder model,[73] in which an unoccupied surface state hybridizes with an occupied MO and an occupied surface state with an unoccupied MO, is not appropriate in the present case, because the bonding orbital is formed by the hybridization of two occupied sp^3 states. The schematic energy levels of MO's of an isolated C_{60} molecule near the Fermi level E_F are described on the left side, and the occupied dangling bond state (DS) of the Si surfaces, on the right side. The LUMO is a threefold degenerate MO with t_{1u} symmetry. The DS is not well defined due to the annealing effect manifested by LEED. According to the interaction between a molecule and the Si surface, the HOMO and the LUMO split as the C_{60} molecule approaches the surface. These split MO's hybridize with the DS and form two bonding states, BS1 and BS2. HOMO' corresponds to the shifted HOMO observed at 1.60 and 1.75 eV, and BS1 to the bonding state observed at 2.10 eV in Fig. 1. LUMO' is the shifted LUMO, and the two antibonding states are depicted as UBS1 and UBS2. Since the partially filled bonding state BS2 consists of the LUMO and the DS, the energy shifts of the C 1*s* core level and MO's might attribute to the BS2. The BS2 also explains well the softening of several vibrational modes reported previously by HREELS,[22,23] because the LUMO is an antibonding MO and the electron-occupied LUMO should soften the bond between two C atoms. The cross section of the partial filling LUMO is always low as reported for C_{60} molecules adsorbed on Au surface[32] and for CO molecules on transition metal surfaces,[74] and, therefore, it is not strange that the BS2 is invisible in Fig. 1.

At last, we mention the S_{a4} component observed in Fig. 5(a), whose energy shift is 0.415 eV. The same energy shift of the S_{a4} component with that of the S_{a7} component suggests its origin to be also the surface Si atoms that dangling bonds hybridize with the LUMO of C_{60} molecules. The existence of the minority species of chemisorbed C_{60} on a Si(001)-(2×1) surface at 300 K with both covalent and ionic characters is consistent with the observation of the split HOMO and the shifts of MO's and the C 1*s* core level at low coverage.[4]

B. Interface structure during the formation of SiC islands

In order to determine the interface structures at 1070 K on the Si(001) surface, and at 1070 and 1120 K on the Si(111) surface, we consider the C 1*s* and the Si 2*p* core level spectra. In the C 1*s* core level spectra obtained at these temperatures, two C 1*s* components are observed as shown in Fig. 4. The intensity ratios I_{C2}/I_{C1} are determined to be 0.390 on the Si(001) surface, and to be 0.180 at 1070 K and 0.530 at 1120 K on the Si(111) surface. I_{C1} and I_{C2} indicate the intensities of C_1 and C_2 described in Table I, respectively. Assuming the same cross sections for the C_1 and C_2 components, approximately $60/(1+0.390)=43$ C atoms of a C_{60} molecule contribute to the C_1 component, and $(0.390\times60)/(1+0.390)=17$ C atoms to the C_2 component on the Si(001) surface. On the Si(111) surface, $60/(1+0.180)=51$ C atoms contribute to the C_1 component and $(0.180\times60)/(1+0.180)=9$ C atoms to the C_2 component at 1070 K, and $60/(1+0.530)=39$ C atoms to the C_1 and $(0.530\times60)/(1+0.530)=21$ C atoms to the C_2 at 1120 K. We consider the C_1 component to be due to the C atoms bonded with a sp^2-like hybridization to other C atoms like in the molecular phase, because the binding energies of these components are equal to those of the C_{60} molecules chemisorbed at 670 and 870 K on both surfaces.

For the C_2 component, two origins are able to be proposed. One is the polymerization of C_{60} molecules on the Si surfaces, because C_{60} polymer is formed under the irradiation of visible or ultraviolet light[75] and by high pressure and temperature.[76] Moreover, the profiles of the valence spectra resemble that of an amorphous carbon film and/or an polycrystalline diamond film.[42,43] The other is the formation of SiC at the interface. Since the polymerization of C_{60} molecules hardly affects the core levels of surface Si atoms and the formation of SiC strongly affects these levels, we use the Si 2*p* core level spectra to determine the origin of the C_2 component.

The energy shift of the S_{a10} component observed in Fig. 5(a) at 1070 K, and those of the S_{b10} and S_{b12} components observed at 1070 and 1120 K in Fig. 5(b) are close to that of the Si 2*p* of SiC,[45–47] and we consider that these components are due to the Si atoms bonded covalently with C atoms.

Taking into account the photon energy, $h\nu = 130$ eV, the binding energy of the Si 2*p* core level, about 99 eV, and the work functions of the samples, 4.9 eV for all samples, we obtain the kinetic energy of the Si 2*p* photoelectron to be about 26 eV. This kinetic energy leads to a mean free path of approximately 0.5 nm for the Si 2*p* photoelectron.[77] In order to determine the thickness of the SiC formed at the interface, we assume that C_{60} molecules do not affect the mean free path because the cages of C_{60} molecules are broken and the density of the C atoms might be low. We also use the assumption that the structures of the SiC islands are cubic and have the same orientations with the Si substrates. Using this assumption, we obtain the thickness of the SiC, Δ_{SiC}, by the relation

$$\Delta_{\mathrm{SiC}} = \frac{I_{\mathrm{SiC}} \times \delta_{\mathrm{SiC}}}{(1 + I_{\mathrm{Si}}) \times \delta_{\mathrm{Si}} + (I_{\mathrm{SiC}} \times \delta_{\mathrm{SiC}})} \times \lambda,$$

where λ is the mean free path of the photoelectron, $(1 + I_{\mathrm{Si}})$ is the intensity of Si atoms that are not bonded with C atoms, and I_{SiC} are the intensities of Si atoms bonded with C atoms. δ_{SiC} and δ_{Si} are the space between two Si layers in a SiC solid and in a Si solid, respectively.

The space between two Si layers is 0.218 nm in the 3C-SiC(001), 0.136 nm in the Si(001), 0.251 nm in the 3C-SiC(111), and the average one is 0.157 nm in a Si(111) solid. On the Si(001) surface, the thickness of SiC is obtained to be approximately 0.253 nm, considering the relative intensity of the S_{a9} and S_{a10} components, 0.399 and 0.894. This thickness suggests the contribution of $(4 \times 3/2) \times (1 + 0.253/0.218) = 13.2$ C atoms per a C_{60} molecule to the SiC formed at the interface. $(4 \times 3/2)$ means the number of Si atoms per layer that contributes to the SiC formation for one molecule, because two C_{60} molecules are adsorbed on the (4×3) superlattice of the Si(001) surface. The outermost layer of SiC should be composed by C atoms and $(1 + 0.253/0.218)$ indicates the C layers number of SiC. On a Si(111) surface, we obtain the thickness of SiC as 0.274 nm at 1070 K and 0.373 nm at 1120 K, using the intensities of the S_{b9}, S_{b10}, S_{b11}, and S_{b12} components, 0.431, 1.087, 0.546, and 2.628. Since seven C_{60} molecules are adsorbed on the (7×7) unit cell of the Si(111) surface, the thicknesses of $(1 + 0.274/0.251) = 2.1$ C-C layers and $(1 + 0.373/0.251) = 2.5$ C-C layers suggest the contribution of $(7 \times 7/7) \times 2.1 = 14.7$ C atoms at 1070 K, and $(7 \times 7/7) \times 2.5 = 17.5$ C atoms at 1120 K. Taking into account the simplicity of our model, these values are close to the number of C atoms that contributes to the C_2 components. Therefore, we consider the origin of the C_2 component observed in Fig. 4 as the C atoms bonded covalently with Si atoms. Moreover, the increment of the covalent bonds between C and Si atoms at higher temperature observed on the Si(111) surface indicates that the progress of the SiC formation is undergoing at the interface.

The qualities and structures of SiC islands are well studied by HREELS[22,23] and STM.[26] However, no information is obtained for the surface except the islands. In the valence spectra, we observed a peak at a binding energy of 0.55 eV after annealing the 1.0-ML C_{60} film adsorbed on a Si(001) surface at 1120 and 1170 K, and two peaks at 0.20 and 0.90 eV after annealing the C_{60} film adsorbed on a Si(111) surface at 1170 K. These energies are the same as those of the surface states of the Si(001)-(2×1) and Si(111)-(7×7) clean surfaces. In the Si 2*p* core level spectra, the same sign of the energy shift and almost the same energy shift with the S_{a2} component of the clean surface, indicate that the S_{a12} and S_{a15} components observed at 1120 and 1170 K are due to the raised atoms of the Si dimer of the Si(001)-(2×1) surface. For the Si(111) surface, the S_{b14} component observed at 1170 K has the same sign of the energy shift and almost the same energy shift with the component due to the rest atoms of the Si(111)-(7×7) surface. In LEED, (2×1) and a (7×7) patterns are observed after the formation of SiC islands. Taking into account these results, we conclude that the surface after the formation of SiC is composed by SiC islands and clean reconstructed Si surfaces between them.

Finally, we consider the formation temperatures of SiC islands that are 50 K lower on the Si(001) surface. Both the dissociation temperature of C_{60} molecules and the mobility of surface Si atoms affect the temperature, because the formation of SiC islands is done by two steps, i.e., the breakdown of the C_{60} cage and the movement of Si atoms. The breakdown of the C_{60} cage implies the breakdown of the bond between C atoms, that results from the thermal-induced vibrational effect and/or the electronic effect. The electronic effect means the softening of the bond between two C atoms due to the charge transfer into the LUMO. Since there is scarcely any difference in the transferred charge on the Si(001) and Si(111) surfaces, the mobility of Si atoms is the most important effect. To move from the initial bonding site, the outermost Si atoms have to break two backbonds on a Si(001) surface and three backbonds on a Si(111) surface for the simplest (1×1) surface structure. Using this simplest model, we recognize the higher mobility of surface atoms on the Si(001) surface. Taking into account the transition temperature on a Si(001) clean surface from (2×1) to c(4×4), approximately 900 K,[78] and that of a Si(111) surface from (7×7) to ''1×1,'' 1100 K,[72] our simple model seems to be sufficient to compare the mobility of the outermost atoms on both surfaces. Therefore, the different SiC formation temperatures on the Si(001) and Si(111) are considered to be due to the different mobility of the outermost Si atoms that results from the different structures of both surfaces.

V. CONCLUSION

We have measured the temperature-dependent valence spectra, the C 1*s* and Si 2*p* core level spectra of the C_{60} molecules adsorbed on Si(001)-(2×1) and Si(111)-(7×7) surfaces using PES. The profile of the valence spectra indicates that the major interaction between C_{60} molecules and Si(001) and Si(111) surfaces is the van der Waals force at 300 K. The physisorbed C_{60} molecules change their bonding natures at 670 K on both Si surfaces. The bonding nature at 670 K is a chemisorption that has both covalent and ionic characters. The covalent character is verified by the observation of the bonding orbital, and the ionic one by the binding energy shifts of the C 1*s* core level and the MO's. The amount of charge transfer is estimated to be 0.19 electrons per C_{60} molecule on the Si(001) surface, and to be 0.21 electrons per molecule on the Si(111) surface from the Si 2*p* core level spectra. Moreover, the changes in LEED patterns suggest that the transition in bonding natures results from the rearrangement of surface Si atoms. After annealing at 1070

K, we observe the breaking of the C_{60} cage on both surfaces. This breaking is accompanied by the progress of the SiC formation at the interface. The formation temperatures of SiC islands are 1120 K on the Si(001)-(2×1) surface, and 1170 K on the Si(111)-(7×7) one. We attribute the difference in formation temperature to the different mobility of the outermost Si atoms that results from the different structures of both surfaces. The LEED patterns and the observation of the surface states indicate that the surface is composed of SiC islands and clean reconstructed Si surfaces between them, at a temperature higher than the formation temperature of SiC.

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