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SiC film formation and growth by the thermal reaction of a C_{60} film adsorbed on a Si(111)-(7×7) surface: Bonding nature of C_{60} molecules and SiC-film surface phonons

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We report here measurements of temperature-dependent vibrational excitations of C_{60} molecules adsorbed on a Si(111)-(7×7) surface, and the formation of a SiC film by thermal reaction using high-resolution electron-energy-loss spectroscopy (HREELS). The interactions of C_{60} molecules with the Si surface are judged from the charge states of C_{60} molecules, determined quantitatively by the energy shifts of the vibrational modes. Most C_{60} molecules interact weakly by van der Waals force at room temperature. At 670 K, two adsorption states, i.e., ionic and covalent bonds, are formed under the rearrangement of surface Si atoms. The amount of charge transfer is estimated to be (4±1) electrons per C_{60} molecule for the ionic bond. At 1070 K, covalent bonds between C_{60} molecules are formed, and at 1170 K $3C$-SiC(111) islands are formed. The formation of $3C$-SiC(111) is verified by the observation of the surface-optical-phonon Fuchs-Kliewer mode. We have grown the $3C$-SiC(111) film, repeating the adsorption of C_{60} molecules, and annealing the sample. Well-oriented films with low step density are obtained. The lower-energy shift of the Fuchs-Kliewer mode, observed for $3C$-SiC(111) films thinner than 30 nm, indicates the softening of the Si-C bond caused by the buffer layer. [S0163-1829(98)04712-2]

I. INTRODUCTION

The interaction of C_{60} molecules with the semiconductor surface is important to understanding the physical and chemical properties of fullerenes and to developing new material functions for C_{60} molecules. Extensive experimental and theoretical studies[1–16] have been performed on the C_{60} molecule adsorbed semiconductor surface. Recent observation of epitaxial silicon carbide (SiC) formation by the thermal reaction of C_{60} with Si(111)-(7×7) and Si(001)-(2×1) surfaces and the possibility of selective SiC growth[8] have led to increased interest in the nature of the bond between the C_{60} molecule and Si surfaces and between C_{60} and the SiC film.

The interaction of C_{60} and Si surfaces is mainly studied by scanning tunneling microscopy (STM). The growth process of a thick C_{60} film,[6] the layer-plus-island growth (Stranski-Krastanov) mode, indicates that the interaction between the first layer C_{60} molecules and the Si surface and that between the nearest-neighbor C_{60} molecules in islands is different. Xu, Chen, and Creager[5] observed the structure of islands by STM, and determined them to be van der Waals solid. These C_{60} islands desorb and a 1 monolayer (ML) film of C_{60} molecules is formed at about 670 K on the Si(111)-(7×7) surface.[12] Seven molecules are adsorbed in the 7×7 unit cell at 1 ML.[9] The C_{60} cage structure is stable up to about 900 K[3]. Chen and Sarid[7] studied the thermal reaction at a coverage of 0.05 ML, and observed the movements of C_{60} molecules at 873 K, which led to the formation of C_{60} dimers. At 973 K, more molecules move from their early adsorption site involving a higher density of C_{60} dimers and the appearance of larger molecular clusters. They also observed the formation of SiC islands at 1123 K. Using low-energy electron diffraction (LEED) and x-ray diffraction (XRD), Hamza, Baboch, and Moalen[8] demonstrated that $3C$-SiC(111) film grows on a Si(111) substrate using C_{60} as a precursor. Recently, Hu *et al.*[13] observed the islands, formed by annealing the 1 ML C_{60} film adsorbed Si(111)-(7×7) surface at 1373 K, using the combined measurements of high-resolution electron-energy-loss spectroscopy (HREELS) and STM. They also observed the surface reconstructions of the islands, and determined them to be cubic ($3C$) SiC(111)-(3×3) surface. Although several studies have been made on the $3C$-SiC(111) film formed by C_{60} molecules as precursor, little is known about the interaction between C_{60} molecules and surface Si atoms at high temperature. HREELS (Ref. 17) with fine resolution is very sensitive to measuring the excitations at surfaces, and is a very suitable technique for obtaining information to elucidate the bonding features and characterize the film.

The C_{60} molecule has four infrared-active intramolecular vibration modes with T_{1u} symmetry, and ten Raman-active modes that have two Ag and eight Hg symmetries.[18–20] The T_{1u} vibrational modes are observed at $\nu_1=65.2$, $\nu_2=71.4$, $\nu_3=146.6$, and $\nu_4=177.2$ meV by infrared absorption spectroscopy[21], and at $\nu_1=66$, $\nu_3=147$, and $\nu_4=178$ by HREELS (Refs. 1 and 11) for solid C_{60}. Recently, Suto *et al.*[15] observed the softening of ν_1, ν_2, ν_4 and two Hg modes of C_{60} molecules adsorbed on a Si(111)-(7×7) surface at room temperature. They estimated the charge transferred from surface Si atoms to C_{60} molecules as (3±1) electrons per molecules at a coverage lower than 0.25 ML with the help of experimental[22–25] and theoretical results.[26]

The Fuchs-Kliewer (FK) mode[27] is a long-wavelength

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surface optical phonon, which is related to the energy of the bulk transverse-optical (TO) phonon (ω_{TO}), the static dielectric constant, (ϵ_s) and the electronic dielectric constant (ϵ_∞), respectively, by

$$\omega_{\mathrm{FK}} = \omega_{\mathrm{TO}} \sqrt{\frac{\epsilon_s + 1}{\epsilon_\infty + 1}}. \tag{1}$$

The FK mode is observed at 116 meV by HREELS for a thick SiC film made by chemical vapor deposition (CVD).[28,29] The energy of the FK mode is a good parameter for getting information about the characteristics of the SiC film, because the energy of the surface phonon reflects the bonding strength between Si and C atoms.

In this paper, we report on the bonding natures of C_{60} molecules adsorbed on the Si(111)-(7×7) surface, and the $3C$-SiC(111) surface formed by the thermal reaction of C_{60} molecules with a Si(111) substrate using HREELS. We also report on the energy of the FK mode, measured with our high resolution, and discuss the characteristics of the $3C$-SiC(111) films. The shifts in vibrational modes indicate the existence of ionic interaction between the C_{60} molecules and the Si(111) surface at 670 K. The amount of charge transferred from surface Si atoms to the C_{60} molecule is estimated to be (4 ± 1) electrons per molecule. Another bonding state in which the vibrational mode does not change is also observed at 670 K. At 1170 K, the formation of SiC is verified by observation of the FK mode. On the $3C$-SiC(111) surface, no energy shift is observed for the vibrational modes of C_{60} molecules from room temperature to 870 K. The lower-energy shift of the FK mode was observed for a $3C$-SiC(111) film thinner than 30 nm. This energy shift is discussed in terms of the buffer layer. The thick $3C$-SiC(111) film made by a C_{60} precursor has a flat surface with small step density.

II. EXPERIMENT

The experiment was carried out in a UHV system that consists of an analysis chamber and a preparation chamber. The analysis chamber is equipped with a HREEL spectrometer, a LEED optics, an Auger-electron spectrometer (AES), and a quadrupole mass spectrometer (QMS). The base pressures were below 1×10^{-10} Torr in the analysis chamber and below 1×10^{-9} Torr in the preparation one. The HREEL spectra were measured with a VSW IB2000 spectrometer with a typical incident energy of 5.0 eV. The full width at half-maximum (FWHM) of the elastically scattered peak were 12 meV for the clean Si(111)-(7×7) surface, from 6 to 8 meV after the deposition of C_{60} molecules, and from 8 to 18 meV for the $3C$-SiC(111) surfaces. The scattering angle was fixed at 60° from the surface normal direction. We changed the incident angle to measure the angular dependent intensities of the energy-loss peaks. All measurements were carried out at room temperature.

The Si(111) sample was a P-doped (n-type) Si wafer that has an electrical resistivity of 1000 Ω cm and a size of $7\times15\times0.5\ \mathrm{mm}^3$. We prepared the Si sample chemically following the Shiraki method[30] and then introduced it into the UHV chamber. The sample was 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(111)-(7×7) surface. The sample was spontaneously cooled for several minutes after heating up to 1520 K before the C_{60} deposition. We checked the quality of the surface by observation of a clear 7×7 LEED pattern. The cleanliness of the surface was verified by AES and the absence of any loss peaks due to the vibrational modes of adsorbed atoms and molecules by HREELS. The sample temperature was measured by an infrared pyrometer with an emissivity setting of 0.64.

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 procedure, 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 h prior to evaporation. The thickness was monitored by a quartz crystal oscillator. The deposition rate was approximately 0.2 nm/min. A thickness of 1.0 nm is estimated to be 1 ML of C_{60} by STM.[15]

III. RESULTS

A. Thermal reaction of C_{60} molecules with the Si(111)-(7×7) surface

Figure 1(a) shows the HREEL spectra of the 1 ML C_{60} film grown on the Si(111)-(7×7) surface at room temperature. Peaks and shoulders are observed at 66, 72, 95, 133, 147, 163, 179, and 193 meV. Taking into account the previous infrared absorption,[21] Raman scattering,[20,21] and HREELS[1,11] measurements, we assign the 66-, 72-, 147-, and 179-meV peaks as the four dipole-active T_{1u} modes of ν_1, ν_2, ν_3, and ν_4, respectively. The 95-, 133-, and 193-meV peaks are the Raman-active Hg modes. The 163-meV peak is observed as a small peak in Raman scattering[20] and neutron scattering.[31] This peak is also analyzed theoretically with the first-principles density-functional method.[32] The surface disorder enhances the intensity of this peak in the HREELS spectra.[11]

The spectra in Figs. 1(b), 1(c), 1(d), and 1(e) are those obtained after annealing the sample at 670, 870, 1070, and 1170 K, respectively. We annealed the sample for 300 sec and then cooled it down to room temperature. At 670 K, we clearly observed the energy shifts of some peaks. The peaks observed at 66, 72, and 95 meV in Fig. 1(a) shift their energies to 64, 70, and 94 meV, respectively. We also observe a new peak at 170 meV. The negligible change in intensity of the ν_1 mode indicates that no C_{60} molecule has desorbed at 670 K. At 870 K, peaks are observed at 64, 70, 94, 132, 147, 170, 179, and 193 meV. The peak energies are the same as those at 670 K.

The profile of HREEL spectrum changes drastically after annealing the sample at 1070 K. The intensities of energy-loss peaks indicating the presence of C_{60} molecules become small, and new shoulders and peaks appear at 87, 97, and 102 meV. An STM image obtained at 1070 K[12] shows the nearest-neighbor distance of C_{60} molecules as 0.93 nm, which is shorter than that in the solid state, 1.004 nm. In the

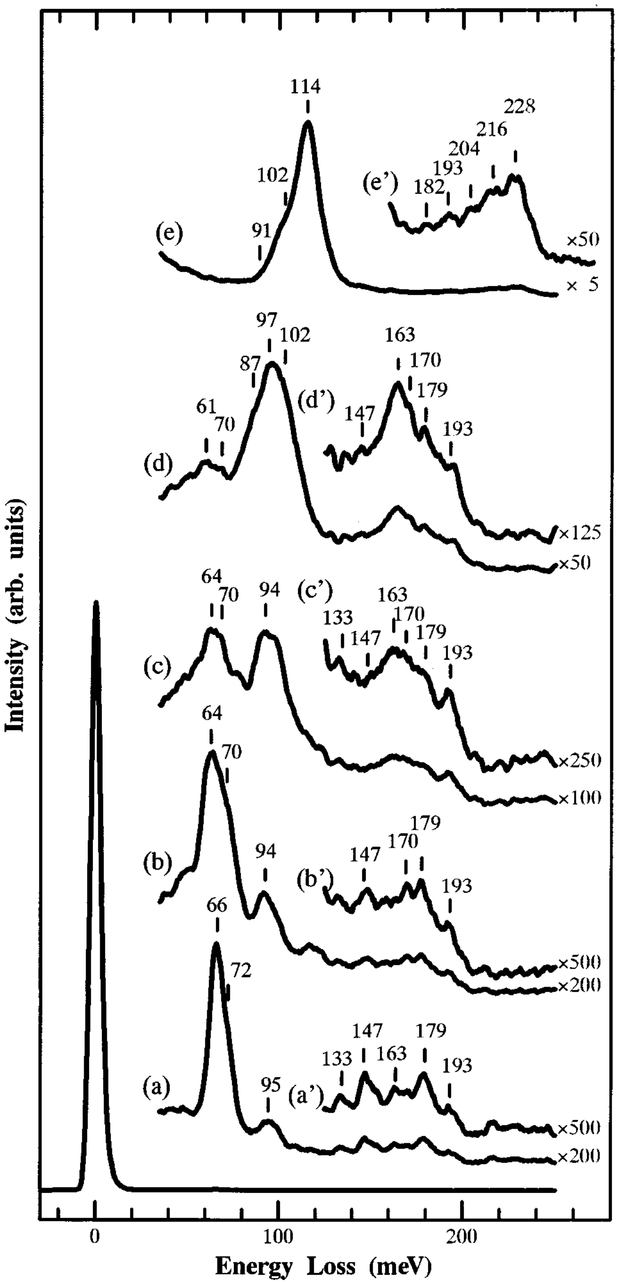

FIG. 1. Temperature-dependent HREEL spectra of C_{60} film on Si(111)-(7×7) surface. (a) shows the spectrum of 1 ML C_{60} deposited at room temperature. (b), (c), (d), and (e) are the spectra measured after annealing the sample at 670, 870, 1070, and 1170 K, respectively. (') indicates the enlarged spectrum of each figure.

infrared-absorption measurements, seven peaks are observed in the energy region between 88 and 99 meV when covalent bonds between C_{60} molecules exist.[33,34] Taking into account the previous studies, the new peaks observed at 87, 97, and 102 meV in Fig. 1(d) result from the formation of covalent bonds between C_{60} molecules. The large intensity of the 163-meV peak indicates that the remarkable roughness is introduced at the surface, involving the formation of covalent bonded C_{60} molecules. The intensity ratio of the 87-, 97-, and 102-meV peaks to those indicating the presence of C_{60} molecules corresponds to the existence ratio of covalent bonds between C_{60} molecules. The shoulders, observed at the higher-energy side of the 94-meV peak in Figs. 1(b) and 1(c), should result from the small number of C_{60} dimers that are created by covalent bonds between molecules. The higher intensity of the shoulder in Fig. 1(c) than that in Fig. 1(b) agrees well with the larger number of C_{60} dimers at higher temperature.

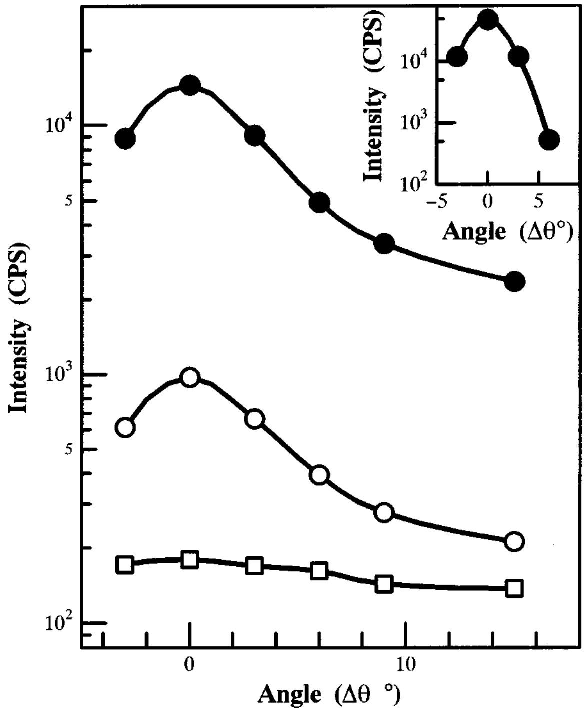

FIG. 2. The angular profile of electrons scattered from the Si(111) surface covered with 3*C*-SiC(111) islands, formed by annealing the 1 ML C_{60} film adsorbed Si(111)-(7×7) surface at 1170 K. The filled circles, open circles, and squares represent the elastic peak, the 102-meV peak and 114-meV peak, respectively. The inset shows the angular profile of the elastically scattered electrons from the Si(111)-(7×7) surface.

After annealing the sample at 1170 K, an intensive peak appears at 114 ± 0.5 meV. Since the loss energy is very close to 116 meV, i.e., the energy of the surface phonon on a thick SiC film,[28,29] we judged it to be the FK mode of SiC. The large intensity supports the idea that the origin of this peak is the coherent motion of ordered surface atoms and not the vibration of an isolated atom. We also observe peaks and shoulders at 91, 102, 182, 193, 204, 216, and 228 meV for the first time, to our knowledge, in our high-resolution measurement. Since no peak is observed around 78, 255, and 456 meV, corresponding to the stretching modes of Si-C, Si-H, and O-H, respectively, all peaks observed in Fig. 1(e) are related to SiC. The peaks observed at 1170 K do not change their energies and intensities until 1370 K is reached, indicating that there is no difference in the characteristics of SiC within this temperature range.

Figure 2 shows the angular profiles of the elastically scattered peak, as well as the 102- and 114-meV peaks observed in Fig. 1(e), at different scattering angles. The filled circles, open squares, and circles correspond to the elastic peak, the 102-meV peak, and 114-meV peak, respectively. At the specular direction, i.e., $\Delta\theta=0°$, the intensity of the elastic peak is only one order larger in magnitude than that at $\Delta\theta=15°$. On a clean Si(111)-(7×7) surface, in which the step density is approximately 50 nm/step, the intensity of the elastic peak is larger by two orders of magnitude at the specular direction than that at $\Delta\theta = 6°$, as shown in the inset of Fig. 2. The elastic peak is equivalent to the Bragg reflected beams observed in LEED. Since the magnitude of change in intensity corresponds to the sharpness of the LEED spot, the rather small angular variation of the elastic peak indicates that the SiC grown on an Si(111)-(7×7) surface is an island and not a flat film. This result agrees well with the previous STM image in which the surface area and height of SiC islands are $10\times10-35$ nm^2 and $2-3$ nm, respectively.[13] The surfaces of these islands are reported as (3×3) reconstructed surfaces by STM.[13] Kaplan[35] showed the existence of various surface reconstructions for the 3*C*-SiC(111) film made by chemical vapor deposition (CVD), and proposed that the 3*C*-SiC(111)-(3×3) surface is terminated by three consecutive Si atom layers. These Si layers contain two adatoms, six first layer atoms, and eight second layer atoms in a unit cell. Although there is a difference in the SiC formation method, the equivalency in reconstruction indicates that the 3*C*-SiC(111) island obtained in our experiment is terminated by Si atoms.

The intensity of the 114-meV peak shows a similar angular profile to that of the elastic peak. Since the increase in intensity as one moves toward the specular direction indicates the dipole scattering mechanism, the 114-meV peak is a vibrational mode resulting from a dipole normal to the surface. The intensity of the 102-meV peak observed at $\Delta\theta = 15°$ is almost the same at that measured in the specular direction. This negligible change in intensity indicates that the 102-meV peak is a ''dipole forbidden'' mode.[17] The dipole forbidden mode is a mode in which the dipole is parallel to the surface or a Raman-active mode, and observed by electrons scattered with short-range interaction, i.e., impact scattering, in contrast to the long-range interaction that contributes to the dipole scattering. Since this impact scattering involves high-order Fourier components of the potential and thus large momentum transfer, electrons scattered with this mechanism are observed inside a broad isotropic scattering angle. The energy, 102 meV, is close to the energy of the Si-C stretching mode[36] (99 meV) and the Si-OH bending modes[37] (102 meV). However, no other peak indicating the presence of contamination by carbon atoms and water molecules is observed in Fig. 1(e). Hence, taking into account the large intensity, we assign the 102-meV peak to the vibrational mode from the coherent motion of ordered atoms, the dipole of which is parallel to the surface.

The lower intensity of the 91-meV peak indicates that this peak comes from the vibration of an isolated atom. Since there is no peak indicating the presence of contamination in Fig. 1(e), the 91-meV peak results from the 3*C*-SiC(111) island. Using HREELS, Daum, Ibach, and Müller[38] observed the vibrational modes of the adatoms on the Si(111)-(7×7) surface at 70.7 meV. The bonding strength is usually stronger when the distance between atoms is shorter, and the lattice constant ratio between the 3*C*-SiC(111) and Si(111) was reported as 4:5 by means of transmission electron microscopy (TEM).[39,40] We assume that the energy of the vibrational mode is proportional to the bonding strength between the Si adatom and first layer Si atom, and in inverse proportion to the lattice constant of the 3*C*-SiC(111) and Si(111) surfaces. Within this rough assumption, the vibrational mode of the adatoms on the 3*C*-SiC(111)-(3×3) surface is estimated to appear at $70.7\times(5/4) = 88.4$ meV. Hence, we consider the 91-meV peak to be the excitation of the Si-Si bond between the Si adatom and first layer Si atom. Since the peaks observed around 200 meV are described by the sum of those observed around 100 meV as

$$\omega_{182} = \omega_{91} + \omega_{91},$$

$$\omega_{193} = \omega_{91} + \omega_{102},$$

$$\omega_{204} = \omega_{102} + \omega_{102},$$

$$\omega_{216} = \omega_{102} + \omega_{114},$$

$$\omega_{228} = \omega_{114} + \omega_{114},$$

we consider them to be the overtones and combination bands. Unfortunately, we are unable to resolve the 205-meV peak, which corresponds to $\omega_{91} + \omega_{114}$, due to the poor resolution (8 meV) on this surface. The assignment of all energy-loss peaks observed in Fig. 1 is summarized in Table I.

B. Growth of 3*C*-SiC(111) film

The 3*C*-SiC(111) film was grown by repeating the anneal of the sample at 1370 K following the adsorption of C_{60} molecules. We refer to the combination of adsorption and annealing as one growing process, tentatively, in this paper. In order to cover the surface perfectly with C_{60} molecules, we adsorbed 3 ML of C_{60} molecules at each process. The HREEL spectra obtained after several processes are shown in Fig. 3. Figure 3(a) displays the spectrum after annealing the 3 ML C_{60} adsorbed Si(111)-(7×7) surface at 1370 K, i.e., after the first process. It is easy to find that the spectrum in Fig. 3(a) shows the same profile as that displayed in Fig. 1(e), though the annealing temperature is different. The spectra in Figs. 3(b), (c), (d), and (e) are those obtained after the third, fifth, fifteenth, and thirtieth processes, respectively. After the thirtieth process, LEED shows a hexagonal (1×1) pattern. The distance between the integer spots was 1.25 times longer than that of the Si(111) surface at the same incident electron energy, indicating the surface of the thick film as 3*C*-SiC(111)-(1×1). This result is consistent with the previous combined LEED and XRD studies, which demonstrated the film grown on an Si(111) substrate using C_{60} as precursor as 3*C*-SiC(111)-(1×1).[8] Since the surfaces of both the thick film and thin film (islands) are 3*C*-SiC(111), we consider that the orientation of the 3*C*-SiC surface is always (111) during the film growth.

Several notable results are observed in Fig. 3 as the number of processes increases. First, the energy of the FK mode shifts from 114 ± 0.5 to 116 ± 0.5 meV. Second, the intensity of the main peak becomes larger. Third, the asymmetry of the main peak observed during the initial processes becomes invisible at the fifteenth process [Fig. 3(d)]. Fourth, the peak around 230 meV becomes sharp with larger intensity. Finally, the tail of the elastic peak becomes longer. The first result supports the growth of the 3*C*-SiC(111) film, because 116 meV is the same energy reported previously for a thick SiC film.[28,29]

TABLE I. Assignments of energy-loss peaks observed in Fig. 1. Asterisks are used to represent the following: (*) modes that result from the covalent bonds between C_{60} molecules, (**) excitation of Si-Si bonds of the $3C$-SiC(111)-(3×3) surface, (***) a mode that results from the surface disorder, and (****) overtones and combination bands.

Room temp.	670 K	870 K	1070 K	1170 K	Assignment
66	64	64	61		T_{1u}
72	70	70	70		T_{1u}
			87,97,102		*
				91	**
				102,114	FK modes
95	94	94			Hg
133		133			Hg
147	147	147	147		T_{1u}
163		163	163		***
179	170,179	170,179	170,179		T_{1u}
193	193	193	193		Hg
				182,193,204,216,228	****

The long tail of the elastic peak observed in Figs. 3(d) and (e) is an outcome of inelastic scattering by a free-electron surface plasmon (ω_{sp}). The energy of ω_{sp} is described by Stroscio and Ho[41] as

$$\omega_{\text{sp}} = \frac{(4\pi n e^2)}{(\epsilon_{\text{s}}+1)m^*}$$

where ϵ_{s}, n, and m^* are the static dielectric constant, the free-electron density, and the electron effective mass, respectively. The free electron comes from the defect of the $3C$-SiC(111) film. When the loss energy of the surface plasmon is small, the matrix element becomes large, and multiple inelastic scattering is likely. This multiple inelastic scattering leads to a long tail of the elastic peak.

In order to understand the growing mechanism of the $3C$-SiC(111) film, we plot the increments in intensity ratio of the FK mode to the elastic peak, I/I_0, against the number of growth processes. Figure 4 shows the intensity ratio at various processes. The horizontal and vertical axes correspond to the number of growth processes and the intensity ratio, respectively. The filled circles are the experimental data. The enlargement in intensity ratio shows two steps. That is, I/I_0 increases rapidly until the third process is reached, and then slows down. Two explanations can be offered for the increase in intensity ratio. First, the formation of the film, SiC in this experiment; and second, the expansion of the flat surface area. Since the formation of the $3C$-SiC(111) film relates to the adsorption of C_{60} molecules on the Si(111) surface in the initial growth processes, it is reasonable to consider that the formation of the $3C$-SiC(111) film changes the intensity ratio following Langmuir's adsorption equation,

$$\frac{I}{I_0} = I_A[1-\exp(-\alpha x)], \tag{2}$$

where I_A is the maximum in I/I_0 for a rough $3C$-SiC(111) surface, α is a constant, and x is the number of growth processes. We consider that at the initial processes, the terrace areas on the $3C$-SiC(111) surface are the same as the surface areas of $3C$-SiC(111) islands observed in STM.[13] Therefore, I_A is the maximum in I/I_0 for a rough $3C$-SiC(111) surface, the terrace of which are approximately $10\times 10-35$ nm^2. However, it is impossible to fit the experimental data with Eq. (2) only. This result indicates that the increment of I/I_0 must come from both explanations described above. The change in I/I_0 resulting from the expansion of the sample surface is assumed to follow an equation identical to Langmuir's adsorption one,

$$\frac{I}{I_0} = I_B[1-\exp(-\beta x)], \tag{3}$$

where I_B is the maximum in I/I_0 for a completely flat $3C$-SiC(111) surface and β is a constant. The broken and dotted lines in Fig. 4, are the fitted lines from Eqs. (2) and (3) with $I_A=0.12$, $\alpha=0.55$ and $I_B=0.02$, $\beta=0.02$, respectively. The solid line in Fig. 4, obtained by adding Eqs. (2) and (3), fits the experimental data well. The values of the parameters show that the effect of the terrace area expansion is small but must not be ignored. Taking into account the fitting lines, we conclude that almost all of the surface area is covered with SiC after the sixth process.

Figure 5 shows the angular variations of the intensities of the elastic peak and FK mode of the $3C$-SiC(111) surface obtained after the thirtieth growth process. The filled and open circles represent the elastic peak and FK mode, respectively. The profile of the elastic peak shows two different results from that shown in Fig. 2. First, the intensity of the elastic peak is 10 times larger than that obtained after the first process at the specular direction. Second, the intensity of the elastic peak is two orders larger in magnitude at the specular direction than that at $\Delta\theta = 9°$, and the magnitude of change in intensity is rather large compared to that after the first growth process, but slightly small compared with that of the clean Si(111)-(7×7) surface. Since the intensities of the elastic peak and its angular variation are reflected by the coherence length of the surface, these results signify the long-range planarity on the thick $3C$-SiC(111) surface. The FK mode shows exactly the same angular profiles as that of the elastic peak, implying that it results from dipoles normal

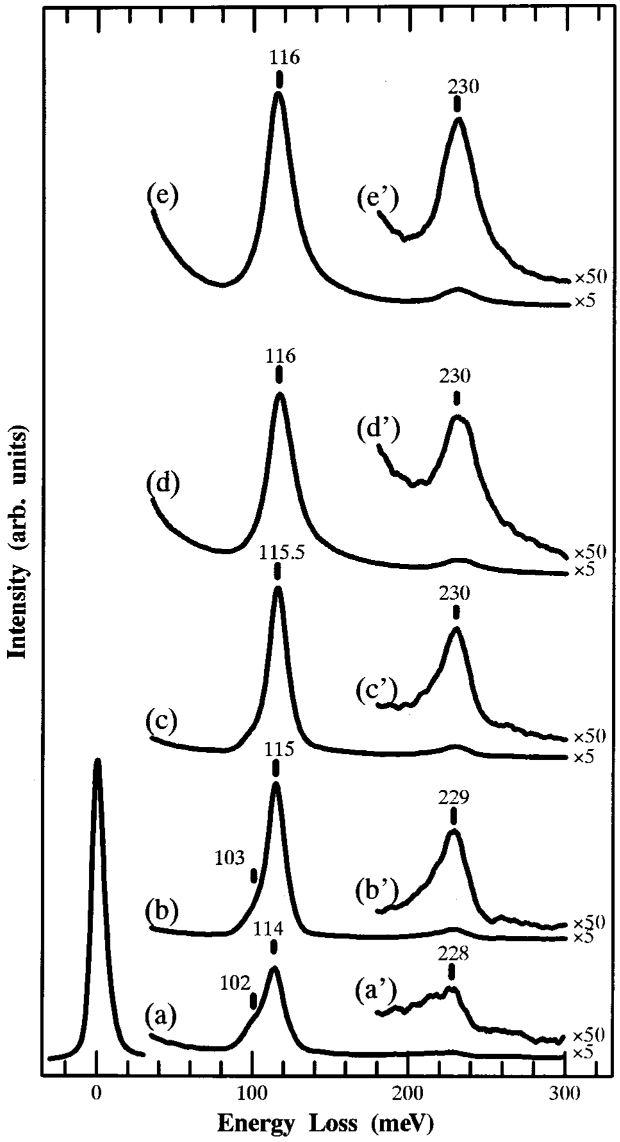

FIG. 3. The HREEL spectra obtained after several growing processes. (a) displays the spectrum after annealing the 1 ML film adsorbed Si(111)-(7×7) surface at 1370 K. The spectra in (b), (c), (d), and (e) are those obtained after the third, fifth, fifteenth, and thirtieth growth processes, respectively. (') indicates the enlarged spectrum of each figure.

to the surface. This dipole direction is consistent with the polarizations of FK mode, which is asserted to be perpendicular to the surface.[27]

Figure 6 displays the HREEL spectra obtained after annealing the C_{60} molecule adsorbed 3*C*-SiC(111) surface at different temperatures. The annealing time was 300 seconds. We adsorbed the C_{60} molecules on the 3*C*-SiC(111) surface obtained after the sixth process, because the influence of the interaction between C_{60} molecules and the Si(111) surface can be ignored at this condition. The LEED of the 3*C*-SiC(111) surface obtained after the sixth growing process shows a hexagonal (1×1) pattern with a higher background compared with that obtained after the thirtieth process. In the LEED experiment, the coherence length of an electron is approximately 10 nm at a primary electron energy of about 100 eV. Hence, the high background indicates that the terraces areas are approximately equivalent as the surface areas of 3*C*-SiC(111) islands observed in STM,[13] $10\times10-35\ \mathrm{nm}^2$, which is consistent with the small terrace area expansion. The HREEL spectrum of the 3*C*-SiC(111) surface obtained after the sixth process is shown in Fig. 6(a). Figure 6(b) shows the C_{60} molecule adsorbed 3*C*-SiC(111) surface. The coverage is 1 ML. We observe clearly the ν_1, ν_3, and ν_4 modes of the C_{60} molecules at 66, 147, and 179 meV, respectively. Since the T_{1u} modes relate to the I_h symmetry, the observation of ν_1, ν_3, and ν_4 modes indicates the

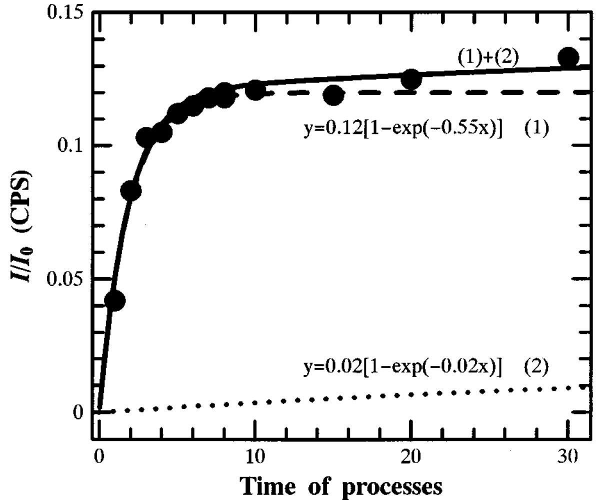

FIG. 4. The change in intensity ratio of the FK mode to the elastic peak. The filled circles are the experimental data. The broken and dotted lines are calculated by Eqs. (2) and (3). The solid line represents the sum of these two equations.

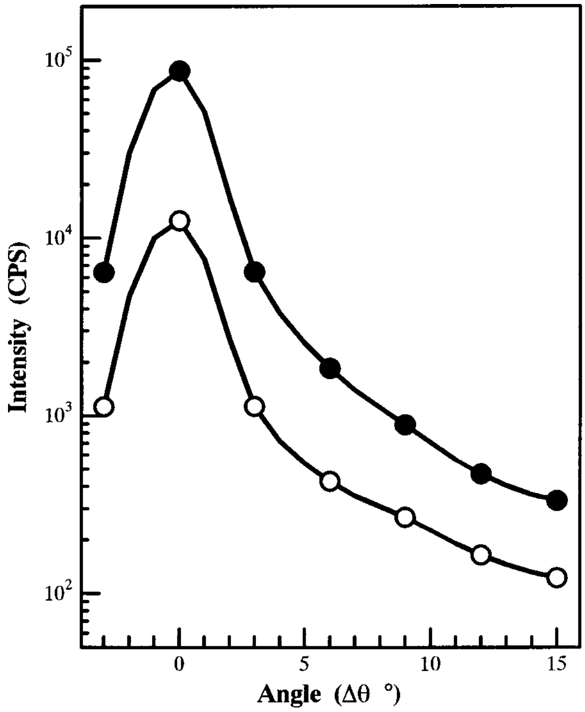

FIG. 5. The angular profile of electrons scattered from the 3*C*-SiC(111) surface obtained after the thirtieth growth processes. The filled and open circles represent the elastic peak and FK mode, respectively. The inset shows the intensities of elastic peaks at various growth processes.

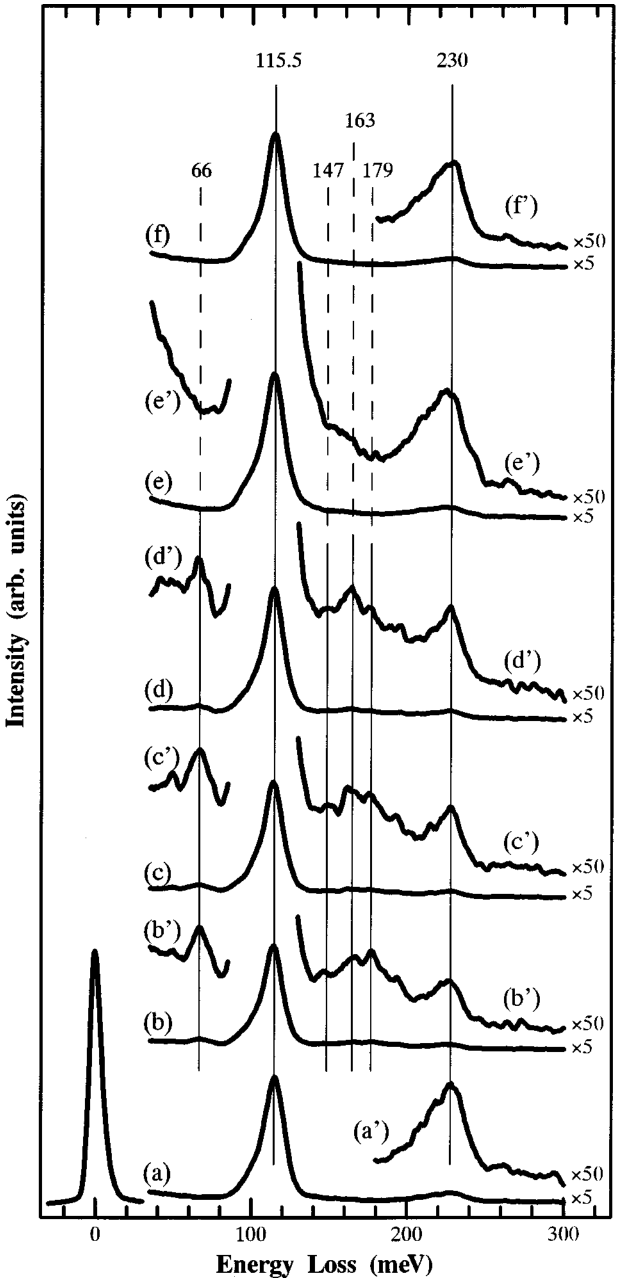

FIG. 6. Temperature-dependent HREEL spectra of the C_{60} molecules adsorbed on 3*C*-SiC(111) surface. (a) shows the 3*C*-SiC(111) surface obtained after the sixth growth processes. (b) is the spectrum measured after adsorbing 1 ML of C_{60} molecules on (a). (c), (d), (e), and (f) are the spectra obtained after annealing the sample at 670, 870, 1070, and 1170 K, respectively. (') indicates the enlarged spectrum of each figure. The solid and broken vertical lines indicate the existence and vanishing of peaks, respectively.

negligible deformation of C_{60} molecules. The large intensity of the 163 meV peak results from the short-range planarity on the SiC substrate, which leads to the disorder of C_{60} molecules. Figures 6(c), (d), (e), and (f) are the spectra after annealing the 1 ML film adsorbed 3*C*-SiC(111) surface at 670, 870, 1070, and 1370 K, respectively. The three T_{1u} modes of C_{60} molecules are visible from room temperature to 870 K.

IV. DISCUSSION

A. Bonding nature of the C_{60} molecule on the Si(111)-(7×7) surface

The bonding nature of solid C_{60} is well established as van der Waals interaction.[42] For the C_{60} molecules adsorbed on surfaces, the charge-transfer scheme[15,22–26] is applied to explain the ionic bonding state. The charges, transferred to the C_{60} molecule, shift the three T_{1u} modes (ν_1, ν_2, and ν_4) and the two Hg modes (95 and 193 meV) to lower energies.[15,22–26] Measuring the alkaline doped C_{60} film, Pichler, Matus, and Kuzmany[23] and Martin, Loller, and Mihaly[24] reported the linear energy shifts of ν_1 and ν_4 modes as -1.25 meV/electron and -1.8 meV/electron, respectively. They also observed a small energy shift of approximately -0.25 meV/electron for the ν_2 mode. The energy shifts of the Hg modes at 95 and 193 meV are estimated to be -0.25 meV/electron and -1.85 meV/electron, respectively, by Raman scattering measurements.[20] Comparing the energies of the peaks observed in Fig. 1(a) with those of the C_{60} solid,[15] no energy shift is confirmed. Therefore, most of the C_{60} molecules are weakly adsorbed on Si(111)-(7×7) surface with van der Waals interaction, like the interaction between C_{60} in the solid state at room temperature. The observation of the (7×7) LEED pattern, with spot intensities weaker than those of the Si(111)-(7×7) clean surface, supports this consequence.

After annealing the C_{60} molecule adsorbed Si(111)-(7×7) surface at 670 K, the 66-meV peak shifts to 64-meV with 1.5 times larger FWHM. The 64-meV peak does not show any decrease in intensity compared to the 66-meV peak. This negligible change in intensity indicates that no C_{60} molecule has desorbed, and the coverage is still 1 ML at 670 K. This result agrees well with the previous STM study[12] in which an image shows the adsorption of a 1 ML C_{60} film at the same temperature. Taking into account the desorption temperature of C_{60} van der Waals islands,[12] we consider that C_{60} molecules, interacting with the van der Waals force on the Si surface at room temperature, desorb at a temperature below 670 K, because the strength of van der Waals interaction between the C_{60} molecules and the Si surface is of the same order of magnitude as that between C_{60} molecules in the solid state.[10] Since 77% of the C_{60} molecules interact with van der Waals force at room temperature for a 1 ML film,[15] the desorption of C_{60} molecules bonded with van der Waals interaction to the Si surface seems to be contradictory to the adsorption of the 1 ML C_{60} film at 670 K. In order to resolve this contradiction occurring between room temperature and 670 K, we observed the LEED pattern. The LEED observed at 670 K shows a different pattern than that obtained at room temperature. The LEED spots originated from the (7×7) structure disappear, and only (1×1) spots and streaks between them are observed. This change in LEED pattern indicates the rearrangement of surface Si atoms. The termination of some Si adatom dangling bonds with C_{60} molecules[15] leads to the change in surface structure at low temperature. In fact, the structural change of the Si(111)-(7×7) surface, the dangling bonds of which are terminated by alkali metal, is observed at 570 K.[43] The different surface structures induce change in the surface electronic state, and therefore interaction between C_{60} molecules and the Si surface should

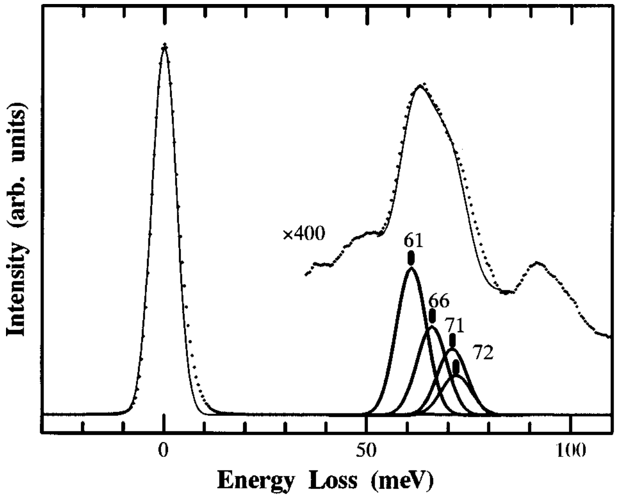

FIG. 7. The HREEL spectrum obtained after annealing the 1 ML C_{60} film adsorbed Si(111)-(7×7) surface at 670 K. The dots, the broken lines, and the solid lines correspond to the experimental data, the Gaussian using the parameter described in Table II, and the fitting curve of the 64-meV peak, respectively.

be changed. Hence, we conclude that C_{60} molecules weakly adsorbed at room temperature change their bonding nature, rearranging the surface Si atoms, and do not desorb.

In order to understand the change in FWHM, we have deconvoluted the 64-meV peak with Gaussian line shapes. The elastic peak is well reproduced by the Gaussian as shown in Fig. 7, and the 64-meV peak is fitted quite well by the sum of four Gaussians. The parameters used for the four Gaussians are tabulated in Table II. Hence, the 64-meV peak contains four vibrational modes the energies of which are 61, 66, 71, and 72 meV. We have assumed the half-width of the four Gaussians to be the same as that of the elastic peak, and the intensity ratio for these peaks to be $I_{71}/I_{61}=I_{72}/I_{66}$, to determine the parameters. Taking into account the charge-transfer scheme,[15,22–26] the energies of 61 and 71 meV agree well with the softened ν_1 and ν_2 modes, respectively, with four electrons transferred to a C_{60} molecule. In this case, the softened ν_4 mode should appear around 171 meV. Since the energy is close to 171 meV, we consider the 170-meV peak observed in Fig. 1(b) to be the softened ν_4 mode. Unfortunately, due to the small shift we could not discuss the lower Hg mode, the unsoftened mode of which must be observed at 95 meV. Because of the tail of the loss peaks observed at 179 meV, the softened higher Hg mode is not observed at 185 meV in Fig. 1(b).

The observation of both softened (61, 71, and 170 meV) and unsoftened (66, 72, and 179 meV) ν_1, ν_2, and ν_4 modes indicates the coexistence of two adsorption states. That is, one state produces the softening of vibrational modes, and the other does not produce any softening. The charge-transfer scheme[15,22–26] suggests the first adsorption state as C_{60} molecules bonded ionically with surface Si atoms. Comparing the energy shifts of the ν_1, ν_2, and ν_4 modes and those reported previously,[15,22–26] we determined the amount of charge transfer to be (4±1) electrons per C_{60} molecule. This number is larger than that for C_{60} molecules adsorbed ionically at room temperature, (3±1).[15] Since C_{60} molecules bonded with van der Waals interaction are not able to exist at 670 K, we suggest the second adsorption state, which does not produce any softening in vibrational modes, as covalently bonded C_{60} molecules. Assuming that the scattering cross sections of ν_1 and ν_2 are equivalent for the ionically and covalently bonded C_{60} molecules, the existence ratio of the ionically bonded C_{60} molecules to the covalently bonded one is suggested to be 1–0.7 from the parameter described in Table II. That is, 59% of the C_{60} molecules of the 1 ML film are adsorbed ionically and 41% covalently with the Si(111) surface at 670 K. This existence ratio and the difference in number of transferred charge for ionic adsorbed C_{60} molecules suggest that both weakly and strongly adsorbed C_{60} molecules at room temperature have changed their interactions under the rearrangements of surface Si atoms.

TABLE II. Fitting parameters used for the line-shape analysis.

Loss energy (meV)	FWHM (meV)	Relative intensity
61	7	1.00
66	7	0.70
71	7	0.39
72	7	0.27

Using the DV-Xα-LCAO method, Yajima and Tsukada calculated the electronic band structures of the 1 ML C_{60} film adsorbed Si(001)-(2×1) surface.[14] Their results indicate a hybridization between the C_{60} molecules and surface Si atoms. However, the HREEL spectra of the C_{60} molecule adsorbed Si(001)-(2×1) surface do not show any softening in vibrational modes.[15] Therefore, our suggestion for the second adsorption state is suitable for the previous studies.[14,15]

The STM image obtained after annealing the C_{60} film adsorbed Si(111)-(7×7) surface at 670 K shows the existence of two kinds of C_{60} molecules on the surface.[12] One forms an ordered domain the area of which is about 10×10 nm^2, and the other a smaller domain in which C_{60} molecules are disordered. The disordered C_{60} molecules are brighter than the others in this image. Furthermore, these C_{60} molecules interact more strongly with the surface Si atoms, since they always pin the ordered domain. Now, we consider carefully this STM image. Since the difference in brightness corresponds to a different height of about 0.2 nm, the value of which is close to the nearest-neighbor atomic distance of Si in the solid state, 0.235 nm, we have to consider the existence of Si adatoms under the disordered C_{60} molecules. The electronic states of the surface Si atom and Si adatom should be different, and it is appropriate to consider different bonding natures between the C_{60} molecule and these Si atoms. The observation of the streaks in LEED signifies the incomplete phase transition from the (7×7) to (1×1) surface structure, and therefore the existence of Si adatoms. In the STM image,[12] approximately 60% of the C_{60} molecules of the 1 ML film form ordered domains and 40% are disordered. Taking into account this ratio and that of the ionically bonded C_{60} molecules to the covalently bonded one, we suggest that the ionic C_{60} molecules make a ordered structure and those bonded covalently with the surface Si atoms make a disordered one.

At 870 K, the equivalency in peak energies suggests the same bonding nature as those observed at 670 K. However, the relative intensities of the dipole-active modes (64, 70, 147, and 179 meV) against those of the Raman-active modes (94 and 193 meV) are different from those observed at 670 K. The intensity ratio of the impact scattering to the dipole scattering is described as

$$\frac{I_{\text{impact}}}{I_{\text{dipole}}} \propto |R_{\text{I}}|^{-2},$$

where I_{dipole}, I_{impact}, and R_{I} are the intensities of the dipole scattering, impact scattering, and elastically scattered beam normalized to the current incident to the sample, respectively.[17] Since the incident current was fixed at 250 pA, the intensity ratio relates only to the intensity of the elastic peak (I_{elas}) as

$$\frac{I_{\text{impact}}}{I_{\text{dipole}}} \propto I_{\text{elas}}^{-2}$$

in our experiment. The intensity of the elastic peak was almost the same as room temperature at 670 K, but decreased above 870 K as the annealing temperature increased. I_{elas} of the sample annealed at 670 K was approximately 1.7 times larger than that obtained after annealing the sample at 870 K. Taking into account the temperature of C_{60} dimer formation observed at a coverage of 0.05 ML,[7] we consider that a few C_{60} molecules move slightly from their earlier adsorption sites at 870 K. This surface disorder leads to a broadening in the scattering angle of the elastic beam, and therefore a decrease in intensity of the elastic peak. The enhancement of the 163-meV peak is consistent with the presence of surface disorder caused by the movement of C_{60} molecules.

B. Bonding nature of the C_{60} molecule on the 3*C*-SiC(111) surface

The bonding nature between C_{60} molecules and the SiC surface atom is identified by the measurement of the temperature-dependent HREEL spectra of the C_{60} molecule adsorbed 3*C*-SiC(111) surface. The observation of the 66-meV peak above 670 K indicates that the interaction between SiC and C_{60} molecules is not van der Waals. If the interaction between the surface atoms and C_{60} molecules is ionic, the softening of some vibrational mode must be observed, as shown for the C_{60} adsorbed Si(111)-(7×7) surface [Fig. 1(b) and Fig. 7]. Since no peak shift is observed for the three T_{1u} modes in Fig. 6(b), we conclude that the interaction between SiC surface atoms and C_{60} molecules is that of covalent bonds. The insignificant peak shift of the T_{1u} modes indicates the negligible change in the chemical nature of the C_{60} molecules on the 3*C*-SiC(111) surface until 870 K, and thus the negligible change in bonding configuration.

On the 3*C*-SiC(111) surface, the ν_1 mode disappears at a temperature lower than that observed for the C_{60} adsorbed Si(111)-(7×7) surface, and the covalent bond between C_{60} molecules is not observed. The weak bonding strength involves the movement of C_{60} molecules and thus the covalent bond between C_{60} molecules. Hence, the covalent interaction between the surface atoms of SiC and C_{60} molecules is stronger than the bonding strength of C_{60} molecules on the Si(111) surface. Taking into account the differences in bonding nature and in bonding strength, we consider the SiC surface atoms of thick film to be carbon atoms. The (1×1) LEED pattern observed for this 3*C*-SiC(111) surface supports our consideration, because the elimination of the Si adlayer was reported by observation of the growth of a plasmon peak in EEL spectra for the 3*C*-SiC(111)-(1×1) surface.[35] The atom species that terminates the surface is different from that of the 3*C*-SiC(111)-(3×3) islands obtained after the first growing process. We consider that this difference comes from the different bonding strengths of surface atoms, since the reconstruction of the surface implies the softening in bonding strengths of the atoms near the surface. The origin of the different bonding strengths is discussed in the following subsection.

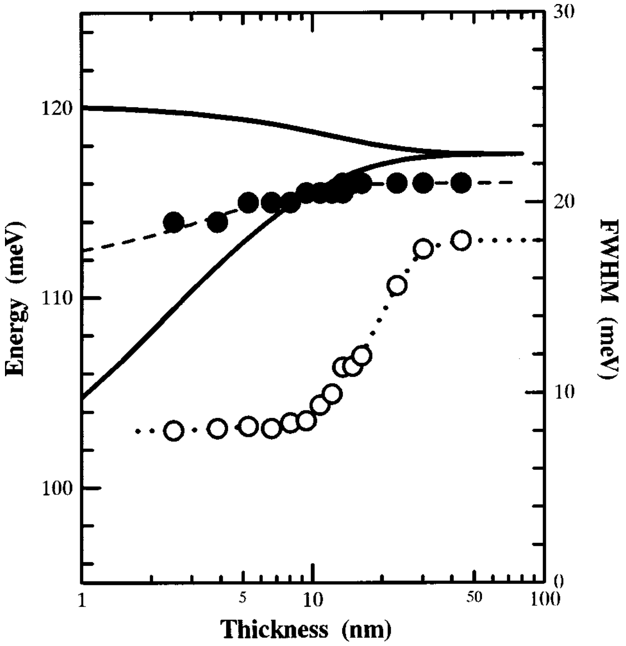

FIG. 8. The energy and FWHM of the ω_+ obtained at various 3*C*-SiC(111) film thickness. The filled circles are the experimental data of the FK mode. The solid lines are the theoretical FK modes. The open circles represent the FWHM of $\omega_{\text{FK}+}$.

C. FK mode of 3*C*-SiC(111) film

Fuchs and Kliewer[27] showed that as the thickness of the film becomes thinner, the FK mode separates into two modes, and the energies of these modes approaches those of ω_{TO} and the bulk longitudinal optical (LO) phonon (ω_{LO}). The bulk phonon modes were reported as $\omega_{\text{TO}}=98.5$ meV and $\omega_{\text{LO}}=120.6$ meV for the 3*C*-SiC solid.[29] Using the macroscopic dielectric theory,[44] indicated by a solid line in Fig. 8, we estimate that the separation of the FK mode occurs at a film thickness of approximately 30 nm. The polarizations of the low-frequency FK mode ($\omega_{\text{FK}-}$) and the high-frequency one ($\omega_{\text{FK}+}$) are parallel and perpendicular to the surface, respectively. Hence, considering the angular variation of scattered electrons and the large intensities, we determine the 102 and 114 meV peaks to be $\omega_{\text{FK}-}$ and $\omega_{\text{FK}+}$, respectively. The observation of $\omega_{\text{FK-}}$ was carried out previously for a thin LiBr layer.[45] However, the intensity of $\omega_{\text{FK-}}$ was very small in that study,[45] and it is difficult to ignore the possibility of it being a loss peak due to contamination. In the present experiment, the large intensity of $\omega_{\text{FK}-}$ explains well the coherent motion of ordered atoms, and the possibility of contamination is neglected from the reasons described in the previous section.

The intensity of $\omega_{\mathrm{FK}-}$ decreases as the SiC film grows, because the expansion of the SiC flat surface area reduces the cross section of electrons scattered from impact scattering. Since the asymmetry of the main peak and the broadening of the 230 meV peak, observed for the initial growth processes, results from the high intensity of $\omega_{\mathrm{FK}-}$, the conversion of $\omega_{\mathrm{FK}-}$ and $\omega_{\mathrm{FK}+}$ and the decrease in intensity of $\omega_{\mathrm{FK}-}$ explain well the third and fourth results observed in Fig. 3.

The thickness-dependent energy of $\omega_{\mathrm{FK}+}$ on the $3C$-SiC(111) surface and the FWHM of the energy-loss peak of $\omega_{\mathrm{FK}+}$ are shown in Fig. 8. We deconvoluted the energy-loss peak with Gaussian line shapes in order to obtain the real FWHM of $\omega_{\mathrm{FK}+}$, because the peak showed extra-broadening due to the overlap of ω_- for the initial growth processes [Figs. 3(a) and (b)]. The filled and open circles are the experimental energy and FWHM of $\omega_{\mathrm{FK}+}$, respectively. We use the STM data[13] to determine the thickness of $3C$-SiC(111) islands formed after the first growth process. Since C_{60} molecules do not desorb at 870 K on the $3C$-SiC(111) surface, and since only little change in the pressure of the analysis chamber and no mass corresponding to carbon atoms was observed during the sample annealing, all carbon atoms of the C_{60} molecule contribute to the formation of SiC. Taking into account the area of the $3C$-SiC(111) surface unit mesh and the lattice constant of $3C$-SiC, and assuming the nearest-neighbor molecular distance between C_{60} molecules to be equivalent with that in the solid state, the thickness of the $3C$-SiC(111) film increases by 1.38 nm at each growth process. This thickness corresponds to approximately 5.5 layers of Si (or C) on the plane of the $3C$-Si(111) surface. The decimal of this value has the possibility to contribute to the terrace area expansion.

The thickness-dependent experimental energy of $\omega_{\mathrm{FK}+}$ are smaller than the theoretical data, and show another profile with the theoretical one. The experimental energy is never above 116 meV, i.e., the energy reported previously for a thick SiC film.[28,29] Only a simple decrease in energy is observed as the $3C$-SiC(111) film becomes thinner. Three possibilities are suggested to explain this phenomenon. First, the size effect of SiC, second the contribution of a microscopic surface phonon, and third the influence of the buffer layer. The SiC buffer layer, suggested by Nishino, Powell, and Will,[46] is a layer in which the large lattice mismatch between Si and SiC layers is accommodated. The Si-C bond must be softened in such a layer.

The size effect[47,48] of the phonon energy is explained by the relaxation of the $q=0$ momentum selection rule. As the size of the microcrystal decreases, the spatial correlation function of the phonon becomes finite due to the effect of the confinement of the phonon into the volume of the microcrystal. Since the dispersion curve of the phonon is not flat in the Brillouin zone, the relaxation of the $q=0$ selection rule leads to an energy shift and asymmetric broadening in the spectrum of the phonon. Both energy shift and asymmetric broadening relate to the slope of the dispersion. That is, when the slope of the dispersion is negative from the Γ point to the end of the Brillouin zone, we observe a lower shift in phonon energy, and a broadening in the FWHM that is accompanied by a tail at the lower-energy side of the energy-loss peak. $\omega_{\mathrm{FK}+}$ has a dispersion in which the energy decreases as the wave number increases for thin film[27]. The minimum in energy is equivalent to that of the thick film, i.e., 116 meV for SiC. However, the energy of $\omega_{\mathrm{FK}+}$ is 116 meV or below at whole thickness, and the FWHM decreases simply as the $3C$-SiC(111) film become thinner as shown in Fig. 8. Taking into account these disagreements, the energy shift observed in our measurement cannot be explained by the size effect.

Senet, Lambin, and Lucas calculated the HREEL spectra of a RhF(001) film on a Ge substrate using shell-model lattice dynamical equations.[49] They showed that the dielectric theory fails in contribution of a microscopic surface phonon for a very thin—a few nm thick—film. However, the thickness dependence of $\omega_{\mathrm{FK}+}$ is different from the dielectric theory for a film thinner than 30 nm in our result. This value is too large to explain the thickness-dependent phenomenon of $\omega_{\mathrm{FK}+}$ with the contribution of a microscopic surface phonon. Furthermore, we do not observe such a microscopic surface phonon in our experiments.

One possible explanation of this phenomenon is the influence of the SiC buffer layer. The thickness of the buffer layer is reported as 1.0–1.5 nm when it immediately takes the unstrained SiC structure,[40] and 30 nm when the composition from Si to SiC changes gradually.[46] The height from the Si(111) substrate to the top of the $3C$-SiC(111) island is reported as 2.0–3.0 nm in the STM study.[13] Therefore, $3C$-SiC(111) island formed by the thermal reaction of a 1 ML C_{60} film adsorbed Si(111)-(7×7) surface is mainly composed of the buffer layer. The difference in the theoretical and experimental energy, i.e., $\omega_{\mathrm{th}}-\omega_{\mathrm{FK}+}$, relates to the extent of influence of the buffer layer. Therefore, the decrease in $\omega_{\mathrm{th}}-\omega_{\mathrm{FK}+}$ signifies that the influence of the buffer layer becomes small as the $3C$-SiC(111) film becomes thick. This result explains well the difference in atom species that terminates the surface of the $3C$-SiC(111)-(3×3) islands, obtained after the first growth process, and the $3C$-SiC(111)-(1×1) surface. That is, the larger influence of the buffer layer for $3C$-SiC(111) islands involves the softer bonding strength of surface atoms, and the (3×3) reconstructed structure that leads the termination with the Si atom. Since, first, the experimental data of the thick $3C$-SiC(111) film are identical with those reported previously,[28,29] and, second, ω_{th} saturates around 30 nm, we conclude that the buffer layer affects the Si-C bonding strength even for a $3C$-SiC(111) film of 30 nm thickness.

The experimental energy of $\omega_{\mathrm{FK}+}$ is smaller than the theoretical one for thick SiC film. It should be noted that the measured value of $\omega_{\mathrm{FK}+}$ is also lower than the calculated one not only for SiC film[28,29] but also for InP,[50] GaP,[50] and LiBr[45] films. This trend is explained quite well by the influence of anharmonicity on the frequency of surface phonons. Actually the phonons have a finite lifetime determined mainly by anharmonic processes. The consistent account of anharmonicity in the lattice dynamics results in the appearance of a complex value of damping in the frequency-dependent dielectric function $[\epsilon(\omega)]$. The real part of this damping corresponds to the anharmonic phonon damping and the imaginary one to the anharmonic shift of the phonon energy. Placido and Hisano[51] calculated the dispersion of surface phonon for NaCl solid including the anharmonic effect. Their result is in good agreement with the experimental result,[52] though the surface phonon energy calculated by harmonic approximation was higher than the experimental one by approximately 2.5 meV. We consider the difference in the experimental and theoretical energies of ω_{FK+} for a thick SiC film as a result of the anharmonicity on the frequencies of the FK mode.

V. CONCLUSION

We have measured the temperature-dependent vibrational modes of C_{60} molecules adsorbed on the Si(111)-(7×7), and the $3C$-SiC(111) surfaces formed by the thermal reaction of a C_{60} film adsorbed Si(111) substrate by means of HREELS. On the Si(111)-(7×7) surface, C_{60} molecules that interact with the van der Walls force with surface Si atoms at room temperature change their bonding natures at 670 K. We find two bonding states at this temperature. One is the ionic bonds between C_{60} molecules and surface Si atoms manifested by the softening of vibrational modes. The other is considered to be the covalent bonds. The amount of charge transfer is estimated to be (4±1) electrons per molecule for the ionic bond. At 1070 K, we observed the formation of C_{60} dimers. The formation of $3C$-SiC(111) islands is verified by the observation of the FK mode at 1170 K. On the $3C$-SiC(111) surface, no softening is observed in the vibrational modes. Taking into account the observation of the C_{60} molecules at 870 K, we consider that C_{60} molecules form covalent bonds with surface atoms. The C_{60} molecules adsorbed on the SiC surface do not change their chemical nature until 870 K, and transform immediately into SiC at 1070 K. The differences in the decomposition temperature and in the SiC formation process, on Si(111) and $3C$-SiC(111) surfaces, indicate the stronger interaction of C_{60} molecules with surface atoms on the SiC surface. Repeating the adsorption and annealing of the sample, the $3C$-SiC(111) islands obtained on the Si(111) surface grow up to thick $3C$-SiC(111) film with long-range planarity on the surface. The softening in the Si-C bond is confirmed by the redshift of the FK mode for $3C$-SiC(111) film thinner than 30 nm.

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