PHYSICAL REVIEW B VOLUME 56, NUMBER 12 15 SEPTEMBER 1997-II

Vibrational properties and charge transfer of C_{60} adsorbed on Si(111)-(7×7) and Si(100)-(2×1) surfaces

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(Received 4 April 1997; revised manuscript received 18 June 1997)

We report here the measurements of vibrational excitation spectra and the temperature dependence of C_{60} molecules adsorbed on Si(111)-(7×7) and Si(100)-(2×1) surfaces using high-resolution electron-energy-loss spectroscopy in combination with scanning tunneling microscopy. A quantitative determination of the molecular charge state is obtained by the lower energy shifts of vibrational modes of C_{60} upon adsorption. On the Si(111)-(7×7) surface, the amount of charge transfer from the surface to a C_{60} molecule is estimated to be (3 ± 1) electrons at the coverage lower than 0.25 monolayer (ML) and (0.7 ± 1) electrons as an average at 1 ML. On the contrary, no indication of charge transfer is observed on the Si(100)-(2×1) surface at a coverage lower than 1 ML. The difference in the charge state on both surfaces is attributed to the difference in the nature of surface states. After annealing 1 ML C_{60} film at 500 K, the strong interaction between the surface Si atom and a C_{60} molecule is indicated by the softening of vibrational modes on both surfaces.
[S0163-1829(97)08336-7]

I. INTRODUCTION

The interaction of C_{60} molecules with the substrates is important to understand the fundamental physical and chemical properties of fullerene and to develop new material functions for C_{60} molecules. Extensive experimental and theoretical studies have been performed on semiconductor surfaces[1–7] as well as metal surfaces.[8–10] In particular, the interaction between C_{60} molecules and silicon surfaces is of great interest because silicon surfaces have the well characterized surface structure and electronic surface states. The clean Si(111) surface reconstructs into the (7×7) structure with 19 dangling bonds in the unit cell[11] and the Si(100) surface has (2×1) structure with two dangling bonds in the unit cell.[12,13] Since these dangling bonds are chemically active, C_{60} molecules are expected to interact strongly with the dangling bonds. In fact, C_{60} molecules do not desorb from the silicon surface even at 1000 K and form a SiC film at 1170 K.[14]

Recently, scanning tunneling microscopy (STM) has been used to study the adsorption and the initial stages of film growth of C_{60} on Si(111)-(7×7) and Si(100)-(2×1) surfaces. On the Si(111)-(7×7) surface, Wang *et al.*[2] reported that C_{60} molecules adsorb most often at the center site of each triangular subunit cell, which is surrounded by three adatoms. Chen and Sarid[3] observed the favor bonding site is the bridge sites of three center adatoms. The existence of the favor bonding site[2,3] and the reduction of tunneling current at the Fermi level[2] indicate the strong interaction of C_{60} molecules with the substrate. The interaction is characterized by charge transfer from the surface Si atom to C_{60} molecules, however the nature and the amount of charge transfer are not yet investigated. On the Si(100)-(2×1) surface, Hashizume *et al.*[4] reported that the interaction is the strong chemisorption while both Chen and Sarid[5] and Klyachko and Chen[6] indicated the physisorption. High-resolution electron-energy-loss spectroscopy (HREELS) (Ref. 15) is very sensitive for measuring the vibrational excitations of surface adsorbates and is a very suitable technique to answer the questions mentioned above.

The icosahedral structure of the C_{60} molecule has the symmetry of the I_h point group. The C_{60} molecule has four infrared-active intramolecular vibration modes with T_{1u} symmetry, and ten Raman-active modes with two Ag modes and eight Hg modes.[16–18] The vibrational modes for bulk C_{60} are measured at $\nu_1=65.2$, $\nu_2=71.4$, $\nu_3=146.6$, and $\nu_4=177.2$ meV by infrared absorption spectroscopy,[19] and observed at $\nu_1=66$, $\nu_3=147$, and $\nu_4=178$ meV by HREELS.[20,21] The ν_2 mode is scarcely observed at 72 meV by HREELS due to the low resolution of about 10 meV compared to infrared absorption spectroscopy of less than 0.1 meV. Some peaks of the Raman-active modes are also observed at the disordered C_{60} films on Si surfaces using HREELS.[21,22]

With the interest in the mechanism of the superconductor of K_3C_{60}, softening of ν_1 and ν_4 modes is observed by infrared absorption spectroscopy by increasing the alkaline doping rate.[23–25] Theoretically, the linear shifts of the two peaks are predicted in the weak electron-molecular-vibration calculation.[26] Recently, Modesti *et al.*[9] and Hunt *et al.*[10] have measured the softening of the ν_1 and ν_4 modes of C_{60} adsorbed on the gold and nickel surfaces, respectively, and estimated the charge state of C_{60} monolayer film with the help of experimental and theoretical results.

In this paper, we report the coverage dependence of vibrational modes and the thermal stability of 1 ML C_{60} film grown on the Si(111)-(7×7) and Si(100)-(2×1) surfaces measured by HREELS. On the Si(111) surface, STM was used to correlate the adsorbate-substrate bonding features given by HREELS with the adsorbate structure reported by other groups.[2–7] The large softening of the ν_1 and ν_4 modes is clearly observed at a coverage lower than 0.25 monolayer (ML) on the Si(111)-(7×7) surface, while energies of vibrational excitations do not shift on the Si(100)-(2×1) surface. These results indicate the strong interaction on the (111) surface, and the weak interaction or physisorption on the (100) surface. The amount of charge transfer from the substrate to the C_{60} molecule at 0.25 ML is estimated to be (3 ± 1) electrons on the (111) surface and (0 ± 1) electrons on the (100) surface. The charge states on both surfaces are discussed in terms of the surface electronic states. We also present the thermal stability of 1 ML film. The strong interaction between the surface Si atom and a C_{60} molecule is indicated by the softening of the vibrational modes on both surfaces after annealing at 500 K.

II. EXPERIMENT

The experiments were performed in a UHV system which consists of two analysis chambers and a sample evaporation chamber. The first analysis chamber is equipped with a high-resolution electron-energy-loss spectrometer, a rear-view low energy electron diffraction (LEED), and an Auger electron spectrometer (AES). The second analysis chamber is equipped with a scanning tunneling microscope (STM). The base pressure in the analysis chambers was below 1.0×10^{-10} Torr and that in the evaporation chamber below 1.0×10^{-9} Torr. Samples were transferred between chambers under UHV conditions. The electron-energy-loss spectra were measured with a VSW IB2000 spectrometer with a typical incident energy of 5.0 eV. The half-widths of the elastically scattered peak were 12 meV for a clean Si(111)-(7×7) surface and 8–5 meV after the deposition of C_{60} molecules. The width at Si(100)-(2×1) surface was 5 meV with and without C_{60} molecules. The incident and the scattering angles were 60° from the surface normal (specular geometry). The STM images were taken with a McAllister STM with software from Digital Instruments. All the measurements were carried out at room temperature.

Commercial n-type Si(111) wafers (phosphorus doped, $\sim1000\ \Omega$ cm) and p-type Si(100) wafers (boron doped, $\sim1000\ \Omega$ cm) were used as sample substrates. Both sample surfaces were etched chemically with the method reported by Ishizuka and Shiraki,[27] and then introduced into a UHV chamber. First, the samples were annealed at 1120 K for 10 min to remove the oxide layer. Second, the clean Si(111)-(7×7) and Si(100)-(2×1) surfaces were prepared by heating the sample up to 1520 K (five times for 3 sec) while passing through the currents directly. The process of chemical etching considerably improves the intensity and the resolution in HREELS measurements. The clear (7×7) and (2×1) structures and patterns were observed by STM and LEED, respectively. The cleanliness of the surface was verified by AES and by the absence of any loss peaks due to vibration modes of adsorbed molecules on both surfaces.

The C_{60} powder was prepared and purified 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. Without the second step, we observed a strong loss peak at 355 meV, which is due to the stretch vibration of the C-H molecule. The C_{60} powder was loaded in a quartz crucible and was heated with tungsten wire in the evaporation chamber. The sample was carefully outgassed below 600 K for over 24 h prior to evaporation. The thickness of the C_{60} layer was monitored by a quartz crystal balance and the deposition rate was approximately 0.2 ML/min. A thickness of 10 Å is estimated to be 1 ML of the C_{60} film by STM.

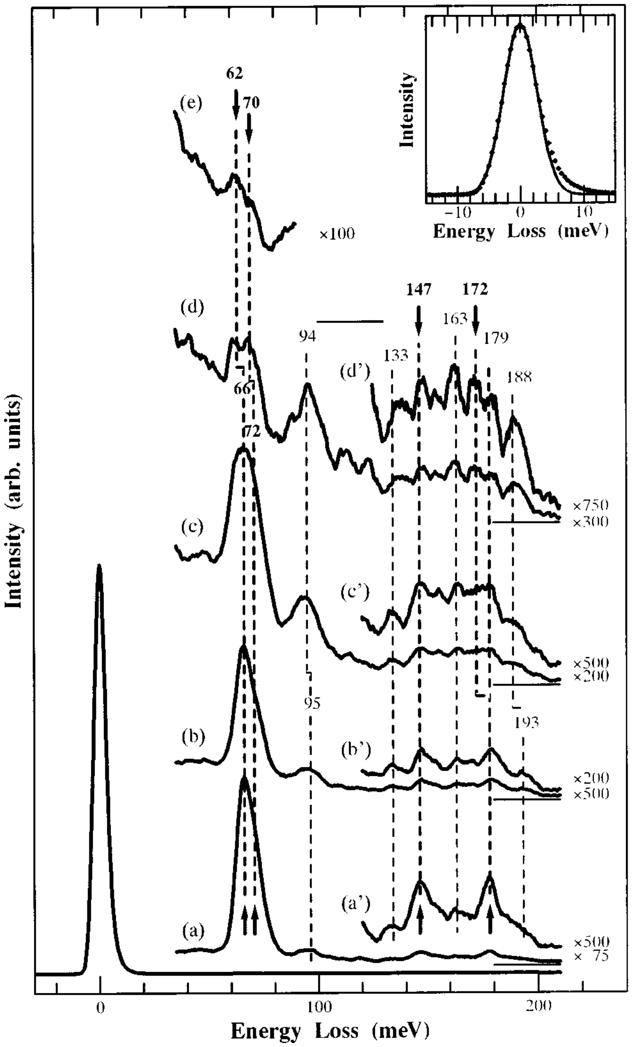

FIG. 1. Electron-energy-loss spectra of C_{60} molecules deposited on Si(111)-(7×7) at 300 K. The coverages are 5 ML (a), 1 ML (b), 0.5 ML (c), 0.25 ML (d), and 0.1 ML (e). Primes indicate the enlarged spectrum at each coverage. Thin solid lines indicate the zero levels of the spectra. These spectra are normalized to the elastic peak. The arrows at the bottom indicate the energies of the dipole-active T_{1u} modes in bulk C_{60}, and those on top indicate the energies of the corresponding modes at a coverage lower than 0.25 ML. The dots in the inset show the enlarged elastic peak, and the solid line is a Gaussian line shape.

III. RESULTS

A. Thickness dependence

Figure 1 shows the electron-energy-loss spectra of C_{60} molecules adsorbed on the Si(111)-(7×7) surface at room temperature. The coverages are 5 ML (a), 1 ML (b), 0.5 ML (c), 0.25 ML (d), and 0.1 ML (e). At the coverage of 5 ML, peaks and shoulders are observed at 66, 95, 133, 147, 163, 179, and 193 meV. The spectral profiles are the same as those for the thick C_{60} film (i.e., bulk C_{60}). The spectra measured by HREELS in specular geometry are dominated by excitations which satisfy the dipole selection rule.[15] The infrared-active (i.e., dipole-active) vibrational modes present the strongest spectral features. Raman-active modes are also observed by the short range electron scattering mechanism, i.e., the impact scattering mechanism. In comparison with the measurements by infrared absorption,[19] Raman scattering,[18,19] and HREELS,[20,21] the 66, 147, and 179 peaks are assigned to be dipole-active T_{1u} modes of ν_1, ν_3, and ν_4, respectively. The Raman-active Hg modes appear at 95, 133, and 193 meV. The peak at 163 meV is assigned to be the mode observed as a small peak in the Raman scattering[18] and neutron scattering[28] at 163 meV. This peak is theoretically analyzed with the first-principles density-functional theory.[29] The surface disorder enhances the intensity of this peak in the HREELS spectra.[21]

At the coverage of 1 ML, the ν_2 mode appears at 72 meV as a shoulder. At the coverage of 0.5 ML, the width of the 66 meV peak becomes broader and the intensity of the 179 meV peak is weaker. At the coverage of 0.25 ML, the 66 meV peak separates into two peaks at 62 and 70 meV. It is noticed that the intensity (i.e., oscillator strength) of the ν_2 mode is larger than that of the ν_1 mode ($I\nu_2/I\nu_1=1.3$). The new peaks at 172 and 188 meV are clearly resolved. At the coverage of 0.1 ML, peaks are observed at 62 and 70 meV. These results show the softening of three T_{1u} modes (ν_1, ν_2, and ν_4), and that of two Hg modes at 95 and 193 meV at 1 ML coverage as shown in Fig. 1 by the dashed lines.

In order to correlate these HREELS spectra with the real structures, STM images are observed with the same samples on the Si(111)-(7×7) surface. Figure 2 shows the STM image of 1 ML C_{60} film grown on the Si(111)-(7×7) surface. At the coverage of 1 ML, the small hexagonal ordered domains are clearly observed, where the C_{60} molecules lie in straight lines. No island formation is observed. At the coverage lower than 1 ML, the C_{60} molecules adsorbed randomly on the (7×7) structure. At 5 ML coverage, well ordered small islands are grown, the surface area of which is about $10\times10\ \mathrm{nm}^2$. The reason we use the combined measurements of HREELS and STM is to check the quality of the film. The STM image shows that the C_{60} molecules grow a single layer at the 1 ML coverage and the spectrum shown in Fig. 1(b) does not include the contribution from the second layers.

Figure 3 shows the electron-energy-loss spectra of C_{60} molecules adsorbed on the Si(100)-(2×1) surface at room temperature. The coverages are 5 ML (a), 1 ML (b), 0.5 ML (c), and 0.25 ML (d). At the coverage of 5 ML, the profile is the same as that on the Si(111)-(7×7) surface without the intensity of the 165 meV peak. Three dipole-active modes are clearly resolved. At the coverage of 1 ML, the intensity of the ν_2 mode becomes larger. In contrast to the Si(111)-(7×7) surface, the peaks at 66, 147, 179, and 193 meV do not shift with reducing the coverage on the Si(100)-(2×1) surface.

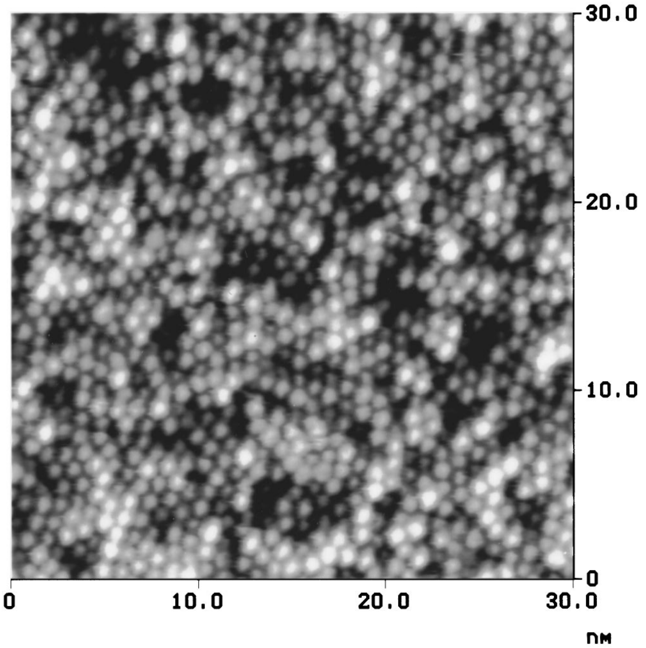

FIG. 2. STM image of the C_{60} film on the Si(111)-(7×7) surface at the coverage of 1 ML. The size of the image is $30\times30\ \mathrm{nm}^2$. Sample bias is 2.7 V and tunneling current is 76 pA.

B. Temperature dependence

Figure 4 shows the electron-energy-loss spectra of 1 ML C_{60} film on the Si(111)-(7×7) surface for different annealing temperatures. The spectrum of the C_{60} film grown at room temperature is displayed in (a). The spectra in (b) and (c) are the spectra obtained after annealing the 1 ML film at 500 and 700 K, respectively. The annealing time was 300 s and then cooled to room temperature. At the coverage of 1 ML, dipole-active T_{1u} modes are clearly observed at 66, 147, and 179 meV. The Raman-active Hg modes appear at 95, 133, and 193 meV. After annealing at 500 K, the 66 meV peak separates into 64 and 70 meV, while the other peaks do not shift clearly.

The electron-energy-loss spectra of C_{60} molecules adsorbed on the Si(100)-(2×1) surface for different annealing temperatures are shown in Fig. 5. The spectrum of the 1 ML C_{60} film grown at room temperature is shown in (a). The spectra in (b) and (c) are the spectra obtained after annealing the 1 ML film at 500 and 700 K, respectively. The annealing conditions are the same as that on the (111) surface. At the coverage of 1 ML, dipole-active T_{1u} modes are clearly observed at 66, 72, 147, and 179 meV. The Raman-active Hg modes appear at 96 and 193 meV. After annealing at 500 K, the 66 meV peak separates into 63 and 71 meV. The intensity of the peak at 179 meV becomes smaller and that of the peak at 173 meV is larger.

In LEED, clear (7×7) and double domain (2×1) patterns are observed on each surface after the 1 ML C_{60} films grown at room temperature. After annealing the film at 500 K, the (7×7) and (2×1) LEED spots become diffusive. At 700 K, the (7×7) pattern disappears and weak streaks are observed between (1×1) spots. The (2×1) pattern is very weak but still observable at 700 K in high background.

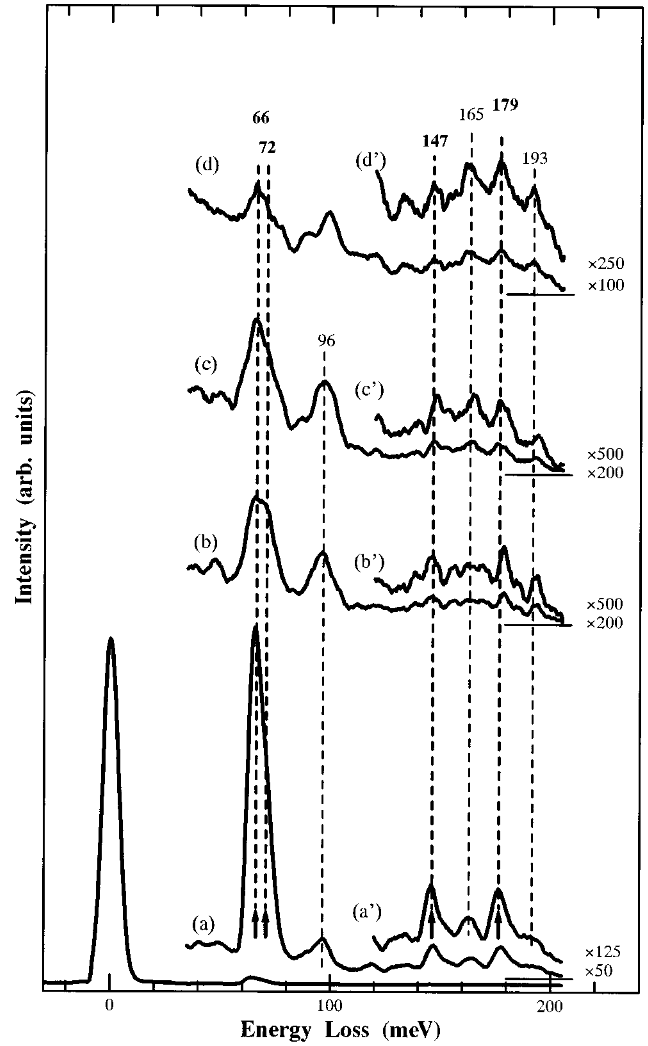

FIG. 3. Electron-energy-loss spectra of C_{60} molecules deposited on Si(100)-(2×1) at 300 K. The coverages are 5 ML (a), 1 ML (b), 0.5 ML (c), and 0.25 ML. Primes indicate the enlarged spectrum at each coverage. The arrows at the bottom indicate the energies of the dipole-active T_{1u} modes in bulk C_{60}.

IV. DISCUSSION

It is well established that the interaction of solid C_{60} is the van der Waals interaction[30] but the interaction between C_{60} molecules and semiconductor surfaces, particularly the Si(111)-(7×7) surface, is not understood. The STM image observed by Xu *et al.*[7] shows a well ordered monolayer film and suggests the interaction of C_{60} with Si(111)-(7×7) is as weak as the van der Waals interaction. On the contrary, the STM image measured by Chen and Sarid,[3] and the image displayed in Fig. 2, shows a monolayer C_{60} film which is made of the small locally ordered domains. These two results indicate a stronger interaction than the van der Waals interaction. At the coverage of 1 ML, the vibrational excitation energies do not shift upon adsorption at the Si(111)-(7×7) surface nor the Si(100)-(2×1) surface, as shown in Figs. 1 and 3. At the coverage of 0.25 ML, however, softening of ν_1, ν_2, ν_4 and the two Hg modes, and the change in the oscillator strength of the ν_1 and ν_2 modes, are clearly observed on the Si(111)-(7×7) surface.

In order to understand the softening and the change in intensity of the ν_1 and ν_2 modes on the Si(111)-(7×7) surface more precisely, we have deconvoluted the loss peaks at 62, 66, 70, and 72 meV with a Gaussian line shape. The elastic peak is well reproduced by the Gaussian peak as shown in the inset of Fig. 1. The peaks at 62 and 70 meV are clearly observed at 0.25 and 0.1 ML coverage and 66 and 72 meV peaks are dominant at 5.0 ML coverage. We assume that the half-width of the Gaussian peak is the same as that of the elastic peak, and that the same intensity ratio of ν_2 and ν_1 occurs at each coverage, i.e., $I_{72}/I_{66}=I_{70}/I_{62}$. The sum of four Gaussian peaks fits the HREELS spectra quite well and the estimated intensities are tabulated in Table I. At the coverage of 5 ML, the ratio of $I_{72}/I_{66}=0.3$ is very close to the ratio of $I_{72}/I_{66}=0.29$ for thick C_{60} film reported by Gensterblum *et al.*[20] The 62 and 70 meV peaks are not observed. The intensity ratios of I_{62}/I_{66} are 0.3 and 0.8 at the coverage of 1.0 and 0.5 ML, respectively. At the coverage of 0.25 ML, the 62 and 70 meV peaks are clearly observed, and the ratios of I_{62}/I_{66} and I_{70}/I_{62} are 10 and 1.3, respectively. These results indicate that there are physisorption and chemisorption sites of C_{60} molecules on the Si(111)-(7×7) surface at the coverage lower than 1 ML, and that C_{60} molecules selectively adsorb the chemisorption sites at the coverage lower than 0.25 ML.

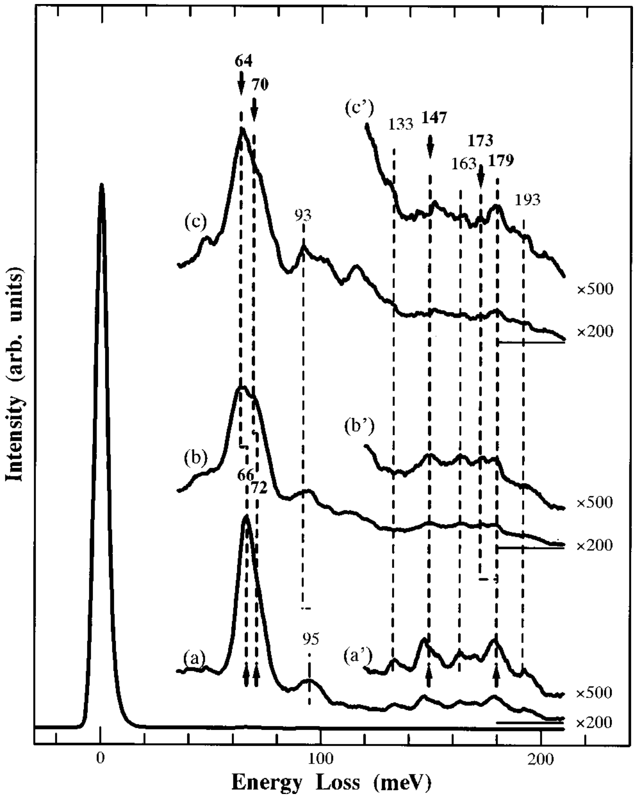

FIG. 4. Electron-energy-loss spectra of 1 ML C_{60} film grown on Si(111)-(7×7) at 300 K (a) and after annealing the sample at 500 K (b) and 700 K (c). Primes indicate the enlarged spectrum at each annealing temperature. The arrows at the bottom indicate the energies of the dipole-active T_{1u} modes in bulk C_{60}, and those on top indicate the energies of the corresponding modes after annealing at 700 K.

We have explained the energy shift and the change in oscillator strength of T_{1u} modes by the charge transfer from silicon dangling bonds to C_{60} molecules. This charge transfer

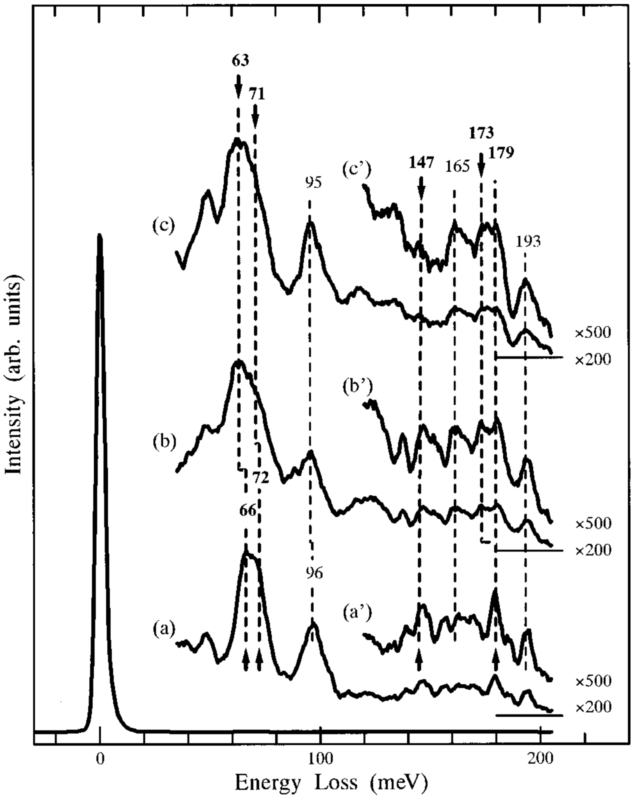

FIG. 5. Electron-energy-loss spectra of 1 ML C_{60} film grown on Si(100)-(2×1) at 300 K (a) and after annealing the sample at 500 K (b) and 700 K (c). Primes indicate the enlarged spectrum. The arrows at the bottom indicate the energies of the dipole-active T_{1u} modes in bulk C_{60}, and those on top indicate the energies of the corresponding modes after annealing the sample at 700 K.

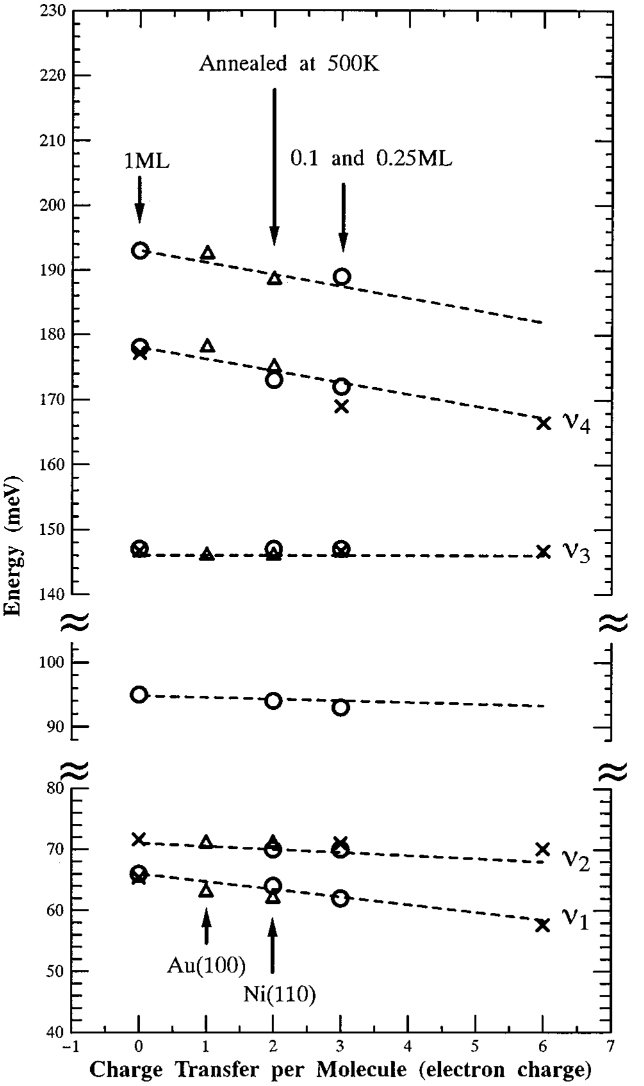

FIG. 6. Energies of the four T_{1u} and two Hg modes of C_{60} molecules adsorbed on Si(111)-(7×7) at the coverage of 1 ML, 0.25 ML, and after annealing the 1 ML film at 700 K (open circles). The crosses show the energies of the dipole-active T_{1u} mode measured by infrared absorption spectroscopy for bulk C_{60}, K_3C_{60}, and K_6C_{60} (Ref. 23). The dashed lines indicate the energies of four T_{1u} and two Hg modes, which depend on the transferred charge. Triangles show the energies of C_{60} molecules on Au(100) (Ref. 9) and Ni(110) (Ref. 10) surfaces.

scheme is first applied to the softening of ν_1 and ν_4 modes of C_{60} on Au(100) by Modesti *et al.*[9] Theoretical calculation by Rice and Choi[26] shows that the energies of ν_1 and ν_4 modes shift linearly towards lower energies with increasing the number of electrons transferred from alkaline metal to the T_{1u} level of the C_{60} molecule. The energies of ν_2 and ν_3 do not shift. This calculation agrees with our results. Recently, Pitcher *et al.*[23] and Martin *et al.*[24] measured the infrared absorption spectra of alkaline doped thick C_{60} films. The observed energies of potassium doped C_{60} are plotted in Fig. 6 with the crosses. The energy shift of the ν_4 mode in bulk K_xC_{60} ($x=0,3,6$) is nearly linear with respect to charge transfer of -1.8 meV/electron. The energy of the ν_3 mode does not shift with charge transfer. The small energy shift is observed for the ν_2 mode. The ν_1 mode disappears in K_3C_{60} and shows up in K_6C_{60}. The peak shift of -1.25 meV/electron is observed. The Hg modes at 95 meV and at 193 meV shift with the slope of -0.25 and -1.85 meV/electron, respectively, which are estimated by the Raman scattering measurements.[18] These energy shifts are shown in Fig. 6 with the dashed lines. The energies of ν_1, ν_2, ν_3, ν_4, and two Hg modes in the present experiments are plotted in Fig. 6 with open circles. The values are in good agreement with the shift. The amount of the charge transfer is estimated to be (3 ± 1) electrons with Fig. 6 at a coverage lower than 0.25 ML. If we assume that the electron scattering cross section of the 66 meV peak per C_{60} molecule is the same as that of the 62 meV peak, the charge transfer is estimated to be (0.7 ± 1) electron as an average at 1 ML

TABLE I. Relative intensity of the energy loss peaks at 62, 66, 70, and 72 meV on the Si(111)-(7×7) surface. Underlines indicate the normalized peak at each coverage.

	Coverage of C_{60}			
Energy (meV)	5.0 ML	1.0 ML	0.5 ML	0.25 ML
66 (ν_1)	1.0	1.0	1.0	0.1
72 (ν_2)	0.3	0.5	0.5	0.1
62 (ν_1)		0.3	0.8	1.0
70 (ν_2)		0.2	0.4	1.3

coverage with the intensity ratio shown in Table I. Though there should be some contribution from the distortion of the C_{60} molecule upon adsorption, the spectra on the Si(100)-(2×1) surface show that a C_{60} molecule does not deform without strong interaction or bonding.

With STM, Wang *et al.*[2] reported that 86% of C_{60} molecules adsorbed at the threefold hollow sites, which is surrounded by three adatoms at a coverage lower than 0.1 ML. Chen and Sarid[3] showed that the C_{60} molecules adsorbed around three center-adatom sites at a coverage lower than 0.1 ML, and adsorbed at bridge sites of two adatoms at the coverage of 1 ML. Though our STM images are not able to specify the adsorption sites, it is plausible that the C_{60} molecules interact three dangling bonds of the Si(111)-(7×7) surface at low coverage and transferred (3 ± 1) electrons from the three dangling bonds to one C_{60} molecule. This result suggests that the C_{60} molecule mainly interacts with surface states of the three adatoms. The (7×7) structure has 19 dangling bonds in the unit cell. Approximately seven C_{60} molecules adsorb on the (7×7) unit cell at 1 ML coverage, and there are two possible positions of threefold hollow sites existing in the (7×7) unit cell. The (7×7) structure indicates that the favorite adsorption sites of the C_{60} molecule are fully occupied at a coverage of about 0.3 ML. At the coverage of 1 ML, C_{60} molecules make a locally ordered monolayer film pinned by the C_{60} molecules which strongly interact with the dangling bond underneath. The softening of vibrational modes is not observed because the HREELS spectrum is the overlap of signals from physisorption and chemisorption sites as shown in Table I. This result shows that the interaction of C_{60} with the Si(111)-(7×7) surface is mainly van der Waals as well as the interaction between C_{60} molecules. If the electron scattering cross section of the 66 meV peak per C_{60} molecule is the same as that of the 62 meV peak, approximately 23% of C_{60} molecules interact strongly with Si dangling bonds. The clear (7×7) pattern in LEED supports this consequence.

On the Si(100)-(2×1) surface, the STM image observed by Hashizume *et al.*[4] shows the internal structure of C_{60} molecules. This result indicates the strong interaction of C_{60} molecules with the surface, while the measurements by both Chen and Sarid[5] and Klyachko and Chen[6] suggest a weak interaction like the van den Waals interaction. In our HREELS measurements, the softening of the vibrational excitations was not observed. This result suggests weak interaction or physisorption, and the transferred charge is estimated to be (0 ± 1) electrons.

There are two aspects of charge transfer.[31] One is ionic in nature. The electronic states or the molecular orbital of adsorbates are not strongly influenced upon adsorption. Another is the covalent bonding, where mixing occurs between orbitals of the adsorbate and the substrate. The model discussed above has ionic character.[26,32] The electronic band structure of monolayer C_{60} on Si(100)-(2×1) is calculated by the $DV\text{-}X\alpha$-LCAO method.[33] A covalent bonding of the C_{60} molecule with the Si dimer atom is assumed in the model. The amount of charge transfer is calculated to be 0.66 electron per molecule. Electronic states of monolayer C_{60} on Si(111)-(7×7) are also calculated by the $DV\text{-}X\alpha$-LCAO method for the model cluster of $C_{60}Si_{101}H_{60}$.[34] The amount of the charge transfer is calculated as 3.35. These numbers agree well with our experimental results at a coverage lower than 0.25 ML on the (111) surface and at a coverage lower than 1 ML on the (100) surface, though the character of the charge transfer is different.

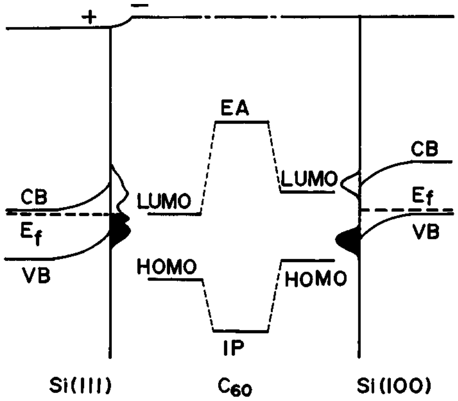

FIG. 7. A schematic diagram of the energy levels of the isolated C_{60} molecule (center), the C_{60} molecule adsorbed on the Si(111)-(7×7) surface (left-hand side), and on the Si(100)-(2×1) surface (right-hand side). On the metallic Si(111)-(7×7) surface, the LUMO level shifts toward the Fermi level (E_F) as suggested by photoemission spectroscopy (Ref. 35).

In order to explain the difference in the amount of charge transfer at the lower coverage on both surfaces, we consider the difference in the character of surface electronic states. Figure 7 shows the schematic energy levels of isolated and adsorbed C_{60} molecules. The ionization potential and the electron affinity of the C_{60} molecule are 7.6 and 2.7 eV below vacuum level. Si(111)-(7×7) has a surface state across the Fermi level, which presents the metallic character of the surface. In contrast, the surface states have a gap on the Si(100)-(2×1) surface as in the semiconductors. Since the work function of Si is about 4.8 eV, the LUMO of C_{60} film lies above the Fermi level shown on the Si(100)-(2×1) surface. Ohno *et al.*[35] studied the electronic structure by photoemission spectroscopy, and showed the LUMO of the C_{60} shifts toward the Fermi level (E_f) in the case of adsorption on the metal surfaces. Since the Si(111)-(7×7) surface has a metallic surface state, the same effect might be expected. Hence, the charge transfer from Si surface states to the LUMO level occurs on Si(111)-(7×7), while the charge at the valence-band maximum does not transfer to the LUMO level of C_{60} on Si(100)-(2×1). In the case of the n-type substrate, the charge transfer may be expected even on the Si(100)-(2×1) surface depending on the doping rate and the band bending of the conduction band, as discussed by Ohno *et al.*[35] and Chen and Sarid.[5]

Finally, the energies of the ν_1 and ν_2 modes shift drastically with increasing the annealing temperature up to 700 K as shown in Figs. 4 and 5. The structure under the 1 ML C_{60} film is distorted as observed by LEED. We tentatively applied the charge transfer scheme, and the charge transfer is estimated to be (2 ± 1) electrons with the softening of the vibration modes as shown in Fig. 6. It is noticed that the softening of the vibrational modes occurs at the low temperature of 500 K. The annealing may induce the charge transfer from the Si surface to C_{60} molecules. Once the charges are extracted from the Si surface, the (7×7) and (2×1) structures become unstable.

On the Si(100)-(2×1) surface, Chen and Sarid[5] studied the temperature dependence of adsorption sites by STM at the coverage of 0.06 ML, and proposed the change in the adsorption characteristics of C_{60} molecules from physisorption to chemisorption at 900 K. At the coverage of 0.25 ML, we observed the same temperature dependence as shown in Fig. 5, though we were not able to specify the adsorption site by STM. The softening suggests that the interaction of C_{60} with the Si(100)-(2×1) surface begins to change at 500 K. The drastic change in HREELS spectra is observed at 1000 K.

V. CONCLUSION

In conclusion, we have measured the vibrational excitation spectra and the temperature dependence of C_{60} molecules adsorbed on Si(111)-(7×7) and Si(100)-(2×1) surfaces by HREELS. On the Si(111)-(7×7) surface, the combined measurements of HREELS and STM are performed. The softening of vibrational modes is observed at a coverage lower than 0.25 ML on Si(111), and the amount of charge transfer is estimated to be (3 ± 1) electrons per one C_{60} molecule. The coverage dependence of HREELS spectra indicates the two adsorption character, i.e., charge transfer and van der Waals interaction. At the coverage of 1 ML, 77% of the C_{60} molecules interact with Si dangling bonds by van der Waals force, and 23% of the C_{60} molecules strongly interact with Si dangling bonds by charge transfer. The amount of charge transfer is estimated to be (0.7 ± 1) electrons as an average. The locally ordered 1 ML film is clearly observed by STM. No softening is observed on the Si(100) surface at a coverage lower than 1 ML. The result shows that the interaction of C_{60} with Si(100)-(2×1) surfaces is mainly van der Waals as well as the interaction between C_{60} molecules. The difference in the charge state on both surfaces is discussed in terms of the character of surface states. After annealing 1 ML C_{60} film at 500 K, the strong interaction between the surface Si atoms and a C_{60} molecule is indicated by the softening of the vibrational modes on both surfaces accompanied by a rearrangement of surface Si atoms.

ACKNOWLEDGMENTS

The authors would like to thank Professor Masaru Tsukada of University of Tokyo for the valuable discussion on the various aspects of charge transfer. The authors also thank Professor Wakio Uchida of Tohoku University, Professor J. Robert Anderson of University of Maryland, and Professor Yuichiro Nishina of Ishinomaki Senshu University for their useful discussions on HREELS measurements. This work was supported in part by Grant-in-Aid No. 08454072 from the Ministry of Education, Science and Culture, and the Kurata Research Grant.

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