

## Bonding state of the C<sub>60</sub> molecule adsorbed on a Si(111)-(7×7) surface

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We report here the measurements of the valence spectra, the C 1s and the Si 2p core-level spectra of C<sub>60</sub> molecules adsorbed on a Si(111)-(7×7) surface, using photoelectron spectroscopy. In the valence spectra, the highest occupied molecular orbital (HOMO) of a C<sub>60</sub> splits into two peaks at a coverage lower than 0.25 ML. The binding energies of the split peaks are 1.8 and 2.4 eV. Taking into account the polarization-dependence of the valence spectra and the binding energy of the C 1s core-level spectra, it is found that the 2.4-eV peak observed in the valence spectra is the covalent bonding state between a C<sub>60</sub> molecule and the Si substrate, and that the 1.8-eV peak is the shifted HOMO. The Si 2p core-level spectra suggest that the bonding site is localized at the interface. We also present the energy-level scheme of the bonding state in terms of the symmetry of the HOMO. [S0163-1829(98)02443-6]

### I. INTRODUCTION

The interaction between C<sub>60</sub> molecules and substrates is important in order to understand the fundamental physical and chemical properties of fullerene and to develop new material functions for C<sub>60</sub> molecules. Extensive experimental studies have been performed on semiconductor<sup>1-7</sup> and metal<sup>8-16</sup> surfaces. In particular, the interaction between C<sub>60</sub> molecules and silicon surfaces is of great interest due to the formation of silicon carbide (SiC) by the thermal reaction.<sup>1-3</sup>

On a Si(111)-(7×7) surface, the favorite bonding sites of C<sub>60</sub> molecules are observed using scanning tunneling microscopy.<sup>4,5</sup> These observations indicate the strong interaction of C<sub>60</sub> molecules with the Si(111)-(7×7) surface. This strong interaction is considered to have an ionic character at a coverage lower than 0.25 ML from the measurement of the vibrational excitations of C<sub>60</sub> molecules using high-resolution electron-energy-loss spectroscopy (HREELS).<sup>7</sup> 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<sub>60</sub> molecule is used.<sup>17</sup>

On metal surfaces, HREELS shows that the interactions between C<sub>60</sub> molecules and Au(110), Ni(110), and polycrystalline Ag surfaces have ionic characters.<sup>8,9</sup> On the other hand, photoelectron spectroscopy (PES) measurements show the full range of interaction. The substrate-dependent interactions of ionic<sup>11-13</sup> and covalent<sup>14,15</sup> characters are discussed from whether the electron occupied LUMO of a C<sub>60</sub> molecule is observed or not. For the C<sub>60</sub> molecules adsorbed on a Au(110) surface, the LUMO is not observed and therefore the interaction is considered to have a covalent character.<sup>14</sup> The hybridization of the molecular orbital (MO) with the substrate bands is proposed to explain the opposite results on the Au(110) surface obtained by HREELS (Refs. 8 and 9) and PES:<sup>14</sup> the hybridization of the LUMO is very

broad and not able to be observed in PES measurements. Therefore, the considerations of the perturbation on the molecular electronic structure are necessary for a complete understanding of the chemical interaction between C<sub>60</sub> molecules and the substrate. Recently, a split of the highest occupied molecular orbital (HOMO), due to the symmetry breaking interaction with the surface, is observed for the C<sub>60</sub> molecules adsorbed covalently on Al surfaces.<sup>15</sup> Nevertheless, the nature of the split peaks and the character of the bonding orbital between a C<sub>60</sub> molecule and surface atoms are not clearly understood.

Although PES is a very suitable technique for obtaining information to elucidate the bonding features as confirmed on metal surfaces, no investigation about the interaction and the electronic states on C<sub>60</sub> adsorbed Si(111)-(7×7) surface was carried out using PES measurement until now.

In this paper, we present the PES measurements of C<sub>60</sub> molecules adsorbed on a Si(111)-(7×7) surface. The split of the HOMO is observed at a coverage lower than 0.25 ML in the valence spectra. Taking into account the polarization-dependent valence spectra and the core-level spectra, we conclude these peaks as the shifted HOMO and the bonding state. The bonding configuration, the energy-level scheme, and two schemes to explain the softening in C<sub>60</sub> vibrational modes observed in HREELS<sup>7</sup> are also discussed.

### II. EXPERIMENT

PES measurements were performed on the beam line BL-18A at Photon Factory of the High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan.

A spherical sector analyzer with a total energy resolution of 100 meV at a photon energy of 21.2 eV and angular acceptance of ±12°, was used for all PES measurements. The analysis chamber was also equipped with a low-energy

electron diffraction (LEED) system, a Mg/Al twin anode x-ray source for the x-ray photoelectron spectroscopy (XPS), and a He discharge lamp. A photon energy of 21.2 eV was used for the valence PES measurements, and photon energies of 125 and 130 eV for the measurements of the Si 2*p* core level using the *p*-polarized synchrotron radiation (SR) light. The He I resonance line of 21.2 eV was also used to measure the nonpolarized valence spectra. The incidence angles of the SR light and that of the He I line were 45° and 15° from the surface-normal direction, respectively. The emission angle was 0° for both lights. All measurements were done at room temperature.

The Si(111) sample was a P-doped (*n*-type) Si wafer, which has the electrical resistivity of 1000 Ωcm and a size of 7×15×0.5 mm<sup>3</sup>. We prepared the Si sample chemically following the Shiraki method<sup>18</sup> 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 s by direct resistive heating in the UHV chamber to obtain the clean reconstructed Si(111)-(7×7) surface. We checked the quality of the surface by the observation of a clear 7×7 LEED pattern. The cleanliness of the surface was verified by the absence of the O 1*s* and C 1*s* signals in the XPS spectra. The sample was spontaneously cooled for several minutes after heating up to 1520 K before the C<sub>60</sub> deposition. The preparation and the adsorption condition of C<sub>60</sub> molecules are described elsewhere.<sup>3,7</sup>

### III. RESULTS

#### A. Valence PES

Figure 1 shows the coverage-dependent valence spectra of the C<sub>60</sub> adsorbed Si(111)-(7×7) surface obtained by the SR light and the He I resonance line. The spectrum of the Si(111)-(7×7) clean surface shows clearly the occupied surface states *S*<sub>1</sub> and *S*<sub>2</sub> at 0.2 and 0.9 eV, respectively. The orbitals of the *S*<sub>1</sub> and *S*<sub>2</sub> states are mainly localized at the adatom sites and rest atom sites of the dimer-adatom-stacking fault (DAS) structure.<sup>19</sup> At a coverage of 5.0 ML, MO's of C<sub>60</sub> molecules are observed at 2.0, 3.3, 5.1, 5.6, 6.8, 8.1, 9.2, and 9.9 eV. In previous reports,<sup>13–16</sup> the binding energy of the HOMO and the second highest occupied MO (HOMO-1) of a C<sub>60</sub> molecule were observed between 2.0 and 2.5 eV, and between 3.3 and 4.0 eV, respectively. Taking into account these energies, the 2.0- and 3.3-eV peaks observed in Fig. 1 are assigned to be the HOMO and the HOMO-1. The HOMO is a fivefold degenerate MO with *h<sub>u</sub>* symmetry in the *I<sub>h</sub>* point group.<sup>20,21</sup> The HOMO-1 is the overlap of fourfold and fivefold degenerate MO's that have *g<sub>g</sub>* and *h<sub>g</sub>* symmetries, respectively.<sup>20,21</sup> The spectral features at 5.0 ML are the same as those of bulk C<sub>60</sub> in which C<sub>60</sub> interacted with van der Waals force. No difference in the binding energy of MO's and in the full width at half-maximum (FWHM) is observed at 1.0 ML, indicating that most of the C<sub>60</sub> molecules interact with van der Waals force with the surface at this coverage. At a coverage lower than 0.5 ML, the valence spectra show the broadening in the FWHM of all MO's. The FWHM of the HOMO at 0.5 ML is 1.2 times larger than that at 5.0 ML. At a coverage lower than 0.25 ML, the HOMO with a binding energy of 2.0 eV disappears and new peaks appear at 1.8 and 2.4 eV. These

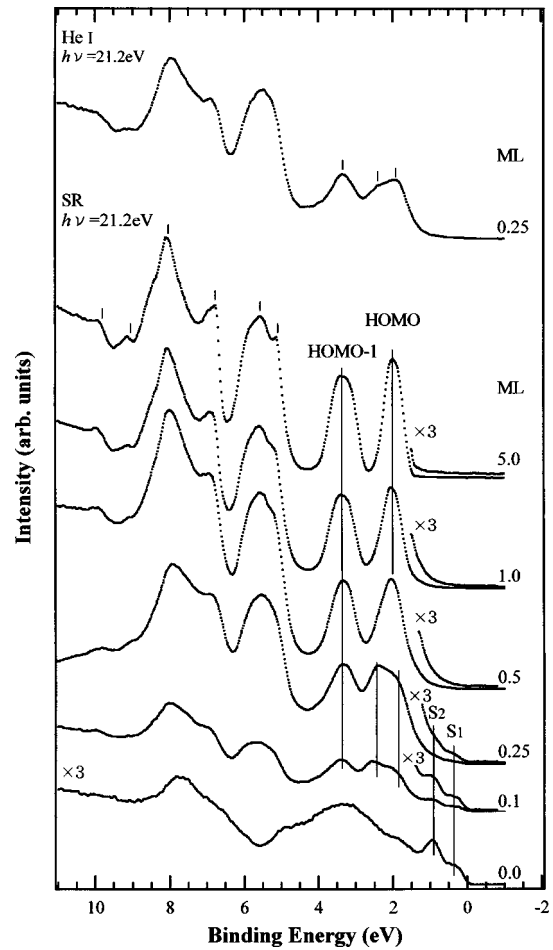


FIG. 1. Coverage-dependent valence photoelectron spectra of the C<sub>60</sub>-adsorbed Si(111)-(7×7) surface measured by SR light of  $h\nu=21.2$  eV, and by He I resonance line.

peaks indicate the strong interaction between C<sub>60</sub> molecules and the Si(111)-(7×7) surface at low coverage. The intensity of the 2.4-eV peak observed by He I line is weaker than that observed by SR light, compared to the 1.8-eV peak. Moreover, intensities from MO's of C<sub>60</sub> decrease and the substrate features become dominant.

We are able to recognize the co-existence of the 1.8-, 2.0-, and 2.4-eV peaks above 0.5 ML in the deconvoluted spectra. The 1.8- and 2.4-eV peaks indicate the presence of chemisorbed C<sub>60</sub> molecules, and the HOMO at 2.0 eV suggests the presence of C<sub>60</sub> molecules interacted with van der Waals force. Therefore, the co-existence of the 1.8- and 2.4-eV peaks, and the HOMO at 2.0 eV suggests the presence of two interactions between C<sub>60</sub> molecules and the Si(111) surface. The presence of two interactions is consistent with the previous HREELS measurement<sup>7</sup> in which both chemisorbed and physisorbed C<sub>60</sub> molecules are observed at the same coverage range.

#### B. Core-level PES

Figure 2 shows the C 1*s* spectra at a coverage of 0.25, 1.0, and 5.0 ML, obtained by the Mg *K*α line with a photon energy of 1253.6 eV. The binding energy of the C 1*s* core level is 284.8 eV and the spectra have a symmetric shape at all coverages. On noble metal surfaces,<sup>10–12,14</sup> a shift to

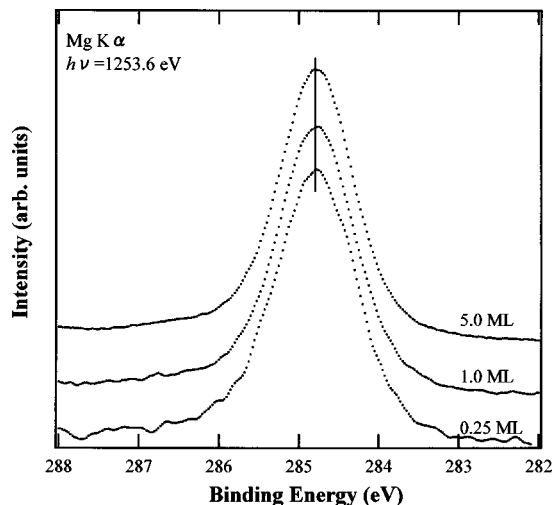


FIG. 2. C  $1s$  core-level spectra for the C<sub>60</sub> molecules-adsorbed Si(111)-(7 $\times$ 7) surface observed by the Mg  $K\alpha$  line. The coverages are 0.25, 1.0, and 5.0 ML.

lower binding energy and an asymmetric energy tail at the higher binding-energy side are observed at a coverage of 1.0 ML. The energy shift and the asymmetric tail ascribe to the final-state screening effect and the electron-hole pair excitation,<sup>14</sup> respectively, and therefore suggest the charge transfer from the metal surface into the LUMO. The present result indicates that the C<sub>60</sub> molecule adsorbed on the Si(111)-(7 $\times$ 7) surface is semiconductor, and that the amount of charge transfer from the Si substrate to a C<sub>60</sub> molecule is very small compared to those on metal surfaces.<sup>10-12,14</sup> Therefore, we conclude the strong interaction between the C<sub>60</sub> molecule and the Si(111)-(7 $\times$ 7) surface to have a covalent character. This conclusion is also supported by the observation in Fig. 1. The binding energies of MO's higher than the HOMO-1 do not change at any coverage. Once the charge transfer occurs, the energies of all MO's shift with the coverage due to the pinning of the LUMO as was observed on metal surfaces.<sup>12,13</sup> The covalent character is also consistent with the result that no new feature except the  $S_1$  and  $S_2$  state of the substrate is observed just below the Fermi level at any coverage in the valence spectra.

The Si  $2p$  spectra of the Si(111)-(7 $\times$ 7) clean surface and the surface covered with a 1.0-ML C<sub>60</sub> film are displayed in Fig. 3. Considering the mean free path, we choose a coverage of 1.0 ML to obtain a uniform sensitivity of electrons emitted from the surface Si atoms covered with C<sub>60</sub> molecules. The photon energies of 130 and 125 eV are used for the clean and the C<sub>60</sub> adsorbed surfaces, respectively. We have used Voigt line shapes, a convolution of a Gaussian and a Lorentzian, to analyze the spectra by a standard least-squares-fitting method. The same parameters are used for the spin-orbit splitting, the branching ratio of  $2p_{1/2}$  and  $2p_{3/2}$ , and the widths of the Gaussian and the Lorentzian on both surfaces in the fitting procedure. The parameters in the procedure are shown in Table I. A polynomial background was subtracted before the decomposition of each spectrum. The filled circles are the experimental data points and the solid lines overlapped with the filled circles are the fitting curves. The solid lines indicate the bulk components, and each hatch different surface components. In order to obtain the best fits

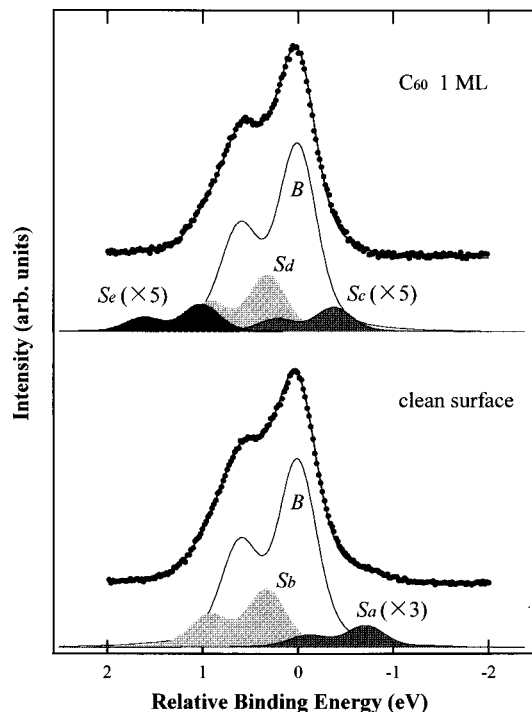


FIG. 3. Si  $2p$  core-level spectra of the Si(111)-(7 $\times$ 7) clean surface and the surface covered with a 1-ML C<sub>60</sub> film measured with photon energies of 130 and 125 eV, respectively. The filled circles are the experimental data, and the solid lines overlapped with filled circles are the fitting curves. Each component is indicated by different hatching. The Gaussian and Lorentzian widths of each components are 0.30 and 0.18 eV.

of the spectrum, three different components, i.e., the bulk component  $B$ , and the surface components  $S_a$  and  $S_b$ , are used for the Si(111)-(7 $\times$ 7) clean surface. For a 1.0-ML C<sub>60</sub> film, we use four different components, i.e., the bulk component  $B$ , and the surface components  $S_c$ ,  $S_d$ , and  $S_e$ . The energy shifts and intensities of the surface components relative to the bulk components are shown in Table I. Taking into account the previous results,<sup>22</sup> the  $S_a$  and  $S_b$  are considered to be due to the rest atoms, and the adatoms and the

TABLE I. The fitting parameters used for the line-shape analysis, and the values of the energy shifts and intensities of the surface components relative to the bulk ones. The positive value of energy shift represents the shift to higher binding energy.

		Clean surface	1 ML C <sub>60</sub>
Spin-orbit splitting	(eV)	0.608	0.608
$2p_{1/2}/2p_{3/2}$		0.500	0.500
Lorentzian width	(eV)	0.180	0.180
Gaussian width	(eV)	0.300	0.300
$S_a$ and $S_c$			
Energy shift	(eV)	-0.716	-0.386
Intensity		0.038	0.025
$S_b$ and $S_d$			
Energy shift	(eV)	0.314	0.314
Intensity		0.310	0.292
$S_e$			
Energy shift	(eV)		1.010
Intensity			0.027

atoms bonded with them, respectively. In fact, the intensity ratio,  $I(S_a)/I(S_b)=8.16$ , agrees well with the number ratio of surface atoms in the  $(7\times 7)$  unit cell, i.e., (adatoms + pedestal atoms)/(rest atoms) =  $(12+12\times 3)/6=8$ .  $I(S_a)$  and  $I(S_b)$  indicate the relative intensities of  $S_a$  and  $S_b$  tabulated in Table I. A pedestal atom is the atom bonded with an adatom in the DAS structure, and therefore the number of pedestal atom is three times larger than that of the adatom in the  $(7\times 7)$  unit cell.

#### IV. DISCUSSION

##### A. Bonding state

In order to determine the origins of the 1.8- and 2.4-eV peaks observed in Fig. 1, we compare the intensity ratio of  $I_{1.8\text{ eV}}/I_{\text{HOMO-1}}$  and that of  $I_{2.4\text{ eV}}/I_{\text{HOMO-1}}$  obtained by the *p*-polarized SR light and the nonpolarized He I line.  $I_{1.8\text{ eV}}$ ,  $I_{2.4\text{ eV}}$ , and  $I_{\text{HOMO-1}}$  indicate the integrated intensity of the 1.8- and 2.4-eV peaks, and the HOMO-1, respectively. We use  $I_{\text{HOMO-1}}$  as the reference intensity, because the cross section of  $g_g$  and  $h_g$  orbitals do not have a polarization dependence. The ratios  $I_{1.8\text{ eV}}/I_{\text{HOMO-1}}$  and  $I_{2.4\text{ eV}}/I_{\text{HOMO-1}}$  are estimated to be 0.77 and 0.86 for the polarized light, and 0.79 and 0.59 for the unpolarized light using Voigt functions with different FWHM's and an integrated background. The equivalency in  $I_{1.8\text{ eV}}/I_{\text{HOMO-1}}$  suggests that the origin of the 1.8-eV peak is a MO. Since a binding energy of 1.8 eV is rather higher than that of the electron occupied LUMO of a  $\text{C}_{60}$  molecule,<sup>23</sup> we consider the 1.8-eV peak as the HOMO that has shifted to lower binding energy. We name the 1.8-eV peak as HOMO' tentatively in this paper. The difference in  $I_{2.4\text{ eV}}/I_{\text{HOMO-1}}$  shows that the origin of the 2.4-eV peak has a dipole moment normal to the surface, and therefore the orbital is almost normal to the surface.

Taking into account the equivalency in the energy shift with that of the Si 2*p* of SiC,<sup>24,25</sup> the  $S_e$  observed in Fig. 3 is considered to be due to the Si atoms bonded covalently with C atoms. This atomic interaction indicates that the covalent bond is formed with the  $sp^3$  hybridizations of Si and C atoms, and that the bonding orbital is located at the interface. In this case, the hybridization of a C atom should transform from the  $sp^2$  hybridized character into the  $sp^3$  one. Since the bond angle of the twelve pentagons of a  $\text{C}_{60}$  molecule is  $108^\circ$  and this value is very close to the angle  $109^\circ 28'$  in ideal  $sp^3$  hybridization, the movements of C atoms and the formation of  $sp^3$  hybridization from  $sp^2$ -like hybridization should not affect strongly to the symmetry of a  $\text{C}_{60}$  molecule. The formation of covalent bond with two  $sp^3$  hybridizations and the direction of the Si dangling bonds suggest the bonding orbital to be almost normal to the surface. Hence, we conclude the 2.4-eV peak observed in Fig. 1 to be the bonding state between surface Si atoms and the rehybridized C atoms of a  $\text{C}_{60}$  molecule.

##### B. Bonding configuration

A sharp  $(7\times 7)$  LEED pattern was observed for the clean surface, and this pattern was still observed for the 1.0-ML  $\text{C}_{60}$  film-covered surface. This observation indicates that the surface structure hardly changes upon  $\text{C}_{60}$  adsorption, and that the number of surface atoms that contribute to the sur-

face components in Fig. 3 is almost equivalent on both clean and 1.0-ML  $\text{C}_{60}$  film-adsorbed surfaces. Moreover, the sum in intensity of the Si 2*p* surface components is almost equal on both surfaces, i.e.,  $I(S_a)+I(S_b)\approx I(S_c)+I(S_d)+I(S_e)$ , at the photon energies used in our experiment.  $I(S_c)$ ,  $I(S_d)$ , and  $I(S_e)$  are the relative intensities of  $S_c$ ,  $S_d$ , and  $S_e$  tabulated in Table I, respectively. In this case, 54 surface Si atoms, i.e., adatom+pedestal atoms+rest atom =  $12+36+6$ , contribute to  $S_c$ ,  $S_d$ , and  $S_e$  in the  $(7\times 7)$  unit cell. Hence, the intensity ratio of  $I(S_e)/[I(S_c)+I(S_d)+I(S_e)]\approx 4/54$  suggests that four surface Si atoms contribute to the covalent bond in the  $(7\times 7)$  unit cell.

Taking into account the sign of the energy shift, the almost same intensity, and the unchanged surface structure,  $S_c$  and  $S_d$  are considered to be due to the rest atoms and the sum of adatoms and pedestal atoms that not contribute to the covalent bond, respectively. The difference in energy shift in  $S_a$  and  $S_c$  is regarded to come from the different charge states of the rest atoms that result from the small distortion of the DAS structure. The relations between  $I(S_a)/[I(S_a)+I(S_b)]\approx 6/56$  and  $I(S_c)/[I(S_c)+I(S_d)+I(S_e)]\approx 4/54$ , and between  $I(S_b)/[I(S_a)+I(S_b)]\approx 48/56$  and  $I(S_d)/[I(S_c)+I(S_d)+I(S_e)]\approx 46/54$  indicate that two adatoms and two rest atoms contribute to the covalent bond in the  $(7\times 7)$  unit cell. Since both adatoms and rest atoms contribute to the covalent bond, we consider that a  $\text{C}_{60}$  molecule adsorbs on the bridge site between an adatom and a rest atom. The bonding of C atoms with both adatom and rest atom suggests the existence of two bonding states. Unfortunately, these two bonding states are not resolved in Fig. 1 due to the finite resolution of the experimental system. However, taking into account that the spacing between an adatom and a rest atom is 4.6 Å and the length of the single bond of a  $\text{C}_{60}$  molecule is approximately 1.45 Å,<sup>26</sup> because a  $sp^3$  hybridization of a C atom is formed breaking a double bond of a  $\text{C}_{60}$  molecule and therefore two  $sp^3$  hybridizations are formed simultaneously, we believe that the bonding configuration mentioned above is plausible. Approximately seven  $\text{C}_{60}$  molecules adsorb in the  $(7\times 7)$  unit cell at 1 ML coverage, and two molecules strongly interact with the surface in the  $(7\times 7)$  unit cell considering the bonding configuration and the number of surface atoms that contribute to the chemical interaction. Therefore, we consider that approximately 30% of  $\text{C}_{60}$  molecules adsorb covalently, and 70% with van der Waals force on the 1-ML  $\text{C}_{60}$  film-covered Si(111)- $(7\times 7)$  surface. This consideration agrees well with the coverage-dependent spectra observed in Fig. 1 and the coverage-dependent bonding natures reported previously.<sup>7</sup>

##### C. Energy level scheme

The intensity ratio,  $I_{\text{HOMO'}}/I_{\text{HOMO}}$ , is estimated to be approximately 0.8 in Fig. 1.  $I_{\text{HOMO'}}$  and  $I_{\text{HOMO}}$  indicate the intensities of the HOMO' and the HOMO at 0.25 and 5.0 ML normalized to that of HOMO-1 at the same coverage. The difference in integrated-intensities suggests the different amount of occupied electron, assuming that the cross sections of both MO's are equal.

Since the HOMO is occupied by ten electrons in the solid phase, the HOMO' might correspond to an orbital occupied with eight electrons. This decrease in the amount of occupied

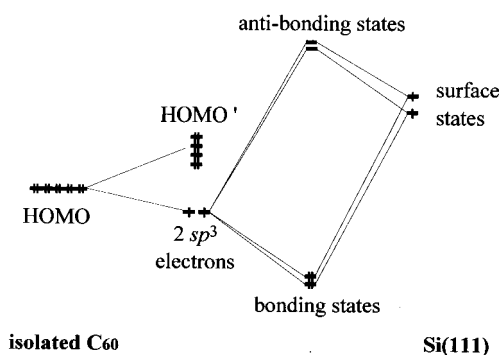


FIG. 4. A schematic diagram of the energy levels for the adsorption of a C<sub>60</sub> molecule on the Si(111)-(7×7) surface. Upon adsorption, the fivefold degenerated HOMO splits into two  $sp^3$  orbitals and the HOMO'. The Si surface states and the two  $sp^3$  orbitals make the bonding state.

electrons indicates that two electrons of the HOMO contribute to the covalent bond; the HOMO splits into five orbitals due to the removal of the degeneracy, and only one of them contributes to the bonding state. The broadening in the FWHM of all MO's except the HOMO observed in Fig. 1, supports the slight removal of degeneracy that results from the strong C<sub>60</sub>-Si interaction.

Since the formation of a  $sp^3$  hybridization of a C atom is done breaking a double bond of a C<sub>60</sub> molecule, a double bond faces to the Si surface just before the adsorption. In this case, one of the  $C_2$  axes of a C<sub>60</sub> molecule corresponds to the surface-normal direction, because the  $C_2$  axis crosses the center of the double bond. Assuming that the interaction between a double bond of a C<sub>60</sub> molecule and the Si surface leads to a distortion of the C<sub>60</sub> along the  $C_2$  axis, the C<sub>60</sub> molecule is deformed into an oblate spheroid and the  $I_h$  symmetry of the molecule changes into a  $D_{2h}$  symmetry. Under this circumstance, the HOMO splits five orbitals into doublet  $A_u$  orbital and singlet  $B_{1u}$ ,  $B_{2u}$ , and  $B_{3u}$  orbitals. The  $B_{1u}$  orbital has no node on the  $C_2$  axis and the  $\pi$  orbital of the double bond interacted with surface Si atoms is symmetric in the initial stage of interaction. Taking into account that the  $\sigma$  interaction between two symmetric  $\pi$  orbitals is stronger than that between two asymmetric  $\pi$  orbital in the Diels-Alder reactions, we consider the  $B_{1u}$  orbital to be the most reactive one. Moreover, the Jahn-Teller effect leads to a consideration that the binding energy of the  $B_{1u}$  orbital is higher, and those of orbitals with other symmetries are lower than that of the HOMO with  $h_u$  symmetry. This model explains well the valence spectra in which the HOMO' has a lower binding energy than the HOMO, and is considered to be occupied with eight electrons. Hence, we conclude that the  $B_{1u}$  orbital contributes to two  $sp^3$  hybridizations and makes the bonding state between a C<sub>60</sub> molecule and Si surface, and the HOMO' is the overlap of the other four orbitals. The schematic energy levels of an isolated C<sub>60</sub> molecule, a C<sub>60</sub> molecule that interacts with the Si surface, the adatom and rest atom dangling bond states, and the bonding and anti-bonding states formed by an orbital mixing of a C<sub>60</sub> molecule and a surface Si atom are displayed in Fig. 4.

The HREELS measurements<sup>7</sup> show the feature of charge transfer from the Si dangling bonds to the LUMO, i.e., the antibonding  $\pi$  orbital, from the softening of infrared-active

vibrational modes<sup>7</sup> that classified with the motions of the double bonds.<sup>27</sup> On the contrary, the present results show evidences of the strong covalency and the neutral charge state of the C<sub>60</sub> molecule. These evidences suggest that the simple charge transfer scheme<sup>7-9,17</sup> is no longer able to explain the softening. We propose two schemes that explain the softening of vibrational modes without the simple charge transfer scheme.<sup>7-9,17</sup> In order to present new schemes, we consider that the softening of double bonds comes from an electronic effect, because the result of HREELS measurement<sup>7</sup> indicates that the softening takes place on the whole molecule and not locally. The first scheme is the interaction like to that so called Blyholder model,<sup>28</sup> in which a MO interacts with an unoccupied Si surface state, and the LUMO with an occupied surface state. When a C<sub>60</sub> molecule adsorbs on the bridge site between an adatom and a rest atom, the distance between this molecule and another adatom is relatively short. In this case the occupied surface electron of this adatom is able to be donated into the LUMO forming a  $\sigma$  interaction, and therefore softened the vibrational modes. Taking into account the reports on carbon monoxide-adsorbed metal surfaces,<sup>29</sup> it is not strange to consider that the cross section of this  $\sigma$  interaction is small and not observed in PES. The second one is the decrement in the amount of electron of the bonding state that might also soften the bond strength. The HOMO and HOMO' are bonding states with different amount of occupied electrons. Hence, the softening of the double bonds might also result from the decrease in amount of electrons of the HOMO.

## V. CONCLUSION

In conclusion, we measured the coverage-dependent valence spectra, the C 1s and Si 2p core levels of the C<sub>60</sub>-adsorbed Si(111)-(7×7) surface by PES. At a coverage lower than 0.25 ML, the valence spectra show the split of the HOMO into two peaks due to the strong interaction with the Si surface. The binding energies of these peaks are 1.8 and 2.4 eV. The polarization dependence of the valence spectra shows that the 1.8-eV peak is the shifted HOMO and the 2.4-eV peak is an orbital almost normal to the surface. Since the charge state of a C<sub>60</sub> molecule adsorbed on the Si(111)-(7×7) surface is determined to be neutral by the binding energy of the C 1s core level, we conclude that the strong interaction has a covalent character. This covalent bonding is suggested to be formed by two  $sp^3$  hybridizations from the analysis of the Si 2p core-level spectra. Taking into account this atomic interaction, we conclude that the 2.4-eV peak observed in the valence spectra is the covalent bonding state between a C<sub>60</sub> molecule and the Si substrate. We also propose that covalently bonded C<sub>60</sub> molecule adsorbs between an adatom and a rest atom. Furthermore, the energy-level scheme of the bonding state is discussed. The HOMO splits five orbitals into doublet  $A_u$  orbital and singlet  $B_{1u}$ ,  $B_{2u}$ , and  $B_{3u}$  orbitals due to the strong interaction with the surface. The bonding state is formed by the contribution of the  $B_{1u}$  orbital, and the shifted HOMO is the overlap of the other four orbitals.

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