Vibrational Modes of C_<60> Fullerene Adsorbed on Si(100)2×1 Surface Studied by High-Resolution Electron-Energy-Loss Spectroscopy

Vibrational Modes of C_{60} Fullerene Adsorbed on Si(100)2×1 Surface Studied by High-Resolution Electron-Energy-Loss Spectroscopy*

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We have measured the inelastic electron-energy-loss spectra of C_{60} on the Si(100)2x1 surface in the infra-red energy range. If C_{60} is evaporated 5 Å (approximately half a monolayer) on Si(100), a strong energy loss peak appears at 65 meV, and weak peaks and shoulders at 72, 144, and 175 meV. In the 12 Å thick film, additional weak peaks at 96, 160, and 189 meV become more apparent. Intensities of these peaks are comparable to those of thick films measured by infra-red absorption and by Raman scattering spectroscopies. Moreover, we have measured the angle dependence of the inelastic electron intensity. These results suggest appreciable interactions between C_{60} and the dangling bonds of Si surface.

KEYWORDS: C_{60}, fullerene, HREELS, Vibrational mode, Si(100)2x1 surface

1. Introduction

The buckminsterfullerene, C_{60}, and its relatives exhibit the third allotropic form of carbon in addition to diamond and graphite structures. Many researchers are trying to find new material functions of this family produced by their interaction with each other or with other substances in contact.

We report here measurements of vibrational excitations of C_{60} molecules adsorbed on Si(100)2x1 surface by high-resolution electron-energy-loss spectroscopy (HREELS). The first layer of Si forms dimer rows and one Si atom contributes one dangling bond. Since such a dangling bond is chemically active, some charge transfer interaction is expected between C_{60} and the silicon surface.

The C_{60} has the symmetry of I_h point group. The C_{60} molecule has four infra-red active vibration modes ($4T_{1u}$) and 10 Raman active modes ($2A_g + 8H_g$). The vibrational excitations for thick films are measured by infra-red absorption spectroscopy and by Raman scattering [1]. Gensterblum et al. [2] reported measurements on the vibrational modes for the 60 Å thick film of C_{60} on Si(100) surface by HREELS. The intensities of the inelastic scattering is very high and is 1/30 of the elastic peak. The electron beam is scattered by dipole moments (dipole scattering mechanism) and by quadrupole moments (impact scattering mechanism) of C_{60} on the surface . Normally, the scattering by the dipole active mode is much stronger than that by impact scattering [3]. They, therefore, observed unusually strong scattering of electrons by Raman active quadrupole moment. Recently, they have attributed them to the surface roughness of the C_{60} film [4].

2. Experimental

2.1 HREELS and UHV system

We have made a UHV system which consists of analysis chamber and sample evaporation chamber. The analysis chamber is equipped with a high-resolution electron energy loss spectrometer (HREELS), a rear-view LEED and Auger electron spectrometer. The HREELS is made up of two 127° cylindrical electrostatic deflectors. The one is for the monochromator and the other for the analyzer. The energy

of the electron beam E_p was 4.8 eV and the half width of the elastically scattered peak was about 7 meV for clean Si(100) surface and 10 to 17 meV after the deposition of C_{60}. The incident and the scattering angles are 65° from the surface normal (specular condition). The angle of the analyzer is varied for the measurements of off-specular spectra. The base pressure of the analysis chamber was 1.4×10^{-8} Pa and the evaporation chamber 1.4×10^{-7} Pa.

2.2 Sample Preparation

We have prepared and purified carefully the C_{60} powder 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. Figure 1 (a) and (b) show the spectra of C_{60} without the second step. The C_{60} was separated by toluene in (a) and by benzene in (b). The strong loss peaks at 100, 252, 352 and 438 meV are due to streching vibration of Si-C, Si-H, C-H and O-H molecule, respectively.

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 300 °C for over 24 hours prior to evaporation. The thickness was monitored by a quartz crystal oscillator. The deposition rate was approximately 4 Å /min.

The thickness of our C_{60} films are 5, 7 and 12 Å. The bulk C_{60} crystal forms the fcc lattice and the nearest neighbor distance is 10.04 Å. Since the C_{60} film of the five-layer island shows the close-packed fcc(111) surface[5], the 5 Å thickness is estimated to be half a monolayer (ML) of the C_{60} film. In order to obtain high scattering intensity in our measurements, the beam current of the HREELS was about 1 nA or above.

The Si(100)2x1 surface was prepared by the method reported by Shiraki [6]. After annealing at 850 °C, the crystal surface shows sharp 2x1 spots as observed in LEED. This 2x1 structure, however, was changed to 1x1 structure if it is covered by C_{60} of thickness less than a few Å. The cleanliness of the surface was verified by Auger electron spectroscopy and by the absence of any loss peaks due to vibration modes of adsorbed molecules on Si(100) surface.
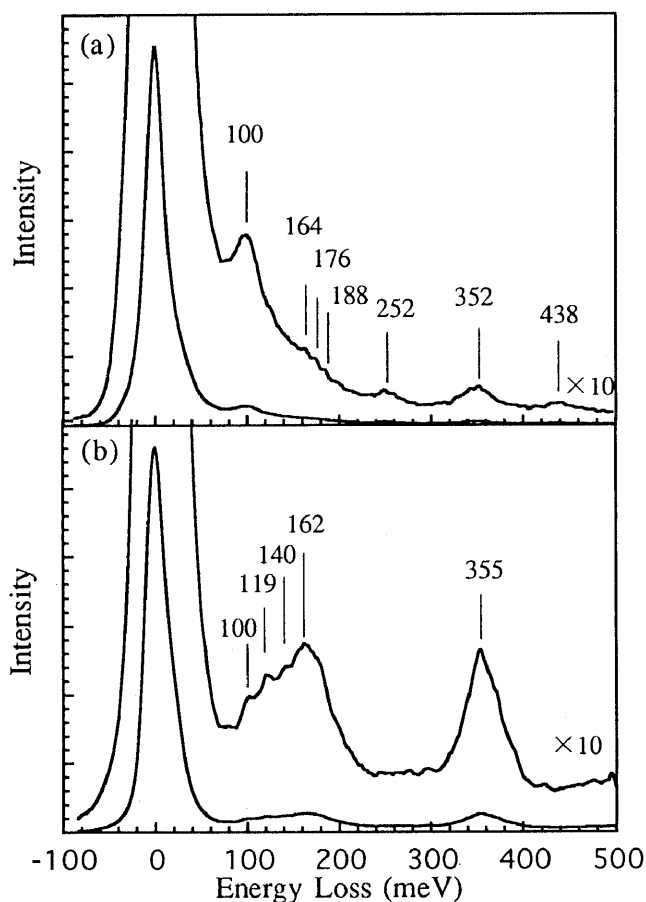
Figure 1. Electron-energy-loss spectra of C_{60} molecules on the Si(100)2x1 surface. The C_{60} molecules are separated by toluene (a) and by benzene (b), respectively, without second step (see in text).

3. Results and Discussion

3.1. Coverage Dependence

Figure 2 shows the electron-energy-loss spectra of C_{60} molecules deposited on the Si(100)2x1 surface with three different coverages; 0.5 ML in (a), 0.7 ML in (b) and 1.2 ML in (c).

At the coverage of 0.5 ML, a strong peak appears at 65 meV with a shoulder at 72 meV. It is noticed that the width of the 65 meV with the shoulder is 18 meV which is broader than the elastic peak width of 11 meV. This broadening indicates that two peaks are overlapping. Weak but discernible peaks appear at 144 and 175 meV. Other weak peaks and shoulders also apparent 96, 109, 129, 158, and 186 meV. With increasing coverage up to 0.7 ML, a profile is essentially similar. At 1.2 ML, the elastic peak is broader than that of (a) and (b). The shoulders at 72, 107 meV disappear. The intensity of the 160 meV peak increases. Except for the 65 meV peak, these spectra are different in energy and intensity as compared with those of 6 ML (60 Å) film by Gensterblum [2]. Table 1 summarizes peaks and shoulders observed in our measurements together with the results by HREELS on Si(100), GaSe(0001) and GeS(001), Raman scattering, and by infra-red absorption spectroscopy. The coverage of the C_{60} film is indicated in the table. The mode assignments for the ordered C_{60} film on GeS(001) are listed in the last column.

We assign the peak at 109 meV as originated not from C_{60} molecules, because the peak intensity becomes weaker
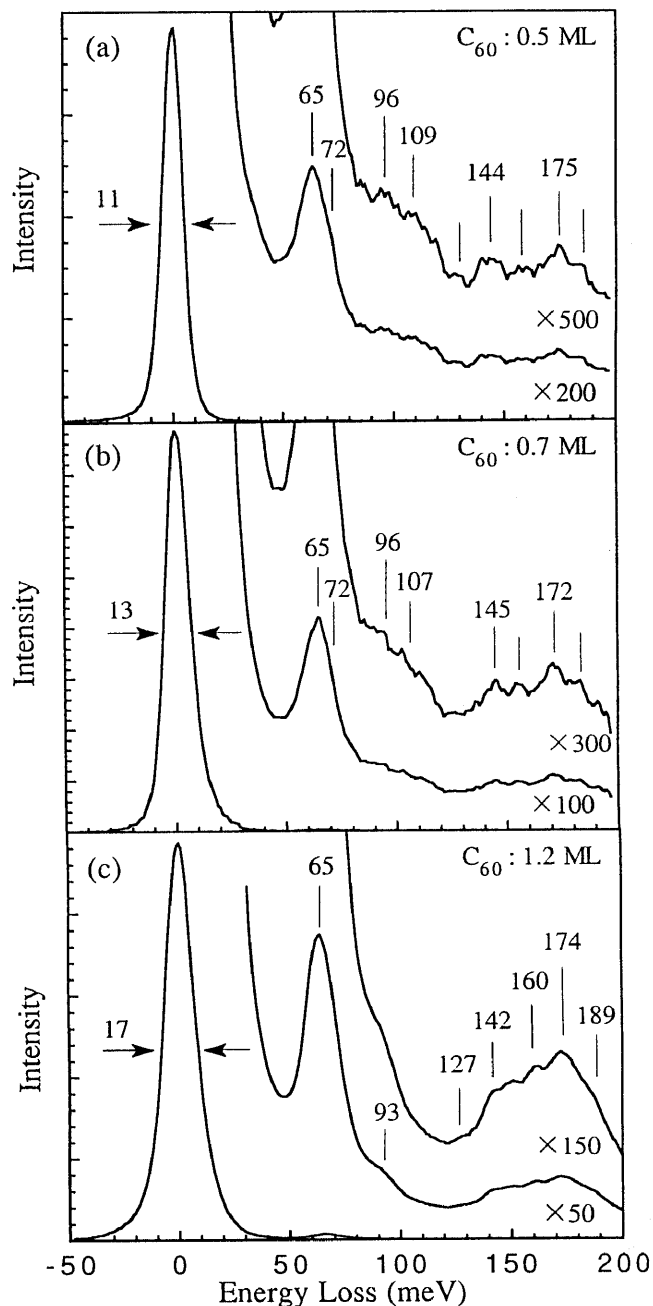

Figure 2. Electron-energy-loss spectra of C_{60} molecules on the Si(100)2x1 with the coverage of 0.5 ML(a), 0.7 ML(b) and 1.2 ML(c).

as the coverage of C_{60} increases from 0.5 to 1.2 ML. In the film of 0.5 ML, the peaks and shoulder at 65, 72, 144, 175 meV are very similar in energy and intensity to the absorption spectrum of thick films. We, therefore, assign them as four T_{1u} dipole active modes. In the film of 1.2 ML, peaks are more pronounced at 93, 142, 160 and 189 meV. Among these, peaks at 93, 160 and 189 meV are very close to the values of Raman active mode observed in measurements for thick films. We have assigned them the mode of H_g, H_g and A_g, respectively, according to the assignment in references 4 and 7.

3.2. Scattering Angle Dependence

To check the mode assignments of vibrational and scattering mechanism, we have measured the angle dependence of scattering cross section. Figure 3 shows the

Table 1 Lists peak positions (in meV) measured by HREELS, infra-red absorption spectroscopy and Raman scattering. The dominant peaks are underlined. The last column is the mode assignment.

Our Results			HREELS		Raman	IRAS	Assignment
0.5 ML	0.7 ML	1.2 ML	6 ML [a]	60 ML [b]	Thick film [c]	Thick film [c]	ordered film [b]
			34		34		H_g
			44	43			T_{2u}
			55	53	55		H_g
					_62_		A_g
_65_	_65_	_65_	_66_	_66_		66	T_{1u}
72				72		72	T_{1u}
			85		89		H_g
96	96	93	_94_	_94_	97		H_g
(109)	(107)						
129		127	120	119			
			136	133	137		H_g
_144_	_145_	_142_		_147_		148	T_{1u}
158	156	_160_	_156_	161	156		H_g
_175_	_172_	_174_	180	_178_	178	178	T_{1u}
186	184	189			_184_		A_g
			_194_	192	196		H_g

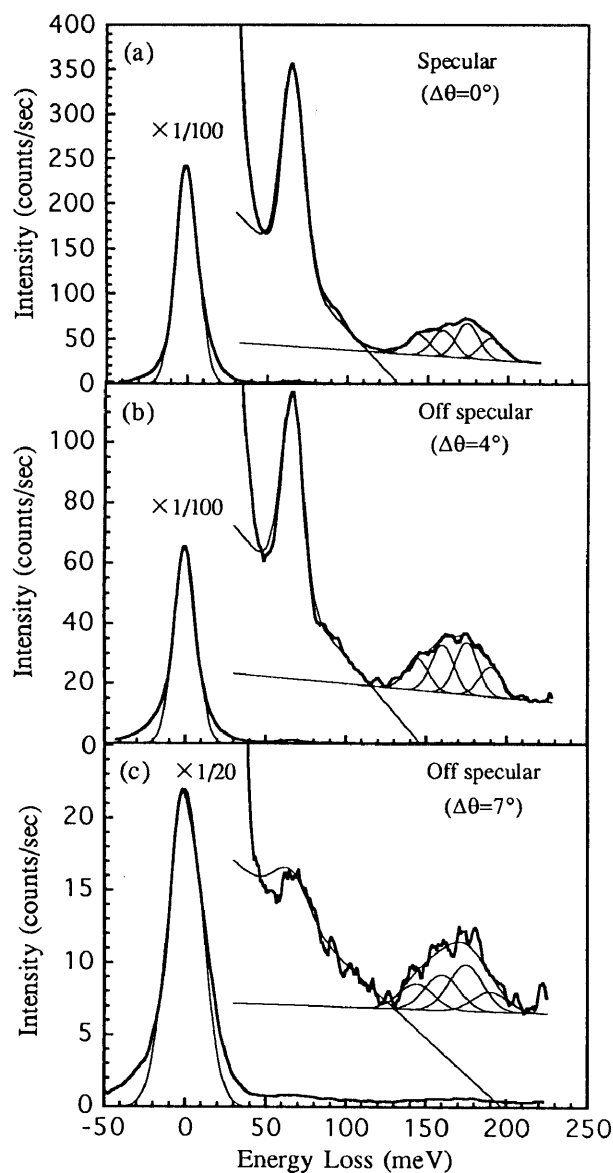[a]Reference 2, [b]Reference 4, [c]Reference 1.

Figure 3. Electron-energy-loss spectra of C_{60} molecules on the Si(100)2x1 with specular(a) and off-specular(b and c) configurations. The coverage is 1.2 ML.

spectra of specular (a) and off-specular (b and c) configurations on the 1.2 ML film. The increase of the scattering angle ($\Delta\theta$) from specular configuration is shown in the figure. First of all, we have deconvoluted the peaks by Gaussian. The thick line is our measured data and the thin lines are the sum of deconvoluted Gaussian line profile. The elastic peak and the whole inelastic spectra are well reproduced by the Gaussian peaks at 65, 144, 160, 175 and 190 meV. These values are very close to those as that for the 60 ML ordered film on GeS within experimental error. It is noted that the intensity of 65 meV peak is comparable to the other peak in Fig. 3(c). The intensities are plotted in the Fig. 4. The scattering intensity of 65 meV peak decreases in the same manner as that of the elastic peak with increasing scattering angle. This result shows that the 65 meV peak arises from a dipole scattering process. The intensities of 144, 160, 175, and 190 meV peak show angle dependence weaker than that of 65 meV peak, but stronger than that of the peak of Raman active modes arisen from impact scattering process. Hence, the Raman active 160 and 190 meV peaks behave like the dipole active 144 and 175 meV, this result indicates that the character of the quadrupole moment is modified on the surface[8].

4. Summary

We have measured the vibration modes of C_{60} at the coverage of 0.5, 0.7 and 1.2 monolayer on Si(100)2x1 structure. The spectra below 1 monolayer are similar to the infra-red absorption spectrum for the thick film . The Raman active 160 and 190 meV peaks are stronger in the 1.2 monolayer film. The scattering angle dependence shows that the peak at 65 meV is purely dipole active (infra-red active) mode. The dependence of the Raman active mode at 160 and 190 meV is the same as the dipole active modes at
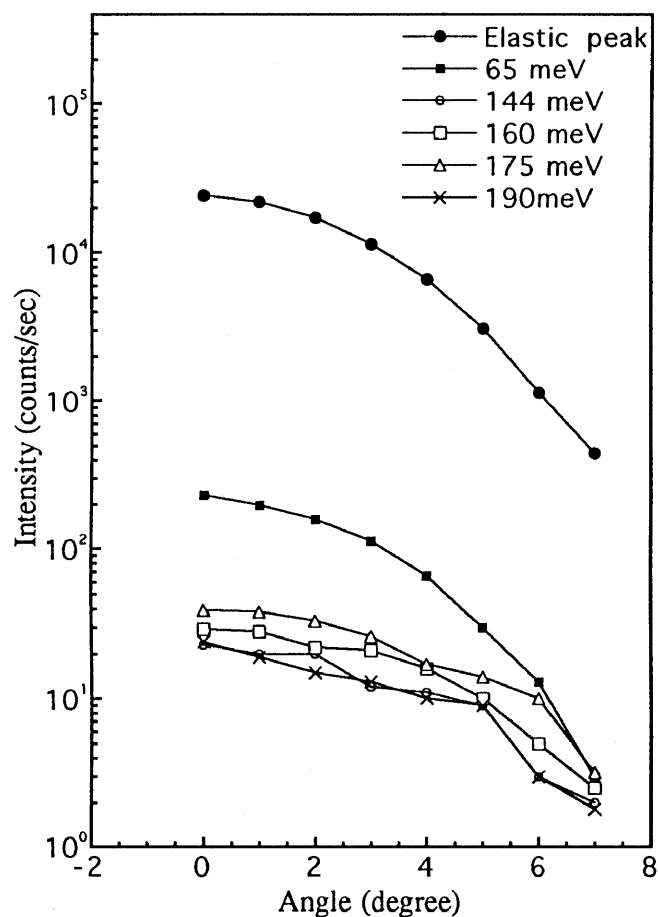
144 and 175 meV. These results suggest that the C_{60} on Si(100)2x1 surface adsorbed like an isolated molecule but there may be small charge transfer effect.

Acknowledgments

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Figure 4. Angular distribution curve for the elastic peak intensity, and for the 65 meV, 144 meV, 160 meV, 175 meV and 190 meV peak intensity measured in 1.2 ML of C_{60} on Si(100)2x1 structure.