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Transition of an adsorption state of C_{60} on a Si(111)7×7 surface revealed by high-resolution electron-energy-loss spectroscopy

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The interaction between C_{60} molecules and a Si(111)7×7 surface has been investigated for various stages of C_{60} coverage by using high-resolution electron-energy-loss spectroscopy (HREELS). In the case of 0.2- and 0.6-ML films, their HREELS spectra indicate the formation of chemical bonds between C_{60} molecules and Si dangling bonds. After the completion of monolayer C_{60} coverage, an R-19° double-domain structure is formed and its HREELS spectrum is quite similar to that of a monolayer C_{60} film grown on a MoS_2 surface. This suggests that bond breaking between C_{60} and Si triggers the transition of adsorption state from a low-coverage disordered structure to the R-19° ordered structure. [S0163-1829(97)02040-7]

Since the discovery of a method to synthesize large amounts of fullerenes,[1] many physical and chemical properties have been studied extensively. In addition, epitaxial growth of fullerene films on various types of substrates has been attempted. Those works were motivated by technological application of fullerene films to electronic devices and by basic research interest for crystal-growth mechanisms, molecule-surface interactions, and so on. Among the various substrates, a clean Si surface is interesting because it provides an ordered dangling-bond structure. Investigation of the adsorption state of the C_{60} molecule on Si and an understanding of the C_{60}-Si interaction are thought to be useful for the control of C_{60} growth on the technologically important material Si.

Recently Xu, Chen, and Creager observed an R-19° double-domain structure in a C_{60}/Si(111)7×7 system by scanning tunneling microscopy (STM).[2] In addition, Sato, Sueyoshi, and Iwatsuki have revealed that the C_{60} film forms the R-19° structure at the coverage of 1 molecular layer (ML), while C_{60} molecules are adsorbed on other sites at lower coverage.[3] This mans that the adsorption state changes with the coverage in the submonolayer region. Therefore it is interesting to clarify the adsorption state of C_{60} on a Si surface at the coverage lower than 1 ML and the mechanism of structural transition in adsorption state.

In this paper, we have investigated the initial stage of epitaxial growth of C_{60} film on a Si(111)7×7 surface by high-resolution electron-energy-loss spectroscopy (HREELS) and reflection high-energy electron diffraction (RHEED). HREELS is one of the powerful methods used to investigate the adsorption state of molecules and has been applied to the study on C_{60} films by several groups.[4–12] However, HREELS measurement on a double-domain structure of the C_{60}/Si(111)7×7 system has not been reported. From the results on RHEED and HREELS we will discuss the interaction between C_{60} molecules and a Si surface and the structural transition of the adsorption state of C_{60}.

The epitaxial growth and HREELS measurements were performed in ultrahigh-vacuum chambers with base pressures of 3×10^{-8} Pa and 1×10^{-8} Pa, respectively. C_{60} powder (99.8% pure) was charged to a Knudsen cell and was preheated at 600 K for half a day under vacuum in order to remove the impurities. A Si wafer was boiled in HCl:H_2O_2:$H_2O=1:1:4$ solution for 10 min. A Si(111)7×7 surface was obtained by annealing the substrate at 1200 K in vacuum. After the substrate was cooled to 350 K, growth of C_{60} was carried out. The film thickness was estimated by a quartz oscillator thickness monitor placed close to the sample holder. The typical growth rate was set at 0.1 ML/min for all films. The surface structure of the substrates and grown films was monitored by RHEED with an incident electron energy of 20 keV. HREELS system (Eiko Engineering EES-10) was composed of two sets of double 127° cylindrical deflectors. The energy resolution was set at about 10 meV. HREELS measurements were performed with an incident electron energy (E_p) of 5.8 eV. The emission angle was fixed at 54° and the incident angle was set at 54° or 36° for specular or off-specular reflection condition, respectively.

RHEED observation was performed during epitaxial growth. Diffraction patterns coming from a C_{60} film were not observed until the completion of 1 ML C_{60} coverage. After the 1 ML C_{60} coverage, a new RHEED pattern appeared, which indicates formation of an ordered structure. Figures 1(a) and 1(b) show RHEED patterns of 1.2-ML C_{60} film grown on a Si(111)7×7 surface. The azimuthal angles of incident beam measured from the $[\bar{1}10]$ axis of a Si substrate are 19° in Fig. 1(a) and 11° in Fig. 1(b), respectively. The lattice constant of the C_{60} film determined from streak intervals is 1.00 nm, which agrees well with that of bulk C_{60} crystals. These RHEED patterns correspond to an R-19° double-domain structure [Fig. 1(c)], which was first reported by Xu, Chen, and Creager.[2] The present RHEED observations indicate that long-range periodicity does not exist below the 1-ML coverage, while the transition to the well-ordered structure occurs after the 1-ML coverage.

Figure 2 shows the HREEL spectra (specular reflection condition) of C_{60} films that have disordered structure (0.2 and 0.6 ML) and the R-19° double-domain structure (1 ML). In the spectrum of a 0.2 ML film, a major peak at 143 meV is observed, whereas peaks for other C_{60} IR active modes (65 and 176 meV) are suppressed. The intensity of IR-active modes changes drastically when C_{60} molecules interact strongly with the substrate. The considerable change in relative IR modes has been also reported in the case of C_{60} film

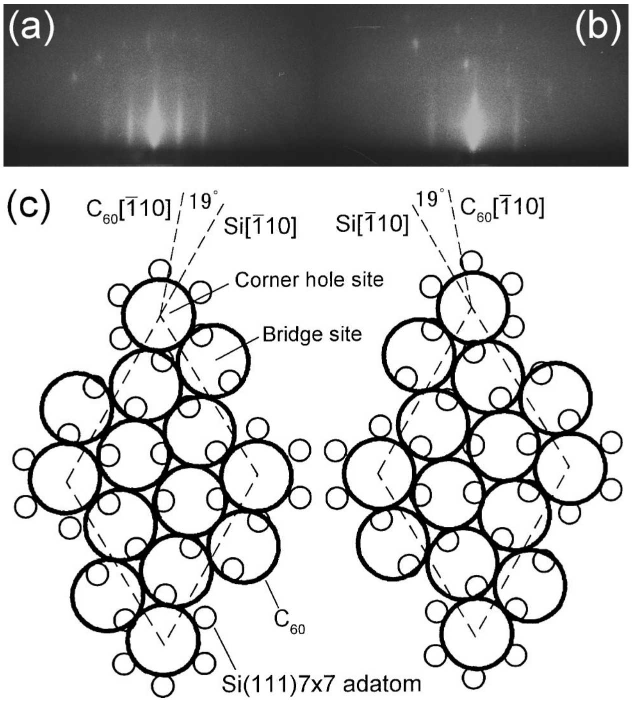

FIG. 1. (a),(b) RHEED images of C_{60} film (1.2 ML thick) on a Si(111)7×7 surface. The direction of incident beam was (a) 19° off the [110] axis of a Si substrate and (b) 11° off the [110] axis. (c) The structure of a C_{60} film on a Si(111)7×7 surface (Ref. 2).

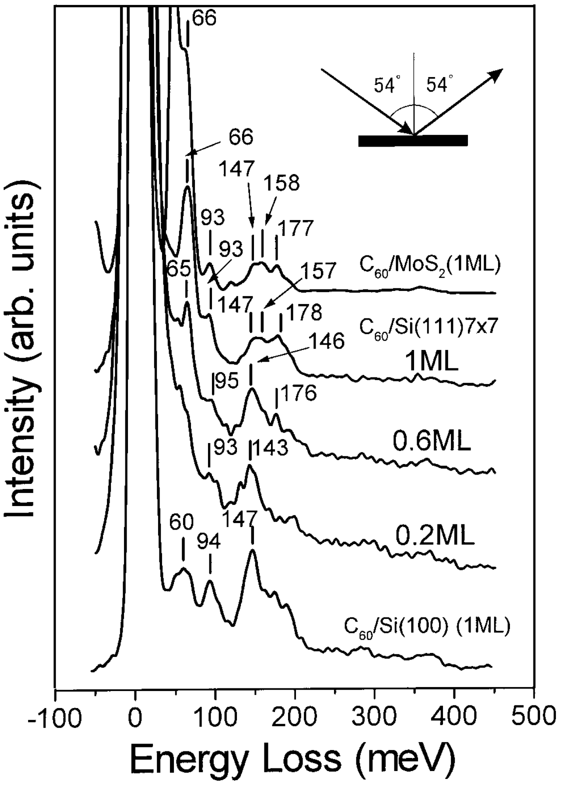

FIG. 2. HREELS spectra of C_{60} films with 0.2, 0.6, and 1 ML coverage on a Si(111)7×7 surface in comparison with those of C_{60} films with 1 ML coverage on a MoS_2 cleaved surface (Ref. 12) and a Si(100)2×1 surface (Ref. 13). These spectra were taken under specular reflection condition.

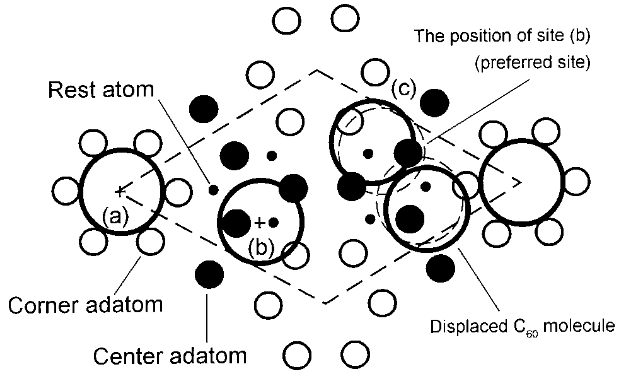

FIG. 3. $(a),(b)$ Preferred adsorption sites of C_{60} molecules on a Si(111)7×7 surface at low coverage which have been observed by Sato, Sueyoshi, and Iwatsuki with STM (Ref. 3). (c) A new site displaced from the site (b) due to steric hindrance.

on K/Au(110) $c2\times2$ by Modesti, Cerasari, and Rudolf. The 0.2 ML spectrum in Fig. 2 resembles that of a C_{60} film grown on a Si(100)2×1 surface,[13] in which a prominent peak appears only at 147 meV. Thus the chemical state of C_{60} molecules at low coverage on a Si(111)7×7 surface is thought to be similar to that of C_{60} molecules on a Si(100)2×1 surface, where C_{60} molecules are locked by the dangling bonds.[14]

Decreasing in the intensity of IR-active modes suggests that C_{60} molecules on a Si(111)7×7 surface are locked by the Si dangling bonds for coverage as low as 0.2 ML. In the Si(111)7×7 surface, a corner hole site [site (a) in Fig. 3] and a site at the center of three adatoms are considered as typical adsorption sites.[2] However, Sato, Sueyoshi, and Iwatsuki reported that C_{60} molecules are adsorbed on sites (a) and sites between center adatoms and rest atoms [sites (b) in Fig. 3] for the submonolayer coverage on a Si(111)7×7 surface.[3] Thus the HREEL spectrum seems to correspond to the adsorption state in which C_{60} molecules are located on both sites (a) and (b).

In the spectrum of a 0.6-ML film, the 143-meV peak of the 0.2 ML film shifts to 146 meV and IR-active modes appear apparently at 65 and 176 meV. The vibrational modes of C_{60} molecules come close to intrinsic vibrational modes of the C_{60} molecule. As the coverage becomes close to 1 ML, C_{60} molecules adsorbed on adjacent (b) sites are likely to cause steric hindrance to each other as shown in Fig. 3. As a result, some displacement from the regular (b) site to the (c) site might occur, which results in a decrease in interaction between C_{60} molecules and Si dangling bonds. It is likely that the bonds between C_{60} molecules and a Si surface begin to weaken at 0.6 ML coverage. This might cause the spectrum of the 0.6-ML film to be similar to that of bulk C_{60} molecules. This intermediate adsorption state seems necessary for the structural transition in the following 1-ML C_{60} film.

In the spectrum of 1-ML film with an ordered R-19° structure, IR-active modes at 66, 147, and 178 and an additional peak at 157 meV are observed. This spectrum is very close to the spectrum of a 1-ML C_{60} film grown on a cleaved MoS_2 surface, in which the peak around 158 meV has also been observed (see Ref. 12). The interaction between C_{60} molecules and MoS_2 is weak because a cleaved MoS_2 surface has no dangling bonds due to its layered crystal structure. Thus the bonds between C_{60} molecules and a Si surface are supposed to be almost broken after the transition to R-19° structure. In this state, most C_{60} molecules are thought to be adsorbed on a bridge site between corner and center adatoms as shown in Fig. 1(c). The spectral resemblance between the C_{60} films on Si(111)7×7 and MoS_2 suggests that the reactivity of the bridge sites in the Si(111)7×7 structure with C_{60} molecules is weaker than that of sites (a) and (b) in Fig. 3. The transition from the strongly adsorbed state on site (a) to the weakly adsorbed state on the bridge site seems to be triggered by the intermediate adsorption state on site (c) in Fig. 3, which is displaced from site (b).

Figure 4 shows a comparison of HREEL spectra of 1-ML C_{60} films on a Si(111)7×7 surface and on a MoS_2 surface under off-specular reflection condition. In the case of C_{60}, the intensity of loss peaks at off-specular condition is close to vibrational density-of-states (VDOS) because the angle dependence of impact scattering cross section is not large due to its isotropic symmetry. The energy of peak observed at 64 meV in the spectrum of C_{60} film on the Si(111) surface is lower than that on the MoS_2 surface.[12] This indicates that some interaction still remains at 1 ML coverage, although the bonds between C_{60} and Si surface are weakened after the transition. The comparison of VDOS between graphite and C_{60} indicates that the peak at about 65 meV in VDOS of C_{60} corresponds to transverse vibrational modes in which motion of C atoms is normal to the carbon network plane. The spring constants of these transverse vibrational modes are associated with the strength of π bonds. Therefore, the redshift of the peak observed at 64 meV in Fig. 4 indicates that the π bonds of C_{60} are weakened. Since the filled surface state on Si(111)7×7 surface is higher than the lowest unoccupied molecular orbital of C_{60} molecules,[15] the weakening of the π bonds of C_{60} could be explained in terms of the small amount of charge transfer from Si dangling bonds to C_{60} molecules at the interface.

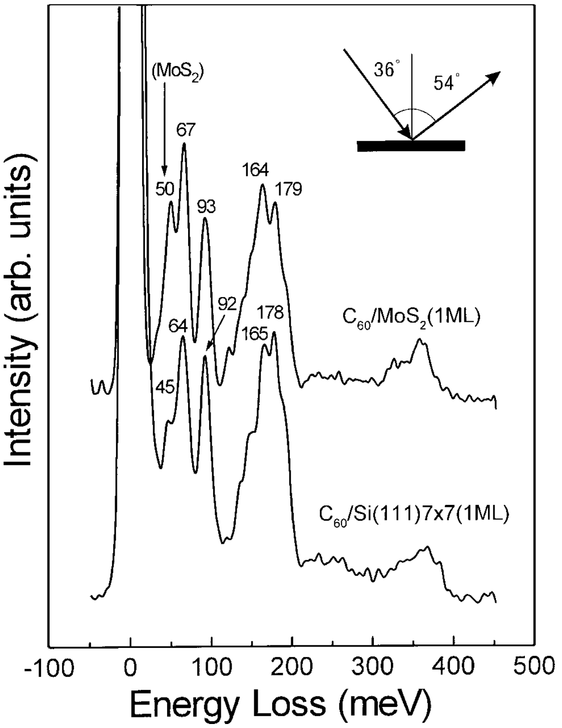

FIG. 4. A HREELS spectrum under off-specular reflection condition of a C_{60} film of 1 ML coverage on a Si(111)7×7 surface in comparison with that of a C_{60} film of 1 ML coverage on a MoS_2 cleaved surface.

In summary, we have measured HREEL spectra of C_{60} films grown on Si(111)7×7 substrate at various stages of coverage and the interaction between fullerenes and a Si(111)7×7 surface has been discussed. The spectra of films with coverage below 1 ML, which have disordered structure, indicate existence of chemical bonds at the interface between C_{60} molecules and Si dangling bonds. With increasing coverage, these chemical bonds are weakened, which results in formation of R-19° double-domain structure. HREEL spectrum of 1 ML coverage film under off-specular reflection condition suggests that the small amount of charge transfer from Si dangling bonds to C_{60} molecules still remains for the 1-ML film.

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