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Behavior of Silicon and Germanium Clusters on a C_{60} Fullerene

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Behavior of silicon (Si) and germanium (Ge) atoms (or clusters) on the surface of a C_{60} fullerene has been revealed by using time-of-flight mass spectroscopy and photoelectron spectroscopy. The mixed clusters of $C_{60}Si_n$ and $C_{60}Ge_m$ were generated by two-lasers vaporization of a molded C_{60} rod and a Si (or a Ge) rod in He carrier gas. The size distributions of anionic and cationic $C_{60}Si_n/C_{60}Ge_m$ clusters monotonically decreased with the number of Si/Ge atoms, and were limited only up to $n = 4$ and $m = 3$. The photoelectron spectra of $C_{60}Si_n^-$ and $C_{60}Ge_m^-$ are similar to that of pure C_{60}^- at n, $m = 3, 4$, whereas the spectra at n, $m =1, 2$ are different from that of C_{60}^-. These results show that Si/Ge atoms assemble together into Si/Ge clusters on the C_{60} cage with an increase in the number of Si/Ge atoms.

1. Introduction

Since the discovery[1] and the large scale synthesis of fullerenes,[2] numerous experimental and theoretical studies have been devoted to endohedrally doped fullerenes (fullerenes with a foreign atom inside).[3−6] In addition to the endohedrally doped fullerenes, heterofullerenes “fullerenes doped with the foreign atom as a part of the fullerene network”, especially silicon-doped heterofullerenes, have also been intriguing because of their novel electronic and geometric structures.[7−12] Among the heterofullerenes, silicon (Si)-doped heterofullerenes are expected to be very reactive at the Si site, because Si atoms strongly prefer sp^3 bonding to sp^2 bonding, which implies that the Si-heterofullerenes are possibly polymerized.

As well as the endohedrally doped fullerenes and the heterofullerenes, exohedrally doped fullerenes (fullerenes with the foreign atom outside) have been studied extensively,[13−15] because there is a strong possibility that the doped fullerene solids may develop novel fullerene-related materials. In particular, the finding of high-T_c superconductivity in $C_{60}K_3$ films,[16,17] largely exhibits that new novel materials might be synthesized with C_{60} as the building units. Among many combinations of C_{60} molecules and heteroatoms, the understanding on interactions between the fullerene and Si or germanium (Ge) atoms is of importance to develop new fullerene-based materials, because the doping of Si/Ge atoms gives an implement to modify the fullerene electronically and geometrically with moderate deformation in bonding. In fact, $C_{60}Si_{60}$ (a C_{60} molecule which is coated by sixty silicon atoms) is theoretically regarded as a promising candidate of the new fullerene-based materials,[18,19] although nobody has succeeded in producing this molecule. Therefore, the understanding on the stability of an intermediate complex, such as $C_{60}Si_n$, seems indispensable to the successful synthesis of $C_{60}Si_{60}$.

Among the various techniques devoted to the investigation of the cluster properties in the gas phase, photoelectron spectroscopy has been shown to be a good probe of the anionic and the neutral cluster geometrically and electronically.[20−22] In the present paper, we investigate the behavior of the exohedrally doped Si and Ge atoms on the C_{60} fullerene cage by using the time-of-flight (TOF) mass spectrometry and the photoelectron spectrometry, and discuss the influence of Si and Ge atoms on the electronic structure of C_{60}.

2. Experimental Section

The experimental setup has been described in details elsewhere.[23] In brief, the binary clusters were produced in a double-rod laser vaporization source. The C_{60} rod has been prepared by pressing purchased C_{60} powder. Both the Si/Ge rod and C_{60} rod were independently vaporized by means of two frequency-double Nd^{3+}:YAG lasers. The laser fluence for the C_{60} was kept sufficiently low to avoid the fragmentation of C_{60} into “C_2 loss”. The vaporized Si/Ge atoms and C_{60} molecules were cooled to room temperature with high-pressure He carrier gas (stagnation pressure; 3.5−5 bar) and then grew into $C_{60}Si_n/C_{60}Ge_m$ clusters. The cluster beam was sent through a skimmer into a second chamber where the anions were accelerated to 900 eV with a pulsed electric field and were separated in time owing to their different mass-to-charge ratios. After the ions are mass-selected, a pulsed electric decelerator strongly reduced their kinetic energy before they entered the photodetachment region of a magnetic-bottle-type electron spectrometer.[23−25] Then the fourth harmonics (266 nm, 4.66 eV) of a pulsed Nd^{3+}:YAG laser was focused onto the only target cluster to detach photoelectrons which were detected by a microchannel plate (MCP) with a strong inhomogeneous magnetic field and subsequently with a weak guiding magnetic field. Then their kinetic energy was analyzed by their TOF. The signal of photoelectron was typically accumulated to 20000−50000 shots.

3. Results and Discussion

3.1. Mass Spectrometry of C_{60}−Si and C_{60}−Ge Clusters. In the present study, TOF mass spectra of anionic and cationic $C_{60}Si_n/C_{60}Ge_m$ were measured. The mass distributions of $C_{60}Ge_m$ cluster anions and cations were almost the same as that of $C_{60}Si_n$ cluster anions and cations. Mass spectra of the $C_{60}Si_n^-$ and

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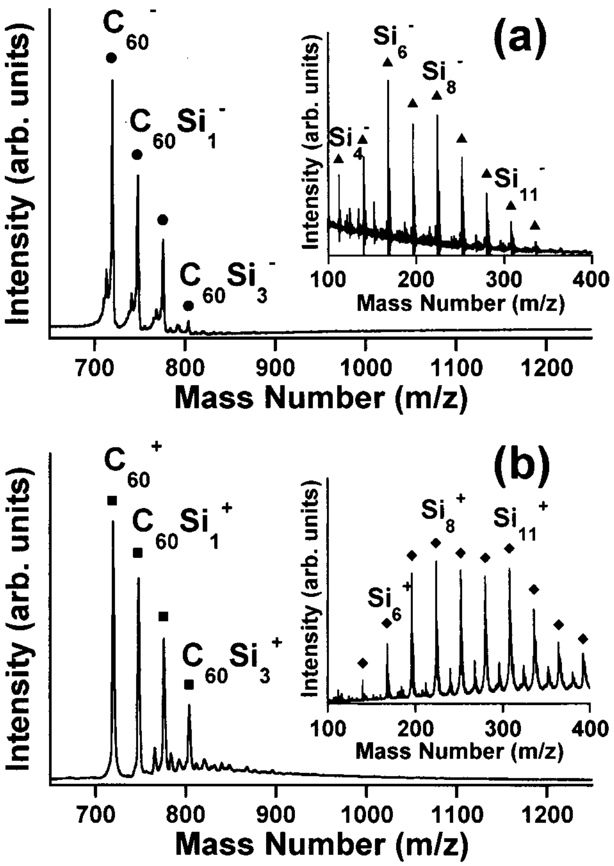

Figure 1. Time-of-flight mass spectra of $C_{60}-Si$ cluster (a) anions and (b) cations. Peaks of the $C_{60}Si_n$ cluster anions and cations at $n = 0-3$ are labeled by the solid-circles (●) and the solid-squares (■), respectively. Typical mass spectra of pure Si_n cluster anions and cations are labeled by the solid-triangles (▲) and the solid-diamonds (◆), respectively, and are shown in the insets.

$C_{60}Si_n^+$ clusters are shown in Figure 1a and 1b, respectively. The mass distributions of $C_{60}Si_n^{-/+}$ cluster monotonically decrease with increasing number (n) of Si atoms, which are in contrast to that of pure Si_n cluster anions and cations. The insets show the typical mass spectra of Si_n cluster anions and cations. As shown in both the inserted mass spectra, intermediate sizes of $n = 4-12$ were strongly observed along with $n = 1$ and 2 for cations (the peaks of Si^+ and Si_2^+ were not shown in the inset spectrum). In the mixed clusters with C_{60}, however, C_{60} can take only a small number of Si atoms ($n = 1-3$). If the Si_n clusters were combined with C_{60}, the signals of $C_{60}Si_4^-$–$C_{60}Si_{11}^-$ and $C_{60}Si_6^+$–$C_{60}Si_{12}^+$ would be observed strongly in their mass spectra. However, these intermediate sizes of Si_n clusters mixed with C_{60} could not be observed at all. This experimental result shows that $C_{60}Si_n^{-/+}$ clusters are generated through the sequential attachment of Si atoms to the C_{60} surface, and that the Si_n clusters interact very weakly with a carbon cage of C_{60}.

According to a theoretical calculation,[27] in the $C_{60}-Si$ complex, a Si atom forms a bridging bond between two C atoms on the sharing bond of two adjacent six-membered rings of C_{60}. Although many sites for the bonding of Si atom still remain, it was difficult to make $C_{60}Si_n$ grow into larger n ($n = 4$). This can be explained well by Si atoms that move around on the surface of C_{60}, and are allowed to make clusters with other Si atoms. Since the averaged Si–Si binding energy of around 3.0 eV [28] is much larger than the calculated binding energy of the Si atom to C_{60} (about 1.5 eV),[27] the "migrating (skating)" of Si atoms should result in the formation of the Si clusters on the C_{60} surface. In fact, this phenomenon of the "migrating" atoms has been reported also for the C_{60}–sodium system.[29] And the existence of the Si_n clusters on C_{60} has been observed also from photofragmentation experiments.[10] Moreover, the clustering of Si/Ge atoms has been observed also on ordered C_{60} overlayers on Si and Ge surfaces.[30]

According to the theoretical study for $C_{60}Si_5$,[27] five Si atoms of $C_{60}Si_5$ preferably aggregate to form a pentagonal shape island (cluster) rather than individual atoms on the C_{60}. However, in hot $C_{60}Si_5$ cluster, it is expected to change the pentagonal shape island of Si_5 to the three-dimensional structure, because larger Si_n ($n = 5$) clusters themselves rather prefer to take three-dimensional ones.[31] Thus, it seems reasonable that Si clusters themselves can be stabilized without a C_{60} surface at larger n. As a result, no signals for anionic and cationic $C_{60}Si_n$ ($n = 5$) clusters were observed. However, $C_{60}Si_n$ cations with large n values have been observed in the mass spectrum reported previously.[10] The explanation for this discrepancy may lie in the difference in internal energy of the clusters. Under the hot conditions, the clusters with large n cannot survive in the cluster beam, because the aggregated Si_n clusters are easily detached from the C_{60} surface, especially for the anions rather than for the cations. Namely, our source condition seems hotter than theirs.[10]

For both anionic and cationic $C_{60}Ge_m$ clusters, a mass pattern similar to that of $C_{60}-Si$ was obtained, although the mass spectra are not shown. Since the behavior of Ge atoms on C_{60} was almost the same as that of $C_{60}Si_n$, it can be deduced that Ge atoms also move around on the C_{60} surface, forming Ge clusters.

3.2. Photoelectron Spectroscopy of $C_{60}Si_n^-$ ($n = 0-4$) and $C_{60}Ge_m^-$ ($m = 0-3$). The photoelectron spectroscopy (PES) for cluster anions is a powerful technique to investigate the electronic and geometric structure of clusters with size selection. The photoelectron spectra were measured for $C_{60}Si_n$ and $C_{60}Ge_m$ cluster anions, to know about the behavior of the Si/Ge atoms on the surface of C_{60}.

Figure 2 depicts the photoelectron spectra of $C_{60}Si_n^-$ clusters for $n = 0-4$ and $C_{60}Ge_m^-$ clusters for $m = 0-3$. In Figure 2, all the spectra exhibit a signal onset followed by a more or less well-defined peak(s). Threshold energy (E_T) was obtained by linear extrapolation of the first onset to the baseline. A downward arrow indicates the position of E_T in each spectrum, and E_T corresponds to the upper limit of adiabatic electron affinity (EA) under no hot band. The EAs and the vertical detachment energies (VDEs) of peaks are given in Table 1. The spectral features are very similar between $C_{60}Si_n^-$ and $C_{60}Ge_m^-$ at each cluster size, and therefore it can be reasonably deduced that behavior of Ge atom(s) is similar to that of Si atom(s) on C_{60}.

For comparison, the PES spectrum of pure C_{60}^- is shown in Figure 2; a small bump peaked at ~2.5 eV has been attributed to the detachment from the t_{1u} state (the lowest unoccupied molecular orbital (LUMO) of neutral C_{60}) and the successive signal onset from ~3.5 eV corresponds to a state of h_u (the highest occupied molecular orbital (HOMO) of neutral C_{60}: the h_u state is located at ~4.6 eV).[32,33] Interestingly, EAs of $C_{60}Si_n$/$C_{60}Ge_m$ are very similar to the EA of C_{60}. This result shows that the electron-detachment occurs from the orbital of C_{60} in the cluster anions, where the negative charge prefers to be located on C_{60} rather than on the Si atom or Si_n clusters. In fact, the EA of C_{60} (2.45 eV) is much higher than those of Si_n at $n = 1-4$: EAs of Si_n are 1.39,[34] 2.18,[35] 2.0,[33] and 1.8 eV[33] at $n = 1-4$, respectively. This picture is also applicable to C_{60}–Ge cluster anions.

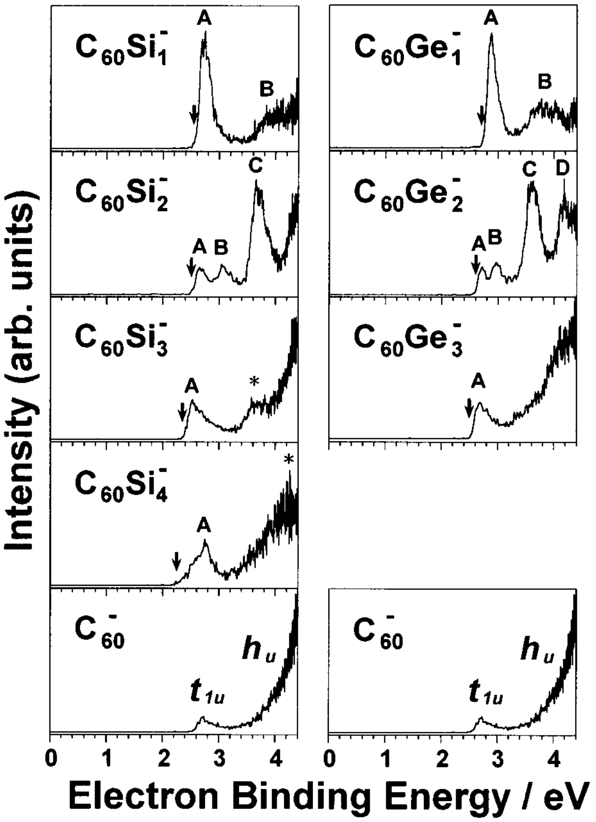

Figure 2. Photoelectron spectra of $C_{60}Si_n^-$ ($n = 0-4$) and $C_{60}Ge_m^-$ ($m = 0-3$) measured at a photon energy of 4.66 eV (266 nm). The downward arrows indicate threshold energies, corresponding to electron affinities. Unassignable peaks are labeled by "*".

TABLE 1: Electron Affinities (EAs) and Vertical Detachment Energies (VDEs) in eV

	E_T (EA)		VDE						
	$C_{60}Si_n$	$C_{60}Ge_m$	$C_{60}Si_n$			$C_{60}Ge_m$			
n,m			A	B	C	A	B	C	D
0	2.45								
1	2.55	2.70	2.75	3.85		2.90	3.80		
2	2.50	2.60	2.65	3.05	3.70	2.70	2.95	3.60	4.20
3	2.35	2.50	2.50			2.70			
4	2.25		2.75						

Furthermore, the overall spectral features of $C_{60}Si_n^-/C_{60}Ge_m^-$ gradually become similar to those of C_{60}^- with increasing n or m. As clearly seen in Figure 2, the features of photoelectron spectra at n, m=1 and 2 are different from that of pure C_{60}^-, although EAs of them are similar to that of pure C_{60}^-. At n, m = 3 and 4, the PES spectra become almost the same between $C_{60}Si_n/C_{60}Ge_m$ and C_{60}. This indicates that Si/Ge clusters (islands) little affect the overall electronic states observed here. The less electronic effect of Si/Ge clusters means that the Si/Ge clusters are weakly attached onto C_{60}; the Si atoms aggregate themselves at n, m = 3, 4. The clustering of Si/Ge atoms on C_{60} is consistent with the result from limited mass distributions of $C_{60}Si_n$ and $C_{60}Ge_m$ at small n, m.

In the spectrum of pure C_{60}^-, the increasing signal above 3.5 eV corresponds to the wing of the h_u state peak completely filled with 10 electrons, and VDE of this peak has been reported to be about 4.8 eV (not observed in Figure 2).[32] Here, it seems that peak "B" in the spectra of $C_{60}Si_1^-$ and $C_{60}Ge_1^-$ corresponds to the h_u state peak of C_{60}, and the intensity of the peak "B" is smaller than that of the h_u state peak. That is, the Si atom strongly interacts with the carbon cage of C_{60}, and this interaction results in the deformation of the electronic structure of C_{60}. The un-degeneracy of the orbital corresponding to the HOMO of neutral C_{60} could result in the observation of a series of peaks.

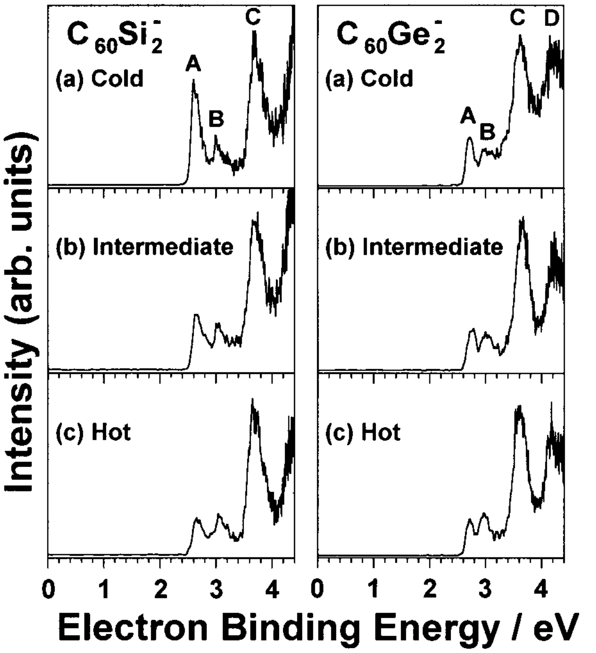

Figure 3. The change of the photoelectron spectra of $C_{60}Si_2^-$ and $C_{60}Ge_2^-$ by the production conditions. Internal temperature of the cluster can be changed by the fluence of the vaporization laser and/or the stagnation pressure of He carrier gas. Spectra (a), (b), and (c) correspond to the spectra in colder, intermediate, and hotter source conditions, respectively. The energies (the mean energies per pulse) of vaporization laser for C_{60} and Si/Ge and the stagnation pressure of He carrier gas on "cold", "intermediate", and "hot" source conditions were (a) "~100μJ, ~15mJ, 4.5~5 bar", (b) "~100μJ, ~15mJ, 3.5~4 bar", and (c) "~100μJ, ~25mJ, 3.5~4 bar", respectively.

The spectra of $C_{60}Si_2^-$ and $C_{60}Ge_2^-$ clearly exhibit three resolved peaks labeled by "A", " B", and "C". Interestingly, their intensity ratios were changed by the cluster source conditions. Figure 3 shows the change of the spectra for $C_{60}Si_2^-$ and $C_{60}Ge_2^-$ under different production conditions; the fluence of vaporization laser and/or the stagnation pressure of He carrier gas. With increasing the fluence of the vaporization laser and/or with decreasing the stagnation pressure of He carrier gas, the relative intensity of the peak "A" to the peaks "B" and "C" decreases without any serious broadening. The dependence of the relative peak intensity can be explained by coexistence of isomers. For $C_{60}Si_2^-/C_{60}Ge_2^-$, two different isomers are conceivable; two Si/Ge separated atoms−C_{60} and Si_2/Ge_2 cluster−C_{60}. This isomer coexistence can be strongly supported by the explanation about the "migrating" behavior of Si/Ge atoms on C_{60}. In the hot source conditions, the migrating atoms preferably result in the formation of the clusters on C_{60}, because the Si−Si binding energy of a Si_2 cluster is larger than the energy between one Si atom and C_{60}. In $C_{60}Si_2^-$ and $C_{60}Ge_2^-$, therefore, the enhanced peaks "B" and "C" in the hot conditions should be attributed to the peaks attributable to the Si_2/Ge_2 cluster−C_{60}, because the migration preferably increases the probability of encountering the Si/Ge atoms. On the other hand, the peak "A" can be assigned to the peak for the two Si/Ge separated atoms−C_{60}. Peak "D" in the spectra of $C_{60}Ge_2^-$ is also assigned to the peak for the two Ge separated atoms−C_{60}, because the intensity ratio between the peaks "A" and "D" is almost constant by changing the production conditions. Namely, two isomers apparently exist in the $C_{60}Si_2^-/C_{60}Ge_2^-$. According to the theoretical calculation, the most stable geometric structure of $C_{60}Si_2$ is the two Si separated atoms$-C_{60}$. Although a theoretical calculation should be examined, for the $C_{60}Si_2^-$, two isomers (two Si separated atoms$-C_{60}$ and Si_2 cluster$-C_{60}$) should be energetically close.

In $C_{60}Si_{3,4}^-$ and $C_{60}Ge_3^-$, $Si_{3,4}$ cluster$-C_{60}$ are the most stable structure in their several isomers. Since the overall spectral features of $Si_{3,4}$ cluster$-C_{60}$ anions are similar to that of C_{60}^-, Si_3 or Si_4 cluster little affects the electronic structure of C_{60}^-. Namely, peaks "A" observed in the spectra of $C_{60}Si_{3,4}^-$ can be attributed to the $Si_{3,4}$ cluster$-C_{60}$ anions, not to separated n-Si atoms$-C_{60}$ anion. This explanation can be applied also to the $C_{60}Ge_3^-$. Then, the peak "A" in the spectrum of $C_{60}Ge_3^-$ can be assigned to the peak for the Ge_3 cluster$-C_{60}$ anion. The overall spectral features of $Si_{3,4}/Ge_3$ cluster$-C_{60}$ anions are almost the same as that of pure C_{60}^-, although there are unassignable peaks at around 3.7 and 4.2 eV (labeled by "*") in the spectra of $C_{60}Si_3^-$ and $C_{60}Si_4^-$, respectively. Precise theoretical calculations on these species are necessary to discuss the peak assignments more quantitatively.

4. Conclusions

Time-of-flight mass spectrometry for the anionic/cationic $C_{60}Si_n$ and $C_{60}Ge_m$ cluster and the photoelectron spectroscopy of $C_{60}Si_n^-$ ($n = 1-4$) and $C_{60}Ge_m^-$ ($m = 1-3$) was employed in order to understand the behavior of Si and Ge atoms (or clusters) on C_{60}. The internal temperature of the "$C_{60}-$Si/Ge atom(s)" cluster is high enough, for the atoms to move easily on the surface of C_{60}. When the atoms form their clusters by themselves on C_{60}, the bulky Si_n/Ge_m clusters at n, $m = 5$ are detached from the C_{60} surface. Thus, the C_{60} surface acts as a field to grow the Si/Ge clusters from Si/Ge atoms.

This result shows that Si and Ge atoms of $C_{60}Si_n$ and $C_{60}Ge_m$ generated by this method prefer to become Si/Ge clusters on C_{60} probably due to high internal temperature in the formation, which never leads to $C_{60}Si_{60}$ and $C_{60}Ge_{60}$ (C_{60} fullerene coated by 60 atoms of Si/Ge). This work shows that the key factor for the successful synthesis of $C_{60}Si_{60}/C_{60}Ge_{60}$ is how to prevent the clustering of Si/Ge atoms on C_{60}.

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