Bonding States of He, Ne and Ar in Solid C_{60}

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(Received November 8, 1999; CL-990953)

He, Ne and Ar are intercalated in a lattice of C_{60} under the conditions of ambient temperature and pressure. The mass-analyzed thermal desorption reveals that rare gases are desorbed above 400 K and their desorption amounts are not in impurity level but in stoichiometric level. X-Ray photoelectron spectra in the C1s and valence band regions show different peak profiles. These results indicate that He, Ne and Ar atoms in a C_{60} lattice are in the bonding state.

The compounds of rare gas elements such as KrF_2, XeF_2, XeF_4, XeF_6 and XeO_4 have been reported.[1-5] The measurements of compressibility for C_{60} using He, Ne and Ar as pressure media and the study of diffusion kinetics in solid C_{60} have been carried out under the conditions of high pressures at around several kbar.[6-9] In this paper, a characteristic interaction was found to exist between C_{60} and rare gas elements under the conditions of ambient temperature and pressure by means of mass-analyzed thermal desorption and X-ray photoelectron spectroscopy .

C_{60} (Hoechst, 99.98% purity) was used without further purification. A sample of C_{60} transferred in situ to an ultra-high vacuum system and heated at 623 K was exposed to rare gases (Nippon Sanso, >99.9999% purity) of 1 to 1.4 atm, at room temperature to 623 K and for 1 to 10 days. After the sample was cooled to liquid nitrogen temperature, the sample tube was evacuated to ultra-high vacuum. The desorbed gas was analyzed by using two mass-spectrometers when the sample was heated with the temperature-rise rate of 5 K/min.[10-12] Before X-ray photoelectron spectrum measurements, a Pyrex glass tube in which a sample of C_{60} exposed to rare gas had been sealed was broken in a glove bag attached to a specimen-introduction device of VG ESCA LAB Mk II, and the sample was pressed onto an electrically-conductive adhesive tape on a sample stage. An MgKα line was used as probe.

Figure 1 shows the thermal desorption spectra for C_{60} exposed to He, Ne and Ar. Desorption processes occurred in the low temperature range of 70-300 K as well as in the high temperature range of 450-900 K. This is a first report on the observation of thermal desorption spectra of rare gases in the temperature region higher than room temperature. The content of rare gas in the sample was determined from the amount of the rare gas integrated over the entire desorption spectrum, the relative sensitivity of the mass analyzer and the pumping speed. Upon exposure to rare gases at 393 K and 1.3 atm for 3 days, the compounds; $C_{60}He_{0.39}$, $C_{60}Ne_{0.074}$ and $C_{60}Ar_{0.09}$ were formed. The contents of the rare gases are not in impurity level but in stoichiometric level. The content of He in the compound is more than those of Ne and Ar in their compounds, which is attributed to the size effect of rare gas on its migration into the

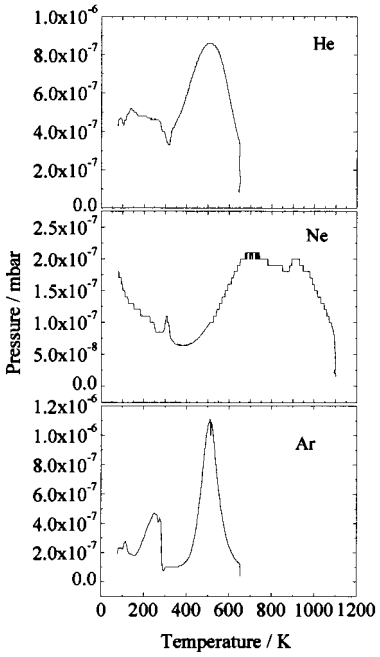

Figure 1. Thermal desorption spectra for C_{60} exposed to He, Ne and Ar.

lattice of C_{60}. The desorption peak of He was observed at 509 K for $C_{60}He_{0.39}$, that of Ne at 706 K for $C_{60}Ne_{0.074}$, and that of Ar at 511 K for $C_{60}Ar_{0.09}$.

Figure 2 shows the X-ray photoelectron spectra in the C1s and Ar regions. The C1s peaks for C_{60} and C_{60} exposed to Ar, Ne, and He were observed at 282-285 eV, and the shake-up satellites based on a $\pi - \pi^*$ transition appeared at ca. 5 eV apart on their higher binding-energy side. A weak peak at 275 eV on the lower binding energy side is ascribed to an X-ray impurity of an MgKα probe. A new peak was obviously observed at 269 eV when C_{60} was exposed to Ar, which is assigned to Ar2p. An Ar2p peak of argon implanted into graphite has been reported to appear at 241.3 eV or 241.6 eV, and those of argon implanted into metals at 240.2-241.9 eV.[13] The Ar2p peak for $C_{60}Ar_x$ is located at ca. 26 eV higher than those for graphite-Ar and metal-Ar systems. The energies for the peaks could not be determined accurately, because the peaks shifted depending on the charging-up of a sample during the measurement. The energy difference between the C1s and the Ar2p peaks is, however, expected to be definite, because they were observed under the same experimental conditions of a sample. Ar is considered to be occluded as a neutral atom in graphite-Ar and metal-Ar systems, and the energy difference between the C1s and the

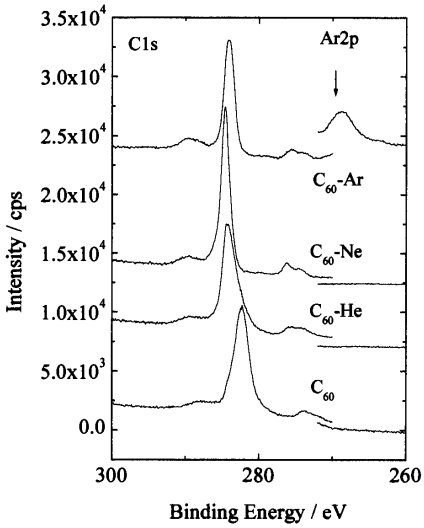

Figure 2. XPS spectra in the C1s region for C_{60} and C_{60} exposed to He, Ne and Ar.

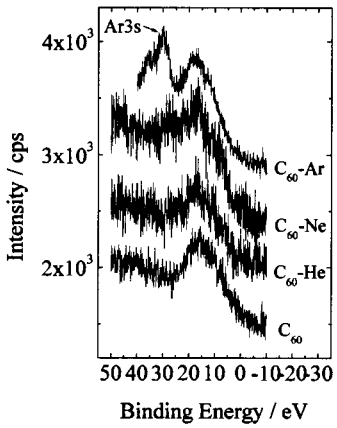

Figure 3. XPS spectra in the valence band region for C_{60} and C_{60} exposed to He, Ne and Ar.

Ar2p peaks for the graphite-Ar system has been reported to be 43 eV, and the Ar2p peaks for the metal-Ar systems to show two-peak profiles due to a spin-orbit interaction.[13] The energy difference for $C_{60}Ar_x$ is 16 eV, and the Ar2p peak shows almost a single-peak profile. The changes of chemical shift and peak profile depend on the chemical bonding state. Since the C1s peaks were observed at 282-285 eV (3 eV difference), the remarkably reduced energy difference and the change of a peak-profile for $C_{60}Ar_x$ indicate that argon atoms in a lattice of C_{60} are in the bonding state.

Figure 3 shows XPS spectra in the valence band region. A new peak appeared at around 30 eV upon exposure of C_{60} to Ar, which is assigned to Ar3s. An Ar3s peak has been reported to appear at 22 eV for the argon implanted into metals,[13] which is located at ca. 8eV lower than that for $C_{60}Ar_x$. This energy difference as *ca.* 8 eV is larger than the energy differences of ca. 3 eV among carbon peak position for C_{60}, C_{60}-He, C_{60}-Ne and C_{60}-Ar systems. Carbon peak profiles for C_{60}-He and C_{60}-Ne systems are also different from that for pristine C_{60}. The XPS spectra of He and Ne have not been reported because of negligibly small photoelectron of He and Ne by X-ray. Therefore, the peak assignment is difficult at the present. The changes in peak profiles for carbon indicate the chemical bonding at least. The energy difference and change in peak profile also suggest that argon atoms in a lattice of C_{60} are in the bonding state. Since the energy difference of carbon valence bands were also observed to be ca. 3 eV as described in the C1s spectra, the observed energy difference of Ar3s as ca. 8 eV is larger than that in the carbon valence band. This indicates that Ar has the positive charge.

The mass-analyzed thermal desorption spectra above room temperature region and the XPS spectra show single-peak profiles. If the interaction of rare gases in a lattice of C_{60} occurs through a simple adsorption, the amount of desorption gas has to be in the order as Ar > Ne > He because their van der Waals forces decrease along this sequence. The experimental results, however, show the reverse order, so that it is reasonable to conclude that the interaction of He, Ne and Ar is caused not by adsorption but by bonding in the lattice. Two experimental results support the bonding state. (1) A hydrogen desorption peak for the KC_8H_x (x~0.6) ternary system appears at 512 K,[10] and desorption peaks for Na-H-C_{60} at around 650 and 900 K,[11,12] in which hydrogen has been concluded to exist as hydride or $H^{\delta-}$. These desorption temperatures are comparable to those of C60-He, Ne and Ar systems. (2) A large isotopic effect is found for the C_{60}-He system: ^{4}He is desorbed at 509 K, while ^{3}He at around 420 K.

The impurities such as another chemical species and defects are difficult to think more, to have the content that helium reaches 40% to C_{60}. Also, the significant impurities are not found out even XPS and ESR measurements. The results obtained from the mass-analyzed thermal desorption and the XPS spectra lead to the conclusion that the He, Ne and Ar atoms in a lattice of C_{60} are in the bonding state.

This work is partially supported by a Grant-in-Aid for Scientific Research No. 11640586 from the Ministry of Education, Science, Sports, and Culture of Japan.

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