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Characteristic Interaction of Na-H-C_{60} and C_{60} with Hydrogen and Rare Gases

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Rare gases such as He, Ne and Ar are trapped in the lattice of solid C_{60} and $(NaH)_4C_{60}$ under conditions of ambient temperature and pressure. The mass analyzed thermal desorption reveals that rare gases are desorbed above 400K and their desorption amounts are in nonstoichiometric level. Ar2p and Ar3s X-ray photoelectron spectra show large chemical shifts. These results suggest that He, Ne and Ar have charge and are in valence state.

Keywords: fullerene; chemical interaction; absorption; XPS; mass analyzed thermal desorption

INTRODUCTION

The compressibility and diffusion kinetics of C_{60} have been investigated by using He, Ne and Ar as pressure media under the high pressure at around several kbar [1]. However, characteristic interaction of Na-H-C_{60} and C_{60} with hydrogen and rare gases under conditions of ambient temperature and pressure are investigated by means of mass-analyzed thermal desorption and X-ray photoelectron spectroscopy (XPS).

Na-H-C_{60} and C_{60} form nonstoichiometric compounds with rare gases such as He, Ne and Ar by exposure under ambient temperatures and pressures. The desorption peaks of rare gases appear at around 70K, 300K, 450-900K. The desorption peak profile for Na-H-C_{60}-A quarternary system (A = He, Ne,

Ar) is different from that for C_{60}. In XPS spectra, a large chemical shift is confirmed in Ar 2p spectrum for C_{60}-A and Na-H-C_{60}-A, indicating the chemical bonding.

EXPERIMENTAL

C_{60} (Hoechst, 99.98% purity) was used without further purification. As to $(NaH)_4C_{60}$, NaH and C_{60} were mixed in the glass tube with the stoichiometric ratio in the glove box, and then calcination at 553K was carried out. Each sample was transferred to an ultra-high vacuum system. For 1 to 10 days each sample was exposed to rare gases (Nippon Sanso, >99.9999% purity) at room temperature to 623K and 1 to 1.4 atm, after vacuum heating at 653K. After cooling it to liquid nitrogen temperature, the sample tube was evacuated to ultra-high vacuum. The desorbed gases were mass-analyzed when the sample was heated with the rate of temperature rise of 5 K/min (The Thermal desorption Spectroscopy) [2-4]. Two mass analyzers have the sensitivities of 10^{-10} mbar. The accuracies of experimental parameters are in about 2-3 magnitude of order. The sample exposed to gases were sealed in Pyrex glass tube. Before X-ray photoelectron spectrum measurement, the sample tube was broken in a glove bag attached to the specimen introduction device of VG ESCA LAB Mk II, and was attached to the electrical conductive adhesive tape on the sample stage. MK_α was used as probe.

RESULTS AND DISCUSSION

C_{60} and $(NaH)_4C_{60}$ absorb H_2, He, Ne, Ar, Kr, and Xe of around 1 atm even at room temperature. To obtain the higher absorption rate, exposures are carried out at 373 to 473K. Figure 1 shows the thermal desorption spectra for C_{60} and $(NaH)_4C_{60}$ exposed to He, Ne, Ar and H_2. Significant desorption processes are observed in the low temperature range of 80-300K and in the high temperature range of 450-900K. This research is for the first time, to report the observation of the thermal desorption spectra of rare gases even in higher temperature range. The gas-element content is able to be decided from the integral value of the desorption spectrum, relative sensitivity in mass analyzer and pumping speed. For example, the compounds of $C_{60}He_{0.39}$, $C_{60}Ne_{0.074}$, $C_{60}Ar_{0.09}$, $Na_4C_{60}H_{0.04}He_{0.55}$, $Na_4C_{60}H_{0.56}Ne_{0.056}$, and $Na_4C_{60}H_{0.87}Ar_{0.041}$ are generated. The content of rare gas decreases in the

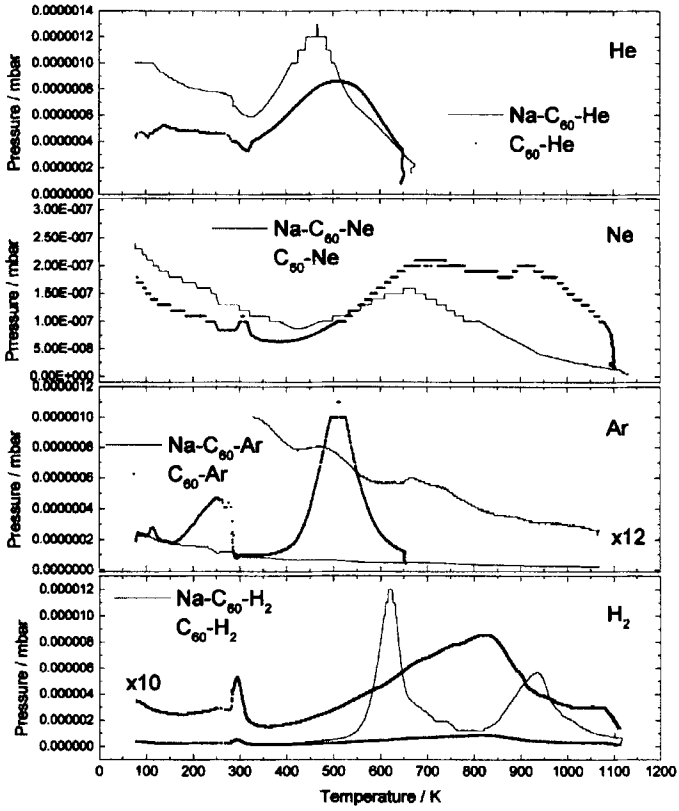

FIGURE 1 Thermal desorption spectra for C_{60} and $(NaH)_4C_{60}$ exposed to He, Ne, Ar and H_2.

order of helium, neon and argon, which is considered to be due to the size effect of rare gas in migration to the bulk at generation process. The desorption peak of helium is observed at 509K and 467K for $C_{60}He_{0.39}$ and $Na_4C_{60}H_{0.04}He_{0.55}$, respectively. The same trend appears in Na-C_{60}-Ne and C_{60}-Ne: the desorption peak of neon is observed at 663K and 706K for $Na_4C_{60}H_{0.56}Ne_{0.056}$ and $C_{60}Ne_{0.074}$. As for argon, the desorption peak appears at

511K for $C_{60}Ar_{0.09}$ and 470K and 700K for $Na_4C_{60}H_{0.87}Ar_{0.041}$.

Up to now, we have reported on the correlation between the existence state of hydrogen and super-conductivity in Na-C_{60}-H ternary system [2-4]. In the KC_8H_x (x~0.6) ternary system, the hydrogen desorption peak appears at 512K [5]. The desorption peaks of hydrogen in Na-H-C_{60} appear at around 650K and 900K in the higher temperature region than alkali-metal-graphite–hydrogen ternary system. For Na-H-C_{60} with superconductive and non-superconductive phases with the almost same hydrogen content, the hydrogen desorption peak for superconductive phase appear at around 10 degree higher than non-superconductive phase. Hydrogen species at around 650K has a strong correlation with super-conductivity. The desorption peak of hydrogen from Na-C_{60}-H ternary system $Na_4C_{60}H_{1.01}$ that shows volume fraction of the superconductive phase as 35% decided by SQUID measurement appears at 644K. This indicates that hydrogen exists as hydride or $H^{\delta-}$. The desorption peak of the hydrogen from $Na_4C_{60}H_{1.39}$ of the non-superconductive phase used in this experiment is observed at 625K. In comparison to the superconductive phase with the almost same hydrogen content, the desorption peak of hydrogen from the non-super-conductive phase is observed lower as about 20K. This suggests that the hydrogen in the non-superconductive phase has a smaller ionicity, a smaller amount of charge transfer, or smaller activation energy of desorption process than the super-conductive phase. The desorption peak of the neon from the Na-C_{60}-Ne and C_{60}-Ne systems are observed in the higher temperature region than the hydrogen desorption from Na-C_{60}-H ternary system. The desorption behavior observed by the mass analyzed thermal desorption spectroscopy indicates that the rare gas atoms of helium, neon and argon form the chemical bond.

Figure 2 shows the X-ray photoelectron spectra of C1s, Ar2p and valence band region for C_{60} and $C_{60}Ar_x$. The C1s peaks of C_{60} and $C_{60}Ar_x$ are observed at 284 and 282.5eV, and the shake-up satellites based on π–π^* transition appear at around 10eV higher binding energy side. The weak peak at 275eV in lower binding energy side is due to the X-ray impurity of MgK_α probe. The peak due to X-ray impurity also appears at around 275eV even in the Ar region. The new peak was observed at 269eV in the case of $C_{60}Ar_x$. Incidentally, the Ar2p peak of argon implanted into graphite is reported as 241.3eV or 241.6eV [6]. Ar2p peak shifts to around 28eV higher binding

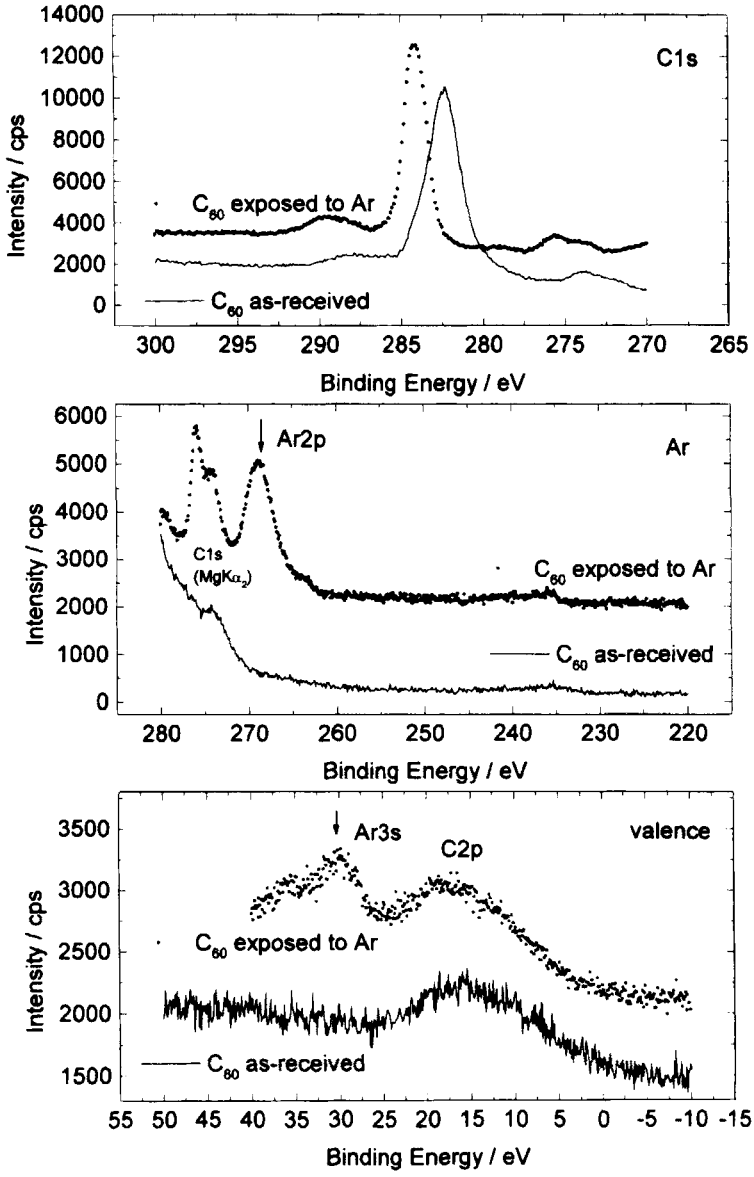

FIGURE 2 X-ray photoelectron spectra of C1s and Ar2p and valence band region for C_{60} and C_{60}Ar.

energy side compared with the reported values of argon implanted into metals as 240.2-241.9eV [6]. The energy difference between C1s and Ar2p for graphite-Ar system is 43eV, while that decrease remarkably to be 16eV in $C_{60}Ar_x$. In addition, while Ar2p peak of argon implanted into metals shows two peak profiles based on the spin-orbit interaction, Ar2p peak of $C_{60}Ar_x$ shows almost single peak profile. For $C_{60}Ar_x$ a new peak appears at around 30eV in the valence band region and be considered to be assigned to Ar3s peak. The Ar3s is reported as 22eV and shifts to around 8eV higher binding energy side. These facts lead to the conclusion that argon has a positive charge: that is, argon exists as cation.

As to application, the compound formation of rare gas can offer new functionability to the separation, enrichment and storage of rare gases. Furthermore, the compound formation with helium gives a possibility of an integral type device for alpha particle measurement and the helium exhaust evacuation or helium gettering in nuclear fusion technology.

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