Polymeric Co-C$_{60}$ Compound Phase Evolved in Atomistically Mixed Thin Films

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A systematic study of the atom-level mixtures between Co and C$_{60}$ has made possible to find a new C$_{60}$-based compound phase, Co$_x$C$_{60}$ ($x \leq 5$). It is confirmed with the EXAFS analysis and the positron annihilation study that the polymeric structure is developed three-dimensionally by bridging two C$_{60}$ molecules with the covalently bonded Co atom.

1. Introduction

The interactions between C$_{60}$ and transition metal elements have attracted much attention for their possible formation of new functional materials,[1,2] and it has been shown that the interesting structures are evolved in the atomistically mixed thin films of C$_{60}$ and transition metals with the poor or the negligible solubility with carbons.[3–6] However, the detailed studies of the microstructures have been limited due to the difficulty in the precise control of sample composition, the decomposition of C$_{60}$ during deposition and the possible contamination from atmosphere. Recently, the mixtures of Co and C$_{60}$ with the broad composition range of $1 < x < 700$ (x: the number of Co atoms per a C$_{60}$ molecule) have been successfully fabricated without the decomposition of C$_{60}$, and the Raman analysis and the characterization of volume-change were performed under the well-defined conditions.[7,8] The systematic study suggests the formation of a new compound-phase between Co and C$_{60}$ (C$_{60}$-based phase, hereafter) with the saturating composition of Co$_5$C$_{60}$ in the Co-dilute mixtures ($x \leq 5$) and the precipitation of the excess Co atoms in the Co-dense mixtures ($x > 5$). The Raman analysis of the C$_{60}$-based phase shows the symmetry-lowering of C$_{60}$ and a relatively small amount of charge transfer (about 0.2 electrons/Co atom) from the bonded Co atom to a C$_{60}$ molecule.[7] In addition, the considerable volume-dilatation was detected in the corresponding mixtures with increasing x ($x \leq 5$).[7,8]

The purpose of this study is to confirm the atomic configuration and the bonding character in the suggested C$_{60}$-based phase. Both of the Co-K edge X-ray absorption fine structure (XAFS) analysis and positron annihilation study are performed to know the short-range structure around the bonded Co atoms together with the size of the intermolecular free-volumes reflecting the spatial configuration of the short-range structure.[9]

2. Experimental

Films of mixtures between Co and C$_{60}$ were prepared using co-deposition technique under the high vacuum condition of 5×10^{-7}–1×10^{-6} Pa. Co (99.99%) and C$_{60}$ (99.99%) were evaporated by using an electron beam evaporator and a Knudsen cell, respectively. The mirror-polished MgO (001) plates were used as substrates, and the substrate temperature was kept at room temperature during the deposition. The distances between the crucibles and the MgO substrate were kept larger than 20 cm to avoid the influence of thermal radiation from the evaporation sources. The films with the compositions of $x = 2$–15 and the thickness of 500–700 nm were prepared by adjusting the deposition rates of the relevant materials, where the protecting layer of Au or Co with a few to several 10's nm thick were deposited additionally to prevent the mixtures from oxidization and the humidity absorption which result in the significant volume-dilatation by up to twice of the as-deposited one.[7,8] The mixtures with the Co content of $x \leq 5$ are composed of nothing but the C$_{60}$-based phase with a composition of Co$_x$C$_{60}$, and those with the Co content range of $5 < x < 15$ have the saturated C$_{60}$-based phase of Co$_5$C$_{60}$, dispersing a small amount of the precipitated Co clusters or nano-crystals.[7,8]

The Co K-edge XAFS spectrum of the mixture with $x = 2.9$ capped with the Au layer was collected in the florescence mode at the BL-27B station of the Photon Factory (KEK, Tsukuba) using Si(111) monochromator. The sample and the fluorescence detector were placed at 45-degree and 90-degree to the incident photon beam, respectively. The XAFS data were analyzed by using the XAFS data analysis software package WinXAS ver. 2.3.[10] The measurements of positron lifetime and Doppler broadening of annihilation radiations were performed for the films of mixtures with the Co content range of $2 < x < 15$ and pure C$_{60}$ polycrystals with the capping layer of Co by using the low-energy positron beam. 7 keV positrons were employed so as to make the most of positrons annihilate within the layer of the mixtures beyond the capping layer. The so-called S- and W-parameters in the Doppler broadening measurements were defined as the ratio of areas on both sides with the smaller-shift (<0.767 keV) and the larger-shift (>3.41 keV) to the total area of the broadened spectrum.
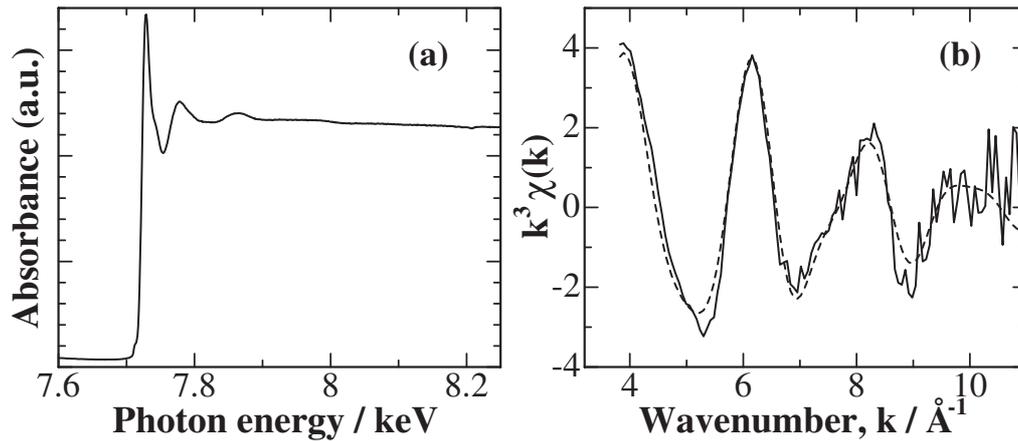
Fig. 1 (a) Co K-edge XAFS spectrum of the mixture with $x = 2.9$ collected by using the fluorescence technique. (b) The normalized EXAFS spectrum extracted from (a) (a solid line) with the simulated pattern (a broken line).
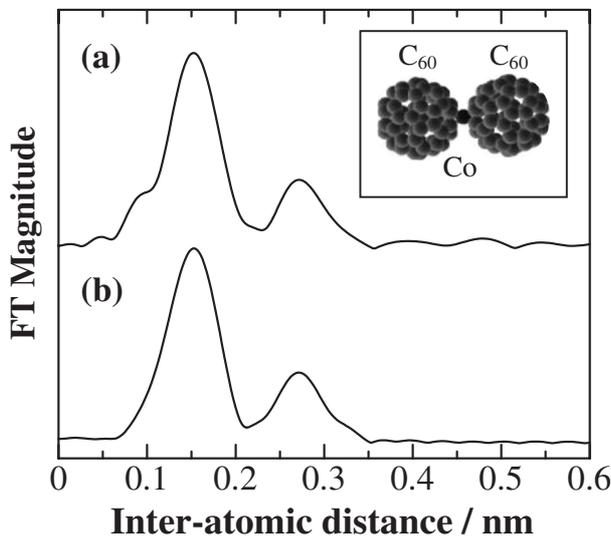

Fig. 2 The calculated radial structural function (a), which is uncorrected for the phase shift, for the mixture with $x = 2.9$ and the simulated patterns (b) for the model illustrated in the inset.

Fig. 3 Examples of the positron lifetime spectra measured for the pure-C_{60} polycrystals ($x = 0$) and the mixtures with $x = 2.1$ and 7.3.

3. Results and Discussion

Figures 1(a) and (b) show the fluorescence Co K-edge XAFS spectrum of the mixture with $x = 2.9$ and the normalized extended X-ray absorption fine structure (EX-AFS) spectrum weighted by k^3 obtained by subtracting the smooth background from the XAFS spectrum, where the simulated pattern based on the model shown below is given together. Figures 2(a) and (b) show the radial structure function (RSF) for the mixture obtained from the EXAFS spectrum, where the inter-atomic distance is not corrected for the phase shift, and the simulated RSF for the model (shown in the inset) by using FEFF 8.2 code.[11] The RSF is definitely different from that of crystalline Co and can be represented well by the model in which one Co atom bridges between two C_{60} molecules. The peaks at about 0.16 nm and 0.28 nm in the RSF scale arise from the Co-C interactions and the multiple scatterings of Co-C-C (3 legs) and Co-C-Co-C (4 legs) on the basis of the simulation. Taking account of the phase shift and
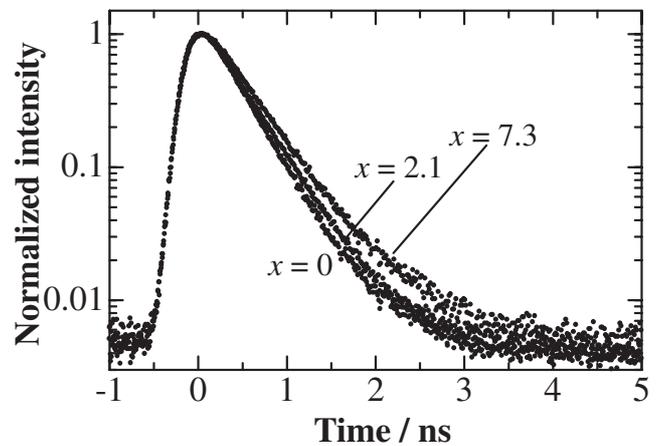
the backscattering amplitude, the Co-C bonding distance and the coordination numbers of the bridging Co atom to the bonded C atoms are determined to be 0.201($\pm$0.001) nm and 6, respectively. The Co-C bonding distance seems to be slightly shorter than the reported one of cobaltcene, $(C_p)_2Co$ (C_p: cyclopentadienyl), (0.207 nm)[12] known as a kind of π-complexes of transition metals but is distinctive from the Co-C nearest neighbor distance in the hexagonal cobalt carbide, Co_3C, (0.268 nm).[13] The coordination numbers obtained suggest that the three carbon atoms on the five- or six-membered rings of C_{60} molecules are bonded to the Co atom. Although the EXAFS measurements at lower temperatures might be desirable for the detailed analysis, the present results at room temperature indicate clearly the bridge-formation between two C_{60} molecules by the covalently bonded Co atom as the composing unit of the C_{60}-based phase.

Figure 3 shows the typical examples of the positron lifetime spectra for the pure-C_{60} film ($x = 0$) and the mixtures with $x = 2.1$ and 7.3. After subtracting the background and extra lifetime components coming from environment, the lifetime spectra are reasonably fitted by a single
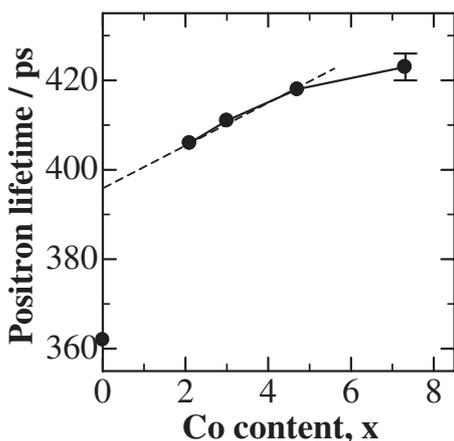
Fig. 4 Positron lifetime as a function of the Co content, x. A broken line is drawn for the linear extrapolation.

Fig. 5 S- and W-parameters estimated from the Doppler broadening spectra as a function of the Co content, x.

component of lifetime. Figure 4 shows the lifetime as a function of x. The positron lifetime becomes longer when positrons annihilate at the sites with the less density of electrons. The positron lifetime of 362 ps for the pure-C$_{60}$ film ($x = 0$) in the present study is consistent with the reported ones, $(360 \pm 10 \, \text{ps})$.[14–16] Both of Jean[14] and Puska[16] pointed out that the observed lifetimes were attributed to the positron annihilation at the octahedral interstitial sites with the size of about 0.42 nm in diameter in fcc-C$_{60}$ crystal from the theoretical calculation. The lifetime of the mixtures with different x increases by about 1%/Co atom in the range of $2 < x < 5$, and then tends to approach the constant value of 420 ps above the saturating composition of the C$_{60}$-based phase ($x = 5$) as confirmed by the Raman analysis.[7,8]

Figure 5 shows the S- and W-parameters of the Doppler broadening spectra as a function of x. The S-parameter reflects the momentum distribution of electrons at the annihilation sites and has a tendency to increase with increasing the probability of annihilation with the valence electrons, and on the contrary, the W-parameter is dominated mostly by the core electrons. The W-parameter usually decreases with the S-parameter-increase, $i.e.$, shows a mirror-like behavior. However, such a tendency is not kept necessarily when the elemental specificity at the positron annihilation sites changes dramatically. The S-parameter of the mixture with $x = 2$ increases by 1% from the pure-C$_{60}$ film ($x = 0$), and then shows a saturating behavior with increasing x. Following the mirror-like behavior, the W-parameters decrease in the region between $x = 0$ and $x = 2$. But the W-parameter-change fails from the mirror-like behavior when x increases beyond the saturating composition of the C$_{60}$-based phase ($x = 5$) nevertheless the S-parameters are almost constant.

The observed single component in the lifetime spectra and the small differences between the S-parameters for the mixtures and the pure-C$_{60}$ film indicate the existence of the intermolecular free-volume with the interstitial nature in the C$_{60}$-based phase. Hence, the lifetime-increase compared with pure-C$_{60}$ crystals in the present case can be ascribed to the enlargement of the intermolecular free-volume by the mixing
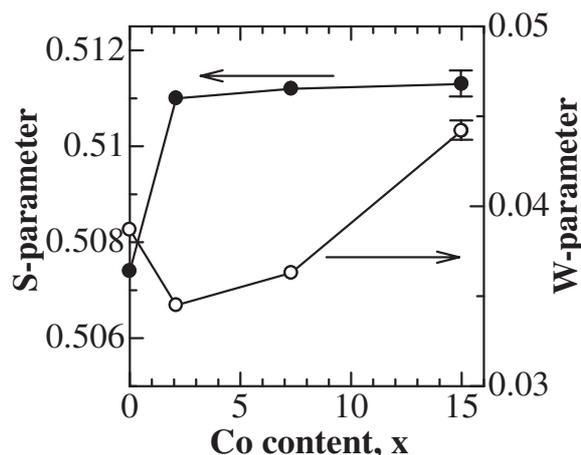
with Co atoms. Also, the S-parameter-increase compared with pure-C$_{60}$ crystals can be attributed to the size-change of the intermolecular free-volume in general, but it might be necessary to consider the role of the transferred electrons from Co atom to π-orbital of C$_{60}$ molecule whose amount is estimated to be around 1 electron per a C$_{60}$ molecule in the saturated C$_{60}$-based phase, Co$_5$C$_{60}$.[7] The elongated lifetime for the present mixtures is in striking contrast to the behavior of the alkali-metal doped C$_{60}$ films in which the metal atoms occupy the interstitial sites in the crystalline lattice of fcc-C$_{60}$ so as to compensate the intermolecular free-volumes without bridging between C$_{60}$ molecules. This result in the decrease of the positron lifetime compared with pure-C$_{60}$ crystals.[16] Here, by assuming that the enlargement of the intermolecular free-volume is in proportion to the lifetime as in the pressure-dependent lifetime measurements,[14] the size of the inter-molecular free-volume is estimated to be around 0.45–0.5 nm in diameter in the saturating C$_{60}$-based phase, Co$_5$C$_{60}$. The observed enlargement of the intermolecular free-volume seems to coincide with the x-dependent volume-dilatation in the C$_{60}$-based phase. In the range of $0 < x \ll 2$ the volume-dilatation of mixtures amounts to 10% compared with that for fcc-C$_{60}$ crystal, and in the following range of $x \leq 5$ the dilatation increases linearly at the rate of 2.5% per a Co atom.[7] The x-dependent dilating behaviors are quantitatively explained by considering the generation of a new phase with the coordination different from pure-C$_{60}$ crystals. The new phase can be realized through the bridge-formation between C$_{60}$ molecules by Co atoms, and hence the enlargement of the intermolecular free-volume is expected at the initial stage of mixing ($0 < x \ll 2$). Further increase of the Co content up to $x \leq 5$ develops the three-dimensionally bridged structure, which results in the continuing dilatation in the C$_{60}$-based phase. The detailed analysis of the behaviors at the initial stage ($0 < x \ll 2$) will be reported elsewhere. Figure 6 illustrates a polymerically coordinated C$_{60}$-based phase deduced from the present study. Our results for the polymeric C$_{60}$-based phase are reasonably consistent with the recent finding of the atomic clusters of transition metals and C$_{60}$ synthesized under the gas phase, where are proposed the
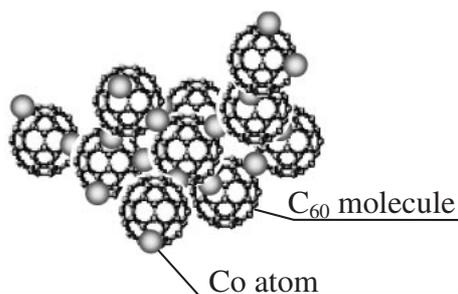
Fig. 6   A schematic drawing of the polymeric C_{60}-based phase developed three-dimensionally through the bridge-formation between two C_{60} molecules by a Co atom.

structures developed from the dimeric C_{60} molecules bonded by a metal atom.[17–19] It can be believed that the polymeric C_{60}-based phase is formed as a non-equilibrium state due to the atomistic mixing achieved by the co-deposition at room temperature. The W-parameter-change deviating from the mirror-like behavior beyond the saturating composition of the C_{60}-based phase implies that positrons annihilate partly with electrons of Co atoms composing of the Co clusters or nano-particles in the region of $x > 5$.[7,8] The saturating behavior in the positron lifetime above $x > 5$ suggests that the precipitated Co clusters or nano-particles in the Co-dense mixtures rarely induce the additional component of positron annihilation.

4.   Summary

We investigated the structure evolution of the C_{60}-based phase, Co_xC_{60} ($x \leq 5$), in the atomistically mixed thin films of Co and C_{60} by employing EXAFS analysis and positron annihilation spectroscopy. The EXAFS analysis reveals the bridge-formation between two C_{60} molecules by the covalently bonded Co atom. Moreover, the positron annihilation study shows that the polymerically coordinated Co-C_{60} phase

is developed three-dimensionally with increasing the Co content. The Co content dependent behaviors in the present study are consistent with the volume-dilatation phenomena reported elsewhere.

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