Eur. Phys. J. D **43**, 141–142 (2007)
DOI: 10.1140/epjd/e2007-00081-1

THE EUROPEAN PHYSICAL JOURNAL D

In situ high-resolution valence photoelectron spectra of a peanut-shaped C_{60} polymer

J. Onoe[1,2,a], T. Ito[3], S. Kimura[3], and K. Ohno[4]

[1] Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152-8550, Japan
[2] Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan
[3] Institute for Molecular Science, and School of Physical Sciences, The Graduate University for Advanced Studies (SOKENDAI), Myoudaiji, Okazaki, Aichi 444-8585, Japan
[4] Yokohama National University, 79-5 Tokiwadai, Yokohama 240-8501, Japan

Received 24 July 2006 / Received in final form 11 October 2006
Published online 24 May 2007 –

Abstract. To elucidate the origins of the metallic properties of the peanut-shaped C_{60} polymer, we examined the valence photoelectron spectra of the polymer using in situ high-resolution photoelectron spectroscopy and found that the density-of-states (DOS) of the polymer clearly comes across the Fermi edge in a manner similar to that of Au film used as a reference, indicating that the peanut-shaped C_{60} polymer exhibits metallic properties.

PACS. 71.20.Tx Fullerenes and related materials; intercalation compounds

1 Introduction

In a previous work [1], we discovered that C_{60} molecules are coalesced to each other to form a peanut-shaped C_{60} polymer by electron-beam (EB) induced polymerization of C_{60} molecules. This polymer exhibited metallic current-voltage ($I-V$) characteristics at room temperature under atmospheric conditions [1].

To reveal the origins of the metallic electron-transport properties of the peanut-shaped C_{60} polymer, we previously examined the valence photoelectron spectra of the polymer in an ultrahigh vacuum (base pressure: 1×10^{-7} Pa), using ultraviolet photoelectron spectroscopy (UPS) with an energy resolution of 50 meV and with non monochromatic HeI emission lines (HeIβ emission line was included), along with graphite as a typical π-electron conjugated semi-metal system [2]. It was found that the density-of-states (DOS) around the Fermi level (E_F) for the peanut-shaped polymer was greater than that for graphite and seemed to come across the E_F. However, the previous measurement conditions (an energy resolution of 50 meV and non monochromatic HeI emission line including not only the main HeIα line but also the minor HeIβ line) were not sufficient to discuss with precision the DOS of the peanut-shaped polymer in the vicinity of the E_F. To clarify the behavior of the DOS of the peanut-shaped polymer in the vicinity of the E_F edge with more accuracy, we have in the present study examined the DOS of the polymer around the E_F using UPS with a higher energy-resolution (10 meV) and with a monochromatic HeI emission line (HeIα line only).

2 Experiments

After a C_{60} film (100 nm thick) formed on a copper substrate (5 mm × 5 mm) by sublimation of C_{60} powder (99.98% pure) at 673 K for 90 min, the pristine C_{60} film was measured in situ by UPS with an energy resolution of 10 meV and with the monochromatic HeIα emission line (21.218 eV) in an ultrahigh vacuum (base pressure: 1×10^{-8} Pa). After the measurements, the film was irradiated with the EB-gun (an incident energy: 3 keV, an electron current: 500 μA) for 12 h. We confirmed by in situ infrared spectroscopy that 12 h of EB-irradiation was sufficient to allow the C_{60} molecules to completely coalesce, thus forming a peanut-shaped C_{60} polymer. After 12 h of EB irradiation, the film was measured in situ by UPS at a substrate temperature of 350 K, because we examined the effect of the charge-up on the UPS spectrum around the E_F as a function of substrate temperature and observed no effect of the charge-up during HeI irradiation of the sample at above 350 K. The zero value in binding energy for the present measurements was determined from the Fermi level (E_F = 0 eV) of a gold film, which was deposited on the same Cu substrate as for the pristine and

[a] e-mail: jonoe@nr.titech.ac.jp

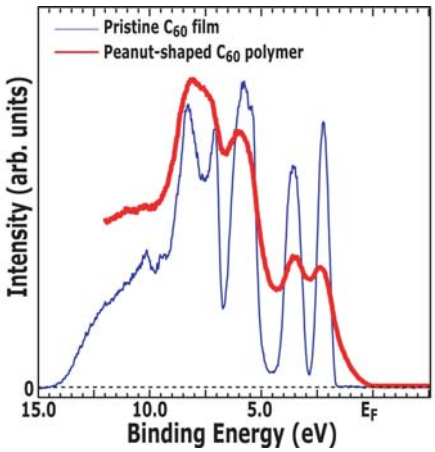

Fig. 1. (Color online) In situ high-resolution UPS spectra of pristine C_{60} film (blue line) and peanut-shaped C_{60} polymer (red line).

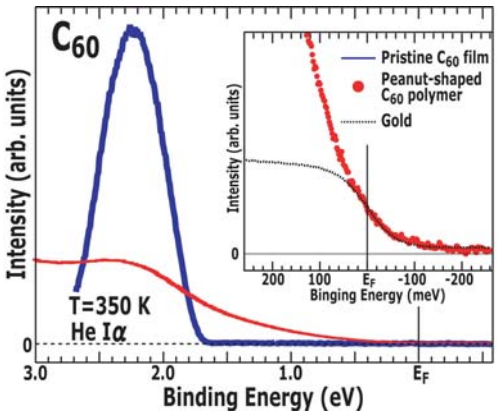

Fig. 2. (Color online) Magnified UPS spectra of Figure 1 in the binding energy range of 0–3 eV. Inset shows the UPS spectrum of the peanut-shaped C_{60} polymer near the Fermi level, together with that of a gold film in situ deposited on the same substrate.

peanut-shaped C_{60} polymer, by fitting its UPS spectrum with a Fermi distribution function at the measurement temperature. In the present substrate temperature, the E_F of a semiconductor is located in the middle between the valence and conduction bands by thermal broadening, and is almost same position as that of a metal with thermal broadening at the temperature.

3 Results and discussion

Figure 1 shows UPS spectra of pristine C_{60} (blue line) and peanut-shaped C_{60} polymer (red line) films obtained at a substrate temperature of 350 K. For the pristine C_{60} film, some intensive narrow bands such as HOMO and HOMO-1 were observed. This result indicates that the band structure of solid C_{60} is strongly reflected by a molecular solid (in other words, molecular orbitals). On the other hand, for the peanut-shaped C_{60} polymer, each band broadened in response to the disappearance of the molecular character caused by EB-induced polymerization between adjacent C_{60} molecules, and the valence density-of-state (DOS) spread toward the E_F.

In order to clarify the behavior of DOS of the peanut-shaped C_{60} polymer in the vicinity of the E_F, we measured more precise UPS spectra of the pristine C_{60} and peanut-shaped polymer films in the binding energy of 3.0 eV below the E_F, as shown in Figure 2. The inset shows the magnified spectrum of the peanut-shaped C_{60} polymer around the E_F, together with that of a gold film in situ deposited on the same substrate. It was found that the DOS of the peanut-shaped polymer is much greater than that of the pristine C_{60} film near the E_F and clearly comes across the Fermi edge in a manner similar to that of a gold film, which indicate that the peanut-shaped C_{60} polymer has a metallic feature. However, the Fermi step was not clearly observed for the peanut-shaped C_{60} polymer, though the DOS of 2D and 3D metals exhibits a Fermi step similar to that for the gold film, as shown in Figure 2. When the spectrum of the peanut-shaped C_{60} polymer was looked carefully, the spectral function around the E_F was similar to that for quasi 1D materials such as $(TaSe_4)_2I$ and $K_{0.3}MoO_3$ in their metallic phase, as shown in Figure 1 of reference [3]. These findings suggest that the peanut-shaped C_{60} polymer also has a quasi 1D structure exhibiting a metal-insulator transition at a given temperature, similar to $(TaSe_4)_2I$ and $K_{0.3}MoO_3$ [3]. This transition would change the electron-transport mechanism of the polymer. In fact, we have recently observed that the electron-transport mechanism was changed at around 90 K by examining the temperature-dependence of the electrical resistance of the polymer [4]. It will be a source of further study to elucidate the structural dimensions of the peanut-shaped C_{60} polymer by optical and photoelectron measurements from the perspective of low-dimensional quantum electronic behaviors such as the Peierls transition [5] and Tomonoga-Luttinger-liquid [6–8].

This work was supported by the program of the Core Research for Evolutional Science and Technology (CREST) and of Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Corporation (JST).

References

1. J. Onoe, T. Nakayama, M. Aono, T. Hara, Appl. Phys. Lett. **82**, 595 (2003)
2. J. Onoe, A. Nakao, A. Hida, Appl. Phys. Lett. **85**, 2741 (2004)
3. B. Dardel, D. Malterre, M. Grioni, P. Wiebel, Y. Baer, F. Levy, Phys. Rev. Lett. **67**, 3144 (1991)
4. J. Onoe, T. Ito, S. Kimura, Y. Ochiai, K. Ohno, J. Phys. Conf. (in press, 2007)
5. R.E. Peierls, *Quantum Theory of Solids* (Oxford Univ. Press, 1955)
6. J. Voit, Rep. Prog. Phys. **57**, 977 (1994)
7. A.E. Mattsson, S. Eggert, H. Johannesson, Phys. Rev. B **56**, 15615 (1997)
8. H. Ishii et al., Nature **426**, 540 (2003)