Electronic and electron–transport properties of peanut–shaped C$_{60}$ polymers

J. Onoe$^{1,2}$, Y. Ochiai$^3$, T. Ito$^4$, S. Kimura$^4$, S. Ueda$^5$, Y. Noguchi$^5$, and K. Ohno$^5$

1) Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152-8550, Japan
2) Japan Science and Technology (JST), Honmachi, Kawaguchi, Saitama 332-0012, Japan
3) Chiba University, Yayoi, Inage-Ku, Chiba 263-8522, Japan
4) Institute for Molecular Science and School of Physical Sciences, The Graduate University for Advanced Studies (SOKENDAI), Okazaki, Aichi 444-8585, Japan
5) Yokohama National University, Tokiwadai, Yokohama 240-8501, Japan

Corresponding author: jonoe@nr.titech.ac.jp

Abstract. When a C$_{60}$ film is irradiated with a 3–kV electron-beam (EB), a peanut-shaped C$_{60}$ polymer with metallic properties is formed. Valence photoelectron spectra of the polymer indicated 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. Interestingly, the spectral function of the peanut-shaped polymer around the Fermi edge resembles that of quasi one-dimensional (1D) materials such as K$_{0.3}$MO$_3$ with its metallic phase. This suggests that the peanut-shaped polymer has also a quasi 1D structure and may exhibit the Peierls transition at a given temperature. If the polymer shows the metal–insulator transition at the given temperature, the transition would change the electron–transport mechanism of the polymer. Then, we examined the temperature–dependence of the electrical conductivity of the polymer in the range of 9K–400K. It is found that the electron transport mechanism was changed at approximately 90 K, suggesting that the valence electronic structure around the Fermi edge was changed at this temperature.

1. Introduction

To synthesize new functional materials by assembling nano–scale building blocks such as fullerenes, nanotubes, DNA, and other nanomaterials, we have hitherto synthesized a new form of nanocarbon materials based on C$_{60}$ through the use of electron–beam (EB) induced polymerization [1–5], and found that C$_{60}$ molecules are coalesced to each other to form a peanut–shaped C$_{60}$ polymer which exhibits metallic current–voltage (I–V) characteristics at room temperature under atmospheric conditions [4]. To reveal the origins of the metallic electron–transport property of the EB–irradiated C$_{60}$ film, we previously examined the valence photoelectron spectra of the peanut–shaped C$_{60}$ polymer film (100 nm thick) on a stainless steel substrate in an ultrahigh vacuum, using ultraviolet photoelectron spectroscopy (UPS) with an energy resolution of 50 meV and with non monochromatic HeI emission lines (HeI$^\alpha$ emission line was included), along with graphite as a typical $\pi$–electron conjugated semi–metal system [5]. It was found that the density–of–states (DOS) around the Fermi level (E$_F$) for the peanut–shaped polymer was eventually greater than that for graphite and seemed to come across the E$_F$. Furthermore, the spectral function in the vicinity of the E$_F$ edge is similar to that of quasi 1D materials such as K$_{0.3}$MO$_3$ with its metallic phase. However, the previous measurement conditions (an energy resolution of 50 meV and non monochromatic HeI emission line including not only the main HeI$^\alpha$ line but also the minor HeI$^\beta$ line) were not sufficient to discuss with precision the DOS in the vicinity of the E$_F$.

In 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 around the E$_F$ using UPS with a higher energy–resolution (10 meV) and with a monochromatic HeI emission line (HeI$^\alpha$). In addition, if the peanut–shaped C$_{60}$ polymer has a quasi 1D structure, it should exhibit a metal–insulator
transition (Peierls transition) at a given temperature, similar to \((\text{TaSe}_4)_2\text{I}\) and \(K_{0.3}\text{MoO}_3\) [6]. Because this transition would change the electron–transport mechanism of the polymer, we examined the temperature dependence of the resistance of the peanut–shaped \(C_{60}\) polymer using four–probe measurements in the range of 9–400 K. We will discuss the high–resolution UPS spectra near the \(E_F\) edge and the electron–transport properties for the peanut–shaped \(C_{60}\) polymer by comparing first–principle calculations of some geometrical quasi–one–dimensional peanut–shaped \(C_{60}\) polymers on the basis of density-functional theory [7].

2. Experiments

For UPS measurements, after a \(C_{60}\) film (100 nm thick) formed on a copper substrate (5 mm x 5 mm) by sublimation of \(C_{60}\) powder (99.98% pure) at 673 K for 90 min in a preparation chamber (base pressure: 2x10\(^{-7}\) Pa), the pristine \(C_{60}\) film was transferred to a UHV analysis chamber (base pressure: 1 x 10\(^{-5}\) Pa) and measured \textit{in situ} by UPS with an energy resolution of 10 meV and with the monochromatic HeI \(\alpha\) emission line (21.218 eV). After the measurements, the film was returned to the preparation chamber and irradiated with the EB–gun (an incident energy: 3 keV, an electron current: 500 µA) for 12 h. We confirmed by \textit{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 irradiation, the film was transferred to the analysis chamber for \textit{in situ} UPS measurements. The Fermi level (\(E_F = 0\) eV) was determined by fitting the UPS spectrum of a gold film, which was deposited on the same substrate in vacuum, with a Fermi distribution function at a given measurement temperature.

For four–probe measurements, after 12-h EB irradiation of a \(C_{60}\) film deposited on a CsI substrate in a UHV chamber (base pressure: 2x10\(^{-7}\) Pa) equipped with infrared spectroscopy, the film was taken out of the chamber and moved into the other vacuum chamber (base pressure: 4x10\(^{-4}\) Pa). A gold electrode was formed on the peanut–shaped \(C_{60}\) polymer through a metal mask and the film resistance was recorded in vacuum as a function of the substrate temperature in the range of 9–400 K.

3. Results and discussion

Fig. 1 shows UPS spectra of pristine \(C_{60}\) (blue line) and peanut–shaped \(C_{60}\) polymer (red line) films polymer in the vicinity of the \(E_F\) at a substrate temperature of 350 K. 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 above 350 K. The inset shows the magnified spectrum of the peanut–shaped \(C_{60}\) polymer around the \(E_F\), together with that of a gold film \textit{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. These findings indicate that the peanut–shaped \(C_{60}\) polymer exhibits metallic properties. In general, the DOS of 2D and 3D metals exhibits a Fermi step similar to that for the gold film. The Fermi step was not, however, clearly observed for the peanut–shaped \(C_{60}\) polymer, as shown in the inset of Fig. 1. Interestingly, the spectral function around the \(E_F\) obtained for the peanut–shaped polymer was similar to that for quasi 1D materials such as \((\text{TaSe}_4)_2\text{I}\) and \(K_{0.3}\text{MoO}_3\) in their metallic phase, as shown in Fig.1 of Ref. 6. 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 \((\text{TaSe}_4)_2\text{I}\) and \(K_{0.3}\text{MoO}_3\) [6]. This transition would change the electron–transport mechanism of the polymer.

We next examined the temperature–dependence of the electrical resistance of the peanut–shaped \(C_{60}\) polymer. Fig. 2 shows the Arrehnius plot of the resistance of the polymer as a function of a substrate temperature. It is found that the electron–transport mechanism is changed at around 90 K. For a substrate temperature above 90 K, the electron–transport properties are behaved on the basis of thermally excited mechanism and the activation energy for electron–transport was obtained to be 60 meV, which is comparable to that of 100 meV for carbon nanotubes (CNTs) [8].
Because the present peanut-shaped C$_{60}$ polymer can be formed only by EB irradiation of a C$_{60}$ film deposited on any substrate by dry (evaporation) or wet (spin coat) processes, this polymer is possible to be superior to CNTs when applied to practical electronic device fabrication. On the other hand, for a temperature below 90 K, although the electron–transport mechanism is considered to change to a variable range hopping mechanism, more measurement points are further needed to clarify the physical meaning of this hopping mechanism such as 1D metallic conduction, Mott–type, and Anderson localization. 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 [9] and Tomonoga–Luttinger–liquid [10–12].

**Fig. 1.** UPS spectra of pristine C$_{60}$ and peanut–shaped C$_{60}$ polymer films 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 Au film in situ deposited on the same substrate.

**Fig. 2.** Arrehnius plot of the resistance of the peanut–shaped C$_{60}$ polymer in the range of 9 – 400 K.
To understand the metallic feature of the peanut–shaped C_{60} polymer, we examined the band structures for three optimized quasi one–dimensional (1D) configurations of the peanut–shaped C_{60} polymer with a cross–linkage consisting of both 6– and 7–membered rings (abbreviated as P67) and of 5– and 8–membered rings (abbreviated as P58), using density–functional theory with a local density approximation [13–19]. Fig. 3 provides a schematic representation of the triclinic unit cell (a–b–c, α–γ=62° and β=90° for P67 and α=80°, γ=63°, β=116.6° for P58) in which P67 or P58 is placed close to two of the adjacent unit cells. The optimized lattice constants are given as follows: a=0.86 nm, b=0.97 nm, c=0.91 nm (P67) and 0.95 nm (P58). From the results of the band structure of the P67 and P58 quasi 1D peanut–shaped C_{60} polymers, the former (P67) is a semiconductor with an energy gap of 0.61 eV, while the latter is a semi–metal which has the cross point between the HOMO and LUMO bands located at the [2+2] bond between adjacent 1D P58 C_{60} polymers [20]. At this stage, the quasi 1D P58 C_{60} polymer (Fig. 3) is a candidate to explain the present UPS results and metallic I–V characteristics of a peanut–shaped C_{60} polymer.

Fig. 3. Schematic representation for the three optimized quasi–one–dimensional unit cells of the peanut–shaped C_{60} polymer with a cross–linkage consisting both of 6– and 7–membered rings (abbreviated as P67) and of 5– and 8–membered rings (abbreviated as P58). Geometry of triclinic unit cell (a–b–c, α–γ=62° and β=90° degrees for P67 and α=80°, γ=63°, β=116.6° for P58) in which P67 or P58 is put toward two of the adjacent unit cells.

4. Summary

In situ high-resolution valence photoelectron spectra of the peanut–shaped C_{60} polymer were presented herein. It was found that the density–of–states (DOS) of the polymer comes across the Fermi edge in a manner similar to that of Au film, indicating that the peanut–shaped C_{60} polymer exhibits metallic properties. It is interesting to note that the spectral function around the Fermi edge for the peanut-shaped polymer is similar to that for quasi one–dimensional materials such as (TaSe_{4})_{2}I and K_{0.3}MoO_{3}, with their metallic phase. In addition, the temperature dependence of the resistance of
the peanut–shaped $C_{60}$ polymer found that the electron–transport mechanism was changed at around 90 K, indicating that the electronic structure in the vicinity of the $E_F$ edge was changed at this temperature. These findings suggest that the peanut–shaped $C_{60}$ polymer has also a quasi 1D structure. According to first-principle calculations of the band structure for quasi 1D peanut-shaped $C_{60}$ polymers with a cross-linkage consisting of both 6– and 7–membered rings and of 5– and 8–membered rings, the former is a semiconductor, while the latter is a semi-metal. This suggests that the latter model structure (P58 shown in Fig.3) possibly explain the present experimental results.

References
[1] J. Onoe et al., Clusters and Nanomaterials (Kawazoe et al. Eds.), Springer-Verlag, Berlin, p.135 (2001) and references therein.
[2] T. Hara, J. Onoe, H. Tanaka, and T. Kazuo, Jpn. J. Appl. Phys. 39, 1897 (2000).
[3] T. Hara, J. Onoe, and K. Takeuchi, J. Appl. Phys. 92, 7302 (2002).
[4] T. Hara and J. Onoe, Eur. Phys. J. D 24, 389 (2003).
[5] J. Onoe, T. Nakayama, M. Aono, and T. Hara, Appl. Phys. Lett. 82, 595 (2003).
[6] B. Dardel, D. Malterre, M. Grioni, P. Wiebel, Y. Baer, and F. Levy, Phys. Rev. Lett. 67, 3144 (1991).
[7] S. Ueda, Y. Noguchi, S. Ishii, J. Onoe, and K. Ohno, J. Metastable and Noncrystalline Mater. 24-25, 249 (2005).
[8] T.W. Ebbesen et al., Nature 382, 54 (1996).
[9] R.E. Peierls, “Quantum Theory of Solids”, Oxford Univ. Press (1955).
[10] J. Voit, Rep. Prog. Phys. 57, 977 (1994).
[11] A.E. Mattsson S. Eggert, and H. Johannesson, Phys. Rev. B 56, 15615 (1997).
[12] H. Ishii et al., Nature 426, 540 (2003).
[13] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
[14] G. Kresse and J. Hafner, Phys. Rev. B 49, 14251 (1994).
[15] G. Kresse and J. Furthmuller, Comput. Mater. Sci. 6, 15 (1996).
[16] G. Kresse and J. Furthmuller, Comput. Phys. Rev. B 54, 11169 (1996).
[17] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
[18] D.M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
[19] J.P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
[20] S. Ueda, K. Ohno, Y. Noguchi, S. Ishii, and J. Onoe, J. Phys. Chem. B, submitted.