

# Electrical property of fullerene films polymerized by argon plasma treatment

Ryuichiro Maruyama

Material Laboratories, Sony Corporation, 2-1-1 Shinsakuragaoka, Hodogaya-ku,  
Yokohama 240-0036, Japan

[Ryuichiro.Maruyama@p.sony.com](mailto:Ryuichiro.Maruyama@p.sony.com)

## Abstract

Photoemission spectral analysis was carried out on plasma polymerized fullerene (C<sub>60</sub>) films prepared by sublimating C<sub>60</sub> under an argon plasma. In the photoemission analysis, the overall distribution of the shallow valence band states of the plasma-treated C<sub>60</sub> was compared with pristine C<sub>60</sub>. These changes suggest that the pi-conjugation of the shallow valence band states of two C<sub>60</sub> molecules is induced by polymerization during the plasma treatment. To investigate the changes in the onset of the shallow valence band states brought about by polymerization, the orbital energy levels in C<sub>60</sub> dimers were examined using the semi-empirical AM-1 method. Calculations showed that the highest occupied molecular orbital (HOMO) levels of the dimers were shallower than that of C<sub>60</sub>.

## Introduction

Fullerene (C<sub>60</sub>) is a promising material for nano-carbon device research. Control of the electrical property of C<sub>60</sub> is necessary for applications. C<sub>60</sub> polymer has great promise because its unique structure allows its electrical and optical properties to be controlled. We reported that argon glow discharge technique using a high-frequency plasma was applied to the polymer synthesis.[1] In this method, because a non-equilibrium gas phase in the glow discharge is induced by the non-equilibrium plasma, C<sub>60</sub> is polymerized without the need for a high temperature. The electrical property of the polymerized C<sub>60</sub> films were investigated using the photoemission and the conductivity measurement.

## Experimental

For thin-film deposition, 50-100 mg of 99.95%-purified C<sub>60</sub> powder was loaded into a molybdenum boat, as shown in Fig. 1. The substrate was located on a steel stage on the anode

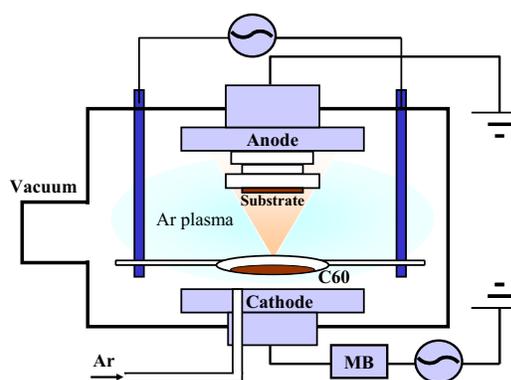


Fig. 1. Block diagram of plasma polymerization system.

and was 10 cm from the boat, which was positioned between the anode and cathode. A quartz-crystal microbalance was used to monitor the rate of deposition and the film thickness. The details of the film-deposition procedure have been reported elsewhere. A steel substrate and a silica-glass substrate that had been deposited with gold electrodes were used to measure the plasma-power dependence of the density of the shallow valence band states and the temperature dependence of the conductivity, respectively. The polymer samples were first deposited in a plasma polymerization chamber, then transferred to an inter-connected chamber to measure the photoemission spectra. They were then transferred to a final inter-connected chamber to measure the conductivity, since oxygen has proved to be one of the most important intercalants that can affect the electrical properties of C<sub>60</sub> films.

The electronic structure of the C<sub>60</sub> dimers was calculated using AM-1 parameterization as implemented in the program system MOPAC. Figure 2 shows the structure of the [2+2] C<sub>60</sub> dimer as a reference, and 4 possible forms of the peanut-type C<sub>120</sub>, all of which were optimized

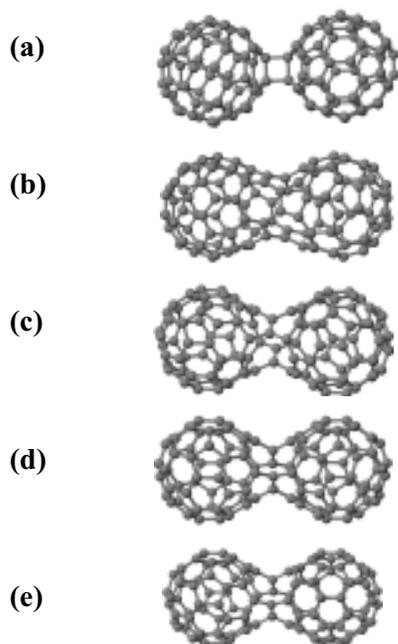


Fig. 2. The structure of the [2+2] C60 dimer and possible forms of the peanut-type C120.

using the MNDO Hamiltonian with the AM-1 parameterization, as implemented in the program system MOPAC. The onset of the shallow valence band states of the polymerized C60 was considered using the highest occupied molecular orbitals (HOMO) for each calculated dimer model.

The valence structures of the prepared C60 polymer and C60 films were measured using photoemission spectra. 50 nm thick films were deposited on the conductive steel stage and measured. Excitation of photoemissions was achieved using the HeI resonance line (21.2 eV) from a discharge lamp attached to the photoelectron chamber and the spectra were acquired at an analyzer resolution of 10 meV. The energy axis of all the photoemission spectra presented in this paper was referenced to the Fermi level of the Au film deposited in situ. Based on this, we obtain a work function of 4.9 eV for Au.

To investigate the electrical transport properties of the films, we fabricated a C60 polymer/gold structure for electrical characterization. Gold was deposited on a silica-glass substrate in the form of coplanar electrodes with a 0.5 mm interelectrode spacing and a 100 mm meander length. A 200 nm thick

film of the C60 polymer was deposited at 0.1 nm/sec on the silica-glass substrate coated by the gold electrodes. During the C60 polymer deposition, 50 W of plasma power was supplied in an argon atmosphere of 3.9 Pa. The temperature dependence of the conductivity of the C60 polymer film was measured in vacuum using the dc conductivity measurement system of a Hewlett-Packard HP4515A.

## Results and Discussion

Figure 3 shows the calculated molecular orbital energy of C60 and C120 near the Fermi level. As a consequence of the nature of the bonds for the orbitals around the Fermi energy, these orbitals are strongly affected by variations in the dimer structure. The HOMO level of the [2+2] and the peanut-type becomes shallow, because the two cages structure lowers the molecular symmetry and induces a split between orbitals of the same level and tends to make the HOMO shallow by dimerization. The lowest unoccupied molecular orbital (LUMO) also decreases. The HOMO levels of C120 with D2v and C2h symmetries increase above the HOMO level of the [2+2]. The shrinkage of the HOMO-LUMO gap of the peanut-type is more than that of the [2+2], because there is an expansion of the pi-electron system over the two cages in the peanut-type. There are no sigma bonds in the peanut-type structure. The structure shows a step in the change from the [2+2] into the final C120 tube, which has a narrow band gap.[2],[3] The HOMO states of C60 are split by the polymerization, and the states in the [2+2] and peanut-type are distributed from -9 to -10 eV. The center of the distribution is equal

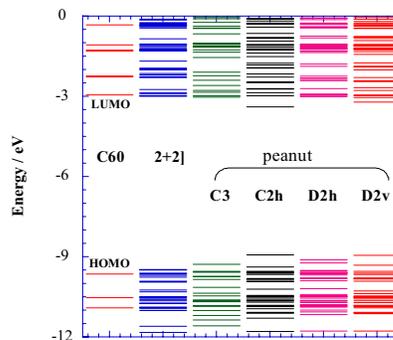


Fig. 3. The molecular orbital energy levels in C60 and C120s calculated by AM-1

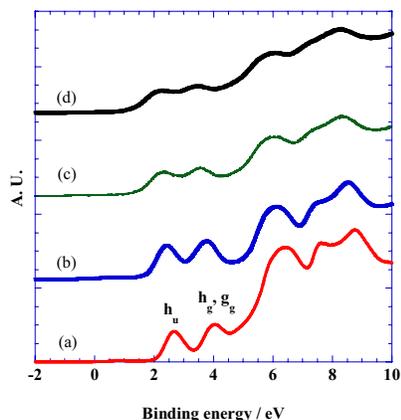


Fig. 4. Photoemission ( $h\nu = 21.2\text{eV}$ ) results for plasma polymerized C60 films (a) 0 W, (b) 20 W, (c) 40 W, and (d) 50 W. The spectra are plotted in arbitrary units

to the HOMO level of C60. This indicates that the polymerization induces the broadening of the onset of the shallow valence band states. Additional evidence supporting this proposition is provided by photoemission measurements of the shallow valence band states of plasma-polymerized C60 (Fig. 4). Figure 4 provides an overview of the distribution of states for C60 and plasma polymerized C60 showing the onset of the shallow valence band states after annealing at 500 K. The plasma polymerized film contains dimers, trimers, polymer chains and planes.[1], [4] The spectra are plotted in arbitrary units. As shown in Fig. 4, the valence electronic structures of the C60 polymer are broadened and shifted by the plasma treatment. The peaks between 0 and 7 eV essentially correspond to the pi-electron states.[5] The valence-band peaks broaden with increased plasma power. Because the [2+2] bond between the two C60 molecules was eliminated by annealing, the broadening of the states with sigma and pi-parentage originate from coalesced fullerene including a peanuts-like structure. This broadening suggests that there is a split of the degenerate states of the C60 molecules brought out by the molecular elongation introduced during plasma treatment.

Given the exponential dependence of the conductivity on the Fermi level in a semiconductor, conductivity measurements can provide an extremely sensitive way of detecting the electronic state in the band gap or near the mobility edge of the polymerized C60. Figure 5

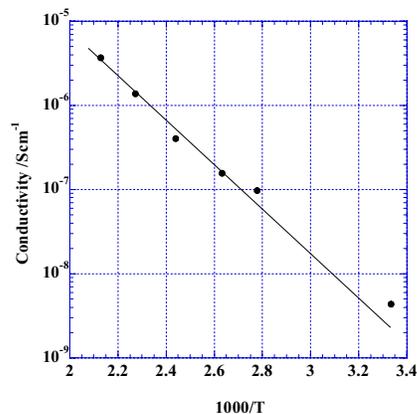


Fig. 5. Conductivity measurement of C60 film polymerized at 50 W. The measured conductivity (log scale) is plotted vs  $1000/T$  on an Arrhenius plot

shows the relationship between the logarithm of the conductivity and the inverse of the temperature for the polymer film deposited in a 50 W argon plasma. The conductivity increased exponentially in the temperature range from 300 to 500 K. The exponential behavior in this temperature range indicates that semiconductor-like properties do dominate and no graphitic character is revealed within the film. In the high-temperature region, the conductivity of the film shows Arrhenius type behavior, thus the conductivity can be described by the Arrhenius equation

$$\sigma = \sigma_0 \exp(-\Delta E_a / kT).$$

Here  $\sigma$  is the conductivity,  $\sigma_0$  is the pre-exponential factor,  $\Delta E_a$  is the activation energy and  $T$  is the absolute temperature. The value of  $\Delta E_a$  estimated from the slope of this Arrhenius plot is 0.42 eV, which is different from the 0.84 eV value for pure C60 reported by Pevzner *et al.*<sup>20</sup>  $\Delta E_a$  for the electron transfer of a semiconductor is typically equal to  $E_c - E_f$  ( $E_c$  is the mobility edge and  $E_f$  the Fermi level). Therefore, the shallow  $E_f$  originates from the narrow mobility gap and the pi-conjugated bonds between the C60 cages brought on by polymerization.

## Conclusion

The molecular orbitals of the C60 dimer, which was the most abundant product after the polymerization process were calculated using the

AM-1 method. This result suggests that the polymerization process causes a narrowing of HOMO-LUMO gap and a broadening of the mobility edge into the gap. With increased plasma power, the overall distribution of onset of the shallow valence band states was detected using photoemission spectra. The [2+2] cycloaddition between two C60 molecules is eliminated by 500 K annealing. Therefore, the structure responsible for the change in the onset of the shallow valence band states is the coalesced structure containing peanut-type material. The electrical properties of the C60 polymer suggest that  $E_f$  is shallow due to the shrinkage of the mobility gap caused by polymerization and the pi-conjugated bonds between the C60 cages.

### References

- [1] M. Ata, N. Takahashi and K. Nojima, J. Phys. Chem., 98, 40, 9960 (1994)
- [2] Y. H. Kim, I. H. Lee, K. J. Chang and S. Lee, Phys. Rev. Lett., 90 (6), 655011 (2003)
- [3] Yufeng Zhao, B. I. Yakobson and R. E. Smalley, Phys. Rev. Lett., 88 (18), 1855011 (2002)
- [4] M. Ata, K. Kurihara and N. Takahashi, J. Phys. Chem. B, 101, 5 (1997)
- [5] N. Troullier and J. L. Martins, Phys. Rev. B, 46 (3), 1754 (1992)