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Enhanced Field-Emission Characteristics of an Electron-Beam Irradiated C_{60} Film

Toshiki Hara, Jun Onoe and Kazuo Takeuchi
RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
Fax: 81-48-462-4702, e-mail: thara@postman.riken.go.jp

The electric-field emission characteristics of an electron-beam irradiated C_{60} film have been investigated. A C_{60} film on a stainless steel substrate was irradiated by a 3-keV electron primary for 10 hours in an ultrahigh vacuum and subsequently for 10 hours in a hydrogen atmosphere. Correlation between the emission current and the applied field behavior of the sample followed the typical Fowler–Nordheim theory. It was found that the onset of the field emission of the C_{60} film was reduced from 75 to 53 V/μm after the irradiation in a hydrogen atmosphere.

Key words: C_{60}, fullerene, field emission characteristics, electron beam, FTIR

1. INTRODUCTION

The structural modification of solid C_{60} has been studied by various techniques, such as photo-irradiation, doping of alkali metals, and high pressure treatment at high temperature[1]. Recently, we studied an electron-irradiation induced reaction in a C_{60} film and found the formation of coalesced dimers with a peanut shape (bucky peanuts) using Fourier transform infrared (FTIR) spectroscopy and laser-desorption mass spectrometry[2].

Because the peanut-shaped dimer has a hollow carbon cage in its structure, the dimer is expected to possess a π conjugated system which is larger than that of C_{60}. The enlarged π electron system affects the electronic structure of this material, such as the density of states, band gap, etc. One of the phenomenon that is strongly correlated with the electronic structure is the field emission characteristics. It is considered that a small band gap and large density of states near the Fermi level enhance the electron emission of the material[3].

In the present study, we investigated the field emission characteristics of an electron irradiated C_{60} film. For carbon-based field emitters, not only the sp^2 carbons, which supply the π electrons, but also the sp^3 carbons are important because they provide emission sites with a lower work function[4,5]. We introduced the sp^3 carbons into the film by forming C–H bonds[4,5] and examined the influences of them on the field emission characteristics of the film.

2. EXPERIMENT

A C_{60} film was formed on a mirror-polished stainless steel substrate (diameter: 20 mm, thickness: 2 mm) in an ultrahigh vacuum (UHV) chamber (base pressure: 2×10^{-9} Torr) by sublimation of the C_{60} powder (more than 99.98% pure) at 673 K for 90 minutes.

After the formation of the film, an electron beam with an energy of 3 keV and an incident current of 530 μA was applied to the film using an electron gun (Omegatron, OME-0032E) connected to the UHV chamber. For uniform irradiation of the sample, the electron beam (spot diameter: 2 mm) was swept over the sample surface (1.8 cm^2) at a frequency of 10 kHz along the x-direction and of 1 kHz along the y-direction. The electron irradiation was cumulatively performed for 20 hours. The first 10-hour irradiation was carried out under a pressure of 5×10^{-9} Torr. In order to introduce C–H bonds to the sample, the last 10-hour irradiation was done under a hydrogen atmosphere of 1×10^{-7} Torr.

The electric-field emission characteristics of the sample was measured before and after the 10- and cumulative 20-hour irradiation in the same UHV chamber. Because the temperature of the sample increased from 297 to 387 K after the first 10-hour irradiation and from 298 to 376 K after the cumulative 20-hour irradiation, the measurement was performed after the sample had cooled to 298 K. For the field emission measurements, a tungsten tip was approached to the sample at a distance (d) of 10–20 μm. Thereafter, an electric voltage (V) in the range of 1–4 kV was applied between the sample and tip. An electric current (I) emitted from the sample was measured by an emission current monitor (Omegatron).

The structural change in the electron-irradiated C_{60} film was examined by FTIR spectroscopy. A C_{60} film was formed on a CsI substrate under the same deposition conditions as for the field emission measurement. The thickness of the film was estimated to be 200 nm from the absorbance of the four fundamental IR-active modes[6]. Thereafter, the C_{60} film was exposed to the electron beam under the same irradiation conditions as for the field emission measurement. The IR spectra were obtained using an FTIR spectrometer connected to the UHV chamber.

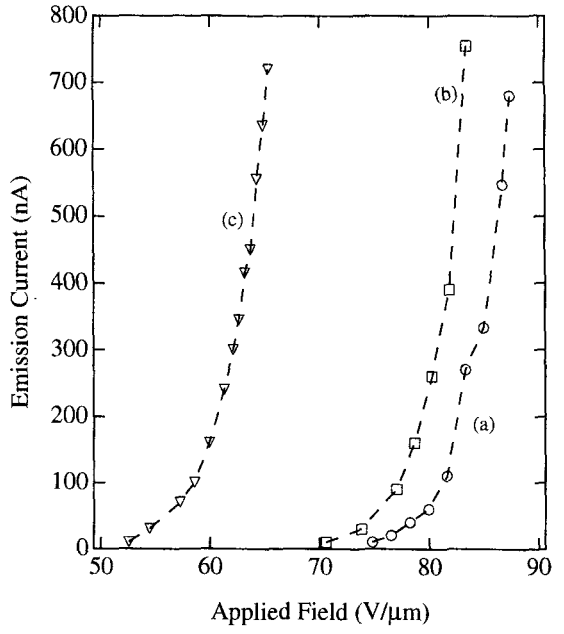

Fig.1 The emission current (I) versus applied field (F) behavior of the C_{60} film (a) before electron irradiation, (b) after the 10-hour irradiation under UHV, and (c) after the subsequent 10-hour irradiation in a hydrogen atmosphere.

3 RESULTS AND DISCUSSION

Figure 1 shows the typical emission current (I) versus applied field ($F = V/d$) behavior of the C_{60} film before and after the 10- and 20-hour electron irradiation. The emission current of 10 nA from the pristine C_{60} film appeared at an onset of 75 V/μm [curve (a)]. After the 20-hour irradiation, it appeared at a lower onset of 53 V/μm [curve (c)]. This indicates that the electron emission was enhanced by the electron beam irradiation. Generally, the behavior of the field emission can be expressed by the Fowler–Nordheim equation[5,7],

$$I = \alpha C_A (\beta \frac{V}{d})^2 \frac{1}{\phi} \exp(-C_B \phi^{\frac{3}{2}} \frac{d}{\beta V}), \qquad (1)$$

where C_A [$= 1.54 \times 10^{-6}$ A(eV)V^{-2}] and C_B [$= 6.83 \times 10^7$ Vcm^{-1}(eV)$^{-3/2}$] are constants, ϕ (eV) is a work function, α (cm^2) is an emission area, and β is a field enhancement factor defined as the ratio of the induced local electric field to the applied external field. The obtained I–F curves in Fig. 1 followed Eq. (1).

For discussion of the three parameters, ϕ, α, and β, Equation (1) is rewritten in a logarithmic form as,

$$\ln(\frac{I}{V^2}) = \ln[\alpha C_A (\frac{\beta}{d})^2 \frac{1}{\phi}] - (C_B \phi^{\frac{3}{2}} \frac{d}{\beta}) \frac{1}{V}. \qquad (2)$$

Table I Field emission parameters $\alpha\phi^2$ and $\phi^{2/3}\beta^{-1}$ of the C_{60} film for each irradiation condition.

Irradiation conditions	$\alpha\phi^2$ (cm^{2}eV^2)	$\phi^{2/3}\beta^{-1}$ (eV$^{2/3}$)
Before irradiation	2.13×10^{-4}	0.29
	2.11×10^{-7}	0.23
	7.28×10^{-5}	0.25
After 10-h irradiation	8.29×10^{-7}	0.19
	8.71×10^{-4}	0.25
	1.06×10^{-2}	0.27
After 20-h irradiation	4.52×10^{-10}	0.10
(10h/UHV+10h/H_2)	1.00×10^{-9}	0.10
	5.64×10^{-8}	0.13

From the slope and intercept of the straight line obtained from the least square fitting of the $\ln(I/V^2)$–$1/V$ plot (Fowler–Nordheim plot), the quantities, $\alpha\phi^2$ and $\phi^{2/3}\beta^{-1}$, were evaluated. Although this analysis does not independently give the three parameters, one can compare the field emission phenomena of the film in each irradiation condition from the two quantities[5]. Table I lists the values of $\alpha\phi^2$ and $\phi^{2/3}\beta^{-1}$ of the C_{60} film before and after the 10- and 20-hour electron irradiation. The values were collected from three different points during each irradiation stage. After the initial 10-hour irradiation, $\phi^{2/3}\beta^{-1}$ slightly decreased from 0.23–0.29 to 0.19–0.27 eV$^{2/3}$. After the subsequent 10-hour irradiation in a hydrogen atmosphere, it further decreased to 0.10–0.13 eV$^{2/3}$. This trend indicates that the field emission from the 20-hour irradiated film was enhanced by decreasing the work function and/or increasing the field enhancement factor.

Unlike the values of $\phi^{2/3}\beta^{-1}$, those of $\alpha\phi^2$ for the three points are very different even in the same irradiation stage. Because the work functions of carbon allotropes are similar (4.9 eV for diamond[8], 4.6 eV for graphite[9], and 4.7 eV for C_{60}[10]), this large variation in $\alpha\phi^2$ is ascribed to the emission area α. This implies that the emission area significantly depends on its position.

Figure 2(a) shows the FTIR transmission spectrum of a pristine C_{60} film. There are four strong absorption peaks originating from the IR-active modes of the C_{60} molecule at 527, 576, 1183, and 1429 cm^{-1}. After the 10-hour electron irradiation of the sample, the IR spectrum changed as shown in Fig. 2(b). A large broad band appeared at around 1388 cm^{-1}. Other new bands were also observed at 722, 1197, and 1340 cm^{-1}. On the other hand, the four original modes of C_{60} decreased. The spectrum in Fig. 2(b) is quite similar to that obtained in a previous study of the electron-irradiated C_{60} film

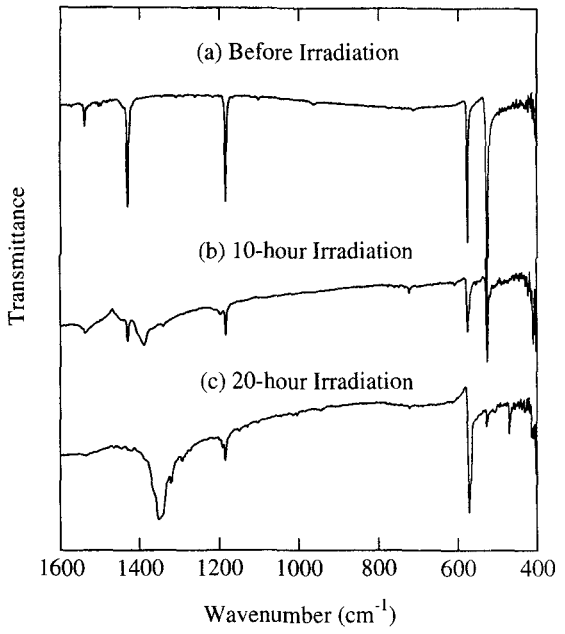

Fig.2 FTIR spectra of C_{60} film (a) before electron irradiation, (b) after the 10-hour irradiation under the UHV, and (c) after the subsequent 10-hour irradiation in a hydrogen atmosphere.

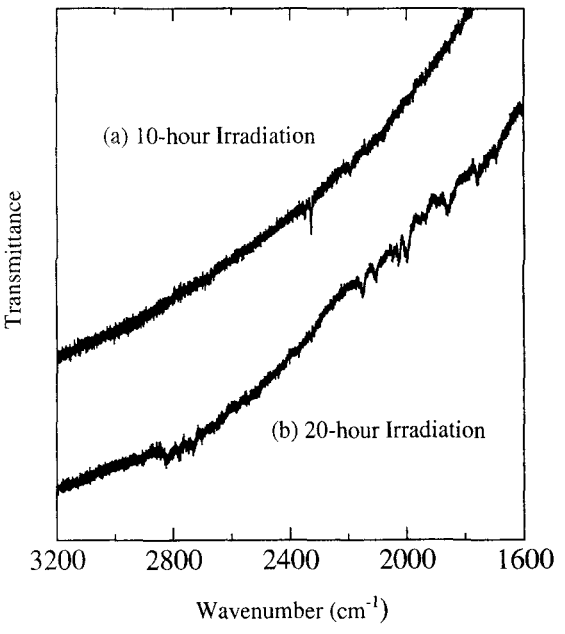

Fig.3 FTIR spectra of C_{60} film (a) after the initial 10-hour irradiation, and (b) after the subsequent 10-hour irradiation in a hydrogen atmosphere.

in which the coalescence of the C_{60} molecules took place[2]. After the subsequent 10-hour irradiation in a hydrogen atmosphere, the IR spectrum shown in Fig. 2(c) was obtained. A large broad band newly appeared at around 1360 cm^{-1}. On the other hand, the band of the original C_{60} at 1429 cm^{-1} completely disappeared. This indicates that the C_{60} molecules in the film were completely consumed by the reaction. Although the structure of the product obtained after the final 10-hour irradiation with the addition of the hydrogen gas is still unknown, it is quite probable that further coalescence which produces the trimers proceeds. In fact, in our previous study[2], there was a small amount of trimers in the mass spectrum of the electron irradiated C_{60} film.

At present, we believe that the field emission of the 20-hour irradiated C_{60} film was improved due to two factors. First, the enlarged π electron system of the coalesced product improved the electric conductivity of the material by decreasing the band gap and by increasing the density of states near the Fermi level. It is important for carbon-based emitters to increase the conductivity because the electrons are emitted from the conduction band[4,5]. Secondly, sp^3 carbons are introduced to the coalesced product by the C–H bond formation. These sp^3 carbons provide emission sites, where the electrons in the conduction band are emitted to the vacuum level. Several groups have reported that the C–H vibrational frequencies for hydrogenated graphite[11] and C_{60} ($C_{60}H_{18}$[12] and $C_{60}H_{36}$[12,13]) appeared in the region of 2700–3100 cm^{-1}. Figures 3(a) and (b) show the FTIR spectra of the C_{60} film after the initial 10-hour irradiation and after the subsequent 10-hour irradiation in a hydrogen atmosphere, respectively. Although the origin of the absorption bands in the region of 1800–2200 cm^{-1} is still unknown, small absorption bands corresponding to C–H vibrations were observed at around 2800 cm^{-1} as shown in Fig. 3(b). It is concluded that the electron irradiation with medium-energy in a hydrogen atmosphere has an advantage of simultaneously inducing the coalescence reaction and C–H bond formation.

In summary, the electric-field emission characteristics of a C_{60} film irradiated by 3-keV electrons have been studied. After the irradiation in a hydrogen atmosphere, the electron emission from the film was observed at a lower onset field than that of the pristine C_{60} film. The enhanced field emission characteristics were interpreted to be due to the enlarged π electron system and increased sp^3 emission sites.

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