

Preparation of Optically Transparent Graphitic Film by Phase Transformation of C₆₀ Molecules

Kazuki Ishii, Maho Iwamura, Takatoshi Yamada,¹ and Toru Kuzumaki*

Department of Metallurgical Engineering, Graduate School of Engineering, Tokai University,
4-1-1 Kitakaname, Hiratsuka 259-1292, Japan

¹Nanotube Research Center, National Institute of Advanced Industrial Science and Technology,
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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We utilized the phase transformation of C₆₀ molecules to develop a new approach for the preparation of transparent electroconductive films on glass substrates. In this study, the effect on film formation of ultraviolet (UV) irradiation in different atmospheres and in the presence of different metal catalysts was investigated. UV irradiation of the C₆₀ films caused phase transformation by either polymerization or decomposition of C₆₀ molecules depending upon the atmosphere. In the presence of a Ni catalyst, an optically transparent film with graphitic structure was formed. The electrical resistivity of the film was on the order of 10⁻⁴ Ω cm.

The polymers of C₆₀ molecules by UV irradiation in vacuum played a role as a solid carbon source and as a reductant, and the optically transparent graphitic film was formed by the surface reaction with C₆₀ and the Ni catalyst on the glass substrate. In contrast, in the case of a Cu catalyst, although a film with a resistivity on the order of 10⁻⁶ Ω cm was formed, it was almost opaque and showed an undeveloped graphitic structure. A transparent film with a rough surface structure was obtained when UV irradiation was carried out at 500 W for 24 h in ambient atmosphere. In this case, interestingly, Raman spectrum mapping revealed that the region with graphitic structure was separated from the area of the Cu catalyst. It is believed that once the graphitic structure was formed on the Cu catalyst, the catalyst migrated.

1. Introduction

With the recent increase in the demand for flat-panel displays, the development of novel transparent electroconductive films has become necessary. Currently, the most widely used transparent electrode is the indium-tin-oxide (ITO) electrode. Indium is a rare-earth element. An increase in the consumption of such elements leads to their depletion, which is a great concern. Therefore, the development of new materials to replace ITO is required.^(1–5) Graphene is a promising candidate for such transparent electrodes.^(6,7) In general, chemical vapor deposition (CVD) of a hydrocarbon gas is used to synthesize large, uniform graphene films.^(8–12) In recent years, a low-temperature synthesis of high-quality graphene films using a microwave CVD technique has been reported.^(13–15) However, the CVD method cannot be used for a wide range of raw materials

*Corresponding author: e-mail: kuzumaki@keyaki.cc.u-tokai.ac.jp
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and is limited to using only gaseous raw materials.⁽¹⁶⁾

In this study, we used fullerene (C₆₀) as the solid carbon source.⁽¹⁷⁾ Since it is possible to form a C₆₀ monomolecular film, its thickness can be controlled at the molecular level. The spherical shell-like structure of C₆₀ molecules is stable. However, it is known that C₆₀ molecules are polymerized by ultraviolet (UV) or laser irradiation in the absence of oxygen.^(18–24) On the other hand, oxygen-exposed C₆₀ molecules are decomposed by UV irradiation.^(25–28) Hence, the phase transformation of C₆₀ molecules yields different structures depending upon the presence or absence of oxygen. The intermolecular bonding of polymerized C₆₀ is dissociated by heating at around 420 K.⁽²⁴⁾ Thus, the formation of a two-dimensional (2D) graphitic structure is expected at relatively low temperatures. Hence, the utilization of the phase transformation of C₆₀ molecules (polymerized, amorphous, and graphite phases) induced by UV irradiation and the control of the interfacial reaction between the carbon atoms and the catalyst by heat treatment is expected to contribute to the development of a novel method for the synthesis of transparent electroconductive films.

In this study, to acquire basic knowledge about the development of optically transparent graphitic films using C₆₀, the effect of UV irradiation in the presence of different atmospheres and metal catalysts on film formation was investigated.

2. Materials and Methods

2.1 Deposition of C₆₀ thin films and UV irradiation

As the source of solid carbon, the C₆₀ thin films (~100 nm) were deposited on quartz glass substrates (15 × 13 × 0.5 mm³) by a vacuum evaporator (JEE-400, JEOL) using C₆₀ powder (99.95% purity, MTR Ltd.). The as-deposited C₆₀ thin films were UV irradiated (HE1000C, SEN Light Corp.) in a vacuum of 10⁻¹ Pa and in ambient atmosphere. The irradiation conditions are given in Table 1.

2.2 Preparation of optically transparent film

In this study, Ni (Ni process) and Cu (Cu process) catalysts were used for the preparation of optically transparent graphitic films. The experimental details are given in the following.

2.2.1 Ni process

The schematic of the Ni process is shown in Fig. 1. It is expected that a Ni catalyst and the carbon atoms originating from C₆₀ molecules make a solid-solution and then a graphitic carbon film is precipitated on the Ni catalyst. In this process, therefore, a Ni film (~20 nm) was deposited

Table 1
UV irradiation conditions for the Ni and Cu processes.

	Ambient atmosphere	Vacuum (10 ⁻¹ Pa)
Ramp type	High-pressure Hg ramp	
Radiation output (W)	500/700	500/700
Irradiation time (h)	24/120	24/18
Specimen temperature at UV irradiation (K)	343/373	343/373

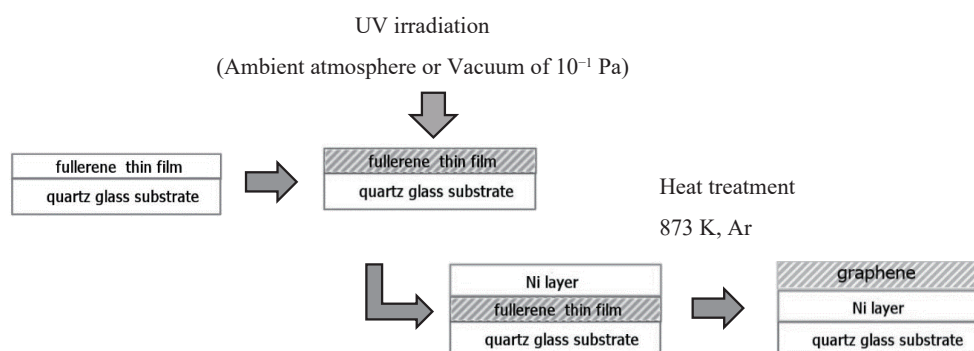


Fig. 1. Schematic of film formation in the Ni process.

on the C₆₀ film by a sputtering system (SC-701HMC II, Sanyu Electron) with and without UV irradiation. The entire specimen was heat treated using an electric furnace (HCP-7000, ULVAC) at 873 K for 10 min in an Ar atmosphere.

2.2.2 Cu process

The schematic of the Cu process is shown in Fig. 2. In this process, the formation of the graphitic film would be dominant due to the interfacial reaction between the carbon atoms and the Cu catalyst. A Cu film (~300 nm) was deposited on the quartz glass substrate by sputtering. The C₆₀ film was then deposited on the Cu film under the same conditions as those used in the Ni process. The UV irradiation was carried out under the conditions given in Table 1. The heat treatment of the specimen was carried out under the same conditions as those used in the Ni process in an Ar + 10% H₂ atmosphere.

2.3 Structural analysis and electrical resistivity measurements

Structural analyses of the C₆₀ films before and after both the UV irradiation and heat treatment were conducted by laser Raman scattering spectroscopy (using a confocal Raman microscope, Renishaw). The laser wavelength was 532 nm and the irradiation time was 10 s. The mean roughness of the films was measured by atomic force microscopy (SPM-9700, Shimadzu). The electrical resistivity of the films was measured by the four-probe method (K-705RH, Kyowariken).

3. Results and Discussion

3.1 Polymerization of C₆₀ molecules by UV irradiation

Figures 3 and 4 show a series of photographs and the corresponding Raman scattering spectra of (a) the as-deposited C₆₀ film, (b) C₆₀ film exposed to UV irradiation at 500 W for 24 h in ambient atmosphere, (c) C₆₀ film exposed to UV irradiation at 700 W for 120 h in ambient atmosphere, (d) C₆₀ film exposed to UV irradiation at 500 W for 24 h in a vacuum of 10⁻¹ Pa, and (e) C₆₀ film exposed to UV irradiation at 700 W for 18 h in a vacuum of 10⁻¹ Pa, respectively.

Figure 3(a) shows the as-deposited C₆₀ film. The film had a light-yellow color. The other

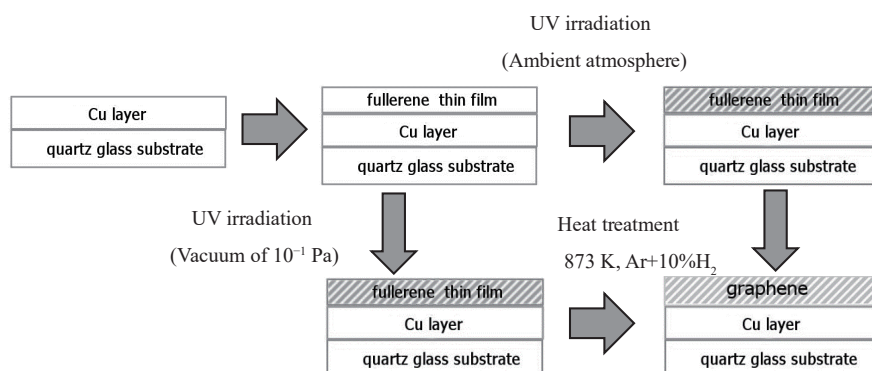


Fig. 2. Schematic of film formation in the Cu process.

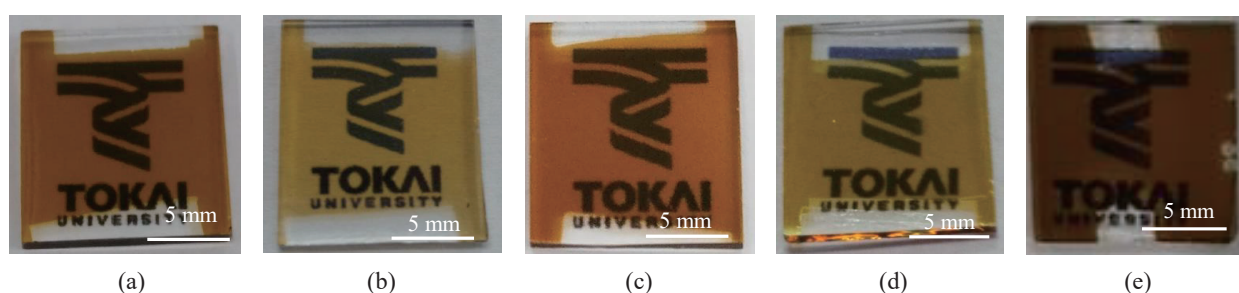


Fig. 3. (Color online) Photographs of (a) the as-deposited C_{60} thin film, (b) C_{60} film exposed to UV irradiation at 500 W for 24 h in ambient atmosphere, (c) C_{60} film exposed to UV irradiation at 700 W for 120 h in ambient atmosphere, (d) C_{60} film exposed to UV irradiation at 500 W for 24 h in a vacuum of 10^{-1} Pa, and (e) C_{60} film exposed to UV irradiation at 700 W for 18 h in a vacuum of 10^{-1} Pa.

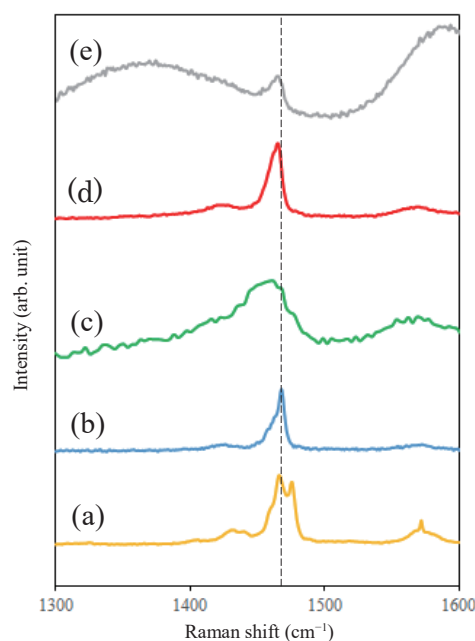


Fig. 4. (Color online) Raman scattering spectra of (a) the as-deposited C_{60} thin film, (b) C_{60} film exposed to UV irradiation at 500 W for 24 h in ambient atmosphere, (c) C_{60} film exposed to UV irradiation at 700 W for 120 h in ambient atmosphere, (d) C_{60} film exposed to UV irradiation at 500 W for 24 h in a vacuum of 10^{-1} Pa, and (e) C_{60} film exposed to UV irradiation at 700 W for 18 h in a vacuum of 10^{-1} Pa. The dotted line shows the position of 1469 cm^{-1} .

films shown in Figs. 3(b)–3(e) displayed different colors depending upon the conditions of UV irradiation. These differences were caused by the changes in the thickness and structure of the films. Each C_{60} film underwent partial sublimation during the UV irradiation. The structural changes in the C_{60} films were examined in Raman spectra near the $A_g(2)$ pentagonal pinch mode, which broadens and shifts from 1469 to 1458 cm^{-1} as the transformation proceeds.^(18–20) Figures 4(b) and 4(c) show the Raman spectra of the C_{60} films exposed to UV irradiation in ambient atmosphere. A peak at around 1469 cm^{-1} , which is the characteristic peak of a pristine C_{60} film, was observed in both spectra. The intensity of this peak (where location is represented by a dotted line) tended to increase with an increase in the UV irradiation output. Figures 4(d) and 4(e) show the Raman spectra of the films exposed to UV irradiation in vacuum. From the figures it can be seen that the intensity of the characteristic peak of C_{60} films observed at around 1469 cm^{-1} tended to shift slightly to lower wave-numbers with an increase in the UV irradiation output.

These results indicate that the UV irradiation in vacuum resulted in the polymerization of C_{60} molecules, whereas that in ambient atmosphere resulted in the decomposition of C_{60} molecules. Under ambient atmosphere, the polymerization of C_{60} molecules was prevented because of oxygen adsorption or intercalation between the C_{60} molecules.⁽²⁵⁾ Oxygen inhibited the polymerization of C_{60} molecules. It has been reported that the oxygen-rich phase obtained by irradiation with UV or visible light is usually referred to as “phototransformed” to differentiate it from the oxygen-free C_{60} polymer.^(25–27) The presence of oxygen molecules promoted the destruction of C_{60} molecules into a glassy graphitic phase.^(28,29) The experimental results demonstrate that the UV irradiation of the C_{60} films resulted in a phase transformation by either polymerization or decomposition of C_{60} molecules depending upon the atmosphere.

3.2 Ni process

Figures 5(a)–5(d) show photographs of the films obtained after the heat treatment with the Ni catalyst. The mean roughness of these films was approximately 20–50 nm whereas that of the films before the heat treatment was approximately 6 nm. This result suggests that the surface structure was changed by the heat treatment. The optical transparency of the films exposed to UV irradiation in the ambient atmosphere shown in Figs. 5(a) and 5(b) was slightly higher than that of the films exposed to UV irradiation in the vacuum shown in Figs. 5(c) and 5(d). However, the

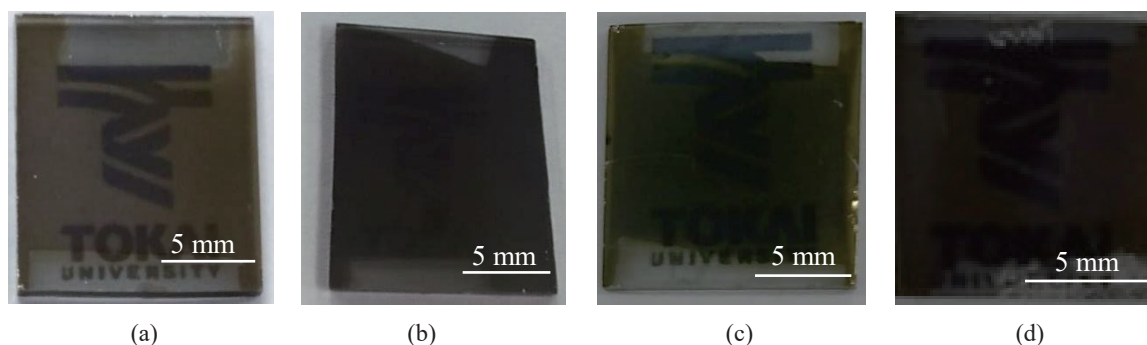


Fig. 5. (Color online) Photographs of the films obtained after heat treatment with the Ni catalyst. (a) The C_{60} film exposed to UV irradiation at 500 W for 24 h in ambient atmosphere, (b) C_{60} film exposed to UV irradiation at 700 W for 120 h in ambient atmosphere, (c) C_{60} film exposed to UV irradiation at 500 W for 24 h in a vacuum of 10^{-1} Pa, and (d) C_{60} film exposed to UV irradiation at 700 W for 18 h in a vacuum of 10^{-1} Pa.

Raman spectra shown in Figs. 6(c) and 6(d) show that the graphitization of the films exposed to UV irradiation in the vacuum was more advanced. The electrical resistivities of the films exposed to UV irradiation in ambient atmosphere and vacuum were on the order of 10^{-3} and 10^{-4} Ω cm, respectively.

It is known that a Ni catalyst and the carbon atoms originating from C_{60} molecules make a solid solution and carbon is then precipitated as a thin film with a graphitic structure. In this study, the carbon in Ni solubility was estimated to be less than 0.1% because the heat treatment temperature was low (873 K). Thus, it can be stated that the graphitic structure was actually formed by the interfacial reaction between the C_{60} molecules and the Ni atoms. The optical transparency of the films exposed to UV irradiation in ambient atmosphere was relatively high. However, the films exposed to UV irradiation under vacuum showed higher graphitization (as observed from the 2D spectrum near 2680 cm^{-1}) and lower resistivity. To understand these results, it is necessary to consider the influence of UV irradiation. In ambient atmosphere, oxygen was absorbed or intercalated between C_{60} molecules, and UV irradiation prevented the polymerization of C_{60} molecules.⁽²⁵⁾ As already mentioned, the presence of oxygen molecules promotes the destruction of C_{60} molecules into a glassy graphitic phase. Here, since the polymerization of C_{60} molecules was inhibited, their destruction and sublimation as a solid carbon source was promoted by UV irradiation in ambient atmosphere.

UV irradiation in vacuum, on the other hand, is expected to yield a C_{60} dimer by a 2 + 2 cycloaddition reaction.^(19,24) During the heat treatment, some of the cross-links dissociated, and then the C_{60} molecules with opened shells easily underwent an interfacial reaction with the Ni catalyst. In the C_{60} films exposed to UV irradiation in vacuum, the sublimation of C_{60} molecules during the heat treatment was less than for the films exposed to UV irradiation in ambient

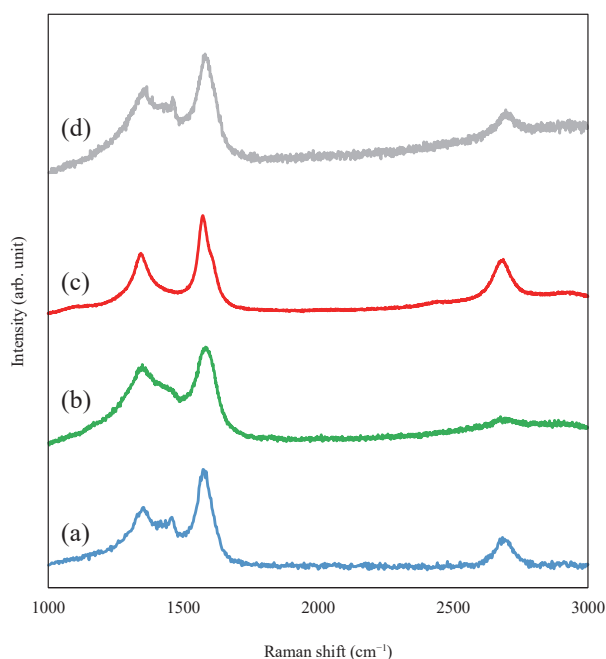


Fig. 6. (Color online) Raman spectra of the films obtained after heat treatment with the Ni catalyst. (a) The C_{60} film exposed to UV irradiation at 500 W for 24 h in an ambient atmosphere, (b) C_{60} film exposed to UV irradiation at 700 W for 120 h in an ambient atmosphere, (c) C_{60} film exposed to UV irradiation at 500 W for 24 h in a vacuum of 10^{-1} Pa, and (d) C_{60} film exposed to UV irradiation at 700 W for 18 h in a vacuum of 10^{-1} Pa.

atmosphere. This is attributed to the polymerization of C_{60} molecules where the films were exposed to UV irradiation in vacuum.

In the Ni process without UV irradiation, an undeveloped graphitic structure was obtained. UV irradiation is essential for the formation of graphitic films from C_{60} films. The results suggest that UV irradiation in vacuum and a subsequent heat treatment using a Ni catalyst contributes to the formation of transparent films. However, optimization of the thickness of the C_{60} and Ni catalyst films exposed to UV irradiation in vacuum is required.

3.3 Cu process

The as-deposited C_{60} thin film formed on the Cu film substrate was opaque and showed an almost coppery color. Figures 7 and 8 show a series of photographs and the corresponding Raman scattering spectra, respectively, of (a) the C_{60} film exposed to UV irradiation at 500 W for 24 h in ambient atmosphere, (b) C_{60} film exposed to UV irradiation at 700 W for 120 h in ambient atmosphere, (c) C_{60} film exposed to UV irradiation at 500 W for 24 h in a vacuum of 10^{-1} Pa, and (d) C_{60} film exposed to UV irradiation at 700 W for 18 h in a vacuum of 10^{-1} Pa when the heat treatment with a reductive gas flow (10% H_2/Ar) was carried out in the presence of the Cu catalyst.

The film obtained by UV irradiation at 500 W for 24 h in ambient atmosphere followed by a heat treatment exhibited optical transparency, as shown in Fig. 7(a). However, the films shown in Figs. 7(b)–7(d) were inhomogeneous and opaque. The Raman spectra in Figs. 8(a)–8(d) show that every film did not exhibit a distinct 2D peak near 2680 cm^{-1} . This suggests that the graphitic structure was undeveloped. Within this experiment, the resistivity of almost all the films exposed to UV irradiation was on the order of $10^{-6}\ \Omega\text{ cm}$. The resistivity of the films was comparable to that of the copper, so that, during the electrical resistivity measurement, the probes penetrated the graphitic film and may have measured the resistivity of the copper catalyst.

In the Cu process, the graphitic film was synthesized by the interfacial reaction between the carbon atoms and the Cu catalyst.^(8,29) The reduction of the Cu catalyst was expected during heat treatment by a flow of 10% H_2 in Ar gas in the Cu process.⁽¹⁹⁾ In this study, unfortunately, an undeveloped graphitic structure was obtained. There are two reasons for this: the first is the effect of UV irradiation and the Cu catalyst on the formation of the C_{60} films. Unlike the case when a quartz glass substrate was used, the surface oxide film of the Cu catalyst (Cu_2O) was reduced by

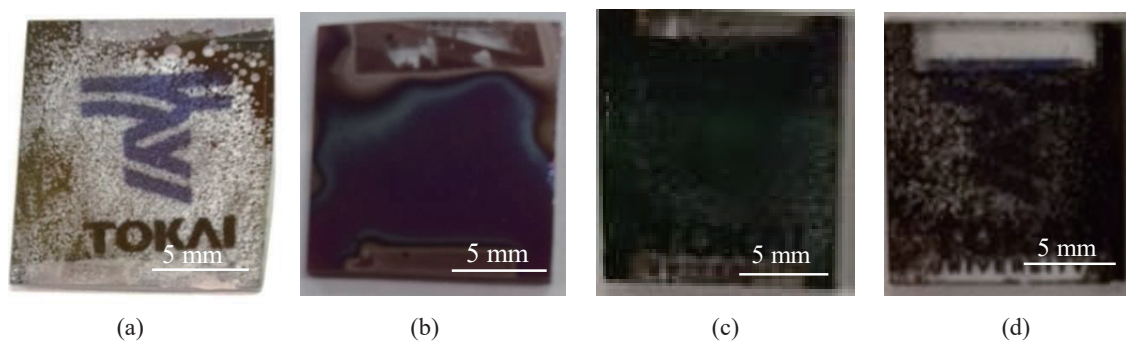


Fig. 7. (Color online) Photographs of the films obtained after heat treatment with the Cu catalyst. (a) The C_{60} film exposed to UV irradiation at 500 W for 24 h in ambient atmosphere, (b) C_{60} film exposed to UV irradiation at 700 W for 120 h in ambient atmosphere, (c) C_{60} film exposed to UV irradiation at 500 W for 24 h in vacuum of 10^{-1} Pa, and (d) C_{60} film exposed to UV irradiation at 700 W for 18 h in a vacuum of 10^{-1} Pa.

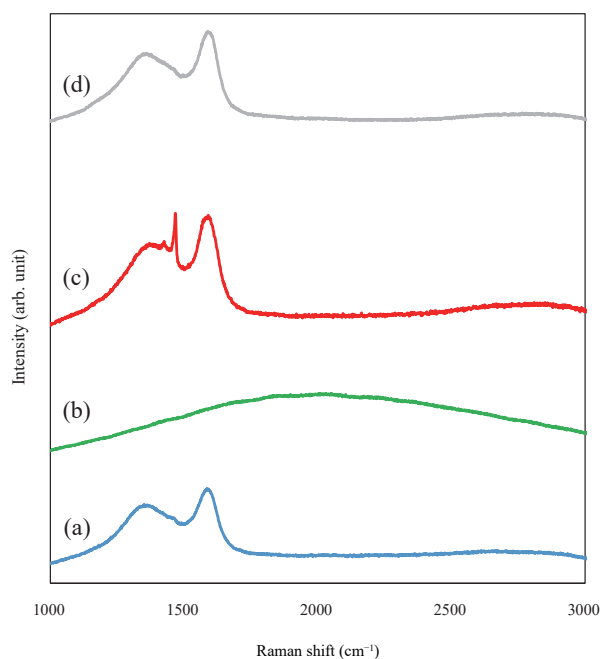


Fig. 8. (Color online) Raman scattering spectra of (a) the C_{60} film exposed to UV irradiation at 500 W for 24 h in ambient atmosphere, (b) C_{60} film exposed to UV irradiation at 700 W for 120 h in ambient atmosphere, (c) C_{60} film exposed to UV irradiation at 500 W for 24 h in a vacuum of 10^{-1} Pa, and (d) C_{60} film exposed to UV irradiation at 700 W for 18 h in a vacuum of 10^{-1} Pa.

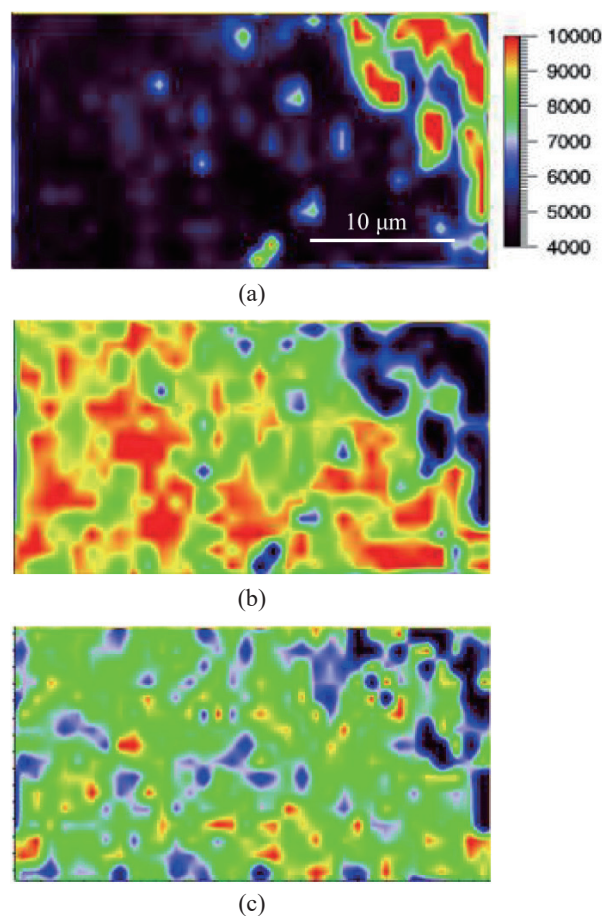


Fig. 9. (Color online) Raman scattering spectrum mapping of the C_{60} film heat treated using the Cu catalyst. UV irradiation was conducted at 500 W for 24 h in ambient atmosphere. (a) The mapping of the Cu catalyst, (b) mapping of the graphitic band, and (c) mapping of the disorder band.

C_{60} molecules under UV irradiation, so that polymerization of the C_{60} molecules did not take place even in vacuum.

The second reason is the influence of the particle size of the Cu catalyst on the domain size of the graphitic film. The Cu catalyst was approximately 300 nm thick. The heat treatment at 873 K for 10 min led to insufficient Cu grain growth, which in turn resulted in the formation of a graphitic film with small domains. Therefore, the film structure as predicted by Raman spectroscopy can be considered to be amorphous. Furthermore, it is possible that the heat treatment temperature was inadequate for the interfacial reaction between the carbon atoms and the Cu catalyst. In a general CVD process, the synthesis of graphene usually takes place at around 1273 K.⁽³⁰⁾

Interestingly, the film shown in Fig. 8(a) exhibited optical transparency unlike the other films. The Raman spectrum mapping of the film shown in Fig. 9 revealed that the graphitic region was separated from the Cu region. This result suggests that once the graphitic structure was formed

on the Cu catalyst, the catalyst migrated. Furthermore, some of the separated Cu was evaporated from the substrate, which facilitated the formation of an optically transparent film, as shown in Fig. 8(a). Under these experimental conditions, the reproducibility of the film was low. It is possible to form optically transparent films directly on glass substrates if the mechanism of phase transformation of C₆₀ molecules on Cu catalysts and the interfacial reactions between them can be precisely controlled.

4. Summary

In this study, the effect of UV irradiation and metal catalysts on the formation of C₆₀ films was investigated to prepare an optically transparent graphitic film on a glass substrate. UV irradiation of the C₆₀ films caused a phase transformation by either polymerization or decomposition of the C₆₀ molecules depending on the atmosphere in which the irradiation was carried out. In the Ni process, the polymerization of C₆₀ molecules by UV irradiation in vacuum contributed to the formation of a graphitic film on the glass substrate. The structural control of C₆₀ film used as a solid carbon source was a key technology for the preparation of the film. The Cu process failed to yield a homogeneous optically transparent film with a graphitic structure. However, an interesting phenomenon of phase separation of the graphitic and Cu regions was observed. The exploration of the mechanism of the migration and vaporization of the copper catalyst may contribute to a novel technique for the direct formation of transparent electroconductive films on glass substrates. Detailed investigations on the optimum thickness of the C₆₀ film or the catalyst film and the crystallinity of the carbon films obtained is required.

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