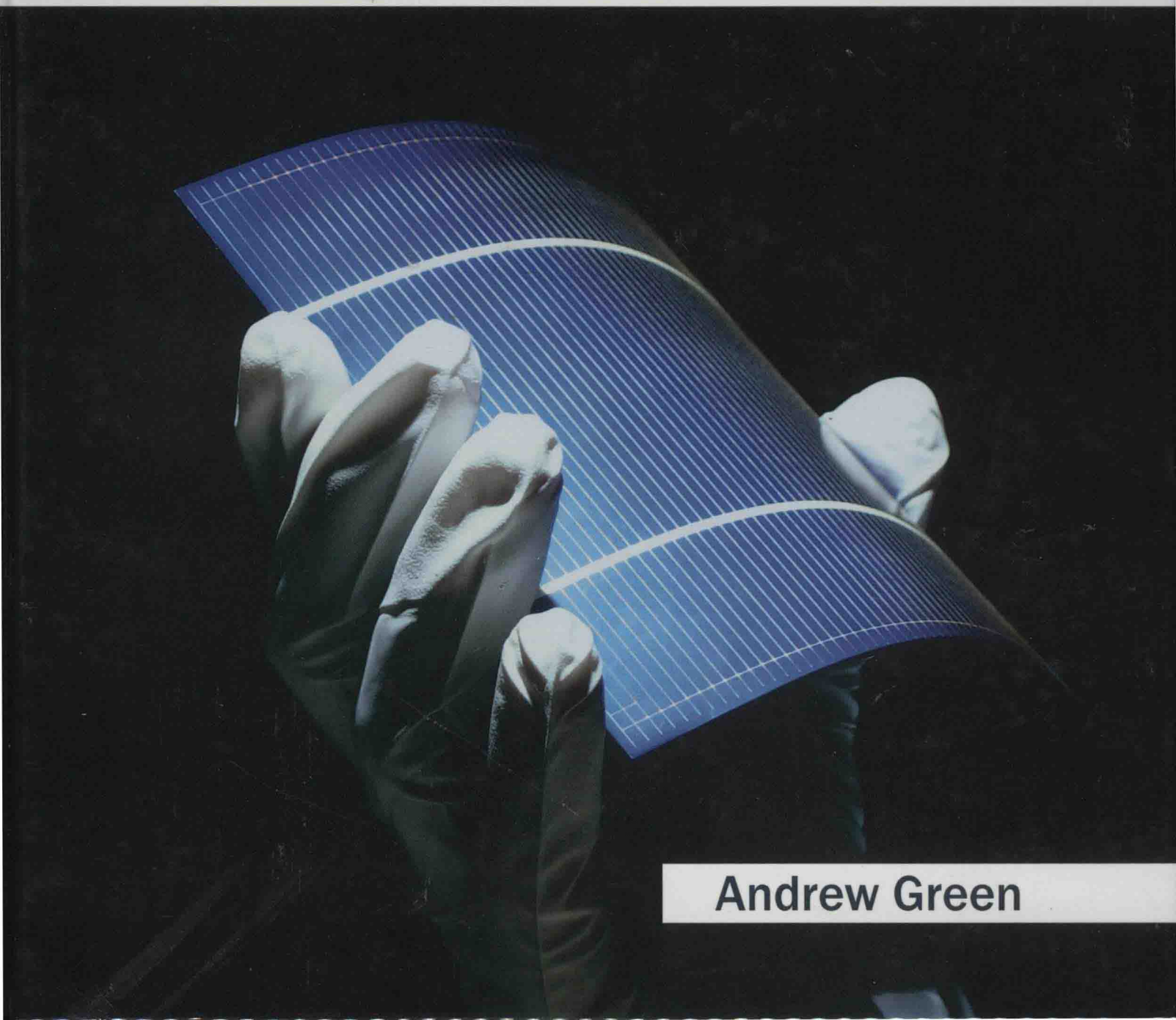
Advances in Nanotechnology

Volume I



Andrew Green

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Preface

This book is a compilation of research material on the emerging field of Nanotechnology. Engineering of functional systems at the molecular scale is referred to as nanotechnology or nanotech. Both the current work and advanced concepts related to this field are covered in this book. Nanotechnology is a technique used to construct an item using the bottoms up approach with high atomic precision. Today, by utilizing the technological advancement and techniques available in the field of nanotechnology, high performance products can be developed.

According to Feynman's vision of miniature factories, to build complex products using nanomachines, advanced nanotechnology should utilize positionally-controlled mechanochemistry guided by molecular machine systems. Nanotechnology is used in various fields of science these days. It plays a key role in areas such as medicine sciences, biotechnology etc. Besides, other applications include green nanotechnology, energy applications of nanotechnology and carbon tube related applications among numerous others.

This book provides a variety of researches and studies based on nanotechnology. It also covers some of the emerging aspects in the field of nanotechnology. I wish to thank all the authors for their efforts and time that they have given to this project. Without their dedication and timely submissions, this publication wouldn't have been possible. I must also acknowledge the editor and the team at the publishing house, who have done a tremendous job. Last but not the least, I wish to thank my family and friends, who have supported me in my life through everything. This book is meant for students, researchers, scientists, and for all those who want to learn and explore this interesting field of science.

Editor

Contents

Raman Laser Polymerization of C_{60} Nanowhiskers

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Photopolymerization of C_{60} nanowhiskers (C_{60}NWs) was investigated by using a Raman spectrometer in air at room temperature, since the polymerized C_{60}NWs are expected to exhibit a high mechanical strength and a thermal stability. Short C_{60}NWs with a mean length of 4.4 μm were synthesized by LLIP method (liquid-liquid interfacial precipitation method). The $A_g(2)$ peak of C_{60}NWs shifted to the lower wavenumbers with increasing the laser beam energy dose, and an energy dose more than about 1520 J/mm^2 was found necessary to obtain the photopolymerized C_{60}NWs. However, excessive energy doses at high-power densities increased the sample temperature and lead to the thermal decomposition of polymerized C_{60} molecules.

1. Introduction

C_{60} nanowhiskers (C_{60}NWs) are the single crystal nanofibers composed of C_{60} molecules [1] and can be synthesized by a facile method called "LLIP method" [2]. C_{60}NWs have a variety of applications and such as field-effect transistors (FETs) [3], solar cells [4], biosensors [5].

C_{60} molecules can be polymerized by electron beam irradiation [6]. Although as-grown C_{60}NWs are composed of the C_{60} molecules that are weakly bonded via van der Waals forces [7], the C_{60}NWs irradiated by electron beams showed the stronger thermal stability [8], the higher Young's modulus [9] than pristine van der Waals C_{60} crystals. Hence, it is of great importance to study the polymerization of C_{60}NWs in order to improve their mechanical and thermal properties.

Laser irradiation is a promising method to obtain the polymerized C_{60} molecules [7, 10]. We first showed the photopolymerization of C_{60}NWs by using the Raman laser beam irradiation [7]. Rao et al. showed that the peak of $A_g(2)$ pentagonal pinch mode of C_{60} shifts downward from 1469 cm^{-1} to 1459 cm^{-1} upon the photopolymerization [11], showing that the shift of $A_g(2)$ peak is a good indicator for the polymerization of C_{60}.

Alvarez-Zauco et al. studied the polymerization of C_{60} thin films in air by the ultraviolet (UV) laser irradiation as a function of laser energy dose (= fluence) from 10 to 50 mJ/cm^2 in order to optimize the photopolymerization of C_{60} films [12]. Likewise, the laser energy dose for the photopolymerization of C_{60}NWs should be optimized. Hence, the present study aims to reveal how the polymerization of C_{60}NWs proceeds as a function of the laser beam energy dose.

2. Experimental

C_{60}NWs were synthesized by a modified liquid-liquid interfacial precipitation method. Isopropyl alcohol (IPA) was gently poured into a toluene solution saturated with C_{60} (MTR Ltd. 99.5%) in a glass bottle to make a liquid-liquid interface, and then the solution was subjected to ultrasonication and stored in an incubator at 10°C to grow short C_{60}NWs. The synthesized C_{60}NWs were filtered and dried in vacuum at 100°C for 120 min. to remove the solvents. In the Raman spectrometry analyses, the C_{60}NWs dispersed in ethyl alcohol were mounted on a slide glass and dried in air.

A Raman spectrometer (JASCO, NRS-3100) with a green laser of 532 nm excitation wavelength was used for the polymerization and structural analysis of C_{60}NWs in air. The power of laser light illuminated onto the specimens was measured by using a silicon photodiode (S2281, Hamamatsu Photonics K.K.). The laser beam power density (D) and

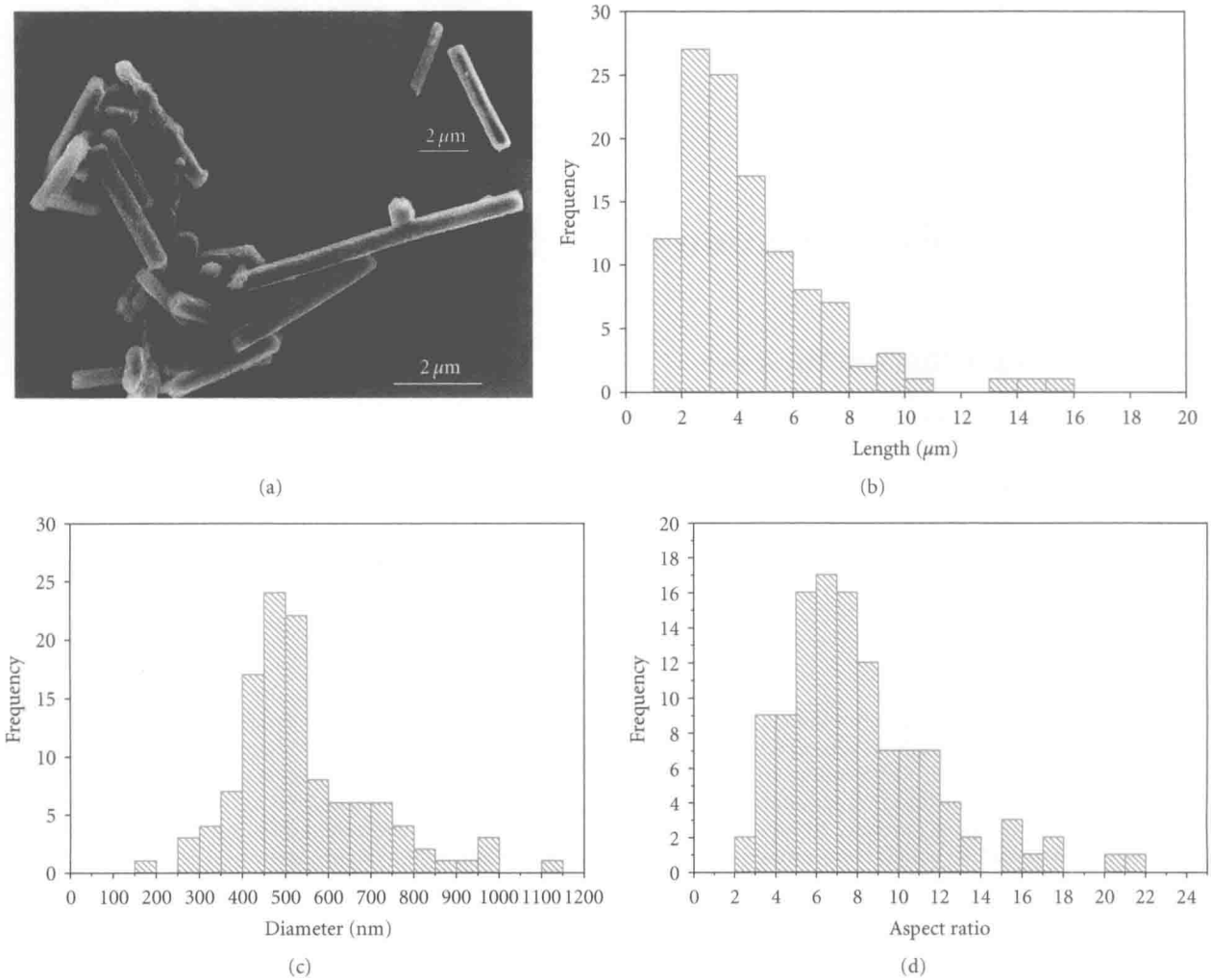

FIGURE 1: (a) SEM images, (b) length, (c) diameter, and (d) aspect ratio (length/diameter) distributions of the synthesized C_{60}NWs.

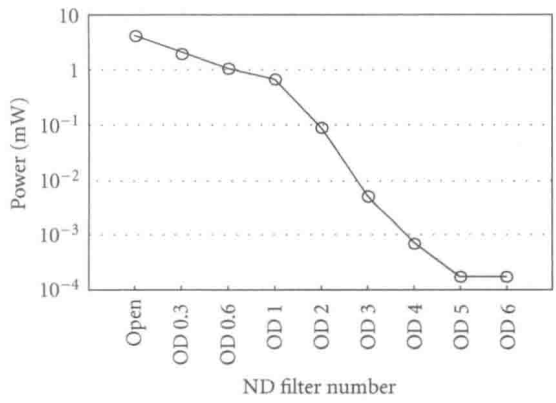

FIGURE 2: Relationship between the neutral density (ND) filter number and the laser beam power.

the energy dose of excitation laser beams in the Raman spectroscopy were controlled by changing ND (Neutral Density) filters, the defocus value of objective lens, and the exposure time of laser beam. D is defined by the following formula in this paper,

$$D\ (\mathrm{mW/mm^2}) = \frac{\text{The power of laser beam (mW)}}{\text{the area of laser beam exposed on the sample (mm}^2\text{)}}. \quad (1)$$

3. Results and Discussion

Figure 1 shows examples of scanning electron microscopy (SEM) images and the size distributions of the synthesized C_{60}NWs with a mean length of 4.4 ± 2.7 μm and a mean diameter of 540 ± 161 nm. The distribution of aspect ratios (length/diameter) is also shown. Most of the C_{60}NWs were found to possess the aspect ratios less than 15.

The power of excitation laser beam can be changed by selecting ND filters. Figure 2 shows the relationship between the ND filter number and the power of laser beam irradiated on samples. The laser beam power could be widely changed

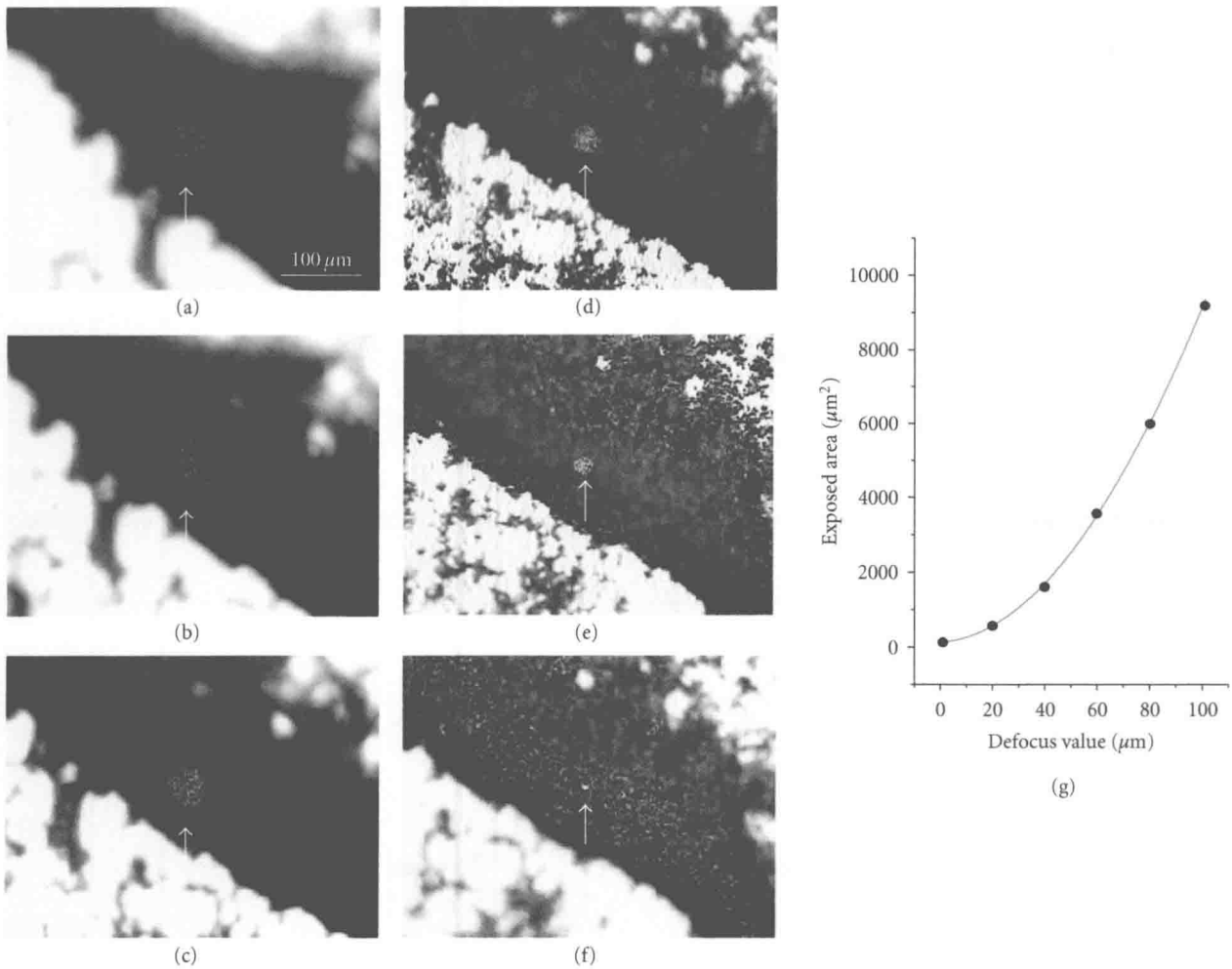

FIGURE 3: Optical microscopy images of the samples of C_{60}NWs irradiated by the excitation laser beams for the defocus values (under focus) of (a) 100, (b) 80, (c) 60, (d) 40, (e) 20, and (f) 0 μm and for the arrowed exposed areas of (a) 9270, (b) 6630, (c) 3480, (d) 1470, (e) 617, and (f) 63.8 μm^2, respectively. Graph (g) shows the relationship between the defocus value and the exposed area.

between OD1 and OD3. The ND filters OD1 (attenuation rate 0.1), OD2 (0.01), and OD3 (0.001) were used in the experiment, since the other filters gave too strong or too weak laser beam energies. The excitation laser beam power density could be varied from about 0.53 to 11800 mW/mm^2 using the above ND filters and by controlling the irradiation area of the laser beams and the defocus value from 0 to 100 μm as shown in Figure 3. The defocus value is defined as the distance from actual image plane and was set to be positive as the distance between the objective lens and the sample surface decreased. The places of C_{60}NWs exposed to the excitation laser beams can be recognized as the green circular areas marked in Figures 3(a)–3(f). The area of laser beam on the samples could be changed from 63.8 to 9270 μm^2 by controlling the defocus value from 0 to 100 μm.

The exposed area (y, μm^2) and the defocus value (x, μm) were plotted as shown in Figure 3(g). The plotted points can be approximated by the fitted quadratic curve, $y = 0.88x^2 + 6.8x + 36$. Figure 4 summarizes the relationship among the laser beam power density, ND filter number, and the defocus value.

Figure 5 shows examples of the Raman spectra of C_{60}NWs taken by using the ND filters of OD1, OD2, and OD3 for an exposure time of about 220 s, where the spot size of laser beam on samples was 9 μm in diameter. Each power density of the excitation laser beam was (a) 11800, (b) 1660, and (c) 71.5 mW/mm^2, respectively. The $A_g(2)$ peak around 1468 cm^{-1} sifted to the lower wavenumbers with increasing the laser beam power density.

Figure 6 shows the $A_g(2)$ peak positions of the Raman spectra of C_{60}NWs as a function of energy dose of the laser beam for each defocus value from 100 μm to 0 μm (just focus). The power density of laser beam on samples was changed by changing the defocus value and the ND filter number as shown in Figure 4. The energy dose was changed by setting the beam exposure time at 215 ± 6 s, 441 ± 10 s, 665 ± 9 s, and 899 ± 29 s for each power density. Hence, as a whole, 72 data points are plotted in Figure 6. As shown in Figure 5, the Raman shifts are found to generally decrease to the lower values with increasing the energy dose. However, the Raman shifts were observed to increase along

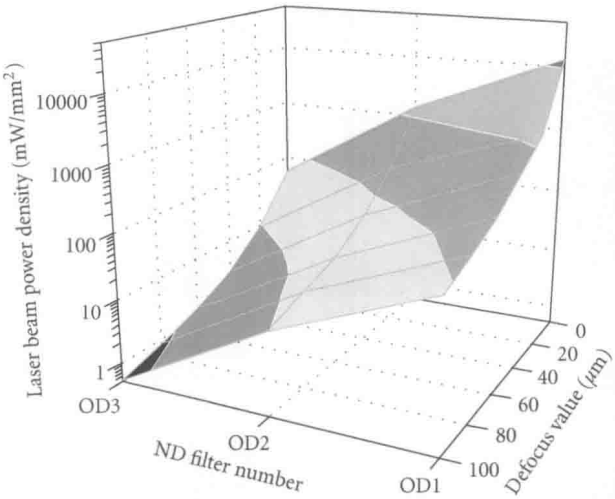

FIGURE 4: Power density of the Raman excitation laser beam measured as a function of ND filter number and the defocus value.

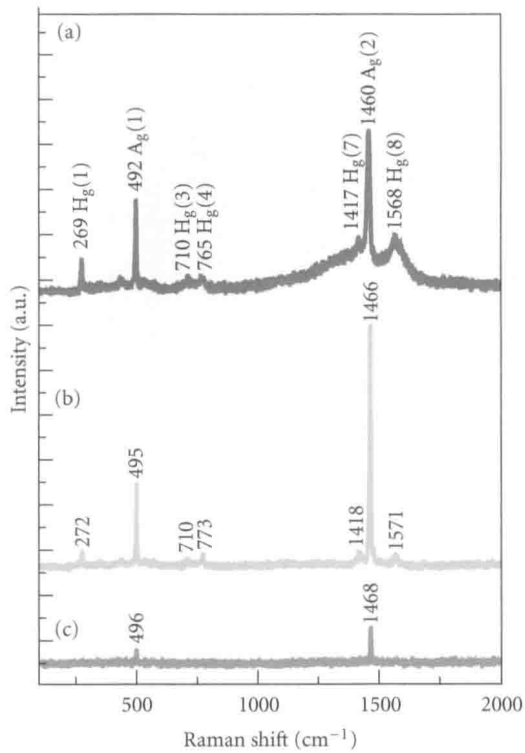

FIGURE 5: Raman spectra of C_{60}NWs. The power density of laser beam (D) is (a) 11800, (b) 1660, and (c) 71.5 mW/mm^2, respectively.

the red arrows for the high energy doses in Figures 6(c), 6(d), 6(e), and 6(f). These phenomena are supposed to be explained by the temperature rise of the C_{60}NWs exposed to the laser beams, since it is known that the photopolymerized C_{60} molecules decompose into their primary monomers and dimers by heating at temperatures higher than about 100°C [13].

The data points obtained using the highest power densities are indicated in each graph of Figure 6 by the black arrows for the exposure time of about 220 s. Figure 7 shows the relationship between the laser beam energy dose and the $A_g(2)$ peak position for the arrowed data points of Figure 6. The fitted curve of semilog plot is expressed as $y = -2.2x + 1467$, where x represents $\log_{10}$ (laser beam energy dose) and y represents the Raman shift of $A_g(2)$ peak. Using this experimental formula, the energy dose more than about 1520 J/mm^2 is found to be necessary for the photopolymerization of C_{60}NWs in air, when the laser light with a wavelength of 532 nm is used.

Since it is known that the photopolymerization of C_{60} progresses through the formation of four-membered rings between adjacent C_{60} molecules [11], it is considered that

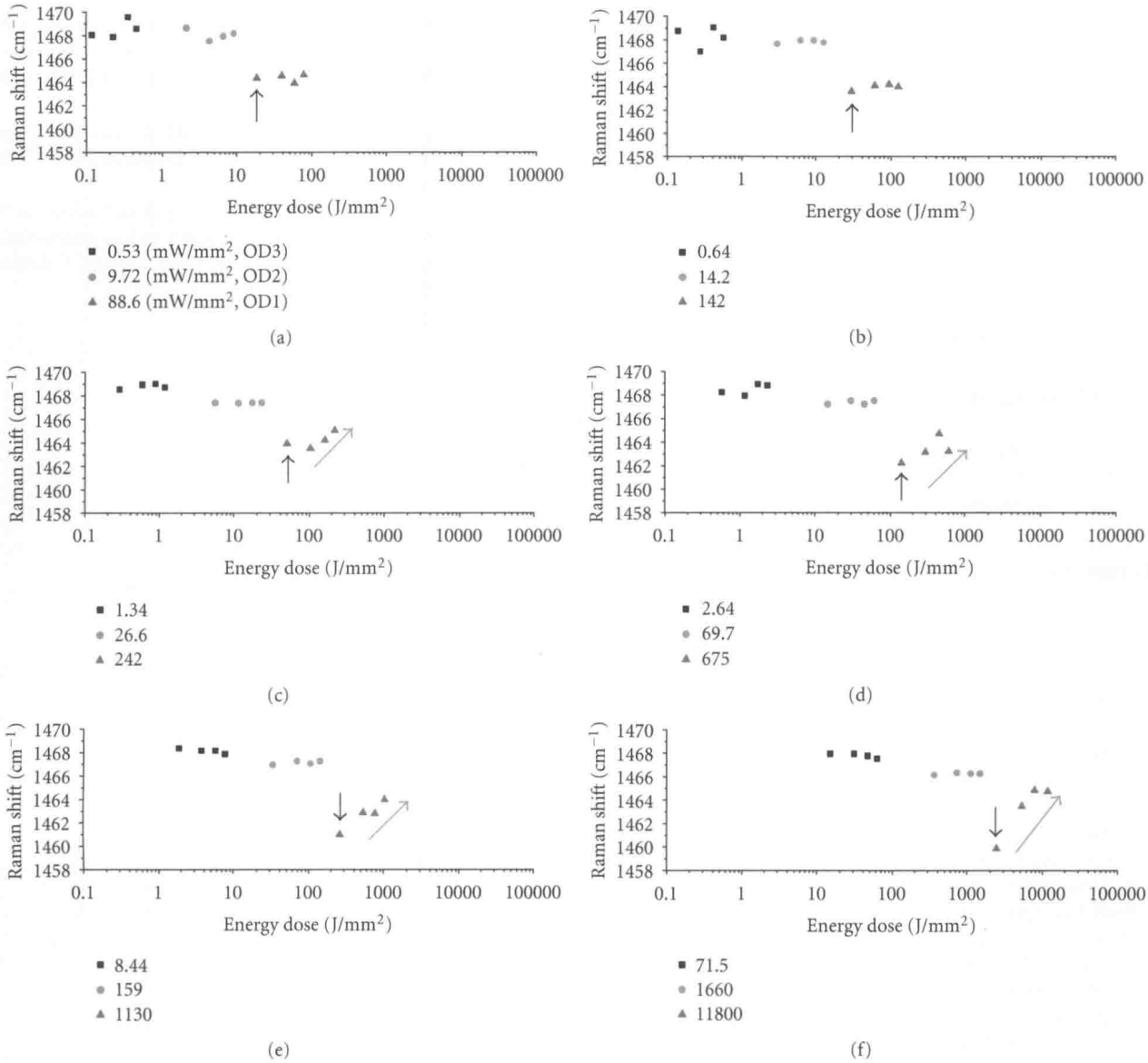

FIGURE 6: $A_g(2)$ peak positions of the Raman spectra of C_{60}NWs under various exposure conditions at the defocus values of (a) 100 μm, (b) 80 μm, (c) 60 μm, (d) 40 μm, (e) 20 μm, and (f) 0 μm (just focus), corresponding to (a) ~ (f) of Figure 3.

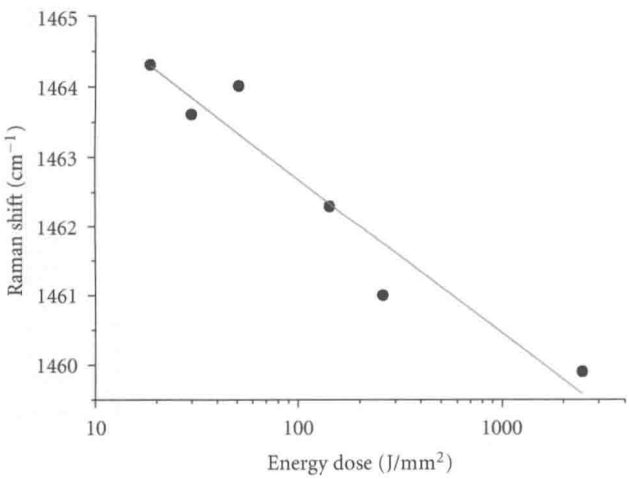

FIGURE 7: Relationship between the Raman shift of $A_g(2)$ peak and the energy dose of C_{60}NWs irradiated by the excitation laser beams.

C_{60} molecules are linearly polymerized by forming the four-membered rings along the growth axis of C_{60}NWs, as was shown in Figure 6 of [2].

In the gas chromatography-mass spectrometry (GC-MS) measurement of solvents contained in the C_{60}NWs that were prepared by use of toluene and IPA, the major residual solvent was toluene, and the content of IPA was very small compared with toluene [14]. Since the residual toluene of C_{60}NWs was measured to be about 0.2% after drying in an Ar atmosphere at 100°C for 30 min. [14], it is considered that the residual toluene of the vacuum-dried samples of C_{60}NWs in the present experiment is negligible and does not influence the Raman profiles.

4. Conclusions

The photopolymerization of C_{60}NWs was investigated by using the Raman laser beam of 532 nm wavelength at various

exposure conditions for the power density and the exposure time in air.

The $A_g(2)$ peak of C_{60}NWs shifted to the lower wavenumbers from that of the as-grown dried C_{60}NWs. However, the $A_g(2)$ peaks were found to move to the higher wavenumbers from the polymerized positions by the irradiation of laser beams for high energy doses at high-power densities, indicating the thermal dissociation of polymerized C_{60} molecules owing to the temperature rise.

An energy dose larger than about 1520 J/mm^2 was found to be necessary for the laser beam of 532 nm wavelength to obtain the photopolymerized C_{60}NWs.

Acknowledgment

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