

## Uniformly dimerized C60 film prepared by deposition under *in situ* photoirradiation

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C60 films with thicknesses of 100–480 nm were deposited on Si reed substrates under *in situ* photoirradiation. In anelasticity measurements, no internal friction peaks associated with rotational motions of the C60 molecules were observed, and Young's modulus was 1.5 times larger than that of a pristine C60 material. X-ray diffraction patterns suggested that the face-centered cubic lattice was contracted by about 3% and locally distorted from the pristine C60 material. Raman spectra very similar to those reported for dimerized C60 were also obtained. These characteristics recovered to those of the pristine C60 materials after annealing the C60 films at 523 K. These results indicate uniform dimerization in C60 films deposited under *in situ* photoirradiation. © 2008 American Institute of Physics. [DOI: 10.1063/1.3003866]

Covalent bonding between C60 molecules (i.e., polymerization) can be generated in a pristine face-centered cubic (fcc) C60 material by several methods, including photoirradiation,<sup>1</sup> high-energy particle irradiation,<sup>2,3</sup> or high-pressure, high-temperature (HPHT) treatment.<sup>4,5</sup> Polymerized C60 materials are regarded as a new type of carbon material in which the  $sp^2$  and  $sp^3$  bonding states coexist.<sup>6</sup> Photoirradiation is an easy way to prepare polymerized C60 films and is applicable for device fabrication. The penetration depth of ultraviolet to visible light in C60 materials, however, is limited to the order of 100 nm.

Recoverable but time-dependent elastic behavior is referred to as anelasticity.<sup>7</sup> The dynamic motion of atoms and molecules or phase transition in solids often induces anelastic relaxation similar to dielectric or magnetic relaxation, with the internal friction giving a measure of the fractional energy loss per cycle in periodic deformation due to anelasticity. Two internal friction peaks associated with the rotational motion of C60 molecules have been reported for C60 materials at around 260 K and below 260 K (referred to hereafter as  $P2$  and  $P1$ , respectively).<sup>8–11</sup>  $P2$  is attributed to a structural phase transition from the fcc phase to a simple cubic phase as a result of orientational ordering about the rotation axis at around 260 K,<sup>8,9</sup> whereas  $P1$  is attributed to thermal jumping between two energetically quasiequivalent rotational configurations of adjacent C60 molecules, in relation to their activation parameters.<sup>12–14</sup> When covalent bonds are formed between C60 molecules,  $P1$  and  $P2$  are expected to disappear through suppression of these rotational motions, whereas the modulus is increased through strengthening of the intermolecular bonding. In the present study, C60 deposition under *in situ* photoirradiation was applied to prepare photopolymerized C60 films with thicknesses up to 480 nm, and the morphology of these films was investigated in terms of their anelastic property, as well as through x-ray diffrac-

tion (XRD) and Raman spectroscopy measurements.

The C60 deposition was carried out on a Si reed substrate (reed dimensions:  $15 \times 3 \times \sim 0.1$  mm<sup>3</sup>) (Ref. 15) at 348 K with a Knudsen cell in ultrahigh vacuum (base pressure below  $10^{-6}$  Pa). The deposition rate was about 0.06 nm/min. Blue light from high-power light-emitting diodes (Lumileds Luxeon K2, peak wavelength: 470 nm) was guided to the vacuum chamber through a viewing port so that the light intensity at the substrate was about 0.25 W/cm<sup>2</sup>. The photoabsorption observed for pristine C60 film at around 2.7 eV (458 nm) is assigned to the intermolecular charge-transfer state.<sup>16</sup> For the *in situ* photoirradiation during C60 deposition, the substrate was tilted to 45° with respect to both the direction to the Knudsen cell and the incident light. The anelasticity was measured by a composite reed vibration technique.<sup>15,17</sup> The dynamic Young's modulus of the C60 film ( $E_{C60}$ ) was estimated from the change in the reed's resonant frequency as a result of the C60 deposition, where Poisson's ratio values of 0.306 reported for a C60 fcc single crystal<sup>18</sup> and of 0.42 for Si were used. The Raman spectrum was measured with a micro-Raman spectrometer (Nano Finder, Tokyo Instruments) under a backscattering configuration. A 488-nm Ar-ion laser beam with a spot size of 0.5 mm  $\phi$  and an intensity of  $\sim 0.05$  mW was used for irradiation, and no spectral changes were found during the measurements. The XRD spectrum was recorded by using a diffractometer (Philips X'pert) with Cu  $K\alpha$  radiation. An evacuation chamber was used to reduce the background scattering, and the remaining background in the raw spectrum was subtracted by assuming a polynomial function.

Figure 1(a) shows the internal friction spectrum observed for a 480-nm-thick C60 film deposited on the Si reed substrate under *in situ* photoirradiation and then subjected to annealing at 523 K for 48 h in vacuum ( $< 4 \times 10^{-5}$  Pa). In Fig. 1(a), the increase in internal friction observed above 200 K for the substrate alone was due to the thermoelastic damping of Si. The internal friction from the C60 film ( $\Delta Q^{-1}$ ) is depicted in Fig. 1(b) after subtraction of the Si reed component. As shown in Fig. 1(b), the  $P1$  and  $P2$  peaks were not

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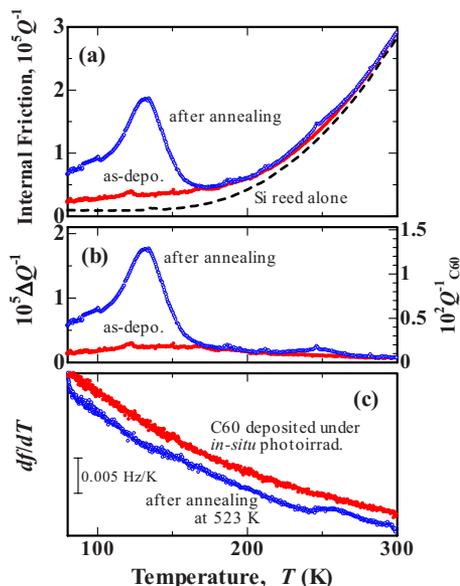


FIG. 1. (Color online) (a) Internal friction spectrum observed for a composite reed of C60 film (480 nm thick) deposited on a Si substrate under *in situ* photoirradiation (red) and that for the same specimen after annealing at 523 K (blue). The dashed line represents the spectrum for the Si reed substrate alone. (b) Internal friction spectra for the C60 film ( $\Delta Q^{-1}$ ) estimated by subtraction of the Si reed component from the spectra in (a), where  $\Delta Q^{-1}$  was converted to the internal friction of the C60 film ( $Q_{C60}^{-1}$ ) on the right-hand axis. (c) Temperature derivative curves of the resonant frequency observed for the composite reed with the C60 film deposited on the Si substrate.

immediately observed for the C60 film deposited under *in situ* photoirradiation (hereafter referred to as *in situ* irradi. C60 film) but did appear after the annealing. Figure 1(c) shows the temperature derivative of the resonant frequency (proportional to the square root of Young's modulus) observed for the *in situ* irradi. C60 film and the film after annealing. The curve of the derivative for the *in situ* irradi. C60 film showed a monotonic decrease with increasing temperature. After annealing, a steplike increase at around 250 K and a dip at around 130 K appeared; these features correspond to *P2* and *P1*, respectively. In the thermodynamic measurement of the C60 subjected to HPHT treatment, the small enthalpy of transition observed at 260 K could be explained by the residual C60 monomers.<sup>19</sup> In the present experiment, no anomalous change in Young's modulus of the *in situ* irradi. C60 film was detected near the temperature corresponding to *P2*. These observations suggest that the rotational motions of the C60 molecules were completely suppressed in the *in situ* irradi. C60 film but revived after the annealing at 523 K. It has been reported that C60 dimers induced by photoirradiation are dissolved by heating to above 473 K.<sup>20,21</sup> Similar results to those shown in Figs. 1(a) and 1(b) were also observed for *in situ* irradi. C60 films with thicknesses of 95 and 150 nm.

Table I lists the  $E_{C60}$  values estimated for the *in situ* irradi. C60 films, where the estimation accounted for the lattice contraction found from the XRD measurements (see below). The  $E_{C60}$  estimated for the *in situ* irradi. C60 films was about 1.5 times larger than that for pristine C60 film or the value of 12–16 GPa reported for polycrystalline C60.<sup>8,22</sup> After annealing at 523 K, the  $E_{C60}$  value decreased to that of pristine C60. It has been reported that one- or two-dimensionally polymerized HPHT C60 materials exhibit a

TABLE I. Dynamic Young's moduli of C60 films ( $E_{C60}$ ) deposited under *in situ* photoirradiation and after annealing at 523 K. The value observed for pristine C60 film deposited without photoirradiation is also listed.

C60 thickness (nm)	$E_{C60}$ (GPa) <i>In situ</i> photoirrad.	After 523 K annealing	Without photoirrad.
95	21.6	17.7	...
150	25.7	22.0	...
480	24.3	17.5	...
165	...	...	16.5

Young's modulus of about 25 or 45 MPa, respectively, and both recover to the fcc C60 material by annealing above 600 K.<sup>23</sup> The Young's modulus and recovery temperature observed here suggest that long polymerized chains were not formed in the *in situ* irradi. C60 films.

Figure 2 shows the XRD spectra obtained for the 480-nm-thick *in situ* irradi. C60 film and the same film after annealing, together with the XRD spectrum for pristine C60 film. The XRD pattern observed for the pristine C60 film can be explained by its fcc structure with a lattice constant of 1.417 nm.<sup>4</sup> For the *in situ* irradi. C60 film, the (111) and (220) reflections exhibited a position shift to a higher angle and peak broadening, as compared with the pristine C60 film. From the (111) and (220) reflections, the lattice parameter was estimated to be about 1.37 nm, suggesting lattice contraction by about 3.3% from the pristine fcc lattice. The reflection at around 21.7° can be identified as the (311) reflection of the contracted fcc lattice. The reflection at around 14°, on the other hand, cannot be expected from the normal reflections of both the pristine C60 fcc lattice and the contracted one, but the peak position coincides with the forbidden (210) reflection of the pristine lattice. In addition to the broadened reflections, the reflection at around 14° suggests that the *in situ* irradi. C60 film had a locally distorted fcc structure. The reflections observed after annealing at 523 K were explained well by the pristine C60 fcc structure and became sharper, suggesting that the contracted, distorted fcc structure nearly recovered to the pristine one. The reflection at around 14°, however, remained, and the other reflections were slightly broader than those of the pristine C60 film. These results indicate that a portion of the lattice distortions remained even after the polymerization dissolved. The fcc

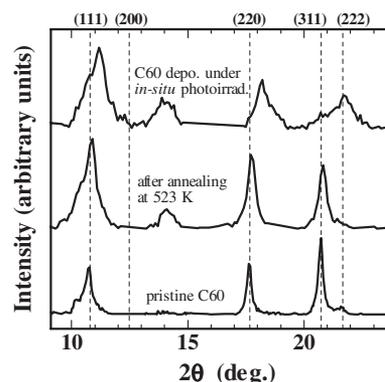


FIG. 2. XRD spectra obtained for a C60 film (480 nm thick) deposited under *in situ* photoirradiation and the same film after annealing at 523 K. The spectrum obtained for pristine C60 film (210 nm thick) is also shown. The vertical dashed lines indicate the peak positions for the C60 fcc structure with a lattice parameter of 1.417 nm.

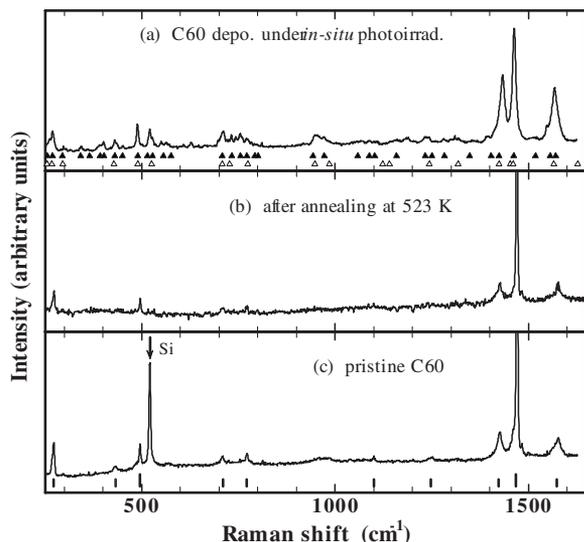


FIG. 3. Raman spectra obtained for (a) a C60 film (480 nm thick) deposited under *in situ* photoirradiation and (b) the same film after annealing at 523 K. In (a), the filled and open triangles indicate the peak positions reported for a dimerized HTHP C60 specimen<sup>27</sup> and a photopolymerized C60 film,<sup>28</sup> respectively. The spectrum obtained for a pristine C60 film (165 nm thick) deposited without photoirradiation is shown in (c), where the peak at 521  $\text{cm}^{-1}$  was due to the Si substrate and the vertical bars indicate the peak positions reported for the pristine fcc C60 material.

structure contracted by 3.7% and its recovery after annealing at 543 K has been reported for an HPHT-treated C60 material (5 GPa at 573 K),<sup>4</sup> and similar lattice changes have been reported for an HPHT-treated C60 crystal (2 GPa at 700 K).<sup>24</sup> The small peak shifts from the perfect fcc position by dimerization are attributed to the distorted fcc structure observed for C60 subjected to HPHT treatment at 1.5 GPa and 423 K.<sup>25</sup>

Figures 3(a)–3(c) show the Raman spectra obtained for a 480-nm-thick *in situ* irradiated C60 film, the same film after annealing at 523 K for 48 h, and a pristine C60 film, respectively. The large peak observed at around 1468  $\text{cm}^{-1}$  for the pristine C60 film [Fig. 3(c)] was identified as the  $A_g(2)$  peak, which is attributed to the pentagon pinching mode of a C60 molecule. It has been reported that the  $A_g(2)$  peak is quenched and other peaks are observed below the  $A_g(2)$  peak because of C60 dimer formation resulting from the 2+2 cycloaddition reaction.<sup>1,26</sup> Instead of the  $A_g(2)$  peak, a large peak at around 1462  $\text{cm}^{-1}$  and small peaks below 1400  $\text{cm}^{-1}$  were observed for the *in situ* irradiated C60 film [Fig. 3(a)]. These peaks are well explained in terms of those reported for an HPHT dimerized C60 crystal (filled triangles)<sup>27</sup> or those reported for a photodimerized C60 film (open triangles).<sup>28</sup> After annealing at 523 K, the  $A_g(2)$  peak revived and the C60 dimer-related peaks disappeared. These observations indicate C60 dimer formation in the *in situ* irradiated C60 film and then dissolution into C60 monomers after annealing. Similar Raman spectra were also observed for the 95- and 150-nm-thick *in situ* irradiated C60 films.

All the present results demonstrate that uniformly dimerized C60 films with a thickness greater than the light penetration depth can be prepared by deposition under *in situ* photoirradiation. We propose that several C60 dimers aligned in a  $\langle 110 \rangle$  direction constitute a fundamental structural unit,

and that the contracted, locally distorted fcc lattice is formed by an aggregate of variants with different orientations. The reflection observed at around  $14^\circ$  in the XRD pattern might be attributed to local fcc lattice distortions induced by variant formation. Since it is reported that the two-dimensional hexagonal C60 photopolymer exhibits a semiconducting property,<sup>29</sup> the electrical conductivity of the present C60 films is of great interest. Further investigations of the electrical property as well as the texture and the formation process are in progress.

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