Morphological change of C_{60} monolayer epitaxial films under photoexcitation

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Thin films of C_{60} were grown under laser irradiation at various intensities $0-200 \ \mathrm{mW/mm^2}$ and their growth shapes were investigated by *ex situ* atomic force microscopy (AFM) observation. The nucleation density of the first layer decreases with increasing laser intensity, probably due to the temperature rise of the migrating clusters. In addition to this gradual laser intensity dependence, an anomalous enhancement of the nucleation density was observed on irradiation at $50 \ \mathrm{mW/mm^2}$, which was attributed to the influence of photopolymerization. As for the second layer, there was a threshold laser intensity ($200 \ \mathrm{mW/mm^2}$) at which the nucleation density increased and the shape of the domains became irregular. This is due to the combined effect of hindered migration caused by the polymerized first layer and photopolymerization of the migrating molecules themselves. Energy transfer from the excited substrate to the migrating C_{60} molecules is strongly suggested.

I. INTRODUCTION

Epitaxial thin film growth under photoirradiation has long been studied. It improves crystallinity through donating migration energies to the photoexcited species, decomposing precursor materials, and changing the chemical route for crystal growth.[1–3] Photoexcited species are commonly involved in the thin film growth recently due to the development of pulsed laser deposition. However, the previous studies have dealt only with strong chemical bond formation, and molecular materials that coagulate via weak van der Waals forces have not been studied. We here report an experimental analysis of C_{60} epitaxial film growth under photoirradiation. C_{60} can be a model material for studying the effect of photoirradiation because it is polymerized by photoexcitation[4] and has a long lifetime ($40 \ \mu s$) of the photoexcited state (T_1).[5,6] In addition, the large migration length on layered material substrates[7,8] is suitable for the study of growth kinetics by atomic force microscopy (AFM).

Since Rao *et al.*[4,9] reported that C_{60} molecules were polymerized by Ar ion laser or UV visible lamp irradiation to a pristine C_{60} film at room temperature, there have been many studies on C_{60} dimers and polymers. It is established that a photo-induced dimer is formed via a $[2+2]$ cycloadditional four-membered ring structure. However, the four-membered ring is thermally broken and the polymers revert to pristine molecules.[10] Many reports have been published about the dependence of photopolymerization kinetics on laser intensity,[8,11,12] irradiation time,[8,12,13] and temperature.[11,12]

In the present study, we investigated the effect of laser irradiation on the interaction between C_{60} molecules that controls the thin film growth. We have chosen a layered material MoS_2 (0001) surface as the substrate. It has been established that C_{60} molecules form close-packed hexagonal lattices on MoS_2 (0001) surfaces and that the crystal axes of the C_{60} films are parallel to the $[11\bar{2}0]$ axis of the substrate.[14,15] A laser beam (532 nm) was irradiated on the

substrate during the growth of C_{60} on MoS_2 (0001). Because the photons with this wavelength are not absorbed by gas phase C_{60} molecules but by solid C_{60}, the present experiment is suitable for studying the effect of excitation of clusters and films. The grown films were observed by AFM, and the morphology of the films was studied precisely.

II. EXPERIMENT

The growth of thin films of C_{60} was performed in an ultra-high vacuum (UHV) chamber with a base pressure of 1×10^{-7} Pa. The C_{60} powder (99.99% pure) was charged into a Knudsen cell (K cell) and was heated at 200 °C for several hours under UHV for degassing. The MoS_2 (0001) surfaces were obtained by cleavage of the natural molybdenite in air just before loading into the growth chamber. The substrate was heated at 300 °C for several hours to remove contaminants prior to the film growth. It was kept at 100 °C during the growth, at which thermal decomposition of the C_{60} polymer does not occur.[10,12] The laser beam was irradiated during the growth of C_{60} on MoS_2 (0001) until the nominal thickness of the films became 1 monolayer (ML). The growth rate was monitored by a quartz crystal oscillator placed near the substrate and was determined to be about 0.2 ML/min. The temperature of the *K* cell was about 300 °C. A Nd:YVO$_4$ laser SHG (wavelength=532 nm) was used as a light source. The laser beam was slightly defocused on the surface of the sample with a spot diameter of 5 mm and was irradiated at normal incidence to the substrate surface. The power density was varied in the range of $10-200 \ \mathrm{mW/mm^2}$. Various sequences of irradiation and film growth were examined to understand the mechanism of the morphological change. The AFM images were taken in the contact mode at room temperature in ambient atmosphere. Raman spectra of the films were taken using a 532 nm laser, a 10 cm monochromator, and a cooled CCD detector.
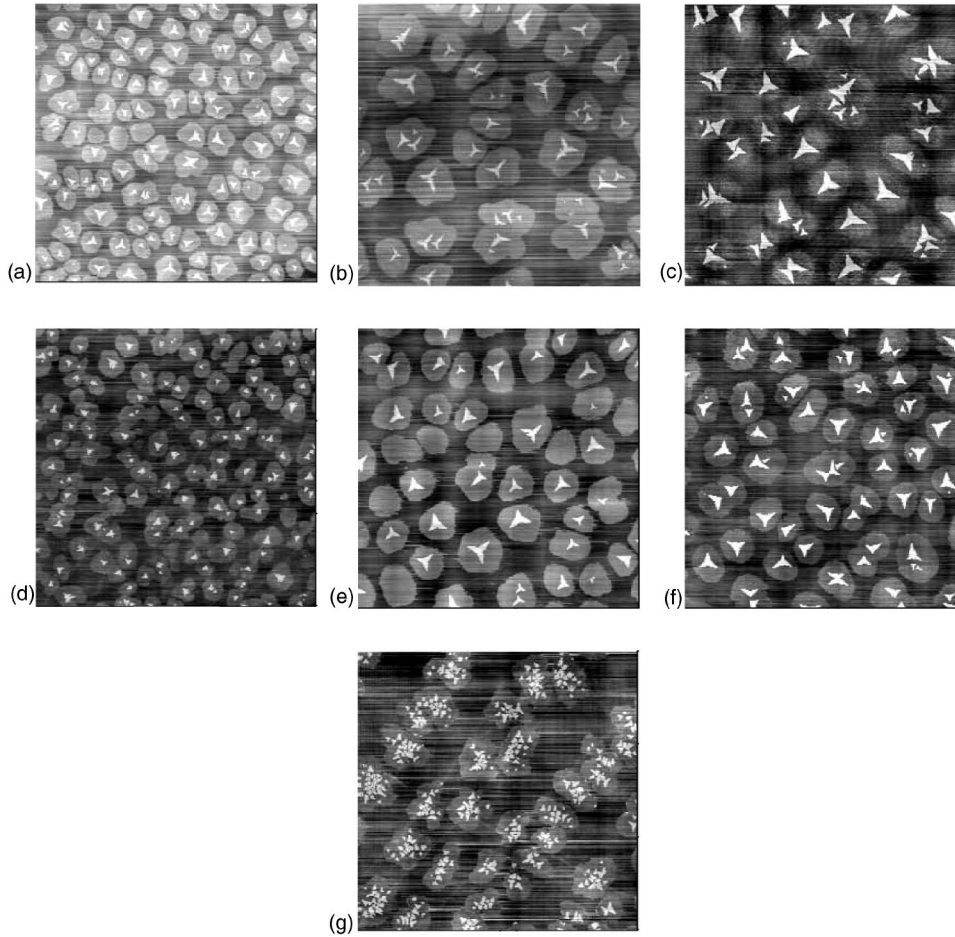
FIG. 1. AFM images of the C_{60} films grown on MoS_2 (0001) surfaces under laser irradiation. The area of the images was 15 μm $\times$ 15 μm. (a)–(g) represent the image under irradiation at 0, 10, 25, 50, 100, 150, and 200 mW/mm^2, respectively.

III. RESULTS

Figure 1 shows the AFM images of C_{60} films grown on a MoS_2 (0001) substrate irradiated at various laser intensities. The films were grown until the nominal thickness was equivalent to 1 ML. Judging from the height of the films, the films were composed of two molecular layers, the gray and white regions corresponding to the first and second layers, respectively. The height of the first and second layer was about 0.8 nm, which is close to the one-layer thickness of an fcc C_{60} lattice (0.81 nm). The shapes of the islands in the first layer of the films irradiated by the 0–150 mW/mm^2 laser [(a)–(f)] were round. Those in the second layer became triangular, probably reflecting the symmetry of the hexagonal lattices of C_{60}. The direction of the triangles was aligned along the axes $\langle 11\bar{2}0 \rangle$ or $\langle \bar{1}\bar{1}20 \rangle$ of the substrate because there are two possibilities of lattice alignment of hexagonally packed double layers. The center of the edges of the triangles was dented under the influence of the Berg effect.[16] When the films grew under irradiation at 200 mW/mm^2 (g), on the other hand, the shape of the first layer was irregular and many small second layer domains were formed with irregular shapes. The edges of the domains aligned along neither of the abovementioned axes in Fig. 1(g).

The diffusion length (ξ) of a molecule can be derived from the universal property of diffusion-limited aggregation (DLA) (Refs. 17 and 18) as follows, which is reported to be valid in a similar system of C_{60} monolayers grown on VSe_2:[8]

$$\xi^2 \approx c^{-1} R^{D-d+2}.$$

Here, R and c are the averaged cluster radius in units of lattice points and the surface concentration of occupied lattice points, respectively. d is the dimension of the system ($=2$) and $D=5/3$ is the universal Hausdorff dimension in DLA independent of the geometry of the lattice. We investigated averaged cluster radii and the concentration of occupied lattice points of the first and second layer grown under various laser intensities and calculated the diffusion length according to the above approximation. We also measured the nucleation densities N_x of each layer. Figures 2(a) and 2(b) show the ξ and N_x of the first and the second layer as a function of laser intensity, respectively. We plotted the nucleation density of the second layer divided by that of the first layer in Fig. 2(c). The value was almost constant for irradiation at 0–150 mW/mm^2, but the value for irradiation at 200 mW/mm^2 was six times larger.

In order to examine the influence of laser irradiation, we changed the irradiation process during growth. Shown in Figs. 3(a)–3(c) are the films prepared as follows, in which the film deposition was performed in two steps. The total amount of the deposited C_{60} was set to be 1 ML equivalent. (a) The first and second halves were grown continuously without laser irradiation. (b) The first half, grown without irradiation, was irradiated by the laser (200 mW/mm^2) for
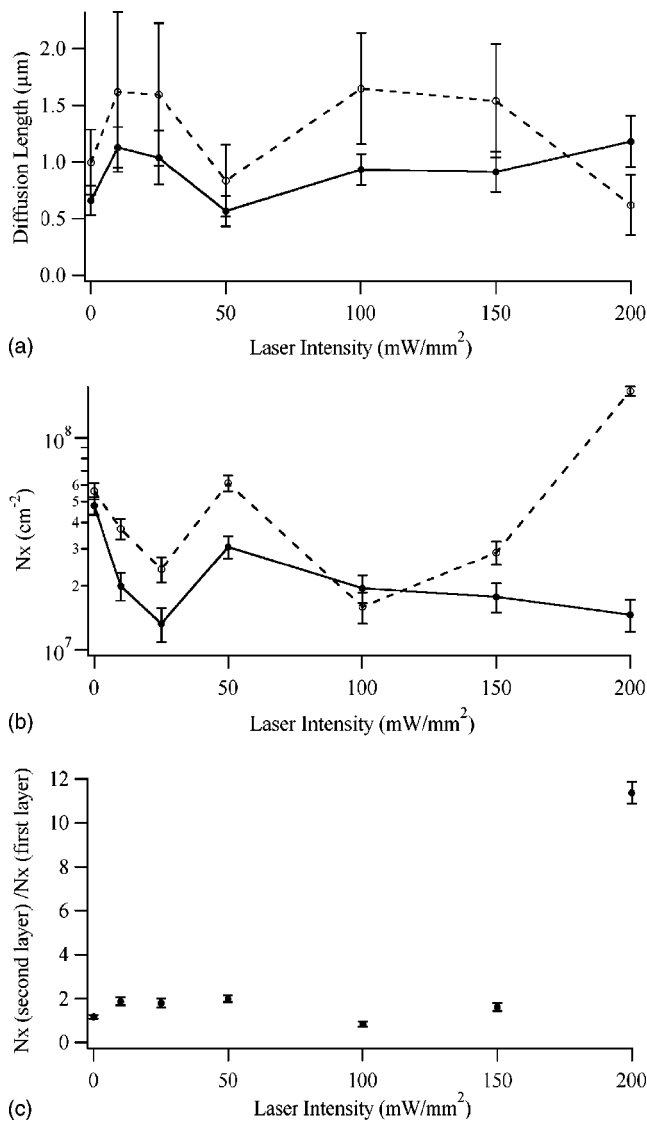
FIG. 2. Laser intensity dependence of the diffusion distance (a) and the nucleation density (b) of the first layer (●) and the second layer (○) obtained from the AFM images in Fig. 1. (c) The nucleation density of the second layer divided by that of the first layer. The error bars show the standard deviation.

5 min after the growth, and the second half was grown without laser irradiation. (c) Just as in (b) but the second half was grown with laser irradiation. In Fig. 3(b), the symmetry of the second layer was almost threefold while many domains with a strong Berg effect can be observed. In Fig. 3(c), the morphology of the second layer was similar to that of Fig. 1(g), which consists of many small irregularly shaped domains. This implies that the second layer of both samples grew in the same way.

It is known that C$_{60}$ is polymerized by photoexcitation in a certain temperature range which can be detected by a Raman spectrum.[11] We therefore have measured the Raman spectra of the films before and after laser irradiation under various conditions including the same condition as in the film growth experiment. Because the Raman intensity of monolayer films is very weak, we have taken the spectra of

50-nm-thick films. The results are shown in Fig. 4. Figures 4(a)–4(c), respectively, show the spectrum of a film without irradiation, that after irradiation at 200 mW/mm^2 for 5 min at 100 °C [same as in Fig. 1(g)] and that after the same irradiation for 2 h at room temperature. A change in the spectrum is observed, from which the polymerization ratio is estimated as shown later.

IV. DISCUSSION

A. The first layer

It was found from Fig. 1 that the contours of the first layer were round with almost constant curvature for growth under irradiation at 0–150 mW/mm^2, while they have an irregular shape at 200 mW/mm^2 irradiation. We also notice from Fig. 2(a) that the nucleation density of the first layer decreases as a function of laser intensity at 0–25 mW/mm^2, increases suddenly at 50 mW/mm^2 and again decreases gradually with increasing laser intensity. We discuss here those two characteristics of the growth of the first layer.

First we must mention the absorption cross section of a C$_{60}$ molecule that is migrating on the surface and that of C$_{60}$ clusters and films. The optical absorption spectra of gas phase C$_{60}$ (Ref. 19) and solid films[20–22] have almost the same shape above 3 eV. The absorption of the gas phase at 532 nm (2.33 eV) is almost 0, whereas solid films show a certain absorption. This suggests that the molecules could not be electronically excited before they arrive at the substrate surface. The larger optical absorption at 532 nm of solid C$_{60}$ is probably due to the dielectric environment of the surrounding C$_{60}$. The ratio of electronically excited C$_{60}$ at various laser intensities is estimated using the reported dielectric constants ($\varepsilon_2 \simeq 0.5$) (Ref. 22) and the refraction index ($n \simeq 2$) (Ref. 20) of C$_{60}$ films at 532 nm, which were obtained by optical absorption and reflection measurements. With the photon density f(cm^{-2} s^{-1}), laser intensity P(mW/mm^2 = × 10 J cm^{-2} s^{-1}), the thickness of the film d, absorption coefficient α derived from $\alpha = 2\pi\varepsilon_2/n\lambda$, the cross-sectional area of a unit cell of C$_{60}$ S, and the lifetime of T_1 state τ, the rate μ at which the molecules are excited is

$$\mu = \alpha d f S \tau = \frac{\alpha d S \tau \lambda P}{10hc}.$$

For example, using $\varepsilon_2 = 0.5$, $n = 2$ (leading to $\alpha = 2.9\ \mu m^{-1}$), $d = 0.71$ nm, $\tau = 40\ \mu s$,[5,6] $\lambda = 532$ nm, $\mu \approx 0.48\%$ and 3.8%, when $P = 25$ and 200 mW/mm^2, respectively.

It should be noted that there is also a possibility of excitation transfer from the MoS$_2$ surface to migrating C$_{60}$ molecules. Because MoS$_2$ shows well-defined exciton peaks at room temperature at 1.92 and 1.96 eV,[23] the excitation lifetime of MoS$_2$ is rather large. A C$_{60}$ molecule has an optically forbidden transition at 1.55 eV (ground state S$_0$→excited state T_1),[24] and the excited energy transfer is expected to occur via the Dexter mechanism[25] which does not require the involvement of optically allowed transitions. If this happens, the population of the excited species will become larger than the estimation above. We will discuss this point later with respect to the growth on the laserirradiated first layer.
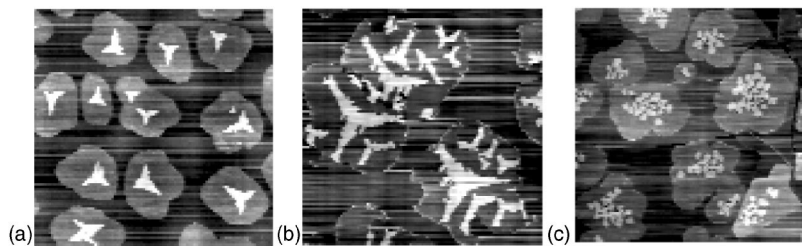
FIG. 3. AFM images of the C_{60} films that were grown in a different manner using two steps. (a) The first and second halves were grown continuously without laser irradiation. (b) The first half, grown without irradiation, was irradiated by the laser (200 mW/mm^2) for 5 min after the growth, and the second half was grown without laser irradiation. (c) Just as in (b) but the second half was grown with laser irradiation. The area of the images is 6 μm $\times$ 6 μm.

Next, let us consider the decrease in nucleation density in the region of 0–25mW/mm^2. This feature is associated with the fact that the saturated nucleation density has a negative dependence on the temperature of the substrates.[16–19] However, we consider that it is not the substrate which is heated but the clusters migrating on the surface for the following reason. The temperature rise of the substrate was less than 5 °C as measured by a thermocouple directly touching the surface during the laser irradiation at 50 mW/mm^2. A temperature difference of 5 °C cannot cause the difference in the nucleation density observed here.[7] A plausible explanation is that the temperature of the migrating clusters increases strongly because the heat capacity of a cluster is smaller than that of the film or of the substrate. The experimental nucleation density of unirradiated film decreases as a function of the substrate temperature as $\exp(-E/k_B T)$ where E =0.26 eV in the temperature range of 80–180 °C.[7] From this empirical form, the temperatures of the photoexcited clusters can be estimated to be 113 °C at 10 mW/mm^2 and 135 °C for 25 mW/mm^2. The decrease in the nucleation density on irradiation at 50–200 mW/mm^2 is probably due to the heating as mentioned above, but the decrease is not as steep as in irradiation below 25 mW/mm^2. We consider that a different mechanism is working in the irradiation at 50–200 mW/mm^2 as explained later.

We assume that the sudden rise in the nucleation density at 50 mW/mm^2 is caused either by a change in the intermolecular force due to laser irradiation (e.g., excimer formation) or by the photopolymerization of C_{60} molecules. First, we examined the former case. Based on the calculation stated above, about 0.48 or 0.96 % of C_{60} molecules are in the excited triplet state at 25 or 50 mW/mm^2 irradiation, respectively. However, it is unlikely that the change in the intermolecular interaction becomes observable when this small ratio of the molecules is excited. Therefore, we thought that the reason for the sudden rise in the nucleation density at 50 mW/mm^2 is the influence of the photopolymerization of C_{60} molecules. When a chemical covalent bond is formed among the C_{60} molecules in a cluster, the molecules will be prevented from dissociation and nucleation will be enhanced. This will increase the saturation nucleation density.

The polymerization proceeds by photoirradiation but the polymers decompose on heating above 420 K.[11] For direct evidence of the polymerization, we have taken Raman spectra of the films. We have measured the films prepared by three different procedures in order to remove the uncertainty of polymerization during the Raman measurement using the same 532 nm wavelength. The results, shown in Fig. 4, indicate that the peak at 1469 cm^{-1} decreased and that the peak

at 1459 cm^{-1} emerged on photoirradiation as previously reported. By curve fitting with two Lorentzians centered at 1469 and 1459 cm^{-1}, the polymerization ratios in Figs. 4(a)–4(c) are estimated to be 5$\pm$5%, 48$\pm$5%, 85$\pm$3%, respectively. Figure 4(b) was prepared at the same irradiation strength and duration and the same substrate temperature as in the present growth experiment [Fig. 1(g)]; therefore it has been confirmed that the polymerization does proceed under the conditions of growth under photoirradiation.

B. The second layer

When the films were grown at 200 mW/mm^2 irradiation, the shapes of the second layer domains were irregular and the nucleation density of the second layer was very high, indicating a very short diffusion distance. In addition, the nucleation density of the second layer divided by that of the
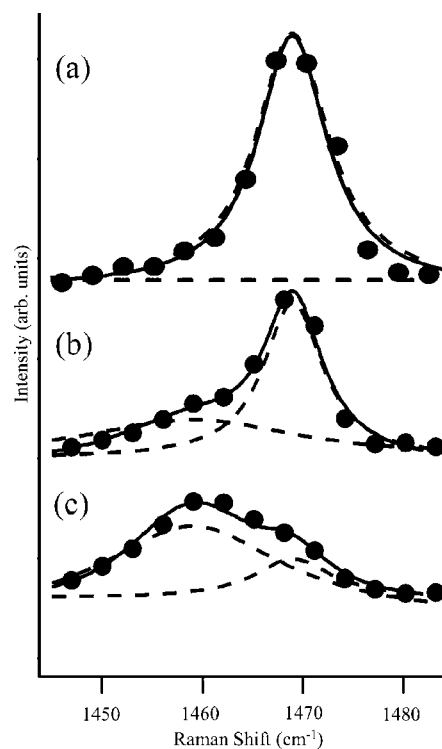

FIG. 4. Raman spectra of 50-nm-thick C_{60} films irradiated by a 532 nm laser under various conditions. (a) Without irradiation. (b) Irradiated at 200 mW/mm^2 for 5 min at 100 °C. (c) Irradiated at 200 mW/mm^2 for 2 h at room temperature. The dots are the raw data and the solid lines are the results of curve-fitting with two Lorentzians (broken lines) centered at 1469 and 1459 cm^{-1}.
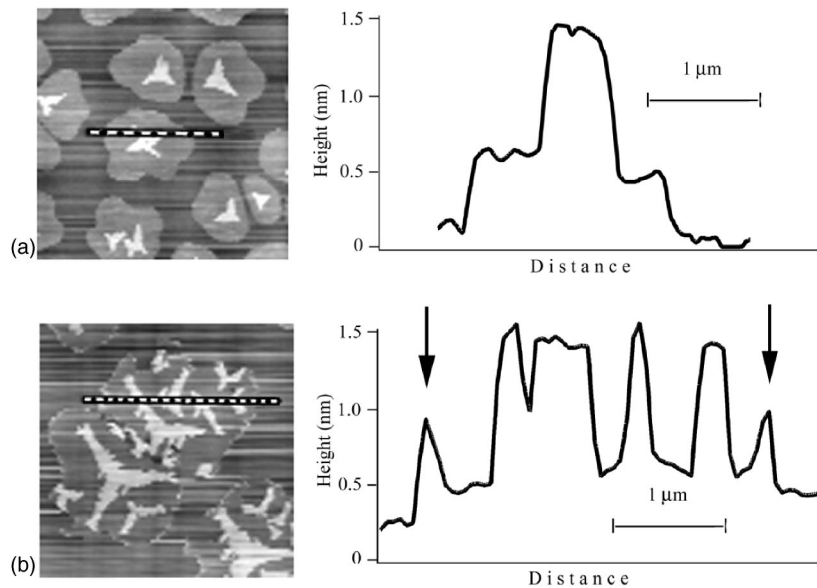
FIG. 5. Cross sections of AFM images of C$_{60}$ films shown in Figs. 3(a) and 3(b). The left panels indicate the lines for the cross section. The height in the cross section is measured from the top of the substrate. The arrows in (b) correspond to the position of the edge of the first layer.

first layer was exceptionally larger by six times only under irradiation at 200 mW/mm^2, whereas it was constant (1–2) for other intensities.

It is difficult to understand that the change occurs only on the irradiation at 200 mW/mm^2 because it is reported that the photopolymerization speed is proportional to the laser power density when the intensity is weak.[11] It becomes even subproportional when the laser density is strong due to thermal dissociation.[12] In order to understand the mechanism of the present results, we have interrupted the deposition in the dark, polymerized the first layer, and then continued the growth with or without laser irradiation. Figure 3 has been obtained for this purpose. As described previously, Fig. 3(a) shows the sample without laser irradiation. The samples (b) and (c) were grown on a partially photopolymerized monolayer C$_{60}$ prepared by photoirradiation (200 mW/mm^2) after half-monolayer growth. The samples shown in (b) and (c) were, respectively, without and with photoirradiation during the growth of the second half of the film.

Three features are observed: First, the denting of the domain contours is strongly observed in Fig. 3(b) compared with Fig. 3(a). Second, the nucleation of the second layer is much enhanced by photoirradiation during the growth on the polymerized substrate [Fig. 3(c)]. Third, the edge of the island in Fig. 3(b) is made of two layers as shown in the cross-sectional images (Fig. 5).

The first feature, the denting in Fig. 3(b), is due to the Berg effect, and it shows a large degree of diffusion limiting in the aggregation process. This can be understood by considering the deformation of the crystal lattice due to the strain caused by photopolymerization.[26] It is impossible to maintain a hexagonal lattice when C$_{60}$ is polymerized,[26–28] which causes stress and distortion in the crystal lattice as observed by AFM (Ref. 26) and STM.[29,30] It is established that the migration of atoms on single crystals is strongly anisotropic as reported for K atoms on W(112),[31] Pt on Pt(100)-hex,[32] and Si on Si(001) 2×1.[33] It is thus expected that the diffusion constant is decreased when the crystal lattice of the surface (first layer) is deformed by partial photopolymerization.

The second feature of enhanced nucleation indicates enhanced polymerization in the growing second layer. This can be explained in terms of the photopolymerization mechanism. It is necessary for polymerization that the pentagonal sites of photoexcited and not-excited C$_{60}$ molecules face each other correctly. If the molecules or clusters are migrating on the substrate, this condition will be difficult to satisfy because a translational degree of freedom exists. In contrast, a molecule or a cluster trapped at a certain site on the first layer would increase the probability of meeting this condition.

The third feature, the double-layer height of the edge of the islands, indicates that the migrating species cannot descend from the top of the partially polymerized first layer onto the substrate even without photoirradiation. This strongly suggests that the particles whose migration is hindered by polymerization of the first layer are not clusters but C$_{60}$ molecules, because the clear bilayer contour will not otherwise be formed. This also suggests that the photopolymer is formed selectively at the edges of the first layer islands, which implies that excitons are concentrated at the edge of an island. This is not due to the diffusion of excitons in the island, because the boundary of an island will not attract the excitons because Frenkel excitons in a molecular solid have higher energies at the boundary with a vacuum than with the bulk because of the lack of attractive interaction among excitation dipoles.[34] The energy transfer from the excited MoS$_2$ substrate to the C$_{60}$ first layer is therefore considered to increase the exciton concentration at the boundary. This hypothesis is supported by the difference in the photointensity threshold for the nucleation feature between the first layer (peaks at 50 mW/mm^2) and the second layer (200 mW/mm^2), which indicates that the aggregating first layer is more easily polymerized than is the second layer.

V. CONCLUSIONS

Thin films of C$_{60}$ were grown under laser irradiation at various intensities, and the growth feature was investigated

by AFM after the growth. The photon energy was chosen so that absorption by molecules in the vapor phase is negligible. The nucleation density of the first layer decreased with increasing laser intensity probably because of the temperature rise of the migrating clusters. It, however, suddenly increased under irradiation at 50 mW/mm^2, which was attributed to the influence of photopolymerization. As for the second layer, there was a threshold laser intensity at 200 mW/mm^2 beyond which the nucleation density increased and the shape of the domains became irregular. This phenomenon can be explained in terms of the combined effect of hindered migration by polymerization of the first layer and photopolymerization of the migrating molecules on the first layer. It seems from the C_{60} bilayer formed at the edges of the islands and the different threshold for the morphological change between layers that the growth is affected by energy transfer from the photoexcited substrate to the migrating molecules.

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