NANO LETTERS

2001
Vol. 1, No. 2
101−103

Molecular Arrangement in C_{60} and C_{70} Films on Graphite and Their Nanotribological Behavior

S. Okita[†] and K. Miura*

Department of Physics, Aichi University of Education, Hirosawa 1, Igaya-cho, Kariya 448-8542, Japan

Received December 7, 2000

ABSTRACT

The nanotribological behavior of C_{60} and C_{70} films on graphite has been studied. C_{60} molecules on graphite begin to grow in a monolayer form, whereas C_{70} molecules begin to grow in a bilayer form. The shear stress between a C_{60} monolayer and graphite was estimated to be about 0.2 GPa. For C_{60}(111) films, a change of tip motion, from one-dimensional stick-slip to two-dimensional zigzag stick-slip with decrease of a loading force, appears.

The mechanical properties of fullerenes have attracted much attention in the field of materials science. Particularly, C_{60} and C_{70} solids have been predicted to be good lubricant materials because of their nearly spherical shape and low surface strength.[1−3] Our previous letter[3] reported on the nanotribological behavior of the C_{60} islands on KCl(001) using frictional force microscopy. Along the different scanning directions of $\langle 1\bar{1}0\rangle$ and $\langle 11\bar{2}\rangle$ of a C_{60}(111) surface, a tip has performed one-dimensional stick-slip and zigzag stick-slip motions on the order of a load of nN, respectively, although at a larger loading force, it destroyed the C_{60}(111) surface. Also, water adsorption on the C_{60} films gave a lower frictional force, indicating that C_{60} molecules rotate or translate at the (111) surface. Thus, the C_{60} films were expected to exhibit various behaviors depending on the loading force, scanning direction, and relative humidity.

In this letter, we report the growth mode of C_{60} and C_{70} films on graphite using atomic force microscopy and frictional force microscopy, and we focus on the nanotribological properties of C_{60} and C_{70} films.

The C_{60} and C_{70} films on highly oriented pyrolytic graphite (HOPG) and KCl(001) were prepared by evaporation from a BN crucible. The temperatures of their substrates during evaporation were kept at range of 150 °C to 200 °C. Normal and lateral forces were measured simultaneously under argon atmosphere at room temperature using a commercially available instrument (Seiko Instruments Inc., SPI-3700). The scan speed was 0.13 m/s. A rectangular silicon cantilever with a normal spring constant of 0.05 N/m was used. Zero normal force is defined as the position at which the cantilever is not bent.

Figure 1 shows the atomic force microscope (AFM: topograph) images of C_{60} and C_{70} islands on a KCl(001) surface. Their islands consist of scores of molecular layers. The (111) facets of the C_{60} and C_{70} islands appear, which form parallel to the KCl(001) substrate. Such island growth occurs in cases where an intermolecular interaction is stronger than a molecule−substrate interaction, as reported in previous papers.[4−6] Thus, it is concluded that C_{60}−C_{60} and C_{70}−C_{70} interactions are stronger than C_{60}−KCl(001) and C_{70}−KCl(001) interactions, respectively. Figure 2 shows the AFM (topograph) images of C_{60} and C_{70} films on a graphite surface at the initial stage of growth. The height of the C_{60} films on the middle of Figure 2 is approximately 1 nm, exhibiting a monolayer. As shown at the bottom of Figure 2, the high-resolution frictional force microscope (FFM) image of the C_{60} monolayer has a periodicity of 0.9 nm, which shows a zigzag motion along the $\langle 11\bar{2}\rangle$ scanning direction of the C_{60} monolayer.[3] Thus, the existence of the monolayer exhibits epitaxial growth on graphite. As shown by Gravil et al.,[7] the growth of this monolayer indicates that C_{60} molecules grow on graphite such that the hexagonal face of a C_{60} molecule pairs with the hexagonal face of the second graphite layer, so as to continue the natural stacking (AB stacking) of the graphite. The height of the C_{70} films in the middle of Figure 2 is about 2 nm, exhibiting a bilayer. Here, it should be noted that there does not exist any C_{70} monolayer on graphite in our experiments. Because the hexagonal face in a C_{70} molecule does not situate on the top of its ellipsoid, as shown on the middle of Figure 2, it may not always be

* To whom correspondence should be addressed. E-mail: kmiura@auecc.aichi-edu.ac.jp.
[†] Present address: Graduate School of Engineering, Nagoya University..

10.1021/nl0055308 CCC: $20.00
Published on Web 01/20/2001

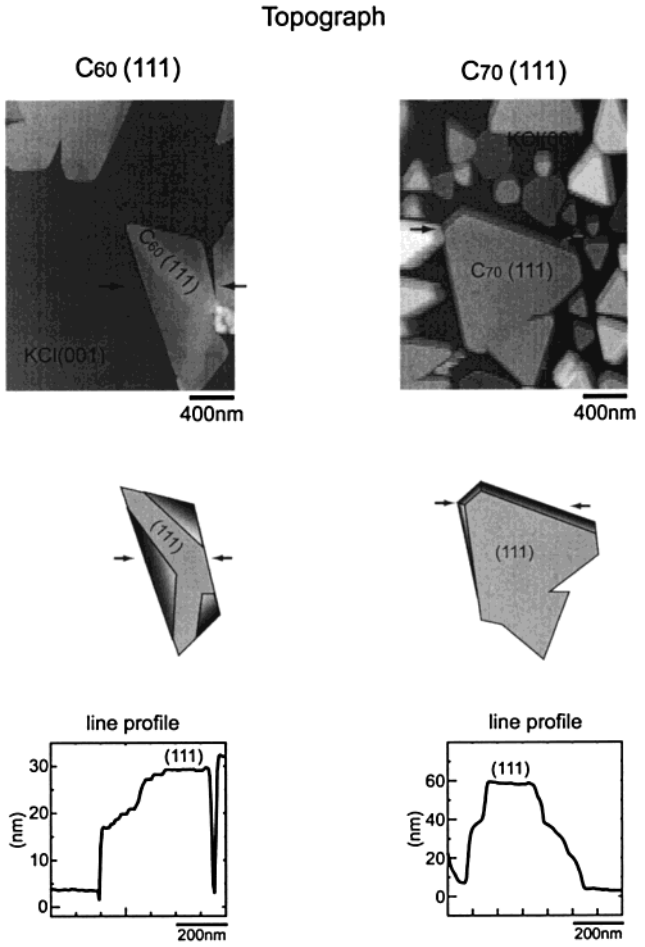

Figure 1. Atomic force microscope (AFM: topograph) images of C_{60} and C_{70} islands on a KCl(001) surface. The (111) facets of the C_{60} and C_{70} islands appear, which form parallel to a KCl(001) substrate. At the bottom, line profiles depicted by the arrows are illustrated.

stable to pair with the hexagon face of the graphite in a monolayer manner.

Figure 3 shows how the AFM image from the C_{60} monolayer of Figure 2 changes by increasing a loading force. One notes that the C_{60} monolayer on graphite is swept up by increasing up to a load of 0 nN. Using the Herztian continuum theory,[8,9] the contact radius versus the tip load estimated using a pull-off force of −10 nN and a tip radius of 15 nm is shown on the bottom of Figure 3. At a loading force of 0 nN, the contact radius between the tip and the C_{60} monolayer surface is estimated to be about 1.3 nm, exhibiting that the contact area between the tip and the C_{60} monolayer is seven molecular dimensions. Then, the mean lateral force was about 3 nN. Thus, assuming that seven molecules are moved by a lateral force of 3nN with the tip, the mean shear force between the single C_{60} molecule and the graphite is estimated to be about 0.4 nN, such that the shear stress between the C_{60} monolayer and the graphite is estimated to be about 0.2 GPa. For similar experiments with C_{70} films on graphite, the C_{70} films were easily swept up at loading forces smaller than those of the C_{60} films. Thus, this exhibits that the interaction between the C_{70}-graphite interfaces is weaker than that between the C_{60}-graphite interfaces.

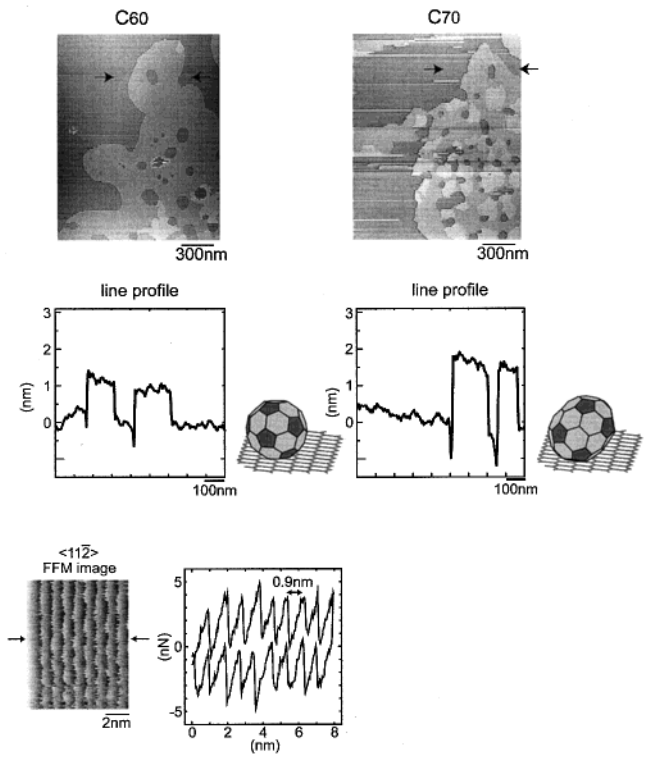

Figure 2. AFM (topograph) images of C_{60} and C_{70} films on a graphite surface at the initial stage of growth. In the middle, line profiles depicted by the arrows are illustrated. The height of C_{60} films is about 1 nm, exhibiting a monolayer. At the bottom of the figure, the high-resolution frictional force microscope (FFM) image of the C_{60} monolayer has a periodicity of 0.9 nm, which shows a zigzag motion along the $\langle 11\bar{2} \rangle$ scanning direction of the C_{60} monolayer. The height of C_{70} films is about 2 nm, exhibiting a bilayer.

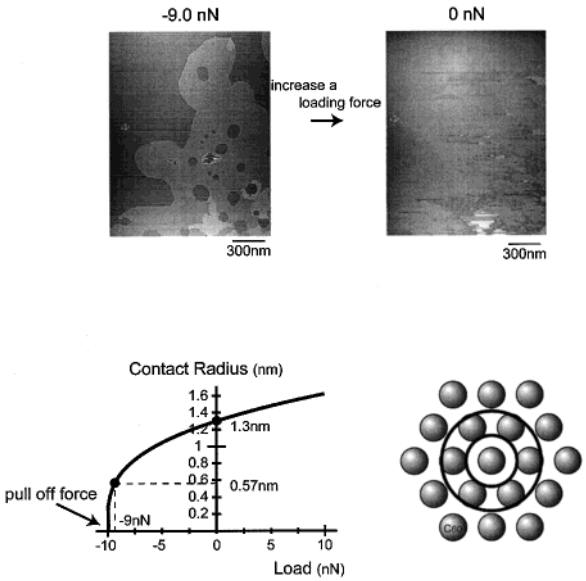

Figure 3. Change of the AFM (topograph) image from the C_{60} monolayer of Figure 2 with an increase in the loading force. One notes that the C_{60} monolayer on graphite is swept up by increasing up to a load of 0 nN. Using the Herztian continuum theory, the contact radius versus the loading force was estimated and is shown at the bottom, where the pull-off force is −10 nN. Contact radii at loading forces of 0 nN and −9 nN are 1.3 nm (solid circle) and 0.57 nm (dotted circle), respectively.

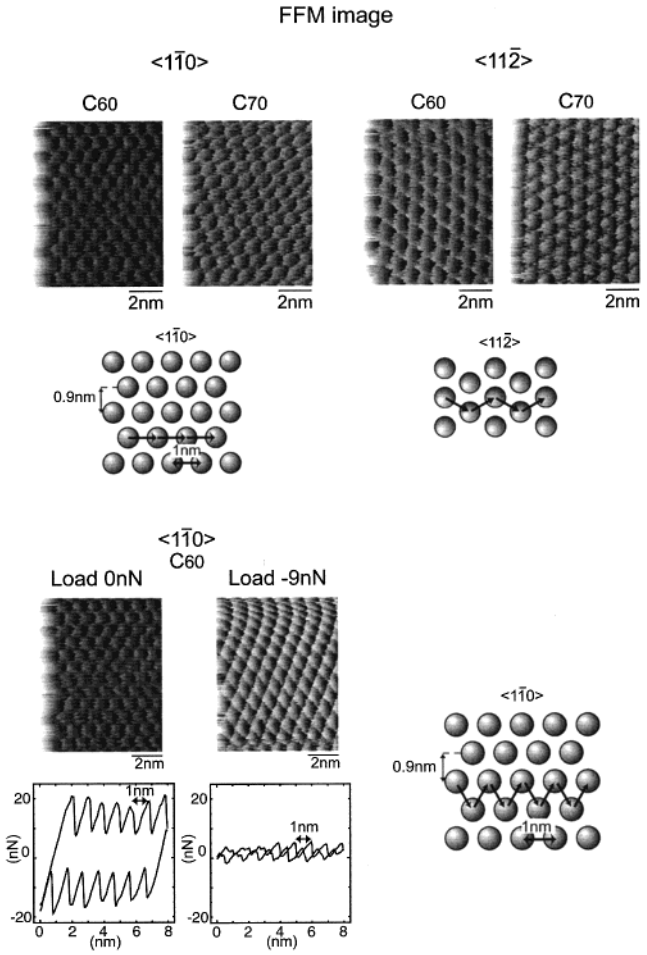

Figure 4. High-resolution FFM images from (111) surfaces of C_{60} and C_{70} films. For the $\langle 1\bar{1}0\rangle$ and $\langle 11\bar{2}\rangle$ scanning directions, the samples exhibit one-dimensional stick-slip and two-dimensional zigzag motions, respectively. In the case of the $\langle 1\bar{1}0\rangle$ scanning direction of the C_{60} (111) films on the bottom of the figure, it should be interesting to note that the image at a loading force of −9 nN (pull-off force, −10 nN) changes from one-dimensional stick-slip to clear two-dimensional motions, exhibiting a single molecular contact with the tip, which gives a mean frictional force of 1 nN.

This result is consistent with the assumption that is stated above, that the C_{60}-graphite interfaces are composed of the natural stacking (AB stacking), whereas the C_{70}-graphite interfaces are not so composed.

Figure 4 shows the high-resolution FFM images from (111) surfaces of C_{60} films and C_{70} films. For the $\langle 1\bar{1}0\rangle$ and $\langle 11\bar{2}\rangle$ scanning directions, the films exhibit one-dimensional stick-slip and two-dimensional zigzag motions, respectively, which is discussed in detail in the previous paper.[3] In the case of the $\langle 1\bar{1}0\rangle$ scanning direction of the C_{60}(111) films, it is interesting to note that the image at a loading force of −9 nN (pull-off force, −10 nN) changes from one-dimensional stick-slip to clear two-dimensional motions, exhibiting a single molecular contact with the probe tip, which gives a mean frictional force of 1 nN.[10] In other words, this is a phase transition of stick-slip motion due to a change from a multi-molecular contact to a single molecular contact. Thus, the shear force between the tip and the single C_{60} molecule is estimated to be 1 nN. It should be noted that the shear force (1nN) between the tip and the C_{60} molecule is lager than that (0.4nN) between the C_{60} molecule and the graphite. This is consistent with the experimental result that a tip scanning at the C_{60} monolayer or bilayer is unstable, whereas a tip scanning at several C_{60} layers is stable.

Acknowledgment. We thank T. Sahashi and S. Kamiya for their assistance with the experiments.

References

(1) Lüthi, R.; Meyer, E.; Haefke, H.; Howald, L.; Gutmannsbauer, W.; Güntherodt, H.-J. *Science* **1994**, *266*, 1979.
(2) Li, Z. Y. *Surf. Sci.* **1999**, *441*, 366.
(3) Okita, S.; Ishikawa, M.; Miura, K. *Surf. Sci. Lett.* **1999**, *442*, L959.
(4) Miura, K. *Phys. Rev.* **1995**, *B52*, 7872.
(5) Miura, K.; Maeda, K.;Yamada, T. *Mater. Sci. Forum* **1997**, *239*−*241*, 663.
(6) Miura, K.; Yamada, T.; Ishikawa, M.; Okita, S. *Appl. Surf. Sci.* **1999**, *140*, 415.
(7) Gravil, P. A.; Devel, M.; Lambin, Ph.; Bouju, X.; Grard, Ch.; Lucas, A. A. *Phys. Rev.* **1996**, *B53*, 1622.
(8) Ishikawa, M.; Okita, S.; Minami, N.; Miura, K. *Surf. Sci.* **2000**, *445*, 488.
(9) Fogden, A.; White, L. R. *J. Colloid Interface Sci.* **1990**, *138*, 414.
(10) The frictional coefficients for both loading forces of 0nN and −9nN are together estimated to be about 1.

NL0055308