

Title	C_<70> close-packed surfaces and single molecule void-formation by local electric field through a scanning tunneling microscope tip
Author(s)	Ohta, Yohei; Mitsuhashi, Ryoji; Nouchi, Ryo; Fujiwara, Akihiko; Hino, Shojun; Kubozono, Yoshihiro
Citation	Applied Physics Letters, 94: 043107-1-043107-3
Issue Date	2009-01-27
Type	Journal Article
Text version	publisher
URL	<a href="http://hdl.handle.net/10119/7866">http://hdl.handle.net/10119/7866</a>
Rights	Copyright 2009 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in Yohei Ohta, Ryoji Mitsuhashi, Ryo Nouchi, Akihiko Fujiwara, Shojun Hino, and Yoshihiro Kubozono, Applied Physics Letters, 94, 043107 (2009) and may be found at <a href="http://link.aip.org/link/?APPLAB/94/043107/1">http://link.aip.org/link/?APPLAB/94/043107/1</a>
Description	

## C<sub>70</sub> close-packed surfaces and single molecule void-formation by local electric field through a scanning tunneling microscope tip

Yohei Ohta,<sup>1</sup> Ryoji Mitsuhashi,<sup>1</sup> Ryo Nouchi,<sup>2</sup> Akihiko Fujiwara,<sup>3</sup> Shojun Hino,<sup>4</sup> and Yoshihiro Kubozono<sup>1,a)</sup>

<sup>1</sup>Research Laboratory for Surface Science, Okayama University, Okayama 700-8530, Japan

<sup>2</sup>WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

<sup>3</sup>Japan Advanced Institute of Science and Technology, Ishikawa 923-1192, Japan

<sup>4</sup>Department of Materials Science and Biotechnology, Ehime University, Matsuyama 790-8577, Japan

(Received 24 November 2008; accepted 5 January 2009; published online 27 January 2009)

A C<sub>70</sub> close-packed surface was formed by a heating of the Si surface, which is covered with C<sub>70</sub> molecules. The close-packed surface is assigned to high-temperature hexagonal close-packed phase. The stability of C<sub>70</sub> close-packed surface and formation of nanometer scale structures are studied by the application of local electric field to the close-packed surface. An application of local electric field from scanning tunneling microscope tip to the C<sub>70</sub> close-packed surface caused molecular scale evaporation. The application of local electric field near strain in the surface produced a very large void by an evaporation of more than 20 of C<sub>70</sub> molecules. © 2009 American Institute of Physics. [DOI: 10.1063/1.3075959]

Fullerenes are suitable molecules for studies with scanning tunneling microscopy (STM) because the molecular size, ~1 nm, is large enough to observe with standard STM equipments. Furthermore, fullerenes are of interests from view of nanoscale manipulation since their arrangements/orientations in bulk crystals can be easily controlled by various perturbations such as heat, light, pressure, and electric field.<sup>1</sup> The growth of C<sub>60</sub> and metal endohedral fullerenes on Si(111)-(7×7) and Si(100)-(2×1) surfaces is described as Stranski–Krastanov type.<sup>1–3</sup> On the other hand, the growth of La<sub>2</sub>@C<sub>80</sub> on hydrogen-terminated Si(100)-(2×1) surface is Volmer–Weber type.<sup>4</sup> Thus, the growth mechanism of fullerene molecules possesses diversity based on a combination of fullerene molecule and substrate.

We recently reported a formation of dark spot by removal of C<sub>60</sub> molecule from the close-packed surface by means of hole/electron injection from STM tip to the surface.<sup>5</sup> The hole/electron injection to C<sub>60</sub> molecule adjacent to the dark spot also enabled ones to move the dark spots. Furthermore, the hole/electron injection to close-packed surface of C<sub>60</sub> also induced a nanoscale chemical reaction to form C<sub>60</sub> polymer ring.<sup>6</sup> Thus, C<sub>60</sub> close-packed surface can provide a stage available for nanoscale chemical reactions as well as formations of nanoscale structures. In this letter, we report STM studies for C<sub>70</sub> molecules on Si(111)-(7×7) surface in order to clarify the nanoscale structures as well as nanoscale chemical reactions of C<sub>70</sub> molecules. Since the STM studies of C<sub>70</sub> are so far limited to those on Si(100)-(2×1) surface for Si substrate,<sup>1,7,8</sup> the growth and formation of C<sub>70</sub> close-packed layer on Si(111)-(7×7) are of interests from view of surface science and technology. Furthermore, an evaporation of C<sub>70</sub> molecules has been achieved by an application of local electric field from STM tip to C<sub>70</sub> close-packed surface.

The well-defined Si(111)-(7×7) surface was formed by the procedure described elsewhere.<sup>9</sup> The C<sub>70</sub> molecules were

deposited on the Si(111)-(7×7) surface by a thermal deposition under  $9 \times 10^{-11}$  Torr, and the temperature of Si substrate was precisely controlled in individual steps for depositions. The STM images were recorded by an observation of the constant current  $I_t$  of 0.2 nA at sample voltage  $V_s$  of 2 V under  $10^{-11}$  Torr at 295 K. The W tip was used for the STM measurement.

The STM image of C<sub>70</sub> molecules on Si(111)-(7×7) surface is shown in Fig. 1(a). 78% of C<sub>70</sub> molecules are adsorbed on A site shown in Fig. 1(b). The A site is surrounded by three Si adatoms with dangling bonds, and a dangling bond exists at the center of the site, i.e., on rest atom. Therefore, the strong chemical bonds are expected to

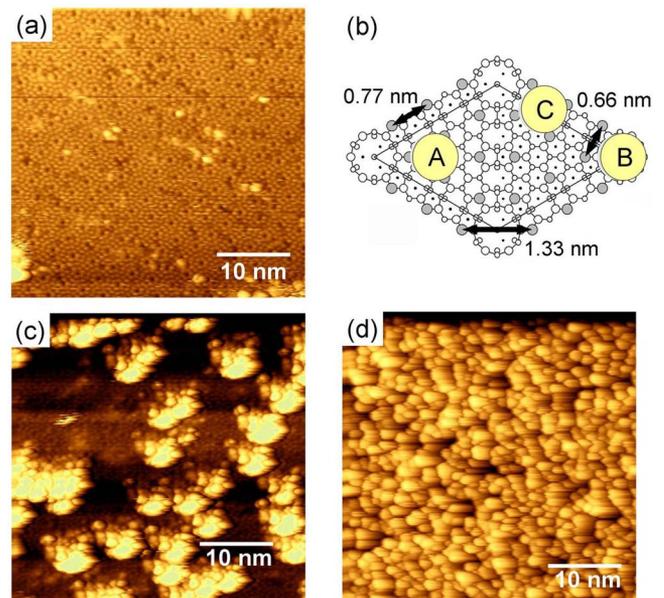


FIG. 1. (Color online) (a) STM image of C<sub>70</sub> molecules on Si(111)-(7×7) surface. Less than 0.1 ML of C<sub>70</sub> molecules are adsorbed. (b) Schematic representation of Si(111)-(7×7) surface. STM images of (c) ~0.5 ML and (d) ~2 ML of C<sub>70</sub> on Si(111)-(7×7) surface.

<sup>a)</sup>Electronic mail: kubozono@cc.okayama-u.ac.jp.

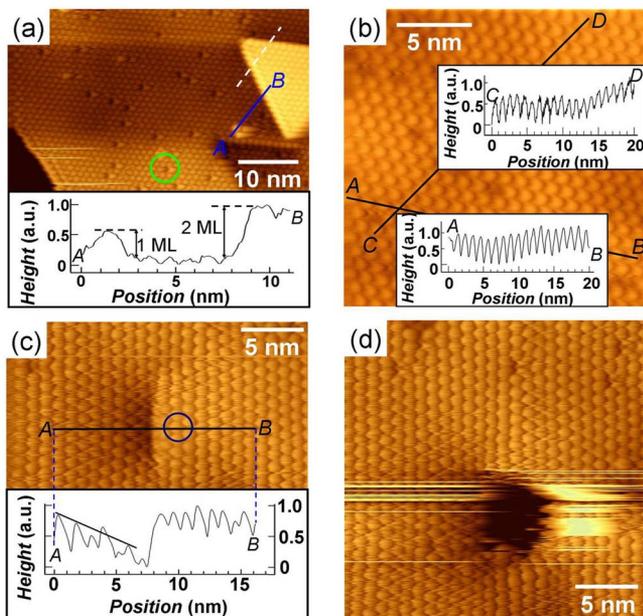


FIG. 2. (Color online) (a) STM image of close-packed surface of  $C_{70}$ . Dim spot is shown by circle and dashed line shows the alignment of  $C_{70}$  spots. Line profile of A–B is shown in the inset in (a). (b) High resolution STM image of  $C_{70}$  close-packed surface; line profiles of A–B and C–D are shown in the insets in (b). (c) STM image of  $C_{70}$  close-packed surface with strain; line profile of A–B is shown in the inset in (c). (d) STM image of  $C_{70}$  close-packed surface with a very large dark spot after electron injection; injection point is shown by circle in (c).

be formed between  $C_{70}$  and Si atoms at the A site. 4% of  $C_{70}$  molecules are adsorbed on B-site [Fig. 1(b)], which is termed “corner hole.” Furthermore, 18% of  $C_{70}$  molecules are adsorbed on C-site, which is termed “dimer line.” The fraction for  $C_{70}$  adsorption in A site is consistent with those, 72%–80%, for  $C_{60}$ , Dy@ $C_{82}$ , and Ce@ $C_{82}$ .<sup>3,9,10</sup> However, the fractions for B and C sites (4% for B and 18% for C) are not consistent with those for  $C_{60}$  (13% for B and 7% for C),<sup>10</sup> but consistent with those for M@ $C_{82}$  (7%–9% for B and 17%–19% for C).<sup>3,9</sup> The low fraction of 4% for adsorption of  $C_{70}$  in B site may be explained by an assumption that the  $C_{70}$  molecules are adsorbed with the long axis (diameter of 1.2 nm) being parallel to Si surface and  $C_{70}$  cannot be deeply trapped into the corner hole, in the same manner as M@ $C_{82}$ .<sup>3,9</sup>

As seen from Fig. 1(c), the aggregates of  $C_{70}$  molecules are observed in the STM image of  $\sim 0.5$  monolayer (ML) of  $C_{70}$ , implying that  $C_{70}$  molecules prefer to form islands on Si surface. Such an island formation was not observed for  $C_{60}$  on Si(111)-(7 $\times$ 7) surface. Thus, the growth mechanism of  $C_{70}$  is not Stranski–Krastanov but Volmer–Weber type. Since  $C_{70}$  has a larger polarizability than  $C_{60}$ , the stronger intermolecular interaction in  $C_{70}$  than  $C_{60}$  can be expected owing to the induced dipole. This may lead to the aggregation of  $C_{70}$ , i.e., formation of islands. The STM image of  $\sim 2$  ML of  $C_{70}$  molecules are shown in Fig. 1(d). The Si surface is densely covered with  $C_{70}$  molecules.

The  $C_{70}$  molecules were subsequently deposited onto the Si surface covered with  $\sim 2$  ML of  $C_{70}$  molecules [Fig. 1(d)] heated to 373 K, and the surface was annealed at 373–393 K for 12 h after the deposition. In this process, the close-packed surface of  $C_{70}$  was observed [Fig. 2(a)]. Here it should be noted that the close-packed surface is not directly

bound to Si surface but a few  $C_{70}$  layers under the surface is formed. On the other hand, the  $C_{70}$  close-packed surface was not formed but some islands of  $C_{70}$  were observed by STM (not shown) without postannealing after the deposition. The STM image [Fig. 2(a)] showed an existence of wider  $C_{70}$  close-packed surface than  $50 \times 50$  nm<sup>2</sup> and a bright triangle  $C_{70}$  close-packed layer is formed on the wide close-packed surface. Dim spots, as shown by circle, are also observed, which can be assigned to the  $C_{70}$  polymers. The difference in height between bright triangle close-packed surface and the wide close-packed surface corresponds to 2 ML of  $C_{70}$  as seen from the line profile [inset in Fig. 2(a)]. Furthermore, the spots on the bright triangle close-packed surface are completely aligned along the spots of the wide close-packed surface, as is shown by the dashed line in Fig. 2(a). This suggests that the close packed-surface is formed by the ‘ABAB’ stacking (not ‘ABCABC’ stacking) because the arrangement of  $C_{70}$  molecule separated by 2 ML is exactly the same.

High resolution STM image of  $C_{70}$  close-packed layer is shown in Fig. 2(b). From the line profile, the  $C_{70}$ – $C_{70}$  distance was estimated to be  $1.06 \pm 0.04$  nm for A–B line and  $1.03 \pm 0.06$  nm for C–D line. The distance of 1.03–1.06 nm is consistent with those in high-temperature crystal phases,<sup>1,11,12</sup> the  $C_{70}$ – $C_{70}$  distances are 1.058 nm in high-temperature hexagonal close-packed (hcp) phase (430 K) and 1.054 nm in face-centered cubic phase (383 K). The  $C_{70}$  molecules freely rotate in these phases, which are stably maintained above room temperature,<sup>11,12</sup> while the phases are also reported to be often maintained down to room temperature.<sup>13</sup> On the other hand, in low temperature phases such as distorted hcp and rhombohedral (rh), the intermolecular distance along the short axis of  $C_{70}$  molecule should be observed in STM because the molecular rotation freezes and the long axis of  $C_{70}$  molecule is oriented along [001] in distorted hcp phase and [111] in rh phase.<sup>1,13</sup> The  $C_{70}$ – $C_{70}$  distance observed by STM can be predicted for the low-temperature phases to be 1.01 nm from the lattice constants determined for these phases.<sup>11–13</sup> The  $C_{70}$ – $C_{70}$  distance observed actually by STM, 1.03–1.06 nm, is larger than that predicted for low temperature phases, showing that the STM image [Fig. 2(b)] is unambiguously assigned to high temperature phase. Further, by a consideration of the fact that this close-packed surface is consisted of “ABAB” stacking, we can assign this surface structure to high-temperature hcp phase.

The STM image of  $C_{70}$  close-packed surface often showed the structure with strain as seen from Fig. 2(c). Since the structures with strain were hardly observed in the  $C_{60}$  close-packed surface,<sup>5,6</sup> it was suggested that the  $C_{70}$  close-packed structure is unstable in comparison with  $C_{60}$  close-packed surface. This result can be reasonably understood because of lower symmetry of  $C_{70}$  ( $D_{5h}$ ) than  $C_{60}$  ( $I_h$ ); the anisotropic  $C_{70}$  shape is difficult to rotate freely to form close-packed layer and it prefers anisotropic rotation. The line profile for the area around strain is shown in the inset in Fig. 2(c). This line profile clearly shows a dislocation of  $C_{70}$  layer in the area of strain, i.e., the  $C_{70}$  layer in the left side slips under the layer in the right side.

We tried to inject electrons from STM tip fixed at the position defined by  $V_s=2$  V and  $I_t=1.5$  nA to the  $C_{70}$  close-packed surface. This position is closer to the surface than that for the STM-image observation ( $V_s=2$  V and  $I_t$

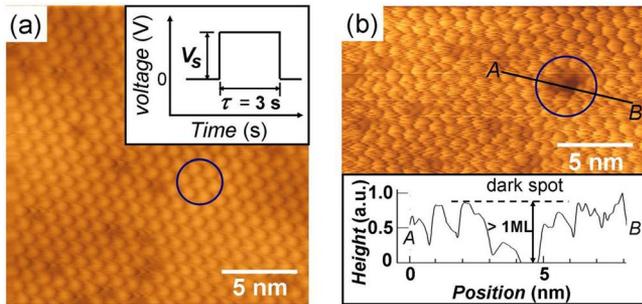


FIG. 3. (Color online) (a) STM image of close-packed surface of  $C_{70}$ . Pulse shape used for electron injection is shown in the inset in (a). (b) STM image of  $C_{70}$  close-packed surface with dark spot formed by electron injection; the injection point is shown by circle in (a). The line profile of A–B is shown in the inset in (b).

$=0.2$  nA). The shape of the applied bias-voltage pulse is schematically shown in the inset in Fig. 3(a). The STM images before/after electron injection are shown in Figs. 3(a) and 3(b), respectively. Figure 3(a) shows  $C_{70}$  close-packed surface without dark spots, and the electrons are injected from the STM tip to the position shown by circle, at the  $V_s$  pulse of 3 V and pulse width (time)  $\tau$  of 3 s. The dark spot was observed at the part where the electrons were injected into the close-packed surface, as seen from Fig. 3(b). The dark spot can be assigned to the void formed by a removal of  $C_{70}$  molecule on the basis of the line profile [inset in Fig. 3(b)] of the close packed surface; the line rapidly dropped by more than 1 ML in the area of dark spot. This result is consistent with that observed after electron/hole injection for the  $C_{60}$  close-packed surface. Thus, the application of  $V_s$  pulse can cause the evaporation of  $C_{70}$  molecule at single molecule scale.

When the electrons were injected to the position near the strain in the  $C_{70}$  close-packed surface, the large dark spots were formed around the strain [Fig. 2(d)]; the STM image of the  $C_{70}$  close-packed surface with strain before the electron injection is shown in Fig. 2(c). Here, it should be noticed that the fixed position of the STM tip ( $V_s=2$  V and  $I_t=1.5$  nA), applied  $V_s$  (2.8 V) and  $\tau$  (3 s) for electron injection are almost the same as those used for the single molecule evaporation [Fig. 3(b)]. Actually, more than 20 of  $C_{70}$  molecules were removed around the strain by electron injection into the position near the strain. As a consequence, an application of local electric field to the close-packed surface may be avail-

able to obtain an indication of instability of surface in nanometer scale because the electric field application to the unstable area evaporates a number of molecules.

In conclusion, the deposition of  $C_{70}$  molecules resulted in Volmer–Weber-type growth for Si(111)-(7 $\times$ 7) surface, and by an annealing of the surface at 373–393 K, the  $C_{70}$  close-packed surface was formed over 50 $\times$ 50 nm<sup>2</sup>. This phase could be assigned to high-temperature hcp phase. The application of local electric field to the  $C_{70}$  close-packed surface from STM tip resulted in evaporation of molecules. Precise control of local electric field achieved a single molecule evaporation of  $C_{70}$ . The instability of close-packed surface of  $C_{70}$  was supported by the existence of strains and the formation of large void around strain by application of local electric field. This study will open a way to an application of their voids toward nanometer scale mold as well as a clarification of basic behaviors of  $C_{70}$  molecules in nanometer scale.

This work was in part supported by a Grant-in-Aid (20045012) from MEXT, Japan.

- <sup>1</sup>M. S. Drreselhaus, G. Drreselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
- <sup>2</sup>X.-D. Wang, Q. K. Xue, T. Hashizume, H. Shinohara, Y. Nishina, and T. Sakurai, *Phys. Rev. B* **48**, 15492 (1993).
- <sup>3</sup>S. Fujiki, Y. Kubozono, Y. Rikiishi, and T. Urisu, *Phys. Rev. B* **70**, 235421 (2004).
- <sup>4</sup>A. Taninaka, K. Shino, T. Sugai, S. Heike, Y. Terada, T. Hashizume, and H. Shinohara, *Nano Lett.* **3**, 337 (2003).
- <sup>5</sup>S. Fujiki, K. Masunari, R. Nouchi, H. Sugiyama, Y. Kubozono, and A. Fujiwara, *Chem. Phys. Lett.* **420**, 82 (2006).
- <sup>6</sup>R. Nouchi, K. Masunari, T. Ohta, Y. Kubozono, and Y. Iwasa, *Phys. Rev. Lett.* **97**, 196101 (2006).
- <sup>7</sup>X.-D. Wang, Q. Xue, T. Hashizume, H. Shinohara, Y. Nishina, and T. Sakurai, *Phys. Rev. B* **49**, 7754 (1994).
- <sup>8</sup>X.-D. Wang, Q. Xue, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina, and T. Sakurai, *Appl. Surf. Sci.* **76**, 334 (1994).
- <sup>9</sup>S. Fujiki, Y. Kubozono, T. Hosokawa, T. Kanbara, A. Fujiwara, Y. Nonogaki, and T. Urisu, *Phys. Rev. B* **69**, 045415 (2004).
- <sup>10</sup>H. Wang, C. Zeng, Q. Li, B. Wang, J. Yang, J. G. Hou, and Q. Zhu, *Surf. Sci.* **442**, L1024 (1999).
- <sup>11</sup>G. B. M. Vaughan, P. A. Heiney, D. E. Cox, J. E. Fischer, A. R. McGhie, A. L. Smith, R. M. Strongin, M. A. Cichy, and A. B. Smith III, *Chem. Phys.* **178**, 599 (1993).
- <sup>12</sup>M. A. Verheijen, H. Meekes, G. Meijer, P. Bennema, J. L. de Boer, S. van Smaalen, G. van Tendeloo, S. Amelinckx, S. Muto, and J. van Landuyt, *J. Chem. Phys.* **166**, 287 (1992).
- <sup>13</sup>K. Prassides, *Phys. Scr.* **T49B**, 735 (1993).