C_{70} close-packed surfaces and single molecule void-formation by local electric field through a scanning tunneling microscope tip

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A C_{70} close-packed surface was formed by a heating of the Si surface, which is covered with C_{70} molecules. The close-packed surface is assigned to high-temperature hexagonal close-packed phase. The stability of C_{70} 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_{70} 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_{70} 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.[1] The growth of C_{60} and metal endohedral fullerenes on Si(111)-(7×7) and Si(100)-(2×1) surfaces is described as Stranski–Krastanov type.[1–3] On the other hand, the growth of $La_2@C_{80}$ on hydrogen-terminated Si(100)-(2×1) surface is Volmer–Weber type.[4] 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_{60} molecule from the close-packed surface by means of hole/electron injection from STM tip to the surface.[5] The hole/electron injection to C_{60} 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_{60} also induced a nanoscale chemical reaction to form C_{60} polymer ring.[6] Thus, C_{60} 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_{70} molecules on Si(111)-(7×7) surface in order to clarify the nanoscale structures as well as nanoscale chemical reactions of C_{70} molecules. Since the STM studies of C_{70} are so far limited to those on Si(100)-(2×1) surface for Si substrate,[1,7,8] the growth and formation of C_{70} close-packed layer on Si(111)-(7×7) are of interests from view of surface science and technology. Furthermore, an evaporation of C_{70} molecules has been achieved by an application of local electric field from STM tip to C_{70} close-packed surface.

The well-defined Si(111)-(7×7) surface was formed by the procedure described elsewhere.[9] The C_{70} molecules were deposited on the Si(111)-(7×7) surface by a thermal deposition under 9×10^{-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_{70} molecules on Si(111)-(7×7) surface is shown in Fig. 1(a). 78% of C_{70} 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

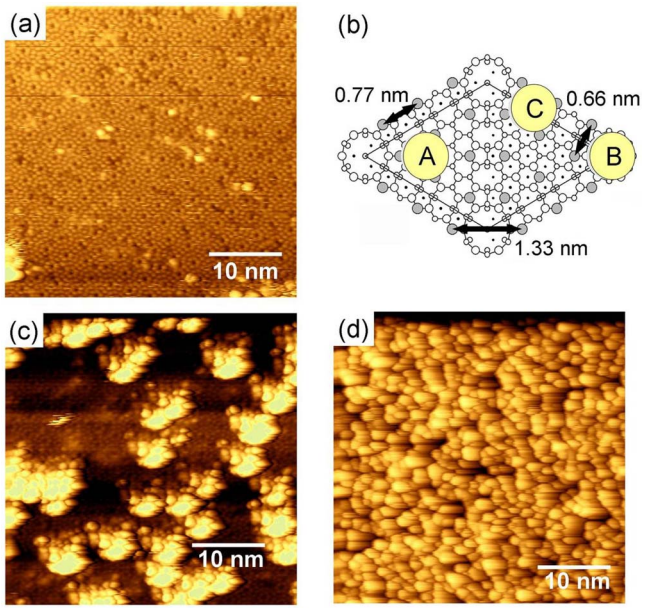

FIG. 1. (Color online) (a) STM image of C_{70} molecules on Si(111)-(7×7) surface. Less than 0.1 ML of C_{70} molecules are adsorbed. (b) Schematic representation of Si(111)-(7×7) surface. STM images of (c) ~0.5 ML and (d) ~2 ML of C_{70} on Si(111)-(7×7) surface.

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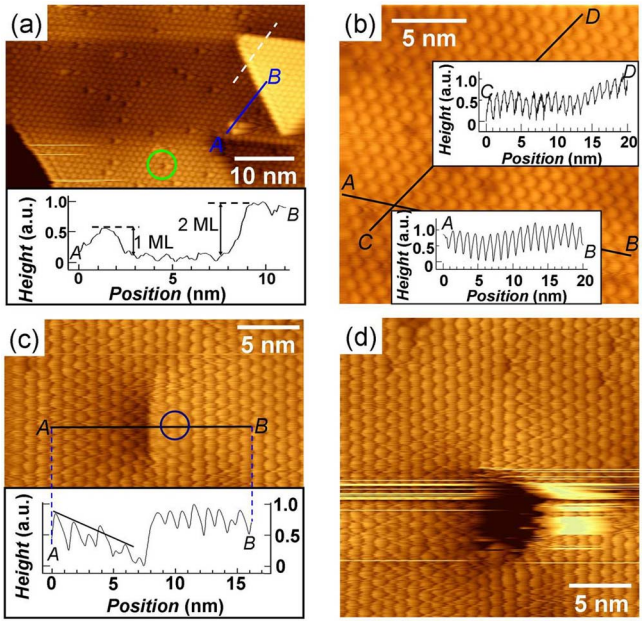

FIG. 2. (Color online) (a) STM image of close-packed surface of C_{70}. Dim spot is shown by circle and dashed line shows the alignment of C_{70} spots. Line profile of A–B is shown in the inset in (a). (b) High resolution STM image of C_{70} close-packed surface; line profiles of A–B and C–D are shown 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 $Ce@C_{82}$.[3,9,10] 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),[10] but consistent with those for $M@C_{82}$ (7%–9% for B and 17%–19% for C).[3,9] 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 $M@C_{82}$.[3,9]

As seen from Fig. 1(c), the aggregates of C_{70} molecules are observed in the STM image of ~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)-(7×7) 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 ~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 ~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 50×50 nm^2 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 ± 0.04 nm for A–B line and 1.03 ± 0.06 nm for C–D line. The distance of 1.03–1.06 nm is consistent with those in high-temperature crystal phases;[1,11,12] 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,[11,12] while the phases are also reported to be often maintained down to room temperature.[13] 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.[1,13] 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.[11–13] 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,[5,6] 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

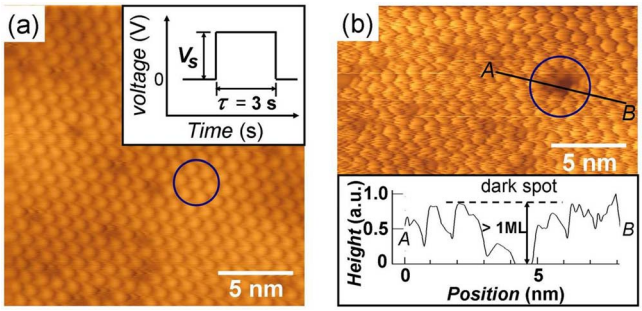

FIG. 3. (Color online) (a) STM image of close-packed surface of C_{70}. Pulse shape used for electron injection is shown in the inset in (a). (b) STM image of C_{70} close-packed surface with dark spot formed by electron injection; the injection point is shown by circle in (a). The line profile of A–B 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) τ 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 τ (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 available 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)-(7×7) surface, and by an annealing of the surface at 373–393 K, the C_{70} close-packed surface was formed over 50×50 nm^2. 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.

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[1]M. S. Drreselhaus, G. Drreselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
[2]X.-D. Wang, Q. K. Xue, T. Hashizume, H. Shinohara, Y. Nishina, and T. Sakurai, Phys. Rev. B **48**, 15492 (1993).
[3]S. Fujiki, Y. Kubozono, Y. Rikiishi, and T. Urisu, Phys. Rev. B **70**, 235421 (2004).
[4]A. Taninaka, K. Shino, T. Sugai, S. Heike, Y. Terada, T. Hashizume, and H. Shinohara, Nano Lett. **3**, 337 (2003).
[5]S. Fujiki, K. Masunari, R. Nouchi, H. Sugiyama, Y. Kubozono, and A. Fujiwara, Chem. Phys. Lett. **420**, 82 (2006).
[6]R. Nouchi, K. Masunari, T. Ohta, Y. Kubozono, and Y. Iwasa, Phys. Rev. Lett. **97**, 196101 (2006).
[7]X.-D. Wang, Q. Xue, T. Hashizume, H. Shinohara, Y. Nishina, and T. Sakurai, Phys. Rev. B **49**, 7754 (1994).
[8]X.-D. Wang, Q. Xue, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina, and T. Sakurai, Appl. Surf. Sci. **76**, 334 (1994).
[9]S. Fujiki, Y. Kubozono, T. Hosokawa, T. Kanbara, A. Fujiwara, Y. Nonogaki, and T. Urisu, Phys. Rev. B **69**, 045415 (2004).
[10]H. Wang, C. Zeng, Q. Li, B. Wang, J. Yang, J. G. Hou, and Q. Zhu, Surf. Sci. **442**, L1024 (1999).
[11]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).
[12]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).
[13]K. Prassides, Phys. Scr. **T49B**, 735 (1993).