Structure transition of a C$_{60}$ monolayer on the Bi(111) surface

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The interfacial structures of C$_{60}$ molecules adsorbed on solid surfaces are essential for a wide range of scientific and technological processes in carbon-based nanodevices. Here, we report structural transitions of the C$_{60}$ monolayer on the Bi(111) surface studied via low-temperature scanning tunneling microscopy (STM). With an increase in temperature, the structure of the C$_{60}$ monolayer transforms from local-order structures to a (7$\sqrt{3} \times 7$) R0° superstructure, and then to a (11 × 11) R0° superstructure. Moreover, the individual C$_{60}$ molecules in different superstructures have different orientations. C$_{60}$ molecules adopt the 6:6 C–C bond and 5:6 C–C bond facing-up, mixed orientations, and hexagon facing-up in the local-order structure, (7$\sqrt{3} \times 7$) R0°, and (11 × 11) R0° superstructure, respectively. These results shed important light on the growth mechanism of C$_{60}$ molecules on solid surfaces.

Introduction

C$_{60}$ molecule, as a prototypical fullerene molecule, has attracted widespread attention due to its potential in endohedral fullerenes, photovoltaic devices, peapod nanotubes, and single-molecule transistors. A C$_{60}$ monolayer grown on solid surfaces is critical for understanding and controlling the interfacial properties of fullerene-derived electronic and photovoltaic devices. STM studies demonstrated that the C$_{60}$ monolayer on the solid surface exhibit a variety of lattice orientations such as the “in phase” (2$\sqrt{3} \times 2\sqrt{3}$) R30°, (7 × 7) R0° and (7$\sqrt{3} \times 7$) R0° superstructure. The individual molecules of fullerene and fulleride within a single domain display different orientations. In the complex orientational ordering (7 × 7) R0° structure, a 7-molecule C$_{60}$ cluster consists of a central molecule sitting atop of a gold atom and six tilted surrounding molecules. In the unit cell of the (7$\sqrt{3} \times 7$) R14.5° structure, 49 C$_{60}$ molecules adopt 11 different orientations. In the (2$\sqrt{3} \times 2\sqrt{3}$) R30° structure, all C$_{60}$ molecules are in the same orientation. The complex chiral motifs have been observed. In C$_{60}$ fulleride films, orientational ordering appears. Moreover, “bright” and “dim” molecules have been widely found in the C$_{60}$ monolayer. However, the “dim” molecules in superstructures reported so far arrange irregularly.

The structure of C$_{60}$ monolayers grown on the solid surface is not only related to C$_{60}$ molecules themselves but also the substrate. In the past reports, there have been a large number of investigation on the C$_{60}$ monolayer structures grown on numerous metals or semiconducting substrates, such as Ag, Au, Cu, Ge, C$_{60}$, or NaCl. However, few reports address the superstructure of C$_{60}$ molecules adsorbed on semi-metal substrates. It is found that thin films of organic molecules grown on a semi-metallic Bi(111) surface shows a lot of interesting phenomena, such as the ordered crystalline layer with the standing-up orientation of pentacene molecules, the chiral self-assembly of rubrene molecules, structural transitions in different monolayers of cobalt phthalocyanine films, and the Moire pattern in C$_{60}$ thin films.

In this study, we use Bi(111) as the substrate and studied the structure transition of the C$_{60}$ monolayer. C$_{60}$ molecules were deposited at 100 K form local-order structures. When the deposition temperature increased to room temperature, the local-order structures turn into a long-range ordered (7$\sqrt{3} \times 7$) R0° superstructure. After annealing at 400 K, the ordered superstructure transforms into the (11 × 11) R0° superstructure. These superstructures are different from the structures of the C$_{60}$ monolayer reported so far. Furthermore, the individual C$_{60}$ molecules in the local-order structure, (7$\sqrt{3} \times 7$) R20° and (11 × 11) R0° superstructure, show the 6:6 C–C bond and 5:6 C–C bond facing-up, mixed orientations, and hexagon facing-up, respectively. The 6:6 (5:6) C–C bond indicates the common side of two adjacent hexagons (pentagon and hexagon) in C$_{60}$ molecules.

Experimental

The experiments were conducted in an ultra-high vacuum low-temperature scanning tunneling microscope produced by Unisoku. The base pressure was kept at ~1.2 × 10$^{-10}$ Torr. An Si(111) substrate was continuously degassed at ~870 K for 8 h
with subsequent flashing to 1400 K for several seconds. The Bi(111) film was prepared by depositing 20 monolayers of bismuth atoms on a Si(111)-7 × 7 surface at room temperature with subsequent annealing at 400 K.\textsuperscript{26} C\textsubscript{60} molecules were deposited onto the Bi(111) surface by heating the tantalum cell to 700 K. The growth rate of C\textsubscript{60} molecules was about 0.4 monolayers per minute. All STM images were acquired with a tungsten tip in constant-current mode at liquid nitrogen temperature (78 K).

## Results and discussion

First, a small number of C\textsubscript{60} molecules were deposited onto the Bi(111) surface when the substrate was maintained at 100 K. Fig. 1(a) shows the atomic-resolution image of the hexagonal lattices of the Bi(111) thin film. The lattice constants of the Bi(111) surface are measured to be $a_1 = a_2 = 0.45 \pm 0.02$ nm, very close to the bulk value ($a = 0.454$ nm) in Bi crystals.\textsuperscript{36} Fig. 1(b) shows the isolated C\textsubscript{60} molecules on the Bi(111) surface presenting round protrusions. When reducing the bias voltage, the round protrusions are separated into two asymmetrical [Fig. 1(c)] or symmetrical [Fig. 1(d)] lobes, corresponding to the two different adsorption configurations, 5 : 6 C–C bond facing-up and 6 : 6 C–C bond facing-up, similar to C\textsubscript{60} molecules on Au(111).\textsuperscript{12} This indicates that there are two stable adsorption orientations of isolated C\textsubscript{60} molecules on the Bi(111) substrate, 6 : 6 C–C bond, and 5 : 6 C–C bond facing-up.

When the coverage increases, C\textsubscript{60} molecules form the close-packed hexagonal structure, as shown in Fig. 2. We noticed that all the C\textsubscript{60} molecules present a uniform height, except a few dim molecules (marked by green dotted circles). The brightness contrast in images stems from the different adsorption sites of C\textsubscript{60} molecules. It is well known that metal surfaces do not behave as rigid templates for the chemisorption of C\textsubscript{60} molecules, but may reconstruct substantially to accommodate the molecules.\textsuperscript{37} We speculate that Dim C\textsubscript{60} molecules are located at the vacancies of the Bi(111) substrate, originating from the reconstruction of the Bi(111) surface, similar to C\textsubscript{60} molecules on Au(111)\textsuperscript{38} and Cu(111).\textsuperscript{18}

According to the arrangement of bright and dim molecules, we can see some local-order structures, though there is a lack of long-range ordering. In Fig. 2(a), there is an (11 × 8) R0° local-order structure (marked by red parallelogram). The lattice directions of (11 × 8) R0° are along with the directions of Bi(111), and the measured lattice constants are 5.00 ± 0.02 nm and 3.64 ± 0.02 nm, corresponding to 11 and 8 times of the lattice constant of the Bi(111) surface. The lattice directions of Bi(111) were obtained on the surface, which was not covered with C\textsubscript{60} molecules. In another domain, shown in Fig. 2(b), the local-order structure is mixed with three types of structures, namely (11 × 8) R0° (red quadrilateral), (11 × 11) R0° (white quadrilateral), and (10 × 8) R10° (blue quadrilateral). In particular, we noticed that C\textsubscript{60} molecules exhibit almost the same orientation in a single domain, and most of the individual C\textsubscript{60} molecules in the local-order structure adopt two favorite orientations (6 : 6 C–C bond and 5 : 6 C–C bond facing-up) as the isolated molecules on Bi(111). For example, most of the molecules shown in Fig. 2(a) present two symmetrical lobes, corresponding to C\textsubscript{60} molecules with a 6 : 6 C–C bond facing up. However, in Fig. 2(b), the molecules present two asymmetric lobes, corresponding to the 5 : 6 C–C bond facing up. We suggest that the formation of a local-order structure is due to the low-temperature growth. Because of the low kinetic energy of C\textsubscript{60} molecules at 100 K, molecular mobility is not high enough to form a long-range ordered superstructure. The C\textsubscript{60} molecules adsorbed on Bi(111) adopt their preferred orientations (6 : 6 C–C bond and 5 : 6 C–C bond facing up), similar to the isolated molecules adsorbed on the substrate. This proves the strong molecule–substrate interaction in the local-order structure.

To investigate the influence of temperature on the structure, we deposited C\textsubscript{60} molecules on Bi(111) at room temperature. It

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**Fig. 1** The initial stage of C\textsubscript{60} molecules adsorbed on the Bi(111) surface. (a) Hexagonal lattices of the Bi(111) surface, 5 nm × 5 nm, −0.1 V. The unit cell is marked with a red box and the orange arrows indicate the directions of the Si(111) substrate. (b) Isolated C\textsubscript{60} molecules adsorbed on Bi(111), 20 nm × 20 nm, 2.2 V. (c) STM image of an isolated C\textsubscript{60} molecule with two asymmetrical lobes corresponding to the 5 : 6 C–C bond facing up, 1.3 nm × 1.3 nm, 400 mV. (d) STM image of an isolated C\textsubscript{60} molecule with two symmetrical lobes corresponding to the 6 : 6 C–C bond facing up, 1.3 nm × 1.3 nm, 200 mV.
is found that C₆₀ molecules aggregate into a hexagonal structure, the same as C₆₀ molecules in the local-order structure. However, the local-order structures, originating from the dim and bright molecules, turn into a long-range ordered (O₂₃/ₐC₂O₉₃) R₂₀/C₁₄ superstructure [Fig. 3(a)]. This superstructure is different from the structures of the C₆₀ monolayer reported so far. There is a misorientation angle of 20° between the lattice directions of the C₆₀ monolayer and the Bi(111) surface. The measured lattice constants of (O₂₃/ₐC₂O₉₃) R₂₀/C₁₄ are \( b_1 = b_2 = 4.38 \pm 0.02 \text{ nm} \), agreeing well with \( \sqrt{93} \text{ times} \) the lattice constant of Bi(111) (0.45 nm). Fig. 3(b) shows the schematic of the (O₂₃/ₐC₂O₉₃) R₂₀/C₁₄ superstructure. Based on the lattice constant of the Bi(111) substrate, the lattice vectors of the (O₂₃/ₐC₂O₉₃) R₂₀/C₁₄ superstructure can be expressed as following matrices:

\[
\begin{pmatrix}
    b_1 \\
    b_2
\end{pmatrix} = \begin{pmatrix} 11 & -4 \\ 4 & 7 \end{pmatrix} \begin{pmatrix} a_1 \\
    a_2
\end{pmatrix}
\]

This ordered superstructure implies two things: first, the intermolecular interaction is getting stronger than that in the local-order structure prepared at low temperature (100 K). Second, the molecule–substrate interaction is also strong since the orientations of the C₆₀ superstructure are commensurate with those of the substrate. Furthermore, we can clearly see that individual C₆₀ molecules adopt various orientations, rather than the favorite orientations as C₆₀ molecules in the local-order structure. As shown in the high-resolution STM image [Fig. 3(c)], C₆₀ molecules in (O₂₃/ₐC₂O₉₃) R₂₀/C₁₄ present various shapes, such as two asymmetric lobes (white circle), two symmetrical lobes (yellow circle), and three lobes (blue circle).

Fig. 2  Local-order structure in the monolayer C₆₀ grown at a low temperature (~100 K). (a) Four unit cells of the (11 \times 8) R₀° superstructure appeared in the C₆₀ monolayer, 20 nm \times 20 nm, −1.2 V. The dim C₆₀ molecules, located at the hollow position of Bi(111), are marked by the green dotted circles. (b) The mixture of three types of superstructures, 20 nm \times 20 nm, −0.9 V. The red, white, and blue unit cells correspond to the superstructure (11 \times 8) R₀°, (11 \times 11) R₀°, and (10 \times 8) R₁₀°.

Fig. 3  (a) The STM image of the (\sqrt{93} \times \sqrt{93}) R₂₀° superstructure, 15 nm \times 15 nm, −1.2 V. (b) Schematic model of the (\sqrt{93} \times \sqrt{93}) R₂₀° superstructure. The yellow balls and black hollow balls represent Bi atoms and C₆₀ molecules. (c) High-resolution STM image of the (\sqrt{93} \times \sqrt{93}) R₂₀° superstructure, 10 nm \times 10 nm, −1.0 V. The individual molecules exhibit different orientations, such as 5 : 6 C–C bond, 6 : 6 C–C bond, and hexagon facing up, marked by white, yellow, and blue solid circles, respectively.
corresponding to the 5:6 C–C bond, 6:6 C–C bond, and hexagon facing up. The diversity of C60 molecular orientations is due to the enhancement of intermolecular interaction in the (5/3 × 5/3) R20° superstructure. The intermolecular interaction enables C60 molecules to overcome the molecule–substrate interaction and adopt other orientations, and then make the (5/3 × 5/3) R20° superstructure stable.

When annealed at 400 K for about 20 min, C60 molecules still revealed a hexagonal lattice, while the superstructure transformed from (5/3 × 5/3) R20° into (11 × 11) R0° superstructure [Fig. 4(a)], indicating that (11 × 11) R0° is more stable than (5/3 × 5/3) R20°. The lattice directions of (11 × 11) R0° are along the directions of the Bi(111) substrate, and the lattice constants are c1 = c2 = 5.00 ± 0.02 nm [Fig. 4(b)], corresponding to 11 times of the lattice constant of Bi(111). Fig. 4(d) is the fast Fourier transform (FFT) image of the (11 × 11) R0° superstructure, where the spots marked by red and green circles correspond to C60 hexagonal lattices and the (11 × 11) R0° superstructure. In the FFT image, the spots of the superstructure are clearly visible, though they are dimmer than the spots of C60 hexagonal lattices, implying that the (11 × 11) R0° superstructure has long-range order. The schematic model of (11 × 11) R0° is shown in Fig. 4(c). From STM images, the (11 × 11) R0° superstructure seems to have the same structure as the reported structure attributed to a Moire’ pattern in ref. 36. However, in our experiment, the (11 × 11) R0° superstructure is transformed from the (5/3 × 5/3) R20° superstructure and have no relationship with the Moire’ pattern. From the close-up view of the (11 × 11) R0° superstructure in Fig. 4(e), it is found that all the C60 molecules reveal a unified three-lobe structure, corresponding to the hexagon facing up, different from favorite orientations in the local-order structure and mixed orientations in (5/3 × 5/3) R20°. With an increase in temperature, the superstructure of the C60 monolayer changes from local order to long-range order and C60 molecules are re-orientated. This is because the thermal diffusivities of C60 molecules and Bi atoms increase with the increase in temperature, which is conducive to the formation of a more orderly and stable superstructure.

**Conclusions**

In summary, the structure of C60 molecules on Bi(111) changes with temperature variation. When deposited on the Bi(111) surface at 100 K, C60 molecules form local-order structures, and the molecules in local-order structures adopt their favorite orientations. As the deposition temperature increases to room temperature, the local-order structures turn into a long-range ordered (5/3 × 5/3) R20° superstructure. The orientations of C60 molecules in (5/3 × 5/3) R20° superstructures are diverse. After annealing at 400 K for about 20 min, the C60 film exhibits a (11 × 11) R0° superstructure, and all C60 molecules in this superstructure take the unified orientation, hexagon facing-up. The appearance of numerous superstructures and the molecular orientations in superstructures is due to the change in the
thermal diffusivity of C\textsubscript{60} molecules and Bi atoms at different temperatures.

**Conflicts of interest**

There are no conflicts to declare.

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