Scanning tunneling microscopy of Dy@C$_{82}$ and Dy@C$_{60}$ adsorbed on Si(111)-(7×7) surfaces

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Dy@C$_{82}$ and Dy@C$_{60}$ adsorbed on Si(111)-(7×7) surface are investigated by scanning tunneling microscopy (STM) at 295 K. The Dy@C$_{82}$ molecules in the first layer are adsorbed on the Si(111)-(7×7) surface without formation of islands and nucleation, and the internal structure of the Dy@C$_{82}$ molecule is first observed on the surface at 295 K. The average heights of the Dy@C$_{82}$ molecules in the first and second layers are estimated to be 7.2 and 10.8 Å, respectively, by STM. These results suggest strong interactions between the Si atoms and the Dy@C$_{82}$ molecules in the first layer. The STM image reveals that the Dy@C$_{60}$ molecule is nearly spherical, showing that the metal endohedral C$_{60}$ possesses a cage-form structure.

I. INTRODUCTION

Metallofullerene molecules have attracted special attention from physicists and chemists owing to their unique structures.[1] Furthermore, the metallofullerenes have been notable as research subjects in nanometer-scale science because the molecular size is ∼1 nm and unique electronic structures are expected at molecular and cluster levels. Scanning tunneling microscopy (STM) is a powerful technique for studying the structures and electronic properties of metallofullerenes at the nanometer scale. Recently, the adsorption characteristics of metallofullerenes on semiconductor surfaces have been studied extensively by STM.[2–6]

A STM image of Sc$_2$@C$_{84}$ adsorbed on Si(100)-(2×1) surface was first reported by Shinohara *et al.* and showed a nearly spherical structure of the Sc$_2$@C$_{84}$ molecule.[2] The first layer of Sc$_2$@C$_{84}$ was not ordered, owing to strong interactions between the surface and the molecules. Further, the Sc$_2$@C$_{84}$ molecules in the first layer possessed no preferential adsorption positions such as terrace edges and defect sites on the Si(100)-(2×1) surface, and showed no specific nucleation. The third layer of Sc$_2$@C$_{84}$ on the Si(100)-(2×1) surface was ordered to form a hexagonally close-packed array, and the nearest-neighbor distance d between the molecules was 11.7 Å, which is slightly smaller than that (12.1 Å) in a close-packed C$_{84}$ array.[7] This implies that the third layer is dominated by van der Waals interactions between the Sc$_2$@C$_{84}$ molecules.

The structure and electronic properties of Dy@C$_{82}$ have been studied by x-ray powder diffraction, x-ray absorption near edge spectroscopy (XANES), and electric resistivity ρ measurements.[8–10] The x-ray diffraction pattern for mixed crystals of Dy@C$_{82}$ isomers I and II at 298 K was indexed in a face-centered cubic (fcc) structure with a lattice constant a of 15.86(1) Å. XANES of a crystalline Dy@C$_{82}$ sample showed that the valence of Dy was +3. The temperature dependence of ρ for a Dy@C$_{82}$ thin film showed a semiconductorlike behavior with the gap energy E_g of 0.2 eV.

Studies of M@C$_{60}$ (M: metal atoms) have scarcely been carried out because of difficulties in obtaining macroscopic amounts of purified samples, although the structures and the expected physical properties such as molecular metals and superconductivity have attracted much interest from physicists and chemists. Recently, Dy@C$_{60}$ was extracted with aniline and purified by high-performance liquid chromatography.[11] XANES of Dy@C$_{60}$ revealed a valence of +3 for the Dy atom. The center frequency ω_0 of the $A_g(2)$ Raman peak for Dy@C$_{60}$ was 1450 cm^{-1}, also showing that the valence of Dy was +3. More recently, the electronic properties of La@C$_{60}$ and Ce@C$_{60}$ adsorbed on highly oriented pyrolytic graphite (HOPG) were studied by STM and scanning tunneling spectroscopy (STS).[4] An energy gap E_g of ∼0.3 eV was observed for Ce@C$_{60}$ by STS at room temperature, while a zero band gap was observed at room temperature for La@C$_{60}$, and the gap opened below 28 K.[4] In the present study, STM images of Dy@C$_{82}$ and Dy@C$_{60}$ molecules adsorbed on Si(111)-(7×7) surfaces are studied at 295 K, in order to clarify the structures and electronic properties at the nanometer scale. The adsorption patterns are observed from the STM images. The structures and electronic properties at the nanometer scale found by STM are compared with those found in the solid and in thin films.

II. EXPERIMENT

Sample preparation and purification of Dy@C$_{82}$ and Dy@C$_{60}$ are described elsewhere.[8,11] The Dy@C$_{82}$ sample used in the present study contained two isomers I and II with a molar ratio of 4:1. The Si(111) substrate was degassed by heating it at 600 °C for 12 h and flash annealing up to

1100 °C for 10 s several times. Furthermore, this substrate was maintained at 700 °C for 3 min and then cooled slowly down to room temperature. The vacuum level was kept below 2×10^{-9} Torr during these procedures to obtain a well-defined Si(111)-(7×7) surface. Powder samples of metallofullerenes were deposited on the well-defined Si(111)-(7×7) surface at 650 °C after annealing the samples at 300 °C for 12 h under $\sim 1 \times 10^{-9}$ Torr. The deposition rate was kept below 0.1 monolayers (ML)/h, and the substrate was not heated during the thermal deposition. All STM measurements were performed by using an ultrahigh-vacuum STM system (UNISOKU Scientific Instruments) with Pt-Ir tips. The STM image was measured in the constant-current mode under $\sim 5 \times 10^{-11}$ Torr. The heights estimated from STM were calibrated with the exact height, 3.1 Å, of the step in the Si substrate. The sample bias voltage V_s and tunneling current I_t were -2.6 to -2.0 V and 0.20–0.25 nA, respectively.

III. RESULTS AND DISCUSSION

A typical STM image of Dy@C_{82} molecules adsorbed on Si(111)-(7×7) at 295 K is shown in Fig. 1(a); the Dy@C_{82} molecule surface coverage is 0.1 ML. The bright spherical spots are the images of the Dy@C_{82} molecules. The monomers of the Dy@C_{82} molecules are adsorbed on the Si(111)-(7×7) surface without formation of islands and nucleation, as in the case of C_{60} molecules on Si(111)-(7×7) and $Sc_2@C_{84}$ molecules on Si(100)-(2×1).[3,12] The adsorption characteristics are different from those of Lu@C_{82} on a C_{60} film, in which an accumulation of Lu@C_{82} molecules is observed near the step edge.[5] The Dy@C_{82} molecules neither migrate toward the step edge nor make significant clusters even after the substrate was heated up to 200 °C; the STM image was measured at 295 K after annealing. These results imply that Dy@C_{82} molecules are strongly bound by the Si surface.

Three possible adsorption sites for Dy@C_{82} on the surface are shown in Fig. 1(b). 72% of the Dy@C_{82} molecules are adsorbed on the A site surrounded by three Si adatoms, and 9% and 19% of the molecules are adsorbed on the corner holes (site B) and on the dimer lines (site C), respectively. Previously, it was shown that 80% of C_{60} molecules were adsorbed on the A site.[12] This value is consistent with that found for the Dy@C_{82} molecules, implying that the A site is very attractive for fullerene molecules. In the case of C_{60}, 13% and 7% of the molecules were adsorbed on the B and C sites, respectively.[12] Contrary to the case of Dy@C_{82}, the adsorption probability on the corner holes was larger than that on the dimer lines.[12] This result may originate from the facts that the van der Waals diameter of the C_{60} molecule is smaller than that of the Dy@C_{82} molecule and that the spacing of the corner holes (B site) is larger than that of the dimer lines (C site). The C_{60} molecules can fall in the corner hole (B site) more deeply than the Dy@C_{82} molecules, as is seen from Fig. 1(c), but the spacing of the dimer lines is too small to let the C_{60} molecule fall deeply into the site; the details of spacing of each site are described later. The deep
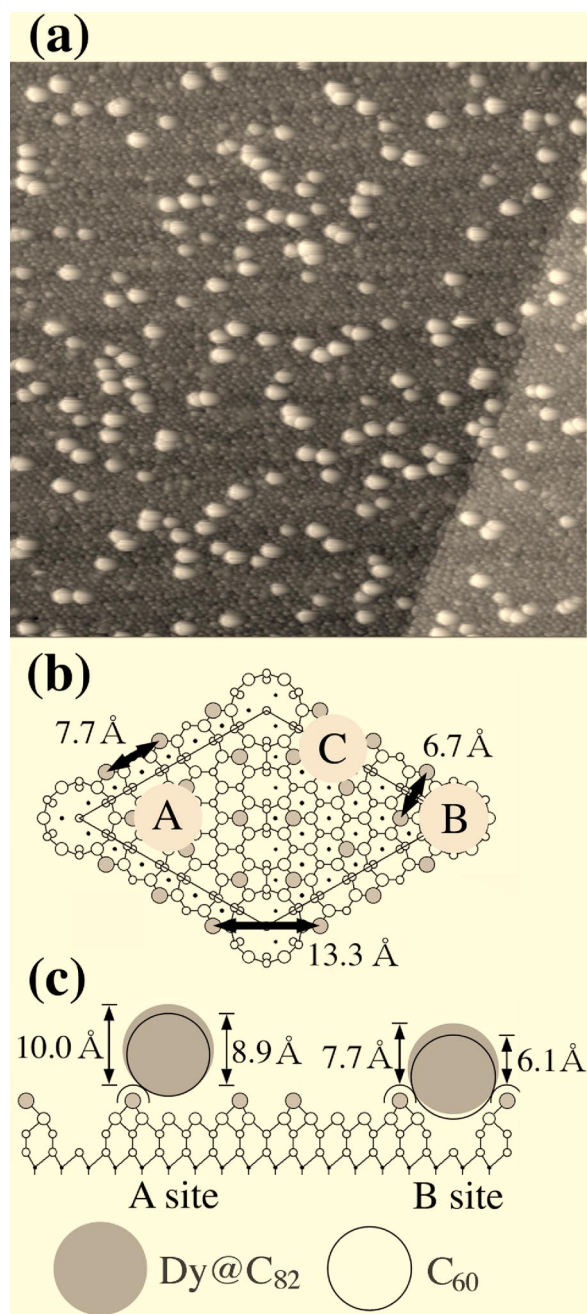

FIG. 1. (a) STM image for 0.1 ML of Dy@C_{82} adsorbed on the Si(111)-(7×7) surface (100×100 nm²). V_s and I_t were -2.0 V and 0.20 nA, respectively. (b) Schematic diagram of three possible adsorption sites on the Si(111)-(7×7) surface. (c) Schematic representation of Dy@C_{82} and C_{60} molecules captured into the basins of the Si surface. The van der Waals diameters of Dy@C_{82} and C_{60} molecules are shown by large gray circles and open circles, respectively, in (c). The small gray circles refer to the Si adatoms in (b) and (c), and the small open circles and the dots refer to the Si atoms except for the adatoms in (b) and (c).

falling of the C_{60} molecule in the corner hole should stabilize adsorption on the site.

It is predicted by taking into consideration only the van der Waals diameters of the Dy@C_{82} molecule (11.4 Å) and Si atom (4.2 Å) that STM will give heights of 10.0 and 7.7 Å

for Dy@C$_{82}$ molecules on the A and B sites, respectively. This feature is schematically represented in Fig. 1(c). These results reflect the facts that the spacing between the Si adatoms is 7.7 Å in one triangular subunit surrounded by three adatoms (A site), and the spacing between the Si adatoms across the corner holes (B site) is 13.3 Å; these values are shown in Fig. 1(b). The heights of the Dy@C$_{82}$ molecules on the A and B sites are experimentally estimated to be 7.3 and 6.6 Å, respectively, from the STM image. These experimental heights are smaller than the predicted ones, 10.0 and 7.7 Å. Furthermore, the experimental height is estimated to be 7.1 Å for the C site, a value also smaller than the predicted one, 8.5 Å; the spacing of the adatoms across the boundary of the triangle (C site) is 6.7 Å. The average height of the Dy@C$_{82}$ molecules observed in the first layer is 7.2 Å. The heights of the Dy@C$_{82}$ molecules cannot be explained only by the fact that the molecules enter basins of the Si surface such as the A, B, and C sites. This implies that the spaces are not large enough to allow the molecules to fall into the basins to reproduce the heights estimated experimentally from the STM. Consequently, we conclude that heights lower than the predicted ones at all sites are realized because of a strong interaction between the Si surface and the Dy@C$_{82}$ molecules, i.e., formation of a Si-C bond.

The schematic representation [Fig. 1(c)] shows clearly that the experimental height of 6.6 Å for the Dy@C$_{82}$ molecule on the B site, lower than those on the A and C sites, 7.3 and 7.1 Å, originates from the fact that the molecule can enter the basin of the B site more deeply than the other sites. At the B site, the difference between the experimental height (6.6 Å) and the predicted one (7.7 Å) is -1.1 Å in Dy@C$_{82}$. The difference is the same as that for C$_{60}$, in which the experimental and predicted heights are 5.0 and 6.1 Å, respectively.[13] This fact implies that the nature of the interaction between the molecules and Si adatoms at the B site is the same for Dy@C$_{82}$ and C$_{60}$. At the A site, the difference between the experimental height (7.3 Å) and the predicted one (10.0 Å) is -2.7 Å in Dy@C$_{82}$, and close to -2.9 Å in C$_{60}$, in which the experimental and predicted heights are 6.0 and 8.9 Å, respectively.[13] This result suggests that the interaction is almost the same for Dy@C$_{82}$ and C$_{60}$ at the A site. Here we note that the Si-C interaction is much stronger at the A site than the B site because the difference is larger by 2.5 times at the A site than at the B site. This result shows that the A site is very attractive for fullerene molecules, and it rationalizes the fact that more than 70% of the Dy@C$_{82}$ molecules and C$_{60}$ molecules are adsorbed on the A site.

High-resolution STM images of the Dy@C$_{82}$ molecules observed at 295 K are shown in Fig. 2. Further, the STM images of three Dy@C$_{82}$ molecules named a, b, and c are enlarged in the figure. Patterns that reflect the charge distribution of the C$_{82}$ cage are clearly observed in these images; this kind of pattern is termed the internal structure of the C$_{82}$ cage. These clear images of the internal structure suggest that the motion of the Dy@C$_{82}$ molecules is frozen on the Si(111)-(7×7) surface even at 295 K. A correlation between the internal structures and the adsorption sites is not clearly seen in Fig. 2, i.e., the high-resolution STM images
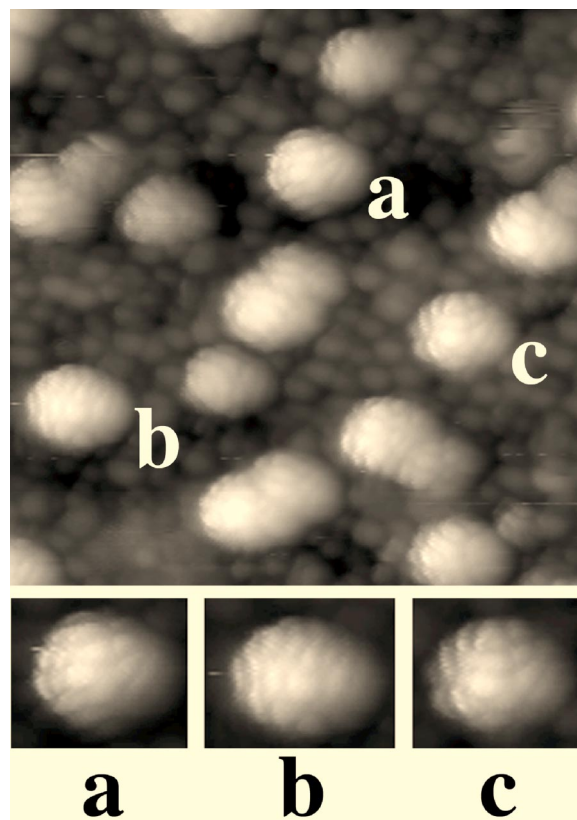

FIG. 2. High-resolution STM image for 0.05 ML of Dy@C$_{82}$ adsorbed on the Si(111)-(7×7) surface (30×30 nm^2). V_s and I_t were -2.0 V and 0.20 nA, respectively.

show that the Dy@C$_{82}$ molecules are randomly oriented on the Si(111)-(7×7) surface. Clear spots ascribable to the Dy atoms inside the cages are not observed for any Dy@C$_{82}$ molecules. This result may originate from a dynamical disorder of the Dy atom inside the C$_{82}$ cage, as suggested from a Rietveld analysis for x-ray powder diffraction.[10]

High-resolution STM images showing the internal structure of metallofullerenes have hardly been reported, although internal structures have been observed for C$_{60}$ molecules on the Si(111)-(7×7) surface at room temperature.[13] The internal structure was not observed in a multilayer film of La@C$_{82}$ on the Si(111)-(7×7) surface.[6] In the present study, the internal structure of the C$_{82}$ cage has been observed owing to the strong interaction between the Si atom and the Dy@C$_{82}$ molecule in the first layer. More recently, Shinohara *et al.* observed the internal structure of La$_2$@C$_{80}$ and La@C$_{82}$ in the first layer of a hydrogen-terminated Si(100)-(2×1) surface at 78 K by STM.[14]

Simulation of the STM image based on a theoretical calculation of electronic structure is necessary to determine the internal structure at the atomic level, because the STM image directly reflects the electronic structure of the molecules near the Fermi level. High-resolution STM images make it possible to identify the molecular orientations of metallofullerenes on the Si surface, when the atomic level structures are determined by analyses of the STM images. The information about molecular orientation helps to clarify the
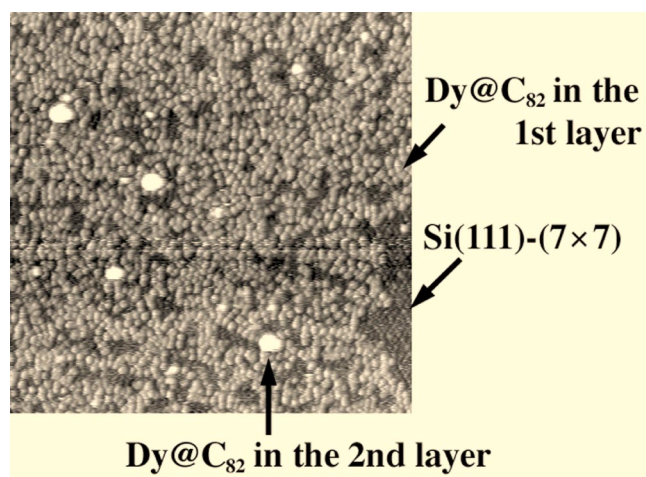
FIG. 3. STM image for ~ 1 ML of Dy@C_{82} adsorbed on the Si(111)-(7×7) surface (80×80 nm^2). V_s and I_t were -2.6 V and 0.25 nA, respectively.

FIG. 4. (a) STM images for ~ 0.01 ML of Dy@C_{60} adsorbed on the Si(111)-(7×7) surface (40×20 nm^2). V_s and I_t were -2.0 V and 0.20 nA, respectively. (b) Close-up of a STM image of Dy@C_{60} molecule (10×5 nm^2).

mechanism for the accumulation of metallofullerenes on the surface. The determination of molecular orientations for various types of metallofullerenes on a semiconductor surface is now in progress, based on the theoretical simulations for their STM images.

The STM image of the Si(111)-(7×7) surface covered with ~ 1 ML of Dy@C_{82} at 295 K is shown in Fig. 3. The dark regions are the bare surface of Si(111)-(7×7). The gray blobs on the Si surface can be ascribed to the Dy@C_{82} molecules in the first layer, and the bright near-circular features can be ascribed to the Dy@C_{82} molecules in the second layer. The STM image shows no specific nucleation in the first layer. The first layer is not ordered, as is seen from Fig. 3, and no second layer islands are observed before completion of the first layer. These results indicate that the interaction between the Si atoms and the Dy@C_{82} molecules in the first layer is stronger than the intermolecular interaction between the Dy@C_{82} molecules. The height of the Dy@C_{82} molecule (bright ball) in the second layer is estimated to be 10.8 Å from the STM image. This value is close to the van der Waals diameter of the Dy@C_{82} molecule, 11.2–11.4 Å.[8] This implies that the electronic structure of the Dy@C_{82} molecules in the second layer is not substantially affected by the Si surface.

The STM image of ~ 0.01 ML Dy@C_{60} molecules adsorbed on the Si(111)-(7×7) surface observed at 295 K is shown in Fig. 4(a). The nearly spherical features can be ascribed to the Dy@C_{60} molecules. This image is similar to a bright spherical feature for La@C_{60} on a HOPG reported previously.[4] It was reported that neither La@C_{60} nor Ce@C_{60} molecules formed an island on the HOPG at room temperature.[4] The Dy@C_{60} molecules are also adsorbed on the surface without islands and do not migrate at 295 K. No spots ascribable to the Dy atoms are observed around the nearly spherical image. A close-up of the image of the Dy@C_{60} molecule is shown in Fig. 4(b), which also exhibits a nearly spherical image. The destruction of the C_{60} cage is not found in this image, i.e., the Dy@C_{60} molecule exhibits a cage-form structure, as suggested from Raman and ex-
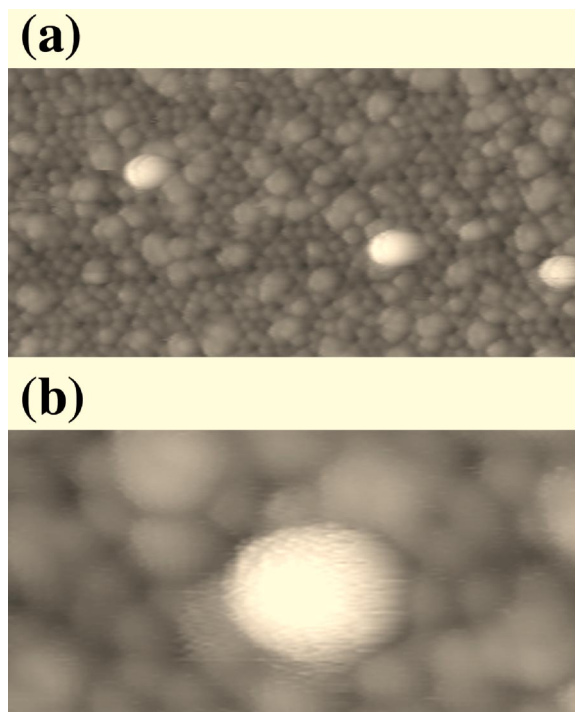
tended x-ray absorption fine structure analyses.[11] The height of the Dy@C_{60} molecule is estimated to be ~ 7 Å, a value suggesting a strong interaction between the Si atoms and the Dy@C_{60} molecules, as in the Dy@C_{82} molecule. In the STM image of the Dy@C_{60} molecules, the spot of the Dy atom could not clearly be observed inside the cage as in the Dy@C_{82} molecules. Internal structures of the C_{60} cage were not observed in this image.

IV. CONCLUSION

The adsorption of Dy@C_{82} and Dy@C_{60} on the Si(111)-(7×7) surface has been studied by STM at 295 K. In the first layer of Dy@C_{82} molecules, the molecules are strongly bound by the Si surface, and the internal structures of the C_{82} cage are clearly observed. The internal structure of the Dy@C_{82} molecule is first observed at room temperature owing to the freezing of its dynamical motion through the formation of chemical bonds between the molecule and the Si adatoms on the Si(111)-(7×7) surface. The driving force for the arrangement of Dy@C_{82} in the second layer is van der Waals interaction. The STM image of the Dy@C_{60} molecule shows a nearly spherical spot. This is direct and important evidence of a cage-form structure because the structure of metal endohedral C_{60} has not yet been established. Information on the structures of Dy@C_{82} and Dy@C_{60} molecules on a semiconductor surface will open doors to build up nanoscale molecular assemblies with high functionality as well as clarifying directly the nature of individual molecules.

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