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## Scanning tunneling microscopy/spectroscopy studies of two isomers of Ce@C<sub>82</sub> on Si(111)-(7×7) surfaces

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Scanning tunneling microscopy images for two isomers of Ce@C<sub>82</sub> were observed on Si(111)-(7×7) at 295 K. The Ce@C<sub>82</sub> molecules in the first layer were bound to the Si surfaces, and the motions were frozen even at 295 K. The multilayer of the Ce@C<sub>82</sub> isomer I (Ce@C<sub>82</sub>-I) produced a close-packed structure in the surface layer by annealing the Si substrate at 473 K. The distance between the nearest-neighboring molecules was 1.15(4) nm whose value was consistent with that, 1.12 nm, estimated from x-ray diffraction of the Ce@C<sub>82</sub>-I crystals. This implies that the close-packed structure is dominated by van der Waals forces, as in crystals of Ce@C<sub>82</sub>-I. The internal structure of Ce@C<sub>82</sub>-I was observed in the first layer due to a freeze of molecular motion caused by strong interactions between the molecule and the Si adatoms in the surface. Scanning tunneling spectroscopy revealed that the energy gaps for Ce@C<sub>82</sub>-I and -II in the first layer opened to gap energies,  $E_g$  of 0.7 and 1.0 eV, respectively. This fact suggests that these molecules are semiconductors with smaller value of  $E_g$  than those for C<sub>60</sub> and C<sub>70</sub>.

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### I. INTRODUCTION

Endohedral metallofullerenes have attracted much interest as promising new materials during the past decade. This is because of their novel physical properties, and possible applications in electronic devices.<sup>1,2</sup> Especially, metallofullerenes have potential applications in molecular electronic devices because of the existence of an electric dipole moment, spin, and charge. For example, when the electric dipole moments in metallofullerenes are controlled by an electric field, this should lead to a switching of electric current on the molecular scale. Recently, the metallofullerenes have also shown promise in the field of quantum computing because their natures allow them to act as quantum bits (qubits).<sup>3,4</sup> Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are powerful techniques for direct observation of the structures and electronic properties of endohedral metallofullerenes at the nanoscale. Several STM studies have been performed to clarify the adsorption characteristics of metallofullerenes on various types of surfaces.<sup>5-12</sup> Among these studies, the interactions between metallofullerenes and well-defined Si surfaces are of much interest because of future applications, in which molecular devices and conventional Si electronics are merged.

STS studies of metallofullerenes have hardly proceeded because of the difficulty in obtaining reliable STS data. STS studies of Ce@C<sub>60</sub> and La@C<sub>60</sub> adsorbed on a highly oriented pyrolytic graphite surface were performed in a wide temperature region.<sup>5</sup> The gap energy  $E_g$  of the Ce@C<sub>60</sub> molecule was estimated to be ~0.3 eV from the STS curve at room temperature, while no gap was observed for the La@C<sub>60</sub> molecule. These results imply that Ce@C<sub>60</sub> is a semiconductorlike material, while La@C<sub>60</sub> is a metal. There was no change in electronic structure of La@C<sub>60</sub> down to

29 K. However, at 28 K an energy gap abruptly appeared. Consequently, it was concluded that the metal-semiconductor transition occurs in La@C<sub>60</sub> at 28 K. Recently, the STS studies of La@C<sub>82</sub> multilayer islands adsorbed on hydrogen-terminated Si(100)-(2×1) at 78 K showed the  $E_g$  of 0.5 eV,<sup>6</sup> whereas the STS for La@C<sub>82</sub> films adsorbed on Si(111)-(7×7) at room temperature showed metallic or semimetallic behavior.<sup>7</sup>

Structural and electronic properties of Ce@C<sub>82</sub> have been investigated by x-ray diffraction, Raman, x-ray adsorption near-edge spectroscopy (XANES), and electric resistivity  $\rho$  measurement.<sup>13,14</sup> The x-ray diffraction patterns for solid samples of the major isomer of Ce@C<sub>82</sub> (Ce@C<sub>82</sub>-I) were indexed as a simple cubic (sc) lattice with a lattice constant  $a$  of 1.578(1) nm.<sup>13</sup> The Raman spectra and Ce  $L_{III}$ -edge XANES for thin films of Ce@C<sub>82</sub> showed that the valence of Ce was +3.<sup>13</sup> The temperature dependence of  $\rho$  for the thin film of Ce@C<sub>82</sub> showed a semiconductorlike behavior, where  $E_g=0.4$  eV for the isomer mixture of Ce@C<sub>82</sub>,<sup>13</sup>  $E_g=0.33$  eV for Ce@C<sub>82</sub>-I, and  $E_g=0.55$  eV for the minor isomer of Ce@C<sub>82</sub> (Ce@C<sub>82</sub>-II).<sup>14</sup> In the present study, the adsorption patterns for the two isomers of Ce@C<sub>82</sub> in a monolayer and a multilayer on Si(111)-(7×7) surface were examined by STM/STS. The structural and electronic properties have also been studied by STM/STS. These properties have been discussed by comparison with those of Ce@C<sub>82</sub> found in the solid and a thin film.

### II. EXPERIMENT

Sample preparation and purification of Ce@C<sub>82</sub>-I and II are described elsewhere.<sup>13</sup> The characterization of the purified samples was performed by time-of-flight mass spectra

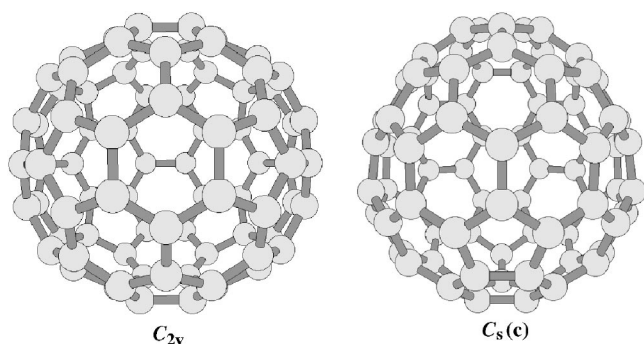


FIG. 1. Molecular structures of  $\text{Ce@C}_{82}$  used in the present study.

and uv-visible-near-infrared (UV-VIS-NIR) absorption spectra. The cage symmetries of the isomers I and II were identified as  $C_{2v}$  and  $C_s$ , respectively, as deduced from the similarity in the UV-VIS-NIR spectra to that of the corresponding isomer of  $\text{La@C}_{82}$ .<sup>15-17</sup> Recently, the symmetry of  $\text{Ce@C}_{82}$ -I was also assigned to  $C_{2v}$  based on  $^{13}\text{C}$  NMR spectra of its anion.<sup>18</sup> The molecular structures of the two isomers,  $C_{2v}$  and  $C_s$ , used in the present study are shown in Fig. 1.

The STM/STS data of two isomers of  $\text{Ce@C}_{82}$  were collected by using an ultrahigh vacuum (UHV) STM system (UNISOKU Scientific Instrument) with Pt—Ir tips under pressure of  $8 \times 10^{-11}$  Torr. Commercially available  $\text{Si}(111)-(7 \times 7)$  surface was prepared according to the following procedure. (1) The substrate was degassed by heating at 873 K for 12 h, and flash annealed up to 1373 K for 10 s five times. (2) The substrate was rapidly cooled to 973 K, and slowly cooled to 295 K. The vacuum level was kept below  $2 \times 10^{-9}$  Torr during the above procedure. The samples of  $\text{Ce@C}_{82}$  introduced into quartz cells for evaporation were degassed in the UHV chamber at 573 K for 12 h. These samples were deposited onto the  $\text{Si}(111)-(7 \times 7)$  surface at 923 K; then the substrate temperature was maintained at 295 K. The deposition rate was kept below 0.1 monolayer (ML)/h to precisely control the deposition of  $\text{Ce@C}_{82}$  on the Si surface, and to avoid nonequilibrium growth of the  $\text{Ce@C}_{82}$  layers. The STM images were collected at sample voltages  $V$  ranging from  $-2.0$  to  $+2.0$  V, in constant-current mode. The current  $I$  was constant for each sample in the range from 0.20 to 0.25 nA. The STS measurements were carried out with  $V$  and  $I$  set points of 1 V and 0.5–1.0 nA, respectively. This was done to obtain a good signal-to-noise ratio. The  $dI/dV$  curves were experimentally measured with a lock-in amplifier; the modulation frequency and amplitude were 3 kHz and 30 mV, respectively.

### III. RESULTS AND DISCUSSION

#### A. STM image of 0.02 ML of $\text{Ce@C}_{82}$ -I

The STM image of  $\text{Ce@C}_{82}$ -I adsorbed by  $\sim 0.02$  ML on the  $\text{Si}(111)-(7 \times 7)$  surface at 295 K is shown in Fig. 2(a). The bright spherical spots are the images of the  $\text{Ce@C}_{82}$ -I molecules. The molecules are randomly adsorbed on the

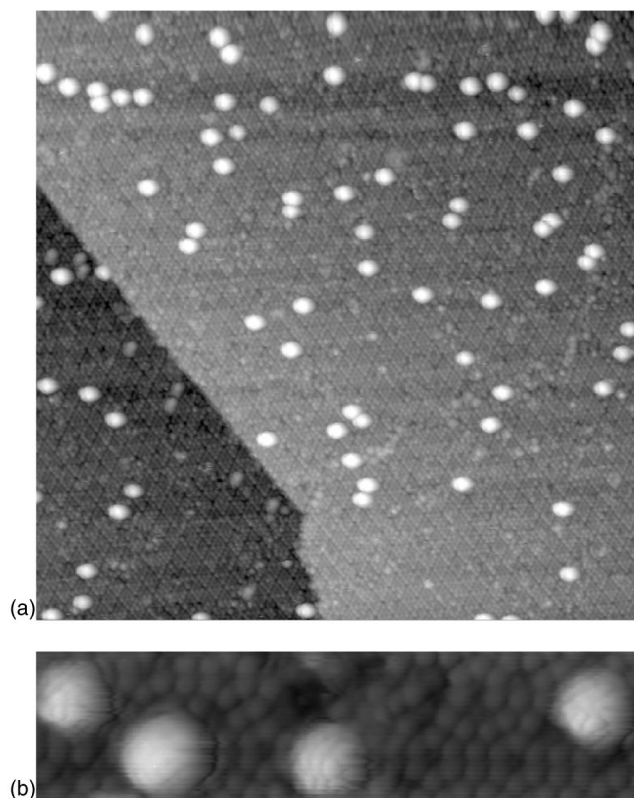


FIG. 2. (a) STM image for 0.02 ML of  $\text{Ce@C}_{82}$ -I adsorbed on the  $\text{Si}(111)-(7 \times 7)$  surface ( $90 \times 90 \text{ nm}^2$ ,  $V = -2.0$  V, and  $I = 0.20$  nA). (b) High-resolution STM image of  $\text{Ce@C}_{82}$ -I ( $20 \times 5 \text{ nm}^2$ ,  $V = 1.5$  V, and  $I = 0.20$  nA). The STM was collected over a region of  $30 \times 30 \text{ nm}^2$ , and an area of  $20 \times 5 \text{ nm}^2$  is shown in (b).

$\text{Si}(111)-(7 \times 7)$  surface. Selective adsorption near step edges is not observed, as in the case of  $\text{Dy@C}_{82}$ .<sup>9</sup> Furthermore, the molecules are adsorbed as single molecules, without the formation of clusters such as dimers and trimers. It should be noted that some dimerlike images found in Fig. 2(a) do not correspond to dimers, because the distances between the molecules are larger than those expected from the usual van der Waals interactions. The lateral broadening of the images caused by tunneling current, which runs obliquely from the STM tip to the molecules, can produce such dimerlike images. The molecules neither migrate toward the step edge nor form clusters at 295 K. These results imply that the interactions between  $\text{Ce@C}_{82}$ -I molecule and the Si adatoms on the  $\text{Si}(111)-(7 \times 7)$  surface are relatively strong in the first layer. A detailed investigation of the adsorption sites in the  $7 \times 7$  unit cell shows that the  $\text{Ce@C}_{82}$ -I molecules are adsorbed on three different sites. Site A is surrounded by three Si adatoms, site B is on the corner holes, and site C is on the dimer lines. The notations A, B, and C, for the three adsorption sites are taken from Ref. 9. The fractions of adsorption of  $\text{Ce@C}_{82}$ -I in the  $7 \times 7$  unit cell were estimated to be 76%, 7%, and 17% at sites A, B, and C, respectively. These values are consistent with those, 72%, 9%, and 19%, in  $\text{Dy@C}_{82}$ , where the  $\text{Dy@C}_{82}$  molecules are adsorbed through chemical bonds between the molecules and Si adatoms.<sup>9</sup>

High-resolution STM images of  $\text{Ce@C}_{82}$ -I are shown in Fig. 2(b). The images show patterns which reflect charge

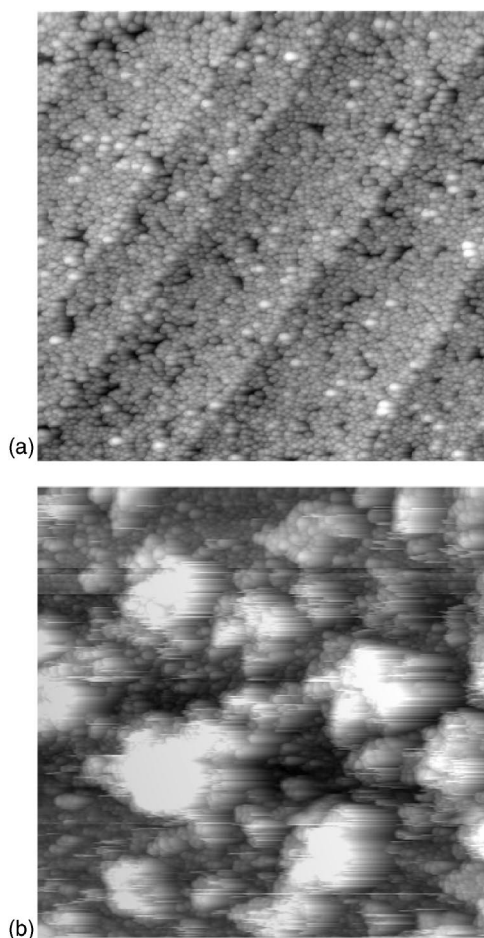


FIG. 3. (a) STM image for 1 ML of Ce@C<sub>82</sub>-I adsorbed on the Si(111)-(7×7) surface (98×98 nm<sup>2</sup>, V=2.0 V, and I=0.20 nA). (b) STM image for 3 ML of Ce@C<sub>82</sub>-I adsorbed on the Si(111)-(7×7) surface (98×98 nm<sup>2</sup>, V=2.0 V, and I=0.20 nA).

distribution of the C<sub>82</sub> cage. This pattern is termed the internal structure of the C<sub>82</sub> cage. These clear images of the internal structures suggest that the motion of the Ce@C<sub>82</sub>-I molecules is frozen on the Si(111)-(7×7) surface at 295 K, which is consistent with the result for Dy@C<sub>82</sub>.<sup>9</sup> The high-resolution STM images suggest that the Ce@C<sub>82</sub>-I molecules adsorbed on Si(111)-(7×7) surface are randomly oriented. This result is consistent with the x-ray standing wave spectroscopy of Ce@C<sub>82</sub>-I on a Ag(111) surface, which showed no specific orientations in the adsorption of molecules.<sup>19</sup>

### B. STM image of the Ce@C<sub>82</sub> layer

The STM images of Ce@C<sub>82</sub>-I adsorbed at ~1 and ~3 ML on the Si(111)-(7×7) surfaces at 295 K are shown in Figs. 3(a) and 3(b), respectively. In Fig. 3(a), no islands are observed before complete formation of the first layer of Ce@C<sub>82</sub>-I. This indicates the strong interaction between the Si adatoms in the Si(111)-(7×7) surface and the Ce@C<sub>82</sub>-I molecule, which is stronger than the van der Waals interaction between the molecules. Further deposition of Ce@C<sub>82</sub>-I causes the formation of islands, as

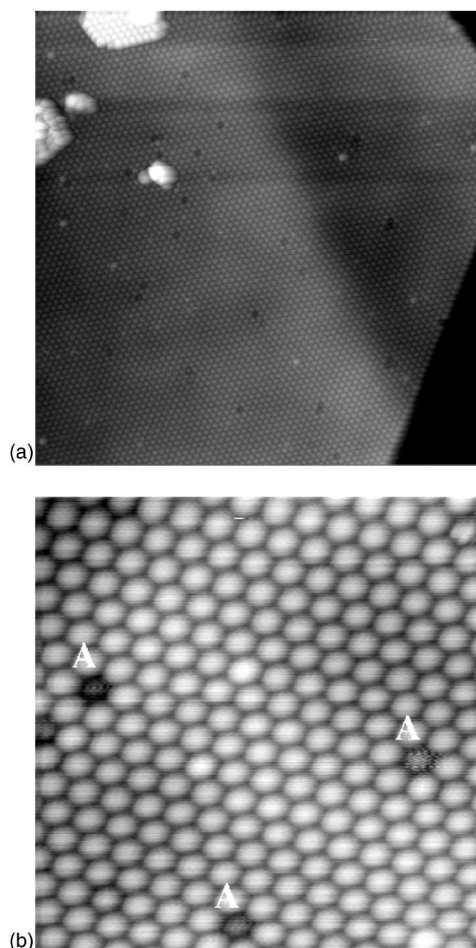


FIG. 4. (a) STM image for the close-packed structure of Ce@C<sub>82</sub>-I (77×77 nm<sup>2</sup>, V=2.0 V, and I=0.20 nA). (b) High-resolution STM image for the close-packed structure of Ce@C<sub>82</sub>-I (15×15 nm<sup>2</sup>, V=2.0 V, and I=0.20 nA). Dim molecules described in text are indicated by “A.”

shown in Fig. 3(b). This type of layer growth is known as Stranski-Krastanov-type growth. This growth is also found in Sc<sub>2</sub>@C<sub>84</sub> on Si(111)-(7×7) and La@C<sub>82</sub> on the Si(100)-(2×1) surface.<sup>10,11</sup> Conversely, the growth of La<sub>2</sub>@C<sub>80</sub> on a hydrogen-terminated Si(100)-(2×1) surface is reported to be of the Volmer-Wever type. It should be noted that no close-packed structures are observed in the STM images shown in Fig. 3. This implies that the Ce@C<sub>82</sub>-I molecules in both the first layer and the multilayer cannot migrate at 295 K to form close-packed structures.

When annealing the substrate covered with 1 ML of Ce@C<sub>82</sub>-I [Fig. 3(a)] at 573 K for 5 min, no close-packed structure was formed on the surface. However, when the Si substrate covered with 3 ML of Ce@C<sub>82</sub>-I [Fig. 3(b)] was annealed at 473 K for 14 h, most of the islands disappeared and a close-packed structure appeared, as is shown in Fig. 4(a). The area of the close-packed structure exceeds 80×80 nm<sup>2</sup>. The high-resolution STM image of the close-packed structure is shown in Fig. 4(b). The area of the close-packed structure increases with increasing annealing time. Here we can point out that the simple cubic structure ( $Pa\bar{3}, Z=4$ ) of Ce@C<sub>82</sub>-I crystals<sup>13</sup> is the same as the face-



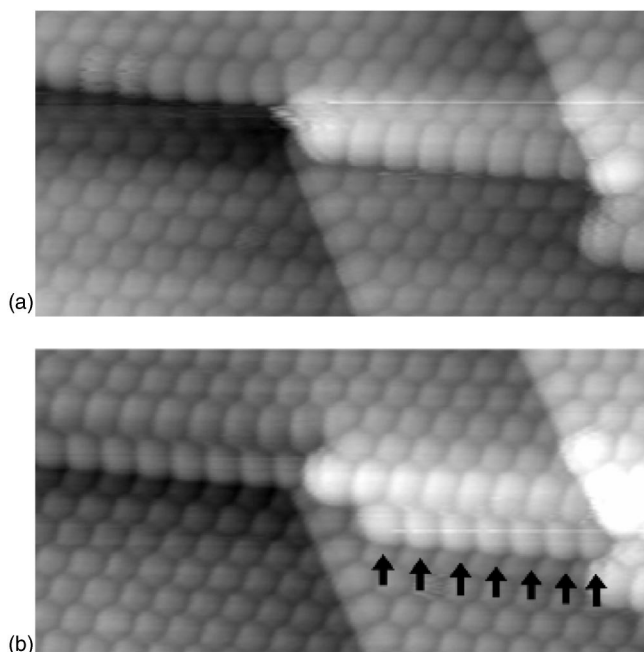


FIG. 5. STM image of the close-packed structure of Ce@C<sub>82</sub>-I ( $20 \times 10 \text{ nm}^2$ ,  $V=2.0 \text{ V}$ , and  $I=0.20 \text{ nA}$ ). The STM was collected over a region of  $25 \times 25 \text{ nm}^2$ , and an area of  $20 \times 10 \text{ nm}^2$  is shown. (a) STM image obtained by the first scanning of the STM tip, and (b) STM image obtained at the tenth scanning.

centered cubic structure regarding the locations of molecules. Thus, for each structure, a Ce@C<sub>82</sub>-I layer perpendicular to [111] direction is observed as a hexagonal structure, indicating a close-packed structure. The height of the step between the molecular layers was estimated to be  $\sim 0.9 \text{ nm}$ , which is consistent with the value,  $0.91 \text{ nm}$ , calculated from the van der Waals distance between the closest molecules,  $1.12 \text{ nm}$ . Further, the height of  $0.9 \text{ nm}$  is consistent with that reported previously for La@C<sub>82</sub> on Si(111).<sup>7</sup> However, it cannot be answered whether the STM images shown in Fig. 4 correspond to the image of the face-centered cubic (fcc) structure viewed along the [111] direction or the hexagonal close-packed (hcp) structure viewed along [001]. Furthermore, due to observation of three layers in the images (Fig. 5), an investigation of the close-packed structures was performed. However, the types of close-packed structure could not be clearly identified because of a stacking fault in the area where three layers were observed. Further STM studies are necessary to determine the type of the close-packed structure.

The distance between the molecules was determined to be  $1.15(4) \text{ nm}$  from the STM image [Fig. 4(b)]. This value is close to that,  $1.12 \text{ nm}$ , determined from x-ray diffraction for the Ce@C<sub>82</sub>-I crystals, which can be explained by van der Waals interactions between the molecules.<sup>13</sup> Therefore, the Si adatoms in the Si(111)-(7 $\times$ 7) surface never effect a rearrangement of the molecular layer above the first layer as in the case of La@C<sub>82</sub> and Dy@C<sub>82</sub>.<sup>7,9</sup> No internal structures of the Ce@C<sub>82</sub>-I molecules were observed in the close-packed structure [Fig. 4(b)]. This implies that the molecular motion is not frozen. However, it cannot be answered from the STM

image whether the molecules rotate freely or jump between some preferred orientations.

Some dim spots are observed in the STM image for the close-packed structure of Ce@C<sub>82</sub>-I shown in Fig. 4(b); the dim spots are indicated by A. The heights of the dim spots are lower by  $0.1\text{--}0.2 \text{ nm}$  than those of bright ones. Moreover, these dim spots seem to exhibit the internal structure. The dim spots were never observed by a hole injection from the tip. Similar dim spots were observed for a close-packed layer of C<sub>60</sub> where the dim spots were assigned to the polymers of C<sub>60</sub>.<sup>20</sup> The polymerization of C<sub>60</sub> was induced only by electron injection, and the height of the dim spots was lower by  $0.1 \text{ nm}$  than that of the monomer.<sup>20</sup> These results are the same as those found for Ce@C<sub>82</sub>-I, indicating that the dim spot originates from a polymerization of Ce@C<sub>82</sub>-I molecules caused by electron injection from the STM tip.

### C. Transfer and removal of Ce@C<sub>82</sub>-I molecules

The STM images of the close-packed structures are shown in Figs. 5(a) and 5(b); these images were observed at the first and the tenth STM scanning, respectively. Seven Ce@C<sub>82</sub>-I molecules shown by arrows [Fig. 5(b)] are observed at different positions from the STM image shown in Fig. 5(a). This result clearly shows that the scanning of the STM tip, for observation of the STM image, can transfer the Ce@C<sub>82</sub>-I molecules near the step edges in the close-packed structure. The  $V$  and  $I$  used for these STM images were  $2.0 \text{ V}$  and  $0.2 \text{ nA}$ , respectively. This corresponds to the gap impedance of  $10 \text{ G}\Omega$ . No transfer was observed for the Ce@C<sub>82</sub>-I molecules on the Si(111)-(7 $\times$ 7) surface, i.e., for the molecule in the first layer, by the STM measurement. Movement of Ce@C<sub>82</sub>-I in the first layer on the Si(111) surface was observed after a STM scanning at  $V$  of  $2.0 \text{ V}$  and  $I$  of  $0.5 \text{ nA}$ , i.e., a gap impedance of  $4 \text{ G}\Omega$ . The C<sub>60</sub> and La@C<sub>82</sub> molecules on the Si surfaces could be manipulated by using STM.<sup>10,21</sup> To manipulate metallofullerene molecules the STM tip was first brought close to the surface near the target molecules by decreasing  $V$  and increasing  $I$ ; then the tip was swept across the surface, so as to push the target molecules. La@C<sub>82</sub> molecules on the Si(100)-(2 $\times$ 1) surface could be manipulated at the threshold gap impedance of  $\sim 1.0 \text{ G}\Omega$  ( $V=2 \text{ V}$  and  $I=2.0 \text{ nA}$ ).<sup>10</sup> The gap impedances  $1\text{--}4 \text{ G}\Omega$  of  $M@C_{82}$  ( $M$  is a lanthanide atom with valence of +3) in the first layer on the Si(111) and Si(100) surfaces were smaller than that,  $10 \text{ G}\Omega$ , used for transfer of Ce@C<sub>82</sub>-I in the close-packed structure. This implies that the STM tip for manipulation of  $M@C_{82}$  in the close-packed structure lies far from the molecule in comparison with the case in the first layer. Therefore, it has been concluded that the Ce@C<sub>82</sub>-I molecules in the close-packed structure can easily be transferred because of weak intermolecular interaction, i.e., van der Waals interaction.

The substrate covered with 3 ML of Ce@C<sub>82</sub>-I [Fig. 3(b)] was annealed at  $773 \text{ K}$  for  $5 \text{ min}$ . The STM image after annealing is shown in Fig. 6(a). Only an island (white lump) was observed on the Ce@C<sub>82</sub>-I layer. No close-packed structure was observed in the STM image [Fig. 6(a)], which differs from the case annealed at  $473 \text{ K}$  (Fig. 4). Recently, a

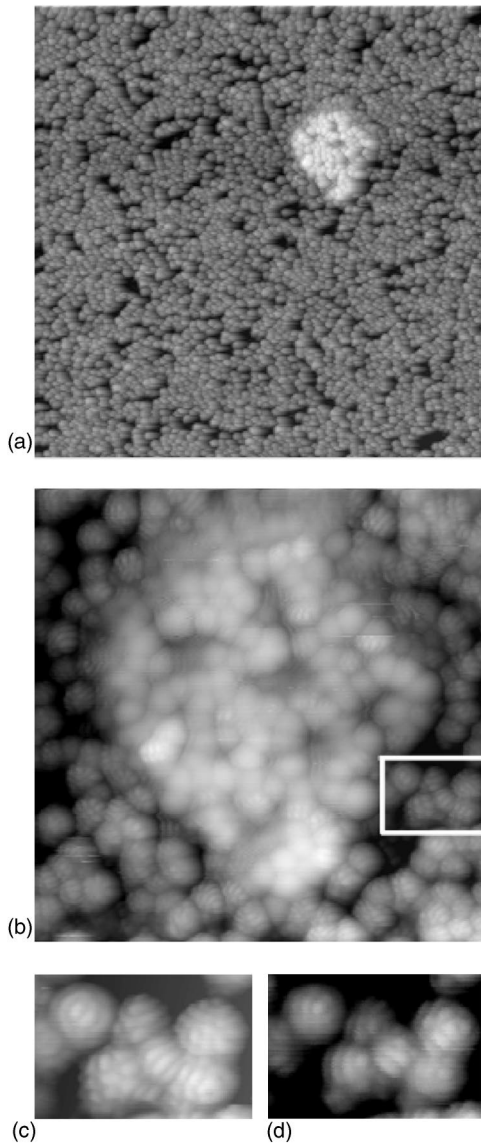


FIG. 6. STM images measured after annealing the Si substrate covered with 3 ML of Ce@C<sub>82</sub>-I at 773 K for 5 min: (a) 98 × 98 nm<sup>2</sup>,  $V=2.0$  V, and  $I=0.20$  nA, and (b) 25 × 25 nm<sup>2</sup>,  $V=1.5$  V, and  $I=0.20$  nA. Close-up images (6 × 4 nm<sup>2</sup>) measured at (c)  $V=1.5$  V and  $I=0.20$  nA, and (d)  $V=-2.0$  V and  $I=0.20$  nA for the part surrounded by the white rectangle (6 × 4 nm<sup>2</sup>) in the STM image shown in (b).

photoemission spectroscopy revealed that the Ce@C<sub>82</sub> molecules in the multilayer were desorbed at 573 K.<sup>19</sup> Therefore the Ce@C<sub>82</sub>-I molecules that constituted the other islands may be removed by annealing at 773 K. The high-resolution STM image of the remaining island is shown in Fig. 6(b). The internal structure of the Ce@C<sub>82</sub>-I molecule around the island is clearly observed, suggesting that the motions of the Ce@C<sub>82</sub>-I molecules are frozen. This indicates that the molecules are strongly bound on the Si surface. This implies that the molecules around the island are in the first layer. Furthermore the bias-voltage dependence of the STM image was investigated in order to observe internal structures ascribable to different electronic states. The STM images for the molecules surrounded by the rectangle [Fig. 6(b)] were collected

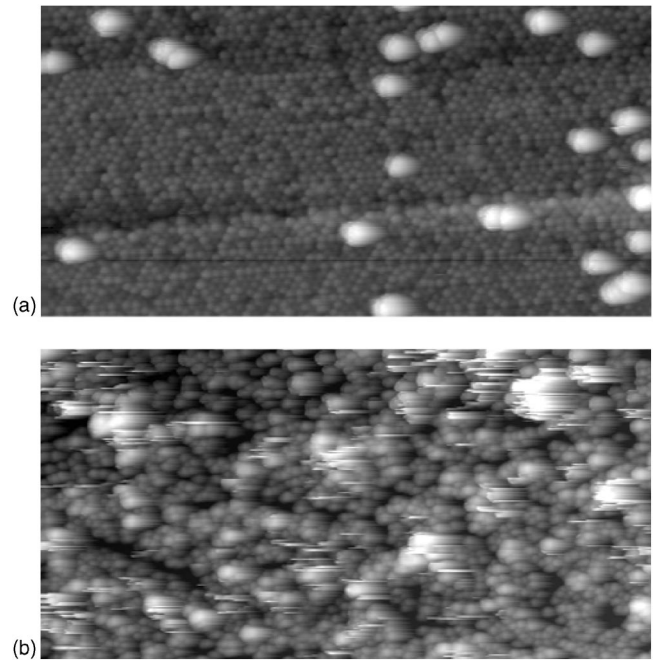


FIG. 7. (a) STM image for 0.02 ML of Ce@C<sub>82</sub>-II adsorbed on the Si(111)-(7 × 7) surface (50 × 25 nm<sup>2</sup>,  $V=-2.0$  V, and  $I=0.20$  nA). The STM was collected over a region of 50 × 50 nm<sup>2</sup>, and an area of 50 × 25 nm<sup>2</sup> is shown in (a). (b) STM image for 1.2 ML of Ce@C<sub>82</sub>-II adsorbed on the Si(111)-(7 × 7) surface (98 × 49 nm<sup>2</sup>,  $V=-2.0$  V, and  $I=0.20$  nA). The STM was collected over a region of 98 × 98 nm<sup>2</sup>, and an area of 98 × 49 nm<sup>2</sup> is shown in (b).

at  $V$  of 1.5 V [Fig. 6(c)] and  $-2.0$  V [Fig. 6(d)]. The image of the internal structure of Ce@C<sub>82</sub>-I depends on  $V$ . This result reflects the distribution of the spatial local density of states at each energy level. Such  $V$  dependence has also been observed in the STM images of La<sub>2</sub>@C<sub>80</sub>, La@C<sub>82</sub> and Dy@C<sub>82</sub>-I.<sup>6,8</sup>

#### D. STM image of Ce@C<sub>82</sub>-II

The STM image of 0.02 ML of Ce@C<sub>82</sub>-II adsorbed on the Si(111)-(7 × 7) surface at 295 K is shown in Fig. 7(a). No aggregation of the molecules are observed on the Si(111)-(7 × 7) surface, as in the case of Ce@C<sub>82</sub>-I [Fig. 2(a)]. The Ce@C<sub>82</sub>-II molecules neither migrated toward the step edge nor formed clusters even after the substrate was heated at 673 K for 5 min. This shows that the Ce@C<sub>82</sub>-II molecules were bound on the Si surface. The STM image of 1.2 ML of Ce@C<sub>82</sub>-II on the Si surface is shown in Fig. 7(b). The first layer of the Ce@C<sub>82</sub>-II molecules shows no close-packed structure. Some small islands (white lumps) are formed on the first layer. This implies Stranski-Krastanov-type growth in the Ce@C<sub>82</sub>-II. Thus, the STM of Ce@C<sub>82</sub>-II shows similar images to those of Ce@C<sub>82</sub>-I. The difference in electronic structure between Ce@C<sub>82</sub>-I and -II cannot be found in their STM images.

#### E. STS of two isomers of Ce@C<sub>82</sub>

The STS ( $dI/dV$ ) curves for Ce@C<sub>82</sub>-I in the first layer at 295 K are shown in Fig. 8(a). The peaks ascribable to the

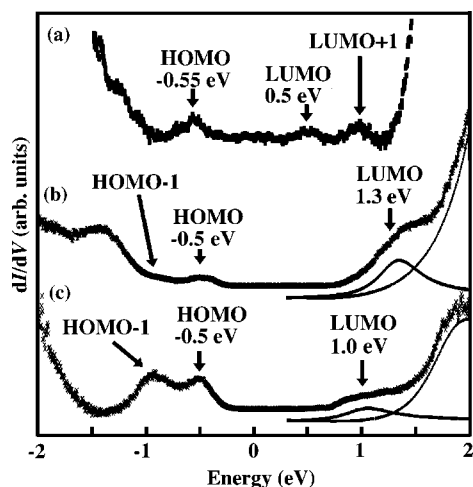


FIG. 8.  $dI/dV$  curves for (a) Ce@C<sub>82</sub>-I in the first layer, (b) Ce@C<sub>82</sub>-II in the first layer, and (c) Ce@C<sub>82</sub>-II in the multilayer. The Lorentz curves determined by the curve fitting for the broad peaks above 0.7 eV are shown in (b) and (c).

highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are observed at  $-0.55$  and  $0.5$  eV, respectively, for Ce@C<sub>82</sub>-I, whose values are close to those,  $-0.8$  and  $0.5$  eV, of La@C<sub>82</sub> in the multilayer reported previously.<sup>6</sup> The  $E_g$  between the HOMO and LUMO for Ce@C<sub>82</sub>-I was estimated to be  $0.7$  eV from the onset of the HOMO and LUMO peaks found in the  $dI/dV$  curve. The  $E_g$  of  $0.7$  eV for Ce@C<sub>82</sub>-I was close to that,  $0.79$ – $0.87$  eV, estimated by surface potential analysis for the thin film of Ce@C<sub>82</sub>-I.<sup>22</sup> Furthermore, the  $E_g$  was close to that,  $0.5$  eV, for La@C<sub>82</sub> in the multilayer.<sup>6</sup> These results show that the electronic structure of Ce@C<sub>82</sub>-I in the first layer is almost the same as that in the multilayer. Thus, the electronic structure of the molecule in the first layer is scarcely affected near the Fermi energy, regardless of the chemical bond with Si adatoms.

As seen from Figs. 8(b) and 8(c), the peaks of the HOMO for Ce@C<sub>82</sub>-II are observed at  $\sim -0.5$  eV for both layers, which is the same as the Ce@C<sub>82</sub>-I. The HOMO-1 peaks are observed at  $-1.0$  eV in both layers, and the peak in the multilayer is enhanced. Furthermore, a peak is observed around  $-1.4$  V for only the first layer of Ce@C<sub>82</sub>-II [Fig. 8(b)], which may originate from the interaction between the molecules and the Si surface. The peak is also observed for the first layer of Ce@C<sub>82</sub>-I [Fig. 8(a)]. The peak at  $0.5$  eV is observed for Ce@C<sub>82</sub>-I, but is not observed for Ce@C<sub>82</sub>-II in both layers. The LUMO peaks are not clearly observed in both layers of Ce@C<sub>82</sub>-II, i.e., the LUMO peaks are involved in the broad peaks observed above  $0.7$  eV. Therefore, the LUMO peaks were separated from the broad peaks by a curve fitting with two Lorentz functions. The LUMO peaks are located at  $1.3$  and  $1.0$  eV in the first layer and the multilayer, respectively. The LUMO peaks for Ce@C<sub>82</sub>-II are observed at higher energy than that,  $0.5$  eV, for Ce@C<sub>82</sub>-I. This seems to directly reflect the difference in electronic structures between Ce@C<sub>82</sub>-I and -II. The  $E_g$  values for Ce@C<sub>82</sub>-II were determined to be  $1.0$  eV in both the first layer and multilayer from the onsets of the HOMO and

the broad peaks including the LUMO [Figs. 8(b) and 8(c)]. These results show that the electronic structure of the first layer of Ce@C<sub>82</sub>-II near Fermi energy is scarcely affected by the Si surface, as in Ce@C<sub>82</sub>-I. These are the first findings on the electronic structure of the minor isomer in metallofullerenes.

The  $E_g$ 's estimated from temperature dependence of  $\rho$  for the thin films of Ce@C<sub>82</sub>-I and -II were  $0.33$  and  $0.55$  eV, respectively.<sup>14</sup> Each  $E_g$  value of Ce@C<sub>82</sub>-I and -II is almost one-half of the value estimated from  $dI/dV$  curves. If the  $E_g$  estimated from  $\rho$  does not correspond to the exact HOMO-LUMO gap but the gap associated with the impurity levels, the  $E_g$  should be smaller than that estimated from STS. Actually, Shiraishi *et al.* assigned the  $E_g$  estimated from the temperature dependence of  $\rho$  to the mobility gap, which corresponds to the difference between the impurity level and LUMO.<sup>22</sup> Furthermore, the origin of the difference between both  $E_g$ 's needs to be fully investigated.

Thus the STS showed that Ce@C<sub>82</sub>-I and -II were semiconductors with smaller values of  $E_g$  than those of C<sub>60</sub> and C<sub>70</sub>,  $1.8$ – $2.2$  eV.<sup>23–25</sup> The origin of the semiconductor-type behavior should be questioned for Ce@C<sub>82</sub>, because the valence of Ce atom is found to be  $+3$ .<sup>13</sup> If the three electrons transfer to the C<sub>82</sub> cage, metallic behavior is expected from a simple electronic picture for  $M@C_{82}$  ( $M$  is a metal atom with the valence of  $+3$ ). In fact, a band calculation for La@C<sub>82</sub> (valence of La is  $+3$ ) predicted metallic behavior.<sup>26</sup> However, all  $M@C_{82}$  [La@C<sub>82</sub>,<sup>2,27,28</sup> Ce@C<sub>82</sub>,<sup>13,22</sup> Pr@C<sub>82</sub>,<sup>29</sup> and Dy@C<sub>82</sub> (Ref. 30)] for which electronic structures have been studied so far showed semiconductor-like behavior. This may imply that  $M@C_{82}$  is a strongly correlated electron material, i.e., the electronic repulsion energy  $U$  results in an opening of the gap. If this is the case, applying pressure to the  $M@C_{82}$  samples should produce metallic phases by an increase in the hopping integral between the molecules.

#### IV. CONCLUSIONS

STM images were observed for two isomers of Ce@C<sub>82</sub>, and the growth mechanism for Ce@C<sub>82</sub> was clarified to be of Stranski-Krastanov type. The growth can be reasonably explained by the fact that the molecules in the first layer are strongly bound on the Si(111)-(7×7) surface through chemical bonds between the C atoms in the molecules and the Si adatoms. The growth mechanism is also supported by the fact that the van der Waals forces dominate the multilayer. Annealing the substrate covered with 3 ML of Ce@C<sub>82</sub>-I at  $473$  K formed a close-packed structure. The distance between the molecules was  $1.15(4)$  nm whose value is consistent with that determined by x-ray diffraction of the crystals,  $1.12$  nm.<sup>13</sup> Thus the adsorption of Ce@C<sub>82</sub> molecules on the Si surface first causes disappearance of dangling bonds of Si adatoms, and the subsequent adsorption of the molecules leads to the formation of molecular clusters and a close-packed structure governed by van der Waals interactions. STS showed the  $E_g$ 's of  $0.7$  and  $1.0$  eV for Ce@C<sub>82</sub>-I and -II, respectively. This implies that Ce@C<sub>82</sub>-I and -II are semiconductors with smaller  $E_g$  than those of C<sub>60</sub> and C<sub>70</sub>.<sup>23–25</sup>



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