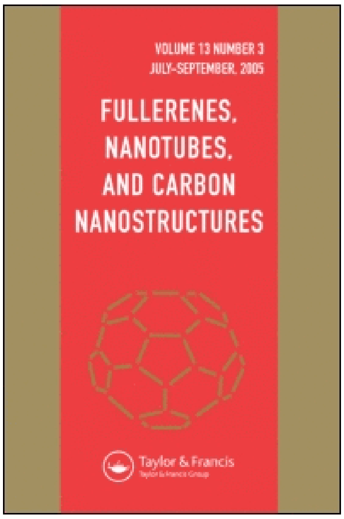

Fullerenes, Nanotubes and Carbon Nanostructures

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Adsorption and Electronic Structure of Single $C_{60}F_{18}$ Molecule on Si(111)-7×7 Surface

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Scanning tunneling microscopy has been used to spatially image individual fluorofullerene $C_{60}F_{18}$ molecules on Si(111)-7×7 surface. The images have been interpreted with the help of ab initio *calculations. $C_{60}F_{18}$ molecules interact with the surface with F atoms pointing down, whereas a large electric dipole moment of the molecule induces strong polarization on the surface but the charge transfer is small. It has been shown that during the time of image collection, some of the F atoms migrate from fluorofullerene molecule due to F binding energy on a Si surface being nearly twice the mean value on the C_{60} molecule.*

Keywords Adsorption Fluorofullerence molecule $C_{60}F_{18}$, Scanning tunneling microscopy, Si(111) surface

Introduction

Thin films of organic materials and self-organized nanostructures compatible with Si-based semiconductor systems are currently of great interest for expanding microelectronic technologies to nanoscale range and for applications in optoelectronic devices (1–3). Among them, carbon fullerences and their derivatives are promising for the fabrication of electroactive elements in photovoltaic solar cells, active layers in organic field-effect transistors (4) and as building blocks for chemical manipulation in nano-science applications to develop new functionalities. While several studies focusing on crystal structures, electrical, and electronic properties of fullerenes have been carried out, the most stable fullerene derivatives — endohedral metallofullerenes and exohedral fullerene fluorides — did not receive the attention they deserve. The latter have been synthesized in a variety of compositions $C_{60}F_x$ ($x = 18$–48). The knowledge of physical & chemical properties of $C_{60}F_x$ molecules on a variety of substrates is essential to determine how the molecule substrate interaction alters the local molecular electronic structure, which is an important step to create controllable single-molecule technologies. Meanwhile, a few attempts have been made to study thin layers of fluorinated C_{60} molecules on Si(111)-7×7 surface using scanning tunneling microscope (STM) (5,6). In these studies, C_{60} was fluorinated under flowing fluorine conditions that resulted in a mixture of $C_{60}F_{46}$ (main constituent) with small amounts of

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$C_{60}F_{42}$, $C_{60}F_{44}$, and $C_{60}F_{48}$. It has been claimed that fluorine atoms often detached from C_{60} core and led to the formation of Si-C covalent bond. Some of the fluorine-adsorbed sites could form thread-like structures suggesting a fluorine "printing" process caused by the rolling movement of the fullerene across the surface. Such molecules were called as "nano-bottle" of fluorine or a low temperature fluorine carrier, a new technological tool to fabricate nanostructures. Some other molecules could release fluorine atoms by the oscillatory motion leading to the formation of nano-scale localized fluorine-adsorbed areas. However, no theoretical calculations in support of such experimental findings have been presented.

Recently, $C_{60}F_{18}$ has been successfully obtained in high abundance and even a crystalline phase has been developed (7). In contrast to $C_{60}F_x$ ($x = 42$–48) molecules, the tortoise-shaped polar $C_{60}F_{18}$ molecule (electric dipole moment > 9 Debye) is asymmetrical (8). The structure of the molecule has been determined to have all 18 fluorine atoms bound to only one hemisphere of C_{60}. The addition of F atoms makes four nearest neighbors around each C atom and the local bonding character changes from predominantly sp^2 to sp^3 type as well as the C-C bonds elongate in the range of 1.5–1.6 Å.[1] There is a 6-membered ring of sp^2 bonded C atoms (alternate bond lengths 1.372 and 1.376 Å), which is isolated from the residual molecular system by a "belt" of sp^3-hybridized C-atoms, each having an F atom. So F atoms flatten this molecule and the I_h symmetry of C_{60} reduces to a 3-fold rotational symmetry (C_{3v}) in $C_{60}F_{18}$. Following the notations in the Schlegel diagram (8), the calculated C–C bond distances lie in the range of 1.37 to 1.68 A, at that the shortest bonds are associated with sp^2 bonded carbon atoms while the longest bonds, with C–C bonds in pentagons having F atoms. The calculated highest occupied lowest unoccupied (HOMO-LUMO) molecular orbital gap of $C_{60}F_{18}$ is 2.41 eV (1.65 eV for pure C_{60}) while the mean calculated binding energy of an F atom on C_{60} is 3.6 eV. So, $C_{60}F_{18}$ is a very stable molecule. Here we present the results of STM imaging of individual $C_{60}F_{18}$ molecules deposited on Si(111)-7×7 surface combined with *ab initio* calculations to obtain the atomic arrangement and electronic structure of these supported molecules.

Experimental

To prepare pure $C_{60}F_{18}$ a method of fluorination of C_{60} in solid-state reactions with transition metal fluorides was employed (7). The deposition of $C_{60}F_{18}$ molecules (rate ~0.05–0.1 ML/min) was performed from Knudsen cell. All experiments were carried out at room temperature using an ultra high vacuum STM (base pressure 2×10^{-11} Torr) equipped with standard preparation facilities (9). A P-doped Si(111) wafer with resistivity of 1.6 Ω·cm was cut into pieces of $20 \times 7 \times 0.5$ mm^3 and then ultrasonically washed in acetone and distilled water. Samples were mounted on a Ta sample holder, and the surface was cleaned by outgassing overnight at 650°C and then flashing at 1250°C for 5s followed by slow cooling. The details of the spatially varying charge density were analyzed from *ab initio* pseudopotential calculations using plane wave projector augmented wave method (10). The exchange-correlation energy has been calculated within generalized gradient approximation (GGA) (11). Isolated $C_{60}F_{18}$ molecule, clean Si surface, and adsorption of $C_{60}F_{18}$ on it have been studied using a supercell with sufficient vacuum space between the molecules/surfaces so that the interaction between the periodic images is minimal. We followed the dimer-adatom-stacking-fault (DAS) model (12) for the 7 × 7 reconstruction of Si(111) surface and studied adsorption using a slab having six layers out of which the bottom three layers were kept frozen. The dangling bonds on the bottom side of the slab have been saturated with H atoms.

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[1] Note that the C–C bond length in diamond structure is about 1.54 Å.

All the ions in the remaining layers as well as the molecule in the supercell were allowed to relax without any symmetry constraints using conjugate gradient method. The Brillouin zone of the supercell was sampled by the gamma point in the case of isolated molecules, while $2 \times 2 \times 2$ Monkhorst-Pack **k**-points were used for the surface calculations (13). Ionic relaxation was continued until the force on each ion became less than 0.01 eV/A and the energy difference between the successive ionic steps was lower than 10^{-5} eV.

Results and Discussion

The lowering of the symmetry of C_{60} by the attachment of F atoms to one part of the cage will influence the properties of the remaining part as well as the ordering and packing of the fullerene molecules on Si(111)-7×7 surface depending upon the interactions of the fullerene cage or attached atoms with the surface. From STM data we can conclude that the initial nucleation of the deposited $C_{60}F_{18}$ molecules occurs on three different positions of the 7 × 7 surface unit cell: the unfaulted half, the faulted half, and the corner hole. In this work we focus on the study of $C_{60}F_{18}$ adsorption on a corner hole. Figure 1 shows STM images of the filled states of a $C_{60}F_{18}$ molecule located above a corner hole of Si(111)-7×7 surface at −1.8 V Figure 1a) and −2.0 V sample bias (Figure 1b and 1c). The images are similar but the bright spot in Figure 1a (in place of the corner hole) is distinctly smaller in comparison with that in Figure 1b. Figure 1c shows the image at −2.0 V sample bias taken moments after the image presented in Figure 1b. One can observe the appearance of black spot shown by an arrow. The STM images of the unoccupied states taken at +1.8 V are shown in Figures 1d and 1e. The central part of the image changes drastically with the applied bias. There is a small spot of high intensity and 5 spots of much lower intensity. One can also notice the appearance of some black spots in the image in Figure 1e (illustrated by white arrows). The black regions in Figures 1c and 1e increase with time and are indicative of some F atoms leaving $C_{60}F_{18}$ molecule.

To understand the adsorption properties of fluorofullerenes, we considered three different orientations of a $C_{60}F_{18}$ molecule on Si(111)-7×7 surface: a "bottom orientation," where most of the F atoms directly interact with the surface (molecule shown in Figure 1a landing on the hole of Si(111)-7×7 surface unit cell in a nearly 3-fold symmetric arrangement); a "top orientation," in which F atoms are in the top position so that only C atoms can interact with the surface; a "side orientation," in which the fullerene is in between the top and bottom orientations and a few F atoms interact with the surface. In all cases the positions of the atoms in the molecule were fully relaxed, as discussed earlier. The adsorption energy of the molecule, E_{ad} is calculated from

$$E_{ad} = E(C_{60}F_{18}) + E(\mathrm{Si}) - E(C_{60}F_{18}/\mathrm{Si})$$

where $E(C_{60}F_{18})$, $E(\mathrm{Si})$, and $E(C_{60}F_{18}/\mathrm{Si})$ are the total energies of a free $C_{60}F_{18}$ molecule, Si (111)-7×7 surface, and the combined system, respectively. Among the three different orientations of a $C_{60}F_{18}$ molecule considered on Si(111)-7×7 surface, the adsorption energy for the bottom orientation is very high (6.65 eV) as compared to 1.75 eV for the top and 1.79 eV for the side orientations. Accordingly, it is expected that $C_{60}F_{18}$ molecule would instantaneously align to the bottom orientation, with the fluorine atoms pointing toward the Si adatoms.

In order to further elucidate the STM images obtained experimentally, we calculated the total and the partial densities of states (DOS) for the bottom orientation case and these are shown in Figure 2. It can be seen that the Fermi energy (E_F) lies in a band of states of Si(111)-7×7 surface, while the occupied and the unoccupied states of the $C_{60}F_{18}$ molecule are energetically separated with a gap of about 2.1 eV. The $2p$ states of F atoms are fully occupied

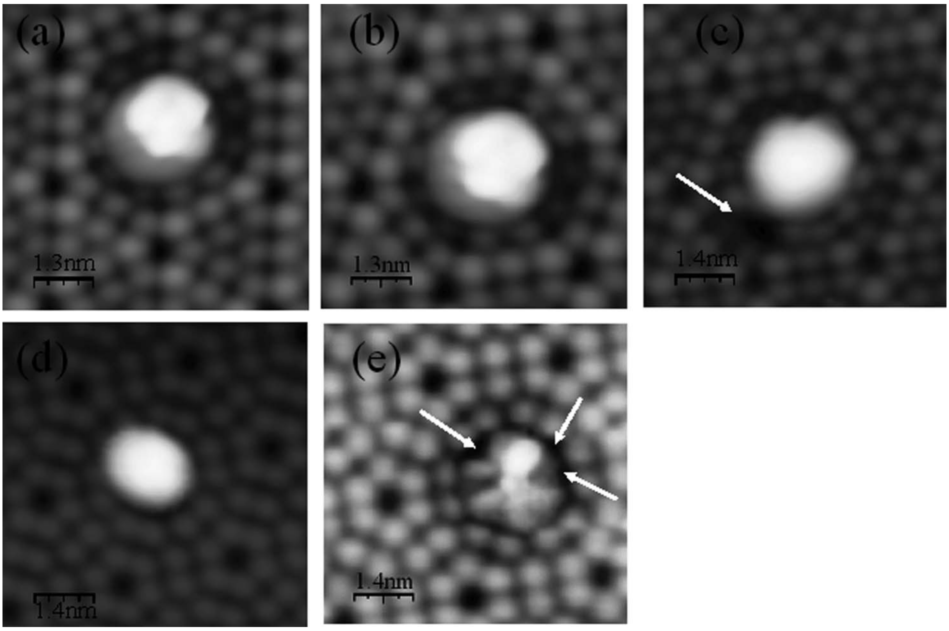

Figure 1. STM images of a single $C_{60}F_{18}$ molecule adsorbed on a corner site of Si(111)-7×7 surface at constant tunneling current $I_t = 20$ pA: (**a**), (**b**), and (**c**) correspond to filled states images at the bias voltages $U_s = -1.8$ V, –2.0 V, and –2.0 V, respectively, the STM image in (c) was obtained some time later than the image in (b); (**d**) and (**e**) show empty states images at $U_s = +1.8$ V; the STM image in (e) was obtained some time later than the STM image in (d). White arrows in (c) and (e) indicate some F atoms leaving $C_{60}F_{18}$ molecule and getting adsorbed on the surface during measurements.

and lie more deeply as compared to the highest occupied 2*p* states of C atoms. So STM images from the filled states in our experiments arise mainly from C-2*p* and Si-3*p* orbitals. From our calculations, no $C_{60}F_{18}$ state lies between E_F and E_F-2.0eV (see the bottom two curves), but some states exist between ~2.1 and 3.9 eV below E_F, predominantly on C atoms (some differences in the calculated and observed values of energies are possible due to the band gap problem in GGA). Accordingly, the STM image of the filled states of the adsorbed $C_{60}F_{18}$ molecule at –2.0 V is largely due to C-2*p* states. As for the empty states STM images (Figure 1d and 1e) we find that in the calculated DOS (Figure 2), again the main contribution is coming from Si and C atoms. There are several peaks in the partial DOS of C atoms in the energy range of E_F and 2.0 eV above it. In the experimental STM image obtained at +1.8 V the $C_{60}F_{18}$ molecule looks as a bright spot surrounded by Si adatoms. Our calculation for +0.8 V bias (a lower value of voltage is taken as the band gap is underestimated in GGA) show similar behavior with three lobs and less bright adatoms as also observed.

The drastic changes in the STM images at –2.0 V Figure 1c) and at +1.8 V bias (Figure 1e) we relate with the detachment of some fluorine atoms from $C_{60}F_{18}$ molecule. In view of the appearance of some black spots, it is concluded that some F atoms have detached from the fluorofullerene molecule in the period of the experiment and moved on to the surface region where black spots are seen. This leads to modification in the electronic structure of the fluorofullerene and the possibility of direct Si–C interaction that modify the image.

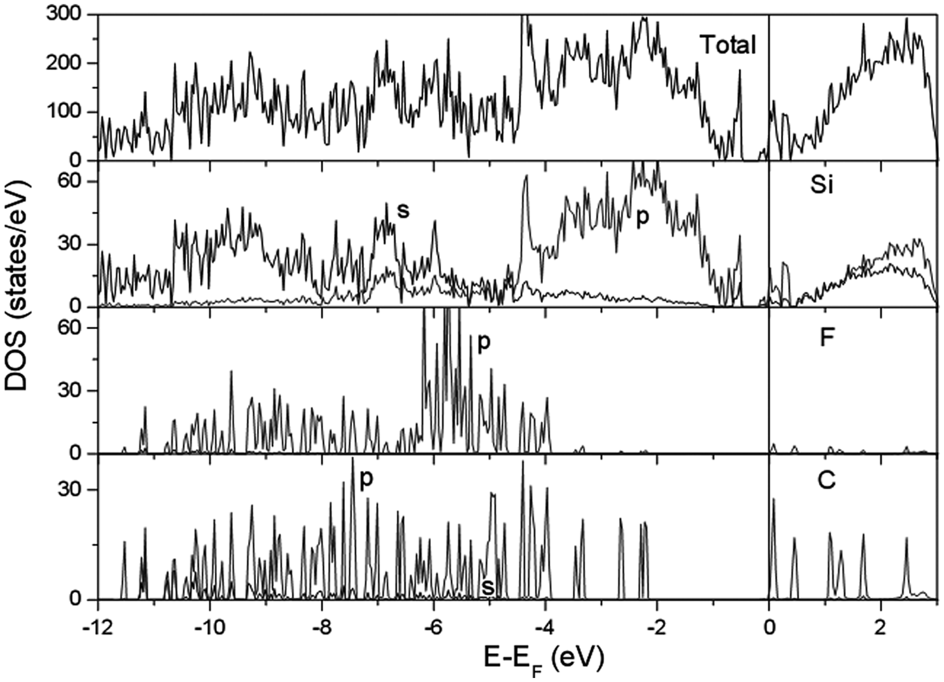

Figure 2. The total and the partial electronic densities of states (DOS) of bottom oriented $C_{60}F_{18}$ molecule adsorbed on Si(111)-7×7 surface. The zero of energy corresponds to the E_F. The partial density of states on F atoms lies mostly about 4 eV below E_F. The lines correspond to total DOS, and *s* and *p* partial DOS of the respective atoms.

We have also calculated the charge contours from filled states by accumulating charge density from states in the energy range of E_F-2.25 eV to E_F and E_F-3.0 eV to E_F and the cuts in planes parallel to the surface and passing above the Si adatoms and above the fluorofullerene are shown in Figures 3a–b. In the plane above the Si adatoms (Figure 3a), one can see high density around the adatoms while the cut above the fluorofullerene shows (Figure 3b) electronic charge density distribution, which has similar features as seen in STM images (Figure 1a and b). Note that the calculated distribution corresponding to −2.25 V is smaller in size as compared to that corresponding to −3.0 V in agreement with the experimental images that show a reduction in size as the bias is reduced from −2.0 to −1.8 V. Figures 3c and 3d correspond to empty states STM image (Figure 1d) as well. Our results of the DOS further confirm that F atoms in $C_{60}F_{18}$ molecule are orientated toward the surface. If F atoms would be on the top position, then we shall see no current in STM images at this bias.

To understand the interaction mechanism of the fluorofullerene molecule with the surface, we calculated the difference ($\Delta\rho$) of the charge densities induced by adsorption for the case of the bottom oriented $C_{60}F_{18}$ molecule on the surface. Figures 3e and 3f show that the main effect of adsorption is the polarization of the Si(111)-7×7 surface whereas the charge density distribution in the molecule is not affected much. The dipole-like formation of the charge density distribution on the surface is observed around six Si adatoms that are near the corner hole where the molecule is adsorbed. This is induced by the large dipole moment in $C_{60}F_{18}$. The electronic charge density distribution of the induced dipole moments closed to the adatom sites is, however, not uniform, and there are alternately low and high

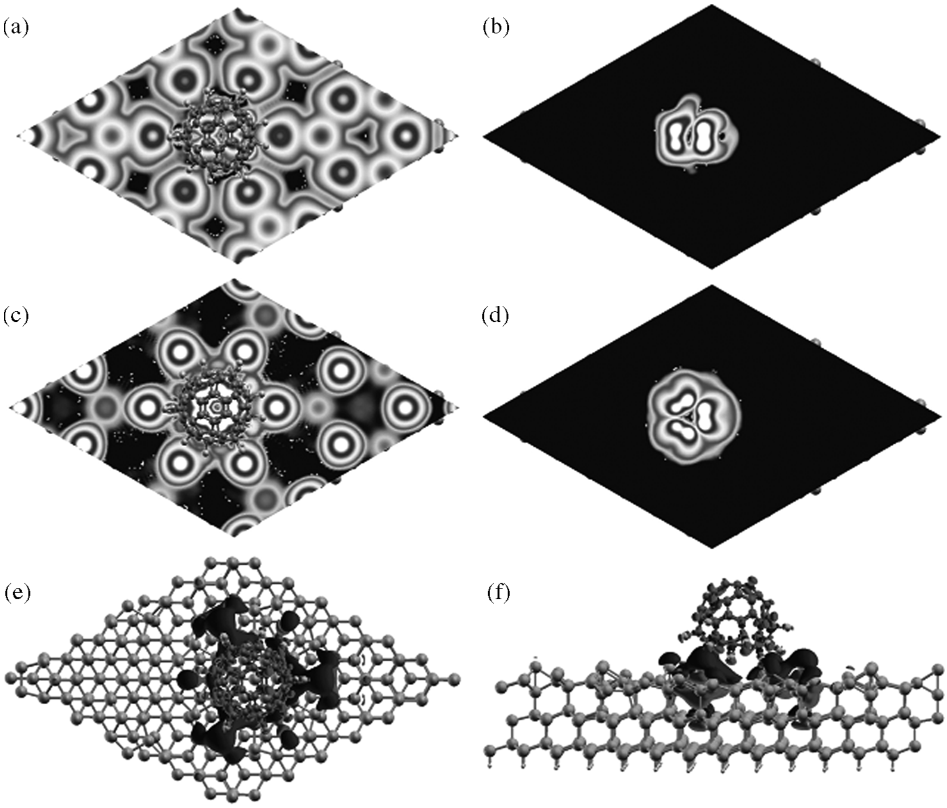

Figure 3. Isocontours (gray corresponds to 0.0 and white to 0.02 e/A^3) of charge density distribution for a single $C_{60}F_{18}$ molecule on a corner hole of Si(111)-7×7 surface in a plane **a**) 1.86 A and **b**) 9.32 A above the center of Si adatom corresponding to filled states with $U_s = -2.25$ V, while **c**) and **d**) correspond to empty states with $U_s = +0.8$ V at heights as in a) and b). (**e**) and (**f**) show top and side views of the difference in the electronic charge densities of the adsorbed system ($C_{60}F_{18}$ + surface) and the sum of the densities of free $C_{60}F_{18}$ molecule and the Si surface, $\Delta\rho = \rho(C_{60}F_{18}/Si) - \rho(C_{60}F_{18}) - \rho(Si)$. More and less dark isosurfaces ($\sim 1.3\times10^{-5}$ electrons/A^3) represent the excess and the depletion of charge, respectively. The excess of charge is more significant around those Si surface adatoms that are close to F atoms with perpendicular to the surface orientation.

densities due to the atomic arrangement in $C_{60}F_{18}$ molecule where F–C–C–F units are located (nearly) parallel and perpendicular to the surface alternatively. In the perpendicular configuration the F atoms are nearer to the surface adatoms and it leads to stronger polarization. There is also higher density of charge on pairs of C atoms sharing a hexagon and a pentagon in the same direction in $C_{60}F_{18}$ fullerene that supports feature that appears to have three lobs in the STM image.

Further, our results show that there is no significant charge transfer between the $C_{60}F_{18}$ molecule and the surface and the large binding energy (~6.65 eV) of the molecule with the surface is due to induced polarization. The smallest Si–F bond distance is approximately 3 Å, and it confirms that there is no significant chemical bonding between the surface and the molecule. Interestingly we also find that the molecule tilts slightly and shifts towards one side of the corner hole to optimize the interaction and it also agrees with the image obtained from experiment which is slightly asymmetrical. The binding energy of F on Si surface is nearly twice the mean value obtained for F atoms on C_{60}. Therefore, there is a very strong energy gain if an F atom moves to the surface, though some compensation can be expected from rebonding within the fluorofullerene and possible chemical bond formation between Si and C atoms. Therefore, our results support the migration of F atoms from $C_{60}F_{18}$ to Si(111) surface. This can be expected to lead to asymmetry seen in the experimental image.

In conclusion, we have performed STM measurements and *ab initio* calculations on the adsorption of individual polar $C_{60}F_{18}$ molecules on Si(111)-7×7 surface. It is found that polar fluorinated carbon fullerene has large binding energy on a corner hole site of Si(111)-7×7 surface due to induced polarization on the Si surface. Calculations also suggest that $C_{60}F_{18}$ molecule binds on the Si surface with F atoms interacting with the surface. F atoms tend to migrate to the surface.

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