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Scanning tunneling microscopy and spectroscopy of individual C_{60} molecules on Si(100)-(2 × 1) surfaces

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Abstract

Individual C_{60} molecules chemisorbed on Si(100)-(2 × 1) surfaces have been studied by scanning tunneling microscopy and spectroscopy. Chemisorption was realized by annealing the samples with room-temperature deposited adsorbates to 600°C. Spectroscopic results on individual adsorbates reveal a transition of their electronic structure from that of a near-free adsorbate to that of SiC, as the adsorbate–substrate interaction increases.

Keywords: Chemisorption; Fullerenes; Physisorption; Scanning tunneling microscopy; Scanning tunneling spectroscopies; Silicon

1. Introduction

It is of interest to investigate the physical and chemical properties of individual fullerene molecules adsorbed on silicon substrates because of the basic scientific knowledge gained by such studies and the development of potential industrial applications. Indeed, the adsorption characteristics of fullerene molecules and films on a variety of metal and semiconductor surfaces have been extensively studied by scanning tunneling microscopy (STM) [1–16]. In particular, the interaction of fullerenes with the well-characterized silicon surfaces have been documented recently [6–8,10–16]. For example, STM images of C_{60} adsorbed on a Si(111)-(7 × 7) surface reveal charge transfer from the silicon dangling bonds to the lowest unoccupied

molecular orbital (LUMO) of the molecule that provides a relatively strong interaction between individual adsorbates and the substrate. The adsorbates were found to be immobilized under typical ultrahigh vacuum STM conditions, making it possible to obtain images at a variety of bias voltages [6]. In contrast, the interaction of C_{60} molecules with the Si(100)-(2 × 1) surface is found to be weaker, and a model employing dipole-induced dipole interactions has been proposed [15,16]. The weak interaction between the adsorbates and the substrate, however, makes it difficult to obtain reliable scanning tunneling spectroscopy (STS) measurements on an individual C_{60} molecule. It has recently been demonstrated that depositing C_{60} molecules on a Si(100)-(2 × 1) surface at room temperature, then annealing to 600°C, altered the bonding nature from physisorption to chemisorption [15,16]. The resultant strong covalent interaction offers an opportunity to study the electronic

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structure of the chemisorbed C_{60} molecules using STS measurements. This Letter reports on such measurements using an ultrahigh vacuum scanning tunneling microscope.

2. Experimental

The experiments were conducted in an ultrahigh vacuum chamber with a base pressure of 8.0×10^{-11} Torr. Commercial *n*-type Si(100) wafers (P-doped, $1.0 \Omega \cdot \text{cm}$, Virginia Semiconductor) were used as sample substrates. The samples were heated with electron beam bombardment from the back. A clean Si(100)-(2 × 1) surface was prepared by outgassing the sample for more than 10 h at 650°C, heating the sample to 1200°C for 2 min while keeping the chamber pressure below 2.0×10^{-9} Torr [17], followed by several minutes at 900°C and finally cooling down over a period of 30 min to room temperature. An optical pyrometer was employed to measure the sample temperature. C_{60} (>99.8%) powder was loaded in a Knudson cell with a BN crucible and outgassed at 300°C for more than 24 h. Submonolayer C_{60} molecules were deposited on the sample surface via sublimation at 280°C. The coverage was estimated directly from STM images, where one monolayer corresponds to 8.4×10^{13} molecules per cm^2 [13]. During C_{60} deposition, the chamber pressure was maintained below 2.0×10^{-10} Torr. STM measurements were performed in situ using a modified McAllister STM, equipped with control electronics by Digital Instruments.

3. Results and discussion

Presented in Fig. 1 are STM images showing samples prepared in the following three steps:

(i) 0.01 monolayer (ML) of C_{60} molecules was deposited on the silicon surface at room temperature (Figs. 1a and 1b); (ii) the sample was then annealed to 600°C for several seconds and cooled back to room temperature (Figs. 1c and 1d); and (iii) a second deposition of 0.01 ML of C_{60} molecules was made on the sample (Fig. 1e).

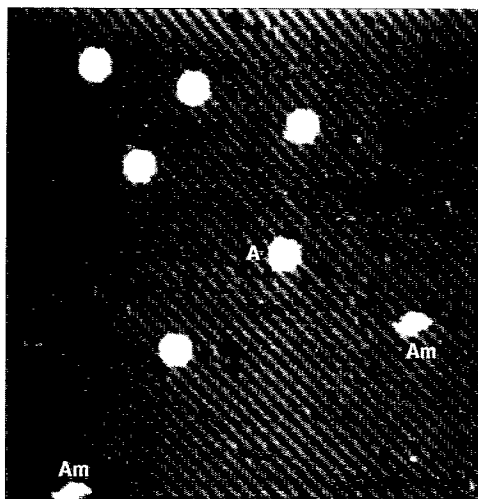
Fig. 1a is a large-scale STM image showing that the pre-annealed C_{60} molecules are randomly distributed on the Si(100) surface without any preferential adsorption at step edges or defects. In agreement with previous studies, these molecules are located in the troughs in between dimer rows. Fig. 1b shows several intact molecules (one of them is labelled "A") and two that were moved by the scanning tip (labelled "A_m"). In contrast, there is no tip-induced movement observed among the post-annealed C_{60} molecules, as shown in Figs. 1c and 1d, indicating a stronger adsorbate–substrate interaction.

Fig. 1c shows adsorbate clustering, preferred bonding of adsorbates to step edges and defects, and small silicon islands. Comparing with Fig. 1a, one can conclude that the annealing process promotes some surface diffusion of both the C_{60} molecules and substrate silicon atoms. Fig. 1d reveals that after the sample annealing there are two types of C_{60} molecules, labelled "B" and "C", that differ in their apparent heights. Note that these molecules are located in between troughs instead of in between dimer rows. In Fig. 1e, both the pre- and post-annealed C_{60} molecules were imaged on the same Si(100)-(2 × 1) surface. This image not only confirms the different locations of the pre- and post-annealed adsorbates, but also reveals their different sizes. The size of the post-annealed molecules is found to be smaller than that of the pre-annealed ones, yielding average heights of 7.0, 5.0 and 3.3 Å for type A, B and C

Fig. 1. (a) A large-scale STM image ($I_t=0.5$ nA, $V_s=-1.9$ V) revealing several pre-annealed C_{60} molecules randomly distributed on a Si(100) surface without any preferential interaction with step edges or defects. (b) An STM image ($I_t=0.5$ nA, $V_s=-1.9$ V) revealing six pre-annealed C_{60} molecules (one of them is labelled "A") and two molecules moved by the scanning tip (labelled "A_m"). (c) A large-scale STM image ($I_t=0.5$ nA, $V_s=-1.8$ V) showing adsorbate clusters, preferred bonding of adsorbates to step edges and defects, and small silicon islands on the substrate after the annealing process. (d) An STM image ($I_t=0.5$ nA, $V_s=-1.8$ V) showing post-annealed C_{60} molecules after annealing to 600°C. The molecules are labelled as "B" or "C" depending on the different type of adsorption. (e) An STM image ($I_t=1.0$ nA, $V_s=-1.8$ V) of a Si(100)-(2 × 1) surface, revealing both pre-annealed (labelled "A") and post-annealed (labelled "B" and "C") C_{60} adsorbates. The line across the type B molecule at the bottom of the image reveals that it is located on top of a single dimer.



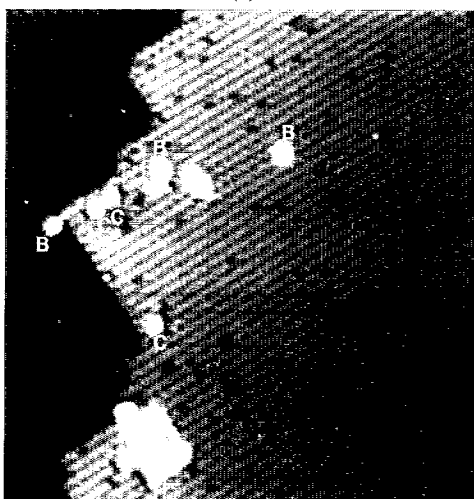
(a)



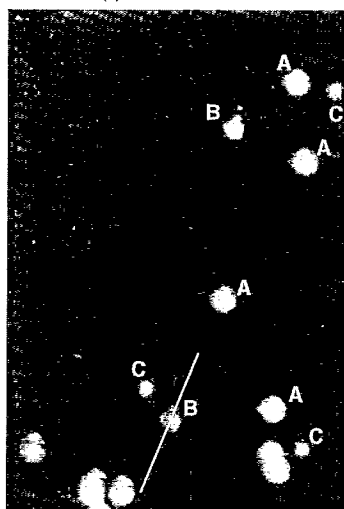
(b)



(c)



(d)



(e)

molecules, respectively. This observation indicates a reduction of the local density of states (LDOS) of the post-annealed adsorbates.

For the pre-annealed C_{60} molecules, the adsorbate-substrate interaction, which originates from the electric polarization of the adsorbate by the dipole moments of the underlying buckled dimer [15,16], is too weak to break the π bonds of the silicon dimers. In contrast, the elevated temperature during the annealing of the sample breaks the π bonds of the silicon dimers, providing two unsaturated dangling bonds on each one, which allow C_{60} molecules to bond covalently on top of them. In other words, the annealing enables the adsorption to overcome the barrier from physisorption to chemisorption.

The STM image shown in Fig. 1e indicates that type B molecules are found on top of a single dimer, suggesting that the π bond of the dimer has been broken to form covalent bonds with the C_{60} molecule. The height difference between a type B molecule at a step edge and a type B molecule on the higher terrace is about 1.4 Å, which is close to the single atomic silicon step height of 1.36 Å, indicating that their charge densities are nearly equivalent. In contrast, type C molecules appear at positions originally occupied by two dimers in the same row. Figs. 1a and 1c have shown that the annealing process involves surface diffusion of both the C_{60} adsorbates and substrate silicon atoms. Such a diffusion gives rise to the bonding of the adsorbates to the step edges of the substrate and the formation of silicon islands around the adsorbates. At step edges, the preferred bonding of the C_{60} molecules is to the end rather than to the side of the dimer row. In our experiments, we found that either a longer annealing time or a higher annealing temperature would convert more type B adsorbates to type C. Therefore, we propose that type C adsorbates might be created by a diffusion process followed by bonding to silicon atoms in the second layer.

As illustrated in Fig. 2, a type C adsorbate can be formed in two ways. First, when a type B molecule diffuses to a substrate step formed by the ends of dimer rows, it tends to bond there. Further growth of the step due to Si surface diffusion around the molecule converts the type B adsorbate

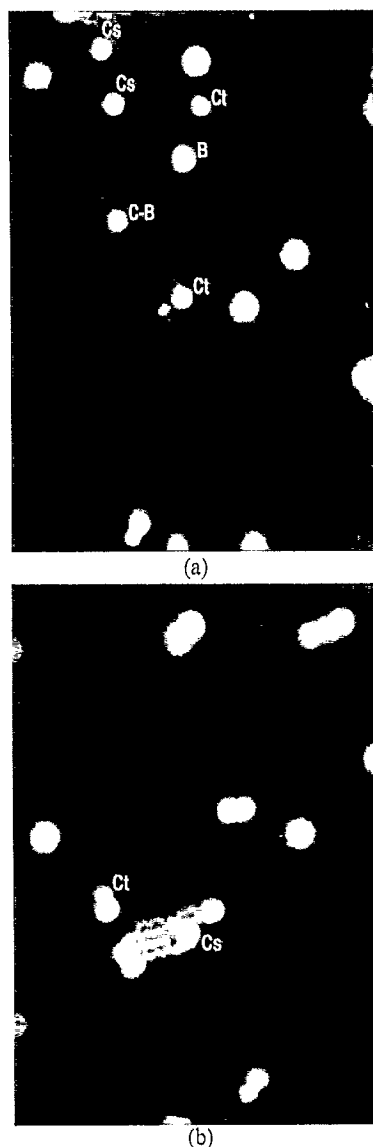


Fig. 2. (a) An STM image ($I_t=0.9$ nA, $V_s=-1.9$ V) showing different type C adsorbates: C_1 , C_2 , and C-B, are as explained in the text. (b) An STM image ($I_t=0.9$ nA, $V_s=-1.9$ V) showing that the formation of silicon islands around the adsorbates also converts type B adsorbates to type C in a newly grown silicon layer, such as the molecule labelled " C_3 ".

into a type C (see the molecules labelled "C"). Note that the molecule labelled "C-B" in Fig. 2a is a type B molecule on a lower terrace, and would have become a type C molecule if Si atoms had grown around it. The formation of silicon islands around the adsorbates, as shown in Fig. 2b, also

converts the type B adsorbates on the terrace to type C in a newly grown silicon layer (see the molecules labelled C_s). Secondly, when a diffusing type B adsorbate finds a surface defect on a terrace, such as a double missing dimer, for example, it tends to bond to the defect and become a type C molecule (see the molecules labelled “ C_r ”).

As discussed above, the type C molecules can form covalent bonds not only with the surface silicon atoms but also with the Si atoms in the second layer. The smaller apparent height of type C adsorbates is consistent with these molecules bonding to the second-layer silicon atoms much more strongly than type B molecules. If the type C molecules bonded to the second-layer silicon atoms with the same strength as type B adsorbates, we would expect a height difference close to the silicon single step height, as observed for type B adsorbates. However, the larger difference of the adsorbate height indicates that the LDOS of type C molecules is smaller than for type B molecules. This reduction in density of states is expected because type C molecules form many more covalent bonds with both the second-layer silicon atoms and the silicon surface, resulting in a much stronger adsorbate–substrate interaction than for type B

molecules. The strong adsorbate–substrate interaction for type C molecules is also evidenced by the local reconstruction around each type C adsorbate, including a missing-dimer like feature and two c-shaped defects in the neighboring dimer rows shown. In contrast, there is no significant reconstruction near type B molecules.

To further characterize the C_{60} molecules, STS measurements have been performed on individual type A, B and C adsorbates. First, a large-scale ($200 \text{ \AA} \times 200 \text{ \AA}$) image was obtained to choose an isolated molecule. Secondly, the scan size was gradually decreased to $20 \text{ \AA} \times 20 \text{ \AA}$. Then STS measurements were made on top of the molecule for 5 s. After that, the molecule was imaged again to check that the thermal drift rate was less than 0.1 \AA s^{-1} . We were not able to obtain reliable STS spectra on type A molecules because they were mobilized by the tip upon changing the bias during the STS measurements. However, stable STS spectra have been recorded on both type B and C molecules because they have been immobilized by covalent bonding to the substrate. All data were averaged over ten voltage scans.

Fig. 3 shows three STS ($\partial \ln i / \partial \ln v$) curves measured on (I) a clean, well-ordered Si(100)-(2 × 1)

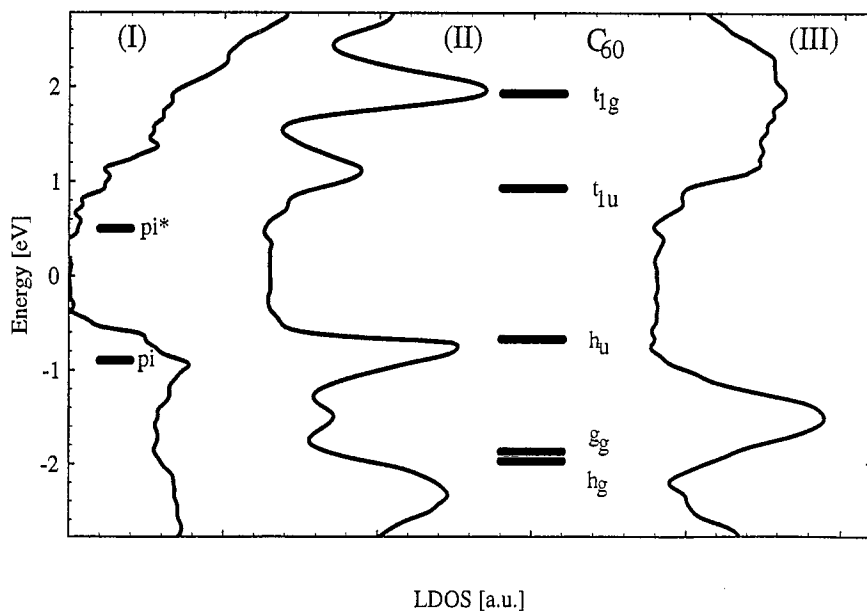


Fig. 3. STS data ($I_t = 1.0 \text{ nA}$, $V_s = -1.8 \text{ V}$) of (I) a bare Si(100)-(2 × 1) surface, (II) a type B adsorbate on a Si(100)-(2 × 1) surface, (III) a type C adsorbate on a Si(100)-(2 × 1) surface, and the energy levels of a free C_{60} molecule.

region, (II) an isolated type B molecule, and (III) an isolated type C molecule, along with calculated positions of free C_{60} energy levels [21]. Curve (I) shows an occupied state located about -0.9 eV below the Fermi level, and a weaker unoccupied state at $+0.5$ eV. These states are derived from the interaction between the dangling bonds on each of the Si dimer atoms and represent the π -bonding and π^* -antibonding combinations, respectively [18-20]. Curve (II) in Fig. 3, reproducibly recorded over several isolated type B molecules, shows four intense peaks near the Fermi level. A close fit between the STS data of type B adsorbates and the energy levels of free C_{60} molecules is apparent [21,22]. Here, the occupied state at -0.7 eV represents the HOMO, while the unoccupied state at $+1.1$ eV represents the LUMO. This observation implies the absence of charge transfer between the chemisorbed adsorbates and the substrate. The wide peak at -2.3 eV corresponds to the two closely spaced h_g and g_g levels, which are separated from the HOMO by about 1.6 eV. Also, the t_{1g} peak is found to be about 0.9 eV above the LUMO level.

Previous STS measurements on a monolayer of C_{60} molecules deposited on an Si(100)-(2 × 1) surface at room temperature [9] yielded a HOMO-LUMO band gap of 0.9 eV, which is much smaller than the 1.6 eV obtained for free C_{60} molecules [21-23]. However, our STS results on individual type B C_{60} molecules after annealing show that the HOMO-LUMO energy gap is about 1.8 eV, which is essentially the same gap as that of free C_{60} molecules. As mentioned above, the type B molecule is located on top of a single dimer, suggesting that the π bond of the dimer has been broken to form two covalent bonds with the molecule. Correspondingly, one of the 90 C-C bonds (30 double bonds and 60 single bonds) of the C_{60} are also broken. Here, the breaking of one C-C bond can be treated as a perturbation of the electronic structure of a free C_{60} molecule. Therefore, the spectra of type B molecules is similar to the energy level of a free C_{60} . On the other hand, a type C molecule forms more covalent bonds with the substrate than a type B molecule because it interacts with both the first- and second-layer Si atoms. This means many more carbon-

carbon bonds on the type C molecule are broken and the adsorbate-substrate interaction cannot be treated as a perturbation to the free C_{60} electronic structure. This is supported by Fig. 2, which also shows the STS (curve III) obtained on individual type C molecules. This spectrum is characterized by the presence of a strong occupied state located at -1.5 eV below the Fermi level and a wide-band structure above the Fermi level. The estimated value of the gap is about 2.2 eV, which is close to the band gap of silicon carbide (2.2 - 2.9 eV) [24]. We attribute the features of curve III to Si-C bonds around the type C molecules. By comparing with curve II, one can see that the strong Si-C interaction has dominated the electronic structure of type C molecules. Furthermore, in order to assess how much the tunneling current modifies the STS spectra, we increased the junction impedance by a factor of five by reducing the current setpoint, and found that the energy levels in the new spectra were unchanged.

4. Conclusion

It was found that a C_{60} molecule deposited at room temperature on a Si(100) surface changes its bonding nature after a thermal annealing process. It is shown that surface diffusion of the adsorbates during the annealing process allows them to preferentially bond to defect sites on terraces and to step edges. STS results suggest that the electronic structure of a chemisorbed C_{60} molecule depends on its interaction with the substrate.

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