

Temperature effects of adsorption of C_{60} molecules on Si(111)-(7 × 7) surfaces

Dong Chen and Dror Sarid

Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

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The adsorption of submonolayer C_{60} molecules on Si(111)-(7 × 7) surfaces, deposited at room temperature and then annealed to various elevated temperatures, is studied using scanning tunneling microscopy. For room temperature adsorption, the C_{60} molecules were observed to favor bonding to adatom bridge sites within a triangular half cell. After annealing to 600 °C, however, they were found to bond dominantly to adatom or restatom sites. The adsorbate-substrate interaction at room temperature is characterized by charge transfer from the substrate to the molecules. After the annealing process, however, the adsorbates bond covalently to the substrate. It is found that the desorption of the submonolayer adsorbates due to the annealing process is minimal. The surface diffusion of the adsorbates begins when annealing the sample to 700 °C, at which point the initial clustering of the adsorbates takes place. When annealing the sample to 850 °C, the C_{60} molecules decomposed on the sample surface and reacted with the Si atoms to form SiC islands.

I. INTRODUCTION

Fullerene-substrate interactions have attracted much attention in recent years since the discovery of a method for synthesizing mass quantities of C_{60} (Ref. 1) and the development of other related fullerene materials. Scanning tunneling microscopy (STM), with its ability to probe surface structural and electronic properties on an atomic scale,²⁻⁴ has been used to study the adsorption of fullerene molecules, and the growth of fullerene films, on a variety of solid surfaces including metal⁵⁻⁷ and semiconductor substrates.⁸⁻¹⁴ Silicon surfaces, due to their inherent scientific interest and technical importance, have been popular substrates for studying the interaction of fullerenes with semiconductor surfaces.¹⁰⁻¹⁴

Two recent STM studies of the adsorption of C_{60} molecules on Si(111)-(7 × 7) surfaces at room temperature^{10,11} showed the relatively strong interaction between these molecules and the surface, where the C_{60} molecule appeared to be immobilized. In particular, Wang *et al.*¹¹ showed that among several available adsorption sites on the (7 × 7) unit cell, the C_{60} molecules adhere most often to the center site of each triangular subunit cell, which is surrounded by three Si adatoms and does not have a Si restatom at its center. In another study, Xu, Chen, and Creager¹³ studied the growth of crystalline C_{60} islands on Si(111)-(7 × 7) substrates. They observed that the C_{60} islands were oriented primarily in two distinct directions. Based on their results, they proposed a model of interface disorder-order transition associated with the pinning of C_{60} molecules at the surface (7 × 7) corner holes and bonding to adatom bridge sites. These studies provided important information regarding C_{60} adsorption properties on Si(111)-(7 × 7) surfaces at room temperature. However, details of bonding properties, as well as the nature and strength of the interaction between the C_{60} and Si(111)-(7 × 7) surfaces, left some questions unresolved. In particular, little work was conducted on the adsorption of C_{60} molecules on

Si(111)-(7 × 7) surfaces at elevated temperatures.

In this paper, we present a study of the adsorption of submonolayer C_{60} molecules on Si(111)-(7 × 7) surfaces at room temperature and subsequent annealing to various elevated temperatures. The results show that the adsorbate-substrate interaction before and after the annealing processes is quite different. For room temperature adsorption, the interaction is characterized by charge transfer from the occupied surface dangling bond states to the lowest unoccupied molecular orbital (LUMO) of C_{60} molecules. Also, the adsorbates are preferentially adsorbed on the adatom bridge sites within a half cell. After annealing the sample to 600 °C the C_{60} molecules bond to the middle adatoms and restatoms, forming Si-C covalent bonds. Further annealing the sample to 700 °C causes breaking of Si-Si bonds on the substrate surface. At this temperature, the C_{60} molecules with Si atoms bonded to them start to diffuse, and form clusters across the surface. Finally, when annealing the sample to 850 °C, the number of Si atoms bonding to the C_{60} molecules is large enough that the molecules decompose on the surface, and react with the Si atoms to form SiC islands that are mostly located at step edges.

II. EXPERIMENT

The experiments were conducted in an ultrahigh vacuum (UHV) chamber with a base pressure of 5.0×10^{-11} Torr. Commercial *n*-type Si(111) wafers (phosphorus doped, $\sim 0.005 \Omega\text{-cm}$) were used as sample substrates. The clean Si(111)-(7 × 7) surface was prepared by heating the sample to 1200 °C with electron beam bombardment on the back of the sample, rapid cooling to 900 °C, and slow cooling to room temperature. Pure (>99.8%) C_{60} powder was deposited with a Knudsen cell equipped with a BN crucible that was mounted 5 cm away from the sample, and outgassed at 300 °C for more than 24 h. Submonolayer C_{60} molecules were then deposited on the

sample surface via sublimation, typically at 280 °C for several minutes. The C₆₀ coverage was measured directly from STM images, assuming that one monolayer corresponds to a full layer of C₆₀ molecules on the surface, each occupying one square nanometer area. An optical pyrometer was employed to monitor the sample temperatures during the annealing process while the chamber pressure was maintained below 5.0×10^{-10} Torr. Annealing times were typically 30 s. All STM measurements were performed *in situ* at room temperature using a McAllister STM (Ref. 15) equipped with electronics and software from Digital Instruments.¹⁶

III. RESULTS AND DISCUSSION

A. Adsorption at room temperature

Displayed in Figs. 1(a) and 1(b) are two STM topographic images obtained sequentially from a Si(111)-(7 × 7) surface, following a deposition of approximately a 0.05 monolayer of C₆₀ molecules at room temperature. Figure 1(a) was acquired with a positive sample bias (+2.0 V, 100 pA), corresponding to tunneling from the tip into the unoccupied states of the sample. Figure 1(b) was acquired with a negative sample bias (−2.0 V, 100 pA) where tunneling occurred from occupied states of the sample into the tip. In addition to the well-resolved (7 × 7) symmetry on the Si(111) reconstructed surface, the images also show the adsorbed C₆₀ molecules, which appear as protrusions on top of the surface in either sample bias. Note that the apparent discontinuities around the adsorbates are caused by the image processing method used to enhance the contrast of the images. This method allows for the observation of the top of the adsorbates while retaining a large contrast of the background surface. The C₆₀ adsorbates appear to be randomly distributed across the surface, and mostly isolated. This indicates a relatively strong adsorbate-surface interaction, which can be contrasted to the case of GaAs(110) surfaces where the C₆₀ molecules form monolayer islands.⁸ Only a few percent of the C₆₀ molecules are observed to adsorb on the (7 × 7) corner hole sites,

consistent with the observation of Wang *et al.*¹¹ Because of the large apparent size of the adsorbates, it is not immediately obvious where their bonding sites are unless they bond to the highly symmetric locations such as the corner hole sites.

Figure 2 shows a schematic of a unit cell of the dimer-adatom-stacking fault (DAS) model of the Si(111)-(7 × 7) surface,¹⁷ consisting of 12 adatoms within a unit cell. The six adatoms around the corner holes are the corner adatoms and the other six are the middle adatoms. Each of these adatoms is bonded to three atoms in the surface double layer. There is a partial stacking fault in the double layer that generates the faulted and unfaulted sides of the unit cell. The Si atoms in the top of the double layer are the restatoms. There are 19 dangling bonds in one unit cell, 12 from the adatoms, six from the restatoms, and one deep inside the corner hole. Also shown in this figure are some dimensional details of the (7 × 7) unit cell and several available bonding sites for C₆₀ molecules. These sites are adatom sites (*A*), adatom bridge sites (*B*), corner hole sites (*C*), restatom sites (*R*), and the center sites of triangular half cells (*M*). It has been shown in previous studies,^{10,11} and observed in our images, that the C₆₀ molecules have similar sticking probabilities on either the faulted or unfaulted halves of the unit cell. Therefore, the correspondent sites of faulted and unfaulted half cells for C₆₀ molecules could be considered to be equal.

The well-resolved substrate (7 × 7) symmetry in the STM images can be used as a scale reference which allows one to determine the bonding positions of the C₆₀ adsorbates on the surface. This is demonstrated in Fig. 3 which shows an image of individual C₆₀ molecules adsorbed on the Si(111)-(7 × 7) surface. Figure 3(b) is a cross section profile along the line *L-L* of the image shown in Fig. 3(a). The distance from the center of the corner hole *A* to the center of the corner hole *B* is 46.56 Å, while that from the center of the corner hole *D* to the position of the C₆₀ molecule *C* is 35.49 Å, indicating that this molecule is bonded to the position corresponding to a restatom site *R* (see Fig. 2). Several individually adsorbed C₆₀ molecules located at different bonding sites are shown in Fig. 1(a), where the white triangles and

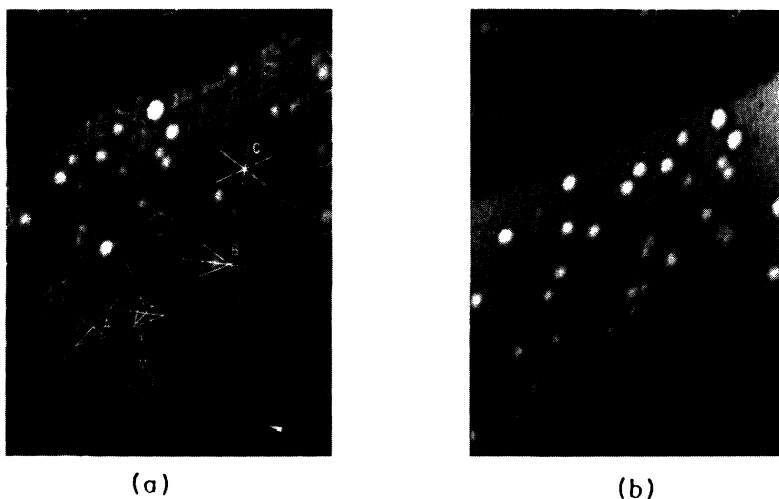


FIG. 1. STM images of a Si(111)-(7 × 7) surface with 0.05 ML C₆₀ molecules deposited on it at room temperature. (a) was acquired with a sample bias of −2.0 V and a tunneling current of 100 pA. (b) was acquired with a sample bias of +2.0 V and a tunneling current of 100 pA.

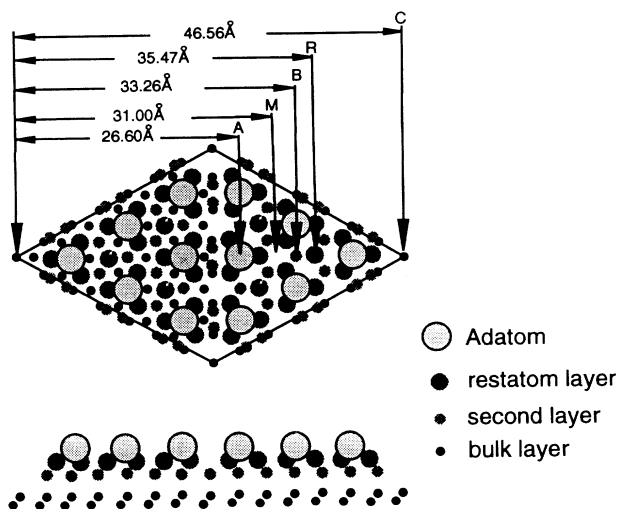
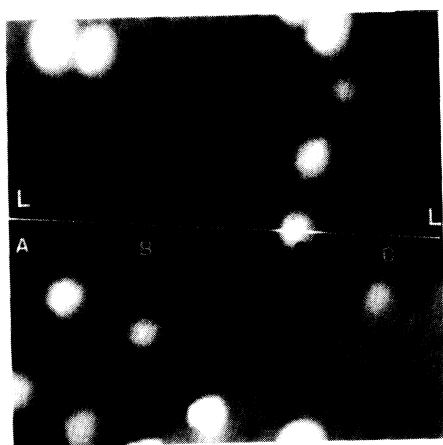
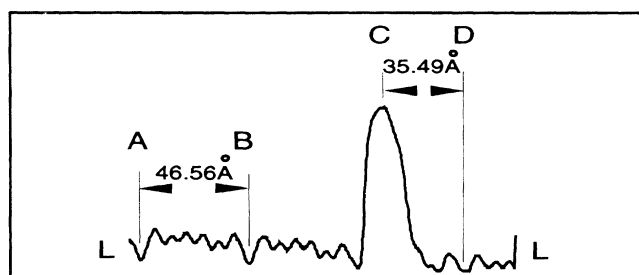


FIG. 2. A schematic of a unit cell of the Si(111)-(7 × 7) DAS model. Some dimensions of the unit cell and several possible C₆₀ adsorption sites are also shown.



(a)



(b)

FIG. 3. (a) A STM image of a Si(111)-(7 × 7) surface with isolated C₆₀ molecules adsorbed on it. (b) A cross section profile of the line L-L shown in (a). The known distance between A and B is used as a reference to measure the distance between C and D, which determines the adsorption position of the C₆₀ molecules in the unit cell.

lines help to determine the symmetries of these bonding sites. Using the method illustrated in Fig. 3, we find from Fig. 1(a) that the C₆₀ molecule labeled A is bonded on top of one middle adatom, the one labeled B is bonded to the bridge site of two middle adatoms, and the one labeled M is located at the center of the triangular half cell. The molecule labeled C is clearly bonded at a corner hole site.

Although some C₆₀ molecules are found to bond to various bonding sites on the surface when deposited at room temperature, most are found to bond to the asymmetric positions which are not on any of the diagonals of (7 × 7) unit cells. One of these adsorbates is labeled X in Fig. 1(a). Careful inspection of the STM images shows that these C₆₀ molecules are bonded to the positions corresponding to the bridge sites between one corner adatom and one middle adatom. This result indicates that when the C₆₀ molecules adsorb on Si(111)-(7 × 7) surfaces at room temperature, the favored bonding sites are those of adatom bridge sites within a triangular half cell. In fact, very few C₆₀ molecules adsorbed on the center of the half cell (site M) at room temperature have been observed in our experiments. Also, almost no C₆₀ adsorbates are found at the positions on the short diagonal of the (7 × 7) unit cell. The observations in our experiments suggest that the C₆₀-Si(111)-(7 × 7) interaction is somehow related to the dangling bond surface states, and is not van der Waals in character. Had the latter been the case, the adsorbates would have favored those surface sites that have a large coordination factor such as C or M sites. The bonding probabilities of C₆₀ molecules on a variety of surface sites, therefore, seems to be proportional to the density of dangling bonds on the surface.

A photoemission and inverse-photoemission study of C₆₀ deposited on different metals by Ohno *et al.*¹⁸ revealed that the energy levels derived from the C₆₀ are aligned with the substrate Fermi level (E_f). The center of the band derived from the highest occupied molecular orbital (HOMO) of deposited C₆₀ was about 2.25 eV below E_f . Therefore, for an approximate 1.6 eV energy gap between the HOMO and the LUMO of C₆₀, the LUMO aligns close to and below E_f , resulting in charge transfer from the substrate into the LUMO of the adsorbed C₆₀. For the Si(111)-(7 × 7) surface, the high local density of states throughout the gap, which strongly pins the Fermi level near the midgap, makes the surface metalliclike. Local tunneling spectroscopy measurements³ show that the adatoms of the (7 × 7) unit cell give rise to substantial tunneling currents even at a very low bias, indicating that they have a high density of states near E_f and are the origin of the surface metallic property. In analogy to the adsorption of C₆₀ on metal surfaces, we believe that the C₆₀-Si(111)-(7 × 7) interaction at room temperature is similar to that of C₆₀-metal interaction, which is characterized by a charge transfer accompanied by a mixing of the LUMO level with the local surface states associated with the dangling bonds on the surface. As shown in Fig. 1, each triangular half cell can be occupied by only one C₆₀ molecule, although the six adatoms in a half cell provide, at most, three X sites which may accommodate three adsorbates. This result implies the ex-

istence of repulsive forces between the adsorbates, which may originate from the charge transfer from the surface states of the Si(111)-(7 × 7) substrate into the LUMO of adsorbates. An occupation of two adsorbates in one half cell is quite rare in this coverage, and only one has been observed in the room temperature deposition case [indicated by an arrow at the bottom of Fig. 1(a)].

A study of C₆₀ adsorption on Si(100)-(2 × 1) surfaces¹⁴ revealed that for a deposition at room temperature, the adsorbates exhibited certain surface diffusion (on a nanometer scale) and preferred to adsorb at step edges or defects, or even cluster at low coverages. In the case of C₆₀ adsorption on Si(111)-(7 × 7) the C₆₀-surface interaction appears to be stronger, as can be seen in Fig. 1, where most of the adsorbates are individually adsorbed and randomly distributed on the surface. The fact that there is no enhanced sticking of C₆₀ at step edges is also observed in these images. Figure 4 shows schematically the energy level diagram of a C₆₀ molecule on the Si(111)-(7 × 7) surface, as well as on the Si(100)-(2 × 1) surface. As mentioned earlier, on the Si(111)-(7 × 7) surface, the high state density near E_f is contributed by the adatom dangling bond state that has its highest state density about 0.15 eV below E_f .³ Therefore, when the LUMO of C₆₀ molecules aligns below the substrate E_f , charge transfer from these adatom dangling bond states to the LUMO of the C₆₀ could occur. In the case of the Si(100)-(2 × 1) surface, however, the electronic structure is described by an occupied π state below E_f and an unoccupied π^* state above E_f , and there is a surface-state band gap between them. Here, E_f is pinned locally by surface defects.¹⁹ When C₆₀ molecules adsorb on a defect-free region of a Si(100)-(2 × 1) surface, charge transfer from the substrate is clearly less likely than for the Si(111)-(7 × 7) surface, because of the existence of the surface-state band gap (see Fig. 4). In fact, it has been observed that the C₆₀-C₆₀ repulsive interaction on a Si(100)-(2 × 1) surface is minimal.¹⁴ The surface states near E_f derive from surface defects, and the charge transfer from these defect states to the adsorbates may occur when they bond to these defect sites. This explains why on a Si(100)-(2 × 1) surface the C₆₀ molecules prefer to stick to surface defects or step edges.

It is of interest to compare the interaction strength of C₆₀ on different semiconductor surfaces. For GaAs(110) surfaces, for example, there are no surface states within the bulk band gap, the C₆₀-surface interaction is weak

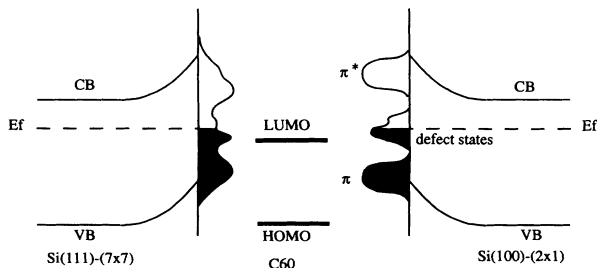


FIG. 4. A schematic shows the energy level diagram of a C₆₀ molecule on a Si(111)-(7 × 7) surface (left-hand side) and on a Si(100)-(2 × 1) surface (right-hand side).

and is van der Waals in nature, and the molecules form ordered two-dimensional close-packed islands.⁸ For a Si(100)-(2 × 1) surface,^{12,14} which has a small surface-state band gap within the bulk band gap, the strength of the C₆₀-surface interaction is increased, as evidenced by the small surface mobility of the adsorbates and the local ordering of adsorbates commensurate with the substrate structure that can be observed in high coverages. For a Si(111)-(7 × 7) surface, however, there is a high density of surface states distributed across the bulk band gap, and the C₆₀-surface interaction is even stronger, so that little surface mobility is observed. Here, the interaction is characterized by charge transfer from the dangling bond surface states into the LUMO of the C₆₀ molecules.



FIG. 5. A STM image measured on the sample surface shown in Fig. 1 following an annealing to 600 °C.

B. Annealing to 600 °C and 700 °C

The relatively weak C_{60} -surface interaction on GaAs(110) surfaces allows the adsorbates to form monolayer islands on the surface even at room temperature.⁸ It was expected, therefore, that annealing our samples to higher temperatures would cause the adsorbates to diffuse on the surface and to form C_{60} islands, or to thermally desorb from the substrate. Figure 5 is an STM image acquired on the same sample surface shown in Fig. 1, following an annealing to 600 °C and subsequent cooling to room temperature. Surprisingly, the image presents no island formation, as the C_{60} molecules remain separately adsorbed on the surface. The C_{60} coverage is measured as 0.05 monolayers (ML), which is the same as before the annealing, implying that the desorption of the C_{60} from the surface at this temperature is minimal. After the annealing, however, some aspects of the adsorption are found to differ from those observed before the annealing.

Figure 6 is a high resolution STM image measured on the same sample surface of Fig. 5, where individually adsorbed C_{60} molecules are shown. After the annealing, these adsorbates are found to bond to positions on the long diagonal of the 7×7 unit cell. A careful measurement of the adsorption locations of some of these C_{60} molecules reveals that they are located on the middle adatom sites (labeled *A*) and restatom sites (labeled *R*). Again, the white triangles and lines in the figure show the symmetries of the adsorbates on the (7×7) unit cell. Actually, the adsorbates labeled *A* are not exactly located above the middle adatoms but rather shift about 1 Å toward the center of the triangular half cell. It is also noted that few of the adsorbates are found to bond to the corner adatoms at this coverage, indicating that the C_{60} molecules preferably react with the middle adatoms. Indeed, it was found in the study of the chemical reactivity of Si(111)- (7×7) surfaces that adatoms around the corner hole are the least reactive among a variety of chemically inequivalent surface sites on the surface.²⁰

Figure 7(a) is a STM image acquired with a sample bias of +0.5 V. As shown in the image, the surface defect density appears higher in comparison with the unannealed case (see Fig. 1). These defects appear mostly in the vicinity of the C_{60} adsorbates (indicated by dark arrows), indicating that the annealing process promotes further interaction between the adsorbates and

the substrate, giving rise to these defects. Also, two C_{60} molecules bonded within one triangular half cell are often observed on the surface after the annealing process. These C_{60} dimers are aligned along the long diagonal of the (7×7) unit cell [see *D1* and *D2* in Fig. 7(a)]. Figure 7(b) is a surface height profile along the line *L-L* shown in Fig. 7(a), which allows us to determine the bonding sites of the molecules in the C_{60} dimer. It is found that one adsorbate (*C*) bonds to a position 28.3 Å away from the corner hole *B* and the other one (*D*) bonds to a site that is 37.0 Å away from the corner hole *B*. A mapping of these locations to the substrate (7×7) unit cell shows that the *C* and *D* molecules of the *D1* are located above a middle adatom and a restatom, respectively, but both shift about 1.5 Å along the long diagonal of the unit cell toward the closer corner hole. The same measurements from two *D1* C_{60} dimers in the image give the same results, indicating that the shift is not due to experimental artifacts. If that were the case, the two *D1* dimers would shift in the same direction, yet the observation is that one shifts downward and the other shifts to the left. The intramolecular distance between the two C_{60} molecules of *D1* is 8.7 Å, which is even smaller than that of the C_{60} fcc close-packed distance. Note that defects are usually created around the *D1* dimers and the isolated adsorbates. From these results, obtained after the annealing process, we deduce that the annealing process involves the formation of covalent bonds between the surface Si atoms and the adsorbates. In the C_{60} dimer labeled *D2*, one of the molecules that appears larger is located at a position corresponding to the top of the corner adatom. The different apparent sizes of the adsorbates on the surface may indicate a difference in the number of Si-C bonds formed on these adsorbates.

Another fact worth noting is that after the annealing process there are no C_{60} molecules adsorbed at corner-hole sites, in contrast to the unannealed case where the adsorption at these sites does occur. This result implies that at room temperature, the C_{60} molecules that adsorbed at these sites interact weakly with the substrate. The measurements of C_{60} coverages on the surface shows that there are no noticeable differences before and after the annealing process, indicating that the C_{60} molecules that adsorbed at these sites diffused to other low energy bonding sites during the annealing process, instead of desorbing from the surface.

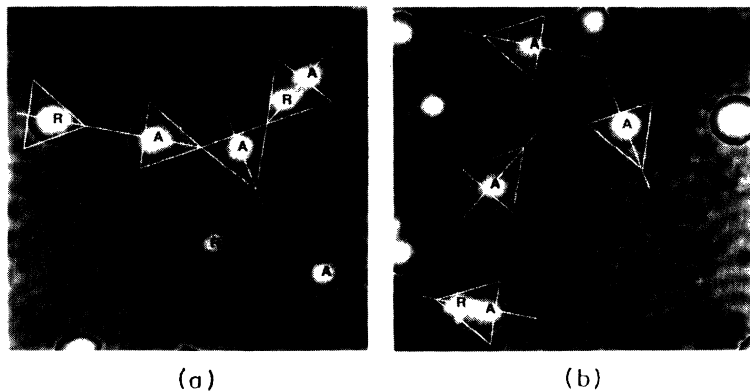


FIG. 6. Two STM images of individually adsorbed C_{60} molecules on a Si(111)- (7×7) surface of the same sample surface shown in Fig. 5.

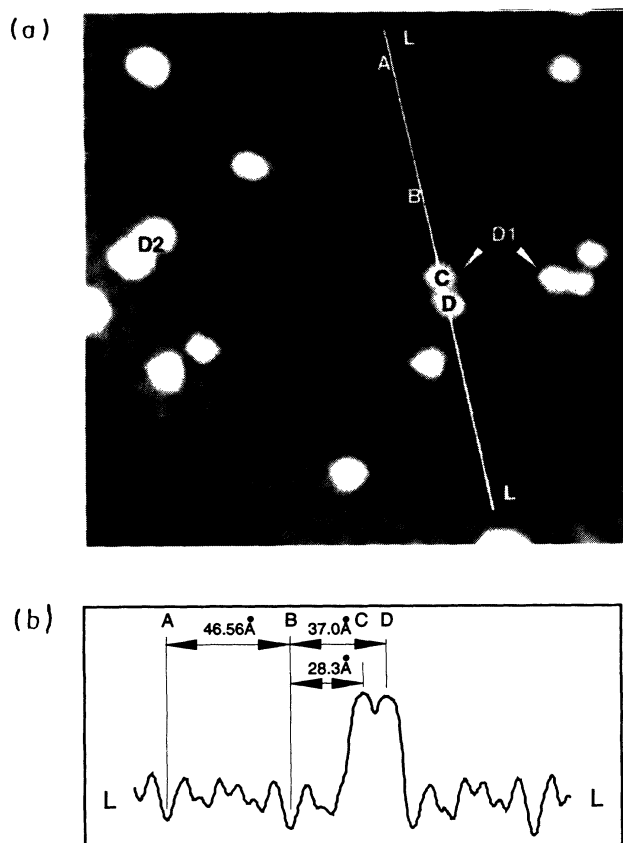


FIG. 7. (a) An image taken from the same sample surface of Fig. 5 showing the C_{60} dimers on the surface and the surface defects created around the adsorbates. (b) A cross section profile of the line $L-L$ in (a).

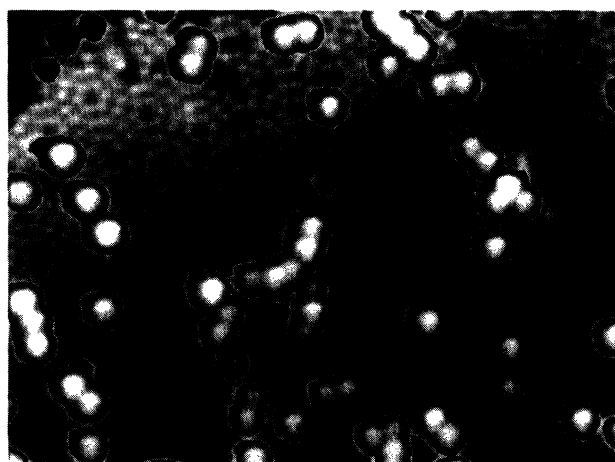
Displayed in Fig. 8 are two STM images obtained from a sample surface which is prepared under the same conditions as the sample surface shown in Fig. 1, except being annealed to 700°C . Even at this temperature, no C_{60} decomposition has been observed, and these molecules remain intact and firmly anchored to the surface. While the adsorption features of the C_{60} molecules on the surface are very similar to those after annealing to 600°C , a higher density of C_{60} dimers and larger molecular clusters are observed on the surface. The clustering of the adsorbates indicates that the annealing process causes some surface diffusion of these adsorbates. Also, more defects appeared across the substrate surface, implying that the diffusion is probably due to the breaking of surface Si-Si bonds other than the C-Si bonds between the C_{60} and the surface. The missing surface Si atoms may have attached to the C_{60} molecules, forming a Si- C_{60} compound.

C. Annealing to 850°C

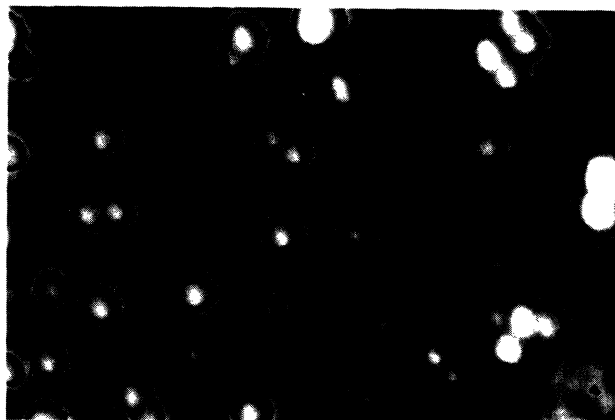
Figure 9 shows two images taken on the same surface of the sample shown in Figs. 1 and 5, following an annealing to 850°C for 20 s. The images show that islands are formed on the surface after the annealing process. The

islands are located mostly at the step edges, have roughly a triangular shape [see Fig. 9(b)], and are oriented with their edges parallel to the substrate $[11\bar{2}]$ directions. Another feature noted in the image is that the monatomic steps on the substrate, compared to the room temperature and to the lower annealing temperature cases, are converted to groups of steps consisting of two or more monatomic steps, indicating the disappearance of layers of surface silicon atoms. It is possible, therefore, that these islands are SiC clusters on the substrate, formed from the decomposition of C_{60} molecules and the released carbon atoms reacting with the Si substrate. The presence of the SiC clusters at the substrate step edges is probably due to the clusters pinning the steps, as is commonly observed on imperfectly cleaned Si surfaces.

Figure 10 is a contrast enhanced STM image of the surface where the total gray scale range has been divided into three ranges which, from low to high, are labeled 1, 2, and 3. In this image, the substrate (7×7) symmetry is resolvable and a (7×7) unit cell is shown. Besides



(a)



(b)

FIG. 8. Two images measured from a $\text{Si}(111)-(7 \times 7)$ surface with submonolayer C_{60} molecules deposited on it at room temperature and subsequently annealed to 700°C .

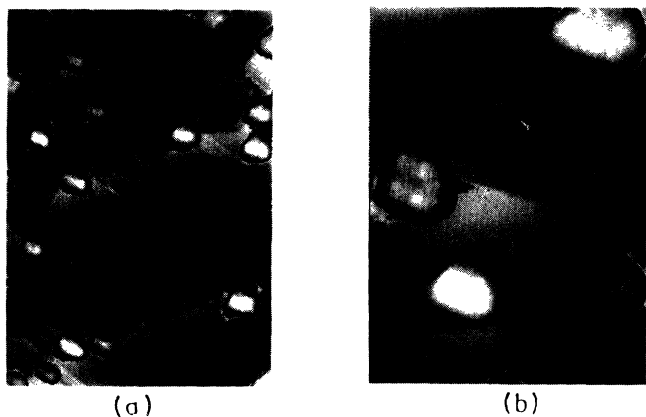


FIG. 9. Two images taken from the same sample surface of Fig. 5 after annealing the sample to 850 °C.

the SiC islands formed on the surface, some islands containing ball-like features are also presented (indicated by arrows). These ball-like features are believed to be the intact C₆₀ molecules. The intermolecular distances of the several undecomposed C₆₀ molecules (indicated by a dark arrow) measure about 17 Å, implying that Si atoms may bond between them. One can envision that during the annealing process, the C₆₀ molecules act as a ball rolling on the Si surface. Because a Si-C bond is stronger than a Si-Si bond, at this elevated temperature, the Si-Si bonds of the surface Si atoms will break and the released Si atoms will bond to the C₆₀. When the number of Si atoms attached to a C₆₀ molecule is small, they will form islands of a Si-C₆₀ compound. However, when the number of Si atoms sticking to a C₆₀ molecule is large, the stress on the molecule would be high enough to open the C₆₀ cage, and the molecule will decompose, forming SiC islands on the surface.

IV. CONCLUSION

In this work, we studied the adsorption of C₆₀ molecules on Si(111)-(7×7) surfaces at room temperature with subsequent annealing to elevated temperatures. For room temperature adsorption, the C₆₀ molecules preferentially adsorb on the bridge sites of the adatoms within a triangular half cell. Compared to Si(100)-(2×1) and GaAs(110) surfaces, the Si(111)-(7×7) surface has a stronger interaction with the C₆₀ molecules. After annealing the samples to 600 °C, the adsorbates are dominantly bonded to the middle adatoms or restatoms. It is found that the annealing promotes the adsorbate-surface

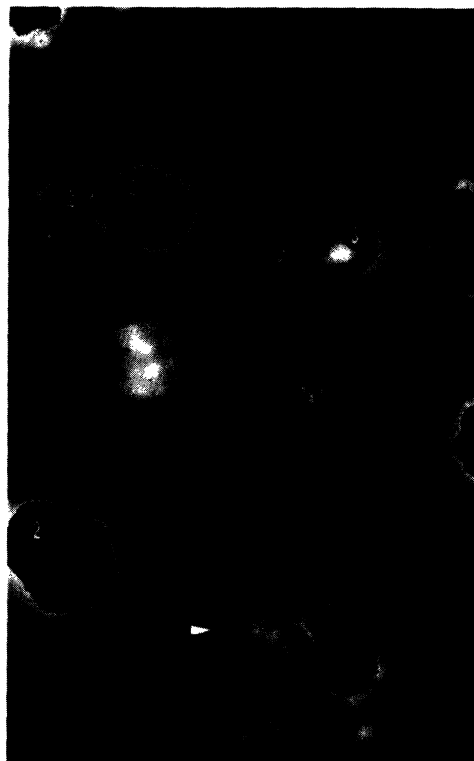


FIG. 10. An image measured from the same sample surface of Fig. 9.

interaction, and is accompanied by the generation of surface defects in the vicinity of the adsorbates. When annealing the samples to 700 °C, the adsorbates start to diffuse across the surface with Si atoms being attached to them, and an initial clustering of the adsorbates starts to take place. Annealing the sample to 850 °C causes the C₆₀ molecules to decompose and form SiC islands on the substrate. This study may open a potential new method for growing SiC films using fullerene materials.

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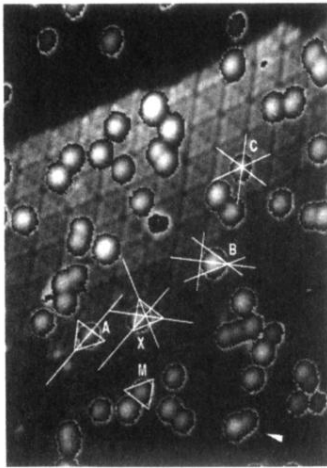
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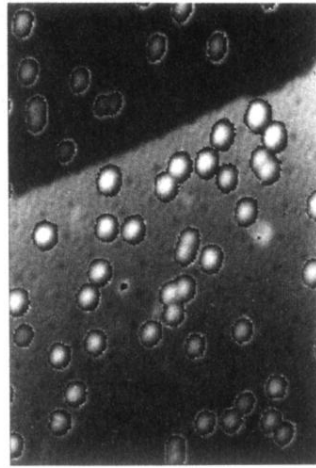
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(a)



(b)

FIG. 1. STM images of a Si(111)-(7 × 7) surface with 0.05 ML C₆₀ molecules deposited on it at room temperature. (a) was acquired with a sample bias of -2.0 V and a tunneling current of 100 pA. (b) was acquired with a sample bias of +2.0 V and a tunneling current of 100 pA.

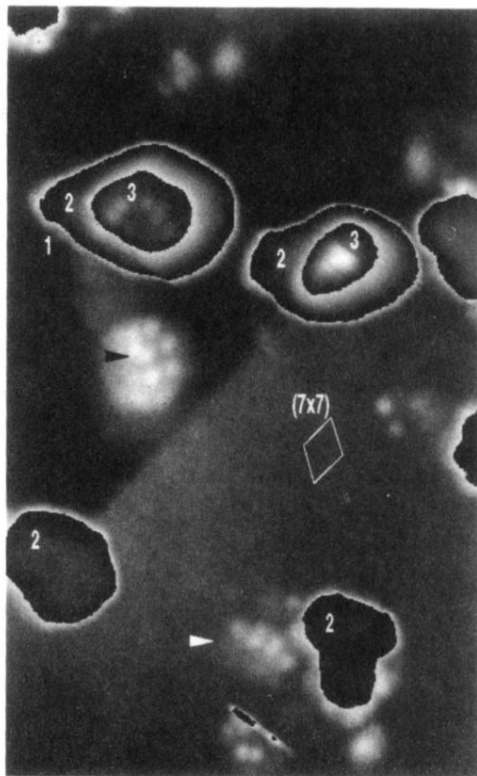


FIG. 10. An image measured from the same sample surface of Fig. 9.

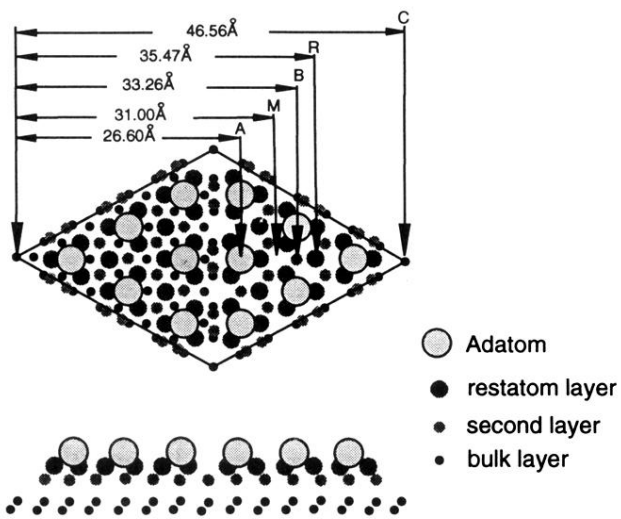
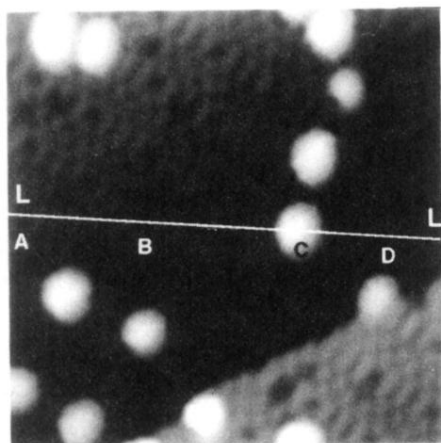
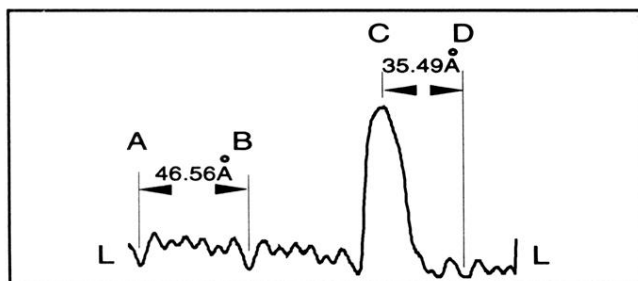


FIG. 2. A schematic of a unit cell of the Si(111)-(7 × 7) DAS model. Some dimensions of the unit cell and several possible C₆₀ adsorption sites are also shown.



(a)



(b)

FIG. 3. (a) A STM image of a Si(111)-(7 \times 7) surface with isolated C₆₀ molecules adsorbed on it. (b) A cross section profile of the line L-L shown in (a). The known distance between A and B is used as a reference to measure the distance between C and D, which determines the adsorption position of the C₆₀ molecules in the unit cell.



FIG. 5. A STM image measured on the sample surface shown in Fig. 1 following an annealing to 600 °C.

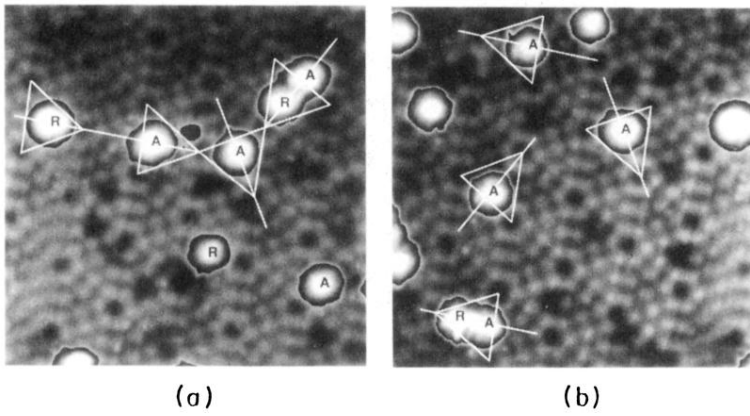


FIG. 6. Two STM images of individually adsorbed C_{60} molecules on a $Si(111)-(7 \times 7)$ surface of the same sample surface shown in Fig. 5.

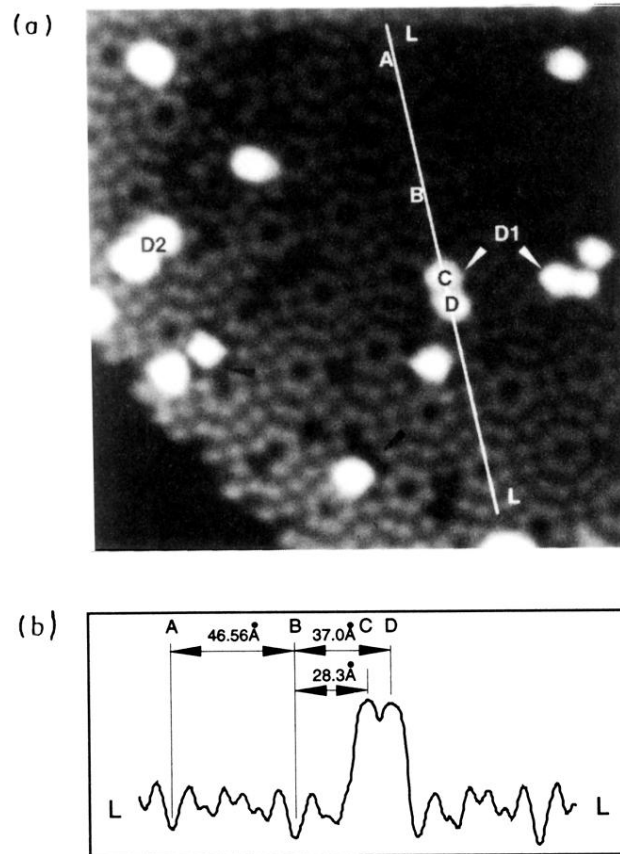
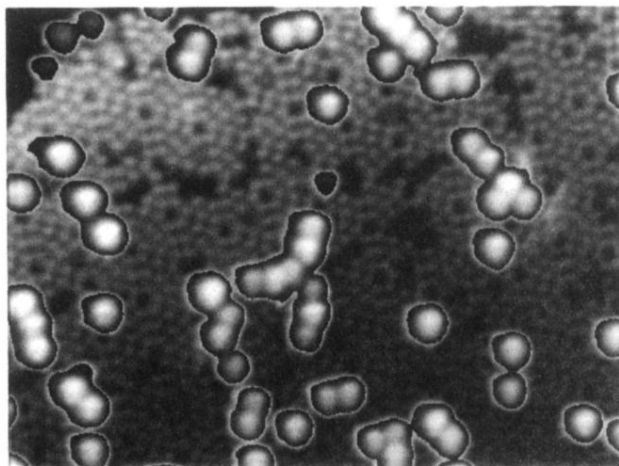
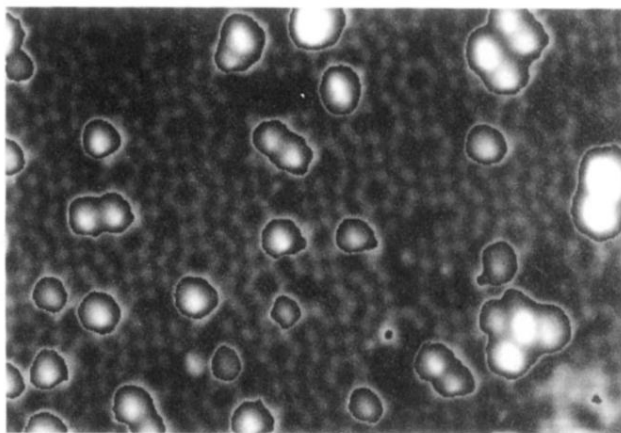


FIG. 7. (a) An image taken from the same sample surface of Fig. 5 showing the C_{60} dimers on the surface and the surface defects created around the adsorbates. (b) A cross section profile of the line $L-L$ in (a).

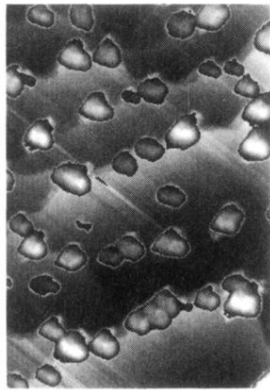


(a)

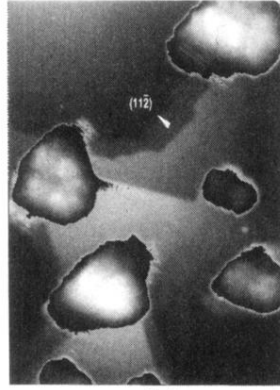


(b)

FIG. 8. Two images measured from a Si(111)-(7 × 7) surface with submonolayer C₆₀ molecules deposited on it at room temperature and subsequently annealed to 700 °C.



(a)



(b)

FIG. 9. Two images taken from the same sample surface of Fig. 5 after annealing the sample to 850 °C.