Stressed C_{60} Layers on Au(001)

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The geometric and electronic structure of a C_{60} molecular layer on the Au(001) surfaces was studied by scanning tunneling microscopy and spectroscopy. The interaction between the substrate and overlayer is strong enough that the C_{60} monolayer is commensurate and uniaxially stressed along the ⟨110⟩ direction. As a result of stress the charge density around the C_{60} molecule appears to be deformed. Charge transfer was observed in ultraviolet photoemission spectroscopy and scanning tunneling spectroscopy, revealing the adsorption mechanism of the C_{60} molecule on this substrate.

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For the last two years, the carbon fullerene molecules have drawn much attention after the recent breakthrough in their synthesis [1]. With macroscopic amounts of molecules, the structural and electrical properties of the smallest C_{60} fullerene have been widely studied. Diffraction methods were used to extract the short-range structural parameters, confirming the proposed buckminsterfullerene structure [2,3]. Scanning tunneling microscopy (STM) has the unique capability of directly observing the three-dimensional charge density of the individual C_{60} molecule [4–8]. These studies have shown the well ordered close-packed fcc layers [4–8], epitaxial growth mechanisms [5], and surface kinetics [5,8] on GaAs(110), Au(111), Au(110), Si(111), and Si(001) surfaces. The observed charge density around C_{60} on these substrates appears to be spherical at any tunneling voltage. The voltage dependent STM images demonstrated the existence of the C_{60} HOMO (highest occupied molecular orbital) -LUMO (lowest unoccupied molecular orbital) band gap [8]. The C_{60} molecules are immobile on some surfaces, indirectly indicating that they may ratchet along one orientation [8]. In the photoemission [9,10] and surface enhanced Raman spectroscopy studies [11], the charge transfer either from surrounding alkali metals in the C_{60} bulk or from the metal substrate in the C_{60} films results in the energy shift of the HOMO state and growth of the LUMO derived state near the Fermi level.

In this study, commensurate C_{60} molecular layers were observed on the Au(001) substrate. Several phases with different unit cell structures are present due to different commensurate periods. We prove for the first time that the charge density around the C_{60} molecule can be deformed to an ellipsoid with a uniaxial stress caused by the lattice mismatch. The driving force for the commensurate structure is a strong overlayer-substrate interaction, studied by ultraviolet photoemission spectroscopy (UPS) and scanning tunneling spectroscopy (STS).

The detailed design of the STM can be found elsewhere [12]. A high purity Au(100) crystal with $<0.16°$ miscut was polished mechanically and electrochemically, then cleaned *in situ* by ion sputtering and annealing until a sharp (5×20) low energy electron diffraction pattern without any trace of impurities in the Auger spectrum was observed. The fullerene was formed by the contact arc method, followed by a liquid chromatography to separate pure C_{60} molecules. The composition of the purified sample was tested by a mass spectrometer, revealing no trace of other fullerenes. A small Knudsen cell charged with the C_{60} molecule was outgassed at 250 °C in a UHV STM chamber for two days before deposition. During deposition the chamber pressure was less than 5×10^{-10} Torr and little trace of other impurities was detected on the Au(001) surface. The coverage of C_{60} molecules was measured by a quartz thickness monitor in the photoemission study. Since the sticking coefficient of C_{60} on the quartz is lower than on the Au(001), the coverage in the photoemission study may be underestimated by as much as 50%. The coverage in the STM study was estimated by counting C_{60} molecules.

The Au(001) surface is known to reconstruct with a surface unit cell of ~5×20 [13]. The driving force of the reconstruction is to expose low energy (111) facets. Atomic density on this surface layer is (20–25)% higher than that in the second layer of the square lattice. Along the ⟨110⟩ direction every fifth atomic row (14.4 Å separation) is buckled outward in order to accommodate the high atomic density [14]. The measured corrugation of the "ridge" by STM was as large as 1.0 Å as shown in Fig. 1(a) (vertical bright lines separated by 14.4 Å). Along the $\langle\bar{1}10\rangle$ direction, a dislocation is present every 18–20 spacings. As C_{60} molecules are deposited on this surface, they preferentially adsorb near the dislocation site and ridge. An isolated molecule is shown in Fig. 1(a), showing symmetric charge density (appearing as a bright circular spot). When the second molecules arrive near an adsorbed one, they often form a weak dimer near the ridge. The detailed interpretation of Figs. 1(b) and 1(c) will be discussed later. With increasing coverage, islands fit to the ridge such that the width is $n\times14.4$ Å (n = integer). In Fig. 1(a), the nearest-neighbor distance

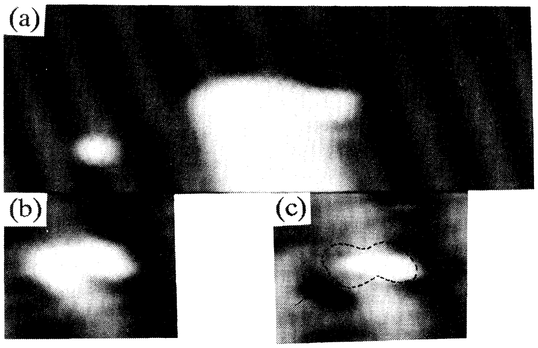

FIG. 1. (a) 140×50-Å gray scale image of an isolated C_{60} molecule and a small island commensurate with the "ridge" rows. (b) Two C_{60} molecules near the ridge at -2 V and (c) at -0.5 V. Two dark spots, the depletion of Au charge density, are indicated by arrows. Broken line shows the positions of the molecules in (c).

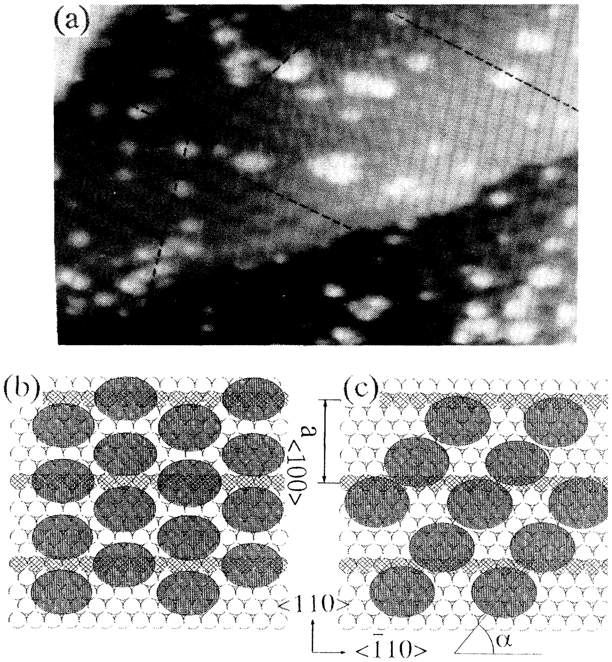

FIG. 2. (a) 240×200-Å image of the C_{60} molecular layer on the Au(001) imaged at -2 V. Broken lines indicate grain boundaries. (b) *A* type compressed layer. The Au(001) (5×20) substrate appears as a near-hexagonal layer and the ridges (shaded atoms) are separated by 14.4 Å. (c) *B* type layer. The angle *α* can vary with the intermolecular distance along the ⟨110⟩. Large ellipses indicate the charge density of C_{60}.

in the island can be 9.6 Å (28.8/3) if three molecules fit to 2×14.4 Å while the nearest-neighbor distance in bulk crystal [3] is 10.0 Å. Stress is present in the island since it grows epitaxially and its perimeter forms the low energy structure (one-dimensional surface tension).

With the coverage of >0.2 monolayer (ML), large monolayer islands, different from the one in Fig. 1, appear. Figure 2(a) shows a typical monolayer C_{60} film on the reconstructed Au(001) surface. This occupied state image was taken at the sample bias of -2 V with the tunneling current of ~0.2 nA. Three terraces are separated by steps with the height of ~2 Å, which is the same as that of the Au substrate. White blobs on top of the distorted close packed layer are C_{60} molecules in the second layer, and the first layer molecules underneath can be revealed once they are removed. Their observed charge density is almost circular (symmetric) like isolated molecules on the Au(001). The first layer C_{60} (shown in middle terrace) forms an ordered island, but showing slight variation of the nearest-neighbor distances. The ordered structure resembles a close packed fcc (111) plane with some distortion. Islands with different amounts of distortion are separated by grain boundaries, shown by broken lines. The detailed structure analysis was possible on the STM images where both the ordered islands and the bare reconstructed Au(001) (5×20) surface coexists. The C_{60} monolayer is commensurate with the Au(001) substrate only along the ⟨110⟩ direction. If *m* C_{60} molecules fit to $n\times 14.4$ Å, the nearest-neighbor distance is $n\times 14.4/m$ Å. When the stress in the film is too big, they grow with tilted angle *α* as shown in Fig. 2(c) (called *B* type grain). Grain boundaries are formed due to the difference in the angle *α* of neighboring grains [Fig. 2(c)], when two neighboring grains grow from separate nucleation sites. The smallest compressed nearest-neighbor distance was as small as ~8.0 Å. Under the uniaxial stress, the charge density around the C_{60} molecule is substantially deformed to an ellipsoid in STM images of *B* type grains. The ratio of major and minor axes of the deformed charge density is a function of the stress, ranging from 1.5 to 4 in both *A* and *B* type grains. The ratio is independent of the tunneling voltage though the charge density appears to be a parallelogram at the HOMO level because of intermolecular bonding which will be discussed later. There is no direct experimental evidence that the C_{60} cage itself is deformed. Further experimental and theoretical study may be necessary to locate atomic positions in the cage. When three molecules fit to 28.8 Å (the compressed nearest-neighbor distance is 9.6 Å), the epilayer reveals the type *A* structure [Fig. 2(b)], which is the structure with the lowest stress among all epitaxially grown monolayers on the Au(001).

If the interaction between the C_{60} molecule and the substrate is small, the film will be incommensurate with the Au(001) substrate. The cohesive energy for the crystallization of C_{60} molecules is known to be the van der Waals interaction. In Figs. 1, 2, and 3, the interaction between the molecule and the Au(001) substrate is strong enough to reveal a commensurate epilayer. On the uniaxially stressed monolayer, stronger than van der Waals in-

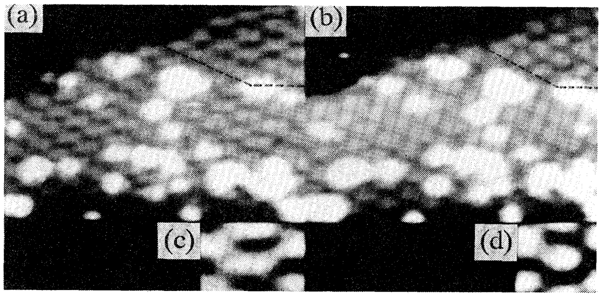

FIG. 3. 120×100-Å gray scale images of the same area at (a) −2 V and (b) 2 V. Broken lines indicate the grain boundaries. Closeup images of a C_{60} molecule at (c) −2 V and (d) 2 V, showing the bonding configuration.

teraction is present among molecules. Figure 3 shows voltage dependent STM images at −2 V (near the HOMO level) and +2 V (near the LUMO level). *A* and *B* type epilayer grains are separated by a grain boundary. At the LUMO level [Figs. 3(b) and 3(d)], the C_{60} molecule reveals a charge density with an ellipsoidal shape of which the ratio of major and minor axes is ∼3 in *B* type and ∼1.5 in *A* type. The closeup view of the molecule does not show the intramolecular structure and shows little evidence of intermolecular bonding. The threefold degenerate π LUMO states (intramolecular structure) may not be easily imaged, since they are surface states on the surface of the ellipsoid and C_{60} molecule may be still rotating around the major axis. However, since the epitaxial layer is highly compressed, the rotational speed may be damped down substantially. If the C_{60} molecule ever ratchets to the substrate, the Au(001) may be one of the best substrates. At the HOMO level, the charge density around the C_{60} molecule resembles a parallelogram. Again intramolecular fivefold degenerate π states are not imaged. There is a strong indication of intermolecular bonding, as shown in Figs. 3(a) and 3(c). The different shapes between the charge densities at HOMO and LUMO levels are due to the intermolecular bonding. As a result of the large stress in the epitaxial layer, an intermolecular bonding with a neck structure and an antibonding with a nodal structure may be present between molecules [Figs. 3(c) and 3(d)]. The existence of the intermolecular bonding and antibonding orbitals was suggested in a recent Fourier transform study [15].

As described earlier, a strong interaction was proved by the commensurate C_{60} monolayer. In C_{60} molecular layers on various metal surfaces, the charge transfer from the metal substrate to the molecule was estimated by measuring the core level shifts in photoemission spectra [9]. On some metal substrates, HOMO-LUMO band gaps and LUMO level shifts were reported [8,9]. We tried to image the charge transfer from the Au(001) substrate to the C_{60} molecule by STM and to measure the change of the electronic structure on the substrate and molecule by STS and UPS. UPS ($h\nu=21.2$ eV) was done for the same Au(001) sample but in a different UHV chamber. In the low coverage UPS spectra, the Au substrate spectrum was subtracted to compare with high coverage spectra which are very similar to the reported results [9,16]. Figure 4 shows the UPS and STS spectra at various coverages. In the UPS spectra, the HOMO level with h_u symmetry shifts to higher binding energy with increasing coverage. The C 1*s* core level of the C_{60} shifts by the same amount in the x-ray photoemission spectroscopy [17]. This result can be explained by the charge transfer from the Au(001) substrate to the molecule at low coverage or photohole screening [18]. By comparing the UPS spectra with STS and STM results, the shift is more likely due to charge transfer. In the STS spectra, the HOMO band is similar to that in the UPS spectra, although the peak position is ∼0.2 eV off, which may be a limit of STS caused by tip effect and weighted **k** integration.

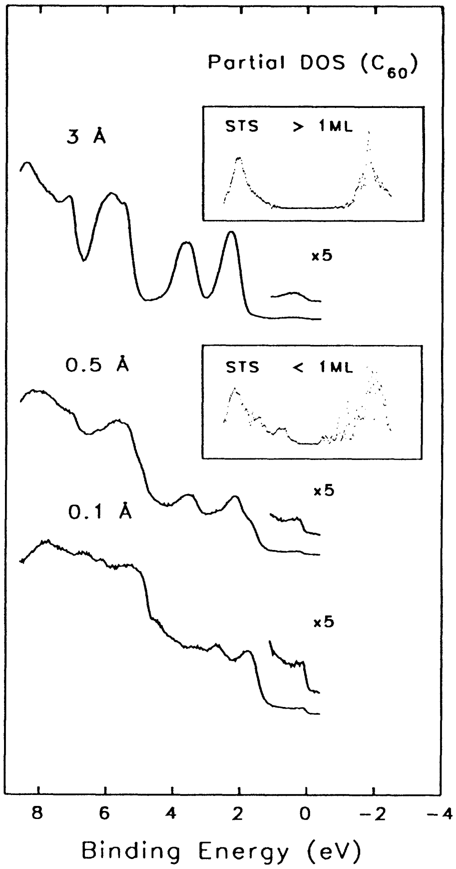

FIG. 4. Photoemission spectra of C_{60} valence band at three different coverages where Au substrate spectra were subtracted. Corresponding STS spectra are inside the insets with the same energy scale.

In the recent surface enhanced Raman spectroscopy of

C_{60} on gold, the symmetry reduction and the perturbation of electronic structure in the adsorbed molecule were observed [11]. During the deposition of an alkali metal on a C_{60} molecular layer, a LUMO derived state (LUMO-metal hybridized state) is present within the HOMO-LUMO gap [9,10]. At low coverage, the LUMO derived state was observed in both STS and UPS spectra. [It is possible to interpret this state as a HOMO derived state (HDS), and the state above the Fermi level can be interpreted as a LUMO derived state (LDS) [17]]. The state decreases in population with increasing coverage. The presence of the LDS and HDS states is more evidence of the charge transfer from the substrate to the molecule. If the amount of charge transfer is big enough, the effect can be observed by STM. Figures 1(b) and 1(c) show the two C_{60} molecules near the Au(001) ridge at the tunneling voltage of -2 and -0.5 V. At -2 V two molecules are visible, but at -0.5 V only one molecule is seen and two dark spots, decreased charge density, were observed around the molecules in the Au substrate. The details of charge transfer among metallic states, HOMO, LUMO, HDS, and LDS will be discussed elsewhere [17]. The existence of HDS and LDS is evidence of chemisorption of the C_{60} molecule on the Au(001) substrate.

In summary, the electronic structures and corresponding geometrical structure are shown by STM, STS, and UPS. The charge transfer from the substrate and to the molecule results in strong chemisorption of the molecule on the Au(001) substrate. As a result of the stress caused by commensurate growth along the ⟨110⟩, the charge density of C_{60} molecules is deformed to an ellipsoidal shape. There is an indication of intermolecular bonding in the compressed C_{60} layer.

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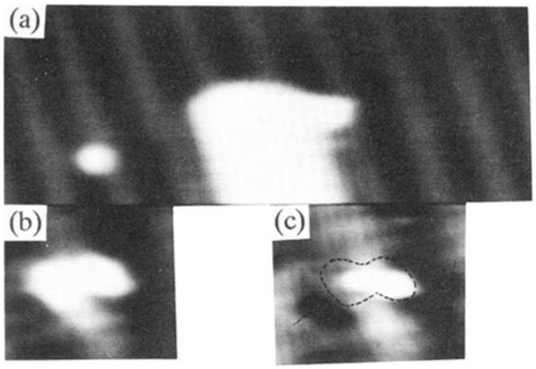

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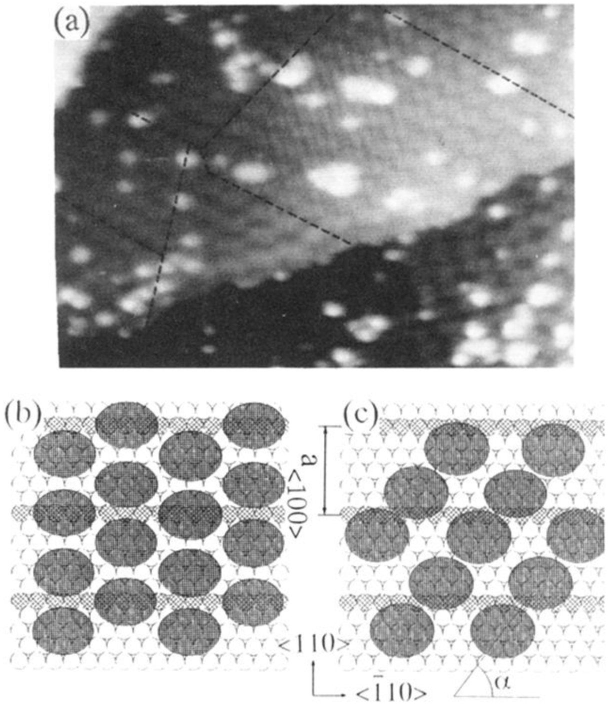

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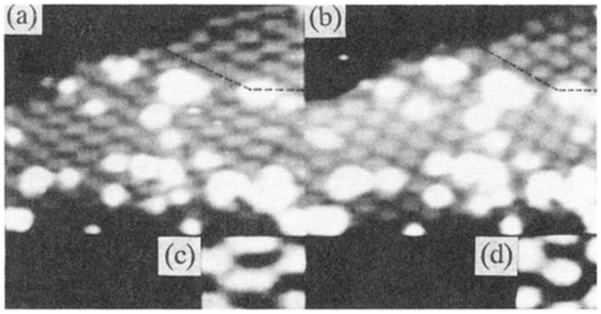

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