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Molecular-scale structural distortion near vacancies in pentacene

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Molecular vacancies form in both of the crystallographic basis sites of thin pentacene crystals. Features in scanning tunneling microscopy images of these crystals correspond to the exposed terminal atoms of molecules. The (001) and $(00\bar{1})$ surfaces of pentacene are distinguishable, which allows for the identification of the absolute orientation of crystals and for the unambiguous assignment of the position of molecules relative to each vacancy. For vacancies in each molecular basis site of the pentacene (001) surface, the image feature associated with one molecular nearest neighbor is displaced by significantly more than other molecules. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2913687]

The importance of defects in controlling many of the properties of organic electronic materials has led to extensive efforts to predict and characterize defects near organic-organic and organic-inorganic interfaces. Extended defects such as dislocations and grain boundaries between crystals of small-molecule organic semiconductors have important roles in transport and crystal growth.[1,2] At a smaller scale, evidence from spectroscopy and theoretical modeling suggests that molecular vacancies trap or scatter charge carriers.[3–5] Electron diffuse scattering has provided structural evidence for distortion of the crystalline lattice near vacancies.[6] Despite these efforts, however, the real-space structure of vacancies is largely unknown. In this letter, we provide evidence for large structural distortions in the vicinity of vacancies in crystalline pentacene islands on a passivated silicon substrate. This structural information should aid in making the connection between the identification of potential defects in monolayer-scale pentacene thin films and the electronic properties of devices based on these layers, for which experimental probes are already available.[7]

We used the chemical attachment of styrene ($C_6H_5CH{=}CH_2$) to the dimers of the Si (001) 2×1 surface to create flat unreactive substrates for the pentacene films. The chemical attachment of similar molecules has been widely described and exploited for other applications.[8,9] In our work, samples from Si (001) wafers (0.07–0.1 Ω cm, phosphorous-doped) were chemically cleaned and heated in ultrahigh vacuum to produce clean Si (001) surfaces. The styrene-modified surface was created by exposing the clean Si (001) surface to styrene vapor at 10^{-7} Torr for 300 s. In comparison with the ordered rows of passivated dimers observed in surfaces passivated with cyclopentene, there was no ordered lattice of styrene molecules.[10] We found that the styrene-modified surface, however, provides better passivation toward impinging pentacene molecules than cyclopentene and thus allowed scanning tunneling microscope (STM) images of the pentacene crystals with higher resolution and repeatability.

Monolayer-thick pentacene crystals on styrene-passivated Si (001) have a similar large-scale structure to pentacene monolayers on SiO_2 or on Si (001) surfaces passivated with other organic molecules or a preliminary layer of pentacene.[11,12] The pentacene films consisted of molecular layers in which a series of terraces exposed either (001) or $(00\bar{1})$ planes. STM images of the third and the fourth molecular layers of two different pentacene crystals are shown in Figs. 1(a) and 1(b). The bias conditions for both images (−3 V applied to the tip and 300 pA tunneling current) were selected to yield images of the highest occupied molecular orbitals.[13] There was no change in the observed topography for bias voltages between −3.5 and −2.2 V and for tunneling currents between 200 and 350 pA. The molecular features form rows differing in height by an average of 20 pm, as visible in the sections shown in Fig. 1. This corrugation is a result of the two inequivalent molecules in the pentacene unit cell in which one molecule extends further along the surface normal and thus appears higher in the STM images.

Diagrams of the (001) and $(00\bar{1})$ surfaces based on the bulk structure of pentacene are shown in Figs. 2(a) and 2(b),

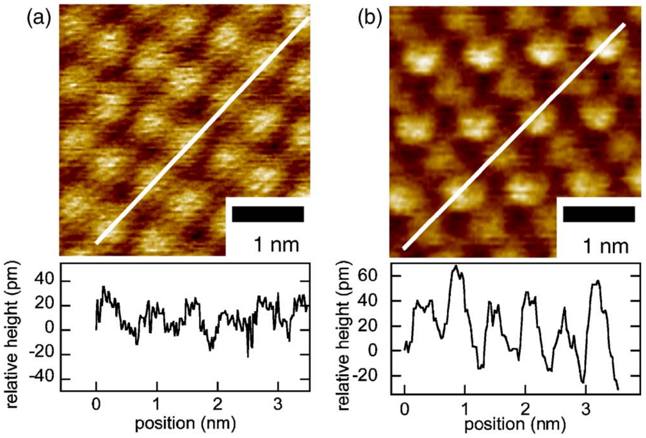

FIG. 1. (Color online) STM images of the (a) (001) and (b) $(00\bar{1})$ surfaces of pentacene. A section along the highlighted line appears beneath each image.

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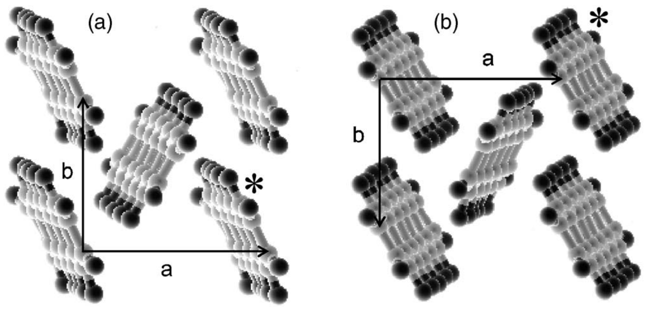

FIG. 2. Molecular models of the (a) (001) and (b) (00$\bar{1}$) surfaces of a pentacene crystal based on crystallographic data from Ref. 14 The molecules closest to a central low molecule are labeled with a star.

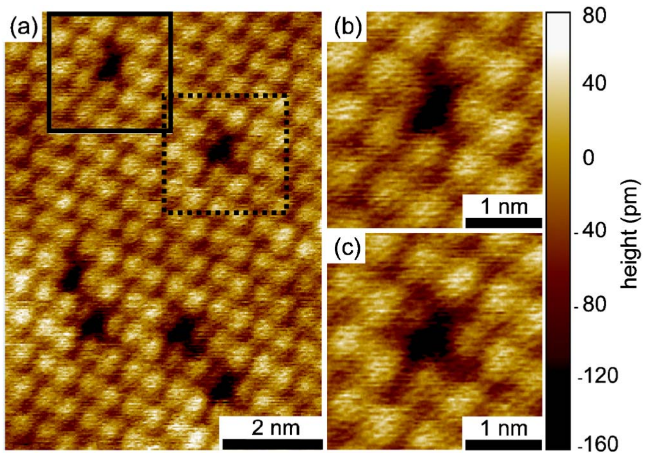

FIG. 3. (Color online) (a) STM images of the (001) surface of pentacene. (b) and (c) show larger images of the areas within the solid and dashed boxes.

respectively.[14] There are distinct structures associated with the (001) and (00$\bar{1}$) faces that allow these faces to be recognized in STM images. This distinction is possible because the structures of the (001) and (00$\bar{1}$) faces are related by the inversion center of the $P\bar{1}$ symmetry of the pentacene crystal rather than by a rotation.

For both the (001) and (00$\bar{1}$) faces, one neighbor of each lower center molecule is significantly closer than all of the others. The (001) surface is shown in Fig. 2(a) with the nearest neighbor of the center low molecule marked with a star. To move clockwise from this molecule to reach another neighbor of the same low molecule requires moving along the longer side of the unit cell, with lattice parameter a. In the (00$\bar{1}$) plane in Fig. 2(b), moving in a clockwise direction from the molecule closest to the low molecule, again marked with a star, traces the shorter side of the unit cell, with lattice parameter b.

The absolute orientations of pentacene crystals can be determined by comparing STM images with the crystallographic model. In Fig. 1(a), the low center molecules are 0.44 ± 0.02 nm away from their closest neighbor. Distances to the other nearest neighbor molecules range from 0.50 to 0.72 nm. Moving in the clockwise direction to another nearest neighbor from the closest neighbor requires traversing the longer edge of a unit cell, indicating that Fig. 1(a) is an image of the (001) plane of pentacene. In Fig. 1(b), the distance between the each low molecule and its nearest neighbor is 0.45 ± 0.02 nm. The next neighbor in a clockwise direction is along the shorter side of the unit cell b. Figure 1(b) is thus an image of the (00$\bar{1}$) plane of the pentacene crystal.

Molecular vacancies appear as low areas within the rows of molecules and occur on both molecular basis sites of the pentacene crystal (Fig. 3). In a scan of a large area, there was no statistically significant difference in the number of vacancies in high and low molecular basis sites. There is thus no preferred site for vacancy formation. Images of vacancies on the higher and lower inequivalent lattice sites appear in greater detail in Figs. 3(b) and 3(c).

Based on images made on several terraces of a single film, the mean fraction of sites occupied by single vacancies in the second, third, and fourth layers was 1.5%. Given the bulk molecular concentration of on the order of 10^{21} cm^{-3}, this corresponds to a concentration of single vacancies in the pentacene thin film of approximately 10^{19} cm^{-3}. This concentration is far higher than the equilibrium concentration of vacancies estimated for a temperature of 300 K from the energy and the entropy of vacancy formation in pentacene, 10^{11} cm^{-3} and other polyacene crystals such as naphthalene and anthracene, 10^{14}–10^{16} cm^{-3}.[6,15] The higher-than-equilibrium concentration of vacancies has been predicted as a consequence of the nonequilibrium kinetics of crystal growth.[16] Other defects including grain boundaries and grain boundary kinks arise from the kinetics of molecular beam deposition.[17]

The molecular features near vacancies in the STM images are displaced from the sites they would occupy in an undisturbed lattice. Comparing measurements of the molecular positions in regions without vacancies to a grid of lattice points shows that the room-mean-square error in measuring the molecular positions is 31 pm. This reflects the accuracy of the assignments of the lattice points in the STM image and sets a practical lower limit for the measurement of displacements.

Several effects can be used to rule out tip-induced artifacts as the origin of the features associated with vacancies in Fig. 3. First, the two vacancies in Fig. 3 clearly appear different from one another. Artifacts resulting from a tip effect would be expected to equally affect all the defects and produce the same structure at each vacancy. Also, the apparent vacancy depth is far greater than the height differences among the pentacene molecules. The tip is thus likely to be a sufficiently well-defined local probe to accurately measure the apparent position of the atoms immediately adjacent to the defect. Finally, the artifacts associated with the shape of probe tips normally affect depressions more than protrusions, since tip effects usually restrict a tip from going into local depressions. We thus believe that the local positions of the protrusions are not likely to be affected by a possibly asymmetric tunneling tips.

Figure 4(a) shows the apparent displacements of molecules from their lattice sites as a function of their lattice site relative to the vacancies. For vacancies in a low basis site, one of the six closest molecules to each vacancy in a low row is displaced from the lattice site by approximately 150 pm. The remaining nearest neighbor molecules are displaced less than 60 pm. Similarly, one molecule adjacent to a vacancy in the higher basis site appears off the lattice site by 70 pm. In both cases, the largest apparent displacement of molecules

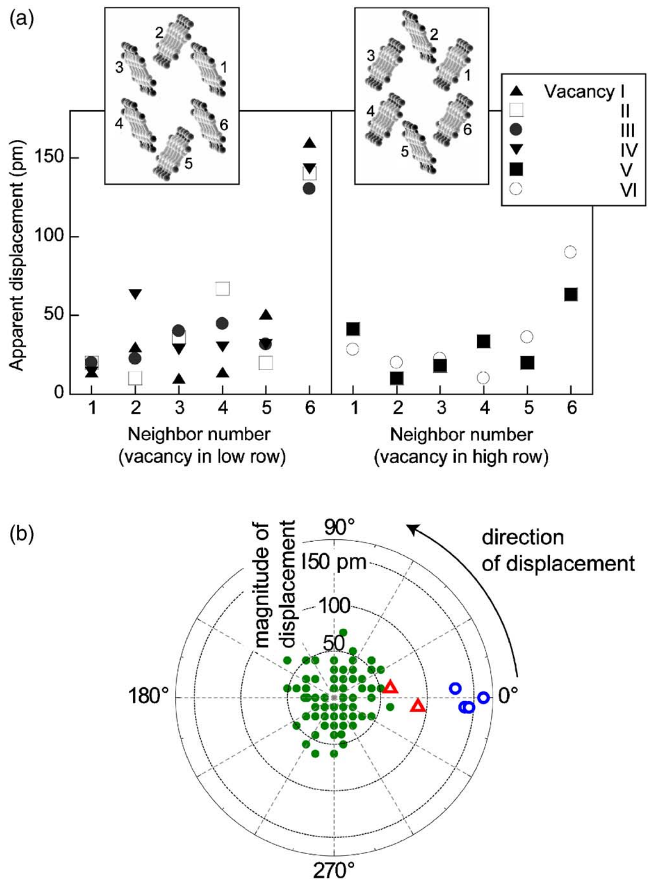

FIG. 4. (Color online) (a) The distances of the molecules near vacancies from their lattice sites in the (001) surface of pentacene for four vacancies in low molecular rows and two vacancies in high molecular rows. The positions of the numbered molecules with respect to the vacancies are given in the insets. (b) The direction and magnitude of displacement of molecules near a vacancy. The circles and triangles indicate molecules in the most displaced position near vacancies in the low and high molecular basis sites, respectively.

adjacent to a vacancy occurs at the molecules numbered 6 in the scheme in Fig. 4.

The relaxation of the molecules near the vacancies occurs in well-defined directions. Figure 4(b) shows the direction and magnitudes of the displacements of molecules from lattice sites in the area of the (001) surface in Fig. 3(a). The molecules associated with the points plotted as circles and triangles in Fig. 4(b) are displaced along the horizontal axis of the image. The remaining molecules have only small random displacements relative to the lattice points that are comparable to the rms displacement of 31 pm that we observed in areas of images far from defects. The points shown as open circles and triangles in Fig. 4 correspond to the molecules displaced by the greatest distances in Figs. 3(a) and 3(b), respectively.

A rotation of the pentacene molecule nearest to the vacancy about its principal crystallographic axes could shift its apparent lateral position with respect to other molecules in the lattice and would also lower its apparent height. In Fig. 2, the molecules with the largest displacements from their lattice sites are lower than their neighbors by 25 ± 4 pm. This value is greater than the 2.5 pm standard deviation in the difference in the heights random pairs of adjacent molecules throughout the image. This difference in height could be accounted for by an increase in the molecular tilt angle with respect to the surface normal by 4.5°, which would move the tops of the molecules down by 25 pm and laterally shift them by 55 pm. This shift, however, is only approximately one third of the total apparent lateral shift of the most shifted molecules in Fig. 4(a), suggesting that molecules near the vacancy are displaced as well as rotated.

The large apparent displacements of molecules near the vacancies are surprising given the widespread expectation of small structural relaxations of approximately 10 pm near vacancies in similar polyacene crystals.[18,19] Electronic structure calculations thus have generally neglected possible changes in the structure around a vacancy.[3] It is interesting to note that the deepest electronic trap near a pentacene vacancy is predicted in calculations to be at the position of the molecules numbered 6 in Fig. 4(a), raising the possibility that electronic effects could be important either in the distortion of the lattice or in the apparent distortion observed in STM images.[3] Imaging defects in this way has the potential to contribute to strategies for controlling molecular-scale defects in organic semiconductor thin films and will lead to another degree of freedom in designing organic-inorganic interfaces.

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