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Abstract
Scanning tunnelling microscopy (STM) has been used to follow the adsorption of tetracene molecules on the Si(100)-2 × 1 surface. Two distinct types of adsorption are indicated by filled state images but three types may be distinguished in empty state images. Molecules aligned both along and perpendicular to the silicon dimer rows can be observed. The calculated charge densities associated with occupied and unoccupied orbitals near the Fermi level are compared with the STM images. Possible bonding arrangements and their correlation with the STM images are postulated.

1. Introduction

There has been much recent interest in the electronic and optoelectronic properties of polyaromatic hydrocarbons, such as tetracene, pentacene and perylene, because of their potential use as organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs) [1, 2]. It is likely that the performance of such devices is strongly influenced by the structural quality of crystals or preferably thin films and by the detailed nature of the interface with other materials. The structure of the first monolayer is crucial to the further development of thin films. Since silicon retains its powerful influence in the microelectronic industry, it is important to consider in detail the interaction between Si(100) surfaces and those molecules, which can contribute to its advanced applications. Pentacene, which is a planar molecule with a linear arrangement of five benzene rings, has been considered as an electroluminescent material [3]. Among the reasons for interest in studying this particular aromatic molecule is the high mobility for hole transport (p-channel) [4], and low defect densities, which can be achieved in FET devices. In general, the electronic structure of polyacene (tetracene, pentacene etc) crystals is characterized by an energy gap of several electron volts between the states derived from the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) [5]. Although previous studies relate to bulk pentacene

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crystals, its adsorption on Si(100)-2 × 1 substrate has also been investigated [6–8]. It has been suggested that the molecule adopts a flat-lying configuration, with orientations both parallel and perpendicular to the dimer rows [6].

The tetracene molecule is also planar and, in this case, four aromatic rings form a linear array. As an isolated species, tetracene has D_{2h} symmetry with a van der Waals' length of 13.63 Å. Here, we present scanning tunnelling microscopy (STM) studies of the initial adsorption of the tetracene molecule on the Si(100)-2 × 1 surface at room temperature, in order to identify the adsorption site of this unsaturated molecule. Although STM provides us with real space images, which might ideally be used to determine the structure, size and shape of organic molecules adsorbed on various surfaces [9–11], it is necessary to keep in mind that the images originate from molecular orbitals, which are modified, perhaps strongly, by adsorption. They are also influenced by different tunnelling factors at the molecular adsorption site, such as effective barrier height, atomic structure and resonant tunnelling [6, 7, 12, 13]. These factors are difficult to address but are likely to be relevant to a detailed interpretation of this system and an understanding of the physical and electronic structure of tetracene on Si(100)-2 × 1.

In order to assist the interpretation of the STM images, density functional theory (DFT) calculations have been carried out to determine the details of the electronic structure of an *isolated* tetracene molecule. Charge densities of specific molecular orbitals close to the HOMO–LUMO gap are then compared with STM images obtained at various bias polarities.

2. Experimental details

The experiments were carried out in a UHV system (base pressure $< 10^{-10}$ mbar) equipped with STM (Omicron), low energy electron diffraction (LEED) and dosing facilities. For the STM study, tungsten tips were used, which were prepared by an electrochemical etching technique. Si(100) samples were cut from on-axis, one-side polished, wafers (P doped) with a resistivity of 1–3 Ω cm^{-1}. Clean Si(100)-2 × 1 was prepared by heating the silicon crystal to 1500 K while maintaining a pressure of $<2 \times 10^{-10}$ mbar. Prior to dosing, tetracene was degassed for 12 h at 333 K. The doser consists of a glass tube with a heating wire and a thermocouple sensor, so the dosing temperature is well controlled and the reproducibility is ensured. Tetracene was dosed at 400 K, with the substrate at room temperature. All STM images were collected at room temperature.

3. Results

3.1. Filled state images

Figure 1(a) shows a filled state image at a tetracene coverage of about 0.1 molecules nm^{-2} chemisorbed on Si(100)-2 × 1, equivalent to 0.03 tetracene molecules per silicon dimer. This filled state image was taken at a tunnelling current of 0.07 nA and a sample bias voltage of −2.6 V. Two silicon terraces are present, separated by a single-height atomic step. On both terraces, the surface structure consists mainly of rows of symmetric, Si–Si dimers. However, at surface defects and at the step edge, zigzag rows of asymmetric dimers can be seen. Chemisorbed tetracene molecules appear as the bright features. The molecules are orientated in two different ways: perpendicular and parallel to silicon dimer rows.

Tetracene molecules arranged perpendicular to the Si dimer rows, labelled A in figure 1(a), show three protrusions, the centre one rather less bright than the outer two. In such STM images, the perturbation induced by the molecule extends from the second silicon atoms belonging to
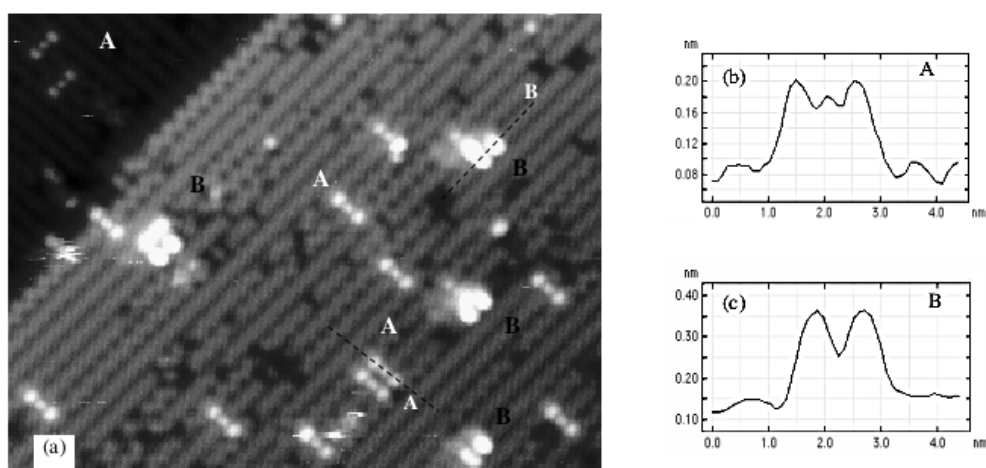
Figure 1. (a) Filled state STM image (25 nm × 18 nm) of tetracene on Si(100)-2 × 1 (70 pA; −2.6 V). Two types of bright feature can be distinguished. Feature A is a tetracene molecule perpendicular to the Si dimer rows, while B corresponds to a tetracene molecule on top of the Si dimer rows. Line profiles of those adsorption sites parallel to the long molecular axis are shown in (b) and (c).

a first dimer row, is centred over two dimers in a second row and continues to the first silicon atoms in a third dimer row. In this case, the length of the tetracene molecule is 13.4 Å, as determined from line profiles, such as that shown in figure 1(b).

A second type of adsorption corresponds to tetracene molecules on top of and aligned parallel with the silicon dimer rows (these are labelled B in figure 1(a)). Here, two even brighter spots indicate the tetracene molecule. The length of the B type features is similar to those of type A, as shown in the line profile β on figure 1(c). Varying numbers of bright features for differing orientations have been similarly reported recently for pentacene on Si(100) [6, 8].

3.2. Empty state image

It is already known that changing the polarity of the bias voltage between the sample and the tip can markedly alter the STM images, particularly for adsorption on semiconductors [8]. The empty state image, shown in figure 2(a), was obtained at a tunnelling current of 0.215 nA and sample bias of +2.6 V. In this image, three distinctive features, as depressions, can be distinguished. One of these, labelled A*, corresponds to a rectangular hole perpendicular to the Si dimer rows. The size of this feature is 13.6 Å, as shown in the line profile (figure 2(b)), which is again in agreement with the van der Waals length of the tetracene molecule. We consider these are correlated with A type features in the filled state image.

A second feature, labelled B*, is also present, which corresponds to a tetracene molecule aligned parallel to the dimer rows but located on top of the silicon dimer row. Here we must make clear that, although the empty state image presented has rows of bright features, these rows are not coincident with the dimers. Instead, these bright rows correspond to inter-dimer sites, since the empty state orbital, which is being imaged, has a nodal plane at the centre of the dimer. B* in the empty state image corresponds to B type sites in the filled state image. A third type of adsorption site (labelled C*) is a rectangular hole whose longer side is again parallel to the silicon dimer rows, but now located between dimer rows, and therefore termed the inter-dimer site. The line profile confirms that the length is similar for both B* and C*
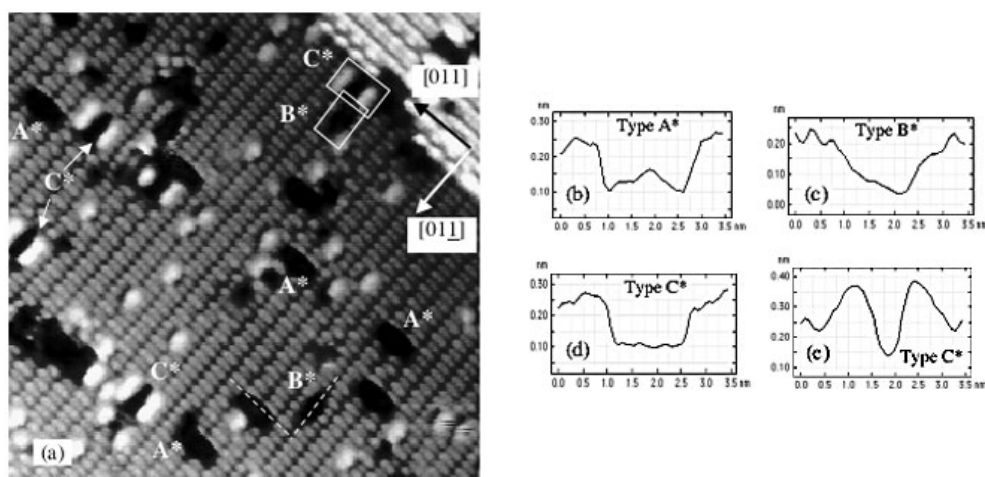
Figure 2. Empty state STM image (22 nm × 22 nm) of tetracene on Si(100)-2 × 1 (0.26 nA; +2.6 V). Three different adsorption types can be seen. The boxes near the top on the right show the difference between tetracene molecules on top of the dimer row (B*) and inter-dimer rows (C*). Line profiles are presented for each type of adsorption parallel to the long molecule axis (b), (c), (d), as well as a line profile perpendicular to type C* (e).

features, as shown in figures 2(c) and (d). Bright borders can be seen parallel and on each side of molecules of type C*, though not for B*. A line profile across type C* features, showing the bright borders, is presented in figure 2(e). Corresponding features have not been recognized in the filled state image.

3.3. Tetracene molecule

DFT calculations (B3LYP/6-31G*) combined with geometrical optimization, using Gaussian 98 [14], were employed to obtain the population analysis, orbital symmetries and energy levels of an isolated tetracene molecule. The LUMO is of B_{1g} symmetry while the HOMO is A_u. The charge density distributions associated with the higher occupied and the LUMO π molecular orbitals are shown in figure 3, together with their calculated energies and symmetries [15].

4. Discussion

The filled state image clearly indicates two different molecular adsorption sites corresponding to orientations perpendicular and parallel to the silicon dimer rows. The former, type A, appears as three bright spots in contrast to the even brighter, two-lobed protrusion of the latter, type B, as shown in figure 1. In favourable cases, we might hope that the STM images would be dominated by tunnelling through a specific molecular orbital located, in energetic terms, by appropriate bias conditions on the tip. Ideally the image would match the charge density distribution in the relevant orbital and most obviously the pattern of its nodal planes. Of course, mixing between adsorbate and substrate orbitals in strongly chemisorbed systems may perturb this simple picture considerably. Noticeably, the HOMO charge density distribution, shown in figure 3, *does not* match the STM images corresponding to either site A or B. In particular, site A shows a lobe at the molecular centre while the HOMO has a node at this point. A more detailed analysis of the other filled molecular orbitals is needed to explore the different nodal patterns, which might be reflected in the STM images. Specifically, we

Energy (eV)
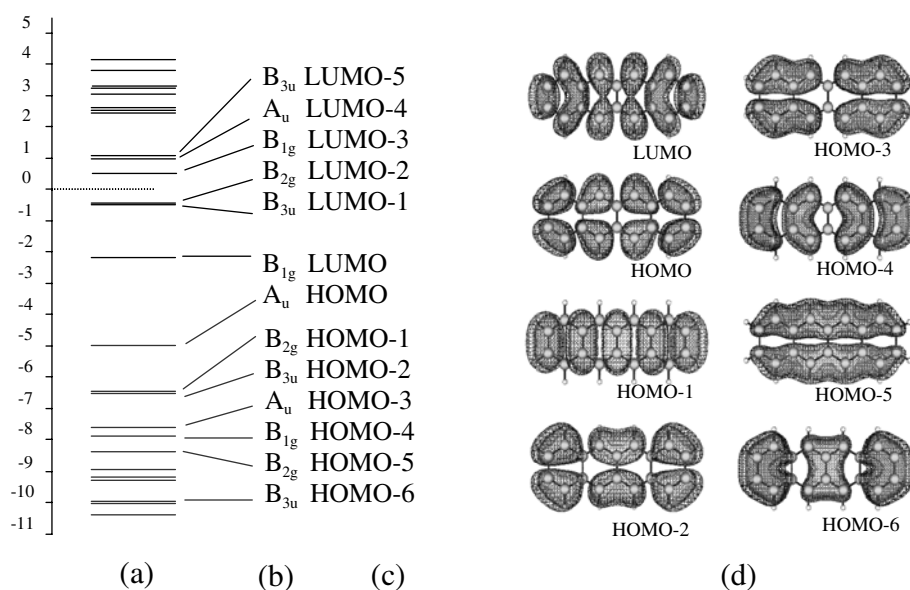
Figure 3. Result of Gaussian 98 calculations showing (a) the energy of molecular orbitals in the range −11 to 5 eV, (b) the symmetries of π orbitals, (c) the label of π orbitals and (d) the charge density distributions of the HOMO, the LUMO and six further occupied molecular π orbitals of the tetracene molecule.

find that the B_{3u} molecular orbitals HOMO-2 and HOMO-6 have three regions of high charge density along the long molecular axis separated by two nodal planes (see figure 3). These may be major contributors to the filled state imaging of molecules in site A, although the latter is energetically probably too far removed (∼6.5 eV) from the mid-point of the HOMO–LUMO gap to contribute and the former, while more energetically reasonable (3 eV from the mid-gap), has a nodal plane containing the long molecular axis, though conceivably this might not be resolved by STM. HOMO-3 and HOMO-4 are ruled out as contributors to type A sites because of their central node as for the HOMO. HOMO-1 also seems to be unlikely since it has five regions of high charge density rather than three.

Molecules in type B sites, parallel to and on top of Si dimer rows, seem to correlate more closely with the charge density of HOMO-3 (A_u) with the possibility of some contributions from the HOMO-4 (B_{1g}) since each of them has the necessary central nodal plane and regions of high charge density which might correlate with the two bright regions of the STM image. Any occupancy of the LUMO (B_{1g}), due to charge transfer into this orbital from silicon could also contribute to the image at site B. As far as the empty state images are concerned, it seems that, with the exception of site C, the molecules are characterized by reduced tunnelling probability, compared with the clean silicon surface. This suggests that, at the bias used, +2.6 V, empty states on the molecule are not accessible, In the case of site C, bright regions in the empty state image are located on Si atoms adjacent to the molecule, which suggests a depletion of charge density from the relevant Si orbitals into orbitals of the molecule or, at least, of the Si–molecule bond. It may be that these states lie in the HOMO–LUMO gap and are therefore energetically unfavourably positioned for contributing to the filled state images at −2.6 V shown in figure 1. At this stage, molecules in adsorption site C are still associated with considerable uncertainty.
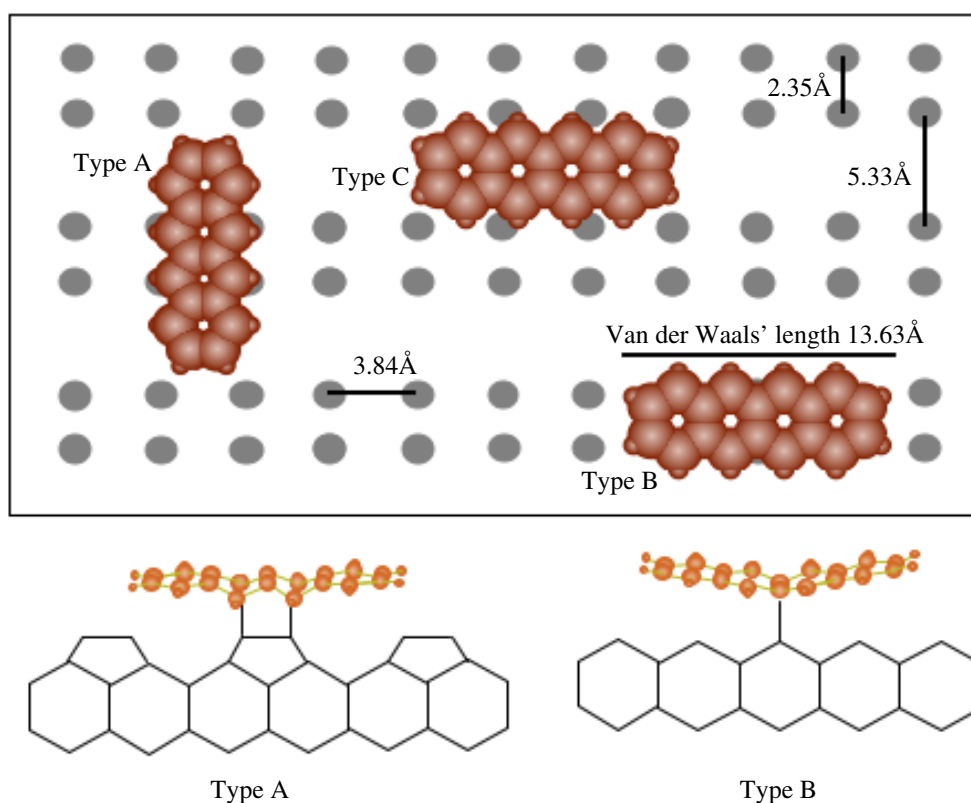
Figure 4. Adsorption sites for tetracene on the Si(100)-2 × 1 surface based on STM images. Orientations of the long molecular axis both perpendicular to the dimer rows, type A, and parallel to the dimer rows, types B and C, are depicted. In addition, a sketch of possible Si–C bonds between the tetracene molecule and Si is shown for sites A and B in cross-section.

(This figure is in colour only in the electronic version)

As an alternative strategy to considering the orbitals of the isolated molecule, it is reasonable to examine the covalent bonding which might occur between the molecule and the Si substrate, based on analogy with the simpler aromatic molecule benzene adsorbed on Si(100)-2 × 1. Benzene is also able to occupy different sites on this surface, with characteristic STM signatures, and these have been correlated with different cycloaddition bonding configurations [16]. For example, one option is (2 + 2) cycloaddition between a double bond of the benzene ring and the Si–Si dimer, resulting in a 1,3-diene attached to the surface through a four-membered, C_2Si_2 ring. An alternative, also postulated to explain STM images, is (4 + 2) addition resulting in a 1,4-diene in which the Si–Si dimer bridges opposite carbon atoms of the ring in the so-called butterfly structure. Before considering the possible bonding configurations and the influence of the substrate bonds on the STM image, knowledge of the registry of the molecule and the substrate is perhaps important.

Careful analysis of the images shows that a tetracene molecule in site A has its centre directly on top of the dimer row, though we note the intensity of this central part seems weak, compared with the two spots at each end, which are located over the valley between silicon dimers, as seen in the line profile of figure 1 taken through a molecule in site A. Registry of the
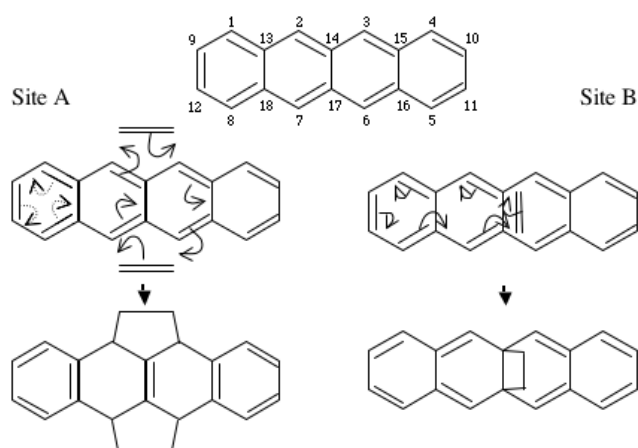
Figure 5. Mechanisms of molecular addition to Si–Si dimer pairs for adsorption at sites A and B. In the latter case, the Si dimer has been displaced for clarity from its position directly below the centre of the molecule.

molecules in site A along the dimer row is harder to determine but, from careful examination of the images, we consider it to be centred directly between two Si dimers. Molecules in adsorption site B, aligned parallel to and on top of dimer rows, appear to be centred on a dimer. These sites, A and B, are shown in figure 4.

Molecules in site A have two carbon atoms in each of the inner aromatic rings ideally placed to bond with the two, underlying Si–Si dimers. These carbon atoms, labelled 2, 3, 6 and 7 in figure 5, can participate in what might be described as a $2 + 8 + 2$ addition mechanism, also shown in figure 5. The result is a molecule attached to the substrate by four Si–C bonds. The outer rings of the molecule remain aromatic while aromaticity is lost from the inner rings, though they are linked at a C=C double bond. The carbon atoms of the Si–C bonds become sp^3 hybridized and buckling of the planar ring structure at these carbon atoms is anticipated, as shown in the lower part of figure 5. One might then speculate that the three-lobed, filled state image corresponding to molecules in site A arises from the π system, with the outer rings giving rise to the two bright lobes and the central C=C providing the weaker lobe in the middle. Turning now to molecules in site B, the model shown in figure 4 indicates that the central Si–Si dimer is well positioned to participate in bonding to the molecule. A possible mechanism is outlined in figure 5. In this case, carbon atoms 14 and 17 contribute to a $(2 + 2)$ addition. These carbon atoms become sp^3 hybridized and the site of buckling away from the planar structure. The resulting molecule retains two regions, each with eight π electrons. Most significantly, there is no π orbital at the centre of the molecule, which is reflected in the node found in the filled state STM image of molecules in site B. Instead, two intense lobes are found where the π systems are located.

5. Conclusions

Highly resolved STM images show that three adsorption sites are possible in the case of tetracene adsorption on Si(100)-2 × 1, corresponding in each case to flat-lying tetracene molecules. Molecules can adopt an azimuthal orientation either perpendicular to Si dimer rows or parallel to the dimer rows. Molecules with the latter orientation can, on the basis of empty state images, occupy sites either on top of the dimer rows or between the rows, although

the latter is not an identifiable site in filled state images. It has not been possible to identify the principal orbital contributions based on charge density calculations for the free molecule to filled state images. However, it has been possible to correlate adsorption sites with possible bonding mechanisms and in turn with the STM images corresponding to those sites.

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