Novel Mechanism for Molecular Self-Assembly on Metal Substrates: Unidirectional Rows of Pentacene on Cu(110) Produced by a Substrate-Mediated Repulsion

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The formation of one-dimensional, unidirectional nanoscopic molecular structures by self-assembly on metal substrates with a long range ordering up to several hundred nanometers has been achieved by a novel mechanism, an oscillatory modulation of the adsorption energy due to charge-density waves related to a surface state. For the case of pentacene ($C_{22}H_{14}$) adsorbed on Cu(110), annealing at 400 K produces a regular pattern of molecular wires one molecule wide (15.6 Å) and a wire-to-wire distance of 28 ± 2 Å. Results obtained for similar compounds suggest that the underlying mechanism is rather general and can be applied also for other linear aromatic molecules.

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The fabrication of nanometer-sized structures on surfaces or interfaces is currently attracting considerable interest. Previous work has shown that linear, one-dimensional structures of atoms and molecules on metal surfaces can be produced by using templates like regular arrangements of surface defects (i.e., steps) [1–3] or special sites within a reconstruction [4]. Since the production of templates can be a challenging task in itself, recently the so-called supramolecular approach has attracted more interest. In this case the formation of molecular nanostructures proceeds by self-assembly on a flat, unstructured substrate by employing directional intermolecular interactions such as hydrogen bonds [5]. Not all molecules, however, are suited for this approach since adding molecular functions required for the intermolecular interactions (e.g., carboxy-units), will in general change the electronic properties of the original molecule and thus limits this approach to a particular class of molecules. Pentacene ($C_{22}H_{14}$, see inset in Fig. 1), an aromatic hydrocarbon, for example, is not suited for such an approach since this molecule cannot form hydrogen bonds.

On the other hand, pentacene has recently attracted a considerable amount of attention due to its fascinating electronic properties [6]. In addition to pentacene single crystals showing superconductivity for both electrons and holes, this material has been successfully used to build high-performance organic field effect transistors (OFETs) and related devices [7,8]. However, the deposition of ultrathin single-crystalline films from this material on a solid substrate has not yet been successfully carried out. This problem is related to the fact that on flat and rather weakly interacting metal surfaces like Cu(111) neither benzene nor molecules with a larger number of aromatic rings show any lateral order. Templates like regular arrays of steps are required to obtain such 2D order [9]. As a result, the growth of ordered pentacene adlayers by epitaxy on these substrates is very difficult or impossible. In contrast, for aromatic molecules with additional functional groups like PTCDA [10] which provide a specific substrate interaction, epitaxial structures with a high degree of order could be grown by using heteroepitaxy on metal substrates [11]. Finding a way to employ self-organization for the formation of two-dimensionally ordered adlayers of pentacene would thus not only allow for the fabrication of nanostructures but would also open the possibility to produce highly oriented pentacene layers by epitaxy for use in electronic devices.

In the present paper we demonstrate that the self-assembled growth of pentacene nanostructures can be achieved by employing a novel scheme, a highly directional substrate mediated repulsion on a Cu(110) surface. The results of a combined scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and x-ray absorption spectroscopy (XAS) study demonstrate that highly stable (up to 450 K) regularly spaced rows of close packed molecules with a separation of 28 ± 2 Å can be produced by annealing a room-temperature deposited pentacene film to 400 K. The fact that identical stripes with the same separation were also obtained for anthracene ($C_{14}H_{10}$) together with an observation of a distinct modulation of the tunneling signal perpendicular to such rows suggests that the underlying mechanism is the formation of charge-density waves which leads to a modulation of the substrate-adsorbate interaction.

The STM and LEED experiments were performed at room temperature using a Omicron-Micro-STM apparatus. The XAS measurements were carried out at beam line I511 of the synchrotron facility MAXlab in Lund (Sweden) [12]. The Cu(110) surface was cleaned in UHV by standard preparation involving repeated cycles of Ar^+ sputtering (800 eV, 20 min) and subsequent annealing (930 K) until a sharp (1 × 1) LEED pattern appeared and the corresponding XPS or STM measurements revealed no traces of contaminations. Pentacene (Fluka, 97%) was evaporated from a Knudsen cell operated at a temperature of 460 K onto the substrate held at RT.

In Fig. 1 we present a STM micrograph showing highly ordered rows of pentacene molecules fabricated on the

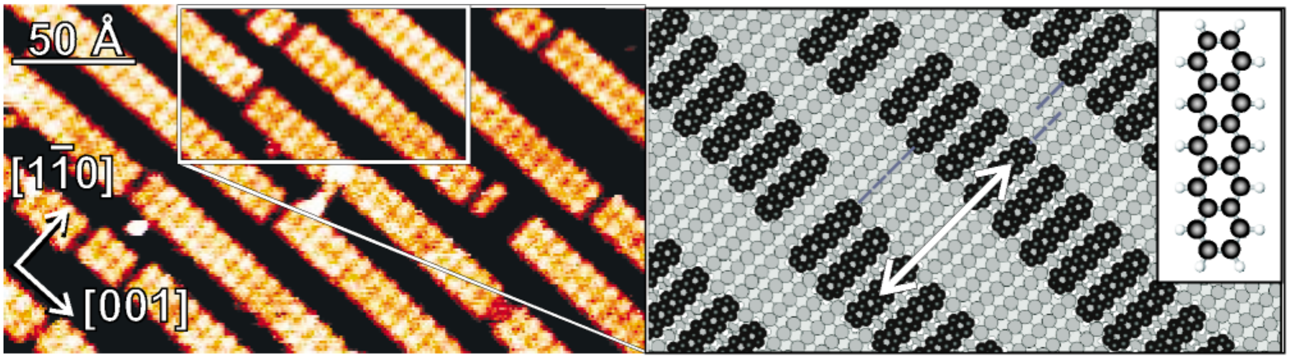

FIG. 1 (color). High-resolution STM image (260 Å × 140 Å, 2 V, 0.5 nA) showing the molecular stripes of pentacene on the Cu(110) surface. The molecular stripes running along the [001] direction are separated by 28 ± 2 Å (white arrow) as shown schematically at the right side together with a stick and ball model of pentacene ($C_{22}H_{14}$).

Cu(110) surface by depositing about 4×10^{13} molecules per cm^2 on the substrate and subsequently annealing to 400 K. Single molecules are resolved and are found to be oriented with their long axis along the [1$\bar{1}$0] direction. Since a direct determination of molecular orientation from the STM data is not straightforward and would require a theoretical modeling of the STM images [13] we have carried out measurements using x-ray absorption spectroscopy. The XAS data (not shown) demonstrate that the pentacene molecules are adsorbed with their molecular plane orientated parallel to the substrate surface [14] thus leading to the structure model shown in the right panel of Fig. 1.

Within the molecular rows the molecules adopt a close-packed side-by-side orientation with a separation of 7.2 Å along the [001] direction which is close to their van der Waals diameter of 6.5 Å and corresponds to twice the lattice spacing of the substrate. For the spacing between the centers of these rows characteristic distances of 28 and 30 Å and occasionally 26 Å were obtained, which are in close agreement with multiple nearest neighbor Cu-Cu distances of 11×, 12×, and 10×, respectively. Although these spacings are quite large the STM data clearly demonstrate the presence of a registration correlation between adjacent rows. For inter-row distances of 26 and 30 Å the pentacene molecules in neighboring rows adopt a head-to-head orientation, whereas for a row separation of 28 Å a staggered conformation is observed (as indicated in Fig. 1).

Room-temperature deposition of the same amount of pentacene used to produce the structure shown in Fig. 1 but without annealing the substrate results in the formation of disordered adlayers (see Fig. 2a). In this disordered phase long-range order is absent, but a significant amount of short-range order favoring a side-by-side arrangement of the molecules is clearly visible. A statistical analysis of the intermolecular spacing yields that separations of about 11 Å are strongly favored. In accord with this result the LEED pattern recorded for this disordered adlayers reveals weak, broad spots at the $1/3$ positions along the [001] direction. For very dilute phases no single pentacene molecules could be imaged with the STM. This observation is attributed to their high mobility at room temperature, an effect which has been reported also for even larger aromatic molecules deposited on the same surface [15]. For larger coverages the molecular mobility is substantially reduced and individual molecules with a uniform orientation of their molecular axis along the [1$\bar{1}$0] direction could be successfully imaged.

After annealing at 400 K all pentacene molecules arrange themselves in well-ordered, evenly spaced molecular rows [see Fig. 2(c)]. For this highly ordered array of stripes the LEED pattern reveals half-order streaks along the [001] direction, consistent with the structural model shown in Fig. 1. The highly ordered pattern of molecular rows remains stable up to temperatures of 450 K where the molecules start to dissociate. This result indicates that the molecular wires are not due to a kinetic stabilization which occurs during the growth of the molecular wires, but instead suggests that it corresponds to a thermodynamically stable structure.

Although the molecular row structure would provide enough space for the adsorption of additional pentacene molecules within the monolayer such a molecular arrangement was not observed. Increasing the coverage instead leads to the formation of ordered multilayers [14] (see below).

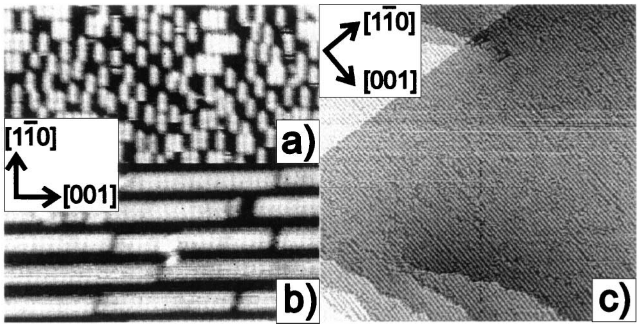

FIG. 2. STM images (250 Å × 125 Å, $U = 2$ V, $I = 0.5$ nA) on the left side compare the pentacene film structure (a) after deposition at RT and (b) after annealing at 400 K which leads to a long-range ordering (c) (2500 Å × 2500 Å).

The formation of ordered striped adsorbate phases on the Cu(110) substrate has been reported previously for other, more strongly interacting adsorbates such as oxygen or carboxylates [16,17]. In the present case, however, the observation of an apparent strong substrate-induced intermolecular interaction is surprising since the interaction of pentacene with Cu substrates mainly arises from a van der Waals–type interaction, which is much weaker than in the chemisorption of O atoms and carboxylates on copper. Note, however, that due to the rather large size of pentacene the total binding energy of the entire molecule (estimated to be 2 eV [9]) roughly equals that of O atoms in the striped Cu(110)–(2×1) O phase [15]. As a result of the rather weak van der Waals interaction the adsorbed pentacene molecules are largely undisturbed and chemical reactions with individual Cu atoms such as, e.g., seen in the case of carboxylic acids deposited on Cu surfaces [16] can be safely excluded.

The presence of essentially undisturbed pentacene molecules is evidenced by our XAS data which reveal sharp π^* resonances with a strong dichroism as expected for a flat-lying, aromatic molecule. A strong substrate-induced distortion of the pentacene molecule as, e.g., observed for aromatic molecules adsorbed on more strongly interacting transition metal substrates [18,19] can thus be safely excluded.

Note that the direct interaction between the pentacene molecules is rather small. In the bulk this interaction is dominated by electrostatic forces resulting from the molecular quadrupole moment, leading to a tilted herringbone type arrangement [20]. In analogy, a herringbone structure would also be expected for a 2D-ordered structure of such a linear, symmetric molecule like pentacene in the absence of additional lateral forces [21]. The parallel packing of the pentacene molecules within the rows as is evident from Fig. 1 is thus not brought about by intermolecular interactions (in fact, a parallel arrangement of pentacene molecules leads to a weak repulsion resulting from the corresponding quadrupole moment), but must result from a tendency to achieve the densest packing of pentacene molecules within confined regions on the Cu substrate which are separated by 12 Å wide stripes of apparently bare Cu surface.

In the search for the mechanism stabilizing the molecular pentacene rows we focused our attention on high-resolution STM images. The scan along the white line in the STM micrograph shown in Fig. 3 actually reveals that the part of the surface between pentacene rows of larger separation shows an additional modulation with a peak-to-peak amplitude of 0.2 Å and a period of about 9.5 ± 1 Å. This rather strong modulation which was observed independently of the scan direction was not seen for the clean Cu(110) substrate. The modulation runs normal to the molecular rows, i.e., along the substrate $[1\bar{1}0]$ direction. Moreover, this modulation was also found at defects (gaps) within the molecular rows, which indicates their registry with respect to the modulations.

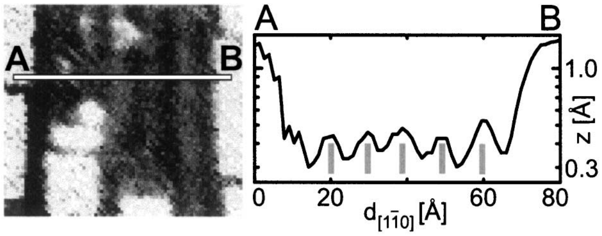

FIG. 3. High-resolution STM image ($U = 2$ V, $I = 0.5$ nA) of the pentacene rows together with a line scan (AB) showing the presence of distinct oscillations with a periodicity of about 9.5 Å which are visible in the case of missing pentacene rows.

This observation suggests that charge-density waves are formed in the surface state 2D electron gas on the Cu surface in the presence of pentacene rows. That such an indirect interaction can become strong enough to affect adsorbate-adsorbate interactions has recently been demonstrated in the case of Cu adatoms on a Cu(111) substrate. Using low temperature STM Repp *et al.* [22] could demonstrate that below 30 K the preferred distances between Cu adatoms amount to multiples of 12.5 Å. This effect was explained by standing waves in the surface-state free electron gas with a wavelength corresponding to $2\pi/k_F$.

When considering this explanation for the present results it is important to note that on Cu(110) the 2D Fermi surface (or Fermi line) of the surface state is not located at the $\overline{\Gamma}$-point-like for Cu(111). In the latter case the Fermi line of the surface state is almost circular, allowing for standing waves running along all surface directions. In contrast on Cu(110) the surface state is located at the $\overline{Y}$ point [23], so that the standing waves for the clean surface should run only along the [001] direction. In fact these waves have been imaged for the clean Cu(110) surface by using a Fourier transform STM method [24]. In the present case, however, we observed a distinct modulation along the $[1\bar{1}0]$ direction. This suggests that the presently observed standing waves which are likely to cause the molecular self-assembly cannot be explained by the electronic structure of the bare Cu(110) substrate, but require a different electronic structure resulting from the interaction with the pentacene molecules. The differences in electronic structure to that of the bare surface are most likely a result of a (small) donation/backdonation between copper substrate and pentacene molecule [25] leading to a modification of existing or creation of new surface states [26,27].

In order to corroborate that the area between the pentacene stripes showing the modulation is electronically different from a clean Cu(110) substrate we have determined the binding energy of a probe molecule, namely CO, on the uncovered copper substrate stripes between the pentacene rows. In contrast to the bare Cu(110) surface and the disordered pentacene layer, where thermal desorption measurements yield a desorption peak at about 210 K (recorded for $\beta = 5$ K/s) for isolated CO molecules, a reduction to 194 K was found in the presence of the pentacene rows.

On the basis of these results we thus propose that the formation of highly unidirectional rows of pentacene molecules results from the formation of standing waves (or Friedel oscillations) in the free-electron gas, in analogy to the explanation provided for explaining recent results in low temperature metal-on-metal epitaxy [24]. In contrast to these previous results obtained for the Cu(111) surface the corresponding surface state for the present system is one-dimensional and is proposed to be oriented along the $[1\bar{1}0]$ direction. From the wavelength of the modulation period between the pentacene rows, $d = 9.5$ Å, we yield a value of $k_F = 2\pi/d = 0.66$ Å^{-1} for the corresponding Fermi wave vector. The fact that in the present case the substrate-mediated adsorbate-adsorbate interactions stabilize structures for temperatures up to 450 K in contrast to the Cu homoepitaxy on Cu(111), where the effects were limited to temperatures below 30 K, is attributed to the one-dimensional character of the related surface state. On Cu(111), in contrast, the surface state at the $\overline{\Gamma}$ point extends in all surface directions, not allowing for the formation of unidirectional structures.

A particularly interesting result of using a substrate with only a two-dimensional symmetry is that the molecular rows are all aligned along the [001] direction of the substrate. This is in contrast to substrates with threefold symmetry used in most previous work reporting the formation of one-dimensional molecular structures [3–5], where the higher symmetry causes the existence of at least three different rotational domains.

The observation of an ordered structure within pentacene monolayers on this particular substrate is of pronounced relevance also for using thin organic adlayers made from pentacene for applications in molecular electronics. Attempts to grow highly ordered epitaxial pentacene multilayers on a variety of substrates have not yet been successful. The present Cu(110) surface appears to be an ideal candidate for achieving pentacene heteroepitaxy. Increasing the coverage of pentacene on the Cu(110) substrate beyond the coverage of the ordered stripe phase leads to the formation of highly ordered double layers. Preliminary results suggest that the growth of ordered multilayers (as evidenced by high-quality LEED patterns) can be achieved on this substrate by starting from the annealed stripe phase and then optimizing the growth parameters [14].

In summary, we have fabricated highly ordered molecular rows of pentacene on a Cu(110) substrate which are stable for temperatures up to 450 K using self-assembly by employing a novel scheme, namely substrate-mediated intermolecular repulsion. Results for other linear, aromatic molecules suggest that the underlying scheme is rather general. The present results are also important for the heteroepitaxy of pentacene on metal substrates, which is a prerequisite for employing the exciting electronic properties of pentacene single crystals in molecular electronics.

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