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*Rapid communication***Growth of 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) on Cu(110) studied by STM**

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Abstract. The structure of thin 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) films on Cu(110) was studied by scanning tunnelling microscopy (STM) from submonolayer to monolayer coverage. While no long-range ordering was found after deposition at room temperature, the formation of a well-defined superstructure is observed after thermal annealing. It appears that the formation of the superstructure is driven by the interaction between the oxygen atoms of the PTCDA and the copper atoms of the substrate. While the distance between the molecules fits well to the atomic lattice of the Cu(110) surface along the $[1\bar{1}0]$ direction, the mismatch along the $[001]$ direction leads to a periodic buckling normal to the surface accompanied by a restructuring of the substrate.

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During the last few years, organic semiconductors have attracted considerable attention. Organic thin films are of interest for various applications, e.g. thin insulators, sensors or light-emitting diodes (LEDs).

Especially the growth of 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) on various substrates has become a prototype for molecular beam epitaxy with organic molecules. Surface-sensitive techniques such as scanning tunnelling microscopy (STM) and low-energy electron diffraction (LEED) are used to characterize the thin organic films. Thin PTCDA films have been studied on different substrates, such as HOPG [1, 2], Au(111) [3, 4], Au(100) [5], Ag(111) [6, 7], Ag(110) [8], GaAs(100) [9] and InAs(001) [10]. It was found that PTCDA forms well-ordered layers. In most cases, the PTCDA layers grow in the herringbone pattern which corresponds to the (102) plane of the bulk crystal. So far two other formations of PTCDA are known. On

Ag(110) the molecules form a “brickwall” structure [7] and on Au(111) a quadratic one [4].

In the present study, we report on the growth of thin layers of PTCDA on Cu(110) varying from submonolayer to monolayer coverage. In contrast to the findings for other substrates, the arrangement of the PTCDA molecules is not planar but reveals a corrugation on a large lateral scale which is attributed to periodic restructuring of the Cu(110) surface.

1 Experiment

The experiments were carried out in an ultrahigh-vacuum system consisting of different chambers for sample preparation and characterization. The typical base pressure is 2×10^{-10} mbar. The preparation chamber is equipped with the standard techniques for sample cleaning. To deposit the organic molecules a small home-built crucible was used. The flow of organic molecules can be controlled by a quadrupole mass spectrometer. The characterization of the samples can be made by X-ray photoelectron spectroscopy (XPS) and LEED, as well as by using a home-built STM, which has been optimized for operation at low tunnelling currents of the order of a few pA.

The Cu(110) surface was prepared by repeated sputtering of a copper single crystal with Ar^+ ions and annealing to 790 K. The bare surface was characterized by XPS and STM. The latter measurement provided a convenient calibration of the STM using the known dimensions of the unit cell of the Cu(110) surface. The PTCDA thin films were prepared by evaporation from a crucible at a temperature of 480 K while the substrate was kept at room temperature. For the preparation of the submonolayer and monolayer, a rate of 0.5 ML/min was chosen. Afterwards, the films were thermally annealed using a linear temperature ramp of 1 K/s, ending at 450 K. During the annealing it was to be controlled by the mass spectrometer if desorption of the PTCDA molecules from the Cu surface took place. However, no desorption from the sample was detected.

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2 Results and discussion

Figure 1 shows an image of the clean Cu(110) single crystal. The individual atoms are clearly resolved. The crystallographic directions are readily identified, as indicated by the arrows. The orientation of the substrate was maintained during the following experiments.

Figure 2 shows a typical image of PTCDA on Cu(110) at a coverage of about 0.6 ML immediately after deposition of the molecules. Since the substrate was kept at room temperature, the mobility of the molecules was relatively low. In consequence they showed a tendency to cluster, but no long-range order was found. Apparently the molecules are lying flat on the copper substrate. The latter was not modified by the adsorption.

After thermal annealing to 450 K the same sample displayed a very striking feature, as shown in Fig. 3. The molecules formed stripes with a significant corrugation. Since no desorption could be detected during the annealing, the

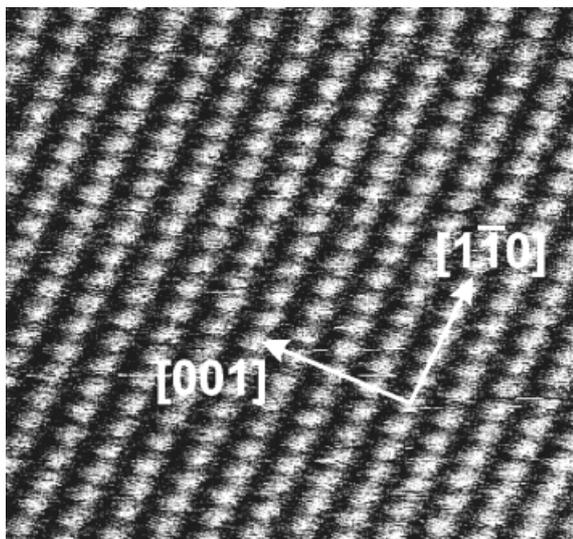


Fig. 1. Atomically resolved image of the Cu(110) surface, $5 \times 5 \text{ nm}^2$, the tunnelling parameters are $U_t = -0.4 \text{ V}$ (at the tip) and $I_t = -225 \text{ pA}$

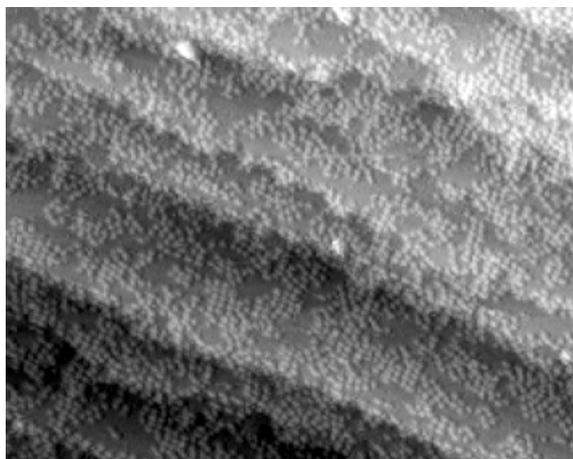


Fig. 2. STM image of a fraction of a monolayer of PTCDA on Cu(110) before annealing; the area is $180 \times 80 \text{ nm}^2$; the tunnelling parameters are $U_t = -0.8 \text{ V}$ and $I_t = 3 \text{ pA}$

coverage equals that in Fig. 2. It can be clearly seen that the molecules have rearranged themselves into islands with a dense packing. They are found preferentially at step edges. Figure 4 shows the arrangement of the molecules in more detail. The superstructure essentially follows a rectangular pattern which has the same orientation as the unit cell of the substrate. However it is not simply a commensurate structure.

Along the $[1\bar{1}0]$ direction the ordering follows a clear scheme. Two molecules form the base, which extends over 10 copper atoms. Every second molecule is rotated by 90° . Figure 5 shows several line scans along this direction.

The situation is more complicated for the $[001]$ direction. Again every second molecule is rotated by 90° ; however, since the distance between the atomic rows is $\sqrt{2}$ times larger than in the $[1\bar{1}0]$ direction, there is no accidental match of the spacing of the molecules and the substrate atoms for a flat arrangement of the molecules. It appears that the tendency of the molecules to lock in specific positions on the substrate is so strong that it causes a large-scale restructuring of the substrate by addition or removal of atomic rows along the $[1\bar{1}0]$

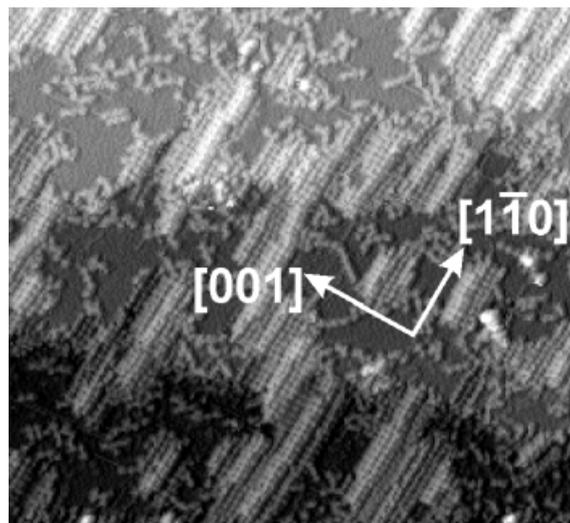


Fig. 3. STM image of the sample after annealing to 450 K; the area is $100 \times 90 \text{ nm}^2$; the tunnelling parameters are $U_t = 2.1 \text{ V}$ and $I_t = 2 \text{ pA}$

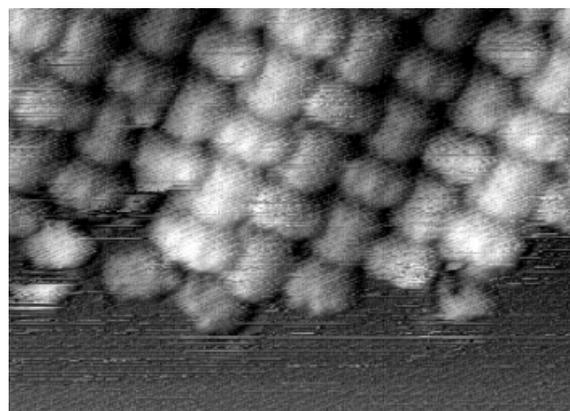


Fig. 4. STM image of the smaller area of the sample after annealing, the area is $10 \times 8 \text{ nm}^2$; the tunnelling parameters are $U_t = -0.45 \text{ V}$ and $I_t = 300 \text{ pA}$

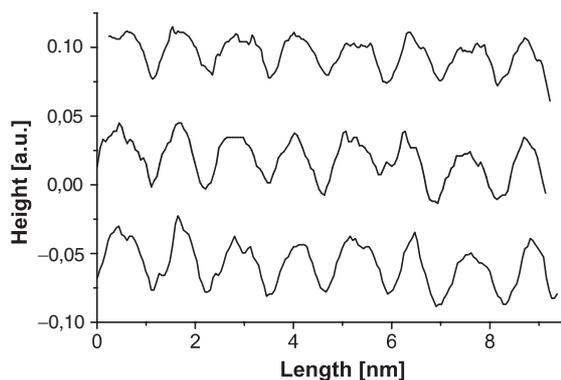


Fig. 5. Cross-sections along the $[1\bar{1}0]$ direction

direction. As a result a corrugation is found which has a periodicity of either four, five or six molecular rows. Figure 6 shows several line scans to illustrate the situation. The large-scale corrugation amounts to 0.18 nm, which is the distance between adjacent layers of the Cu(110) substrate.

For several reasons we rule out the idea that the corrugation is due to the formation of a second layer of PTCDA molecules which might lead to a similar difference in height. First of all, if one compares the relative portion of the surface which is not covered by molecules before and after thermal annealing, it is found to remain unchanged. However, if a second layer were partially formed, the uncovered surface should increase. Second, the molecules between the upper and the lower regions appear to be tilted, which is not expected for a step to the next molecular layer. The observation is independent of tunnelling voltage and current. Hence, the idea that it is due to an effect of the electronic structure may be excluded.

If the coverage is increased to one monolayer, the superstructure discussed above expands all over the surface. Figure 7 shows a monolayer of PTCDA after annealing to 450 K.

The presented superstructure differs from those found so far on other substrates. For many substrates the “herringbone” structure is found which is equivalent to the (102) plane of the PTCDA bulk. The reported ordering represents the first example of a non-planar superstructure of PTCDA. Furthermore, it induces a restructuring of the substrate which is accompanied by a massive transport of substrate atoms.

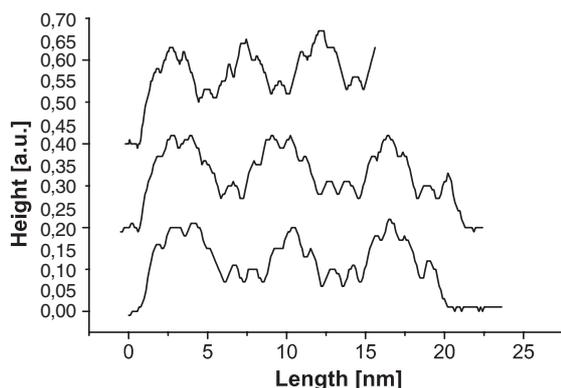


Fig. 6. Cross-sections along the $[001]$ direction

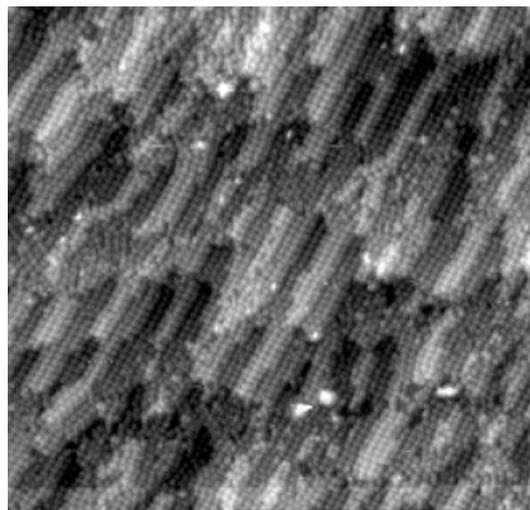


Fig. 7. STM image of about one monolayer of PTCDA on Cu(110), annealed to 450 K; the area is $91 \times 87 \text{ nm}^2$; the tunnelling parameters are $U_t = 2.6 \text{ V}$ and $I_t = 2 \text{ pA}$

A similar case of surface restructuring induced by organic molecules has been reported for C_{60} on Ni(110) [11].

3 Summary

The growth of thin films of PTCDA on Cu(110) was studied by STM in UHV. The ordering of the molecules is commensurate along the $[1\bar{1}0]$ direction, leading to a perfectly regular pattern. However, there is a mismatch between the intermolecular distances and the atomic distances of the unreconstructed Cu(110) surface along the $[001]$ direction. In connection with the strong interaction between the molecules and the substrate, this leads to a rearrangement of the atomic rows of the substrate, resulting in a quasi-periodic corrugation of 0.18 nm, which equals the height of a mono-atomic step. The ordering exhibits some variation; the periodicity varies between four and six molecular rows.

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