

Highly ordered thin films of perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) on Ag(100)

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ABSTRACT

We report experiments performed on vacuum deposited perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) films on Ag(100) by spot profile analysis low energy electron diffraction (SPA-LEED) and scanning tunnelling microscopy (STM). Up to a coverage of 1 ML, PTCDA forms a commensurate $c(8 \times 8)$ structure with two molecules per primitive unit cell, which are perpendicularly oriented to each other (four molecules per $c(8 \times 8)$ unit cell). The PTCDA islands exhibit an equilibrium shape that corresponds to the symmetry of the Ag(100) surface. The structural order is stable up to a temperature of ~ 670 K, at which a phase transition to a disordered phase occurs. Upon cooling back to room temperature, the order is partly re-obtained, although there is evidence that molecules have partly desorbed and dissociated at the high temperature. At coverages above 1 ML, a second layer orders in a *herringbone* structure on top of the $c(8 \times 8)$ -ordered first layer. The corresponding unit cell is very similar to that of the (102) plane of PTCDA bulk crystals.

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1. Introduction

The fast development of organic semiconductor devices over the last years [1–3] has motivated detailed investigations on the interface properties of large π -conjugated molecules. In order to improve the quality of thin film devices based on organic molecules, it is important to understand the basic mechanisms which control the initial growth of organic films on surfaces [4]. Perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) is one of the most studied π -conjugated molecules that forms ordered structures on a wide range of metal surfaces [5–14]. Fig. 1 shows the structural formula and a hard sphere model of PTCDA. The free molecule is planar. However, recent normal incidence X-ray standing waves measurements have shown that on Ag(111) [14] and Cu(111) [15], the anhydride and carboxylic oxygen atoms are differently attracted by these surfaces, and hence cause that the adsorbed molecules is not planar. For coverages above 1 ML PTCDA commonly orders in a *herringbone* structure which corresponds to the (102) plane of the PTCDA bulk crystal structures [16–18].

On close-packed noble metal surfaces with a small density of states near the Fermi edge and moderate adsorbate–substrate interactions, PTCDA monolayers exhibit *herringbone* structures with lattice constants that are also very close to those of the (102) plane of the bulk structure. The angle between the two molecules in the unit cell is about 80° [6]. Examples for this are PTCDA

monolayers on Ag(111) [6,11] and Cu(111) [12,13]. Depending on the particular deposition rate and the substrate temperature, the 2D unit cell of the PTCDA monolayer can even vary to some extent, e.g. Mannsfeld et al. [7] and later Kilian et al. [8] observed two slightly different *herringbone* structures on Au(111). A *herringbone* structure is also formed by PTCDA on the reconstructed Au(100) surface [7,19].

Structures which differ more strongly from the *herringbone* structure can be observed on the (100) and (110) surfaces, e.g. on Cu(100) Schmidt et al. [10] found a PTCDA structure with two molecules per unit cell oriented with their long axes exactly perpendicular to each other (“L-shape arrangement”). A structure, which differs even stronger from the *herringbone* structure is formed on Ag(110). There the molecules form a brick-wall structure with one molecule per unit cell and the long molecule axes oriented perpendicular to the close-packed Ag rows [5,6]. On some more reactive surfaces, like Ni(111) [11], or semiconductor surfaces like Si(111) [20,21] or Ge(100) [22], PTCDA forms only disordered monolayers.

Although the ordered monolayer structures of PTCDA on Ag(111) and Ag(110) have been analysed over the last years, the structure of PTCDA on Ag(100) was not reported so far. Here, we present a structural analysis of the first monolayer and the second layer of PTCDA on the Ag(100) surface which is based on spot profile analysis LEED (SPA-LEED) and STM. In addition to the measurements at room temperature, we took data at elevated temperatures which give information about the thermodynamic stability of the ordered structure. As we will report, PTCDA on Ag(100) constitutes

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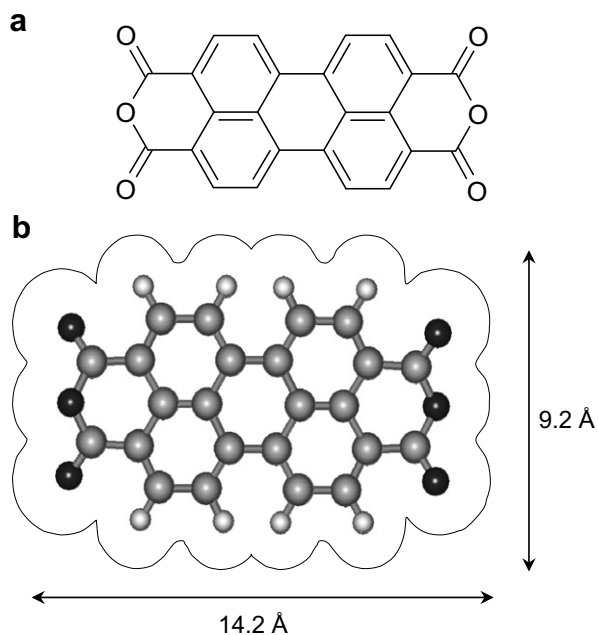


Fig. 1. Lewis structure formula (a) and hard sphere model of the PTCDA molecule (b). H atoms: white, C atoms: grey, O atoms: black. The van der Waals radii are indicated [6].

an interesting intermediate case between the situations on Ag(111) and Ag(110). On the one hand, the stronger surface corrugation causes a deviation from the dense and energetically most stable *herringbone* structure, found on Ag(111), and forces the molecules into a structure with a “T-shape arrangement”. On the other hand, the symmetry of the Ag(100) surface still allows two perpendicular orientations of the molecules, contrary to the Ag(110) surface, and hence enables attractive intermolecular interactions between the oxygen containing anhydride groups and the hydrogen terminated perylene cores.

2. Experimental

The SPA-LEED experiments were performed in a UHV-chamber at a base pressure of 4×10^{-10} mbar. The chamber is equipped with SPA-LEED apparatus manufactured by Omicron NanoTechnology GmbH. For deposition control, a mass spectrometer and a quartz-microbalance were used. The sample was mounted on a manipulator cooled by liquid nitrogen. During the measurements, the sample could be cooled down to 170 K and heated up to 900 K by a tungsten filament or electron bombardment.

The STM measurements were performed in a second UHV-chamber equipped with a temperature variable STM from RHK Technology. During the measurements the pressure was about 1×10^{-10} mbar. The sample holder was connected to a He-cryostat to allow measurements at low temperatures down to 35 K. On the STM sample stage, the sample was also heated by a tungsten filament for the high temperature measurements.

The Ag(100) crystal was prepared by subsequent cycles of sputtering and annealing. The first sputter cycle was done prior to the bake-out of the vacuum system. This removed possible residues from the polishing process and silver oxides from the crystal surface, which otherwise could have lead to formation of step bunches and faceting, during the bake-out. The following sputter-annealing cycles were used: sputtering with Ar⁺ ions of 800 eV kinetic energy, using an ion current of 1–2 μA on the sample, for about 30 min, subsequent annealing at 900 K for about 15 min. This routinely yielded atomically flat terraces of about 300–500 nm in diameter.

PTCDA was deposited from a home-made Knudsen-cell. Because of the different geometries of the two vacuum chambers, different cell temperatures and deposition times were used. For 1 ML coverage in the SPA-LEED chamber, PTCDA was evaporated at a cell temperature of 790 K for about 120 s; in the STM chamber, for the same coverage a temperature of 650 K for 5 s was used. Usually, the sample was held at room temperature during the deposition, except for some STM experiments dealing with the initial growth, for which lower sample temperatures were used.

3. Results and discussion

3.1. The structure of the monolayer

A SPA-LEED pattern of about 1 ML PTCDA on Ag(100) is shown in Fig. 2a. The (0,0) and the first order spots from the Ag(100) surface are marked. In the PTCDA diffraction pattern we find systematic absences of the $(n,0)$ and $(0,k)$ spots, when n and k are odd numbers [23]. This is explained by the presence of two glide planes in the superstructure (see below). From the SPA-LEED pattern we find a commensurate superstructure with a quadratic unit cell. A simulation of the LEED pattern is plotted in Fig. 2b, showing the primitive unit cell and the unit cell vectors. Interestingly, the superstructure spots in the intermediate k -range of Fig. 2a are strongly suppressed, which we believe is due to dynamic effects in the scattering process.

The proposed structure model is given in Fig. 3a. It is in a good agreement with the SPA-LEED measurements and was also proved by STM images (Fig. 3b), which we will discuss below. The unit cell is quadratic and belongs to the symmetry group $p4gm$, which exhibits two glide planes parallel to the unit cell vectors. The superstructure is commensurate, and the unit cell vectors \mathbf{b}_1 and \mathbf{b}_2 are described by the matrix

$$\begin{pmatrix} \mathbf{b}_1 & \mathbf{b}_2 \end{pmatrix} = \begin{pmatrix} 4 & 4 \\ -4 & 4 \end{pmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{pmatrix}, \quad (1)$$

where \mathbf{a}_1 and \mathbf{a}_2 are the basis vectors of the substrate. In the Wood's notation this is a $(4\sqrt{2} \times 4\sqrt{2})R45^\circ$ superstructure. There are two PTCDA molecules in the unit cell, which are perpendicularly oriented to each other (T-shape arrangement) and which are both planar to the Ag(100) surface. For this unit cell on Ag(100), we calculate an area of 267 \AA^2 which is by 11.1% and 12.1% larger than the unit cell of the (102) plane of the bulk crystal α - and β -phases, respectively (see Table 1) [17] and 11.9% larger than the unit cell of the commensurate monolayer of PTCDA on Ag(111) [6]. We note that the superstructure may alternatively be described by a centred quadratic unit cell as a $c(8 \times 8)$ superstructure with unit cell vectors parallel to those of the substrate. This unit cell consists of four molecules and is also shown in Fig. 3a. The principal axes of the molecules are oriented parallel to the close-packed rows of the Ag(100) substrate, i.e. the directions of the unit cell vectors of the substrate. We define the coverage of this ideal monolayer structure as 1 monolayer (1 ML).

Although from the SPA-LEED and STM measurements the exact adsorption sites of the molecules were not determined, an argument can be given from the symmetry of the structure. Under the reasonable assumption that the molecules are adsorbed on high symmetry sites, i.e. the centres of the molecules are on a four-fold hollow site or an atop site, one deduces from the model in Fig. 3a that both molecules in the unit cell are adsorbed on equivalent sites. Hence they are chemically and structurally fully equivalent. Here we note the difference in comparison to the PTCDA structure observed on Cu(100) [10], where the two molecules in the unit cell have different adsorption sites corresponding to the lower symmetry of the unit cell (L-shaped instead of T-shaped

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