

A refined structural analysis of the PTCDA monolayer on the reconstructed Au(111) surface—“Rigid or distorted carpet?”

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Abstract

The superstructures (**H1** and **H2**) of perylenetetracarboxylicacid-dianhydride (PTCDA) monolayers on the $(22 \times \sqrt{3})$ reconstructed Au(111) surface reported by Mannsfeld et al. [S. Mannsfeld, M. Toerker, T. Schmitz-Hübsch, F. Sellam, T. Fritz, K. Leo, *Org. Electron.* 2 (2001) 121] are reinvestigated by high resolution low energy electron diffraction (SPALEED). The purpose of this investigation is to elucidate in detail the point-on-line (p-o-l) structural relation of the homogeneous adsorbate layer with respect to the three reconstruction domains of the Au(111) surface. For the **H2** (non-equilibrium) structure, diffraction patterns without a spot splitting are found, indicating an almost perfect undisturbed overgrowth of the domain boundaries of the $(22 \times \sqrt{3})$ reconstruction. As a consequence, the superstructure does *not* follow strictly the p-o-l relation, but only in an averaged manner. Contrary for the **H1** phase (equilibrium structure), a spot splitting is observed, which indicates that superstructure domains on different Au(111) reconstruction domains exhibit slightly different angular orientations, thus adopting p-o-l relations on all Au(111) reconstruction domains. The PTCDA layer on Au(111) may be thus considered as a *rigid* or *distorted carpet*, depending on the preparation conditions.

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1. Introduction

The structural relations between densely packed monolayers of large π conjugated molecules and underlying substrate surfaces has been subject of numerous investigations in the last years [2]. For a strong site specific bonding to the substrate, *commensurate* superstructures are typical, whereas weak adsorbate substrate interactions usually lead to *incommensurate* structures [3]. In addition to these two possibilities, the structural relation to the substrate may be of the so-called *point-on-line* (p-o-l) type, which constitutes a structural relation of the adsorbate layer to the underlying substrate which is between that of an incom-

mensurate and a commensurate layer. In this case, all lattice points of the adsorbate layer fall onto lattice points of the substrate surface, which minimizes the interface energy to the substrate, while only small distortions of the structure of the organic layer with respect to the optimal lateral packing are induced [3,4]. Indeed, p-o-l type structural relations have been found for close packed layers of organic adsorbates on surfaces of weak or negligible chemical reactivity and lateral corrugation of the bonding potential in many cases [3,5], which demonstrates that the p-o-l relation does effectively reduce the interface energy.

1.1. PTCDA on Au(111)

Monolayers of 3,4,9,10-perylenetetracarboxylicacid-dianhydride (PTCDA, see Fig. 1(c), below) have been studied on many surfaces (see Refs. [6–8] and references therein). On the Ag(111) surface, a commensurate

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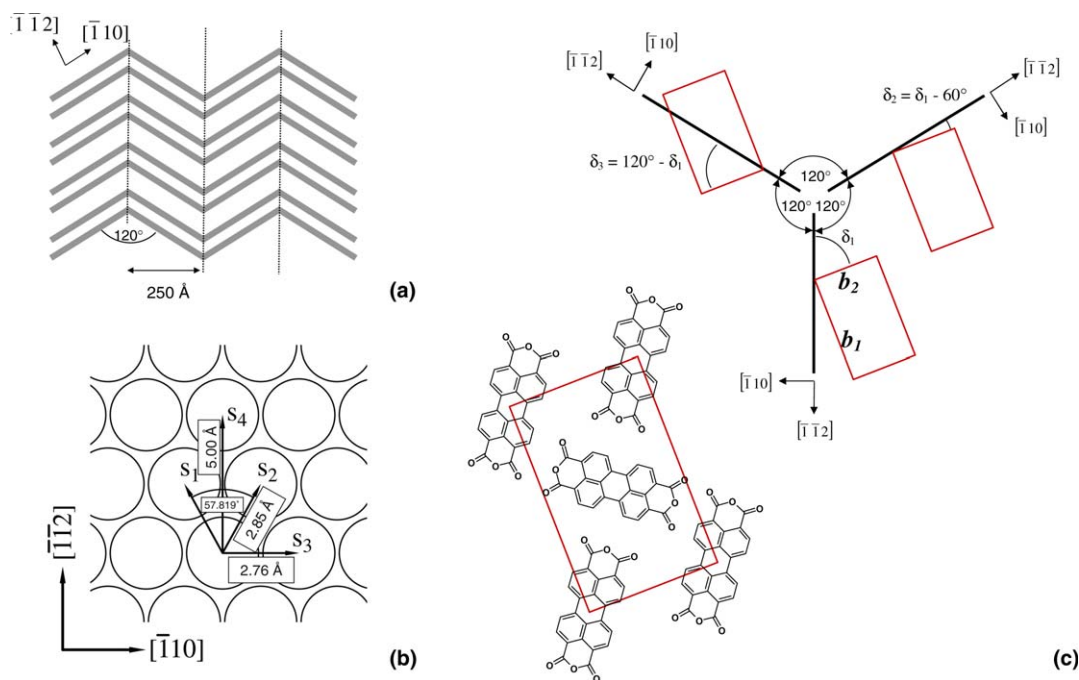


Fig. 1. (a) Schematic illustration of the $(22 \times \sqrt{3})$ reconstructed Au(111) surface. The zig-zag arrangement of the corrugation lines leads to a stripped arrangement of the $(22 \times \sqrt{3})$ reconstructed domains. The vertical direction is expanded by about a factor of 2. (b) Hard-sphere model of the top layer of the $22 \times \sqrt{3}$ reconstructed Au(111) surface showing the local geometry under the assumption of a uniform compression in $[\bar{1}10]$ direction. The unit cell can be chosen as a pseudo-hexagonal (s_1, s_2) or rectangular unit cell (s_3, s_4). (c) Schematic presentation of the three symmetry equivalent orientations of the reconstruction domains of the Au(111) surface (indicated by the corrugation lines in the $[\bar{1}\bar{1}2]$ direction) and the relative orientation of an adsorbate domain (represented by one unit cell) to each of these reconstructions, described by the angles δ_1 , δ_2 , and δ_3 (adapted from [1]). One unit cell with schematically drawn PTCDA molecules is shown at the bottom. Further details see text.

superstructure is formed [6] due to the chemisorptive bonding [9–12], whereas on HOPG [5] and on Au(111) [1,13] the weaker bonding leads to superstructures of the p-o-l type. The monolayer structures of PTCDA on Au(111) have been so far investigated by STM [1,13,14], RHEED [13,15], LEED [1], and XRD [16]. On all of the above mentioned substrates the lateral arrangement of the PTCDA molecules is very similar to that within the (102) plane of the two known bulk phases [6]. There are two flat-lying molecules per unit cell, arranged in a herringbone structure (see Fig. 1(c), below). This lateral arrangement is presumably caused by electrostatic forces between the negatively charged anhydride groups and the perylene cores [6]. As it will turn out in our analysis, this lateral arrangement is rather robust and tolerates only small deviations in order to optimize the interaction with the substrate if this is relatively weak, as in the Au(111) case.

By LEED measurements Mannsfeld et al. [1] identified two superstructures (**H1**, **H2**) with rectangular unit cells for the PTCDA monolayer on Au(111). The coverage ratio of these partially coexisting two structures was found to depend on the substrate temperature and the molecular flux during film growth. The structure **H1** grows preferentially under “equilibrium conditions”, i.e. at high substrate temperatures and small fluxes; whereas the structure **H2** grows under “non-equilibrium conditions”, i.e. at low substrate temperatures and high fluxes. An additional struc-

ture with a squared unit cell (“square phase”) could be detected by STM covering only minor areas of the sample [1,13]. Mannsfeld et al. classified the two structures **H1** and **H2** both as p-o-l structures [1].

The STM images demonstrate that the $(22 \times \sqrt{3})$ reconstruction of Au(111) is *not* lifted by the adsorbed PTCDA monolayer, pointing to a very weak interaction with PTCDA, as also observed by photoelectron spectroscopy data [17,18], similar to PTCDA on Au(100) [19]. An important and interesting finding of the STM measurements for our analysis was that the size of PTCDA adsorbate domains is by far larger than the size of the reconstruction domains of the Au(111) substrate [1]. In particular, it is seen that PTCDA domains overgrow the reconstruction domain boundaries homogeneously without any large changes of the geometric structure, i.e. the size of the unit cell or its orientation. From this observation it was concluded that three *symmetry inequivalent* orientations $\delta_1 = \delta$, $\delta_2 = \delta - 60^\circ$, and $\delta_3 = 120^\circ - \delta$ between the PTCDA overlayer and the three rotational Au(111) reconstruction domains exist for both structures **H1** and **H2**. This is illustrated in Fig. 1(c) [1]. A direct consequence is that the structures **H1** and **H2** cannot strictly obey the p-o-l relation on all three Au(111) reconstruction domains simultaneously and that thus the structural relation must be more complicated. This was already noted by Mannsfeld et al. [1], but could not be answered within the resolu-

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