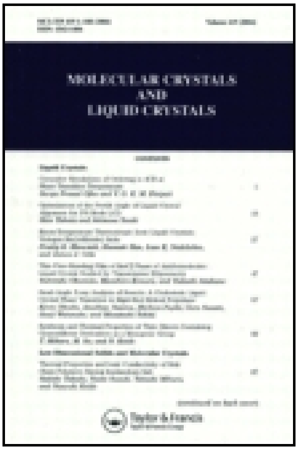

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Heteroepitaxially Grown Overlayers of PTCDA on Au(111) Surfaces: Structural and Fluorescence Properties

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Heteroepitaxially Grown Overlayers of PTCDA on Au(111) Surfaces: Structural and Fluorescence Properties

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We have investigated the crystalline structure of PTCDA overlayers on reconstructed Au(111) surfaces by the combination of scanning tunneling microscopy (STM) with *in situ* reflection high energy electron diffraction (RHEED). Large domains of PTCDA (up to 200 nm) are found on the still reconstructed Au surface. These structurally well-characterized PTCDA samples have been optically examined in detail, mainly by cw- and time-resolved fluorescence. An important finding is the occurrence of a new spectral feature in the emission around a wavelength of 590 nm. Temperature and intensity dependent measurements reveal that the very broad emission around 700 nm (commonly considered to be caused by excimer emission) consists of several sub-bands with different origin.

Keywords: PTCDA layers; organic-inorganic heteroepitaxy; structural characterization; fluorescence properties

INTRODUCTION

The optical and electrical properties of crystalline organic dyes continue to be of interest due to their potential applicability for electronic and optoelectronic devices such as organic light-emitting diodes, optical sensors, and waveguides. Of particular interest is the dependence of their optical and electrical properties on the structure. A drastic difference is expected between common polycrystalline layers and highly ordered films, the latter achieved by organic-inorganic heteroepitaxy, or *Organic Molecular Beam Epitaxy* (OMBE).

Of the various substances previously used for OMBE studies, much work has been focused on 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA)[1-4] since this organic dye exhibits interesting optical and semiconducting properties and the brick-shaped molecule easily forms well-ordered films on various substrates.

Here, we report on the structural and optical properties of highly ordered PTCDA layers on reconstructed Au(111) surfaces.

EXPERIMENT

The gold surfaces were prepared in a separate chamber under UHV conditions ($p < 10^{-7}$ Torr) by evaporation of pure gold (99.99 %, Degussa) onto freshly cleaved and thoroughly annealed (500 °C, 10 h) mica (0001) surfaces (high grade, Ted Pella). At this substrate temperature and at high evaporation speed (ca. 0.5 nm/s) epitaxial gold films with flat (111)-terraces[5,6] (terrace width typically 200..500 nm), which exhibit the well-known ($22 \times \sqrt{3}$) surface reconstruction[7], are obtained.

The PTCDA (Aldrich) was purified by gradient sublimation and then deposited in the main chamber at a substrate temperature of approx. 25 °C at a rate of 2 monolayers per minute (checked with a quartz balance). The Knudsen cell was held at 400 °C and the pressure was in the range of 10^{-9} Torr while depositing. To investigate the dependence of the optical properties on the structure, disordered polycrystalline layers (so-called evaporated dye layers - EDLs) were prepared at a high deposition speed (ca. 0.5 nm/s) by thermal evaporation in a HV chamber (ca. 10^{-5} Torr) onto the same single crystalline Au-substrates as described before.

The STM images were taken under ambient conditions using a NanoScope II (Digital Instruments). Structural data were obtained during the actual deposition using a RHEED system (Staib Instruments) with a CCD camera. The recorded images were averaged in the streak direction and then differentiated in the direction perpendicular to the streaks, in order to enhance the visibility of the usually weak streaks of PTCDA. Fluorescence measurements were carried out with a commercial cw-fluorescence spectrometer (FluoroMax, SPEX) and with a streak camera system (Hamamatsu).

RESULTS AND DISCUSSION

Figure 1 shows a typical RHEED image, taken at a PTCDA coverage of 1..2 monolayers. A variety of rather weak Bragg reflexes, stemming from the PTCDA lattice, can be seen. No azimuthal angular dependence of those reflexes could be found. The elongated streaks are rather narrow, which proves good crystallinity of the grown layer. At this low coverage, the diffraction streaks of the Au$[\bar{1}10]$ lattice rods are still visible (the outer strong lines) and can be used to accurately calibrate the images. For the PTCDA we do not find a significant relaxation of the lattice parameters with increasing layer thickness (up to several tens of nm).

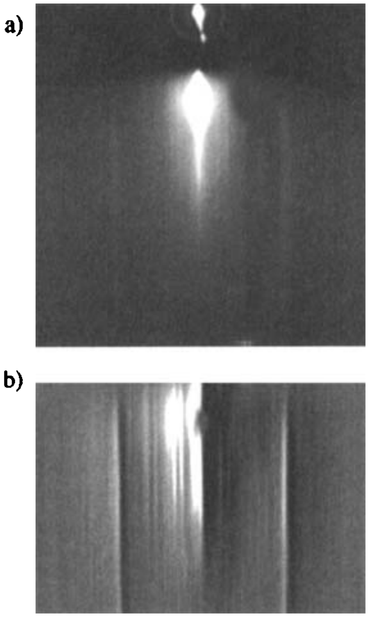

FIGURE 1
RHEED pattern of PTCDA/Au(111):
(a) as recorded, (b) differentiated

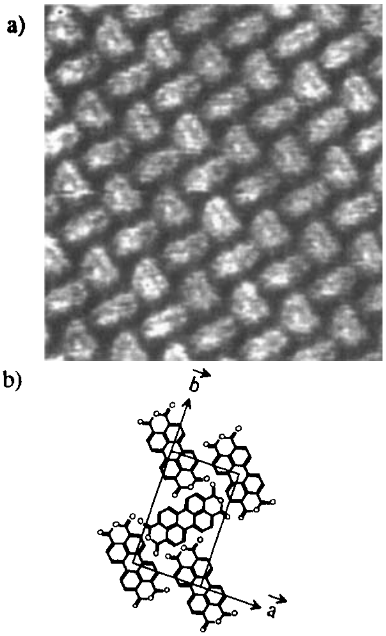

FIGURE 2
(a) STM current image (9 x 9 nm^2) of PTCDA/Au(111), V = 100 nm, I = 3 nA, (b) 2-dim. unit cell

To understand the complexity of the observed RHEED patterns and to deduce the lattice parameters, additional information about the molecular arrangement in the films is required. This information is provided by high-resolution STM images (Fig. 2): similar to the (102) plane of the molecular crystal[1] the molecules are arranged in a two-dimensional fashion, forming a rectangular lattice with two flat lying molecules per unit cell. Because neither RHEED nor STM data reveal any information about the growth in the direction perpendicular to the substrate, we restrict our following analysis to this two-dimensional lattice parameters.

As seen in large scale STM images, the PTCDA domains are extended over some hundred nm, and the Au surface reconstruction is not lifted by the deposition of the organic material. This allows us to determine precisely the orientation of different PTCDA domains. An important experimental finding is that only three basically different lattice alignments exist, which gives in total a number of 18 different domains[8]. All those domains can be explained as coincident structures, following the point-on-line concept[2]. It is obvious from these STM results, that the observed RHEED patterns consist of streaks from domains at different azimuthal orientations and therefore show no azimuthal angular dependence. From the combination of STM and RHEED data, the unit cell parameters were determined as $a = 12.2 \pm 0.2$ Å and $b = 19.7 \pm 0.4$ Å, but do not allow us to clearly identify the lattice as either α-, β- or new polymorph. Within error, these lattice constants are similar to those found previously by other authors[1-4].

A complete description of the optical properties of PTCDA in the solid phase is extremely difficult due to various intermolecular interactions. Absorption and emission of isolated PTCDA molecules are well understood as strong π-π^* transitions with vibronic progressions [9,10]. The absorption of thin polycrystalline PTCDA films shows two broad bands at 478 nm and 555 nm instead of the monomeric peak at 520 nm (in chloroform). At present there exist different models to explain the nature of such bands in PTCDA or related dyes. One approach is to assign the 555 nm peak to a extended charge transfer exciton [10]. Another approach is to consider the splitting of the excited state into an exciton band due to dipole-dipole interactions [11] or due to direct overlap of the π orbitals [12]. The emission properties of solid PTCDA are even more complicated due to excimer formation. There exist at least two excimer states which emit in the region between 600 and 800 nm [13]. These excimer states might be compared to the *Y* and *E* state in α-perylene [14] but the microscopic nature of these states is not yet understood. Since the emission properties of the excimer states strongly depend on the geometrical arrangement of the molecules, we used fluorescence to obtain information about structural differences in differently grown layers.

First, we investigated the absorption properties of our well-ordered PTCDA samples. Because of the almost opaque Au substrates, a direct measurement is not possible. However, by excitation scans we can prove that no distinctive difference exists in the absorption behavior between polycrystalline and highly ordered PTCDA samples, at least in the thickness range investigated (4..20 nm). Prior to measurements of PTCDA on Au we checked the validity of the method on polycrystalline samples on transparent substrates by the comparison of the direct absorption measurements (A = 1 - R - T, R and T being the reflectance and transmittance, resp.) and the excitation scans for samples of different thickness. The detection wavelength was always set to 713 nm, i.e., within the excimer emission region.

Second, the cw-emission of ordered and polycrystalline samples is compared in Fig. 3 with the monomer fluorescence (PTCDA in chloroform). All layers show an emission peak in the range between 600 nm and 800 nm. This emission is strongly red shifted (compared to the monomer) and very broad, therefore commonly ascribed to excimer fluorescence. The thinner the OMBE-layers are, the less red shifted is this excimer emission, pointing to fewer structural defects in the thinner films: Assuming a flatter van-der-Waals potential for structural relaxation at crystal defect sites, the excimer energy should be decreased and the red shift increased. As an important experimental finding we state that only in OMBE-layers a sharp new characteristic emission at 580..590 nm is observed (hereinafter referred to as *O-peak*). Because the absolute O-peak emission intensity of the 20 nm thick OMBE-layer is approximately two orders of magnitude larger than in case of the 4 nm layer, it is readily conceivable that the O-peak emission stems not from the substrate-deposit interface.

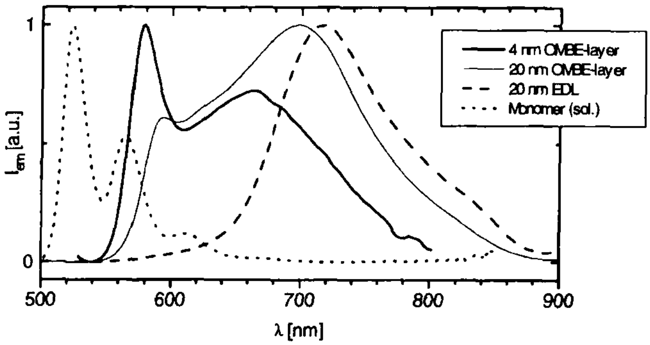

FIGURE 3 cw-Emission of PTCDA at room temperature (excit. at 478 nm)

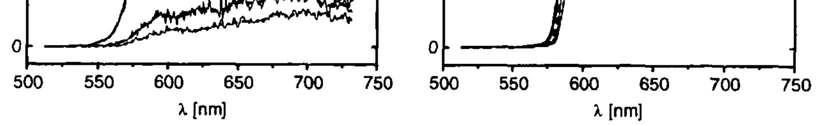

FIGURE 4 Time-resolved emission of 20 nm OMBE-layer (excit. at 427 nm)

In Fig. 4, an example for the temperature dependent time-resolved fluorescence of PTCDA OMBE-layers is depicted. Our experiments also included the polycrystalline samples. Again, the O-peak is observable in all OMBE-layers, but not in the EDLs. It is found that the decay of this emission is much faster than the excimer decay. The

O-peak does not exhibit spectral relaxation, and its linewidth is small and temperature independent. In contrast, the excimer peak shows spectral relaxation and a complicated substructure in the low temperature regime. While the origin of the O-peak still remains unclear, we observe no feeding of excimer states by the O-peak. The decay dynamics of the O-peak is strongly temperature dependent. The higher the temperature is, the more non-exponential and faster the decay process becomes. Therefore, the short decay times cannot be explained exclusively by direct quenching by the metal substrate. Instead, there is strong evidence for transport processes towards the substrate or other quenching centers.

CONCLUSION

Highly ordered and well-characterized PTCDA layers on Au(111) have been grown. While the absorption properties of those layers differ not remarkable from EDLs of the same dye, we found new optical features in the emission: at around 585 nm, a short living narrow emission peak is observed. The dynamics of all emitting states are strongly influenced by transport processes.

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