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Rapid Note

Molecular resolution of an organic monolayer by dynamic AFM

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Abstract. We report molecularly resolved dynamic AFM-measurements of a monolayer of perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) epitaxially grown on Ag(110). Preparation and experiments were performed under UHV conditions. The frequency-modulation AFM technique was applied.

PACS. 61.16.Ch Scanning probe microscopy: scanning tunneling, atomic force, scanning optical, magnetic force, etc. – 68.55.-a Thin film structure and morphology

Recently, the wide range of application of atomic force microscopy (AFM) has been expanded to high resolution imaging. Doubts about the principal capability of high resolution imaging *via* AFM have been dismissed by the demonstration of true atomic resolution on different inorganic and hard materials [1–5]. In most cases dynamic modes of operation of the AFM were applied [1–6].

Intermolecular distances on thin films by AFM have been resolved on self-assembly films [7], and Langmuir-Blodgett (LB) films [8]. However, imaging monolayers of LB-films with high spatial resolution has proven to be difficult [9,10]. On LB-films only the end-groups of long organic chain molecules can be imaged.

Here, we report the first measurements of a molecularly resolved monolayer of small and flat organic molecules under UHV conditions. In our case we can resolve whole molecules lying on the sample surface. The molecules were perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) (see Fig. 1) grown on an Ag(110) single crystal. This system and its preparation by MBE is well-known from LEED and STM examinations [11,12].

Dynamic AFM-techniques appear to be more promising for imaging these layers than contact AFM. This is because the lateral forces between the probing tip and the adsorbed molecules can easily damage the molecular layer. We used a commercial AFM (Omicron instruments) and silicon tips (Nanosensors) that were cleaned by sputtering with Argon ions ($I_{target}/Area = 8\ \mu\text{A/cm}^2$, $U_{bias} = 500$ V) for 10-20 minutes.

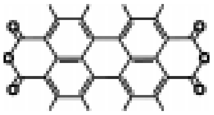

Fig. 1. Molecular structure of PTCDA.

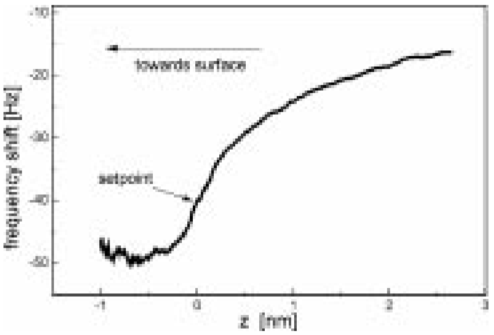

Fig. 2. Frequency shift *versus* distance dependence measured with the same tip as used for imaging (see Fig. 3). Parameters: $f_0 = 275804$ Hz, k about 42 N/m, $U_{gap} = 1.5$ V, vibrational amplitude of the order of 20 nm (peak-to-peak). The frequency shift used for imaging was at -40 Hz.

For imaging the molecular layers the frequency modulation (FM) technique [6] was applied: the force-induced frequency shift of a vibrating cantilever is used as a distance control. Hereby it is possible to operate the AFM with purely attractive (adjustable) forces acting between tip and sample [13].

An example of the frequency-distance dependence is shown in Figure 2. The setpoint used for the images below is indicated by an arrow. The resonance frequency of the vibrating cantilever runs through a minimum when moved towards the sample. At this minimum stable distance control is not possible. Unfortunately, the optimum setpoint for imaging in the noncontact regime with high resolution lies close to that minimum. For a more stable operation in the desired regime (falling values of the frequency shift when moving towards the sample) we found it helpful to

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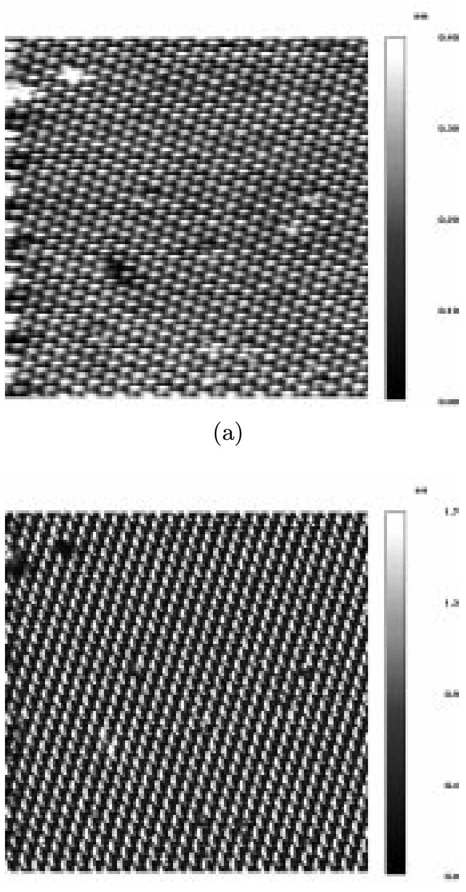

(a)

(b)

Fig. 3. (a) Dynamic AFM topographical image of a monolayer of PTCDA on Ag(110), scan range: 30×30 nm^2, $U_{gap} = 1.5$ V, $\Delta f = -40$ Hz. The image only contains raw data and was not filtered. (b) Simultaneously recorded mean tunnelling current.

apply a bias voltage between tip and sample of about 1 V that induces an additional attractive force. The setpoint implies an operation in the attractive regime [13] with purely attractive forces acting between tip and sample at any time. This applies to the net forces, that are a sum of the attractive van-der-Waals forces integrated over the tip apex, the repulsive force of the outermost part of the tip (if close enough to the sample) and, in this case, an additional electrostatic contribution. Hence, there might be a repulsive contribution at the tip apex although the overall force acting on tip is still attractive. In this type of measurement it can therefore not be excluded that the AFM effectively undergoes an intermittent contact for imaging. Thus, the molecular image contrast may be dominated by either of the three tip-sample interactions mentioned above.

Figure 3a shows a topographical AFM image of the monolayer. The distance regulation time constant was relatively large so that there is a contrast in the frequency signal (not shown here). The epitaxial structure of the molecules observed in the dynamic AFM image Figure 3a can be compared with previous STM examinations [11]. Not only the periodicity of the grown superstructure, but also various point defects can be recognised. The defects appear as additional or missing material.

As the cantilevers are electrical conductors a mean tunneling/point contact current can be recorded during AFM operation [4]. The current is averaged over the oscillations and can be recorded simultaneously with the AFM topography. The current image corresponding to Figure 3a is shown in Figure 3b. Note that the tip-sample distance was controlled purely *via* the frequency shift and not *via* the current. A characterization of the defects and of the layer can be supported by the tunnelling current.

With regard to these results we hope that it is also possible to image multilayers of PTCDA or other soft organic adsorbate layers, and directly observe the molecular order. Characterizing multilayer growth is a crucial step towards controlled manufacturing of highly ordered dye layers. While mono- or bilayers can be imaged very well *via* STM, multilayers, however, usually require different techniques such as AFM for a real space characterization. This is because most of the molecular systems are poor electrical conductors. High resolution AFM is therefore highly desirable.

In summary, monolayers of PTCDA have been imaged with molecular resolution *via* AFM. This demonstrates the general capability of dynamic AFM techniques to image soft (chemisorbed) molecular layers and may lead us to new physical insight into tip-sample interactions on soft organic material using dynamic force microscopy.

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