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# From interfaces to surfaces: soft x-ray spectromicroscopy investigations of diindenoperylene thin films on gold

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## Abstract

We present the results of photoemission electron microscopy investigations on diindenoperylene (DIP) thin films deposited on polycrystalline gold, prepared in order to have a roughness much larger than the molecular size. Our investigations revealed the ability of the DIP molecule to form well-organized films, exhibiting a different molecular orientation with respect to the already known  $\lambda$  and  $\sigma$  phases. In locally thicker film regions, the energy of the films is minimized by a molecular arrangement that has an asymptotic tendency to the  $\sigma$  phase.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

In the past, organic materials were considered very appealing not only because of a purely academic interest but also because of their promising properties for electronic applications [1]. Nowadays we can affirm that these materials kept their promise and they are widely present on the market. However, some of their properties demand deeper investigations and a better understanding. A general property that has been found investigating the growth of organic materials is that thin film characteristics are influenced by preparation conditions, substrate and post-growth treatment [1–3]. An aspect that can be investigated in order to gain information about the film structure is the orientation of the molecules in the film with respect to the substrate plane [3–6].

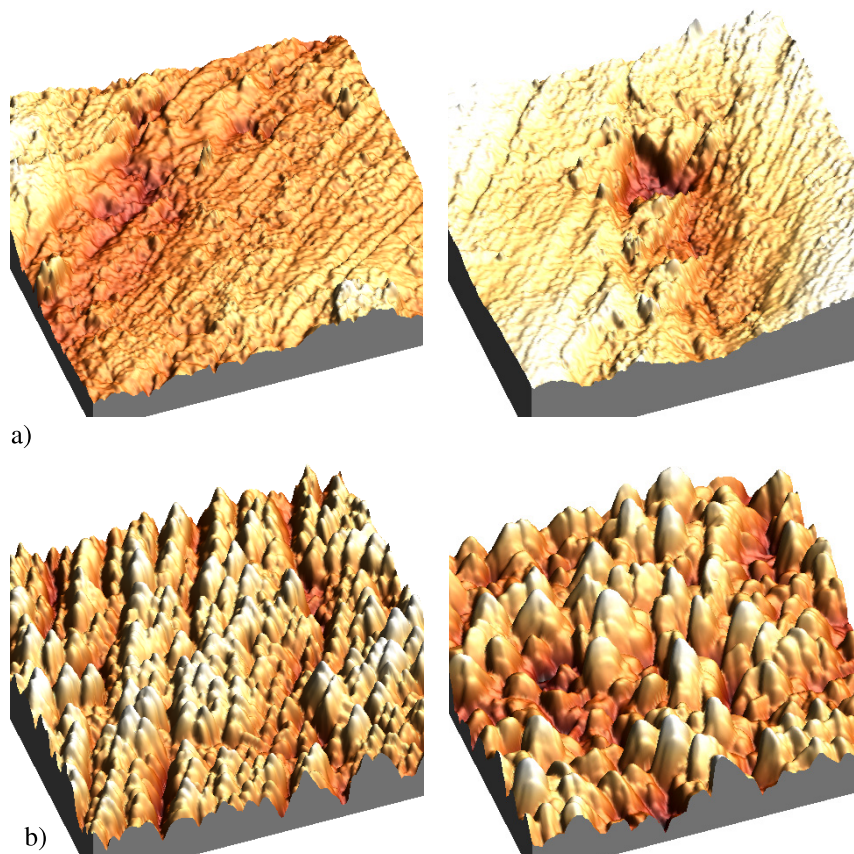
Diindenoperylene (DIP, C<sub>32</sub>H<sub>16</sub>) is a perylene-based molecule that shows a very high hole mobility already in thin films [7], good film forming properties and thermal stability [8, 9]. Two main phases have been identified so far: an upright standing molecule configuration ( $\sigma$  phase) in the thin films grown on rubrene and SiO<sub>2</sub> [10], while the  $\lambda$  phase, i.e. flat lying molecules, has been found in thin films

deposited on polycrystalline gold [11]. We investigate DIP films deposited on polycrystalline gold foils, with roughness larger than the molecular size, with a bunch of soft x-ray-based techniques in order to probe (1) the ability of the DIP molecule to form well-organized films also on a non-ideal substrate and (2) the influence of the substrate roughness on the molecular orientation. In this work, we present the results of photoemission electron microscopy (PEEM), further supported by standard near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, focusing on a detailed pre-characterization of the substrate.

## 2. Experiment

The measurements were performed at the IFP soft x-ray beamline WERA at ANKA (Karlsruhe, Germany). The PEEM chamber is equipped with a FOCUS-PEEM (FOCUS GmbH). WERA is a dipole beamline; thus the PEEM experiment had to be performed under a fixed geometry (the angle between the normal to the sample surface and the incident photons is  $\theta = 65^\circ$ ). However, a dipole beamline presents the big advantage of reducing the order of magnitude of the photon flux density on the sample in comparison to an undulator beamline making

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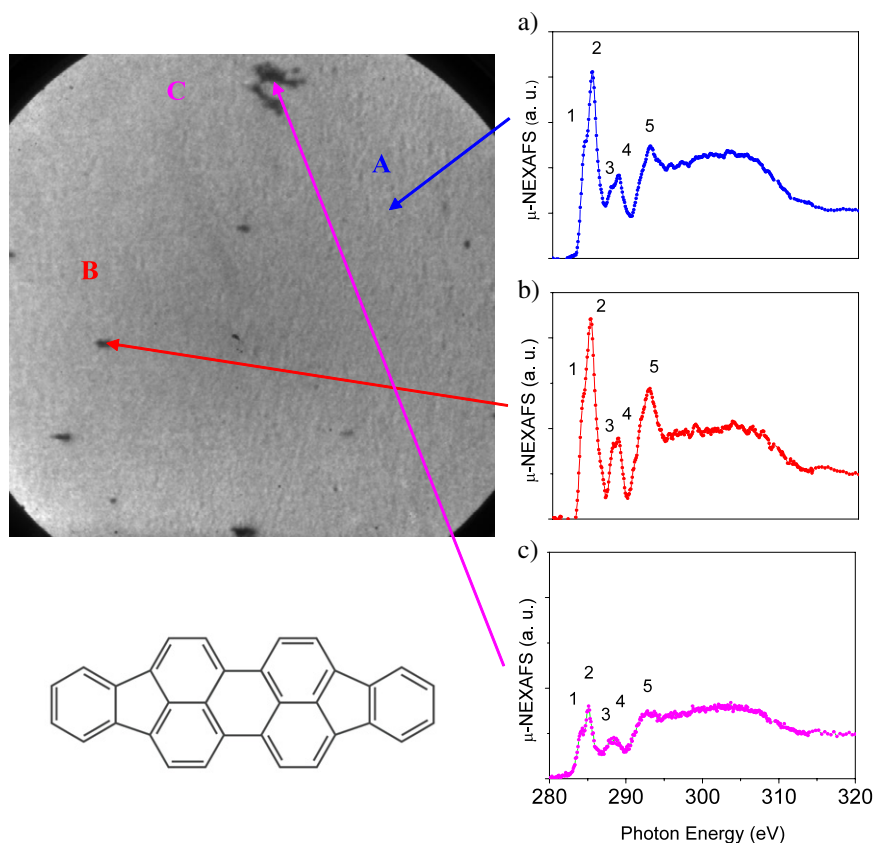
**Figure 1.** (a)  $3\ \mu\text{m} \times 3\ \mu\text{m}$  AFM images of polycrystalline gold after preparation. (b)  $5\ \mu\text{m} \times 5\ \mu\text{m}$  (left) and  $3\ \mu\text{m} \times 3\ \mu\text{m}$  (right) AFM images of a nominally 15 nm thick DIP film deposited on polycrystalline gold at room temperature. The  $z$  axis is strongly expanded in comparison with the  $x$  and  $y$  axes.

it possible that short measuring runs (not longer than 1 h) do not damage the samples. The effective lateral resolution of the experiment corresponding to the chosen field of view was about 300 nm. The energy resolution for the micro-near-edge x-ray absorption fine structure ( $\mu$ -NEXAFS) spectroscopy was about 0.14 eV and the polarization degree was 0.80. Because of the fixed geometry of the PEEM experiment, the spectra were obtained only for one direction of the polarized incident radiation and we could not quantitatively determine the molecular orientation only by using these data [12]. Thus, we also performed standard NEXAFS. We carried out standard NEXAFS (energy resolution  $\sim 0.095$  eV and polarization degree = 0.95) in the partial electron yield mode in grazing incidence ( $\theta_2 = 80^\circ$ ) and normal incidence ( $\theta_1 = 0^\circ$ ). In this way, we were able to calculate the molecular orientation ( $=47^\circ$ ) [12–14], i.e. the angle between the molecular axis and the surface plane. The gold foil (Goodfellow, purity 99.99%) was cleaned in ultra-high vacuum (UHV) by means of repeated cycles of Ar sputtering and checked by using XPS and ultraviolet photoelectron spectroscopy (UPS) *in situ* and by *ex situ* atomic force microscopy (AFM). The AFM measurements were performed under ambient conditions in tapping mode with a Nanoscope IIIa (Digital Instruments) scanning probe microscope. DIP was deposited *in situ* by using organic molecular beam deposition (OMBD). The nominal

thickness was determined by using a quartz microbalance and cross-checked by using the attenuation of the XPS substrate signals (Au 4f). The deposition rate ( $\Phi$ ) and the substrate temperature ( $T_{\text{sub}}$ ) were kept constant for each film preparation ( $\Phi = 3\ \text{\AA}\ \text{min}^{-1}$ ,  $T_{\text{sub}} = \text{room temperature (RT)}$ ). PEEM images have been recorded in sets of frames in 0.15 eV steps of the photon energy at the C 1s edge between 280 and 330 eV. By overlapping each frame in this range along the direction of increasing photon energy and looking at the intensity of the emitted photoelectrons for the single pixel, the  $\mu$ -NEXAFS spectra of the investigated region are obtained. Full details of the experiment, technique, data analysis and normalization are given elsewhere [14].

### 3. Results and discussion

To investigate the substrate morphology, first we characterized the gold foil by using AFM. Figure 1(a) shows two typical AFM micrographs of the gold foil after the standard preparation, namely cycles of sputtering to reach the necessary cleanliness, checked by XPS, and work function (5.2 eV) checked by UPS before depositing DIP on it. The average roughness of the gold foil as received was 4.5 nm. After the cleaning procedure it increased up to around 10 nm. The maximum corrugation was of the order of 35 nm. The surface



**Figure 2.** PEEM stack (the field of view is  $130 \times 130 \mu\text{m}^2$ ) of a 12 nm thick film, integrated in the photon energy range between 280 and 320 eV, together with the  $\mu$ -NEXAFS spectra (a)–(c) for three representative regions as indicated. The  $\mu$ -NEXAFS spectra have the same scale to facilitate comparison. The DIP molecular structure is also shown.

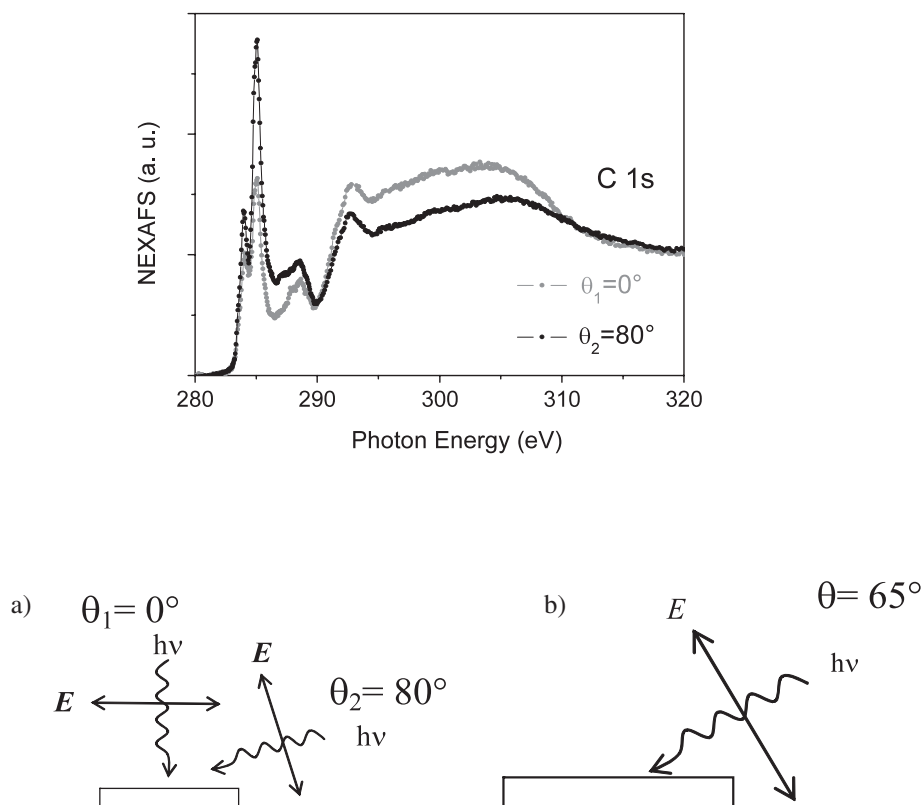
showed narrow terraces (on average 40 nm large). 15 nm nominally thick DIP films were deposited onto the clean Au surface. Figure 1(b) shows a typical AFM micrograph of the obtained films. The islands are clearly visible and large. The average grain size is above 300 nm and the minimum grain size is about 200 nm, while the average film roughness is 25 nm. Their shape and distribution are in nice agreement with the Stranski–Krastanov growth mode already reported [15] and with previous works [11].

Figure 2 shows one of the PEEM stacks (the field of view is  $130 \mu\text{m} \times 130 \mu\text{m}$ ) together with the normalized  $\mu$ -NEXAFS spectra for three areas as indicated, for a 12 nm nominally thick film. The  $\mu$ -NEXAFS are representative of regions of the DIP film surface, chosen depending on their different contrast. We see that the main features of the spectra remain constantly present but their intensity varies. Two main groups of resonances dominate the spectra: the  $\pi^*$  region up to 288 eV and the  $\sigma^*$ -region above 288 eV [15].

We can deduce some information about the local molecular arrangement by comparing  $\mu$ -NEXAFS and standard NEXAFS spectra presented in figure 3. This comparison is based on the fact that the geometry of the PEEM experiment is similar to the geometry of the standard NEXAFS experiment in grazing incidence (see figures 3(a) and (b)). A different alignment of the molecular orbital with respect to the incident electric field vector implies different

resonance intensities [12]. If the molecules are lying flat on the surface the angle between the electric field vector and the orbital pointing out of the substrate plane is smaller than in our reference spectra, i.e. the standard NEXAFS: the  $\pi^*$ -resonance intensities should be stronger. The opposite should be expected when comparing spectra coming from regions with upright standing molecules, because the angle between the electric field vector and the molecular orbital is larger than  $47^\circ$ . In figure 2(a), feature 2 is very intense and comparable with the corresponding one in the  $\theta_2$  curve (see figure 3). Thus we can assume that the molecular orientation in region A resembles that of the average value. Looking at the  $\mu$ -NEXAFS spectrum belonging to region B (figure 2(b)), we observe that the main characteristics remain unchanged. Feature 2 still has a high intensity. This leads to the conclusion that in regions with characteristics like B, the molecular orientation is also consistent with the value determined by using standard NEXAFS. Finally, the strongest changes are revealed by the region C spectrum (figure 2(c)). The relative intensities in the  $\mu$ -NEXAFS spectrum are different and the orientation of the molecular axis is drastically changed, indicating that the molecules in this region have a position closer to the upright standing one.

Observing the PEEM images and the  $\mu$ -NEXAFS spectra we can deduce that the morphological and structural properties of the films are quite constant for large regions where the



**Figure 3.** C 1s standard NEXAFS spectra (same scale as in figure 2) for the same film as in figure 2, together with the geometry of the two experiments: (a) standard NEXAFS. The spectra were taken in grazing (black curve) and in normal (grey curve) incidence. (b) PEEM.

films are homogeneous (at least  $130 \mu\text{m} \times 130 \mu\text{m}$  field of view, see figure 2). In addition, they are very similar for film regions with analogous morphology. Comparing regions A and B we observe that, despite the strong contrast between the two regions, their  $\mu$ -NEXAFS spectra have very close characteristics (see figures 2(a) and (b)), and again a good similarity with the collected standard NEXAFS spectra. Sampling randomly the surface, we have always obtained very similar  $\mu$ -NEXAFS spectra, i.e. the same molecular arrangement, in those regions with morphological characteristics like A or B. It is important to mention that the different contrast in the PEEM images is due to different film thicknesses. We have demonstrated and discussed this result, evaluating in detail the morphology of the DIP films not only with synchrotron radiation but also with a mercury high pressure lamp, showing that darker regions are thicker film regions [14]. The complete discussion is reported in [14].

The value obtained for the molecular orientation is now different than in standard NEXAFS spectroscopy: it is not anymore averaged on a large area (beam spot) but it comes from delimited and well-known micro-areas (300 nm/pixel) of the samples. Note that the average island size is of the order of magnitude of a pixel. Thus, we can confidently assume that the  $\mu$ -NEXAFS spectra give a plausible value of the molecular orientation, excluding scenarios where an intermediate value for the molecular orientation could be interpreted as due to the mean value between two domains with flat lying and upright standing molecules.

Our work shows that, within the resolution of our experiment, (1) DIP films are rather homogeneous in term of molecular orientation, despite the roughness of the substrate, (2) a molecular orientation between the  $\lambda$  and the  $\sigma$  phases occurs at intermediate coverage (see regions A and B) and (3) the molecular orientation shows the asymptotic tendency to the  $\sigma$  phase (see region C). According to our previous NEXAFS results [15] in the monolayer regime, the interaction between substrate and molecule is strong enough to force the molecules themselves into a flat lying configuration. Already after depositing a second layer, this interaction is overwhelmed by the intermolecular interaction. The real molecular arrangement of the few layers after the one on top of the gold is not yet clear. However, because of the information depth of the PEEM experiment (maximum 10 nm), we can also exclude that the present result is affected by contributions due to the first layer. In addition, we can also exclude the occurrence of a pure upright standing phase on top of a pure flat lying one, because we have never detected a pure  $\lambda$  phase, or conversely a pure  $\sigma$  phase, even in thinner films.

Further work is still needed to understand whether the molecules switch immediately to the intermediate angle or whether they assume different orientations in between the flat lying and the intermediate angle configuration itself.

Crystallographic orientation, roughness and terrace size of the substrate have a strong influence, leading to different phases under the same preparation conditions [4]. Comparing our results with those previously obtained on smooth



polycrystalline gold [11], we can deduce that the different roughness in a substrate of the same metal plays the major role. In fact we kept all parameters constant during preparation, intending to limit the number of variables. In addition, for an easier comparison, we also used preparation parameters similar to those used in [11]. In conclusion, this work shows that the substrate roughness does not hamper the ability of DIP molecules to form well-organized films, as could have been expected for such a small molecule deposited on a very rough surface, but it influences the film structure in terms of molecular orientation. In fact, we could not detect the same molecular arrangement as on smooth evaporated polycrystalline gold.

Our finding also has an impact when considering device applications. Gold is often used as an electrode in electronics. Several device configurations are based on the organic film deposition on gold; thus differently prepared electrodes lead to different device performances, including shorter lifetime, also under the same preparation routine of the organic materials, because the molecular orientation will be different.

Relating the molecular arrangement in thin films deposited on substrates with well-known local defects, on the one hand, and bridging the gap between ideal substrates and real surfaces, on the other, using the same methodology in both cases, will help to identify in very great detail the influence that the substrate has when growing the films under the same preparation conditions.

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