

Nucleation in Organic Thin Film Growth: Perylene on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111)

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The molecular orientation of perylene thin films has been investigated using near-edge X-ray absorption fine structure spectroscopy. The presence of different molecular orientations in the monolayer, ranging from flat-lying to more upright-standing molecules, has been found and related with the different sets of growth parameters used for each sample preparation. The same molecular tuning has been observed in the multilayer regime. It is shown that it is possible to explain these results by using concepts of the atomistic theory of nucleation. Regarding perylene on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) as a model system for organic layers in, for example, organic field effect transistors, our findings raise some questions about the suitability of perylene as an active layer in a real device.

## Introduction

Organic electronic devices offer an interesting alternative to inorganic semiconductor electronics due to low-cost deposition methods, flexible substrates, and simple packaging.<sup>1,2</sup> Organic field effect transistors (OFETs) are part of this rapidly developing field and a technological challenge of modern solid-state science.<sup>3–5</sup> Many different components of a device need to be optimized, in view of both their own intrinsic properties as well as their interplay with other components. This is, of course, particularly true for the organic layer(s) in the device. Organic single crystals of tetracene<sup>6</sup> or pentacene<sup>7</sup> have been used in OFETs, reaching relatively high room-temperature mobilities. On the other hand, the growth of a single crystal to be used in an OFET is not an easy task. Organic single crystals are often fragile and small. Their integration in a device is rather difficult, in particular, regarding the interfaces with the insulator and with the metal contacts. An alternative way is given by producing devices with thin films of small molecules. In a bottom-gate thin film transistor, the molecules can be vapor-deposited under vacuum, spin-coated, dip-coated, or printed on the insulator. All these techniques minimize the problems related with handling a single crystal and, not less important, are crucial for low-cost electronics.

It has been shown by Garnier et al.<sup>8</sup> and, lately, by Dimitrakopoulos et al.<sup>9</sup> that the mobility in OFETs depends strongly on the degree of overlap of delocalized molecular  $\pi$  orbitals. In other words, the charge transport is facilitated in films where the current flows in the direction parallel to the layers. In fact, the highest mobilities in bottom-gate thin film transistors are reached when the molecules are standing upright on the insulator surface.<sup>5</sup> These results indicate the two main goals of most of the recent research efforts: control of the

interfaces and growth of films with physical and electronic properties dominated by high structural order. This requires a deep understanding of the growth mechanisms and their strict control during preparation as well as the knowledge of the chemical and electronic structure at the organic/insulator interface.

Perylene (C<sub>20</sub>H<sub>12</sub>) is one of the simplest aromatic hydrocarbons, and its crystal and molecular structure has been thoroughly studied in the 1960s.<sup>10,11</sup> Its high hole (0.4 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and electron (5.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, when the electric field is parallel to the *b* crystallographic axis) mobilities<sup>12</sup> at room temperature (rt) make perylene an interesting system for a better understanding of growth mechanisms, intermolecular interactions, and interface properties, that is, the basic ingredients necessary to build an efficient device by design.

Only few experiments have been performed so far to investigate the thin film growth dynamics of perylene and its interaction with different metal substrates, and very little has been done on oxide substrates.<sup>13</sup> Seidel et al.<sup>14</sup> investigated the growth of perylene up to a monolayer on several metal surfaces by using low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Perylene on Ag(110) and Au(111) shows transitions between two-dimensional gas, fluid, and crystalline phases, which are reversible above rt. Eremitchenko et al.<sup>15</sup> found by using STM and electron energy loss spectroscopy that, in perylene-based molecules, the perylene backbone supplies the potential for an efficient recognition center, which has its activity increased by electronegative side groups. Identical investigations on perylene on Ag(111) indicate that, also, perylene has a preference toward a specific absorption site when the influence of the intermolecular interaction is inhibited.<sup>16</sup> Epitaxial growth of a new large-scale crystalline structure of perylene on Cu(110), where the molecular planes are parallel to the substrate, has been studied by Chen et al.<sup>17</sup> This result has been recently questioned by Hänel et al.,<sup>18,19</sup> who found that, for multilayers exceeding a 10 nm thickness deposited on Cu(110), the molecules grow in a bulklike structure. Verlaak et al.<sup>20</sup> have adapted the microscopic theory of nucleation for

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the epitaxial growth of inorganic material to the nucleation of several organics, including perylene, on an inert substrate. All of these investigations lead to a common important result: perylene behaves differently from perylene-based molecules. Therefore, there is the need for more comprehensive investigations, especially on passivated substrates.

An important point, not yet completely explored because of its complexity, is to what extent the growth parameters influence the morphology and the structure of the perylene thin films. As already known, the thin film structure of 1,4,5,8-naphthalene tetracarboxylic acid-dianhydride (NTCDA),<sup>21</sup> and 1,8-naphthalene dicarboxylic acid-anhydride (NDCA) can be influenced by changing the substrate temperature or by using an oxygen precovered substrate.<sup>22</sup> A good indicator of this change is the molecular orientation. The ideal technique to study this aspect of the film structure is the near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

In this work, we report a systematic investigation of the influence of the growth parameters on the molecular orientation in thin films of perylene grown on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111). The choice of Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) represents a key point because the oxidation of a single crystal of Ni<sub>3</sub>Al(111), if performed correctly, produces a thin layer of Al<sub>2</sub>O<sub>3</sub> that is closed, highly ordered, and free of grain boundaries.<sup>23</sup> This has a strong influence on the interface properties and on the organic thin film growth.<sup>24</sup> It can be also seen as a simulation of insulating oxides used in a large variety of electronic devices. Last, but not least, these results are explained by using basic concepts of the atomistic theory of nucleation, thus providing new insights into the issue of organic thin film growth.

## Experimental Section

The measurements were performed at the beamline UE52-PGM at BESSY (Berlin, Germany). This beamline is characterized by a plane-grating monochromator, a photon energy range from 100 to 1500 eV, and an energy resolving power of  $E/\Delta E = 10500$  at 401 eV ( $c_{ff} = 10$ , 10  $\mu\text{m}$  exit slit). The experimental end station has two ultrahigh vacuum (UHV) chambers: a preparation chamber (base pressure,  $6 \times 10^{-10}$  mbar) equipped with a sputter ion gun, two separated gas dosing systems for argon and oxygen, a quadrupole mass spectrometer, a LEED optics, and a homemade Knudsen cell. The main chamber (base pressure,  $2 \times 10^{-10}$  mbar) is equipped with a standard twin anode X-ray source, a SCIENTA SES200 electron energy analyzer, and a homemade partial electron yield detector. We carried out NEXAFS measurements in the partial electron yield mode (PEY), using a retarding voltage of 50 V, in grazing incidence (70° with respect to the sample normal). To investigate the molecular orientation, we measured the spectra by using linearly polarized synchrotron radiation parallel (s-pol) and normal (p-pol) to the surface, changing the direction of the polarization by means of the undulator. Finally, the spectra were normalized by taking the  $I_0$  current and the clean substrate signal into account, as discussed in refs 25 and 26, and then scaling all spectra to give an equal edge jump.

The Ni<sub>3</sub>Al(111) single crystal (MaTeck, Germany) was oriented with an accuracy better than 0.4° and mechanically polished on one side. The surface was cleaned in UHV by means of repeated cycles of Ar sputtering and subsequent annealing. The preparation of the oxide was carried out by exposing the single crystal at 1050 K to oxygen gas (partial pressure,  $3 \times 10^{-8}$  mbar). After the exposure, the sample was annealed for 5 min in UHV. This method gives highly ordered large domains and a relatively thin oxide layer, 5 Å,<sup>23</sup> suitable for investigation

**TABLE 1: Preparation Parameters of the Investigated Samples**

sample	thickness (Å)	$T_{\text{sub}}$ (K)	$\Phi$ (Å min <sup>-1</sup> )
<b>1</b>	4	90	1
<b>2</b>	10	200	2.5
<b>3</b>	11	240	3.6
<b>4</b>	24	99	4
<b>5</b>	>60	300	>6
	3	120	2
	4	100	0.2
	13	200	13
	30	240	1

by electron spectroscopies without the occurrence of charging phenomena. Each step of the substrate preparation was checked by using X-ray photoelectron spectroscopy (XPS) and NEXAFS.

Perylene (Aldrich Chem. Co) was purified by using thermal gradient sublimation and deposited in UHV conditions on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) by using organic molecular beam deposition (OMBD) in situ. The deposition was monitored with a quadrupole mass spectrometer, and the nominal thickness was determined by using the attenuation of the XPS substrate signals<sup>27</sup> (Al<sub>2p</sub> and Ni<sub>3p</sub>) with the corresponding inelastic mean free path of the photoelectrons taken according to ref 28. Furthermore, the homogeneity of the film thickness was probed on the local and global scale by using XPS. The deposition rate ( $\Phi$ ) was varied in the range between 1 and 20 Å min<sup>-1</sup>. The substrate temperature ( $T_{\text{sub}}$ ) was varied between 90 K and room temperature to probe a wide range of different preparation conditions and their influence on the films (Table 1). The temperature was read with a K-type thermocouple spot-welded on the tantalum foil, which clamped the Ni<sub>3</sub>Al(111) single crystal.

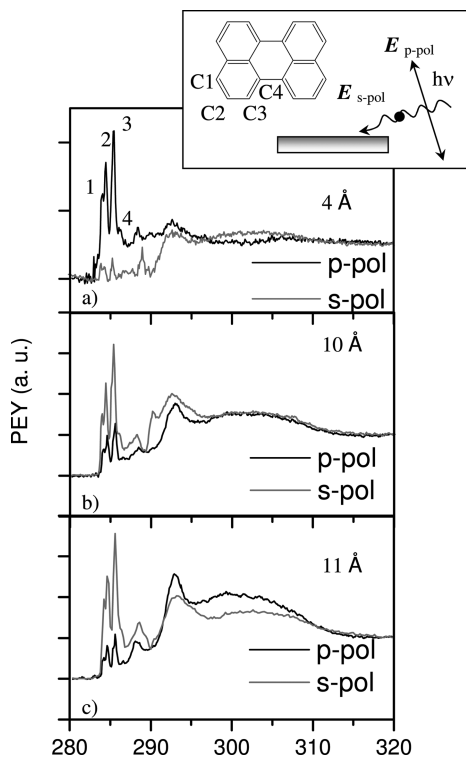
The spectra of the thick films were recorded at the PM-1 bending magnet beamline at BESSY ( $E/\Delta E = 3000$ , at 400 eV,  $c_{ff} = 2.08$ , 50  $\mu\text{m}$  exit slit). They were normalized according to the same procedure described above. The experimental end station has been described elsewhere.<sup>29</sup>

All samples were carefully monitored for radiation damage during beam exposure. The measurements were always performed on freshly prepared films unless specified differently in the text. This is an important point to be mentioned since perylene has a very high vapor pressure at rt ( $\sim 7 \times 10^{-10}$  mbar<sup>12</sup>).

## Results

NEXAFS spectra are characterized by resonances due to the excitation of a core electron to an empty state. Their intensities exhibit a strong dependence on the direction of polarization of the incident X-ray radiation. Measuring their detailed polarization dependence, it is possible to determine the molecular orientation with respect to the surface of the sample.<sup>30</sup> The NEXAFS signal is integrated over the area sampled by the incident spot, and the obtained molecular orientation is, thus, an average value. Nevertheless, the obtained values, especially in the case of strong dichroism, give a clear indication of the molecular arrangement in the film.

**Different Molecular Orientation in Perylene Monolayers on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111).** Figure 1 shows the C 1s NEXAFS spectra for samples 1–3 (Table 1 lists the preparation parameters of the investigated samples). The spectra were taken in grazing incidence for p-polarization (black curves), that is, out-of-plane, and s-polarization (gray curves), that is, in-plane. The low photon energy range between 284 and 290 eV is dominated by several well-resolved prominent peaks corresponding to the  $\pi^*$



**Figure 1.** C 1s NEXAFS spectra (a–c) for samples 1–3, respectively. They were taken in grazing incidence for p- (black curves) and s-polarization (gray curves). The perylene molecular structure is shown in the inset together with the geometry of the experiment.

resonances. It is worth mentioning that the energy resolving power of the UE 52 beamline gives the opportunity to perform highly resolved measurements and the spectra exhibit the presence of features that, in our previous results, were not resolved.<sup>31</sup> In particular, it is very interesting to focus on the resonances 1 and 2. In a study of perylene  $\alpha$  single crystals, they were seen as a small splitting of a peak at around 284 eV, the splitting being due to the transition from C 1s levels of nonequivalent C atoms into the lowest unoccupied molecular orbital (LUMO).<sup>31</sup> In the present spectra, they are two distinct well-resolved peaks. Recent ab initio calculations<sup>32</sup> based on the GSCF3 package<sup>33</sup> show that peak 1 is due to transitions from the carbon atoms C1 and C3, whereas peak 2 has contributions from the atoms C2 and C4 (see inset in Figure 1). An analogue observation holds for resonance 4. It arises from transitions from C 1s states of the site C4 and is clearly observable in our spectra, in contrast to previous measurements.<sup>29</sup>

Figure 1a shows the C 1s NEXAFS spectra for sample 1: a  $4 \pm 3$  Å thick layer of perylene on  $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$  grown at 90 K with a deposition rate of 1 Å/min. A strong dichroism is clearly evident. The  $\pi^*$  resonances are intense and well-resolved when the incident radiation is polarized in the plane perpendicular to the substrate, whereas they are almost completely quenched for in-plane polarization. This suggests flat-lying molecules in the film, that is, molecules with their delocalized  $\pi^*$  orbitals perpendicular to the surface.

The development of a quantitative approach to determine the molecular orientation is based on the fact that the polarization dependence stems from the dipole selection rules.<sup>30</sup> The  $\pi^*$  or the  $\sigma^*$  resonances are largest when the electric field vector of the incident radiation is along the  $\pi^*$  or the  $\sigma^*$  orbitals, respectively. This not only explains the dichroic NEXAFS behavior but also allows us to determine quantitatively the molecular orientation. It can be shown directly from the dipole

selection rules that, for a vector-type orbital, that is, an orbital that points in a specific direction, such as the  $\pi^*$  orbital in an aromatic ring, measuring the intensity for two different polarization directions with respect to the surface, s-pol and p-pol, it is possible to determine the angle  $\alpha$  from the following equation<sup>35</sup>

$$\frac{1}{\tan^2 \alpha} = \frac{1}{2} \left( 1 - \frac{1 - q}{\sin^2 \theta_{\text{p-pol}} - q \sin^2 \theta_{\text{s-pol}}} \right) \quad (1)$$

where we assume perfect polarization (this condition was satisfied during our measurements at the UE52-PGM beamline),  $\alpha$  being the angle between the surface normal and the orbital,  $\theta$  the angle between the incident radiation and the surface normal, and  $q$  is the ratio between the intensities of the chosen resonances for the two different polarizations

$$q = \frac{I(\theta_{\text{s-pol}})}{I(\theta_{\text{p-pol}})} \quad (2)$$

In this work,  $\theta_{\text{s-pol}} = 0^\circ$  and  $\theta_{\text{p-pol}} = 70^\circ$ . Equation 1 can be rewritten as

$$\frac{1}{\tan^2 \alpha} = \frac{1}{2} \left( 1 - \frac{1 - q}{\sin^2 70^\circ} \right) \quad (3)$$

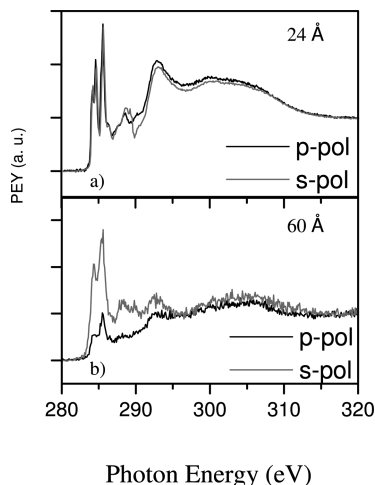
We performed molecular orientation calculations by using only the intensities of the  $\pi^*$  resonances because, in our spectra, they are very sharp. In particular, the values given in this work are calculated using resonance 3 and cross-checked with the others.

With this analysis, we find that the molecules in the monolayer (sample 1 in Figure 1a) lie flat (tilt angle  $\leq 10^\circ$ ) on the  $\text{Al}_2\text{O}_3$  surface, as mentioned above. Figure 1b shows the C 1s NEXAFS spectra for sample 2. The thickness of this sample is  $10 \pm 3$  Å, whereas the molecular orientation is derived to be  $67^\circ \pm 5^\circ$ . This value of the molecular orientation could be reached by tilting the molecules around their short axis or their long axis. The values of thickness and angle agree well with the growth of a monolayer formed by molecules with their long axis oriented at an angle of  $67^\circ$  with respect to the surface. The length of a perylene molecule is  $11.800$  Å;<sup>36</sup> therefore, the thickness of a monolayer under these conditions is expected to be  $10.862$  Å.

From the comparison of the two samples together with their preparation conditions (Table 1), it is immediately evident that a change in the substrate temperature and/or in the deposition rate induces a change in the molecular orientation of the film. To shed further light on the molecular orientation as a function of preparation parameters, sample 3 was grown with a deposition rate of  $3.6$  Å/min at a  $240$  K substrate temperature. The C 1s NEXAFS spectra are shown in Figure 1c. The quantitative analysis gives a molecular orientation of  $73^\circ \pm 5^\circ$  for a thickness of  $11 \pm 3$  Å. Also, sample 3 is interpreted as monolayer since the theoretical thickness of a perylene layer formed by molecules with a long axis orientation of  $73^\circ$  with respect to the surface is  $11.28$  Å.

In summary, changes in the substrate temperature and in the deposition rate influence the molecular orientation of the perylene monolayer on  $\text{Al}_2\text{O}_3$ . By simultaneously increasing the substrate temperature and the growth rate, the molecular orientation changes from flat-lying (at low temperatures and



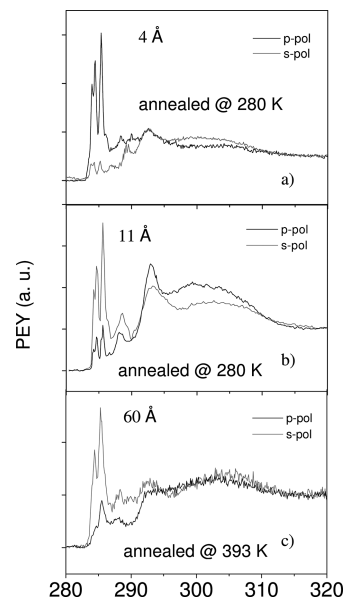


**Figure 2.** C 1s NEXAFS spectra (a, b) for samples 4 and 5, respectively. They were taken in grazing incidence for p- (black curves) and s- (gray curves) polarization.

growth rates) to almost upright (at high temperatures and growth rates). This indicates the possibility of a priori tuning the molecular orientation in a perylene monolayer by using appropriate growth conditions and, thus, the possibility to optimize such layers for the use in organic electronic devices.

**Multilayer Films of Perylene on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111).** Figure 2 shows the C 1s NEXAFS spectra for samples 4 and 5. It is worth emphasizing that the resonances found in the monolayer spectra are present also in the multilayer spectra. In contrast, the monolayer and multilayer C 1s NEXAFS spectra of perylene on substrates such as, for example, Si(111) or Cu(110), are significantly different.<sup>34</sup> In those cases, the monolayer spectra exhibit only a broad feature in the  $\pi^*$  region, that is, the intensity of the resonances 1 and 2 of the multilayers is strongly reduced. This can be explained by a partial occupation of the LUMO due to a charge transfer from the substrate, that is, a strong covalent coupling between perylene and the substrate. In our case, there is neither an indication of such a broadening nor an indication of an intensity reduction for resonances 1 and 2 when comparing monolayer and multilayer spectra. This result implies that the coupling between the perylene  $\pi$  system and the Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) substrate is weak. Figure 2a shows the C 1s NEXAFS spectra for a  $24 \pm 3$  Å thick film deposited on a substrate at 99 K with a deposition rate of 4 Å/min. The observed dichroism is not very pronounced, and the corresponding quantitative analysis gives a molecular orientation of  $53^\circ \pm 5^\circ$ . As mentioned, note that the same molecular value could be obtained if half of the molecules are upright-standing and half are flat-lying on the surface. Thus, we also investigated thicker layers deposited with a high deposition rate ( $>6$  Å/min) on the substrate kept at rt in order to investigate the tendency of the molecular arrangement with increasing the thickness. The C 1s NEXAFS spectra were recorded at the PM 1 beamline at BESSY, and an example is shown in Figure 2b. The dichroism in this case is, again, pronounced and similar to the dichroism shown by samples 2 and 3 (i.e., grown at elevated substrate temperatures). This direct observation is supported by the determined molecular orientation of  $76^\circ \pm 8^\circ$ . These two multilayer results, selected from a set of nine samples not shown here, suggest that also in multilayers the average molecular orientation changes toward more upright-standing molecules with increasing substrate temperature and deposition rate.

**Thermal and Vacuum Stability.** Because of the interesting transport properties, the above-discussed findings appear prom-

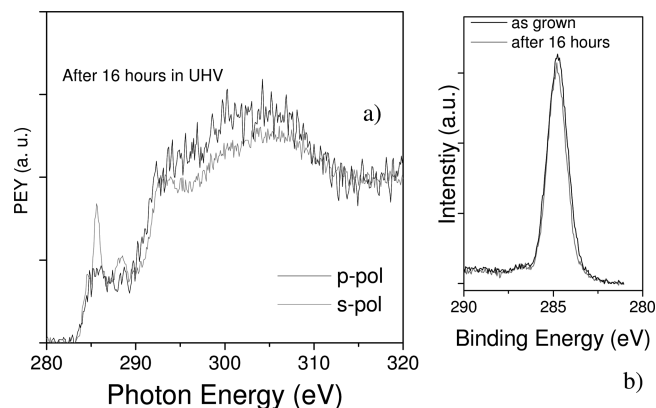


**Figure 3.** C 1s NEXAFS spectra for samples 1 (a), 3 (b), and 5 (c) after annealing.

ising for the preparation of organic thin films with high  $\pi$ -system overlap (and, thus, favorable transport properties parallel to the surface) at room temperature and high deposition rates.

For a long-term stable device, thermal and vacuum stability of the films is also very important. To test these aspects in the case of perylene on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111), we annealed the samples for 10 min at different temperatures depending on the starting preparation conditions and investigated the chemical and structural changes with XPS and NEXAFS. In Figure 3, we show results for three representative samples. Sample 1 was heated by using a ramp of 1 K s<sup>-1</sup>, kept at the chosen temperature for 10 min, and then cooled down. The sample was successively annealed at 150, 200, 255, and 280 K, respectively, and Figure 3a shows the C 1s NEXAFS spectrum after the last annealing cycle. On comparison with Figure 1a, the molecular orientation of flat-lying molecules in the monolayer remains virtually unchanged. Similarly, sample 3 was annealed at 315 K, and Figure 3b shows the corresponding C 1s NEXAFS spectrum after the annealing cycle. Also, in this case, the molecular orientation of almost upright-standing molecules is not affected by the annealing step (compare Figure 1c). A further increase of the temperature up to 380 K produces a significant degradation of the sample (not shown). Sample 5 (upright-standing molecules in a multilayer) was annealed at 343 and 393 K, and the C 1s NEXAFS spectrum after the last annealing cycle is shown in Figure 3c. Again, no major changes in the molecular orientation can be observed upon annealing. Thus, our results indicate that a once-established preferred molecular orientation is relatively stable upon annealing (at least below some critical temperature).

We also probed the vacuum stability of our ordered perylene thin films. We prepared a thick film with the same growth parameters used for sample 5, and we measured NEXAFS and XPS C 1s on the sample as prepared (NEXAFS spectra are identical to the spectra in Figure 2b) and after keeping it in UHV ( $7 \times 10^{-10}$  mbar) for 16 h. The measured spectra of the aged sample are shown and compared in Figure 4. In this case, the resulting NEXAFS spectra are noisy and the molecular orientation does change drastically as well as the electronic structure. Also, the XPS spectra indicate a clear change with time. The C 1s XPS edge becomes sharper and less intense,



**Figure 4.** C 1s NEXAFS (a) and C 1s XPS (b) of a sample grown with the same parameter set as that of sample 5. The spectra were recorded after keeping the sample 16 h in UHV.

opening a technologically relevant question on the vacuum stability of perylene films over a longer time scale.

## Discussion

**Molecular Orientation and Growth Mechanisms.** When the obtained results are merged, a picture of perylene growth on  $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$  can be drawn. The films show high orientational order, in both monolayers and multilayers. We observe the possibility of “tuning” the molecular orientation by choosing an appropriate set of growth parameters during the deposition. As a consequence, the monolayer can be deposited, varying the molecules’ orientation from flat-lying on the substrate toward a more upright-standing position. Because of the relationship between the films’ thickness and the molecular orientation, we conclude that the molecules have their short axis parallel to the substrate plane, whereas the long axis is out-of-plane. In the multilayers, the minimum obtainable value for the molecular orientation is  $53^\circ$ . In this case, we cannot discern by using only NEXAFS data whether it is a real intermediate phase or it is a coexistence of several phases. In thicker films prepared by using a higher deposition rate and keeping the substrate at rt, we obtain an almost upright molecular orientation close to the single-crystal value. Perylene exists in two different crystalline phases: the  $\alpha$  and the  $\beta$  form. Both of them belong to the monoclinic space group  $P2_1/a(C_{2h}^5)$ . Whereas the  $\alpha$  form has a dimeric structure and four molecules in the unit cell,<sup>10</sup> the  $\beta$  form is monomeric and its unit cell contains only two molecules.<sup>11</sup> NEXAFS measurements on  $\alpha$  single crystals have shown that the average inclination of the molecules relative to the cleavage plane is  $85^\circ$ .<sup>31</sup> In the  $\beta$  form, the molecular plane is orientated with an angle of  $70^\circ$  with respect to the cleavage plane. Both phases are stable at and below rt.<sup>11</sup> The comparison between our results and the single-crystal data indicates that, in the multilayers (samples 4 and 5), the molecules arrange in a bulk fashion, where the substrate plays a similar role as the cleavage plane in the crystalline forms. The NEXAFS spectra in Figure 3 show that there is no evidence for any reorientation of the molecules upon annealing. This means that the possibility to tune the film structure is directly related with the adsorption mechanism.

The growth of organic thin films has been the focus of intensive investigations that, in recent years, have gained knowledge about the involved mechanisms regarding substrate–molecule interaction and substrate temperature.<sup>37,38</sup> However, those concepts are not enough to explain our results. We keep the same substrate (i.e., same substrate interaction with mol-

ecules of the first layer on top of it and with those of further layers). We see that changes in preparation conditions influence the film structure. A comprehensive theory that relates different preparation conditions with the film structure and, more important, that takes into account the molecular orientation does not exist so far.

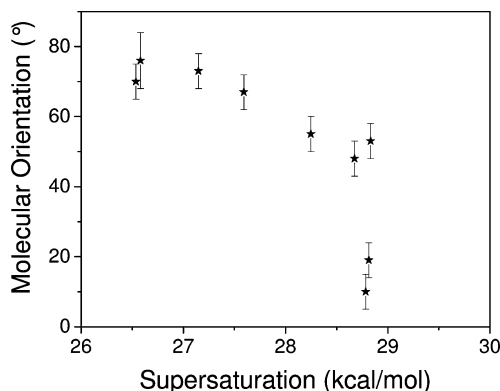
Atomistic theories, based on a general thermodynamic approach, describe the role of individual atoms or small clusters during the earliest stage of the film formation.<sup>39,40</sup> The growth of organic thin films is actually easier to model because the interactions that prevail in this case are weaker than those for inorganic clusters. We apply this approach to the molecules, seen now as the elemental building blocks. The reason for this choice is based on the fact that (1) this theory answers the questions why, how, and where different preparation conditions play a role in the film growth; (2) it relates the preparation with a different dimensionality of the growth; and (3) it has been already applied to the growth of tetracene, pentacene, and perylene thin films, which shows how the growth of organic thin films on inert substrates closely mimics the epitaxial growth of inorganic materials.<sup>20,41</sup>

The diffusion of a perylene molecule on  $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$  is the first process in the film growth. Given a certain deposition rate, the molecule on the surface can join an existing island or find another molecule to create a new island. When a molecule joins an island, the free energy of the island is negative. This implies that the cohesive energy between the molecules does not allow island dissociation. For small islands, also, the free energy is small and the surface tension can dominate: the island is not stable anymore. If we apply the nucleation theory to our case, we can define a critical island size as the size at which the island becomes stable with the addition of only one more molecule. This critical size depends on the supersaturation  $\Delta\mu$ . Usually, this physical quantity is expressed in terms of macroscopic quantities that cannot be known with certainty. However, in first approximation, it can be shown that the supersaturation is a function of substrate temperature and deposition rate.<sup>39</sup> According to ref 20, the supersaturation is, therefore, given by

$$\Delta\mu = \Delta H_{\text{sub}} + RT_{\text{sub}}[\ln(\sqrt{2\pi MRT_{\text{sub}}}\Phi) - A] \quad (5)$$

where  $\Delta H_{\text{sub}}$  is the heat of sublimation,  $R$  the gas constant,  $M$  the molecular weight, and  $A$  an empirical constant related to the entropy of sublimation.<sup>42</sup> We have calculated the supersaturation for each set of preparation parameters used to grow the samples here investigated. Figure 5 shows the experimentally obtained dependence of the molecular orientation versus supersaturation.

Sample 1 has been prepared at 90 K and with a deposition rate of  $1 \text{ \AA}/\text{min}$ . It shows flat-lying molecules. Under these preparation conditions, the supersaturation is so high that one molecule is already a critical nucleus,<sup>39</sup> the surface diffusion is low, and the coupling with the substrate is strong enough to allow a two-dimensional development of a planar layer. On the contrary, a higher  $T_{\text{sub}}$ , that is, lower supersaturation, implies the increase of the critical island size, together with enhanced surface diffusion. The probability of a three-dimensional growth becomes different from zero. The energetic arrangement of the molecules on the surface requires an energy minimization similar to that in the bulk. This is a continuous process leading to the occurrence of several different phases in which the molecular orientation slowly varies, for each set of preparation conditions,



**Figure 5.** Calculated molecular orientation versus supersaturation. The values of the supersaturation were calculated for each set of preparation conditions used for the investigated samples.

from the flat-lying molecule configuration toward the more upright one. These phases, which have never been reported before, are a priori produced by a convenient choice of preparation conditions or, in other words, by opportunely varying the balance between kinetics and thermodynamics at the surface and “freezing” it. This argument is in agreement and further confirmed by the results obtained on the multilayers. As discussed, from the comparison between the NEXAFS spectra of the monolayer and those from the multilayers, the interaction between the molecules and the substrate is rather weak. At the very beginning, in the monolayer regime, it is still enough to force the molecules in a flat-lying configuration, but as soon as the coverage increases, the substrate–molecule interaction is overwhelmed by the molecule–molecule interaction. This means that, under these preparation conditions, the substrate plays a minor role and it cannot act as a template for the layer growth. The energy is minimized by a molecular arrangement that has an asymptotic tendency to the bulklike structure. For higher supersaturation values, the molecular orientation has small values showing the tendency to the flat-lying configuration; in these conditions, the critical nucleus is established by a single molecule. In other words, the diffusion coefficient is reduced,<sup>40</sup> and the molecule, once onto the substrate surface, stays on this site, forming a stable “site plus molecule” system. The probability of the growth is higher than the probability of the decay of this system, leading to the formation of a homogeneous flat-lying molecule monolayer. When the supersaturation is decreased, the critical nucleus is established by more than a molecule. The adsorbed molecules have the tendency to move to reach a stable configuration that is given by the monomeric/dimeric arrangement in the mentioned bulklike fashion. The growth is no longer driven by nucleation but by diffusion.

According to this discussion, we cannot exclude the possibility to form multilayers with flat-lying molecules. This could be achieved by cooling down the substrate to lower than 90 K and choosing an appropriate evaporation rate to favor the substrate–molecule interaction. In the present work, the limit of 90 K has been set by the characteristics of our experimental system.

**Molecular Orientation and Thermal and Vacuum Stability.** When one looks at the NEXAFS spectra in Figure 3, the first impression is that no big changes occur on the molecular orientation upon annealing up to 100 K above the substrate temperature during preparation. Actually, the molecular orientation does not change relevantly, but the electronic structure of the annealed films changes in several details. The strongest

changes are noticeable in the thicker films with highest molecular orientation. This is due to the fact that the annealing temperature, in that case, becomes quite high, approaching the temperature, 550 K, at which perylene molecules are desorbed from the substrate, leaving the oxide completely clean. Under these conditions, the film becomes less stable and the molecule–molecule interaction changes, leading to a change in the electronic structure. An analogous effect, although more drastic, has been shown by the NEXAFS spectra (Figure 4a) performed in order to investigate the vacuum stability. In this case, the changes in the electronic structure can be explained by the fact that the perylene molecules at the film surface, for example, the molecules that are weakly bonded, desorb at room temperature. This effect is shown by the XPS spectra in Figure 4b where the spectrum taken 16 h later is sharper and less intense. This result, although surprisingly strong, is not completely unexpected since the high value of the vapor pressure at rt characterizes perylene.

## Conclusion

The presented NEXAFS results give detailed insight into the growth of perylene thin films on  $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$ . They represent the first systematic study of perylene deposited on a well-oriented oxide substrate, providing information on the occurring adsorption mechanisms. We have reported on perylene monolayer and multilayer regimes. Their investigations revealed the existence of different molecular orientations depending on the growth parameters. We have shown that this can be explained by using concepts derived by the atomistic theory of nucleation.

The results of the investigation on the thermal and vacuum stability of perylene thick films characterized by high values of molecular orientation open a question regarding the possible use of perylene in real devices. As a matter of fact, the efficiency of the devices could be drastically reduced by the changes in the electronic structure due to the operating temperature kept in a device for a period of time longer than the annealing cycles that have been used during our tests. In addition, the lifetime could be heavily shortened by the poor vacuum stability shown by perylene thin films.

In conclusion, with this paper, we also aim to stimulate further discussions and experiments, for example, by using techniques, such as Penning ionization electron spectroscopy and photoemission electron microscopy, that deliver sensitive results regarding details of the molecular conformation and orientation in organic thin films<sup>41,44–45</sup> in order to explore to which extent theory and concepts developed for inorganic materials may describe also growth phenomena in organic thin films.

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