

Role of Molecular Conformations in Rubrene Thin Film Growth

D. Käfer, L. Ruppel, G. Witte, and Ch. Wöll

Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, D-44780 Bochum, Germany

(Received 27 May 2005; published 11 October 2005)

A systematic analysis of the growth of rubrene ($C_{42}H_{28}$), an organic molecule that currently attracts considerable attention with regard to its application in molecular electronics, is carried out by using x-ray absorption spectroscopy and thermal desorption spectroscopy. The results allow us to unravel a fundamental mechanism that effectively limits organic epitaxy for a large class of organic molecules. If the structure of the free molecule differs substantially from that of the corresponding molecular structure in the bulk, the crystallization is severely hampered.

DOI: [10.1103/PhysRevLett.95.166602](https://doi.org/10.1103/PhysRevLett.95.166602)

PACS numbers: 72.80.Le, 61.10.Ht, 68.55.-a, 81.10.-h

When replacing inorganic, hard materials by organic, soft compounds quite often the physics underlying apparently simple phenomena can change significantly. The basic mechanism governing charge-carrier transport in organic materials, for example, is quite different from that in conventional semiconductors such as Si and GaAs. The hopping mechanism describing charge-carrier transport in organic semiconductors at elevated temperatures transforms into a bandlike mechanism at lower temperatures [1]. Notwithstanding a growing commercial interest in the development of plastic electronics [2] forming the basis of future cheap electronic devices, e.g., in connection with display drivers or identification tags, the mechanism underlying this bandlike transport is still only poorly understood. The molecular electronic devices presently showing the highest mobilities (reaching almost the values of polycrystalline silicon) have been fabricated by gently attaching flexible metallic contacts to macroscopic single crystals of aromatic molecules [3]. Although the technical performance of these organic field effect transistors (OFETs) is rather impressive, there are two major drawbacks related to this approach. First, from a fundamental point of view, the precise description of charge-carrier injection into the molecular material is virtually impossible due to contaminations on the metal electrodes present before the contact to the molecular crystals is made. Second, because of technological problems, organic single crystals cannot possibly form the basis for a future mass production of molecular electronic devices.

A different approach to the realization of molecular electronic devices is based on the fact that the active layer, e.g., in an OFET, is very thin; values as small as 1 nm have been reported in the literature [4]. Therefore, currently significant attention is being paid to organic molecular beam deposition (OMBD). Here the goal is to grow high-quality, possibly single-crystalline, layers of molecules on appropriate substrates [5].

An intense amount of research has been focused on unraveling the principles governing the growth of soft molecular materials on hard inorganic substrates using OMBD in recent years. The initial belief that concepts

can be borrowed from the knowledge gained in the previous studies on metal-on-metal or semiconductor-on-semiconductor growth soon had to be replaced by realizing that due to the anisotropic shape of the molecules and the peculiarities of the crystal structure the principles governing the growth of molecular adlayers are quite different from those developed to describe inorganic epitaxy [5]. These problems are reflected by the fact that thin film devices prepared by OMBD always show lower mobilities than the intrinsic properties of the organic single crystals [1,2].

In this Letter we focus on a fundamental problem in organic molecular beam deposition: namely, the importance of the flexibility of the molecular entities. Because molecules are, in contrast to inorganic materials, rather flexible, the precise geometry of the molecules in the bulk and for the free molecule can differ substantially. We demonstrate the importance of this effect for OMBD by presenting high resolution x-ray absorption fine structure (NEXAFS) spectroscopy data obtained for thin films of rubrene grown on different substrates. Rubrene ($C_{42}H_{28}$) is an aromatic molecule consisting of a tetracene backbone and four phenyl side groups [see Fig. 1(a)]. OFET devices made from rubrene or pentacene single crystals have been demonstrated to exhibit very large charge-carrier mobilities [3,6]. Surprisingly, so far it has not been possible to produce also thin film rubrene OFETs with satisfying electronic properties by OMBD [7], in contrast to penta-

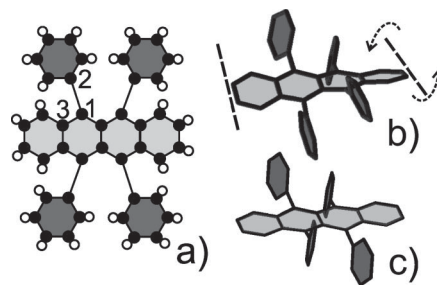


FIG. 1. Schematic structure of rubrene ($C_{42}H_{28}$) (a) together with its molecular geometry in the gas phase (b) and the crystalline phase (c).

cene, where high-performance devices with large mobilities have been fabricated by a number of different groups. This apparent impossibility to grow high-quality rubrene thin films by OMBD has so far not been understood.

The UHV experiments described here were performed for thin films of rubrene grown on well defined Au(111) and SiO₂ substrates. The NEXAFS measurements were carried out at the electron synchrotron BESSY II (beam line HE-SGM) in Berlin and allow for a determination of the position of the unoccupied molecular electronic levels and the orientation of the molecules [8]. A detailed description of the instrument and the corresponding NEXAFS data analysis have been provided elsewhere [9]. In a separate apparatus the thermal stability of the films was characterized by using thermal desorption spectroscopy. In both instruments (base pressure $< 5 \times 10^{-10}$ mbar) photoelectron spectroscopy was used to check the cleanliness of the substrates that had been cleaned before deposition by sputtering and annealing and to gather information about the deposited organic thin films. The thin films of rubrene (Acros, purity $> 99\%$) were deposited at a pressure of less than 8×10^{-9} mbar from a Knudsen cell operated at temperatures between 480 and 550 K yielding growth rates of 2–7 Å/min, and the amount of deposited material was monitored by means of a quartz crystal microbalance. The actual thickness of the thin films was determined from the attenuation of the substrate photoelectron signal that had been cross-calibrated by corresponding measurements for a decanethiolate monolayer.

In Fig. 2 we show a typical C1s NEXAFS spectrum obtained for a multilayer film of rubrene (40 nm) deposited at room temperature on a Au substrate. The π^* region of the spectrum consists of three sharp, well defined peaks, α , β , and γ , located at energies of 284.25, 285.15, and 285.75 eV. The NEXAFS spectra recorded for thick multilayer films closely resemble those obtained for rubrene single crystals (not shown). Based on a comparison with NEXAFS data obtained for multilayer films of benzene [8] and tetracene (see Fig. 2), the most intense resonance β can be related to excitations within the 4 phenyl side groups of rubrene. The two other resonances α and γ are assigned to excitations within the tetracene-backbone part of the rubrene molecule. This assignment is corroborated by additional experiments [10] where rubrene films were doped with alkali atoms. This leads to a donation of electrons from the alkali atoms to the tetracene part of the rubrene molecules, filling of the π^* orbitals, and thus quenching of the π^* excitations in the NEXAFS data. For the Cs-doped rubrene layers only a somewhat broadened β resonance at 285.2 eV (assigned to the phenyl units in the molecule) remained in the NEXAFS spectra.

Additional AFM and SEM measurements that have been carried out *ex situ* after room temperature deposition reveal homogenous films without any island formation. Thus possible dewetting phenomena that have been observed,

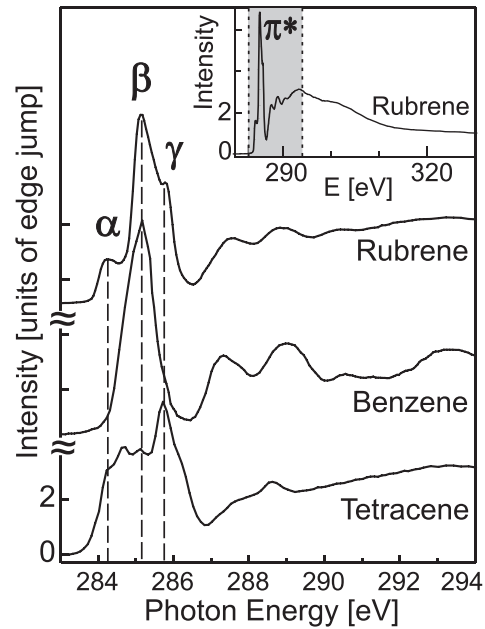


FIG. 2. High resolution C1s NEXAFS spectra of the π^* region recorded for multilayer films of rubrene, benzene, and tetracene at an angle of incidence of 55° of the incident field vector \vec{E} relative to the surface normal. The inset shows the entire NEXAFS spectrum of rubrene.

e.g., for organic thin films of pentacene grown on Au substrates [11] are absent in this case.

In Fig. 3(a) we present NEXAFS data recorded for a submonolayer of rubrene (thickness about 0.5 nm) deposited on a clean Au(111) surface at a temperature of 170 K. In addition to the resonances α , β , and γ seen for the multilayer, a fourth resonance, denoted α' , appears at an energy of 283.75 eV. Despite a somewhat reduced intensity, this new resonance was also obtained for thin rubrene films grown at room temperature on the gold substrate as depicted in Fig. 3(b). This unexpected appearance of a new peak indicates a difference in electronic structure between rubrene molecules in thick multilayer films and those in thin films. Such an electronic modification is surprising since gold is one of the most inert substrates and chemical adsorbate-substrate interaction should be absent.

In order to rule out that the change in electronic structure is caused by a chemical interaction or a charge transfer, we have carried out additional NEXAFS experiments where the Au substrate was coated by a self-assembled monolayer (SAM) of decanethiolate prior to rubrene deposition. The SAM effectively acts as a spacer layer (consisting mainly of saturated hydrocarbons) with a thickness of 1.2 nm and hence effectively avoids any electronic coupling between the rubrene molecules and the gold substrate. Thin films of rubrene deposited on top of this SAM yielded NEXAFS spectra which are qualitatively very similar to those obtained for thin rubrene films grown on the gold substrate. Moreover, the corresponding NEXAFS data are virtually identical to those obtained for thin rubrene films which

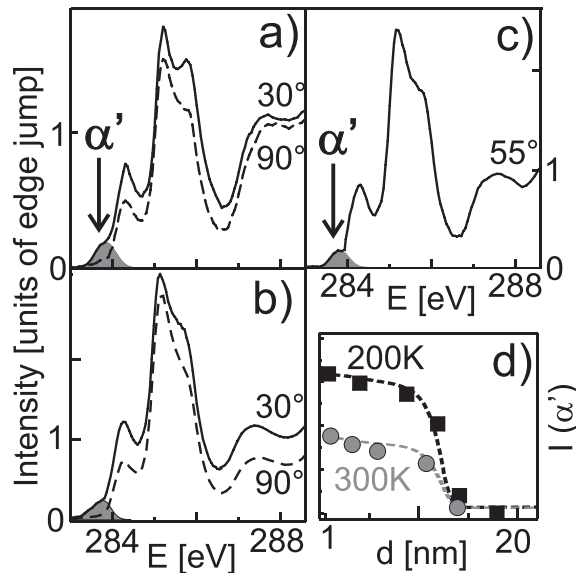


FIG. 3. High resolution C1s NEXAFS data showing the π^* region of various OMBD grown rubrene films: (a) 0.5 nm grown at 170 K on Au(111), (b) 2 nm grown at 300 K on Au(111), (c) 2 nm grown at 300 K on SiO₂. The evolution of the α' peak intensity with increasing film thickness d is displayed in (d) for films grown at 200 K on clean Au and at 300 K on SAM/Au or SiO₂.

were grown on SiO₂ and again reveal the additional α' resonance at 283.75 eV [see Fig. 3(c)]. With increasing film thickness, the intensity of the α' resonance reduces slightly and was no longer observed for films exceeding a thickness of about 12 nm [see Fig. 3(d)], yielding NEXAFS data typical for thick rubrene multilayer films (as shown in Fig. 2).

In order to resolve this unexpected electronic anomaly seen for rubrene molecules in thin films grown on various solid substrates, high-quality *ab initio* electronic structure calculations [12] have been carried out. One first, important, result of these calculations is that the structure of a free rubrene molecule is significantly different from that determined by x-ray structure analysis for bulk single crystals [13]. For a free rubrene molecule in the gas phase the tetracene backbone is considerably twisted and the lines defined by the exterior carbon atoms of the outermost aromatic atom rings form an angle of 42° [see dashed line in Fig. 1(b)], thus yielding an axial chirality. In contrast, in the crystalline phase the tetracene backbone of the rubrene molecule is basically planar without any chirality as depicted in Fig. 1(c). Deviations of the backbone C atom from the plane are smaller than 0.1 Å, and the angle considered above amounts to 0°. According to the electronic structure calculations, the energy difference between the two rubrene geometries amounts to 210 meV, with the twisted conformation being the more stable one. When rubrene molecules condense from the gas phase to form crystallites exhibiting the bulk structure, the energy needed to planarize the backbone is compensated by the more

efficient packing of the planarized rubrene molecules in the bulk, i.e., by the lattice energy.

Because of the rather weak, mostly van-der-Waals-type interaction between hydrocarbons and the SiO₂ or gold surfaces [14] only very minor changes of the rubrene molecule are expected upon adsorption on these substrates, and the deposited molecules will retain the twisted geometry of the free molecule. Deposition of further molecules will not change this situation, since the 2D packing will not yield enough crystal energy to cause a transition to the bulk planar rubrene conformation.

Accordingly, we explain the difference in the NEXAFS data between the thin rubrene films and the bulk data by a slight difference in electronic structure between the free (twisted) rubrene molecule and rubrene with the (planar backbone) bulk molecular geometry. Compared to the planar geometry, the α' resonance of the twisted geometry is shifted to slightly lower energies. This assignment of the α' resonance is corroborated by previous calculations for tetracene [15] where it was shown that the C1s NEXAFS resonance with the lowest energy is associated with excitations of carbon atoms located in the inner rings labeled 1 in Fig. 1(a). In case of rubrene these atoms form the connection to the phenyl groups and are thus expected to be very sensitive to changes of the molecular conformation. To illustrate the effect of the different molecular geometries on the electronic structure of rubrene, an analysis of the charge distribution (Mulliken population analysis) of the various carbon atoms has been carried out for the two molecular conformations. Indeed, significant charge redistributions are seen only for these carbon atoms [atoms labeled 1, 2, and 3 in Fig. 1(a)]. The changes when going from a planar to a twisted geometry amount to $-0.78e$, $+0.67e$, and $+0.58e$. In contrast, the changes for all other atoms are negligible ($< 0.1e$).

Recently, fine structures of π^* resonances were observed in high resolution NEXAFS data of organic multilayer films, which have been interpreted as vibronic coupling to electronic excitations [16]. In the present case, however, no such fine structures were observed, and instead all well resolved π^* resonances revealed no noticeable broadening. Moreover, because of the disappearance of the α' resonance with increasing film thickness a vibronic coupling cannot account for this new resonance because maximal vibronic coupling would be expected for soft organic multilayers.

The slightly higher interaction of the molecules in the first monolayer with the gold substrate (the thermal desorption peak shifts from 416 K for the multilayer to more than 435 K for the monolayer) causes an orientational anisotropy with the tetracene backbone being oriented mainly parallel to the substrate. This preferential orientation is evidenced by a small but distinct linear dichroism, the π^* resonances for the monolayer film being strongest for grazing incidence [see Fig. 3(a)]. The quantitative analysis of the dichroism [8] yields a tilt angle of the backbone relative to the surface of about 38° as depicted

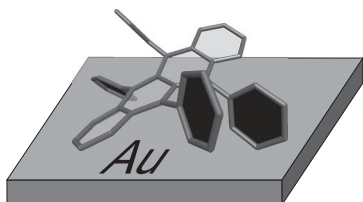


FIG. 4. Schematic representation of the molecular orientation and geometry of rubrene in the thin films grown on gold.

schematically in Fig. 4. In contrast, for thin rubrene films grown on SiO_2 or on a SAM covered gold surface no dichroism was obtained and hence indicates the absence of any orientational alignment.

The particular type of growth proposed above very well explains the difficulties in growing high-quality or even epitaxial layers of rubrene on a solid substrate. Since molecules in direct contact with the substrate exhibit a different molecular geometry than those in the bulk, a transfer of orientation from the substrate to the organic thin layer, a necessary requirement for OMBE, is made impossible and the growth of subsequent layers effectively occurs on an organic surface made up of twisted rubrene molecules. Upon further deposition, a formation of small nuclei with a bulklike structure of rubrene molecules with the planar conformation takes place which is stabilized by the crystal energy. For all presently studied substrates the α' resonance disappears above a critical film thickness of about 12 nm. This value is distinctly larger than the mean probe depth of NEXAFS, which amounts to about 5.5 nm for the present conditions as determined from the attenuation of the simultaneously measured C1s NEXAFS resonance of the alkanethiolate SAM beneath the rubrene films (not shown). A comparison with the (001)-layer spacing of crystalline rubrene ($d_{(001)} = 1.34$ nm) thus indicates that a critical thickness of more than 9 ML is required to stabilize the crystalline packing motive. Because the seed layer on the substrate is rather disordered, this nucleation is rather inhomogeneous and hence only disordered polycrystalline films are formed. In turn, such small crystallites are rather immobile and thus will not aggregate further at room temperature. Accordingly, growth at room temperature leads to the formation of nanocrystalline films, and additional energy is required to activate the growth of crystalline films as demonstrated recently by hot wall deposition [17].

Since the presence of rather large changes in geometry upon condensation of organic molecules is quite common, the phenomenon observed here, namely, the presence of structural contaminations inhibiting any molecular epitaxy on solid substrates, is not an exception but is of general importance. For example, also para-phenylenes, where benzene units are linked by a C-C single bond, show rather surprising growth phenomena when deposited on solid substrates. In the case of *p*-sexiphenyl the formation of needles is observed which show a very sensitive dependence on the condition of the substrate [18,19]. We propose

that also in this case the nucleation is strongly affected by the geometry of the free molecule (with the phenyl units being twisted relative to each other by about 40°) being considerably more stable than that in the bulk structure (with a planar geometry).

In conclusion, we have identified a fundamental mechanism that impedes a true epitaxy of nonplanar organic molecules on solid substrates. In the—rather common—situation where the structure of the free molecules is different from that in the bulk phase, molecules in direct contact with a substrate act as structural contaminations, and the growth of crystallites with a bulk structure can occur only at particular nucleation sites.

This work has been funded by the Deutsche Forschungsgemeinschaft (focus program SPP1122 OFET). D. K. is grateful for support by the *Studienstiftung des Deutschen Volkes*.

-
- [1] N. Karl, *Organic Electronic Materials*, edited by R. Frachioni and G. Grosso (Springer, Berlin, 2001), p. 283.
 - [2] C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.* **14**, 99 (2002).
 - [3] R. W. I. de Boer, M. E. Gershenson, A. Morpurgo, and V. Podzorov, *Phys. Status Solidi (a)* **201**, 1302 (2004).
 - [4] G. Horowitz, *J. Mater. Res.* **19**, 1946 (2004).
 - [5] G. Witte and Ch. Wöll, *J. Mater. Res.* **19**, 1889 (2004).
 - [6] V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, and J. A. Rogers, *Science* **303**, 1644 (2004).
 - [7] H. H. Fong, S. K. So, W. Y. Sham, C. F. Lo, Y. S. Wu, and C. H. Chen, *Chem. Phys.* **298**, 119 (2004).
 - [8] J. Stöhr, *NEXAFS Spectroscopy* (Springer, New York, 1992), Vol. 25.
 - [9] S. Reiß, H. Krumm, A. Niklewski, V. Staemmler, and Ch. Wöll, *J. Chem. Phys.* **116**, 7704 (2002).
 - [10] D. Käfer *et al.* (unpublished).
 - [11] G. Beernink, T. Strunskus, G. Witte, and Ch. Wöll, *Appl. Phys. Lett.* **85**, 398 (2004).
 - [12] GAUSSIAN 98, Revision A. 11.1, Gaussian, Inc., Pittsburgh, PA, 2001.
 - [13] I. V. Bulgarovskaya, V. M. Vozzhennikov, S. B. Aleksandrov, and V. K. Belsky, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **4**, 53 (1983).
 - [14] K. A. Fosser, R. G. Nuzzo, P. S. Bagus, and Ch. Wöll, *Angew. Chem.* **41**, 1735 (2002).
 - [15] H. Ågren, O. Vahtras, and V. Carravetta, *Chem. Phys.* **196**, 47 (1995).
 - [16] A. Schöll, Y. Zou, L. Kilian, D. Hübner, D. Gador, C. Jung, S. G. Urquhart, Th. Schmidt, R. Fink, and E. Umbach, *Phys. Rev. Lett.* **93**, 146406 (2004).
 - [17] D. Käfer and G. Witte, *Phys. Chem. Chem. Phys.* **7**, 2850 (2005).
 - [18] E. Zojer, N. Koch, P. Puschnig, F. Meghdadi, A. Niko, R. Resel, C. Ambrosch-Draxl, M. Knupfer, J. Fink, J. L. Bredas, and G. Leising, *Phys. Rev. B* **61**, 16 538 (2000).
 - [19] F. Balzer and H. G. Rubahn, *Adv. Funct. Mater.* **15**, 17 (2005).