Anomalous roughness evolution of rubrene thin films observed in real time during growth

S. Kowarik,*[ab] A. Gerlach,[ab] S. Sellner,[b] F. Schreiber,*[ab] J. Pflaum,[c] L. Cavalcanti[d] and O. Konovalov[d]

Received 16th December 2005, Accepted 8th February 2006
First published as an Advance Article on the web 23rd February 2006
DOI: 10.1039/b517866e

We study the growth and structure of thin films of the organic semiconductor rubrene during organic molecular beam deposition (OMBD) on silicon oxide *in situ* and in real time using X-ray scattering. Using *in situ* grazing incidence diffraction (GID) we find a small degree of local order but an otherwise largely disordered structure, consistent with out of plane scans. Monitoring the surface morphology in real time during growth, we find relatively smooth films (surface roughness σ below ~ 15 Å for thicknesses up to at least 600 Å) and a significant delay before the onset of roughening. This anomalous roughening in the beginning and crossover to normal roughening later during growth may be related to conformational changes of rubrene in the early stages of growth.

Introduction

Organic electronic materials offer significant potential for a variety of device applications ranging from light emitting diodes and solar cells to memory and field effect transistors.

Rubrene ($C_{42}H_{28}$, 5,6,11,12-tetraphenylnaphthacene, Fig. 1) has recently been identified as a very promising organic semiconductor, and single crystal transistors[1] with high effective hole mobility (~ 15 cm^2 V^{-1} s^{-1}) at room temperature and efficient electroluminescent devices[2] have been reported. Rubrene can be purified by recystallisation from solution, as its side groups promote solubility. It is therefore considered to be a good candidate in the search for a material in which the electrical properties are not determined by extrinsic, uncontrolled impurities. Although a recent study reports effects related to surface contaminations, work on single crystals is encouraging, spurring interest in thin films which are practicable for devices.[3]

However, controlling the growth of molecular organic semiconductors poses several new fundamental challenges. While inorganic materials are dominated by strong binding energies, molecular semiconductors are bound by relatively weak van der Waals forces, and frequently display polymorphism. Furthermore, highly anisotropic non-planar organic molecules have additional degrees of freedom compared to inorganic materials, as their internal conformation as well as their orientation can change during growth.

Specifically rubrene appears to exhibit a particularly peculiar structural behavior, with very good bulk crystals on the one hand, and thin films grown by organic molecular beam deposition (OMBD)[4,5] with very low order on the other. Recently Käfer *et al.* have shed some light on this problem by pointing out that changes in the conformation of the molecule affect the OMBD growth, but several fundamental issues related to the statistical description of the growth such as evolution of roughness or correlation lengths remain open.[3,6]

In this paper we show by real time *in situ* X-ray scattering, that rubrene thin films grown by OMBD are very smooth and, surprisingly, exhibit an anomalous evolution of the film roughness. The findings are complementary to very recent data by Käfer *et al.*[6] and contribute to a comprehensive picture of the growth of this promising but unusual material.

Experimental

Rubrene was purchased from Acros with an elemental purity of $> 99\%$. In one set of experiments the material was used as received for growth and in a second set it was used after additional purification by gradient sublimation, cleaning the material and removing a significant fraction of residue (consisting of molecules other than rubrene but containing the same elements). Rubrene thin films were grown on oxidized (~ 15 Å) silicon wafers with (100) orientation. The wafers were cleaned by sonication in HPLC grade acetone and isopropanol (Sigma), and ultrapure water, followed by heating to 600 °C for 10 min in a vacuum. Film growth was performed using a portable vacuum chamber,[7] equipped with a Be window, enabling us to perform *in situ* measurements after growth as well as real time measurements during growth. Typical growth rates were around 20 Å min^{-1}. We performed X-ray diffraction experiments at the ESRF beamline ID10B in Grenoble, France, with a wavelength of 0.964 Å. The resolution of the reflectivity scans (used to probe the structure perpendicular to the sample surface) was 8×10^{-4} Å^{-1} for the out of plane momentum transfer $q_{\perp}$. For grazing incidence diffraction

[a] *Physical and Theoretical Chemistry, Oxford University, South Parks Road, Oxford, UK OX1 3QZ*
[b] *Institut für Angewandte Physik-Universität, Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany*
[c] *3. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany*
[d] *European Synchrotron Radiation Facility, 6, rue Jules Horowitz-B.P. 220, 38043, Cedex 9 Grenoble, France*

 This journal is © the Owner Societies 2006

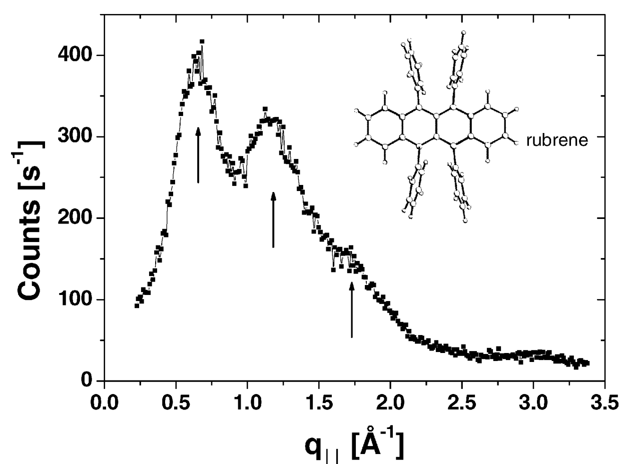

Fig. 1 Grazing incidence scan for a 384 Å rubrene film grown at a rate of 22 Å min^{-1} on silicon oxide at 10 °C substrate temperature. In-plane (parallel to the sample surface) length scales of about 10 Å are observed for rubrene. No sharp Bragg reflections from crystalline structures are found.

(GID) at an incident angle of 0.108° the resolution was reduced to 8×10^{-3} Å^{-1} in $q_\perp$ and half that value in $q_\parallel$.

Results and discussion

Fig. 1 shows a GID scan on a 384 ± 2 Å thick purified rubrene film, probing the structure in the plane of the thin film. The absence of sharp Bragg reflections indicates that there are no crystallites in the film. This is consistent with the relatively low charge carrier mobility in thin film devices of rubrene.[8] Only broad features can be seen, with a typical length scale of ~10 Å (*i.e.* of the order of the dimensions of individual molecules), but with an otherwise disordered structure.

The post-growth specular reflectivity of the same film, shown in Fig. 2, also shows no sharp Bragg reflections but slight enhancements in reflectivity again at $q_\perp = 0.65$ Å^{-1} (as in GID). This confirms the above conclusions that there are no crystalline regions, but some degree of short-range order.

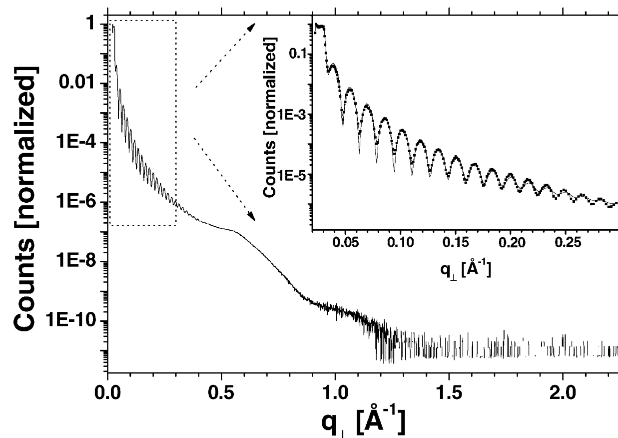

Fig. 2 Post growth X-ray reflectivity scan of a 1280 Å rubrene film. Pronounced finite thickness oscillations at low q indicate a very smooth surface (Inset: Enlarged image for low q range, solid line is a fit to the data).

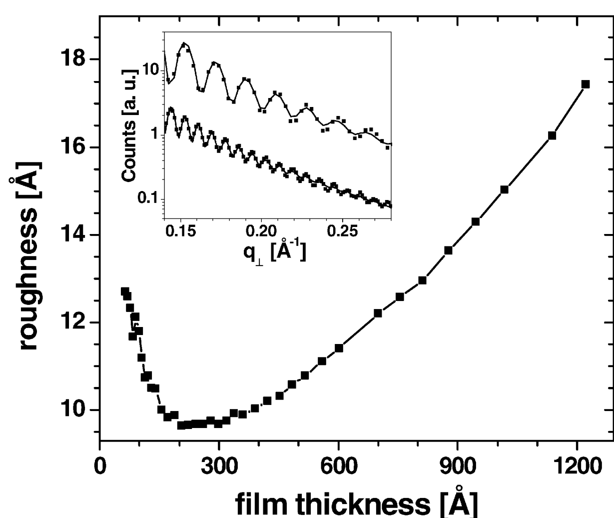

Fig. 3 Evolution of the root mean square roughness with film thickness during OMBD growth of rubrene at 10 °C substrate temperature. The absolute error bar is ±7 Å, while the relative uncertainty is ±2 Å. The film is very smooth and only becomes rough at around 400 Å. Inset: Typical real time reflectivity scan and fit (solid line) corresponding to 338 and 755 Å thickness.

Importantly, the specular reflectivity shows pronounced finite thickness oscillations (Kiessig fringes), due to a very low film roughness of 10 ± 2 Å, as determined from a fit of the data using the Parratt formalism (see Fig. 2, inset), which takes into account scattering from all interfaces including multiple scattering effects (for details see ref. 9).

To further investigate the remarkably smooth morphology of this amorphous film, we followed the roughness evolution of rubrene with film thickness in real time, scanning the specular reflectivity repeatedly during OMBD. We were able to scan a range between 0.14–0.29 Å^{-1} with sufficient counting statistics within 1 min, so that during a 1 h growth run we obtained a detailed picture of the changes during growth.[10]

The evolution of the film roughness with film thickness is plotted in Fig. 3. As we have only part of the specular reflectivity for the fits, the absolute value of the roughness can be determined with an accuracy not much better than ±7 Å. However the relative uncertainty between successive fits of ±2 Å, which is the relevant quantity for our analysis, is significantly smaller.

As seen in Fig. 3 the roughening of the rubrene film shows a delay in time (*i.e.* film thickness), with an increasing roughness starting only at around 250 Å. Fig. 3 even suggests a certain degree of smoothing (*i.e.* reduction of roughness with thickness) in the initial stage of the growth, but this point may be difficult to firmly establish within the experimental uncertainty.

In our experiments this behaviour of delayed roughening is universally found for a variety of growth conditions from 10–80 °C substrate temperature and for unpurified as well as purified rubrene. For unpurified material we find an absence of finite thickness oscillations in the beginning of growth (up to ~100 Å), indicating that the film roughness and film smoothing in the beginning is higher for the pristine compound than

This journal is © the Owner Societies 2006

for purified material. For a substrate temperature of 100 °C we find relatively rough films, with no thickness oscillations occurring.

The most important finding, however, is the delayed roughening or even smoothing at $T \leq 80$ °C in the initial stage of the growth. This is in contrast to most other growth scenarios of molecular materials, where the roughness σ exhibits a monotonic increase with thickness D, as expressed in a scaling law $\sigma(D) \sim D^{\beta}$ with the roughening exponent $\beta > 0$ depending on the material.[4,11,12] As shown in Fig. 3 the early stages of rubrene growth are characterized by an anomalous value of $\beta \leq 0$ followed by a crossover to $\beta > 0$. The comparison with a previous detailed study of the crystalline organic semiconductor diindenoperylene (DIP) where even enhanced (rapid) roughening was observed makes the present finding even more remarkable.[12]

The underlying reason for the different behaviour (rubrene *vs.* DIP) may be related to amorphous (rubrene) as opposed to crystalline (DIP) growth modes. A recent study by Blüm *et al.*[13] directly images chiral rubrene molecules absorbed on a gold surface, and according to Käfer *et al.*[3,6] the chirality of the rubrene molecules prevents the initial formation of crystalline layers in OMBD on silicon oxide. For films thicker than 140 Å, a change from the chiral to the planar conformation of rubrene, which may form crystallites, has been reported.[6] Nevertheless from the scan in Fig. 1 no long-range order (crystallinity) can be deduced even for films with a thickness of 384 Å.

Our observations provide an independent manifestation of the anomalous effects observed for rubrene. We speculate that the anomalous roughness evolution is also related to the conformational change of planarizing the chiral molecule, which obviously strongly influences the initial stages of the growth. Remarkably, the length scale for the change in molecular conformation ($\sim$140 Å) is consistent with thickness range of the crossover in the scaling exponent β, assuming that the change in β is triggered by the change from chiral molecules to more strongly interacting planar molecules.

Conclusions

In conclusion, OMBD grown rubrene films exhibit a very smooth surface for an organic semiconductor. One of the implications is that rubrene thin films in a thickness range of 150–300 Å are well suited as model substrates, offering a very smooth and weakly interacting organic semiconductor surface.

Studying the surface morphology of amorphous rubrene films in real time we find a crossover between a scaling of film roughness with $\beta \leq 0$ (that is, no roughening or even smoothing) to the expected monotonic increase in roughness ($\beta > 0$), possibly triggered by the change of molecular conformation.[6] Clearly, the internal degrees of freedom of organic semiconductors introduce new complexities. However, these are also opportunities for tailoring the growth, and they may well be exploited in heterostructures for devices.

Acknowledgements

We gratefully acknowledge financial support from the EPSRC.

References

1 (*a*) V. Podzorov, V. M. Pudalov and M. E. Gershenson, *Appl. Phys. Lett.*, 2003, **82**, 1739–1741; (*b*) A. F. Stassen, R. W. I. de Boer, N. N. Iosad and A. F. Morpurgo, *Appl. Phys. Lett.*, 2004, **85**, 3899–3901; (*c*) V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson and J. A. Rogers, *Science*, 2004, **303**, 1644–1646.
2 (*a*) G. Li and J. Shinar, *Appl. Phys. Lett.*, 2003, **83**, 5359–5361; (*b*) H. Aziz and Z. D. Popovic, *Appl. Phys. Lett.*, 2002, **80**, 2180–2182; (*c*) G. Sakamoto, C. Adachi, T. Koyama, Y. Taniguchi, C. D. Merritt, H. Murata and Z. H. Kafafi, *Appl. Phys. Lett.*, 1999, **75**, 766–768.
3 D. Käfer and G. Witte, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2850–2853.
4 F. Schreiber, *Phys. Status Solidi A*, 2004, **201**, 1037–1054.
5 (*a*) W. Brütting, *Phys. Status Solidi A*, 2004, **201**, 1035–1035; (*b*) G. Witte and C. Wöll, *Phase Transitions*, 2003, **76**, 291–305.
6 D. Käfer, L. Ruppel, G. Witte and Ch. Wöll, *Phys. Rev. Lett.*, 2005, **95**, 166602.
7 K. A. Ritley, B. Krause, F. Schreiber and H. Dosch, *Rev. Sci. Instrum.*, 2001, **72**, 1453–1457.
8 H. H. Fong, S. K. So, W. Y. Sham, C. F. Lo, Y. S. Wu and C. H. Chen, *Chem. Phys.*, 2004, **298**, 119–123.
9 M. Tolan, *X-ray Scattering from Soft-Matter Thin Films: Materials Science and Basic Research*, Springer, Berlin, 1999.
10 Again, the Parrat formalism was used to fit the reflectivity, taking into account the slight change in thickness during each scan.
11 J. Krug, *Adv. Phys.*, 1997, **46**, 139–282.
12 A. C. Dürr, F. Schreiber, K. A. Ritley, V. Kruppa, J. Krug, H. Dosch and B. Struth, *Phys. Rev. Lett.*, 2003, **90**, 016104.
13 M.-C. Blüm, E. Cavar, M. Pivetta, F. Patthey and W.-D. Schneider, *Angew. Chem., Int. Ed.*, 2005, **44**, 5334–5337.

This journal is © the Owner Societies 2006