

Organic molecular beam deposition: Growth studies beyond the first monolayer

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We review recent work on organic molecular beam deposition (OMBD) with emphasis on growth studies beyond the first monolayer, i.e. the evolution of the film structure and morphology. First, we briefly discuss general issues related to growth physics, including epitaxial relations, surface and interface energies, growth modes, correlation functions, dynamic scaling, and growth exponents. We also point out the general features that distinguish organic systems from inorganic systems, such as the different interaction potentials and the internal degrees of freedom of organic molecules. Then we discuss selected case studies, organised according to the role of the substrate (insulators, metals, semiconductors), covering examples from various organic semiconductors, namely perylene-derivatives (in particular diindeno-perylene (DIP) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA)), phthalocyanines, and oligoacenes (anthracene, tetracene, pentacene). Finally, we briefly discuss organics-based heterostructures and indicate some open problems and future directions.

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1 Introduction

Organic semiconductors exhibit a range of interesting properties, and their application potential is rather broad, as seen in many other contributions in this issue. For the crystalline ‘small molecule’ systems, grown by organic molecular beam deposition (OMBD), subject of the present contribution, it is generally agreed that the structural definition is important for the functional properties. The following list should serve to illustrate the various aspects:

1. The definition of interfaces (degree of interdiffusion and roughness)
 - (a) Organic-organic (e.g., in organic diodes)
 - (b) Organic-metal (e.g., for electrical contacts)
 - (c) Organic-insulator (e.g., in transistors (insulating layer between gate and semiconductor))
2. The crystal structure
 - (a) Which structure is present? (Note that polymorphism is very common in organics).
 - (b) Are different structures coexisting?
 - (c) Orientation of the structure (epitaxy)?
 - (d) Is the structure strained (epitaxy)?

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3. Crystalline quality/defect structure

- (a) Mosaicity (Note that in a thin film one has to distinguish between quality in the xy plane and in z direction (surface normal).)
- (b) Homogeneity within a given film (density of domain boundaries etc.)
- (c) Density of defects (and their nature), which also impacts the electronic properties.

Since the structure has a strong impact on the functional properties, understanding the structure formation, i.e., the growth process, and finding ways to optimise the structural definition is a prerequisite for technological progress. Moreover, understanding the physics of the growth process provides several fundamental challenges.

We will mostly focus on 'thicker' films, their growth modes and the evolution of the morphology for thickness ranges which are typically employed in organic semiconductor applications. We will discuss only to a limited extent the work on the first monolayer, although as the 'seed layer' for the following layers this is obviously important. Thus, some of the classical surface science issues, such as binding site, epitaxial relation etc., are not in the focus of this review. For these issues and also for information on the history of the field, we refer to Refs. [1–9]. Also, we will not discuss issues related to chirality, although they are undoubtedly intriguing [9–12].

In terms of growth technology, the equipment is essentially the same as for inorganic molecular beam epitaxy. Evaporation cells on a vacuum chamber are used to provide a flux of molecules at the substrate surface (typically some range around 1 Å/sec to 1 Å/min), and ideally the growth can be monitored *in situ*. Virtually all surface and interface techniques have been used for OMBD-grown films, and we refer to standard textbooks for details of the experimental methodology.

This review is organised as follows. We first present some of the general issues in thin film growth and then what is specific and potentially different for organics (Sec. 2). In Sec. 3, we give an overview of the most popular systems. Sec. 4 contains a number of case studies, trying to highlight the issues that we feel are particularly relevant and typical for OMBD. The case studies are based on four different compounds. They are organised according to the (inorganic) substrates, covering, insulators, metals, and semiconductors. In Sec. 12, we briefly indicate the issues for organics-based heterostructures. Some conclusions are given in Sec. 9.

In a review with limited space such as the present one, it cannot be our goal to give a complete and exhaustive overview. Instead, the examples are centred mostly around our own work, which we try to discuss in the context of the general field. This selection is obviously unbalanced, and we apologise for omissions of important other work.

2 Organic molecular beam deposition

2.1 General concepts of thin film growth

Crystal and thin film growth are enormously rich subjects with many different facets and theoretical approaches. For a thorough treatment of the underlying concepts, we refer to Refs. [13–16]. Here we shall only briefly touch on selected aspects which we feel are important in the present context and help to appreciate the issues related to thin film growth (see also Fig. 1).

One approach to describe the various relevant interactions uses the concept of surface and interface energies, γ , similar to what is done for wetting phenomena. Typically, the surface energies (i.e., the relative contributions of the free substrate surface, γ_s , the film surface, γ_f , and the film-substrate interface, γ_i) are then related to the different growth modes, i.e. Frank-van-der-Merwe (layer-by-layer), Stranski-Krastanov (layer plus islands after a certain critical thickness), and Vollmer-Weber (islands starting at the first monolayer).

We will not discuss issues related to the epitaxial relation in much detail. (For clarity, we should emphasize that under epitaxial relation we understand the crystallographic relation between film and substrate, which does not necessarily imply smooth film growth.) However, we should point out that, generally, the surface energies depend on the strain field induced by the lattice mismatch at the film-

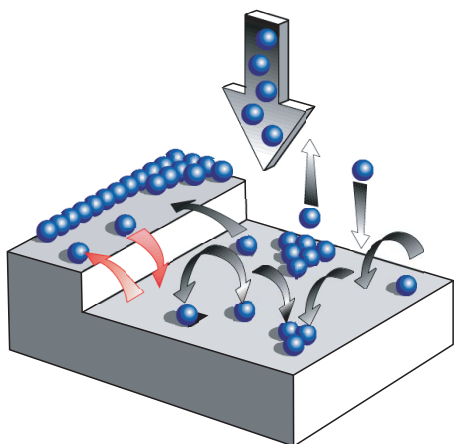


Fig. 1 (online colour at: www.interscience.wiley.com) Schematic of processes relevant in thin film growth, such as adsorption (as a result of a certain impingement rate), (re-)desorption, intra-layer diffusion (on a terrace), inter-layer diffusion (across steps), nucleation and growth of islands.

substrate interface, and thus also on the number of layers of the film. Therefore, the epitaxial relation of film and substrate is important not only in a crystallographic sense but also for the growth behaviour.

It should be emphasized that growth is actually a non-equilibrium phenomenon, and equilibrium or near-equilibrium energy considerations alone cannot properly account for all growth scenarios. Thus, a dynamic description is needed. This description has to take into account the flux of adsorbates towards the surface (corresponding to a certain supersaturation), the adsorption and re-desorption probabilities, and the diffusion processes on the surface (interlayer and intralayer) and their respective barriers. In the last two decades a theoretical framework has been established, which relates growth mechanisms to a set of scaling exponents describing the dependence of the surface roughness on film thickness and lateral length scale. Much effort has been spent to theoretically predict scaling exponents for certain growth models, as well as to determine them experimentally [13–18].

The scaling theory of growth-induced surface roughness is based on the behaviour of the height difference correlation function (HDCF), the mean square height difference $g(R) = \langle [h(x, y) - h(x', y')]^2 \rangle$ of pairs of points laterally separated by $R = \sqrt{(x - x')^2 + (y - y')^2}$. The HDCF displays distinct behaviours for $R \ll \xi$ and $R \gg \xi$, where ξ denotes the correlation length. For $R \ll \xi$ one expects a power law increase as $g(R) \approx a^2 R^{2\alpha}$, where α is the static roughness exponent and the prefactor a is a measure of the typical surface slope. For $R \gg \xi$ the heights at distance R become uncorrelated. Hence $g(R)$ saturates at the value $g(R \gg \xi) = 2\sigma^2$, where $\sigma = \langle (h - \langle h \rangle)^2 \rangle^{1/2}$ is the standard deviation of the film height (or ‘rms roughness’). The three parameters σ , ξ and a evolve with film thickness according to the power laws $\sigma \sim D^\beta$, $\xi \sim D^{1/z}$ and $a \sim D^\lambda$, defining the growth exponent β , the dynamic exponent z and the steepening exponent λ . Assuming that the regimes $R \ll \xi$ and $R \gg \xi$ are connected through a scaling form $g(R) = 2\sigma^2 \tilde{g}(R/\xi)$, it follows that the scaling exponents are related by $\beta = \alpha/z + \lambda$. For $\lambda = 0$ (no steepening) one has $\beta = \alpha/z$. Scaling with $\lambda > 0$ is referred to as anomalous [15]. The HDCF can be determined experimentally by real space methods (such as atomic force microscopy) or diffuse scattering, each having their advantages.

2.2 Issues specific to organic thin film growth

While the general considerations presented above apply to inorganic as well as organic thin film systems, there are a few issues specific to organics (Fig. 2), which can lead to quantitatively and qualitatively different growth behaviour.

1. Organic molecules are ‘extended objects’ and thus have *internal degrees of freedom*. This is probably the most fundamental difference between growth of atomic and growth of organic systems.

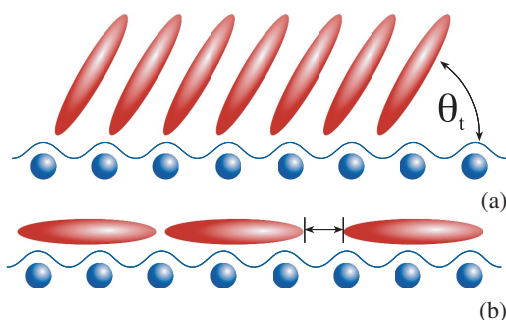


Fig. 2 (online colour at: www.interscience.wiley.com) Issues specific for organics in the context of thin film growth. (a) Orientational degrees of freedom, potentially leading to orientational domains (additional source of disorder). They can also give rise to orientational transitions during growth. (b) Molecules larger than the unit cells of (inorganic) substrates, thus leading to translational domains. Generally, this can also lead to a smearing-out of the corrugation of the substrate potential experienced by the adsorbate.

- (a) The *orientational degrees of freedom* which are not included in conventional growth models can give rise to qualitatively new phenomena, such as the change of the molecular orientation during film growth (Fig. 2). Also, even without considering a *transition* during the growth, the distinction of 'lying-down' and 'standing-up' films is important and obviously only possible for molecular systems.
 - (b) The *vibrational degrees of freedom* can have an impact on the interaction with the surface as well as the thermalisation upon adsorption and the diffusion behaviour.
2. The *interaction potential* (molecule-molecule and molecule-substrate) is generally different from the case of atomic adsorbates, and van-der-Waals interactions are more important.
 - (a) The response to strain is generally different. Potentially, more strain can be accommodated and in those systems, where the build-up of strain leads to a 'critical thickness' (before the growth mode changes), this thickness can be greater for 'softer' materials. The different ('softer') interactions with the substrate and the corrugation of the potential have also been discussed in terms of 'van-der-Waals epitaxy' and 'quasi-epitaxy' [3].
 - (b) The importance of van-der-Waals interactions implies that the relevant temperature scales (for evaporation from a crucible and also for diffusion on the substrate) are usually lower. It should be emphasized, however, that the *total* interaction energy of a molecule (integrated over its 'contact area' with a surface) can be substantial and comparable to that of strongly interacting (chemisorbing) atomic adsorbates. Nevertheless, in terms of interaction energies *per atom* those of the organic molecules considered here are usually weaker.
 - (c) Since we are concerned with closed-shell molecules and van-der-Waals-type crystals, there are no dangling bonds at the organic surface, and thus the surface energies are usually weaker than for inorganic substrates.
 - (d) Importantly, however, if the surface of the *substrate* is 'strongly interacting', this results in limited diffusion and thus the evolution of well-ordered films is hampered. In the extreme case of a 'very reactive' surface (e.g., with dangling bonds available), the molecules may even dissociate upon adsorption.
 3. The *size of the molecules and the associated unit cells* are greater than that of typical (inorganic) substrates.
 - (a) The effective lateral variation of the potential is smeared out (i.e., averaged over the size of the molecule), making the *effective corrugation* of the substrate as experienced by the molecule generally *weaker* than for atomic adsorbates.
 - (b) The size difference of the unit cells of adsorbate and substrate implies that there are more translational domains (see Fig. 2).
 - (c) Moreover, organics frequently crystallize in low-symmetry structures, which again can lead to multiple domains (not only translational, but also orientational domains). Importantly, both are a source of disorder, *in addition* to those known from inorganic systems (e.g., vacancies).

Generally, most of the above points directly or indirectly impact the interactions and thus also the barriers experienced during diffusion. Thus, not only the static structure, but also the growth dynamics exhibit differences compared to inorganic systems.

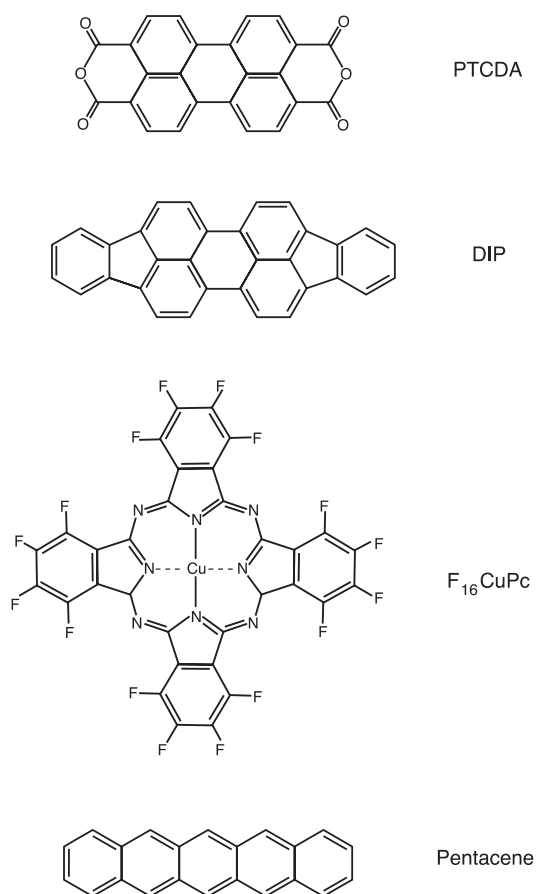


Fig. 3 Some popular organic semiconductors discussed in this review.

2.3 Overview of popular OMBD systems

Organic chemistry provides obviously a vast number of dyes and semiconductors, which are potentially interesting for thin film studies, and there is the additional possibility of specifically modifying certain functionalities. A fairly large number of compounds has indeed been employed for thin film work, but not for all of these have detailed growth studies been performed. We will limit ourselves to only selected systems, largely based on examples from our own work (see Fig. 3).

1. PTCDA

The perylene-derivative PTCDA (3,4,9,10-perylene-tetracarboxylic dianhydride, $C_{24}H_8O_6$, a red dye) has long been regarded as a model system for OMBD [2, 3, 19–26]. Its bulk structure (actually α and β phase) exhibits layered molecular planes, and it was expected that the regular stacking of these planes (along the [102] direction in α phase notation) is favourable for well-behaved film growth, which turned out to be not necessarily correct. The optical properties [27–31] as well as the vibrational properties [31–34] have been thoroughly studied.

2. DIP

Diindeno(1,2,3-*cd*,1',2',3'-*lm*)perylene ($C_{32}H_{16}$, DIP, a red dye) has the same perylene core as PTCDA, but it has been studied much less. It has recently been shown to exhibit excellent out-of-plane ordering behaviour [18, 35–37] and, associated with this, very good charge carrier transport properties [38], suggesting that DIP will be studied and exploited more in the future.

3. Phthalocyanines

Phthalocyanines (Pc's) are rather popular [39–44], and some of the early work on OMBD has employed Pc's [39]. They exhibit a certain degree of "specific tunability", due to the possible central metal ion, which can be changed within a broad range, and due to the choice of the sidegroup(s) [40, 41]. $F_{16}CuPc$ is particularly attractive, since it is considered a good candidate as an n-type conducting organic material [45]. As a blue dye [43] it is also interesting for optoelectronic applications [44, 40].

4. Oligoacenes (anthracene, tetracene, pentacene)

The oligoacenes and in particular pentacene have recently attracted considerable attention, since their charge transport properties were reported to be excellent [7, 38]. An important feature of

pentacene seems to be that it can be grown in well-ordered thin films, although the 'bulk structure' and a 'thin film structure' appear to be competing. It does not appear to be entirely clear whether or not there is indeed an identifiable special feature of pentacene that makes it superior to other compounds in terms of transport properties.

There are, of course, many other popular systems, which, however, we cannot discuss due to the limited space. These include, e.g., oligothiophenes, oligophenyls and also 'sheets of graphite'. Besides the crystalline systems, there are also amorphous small-molecule organic semiconductors prepared by OMBD, such as Alq₃ and TPD. In terms of the growth physics, amorphous systems exhibit obviously some differences (no strain due to epitaxy; different diffusion barriers; no crystallographic domains; etc.). They are worth studying in their own right, but we cannot discuss them here. For examples from various other systems we refer to Refs. [1–9].

3 Films on oxidized silicon

Silicon wafers are among the most common substrates for thin film growth. They are stable in air with their oxidised surface layer, the thickness of which can be 'tuned' by thermal oxidation (from some 15 Å (native oxide) to several 1000 Å). Also, they are very flat and relatively easy to clean.

In the context of organic electronics, of course, they are very popular as a substrates for thin-film transistors (TFTs), since the oxide can serve as the insulating layer between the silicon as the bottom contact (gate) and the active organic semiconductor on top.

We should also mentioned that oxidised silicon surfaces are suitable for surface modification using self-assembled monolayers (SAMs) [46, 47], which has been exploited, e.g., for the growth of pentacene [48].

3.1 PTCDA

It was expected that the regular stacking of PTCDA molecules in the [102] direction (in α phase notation) of the bulk structure would give rise to well-behaved film growth. This regular stacking is indeed observed on siliconoxide and many other substrates, unless the growth temperature is too low and no well-defined structure evolves or a too strong interaction with a very 'reactive' substrate leads to other orientations of the first PTCDA monolayer. However, it is important to realise that a regular stacking and well-defined orientation of the molecules within the films does not necessarily imply smooth surfaces.

In an early study, it was already found that PTCDA on oxidised silicon exhibits smooth surfaces only for growth at low temperatures ($T < 50$ °C for deposition rates around 1 Å/s), where the crystallinity was not very good [49]. For growth at higher temperatures, the films exhibited good crystallinity, but showed a tendency to island growth ('dewetting').

These results demonstrate a not uncommon feature of growth on substrates with low surface energies. If the films tend to dewet from the substrate near equilibrium, then the above pattern (relatively flat, but low-crystallinity films for low T , and dewetting (i.e. rough) morphologies with good crystallinity for high T) is quite frequently found.

3.2 DIP

DIP has the same perylene core as PTCDA, but the indeno endgroups instead of the anhydride endgroups give rise to a completely different structural behaviour compared to PTCDA. DIP has recently been studied in detail [18, 35–37, 50–52], and it was found to exhibit excellent out-of-plane order on siliconoxide surfaces.

Films with various film thicknesses ($69 \text{ \AA} \leq D \leq 9000 \text{ \AA}$) were prepared on oxidized (4000 Å) Si(100) substrates at a substrate temperature of 145 ± 5 °C and at a deposition rate of 12 ± 3 Å/min. The out-of-plane X-ray spectra exhibit well-defined Bragg reflections corresponding to a lattice spa-

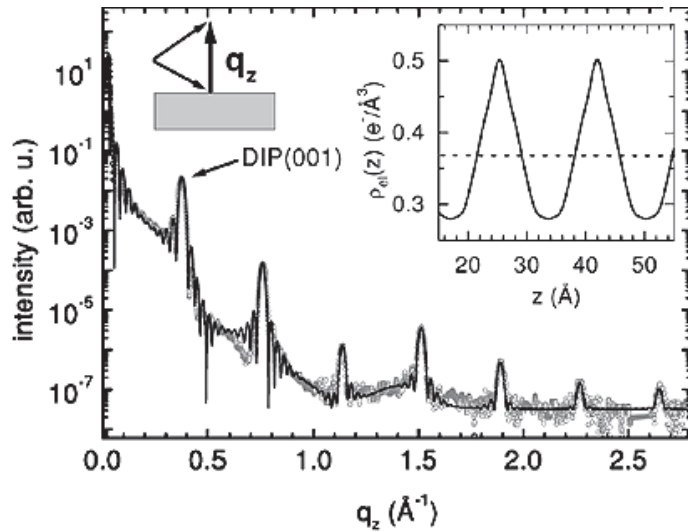


Fig. 4 Specular X-ray scan of a 206 Å thick DIP film. Many higher-order Bragg reflections are observed, which can be used for the reconstruction of the electron density profile using the various Fourier components (close-up shown in the inset). From Ref. [35] with permission.

cing of $d_{\text{DIP}} \approx 16.55 \text{ \AA}$ (suggesting essentially upright-standing molecules) and associated Laue oscillations, the analysis of which shows that the films are coherently ordered across the entire thickness [35]. The rocking width, which is a measure of the distribution of the out-of-plane lattice planes, is 0.01° and lower [35, 37]. The lattice spacing is consistent with a model of molecules standing essentially upright with a tilt angle θ_{tilt} presumably around 15° – 20° . The large number of higher-order Bragg reflections could be used to deconvolute the out-of-plane electron density distribution in a Fourier series (Fig. 4)

$$\rho_{\text{el}}(z) = \rho_0 + \sum_n A_n \cos\left(n \frac{2\pi}{d_{\text{DIP}}} z + \phi_n\right) \quad (1)$$

where the Fourier amplitude, A_n , is associated with the intensity of the n th Bragg reflection [35]. We can speculate that the shape of DIP with its slightly narrow head and tail may be favourable for an ordering mechanism with some degree of interdigitation of molecules from neighbouring (i.e., top and bottom) lattice planes.

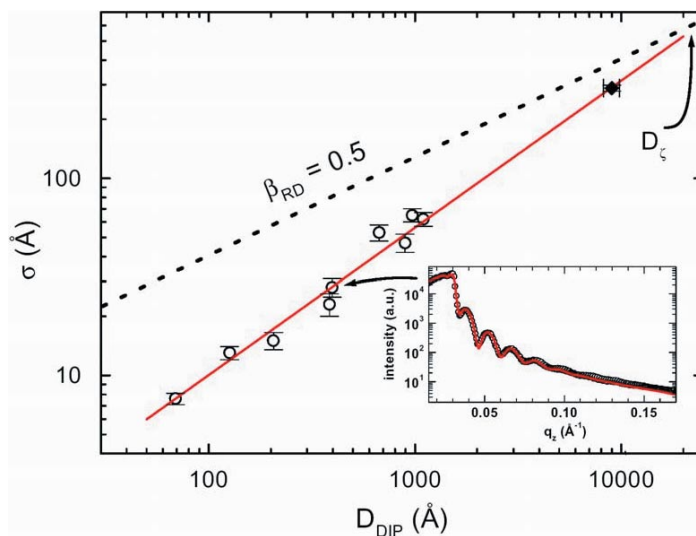


Fig. 5 Root-mean-square roughness σ of DIP films as a function of thickness D_{DIP} . The inset shows a typical X-ray reflectivity dataset and a fit to the data. The solid line in the main plot is a linear fit to the data and the growth exponent is obtained as $\beta = 0.748 \pm 0.05$. The dotted line denotes the random deposition limit $\beta_{\text{RD}} = 0.5$. From [18] with permission.

On siliconoxide, the in-plane structure is, of course, a 2D powder. The packing appears to follow a herringbone motif. The structure will be discussed also in the context of growth on Au (Ref. [36] and Sec. 5).

The growth including the evolution of the HDCF and the associated growth exponents, α , β , and $1/z$, were studied using AFM and X-ray scattering (specular and diffuse) [18]. Whereas the static roughness exponent α (average of AFM and X-rays 0.684 ± 0.06) is similar to that observed in many other growth experiments [14], the values for $1/z$ (0.92 ± 0.20) and β (0.748 ± 0.05) were found to be rather large (Fig. 5). Specifically, the DIP films belong to the class of systems which display the phenomenon of *rapid roughening*, for which $\beta > 1/2$, i.e., the roughness increases faster with thickness D than the random deposition limit $\beta_{RD} = 0.5$ [15]. This effect appears hard to rationalise in the absence of a thermodynamic driving force (e.g., dewetting). A model which is consistent with the scaling exponents involves random spatial inhomogeneities in the local growth rate, which are fixed during the growth process [53, 18]. It is plausible that when certain regions of the surface persistently grow faster than others, the surface will roughen very rapidly. It was suggested that the spatial inhomogeneities may be related to the different tilt domains of the film and the inevitable grain boundaries in between these [18].

3.3 Phthalocyanines

Phthalocyanines also tend to grow in a standing-up configuration in thicker films on 'inert' substrates. Films of F16CuPc between 120 and 450 Å were recently found to exhibit very good crystalline out-of-plane order with rocking widths around 0.01° and well-defined Kiessig interferences and Laue satellites around the out-of-plane Bragg reflection [54].

The in-plane structure is, of course, azimuthally disordered, since the substrate is isotropic. One of the complications for phthalocyanines is a strong anisotropy of the crystal structure and the associated growth properties, which can lead to needle-like features, both for F16CuPc [55] as well as for H16CuPc [56].

3.4 Pentacene

Pentacene on siliconoxide has been studied intensely due to its relevance for OFETs [7]. Ruiz et al. studied the initial stages of the growth [57]. Their analysis of the island distribution in (sub)monolayer films by dynamic scaling showed that the smallest stable island consists of four molecules. Meyer zu Heringdorf et al. showed that under appropriate growth conditions the single-crystal grain sizes can approach 0.1 mm [58].

For thicker films, pentacene thin films exhibit some complication in the sense that there is a 'thin film structure' and a 'bulk structure', which can coexist, depending on the growth conditions.

An interesting idea is that of surface modification involving self-assembled monolayers (SAMs) [47]. Shtein et al. studied the effects of film morphology and gate dielectric surface preparation on the electrical characteristics of organic-vapour-phase-deposited pentacene thin-film transistors including surface modification using SAMs [48]. Meyer zu Heringdorf et al. employed cyclohexene-saturation of Si(001) to modify the growth dynamics [58]. Voigt et al. studied the growth of tetracene on oil-covered surfaces [59]. While they actually used ITO as solid substrates, the concept might equally well be applicable to siliconoxide surfaces. For recent work on the growth of pentacene on polymers, see Ref. [99].

4 Films on aluminium oxide

Interfaces of organics with insulators are of obvious relevance for organic electronics, and aluminium-oxide is one of the most commonly used insulators. Unfortunately, sputtered aluminiumoxide layers frequently exhibit a rather high roughness and not well-defined starting conditions for growth studies. Sapphire is aluminiumoxide (Al_2O_3) in its purest and best ordered form. It is also a popular substrate

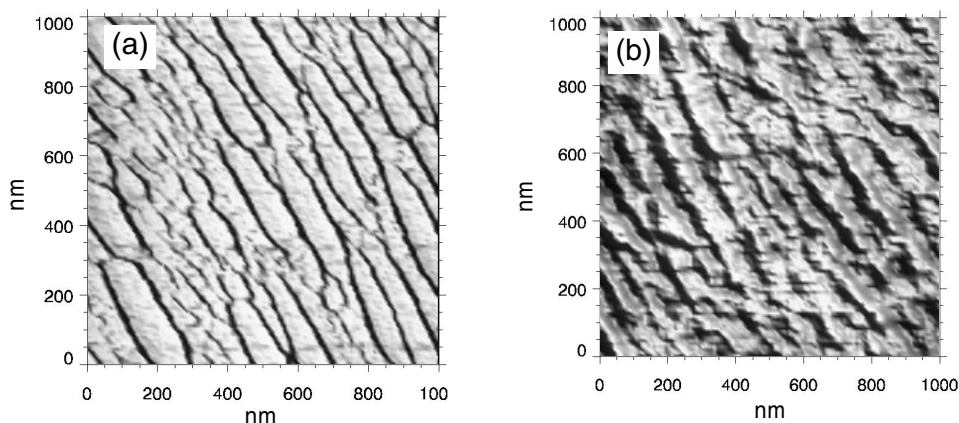


Fig. 6 Topography of an A-plane sapphire substrate (a) and an F16CuPc film (120 \AA) film (b) on this substrate determined by non-contact AFM. The step pattern of the substrate serves to azimuthally align the film (see text). From Ref. [63] with permission.

for epitaxy of metals and inorganic semiconductors, and it can be obtained in very high crystalline quality. We will focus here on sapphire, since it is very suitable for model studies of the growth of organics on insulator surfaces (see Sec. 6 for other substrates).

Surfaces of ionic substrates, which are not charge-balanced, tend to be unstable and/or exhibit strong relaxations/reconstructions. In the case of sapphire, the $(11\bar{2}0)$ surface ('A plane') is charge balanced and rather inert, and it has been used for growth studies. An important feature to realise for surfaces of crystals is that they commonly exhibit a miscut, i.e. a difference between the physical surface and the (low-index) crystallographic plane. This gives rise to a step pattern, which in the case of essentially perfect crystals like sapphire is the dominating feature of the surface morphology (Fig. 6). Issues related to the surface preparation have been discussed in Ref. [60].

4.1 PTCDA

PTCDA on sapphire has, to our knowledge, not been studied in detail. Test results, however, indicate that the overall behaviour is similar to that for PTCDA on oxidized silicon, i.e., that for growth at high temperatures the films tend to (partially) dewet [61].

The overall growth scenario is most likely not changed significantly by the presence of steps, but the in-plane order of PTCDA may be affected. However, even with alignment at the step edges PTCDA would most likely still exhibit multiple domains (see also the discussion of PTCDA on metals).

4.2 DIP

Based on the results for DIP on siliconoxide it is expected that DIP would also exhibit good out-of-plane ordering on the similarly 'inert' sapphire. Preliminary data indicate that this is, in fact, the case [62]. In addition, the stepped sapphire substrate can induce in-plane ordering, as first demonstrated for the growth of phthalocyanines [63] (see below), which was indeed also found for DIP [62].

4.3 Phthalocyanines

As described above, the regular surface steps associated with miscut sapphire can serve as templates for film growth with azimuthal alignment. While the concept of stepped substrates has been used

frequently for monolayer adsorbates, its use for comparatively thick films (5 to 50 ML) of relatively large molecules was first demonstrated by Osso et al. for F₁₆CuPc on A-plane sapphire [63]. The resulting azimuthal ordering has been shown by four methods sensitive to different aspects [63]. AFM was used to image the surface morphology of the bare substrate. After film growth, the characteristic step pattern of the bare substrate was shown to be basically replicated, suggesting an azimuthal coupling of the film structure to the substrate morphology (Fig. 6). In-plane X-ray diffraction (GIXD) showed that the crystal structure of the film was indeed not a 2D powder, but was aligned. The distribution width ('mosaicity' of the in-plane lattice) was several degrees broad, which suggests a rather "soft" driving force for the ordering. The in-plane order was also visible in the azimuthal intensity distribution of the vibrational modes detected by Raman scattering. Finally, the resulting anisotropy of the dielectric function was studied by spectroscopic ellipsometry, offering the chance to study the 'intrinsic' behaviour of these systems without a strongly reduced disorder-induced broadening of the optical transitions. We should note that the strong optical anisotropies of these systems are an interesting field of study in their own right, and give rise to non-trivial effects in the propagation of light [43].

A discussion of the mechanisms responsible for the azimuthal alignment and in particular the possible competition between the effects of the step edges themselves and the underlying lattice (epitaxial driving forces) is found in Ref. [55].

The out-of-plane ordering was similarly good as for F₁₆CuPc or DIP on siliconoxide, i.e. a well-defined Bragg reflection with Laue oscillations and mosaicities around 0.01°, although the tendency of phthalocyanines to grow in needles can cause some complications. We note that the tilt angle of the molecules as well as the out-of-plane lattice parameter was found to depend on the growth temperature (and are different from the bulk structure parameters), indicating that the structure may not be in full equilibrium.

4.4 Pentacene

Similar concepts and mechanisms as observed for DIP and F₁₆CuPc in terms of azimuthal alignment should be applicable to pentacene on sapphire, but to our knowledge there are no published results yet.

5 Films on metals

Interfaces with metals are of obvious relevance for contacting organic semiconductors. The choice of the metal is frequently determined more by the desired work function and thus electron or hole injection properties than by growth considerations. Nevertheless, there is a wide variety of metals in terms of behaviour as substrates for organic thin film growth, and it is important to realise that this can have a profound impact on the growth and the resulting structural and functional properties. Besides issues related to the surface morphology, crystalline quality, potentially crystalline orientation and size of the unit cell (epitaxy), it is very important how 'reactive' or 'inert' the metal is, since this determines the mobility of the molecules on the surface and thus the growth.

For strongly reactive substrates, the molecules tend to behave almost in a 'hit-and-stick' fashion, i.e. without significant mobility and thus no long-range order. Less reactive metals such as noble metals, to which we will limit ourselves here, turned out to be rather popular and suitable.

We will concentrate on metal single crystals. From a practical point of view, for growth studies it is important that their surfaces can be 'recycled' by sputtering and annealing, i.e. several growth experiments can be performed on the same substrate and on (essentially) the same surface. Less reactive metals are also easier to keep clean before growth. Obviously, with metal substrates the application of electron-based surface science methods is possible, since the signal does not suffer from charging effects. This has been used excessively by the surface science community in particular for molecular monolayers on surfaces of metal single crystals.

We should also mention that metal surfaces are suitable for surface modification using self-assembled monolayers (SAMs) [46, 47], which has been employed in particular for Au(111). Examples include the growth of PTCDA on alkanethiol SAMs [64–67].

5.1 PTCDA

PTCDA on metal surfaces has been thoroughly studied, with the noble metals being particularly popular.

5.1.1 Structure and epitaxy of PTCDA/Ag(111)

On Ag(111), very well-defined epitaxial growth of PTCDA(102) has been observed [2, 19, 23, 25]. The 2D structure is characterised by a herringbone arrangement of the flat-lying molecules, which corresponds to a layer of the (102) plane of the bulk structure, with a small degree of distortion (strain). Possible mechanisms leading to the well-behaved 2D structure of PTCDA on Ag(111) were recently discussed in Ref. [68]. The vertical PTCDA-Ag(111) spacing was found to be $2.85 \pm 0.1 \text{ \AA}$ based on X-ray diffraction [24], but it may differ for low-temperature deposition if the adsorption state differs.

For growth extending beyond the monolayer, a more complex azimuthal distribution arises, and, depending on the growth temperature, also domains non-collinear with principal axes of the substrate can form to relieve strain [23]. Interestingly, the epitaxial relations could be rationalised similar to the Nishiyama-Wassermann vs. Kurdjumov-Sachs relations for fcc(111)/bcc(110) growth, although, of course, the PTCDA structure is not bcc [23].

5.1.2 Comparison with other substrates

The comparison with PTCDA/Au(111) yields a qualitatively similar picture [21, 26, 69], although details of the epitaxy appear to differ, which is not too surprising given that structure is a result of a rather delicate balance of different factors and given that the corrugation of the substrate potential experienced by PTCDA is different. Of course, Au(111) exhibits a reconstruction, and also the substrate-molecule interaction may differ slightly if the overlap of the outermost orbitals is different.

On the more open Ag(110) surface, an entirely different structure already in the monolayer was found, characterised by a 'brick-stone' arrangement, [19]. Phase transitions of PTCDA/Ag(110) were studied in Ref. [70].

Growth on Cu(110) was studied by Möller's group [71–73]. The monolayer was found to differ from those known from other substrates. For thicker films, Stranski-Krastanov growth was found, similar to the case on Ag(111) (see below).

5.1.3 Dewetting and thermal properties

While the structure and epitaxy in the monolayer regime are well-defined, the later stages of the growth (potentially after a certain threshold thickness) can, of course, exhibit islanding and a very rough resulting morphology. It was recently found that PTCDA on Ag(111), a well-behaved system in the monolayer regime, exhibits indeed Stranski-Krastanov growth. At growth temperatures $T \lesssim 350 \text{ K}$, relatively smooth epitaxial films have been found, whereas at $T \gtrsim 350 \text{ K}$, well-separated crystallites with bulk crystalline structure on top of a 2 ML thick wetting layer have been observed [23, 24, 74, 75]. These results are qualitatively the same as those for PTCDA on Au(111) [21].

The thermally-induced post-growth dewetting of 'low-temperature' grown films was also studied, confirming that the films tend to dewet if given sufficient thermal energy [24]. In these experiments, also the thermal expansion of PTCDA was determined ($1.06 \pm 0.06 \times 10^{-4} \text{ K}^{-1}$ out-of-plane) [24]. For a comparison with other systems (Alq₃ and TPD), see Ref. [76]. While islanding of the films is usually not desirable, it should be pointed out there might also be ways to exploit islanding or dewetting and the formation of small crystallites for 'self-organised nanostructures' (similar to Si-Ge quantum dots).

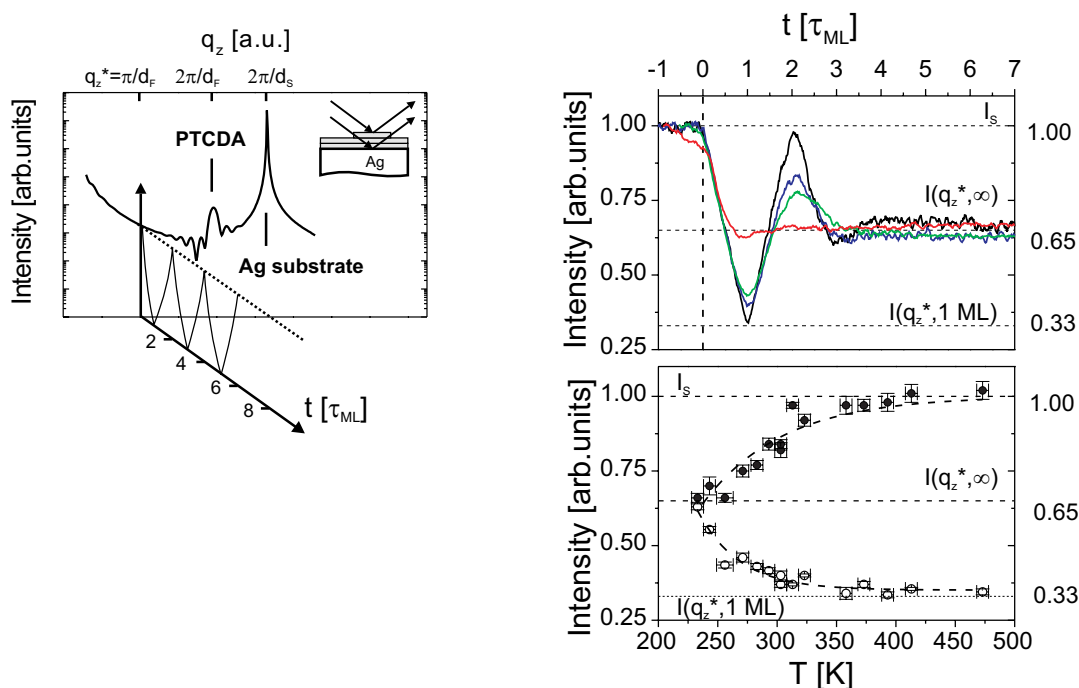


Fig. 7 (online colour at: www.interscience.wiley.com) Simulation of the specular rod scattering of a thin PTCDA film on Ag(111) as a function of the out-of-plane momentum transfer q_z (top left). The time axis in this figure (for a fixed q_z) indicates the intensity oscillations at the anti-Bragg point during growth (see text for explanation). The top right figure shows the time dependence (in units of monolayer deposition times) of the normalised scattered intensity at the anti-Bragg point for various temperatures (233 K (red); 283 K (green); 303 K (blue); 358 K (black)). The bottom figure shows the temperature dependence of the deviation from layer-by-layer growth expressed in terms of the intensity of the minimum (open symbols) and of the maximum (filled symbols) of the scattered intensity at 1 ML and 2 ML, respectively (see text for details). From Ref. [75] with permission.

5.1.4 Real-time growth

In order to shed light on the dynamics and the temperature dependence of the 2D-3D transition (layer-by-layer to islanding), a real-time X-ray diffraction study of the growth of PTCDA on Ag(111) was performed [75]. The idea is as follows (Fig. 7). In kinematic theory the specular X-ray scattering intensity is the sum of the scattering contributions from the film and the substrate,

$$I(q_z, t) = |F(q_z, t)|^2 = \left| f_F \sum_{n=1}^{\infty} e^{iq_z d_F(n-1)} \theta_n(t) + f_S \frac{1}{1 - e^{-iq_z d_S}} e^{-iq_z d_0} \right|^2. \quad (2)$$

f_F and f_S are the form factors of the film and the substrate, d_F and d_S are the corresponding lattice spacings, and $d_0 = 2.8 \text{ \AA}$ is the distance between the substrate and the first layer of the film [23]. $\theta_n(t)$ is the time-dependent fractional coverage of the n th layer within the organic film. At the anti-Bragg point of the PTCDA film ($q_z^* = \pi/d_F$) the first term in Eq. 2 equals $f_F \sum (-1)^{(n-1)} \theta_n(t)$. Therefore, the coverage difference

$$\Delta\theta(t) = \sum_m \theta_{2m+1}(t) - \sum_m \theta_{2m}(t) = \theta_{\text{odd}}(t) - \theta_{\text{even}}(t) \quad (3)$$

can be deduced from the measured intensity $I(q_z^*, t)$. Specifically, it is possible to distinguish the coverage of the first and the second layer in the initial stage of the growth. In the case of layer-by-layer growth, characteristic intensity oscillations are observed.

Figure 7 shows typical time-dependent intensity data during growth in a dedicated chamber [77], measured at various substrate temperatures between 233 and 258 K [75]. $t = 0$ is defined as the starting time of the deposition. The signal is normalized to the substrate scattering intensity, $I_S = I(q_z^*, t < 0)$, and the time is normalized to the deposition time, τ_{ML} , of one monolayer, which corresponds to the intensity minimum. A typical growth measurement exhibits distinct intensity oscillations for $t \lesssim 3\tau_{ML}$, followed by a constant intensity during further deposition, similar to the observations for PTCDA/Au(111) [78]. The intensity oscillations correspond to layer-by-layer growth. The transition to a constant intensity indicates the breakdown of layer-by-layer growth and the onset of islanding characteristic of SK growth. As can be seen from the transition to a time-independent scattering signal (associated with an equal probability for a given molecule to be accommodated in even and odd layers), the islanding starts rapidly after completion of a 2 ML “wetting” layer.

Comparing the growth data for different temperatures (Fig. 7), we find that for $T \geq 358$ K the oscillations are not visibly damped for $t < 2\tau_{ML}$. They are followed by a sharp transition to a time-independent intensity (islanding). For lower temperatures, the oscillations are progressively damped, and the 2D–3D transition is smeared out as the temperature is lowered.

The experimental data, i.e., in particular the 2D–3D transition, could be modelled by kinetic Monte-Carlo simulations using a relatively simple model for the energies/barriers, the most important feature of which is the dependence of the interlayer transport barrier, E_{inter} , on the layer number n , namely $E_{inter}(n \leq 3) = 0$ and $E_{inter}(n > 3) > 0$ [75].

Moreover, for elevated temperatures strong post-growth diffusion was observed [79].

5.2 DIP

In the monolayer regime, DIP as many other organic semiconductors, was studied by STM. The molecules were found to be lying down flat on the substrate [80]. The interaction of DIP with Au was found to be physisorptive [36]. In the regime of thicker films, DIP was recently studied in detail *on* Au contacts [36] (and as substrate for Au contacts evaporated *on* DIP [36, 50–52]). Importantly, in contrast to growth on siliconoxide, due to the stronger interaction with the Au substrate, the lying-down configuration tends to prevail not only for monolayers, but also for multilayers. Since the standing-up configuration (which again followed a herringbone-like motif) appears to have the more favourable surface energy (as seen on siliconoxide), there is obviously a competition between the two configurations (standing-up vs. lying-down), and they are found to coexist [36]. From the point of view of growth kinetics this competition is very interesting, but it is certainly a further complication and an additional source of disorder which is usually undesirable.

5.3 Phthalocyanines

Phthalocyanines were among the first ‘large’ molecules that were studied by STM with (sub)molecular resolution [39]. In the monolayer regime, the molecules are lying down flat on the surface, and the 2D structures have been thoroughly studied. Recently, the (vertical) bonding distance to the metal substrate was determined using XSW [81]. For thicker films, there is a competition between the lying-down configuration of the first layer and the tendency to stand up. The impact of roughness on the ordering behaviour was studied in Ref. [82].

5.4 Pentacene

Acenes on metal substrates were studied by several groups. Early work on the orientation of various aromatic hydrocarbons including tetracene on metal surfaces using NEXAFS was done by Koch and collaborators [83].

More recent work focussed on pentacene. Pentacene structures on Au(111) as a function of coverage (up to the equivalent of around 2 ML) were studied by Parkinson’s group [84]. In the monolayer regime of pentacene on Cu(110), Lukas et al. reported a novel mechanism giving rise to long-range

order on Cu(110), based on the modulation of the adsorption energy due to charge-density waves related to a surface state [85].

While it is not too surprising that the molecules in the monolayer regime tend to be lying more or less flat on the surface, importantly, for the growth of thicker films on Cu(110) an orientational transition from a lying-down configuration to an essentially standing-up configuration was observed [86].

An interesting study of the 'hyperthermal' growth of pentacene (exhibiting hyperthermal energies in a seeded supersonic molecular beam) on Ag(111) was presented by Casalis et al. [87]. They found that at low substrate temperatures (200 K) highly ordered films can be grown by hyperthermal deposition when thermal deposition leads only to disordered films. The results were interpreted as a result of 'local annealing' due to the impact of the hyperthermal molecules. This technique appears to have the potential to tailor the growth of molecular systems in addition to what is possible by changing the impingement rate and the substrate temperature, and it may be further tested in the future.

6 Films on other substrates

Many other substrates than the above have been employed, which we cannot all review. We shall only mention some of the most important other substrates.

Quite popular for growth studies is graphite, since it is easy to prepare. In our general classification of substrates, graphite would be 'weakly interacting', and, e.g., PTCDA would probably also exhibit (partial) dewetting. Other examples from this group of layered substrates are MoS₂, GeS, and Sb₂S₃ [4].

Also rather weakly interacting would be MgO, which falls essentially in the same category as sapphire and siliconoxide. Mica, which can be easily prepared by cleavage, may also be seen in the category of rather inert substrates.

Alkalihalogenides, such as NaCl and KCl, are quite popular as simple substrates for growth studies, since they are easy to prepare. For some studies, they have the additional benefit that they can be easily dissolved and the film can be studied by TEM.

Metals, as indicated above, span a broad range from the noble metals to very reactive substrates.

A very important class of substrates are certainly (inorganic) semiconductors such as Si and GaAs, since they may be used in the integration of organic-inorganic hybrid devices. Moreover, they are very well-defined in terms of their surface and overall structural quality, which is favourable for growth studies. If the surface is clean, however, they can exhibit 'dangling bonds' and be rather reactive. In these cases, the organic adsorbates then tend to 'hit and stick', i.e. they usually do not diffuse over significant distances, hence they do not form long-range ordered structures. A strategy to avoid these problems, but still benefit from the above advantages, is the use of surface-passivated semiconductors, such as H-Si or Se-GaAs.

Polymeric substrates and possible routes for oriented growth of pentacene have been studied in Ref. [88].

7 More complex heterostructures and technical interfaces

Organic semiconductor devices usually do not only consist of a film on a substrate, but involve additional layers such as metal contacts or insulating layers or also different organic components in a multilayer structure.

Metal contacts are one obvious requirement for many applications of organic semiconductors. It turns out that the controlled deposition of metals *on* organics ('top electrode') is non-trivial. In order to reduce problems related to interdiffusion (and ultimately short-circuiting) and traps related to surface states, different strategies can be pursued.

1. Deposition at low temperatures to 'freeze in' the interdiffusion;
2. Deposition at (moderately) high rates with the idea that the metals are quickly forming larger aggregates which are then less mobile and diffuse less far into the organic film;
3. Use of 'suitably reactive' metals and/or organics, so that a strong interaction at the top layer(s) of the organic material prevents interdiffusion;

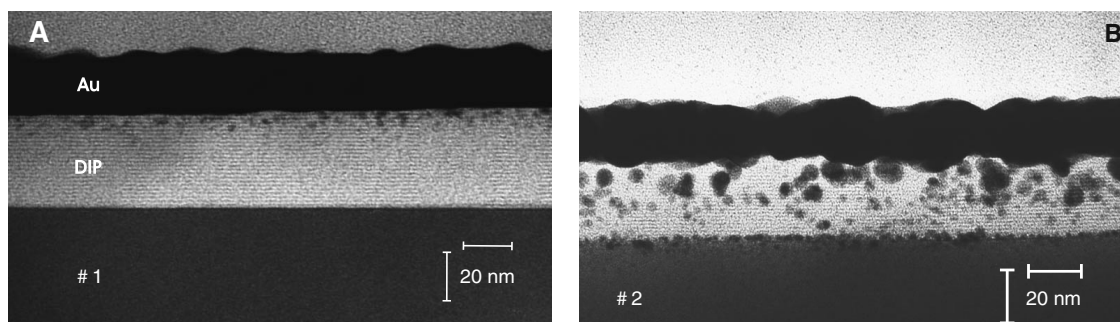


Fig. 8 Cross-sectional TEM images of two Au/DIP/siliconoxide heterostructures. While the Au contact prepared at $-120\text{ }^{\circ}\text{C}$ and a rate of $23\text{ }\text{\AA}/\text{min}$ (left) exhibits rather well-defined interfaces, the Au contact prepared at $70\text{ }^{\circ}\text{C}$ and a rate of $0.35\text{ }\text{\AA}/\text{min}$ (right) shows strong interdiffusion. Note that individual lattice planes of the DIP film can be resolved. From Ref. [50] with permission.

4. ‘Soft deposition’ by ‘thermalising’ or at least reducing the energy of the impinging metal atoms by ‘baffling’ these using a noble gas or other means [89];
5. Miscellaneous other non-thermal deposition strategies including, e.g., electrochemical deposition may be attempted.

Recently, we performed studies of the deposition of gold, which is widely used as a hole injection material, onto well-defined DIP thin film surfaces to study the interdiffusion (Fig. 8). The study followed the ‘classical’ approach without specific precaution against interdiffusion except for variation of the temperature and the rate [36, 37, 50–52]. The important result was that under rather typical deposition conditions near room temperature the metal interdiffusion was already significant, and the layers would exhibit electrical shorts (Fig. 8). If the substrate, however, is cooled, fairly well-defined interfaces could be obtained. We note that Faupel’s group studied similar issues in detail for metal deposition on polymers [90].

Recently, Sellner et al. [91] have studied aluminium-oxide/DIP interfaces, which apparently exhibit a very different interdiffusion behaviour. This is to be further investigated.

We should note that for device structures one also has to take into account the effect of the morphology of technical interfaces and surfaces on the growth behaviour of organics [82].

Another important interface, which has not been excessively studied with regard to growth and structure, is the organic-organic interface as found, e.g., in OLEDs. Some early work on superlattices and bilayers can be found, e.g., in Refs. [92–95]. PTCDA on self-assembled monolayers (SAMs) as well-defined organic model surfaces has been studied in Refs. [64–67]. PTCDA on hexa-peri-hexabenzocoronene (HBC) was investigated in Ref. [96]. A number of different polynuclear aromatic hydrocarbons including DIP and perylene were studied by Kobayashi’s group [97]. Other studies were concerned with the post-growth stability of the organic-organic interface and the interdiffusion behaviour [76, 98].

8 Summary and Conclusions

This review does not claim to be complete in any way. We have rather presented a few case studies, which we hope serve to highlight a few of the issues specific to the growth of organic thin films. We shall summarise some of these.

1. Epitaxial relations can be complicated, and the films can exhibit a large number of symmetry-equivalent domains. Moreover, the coexistence of different phases can give rise to complications.
2. Islanding (after some critical thickness) is not uncommon, and is, of course, not prevented by well-defined structural relation between the film in the monolayer regime and the substrate.
3. Even for systems that tend to ‘wet’ the substrate, overproportional roughening may occur, and the growth exponents may be very different from those expected based on conventional theories.

4. The controlled preparation of organics-based heterostructures can be particularly difficult, given the tendency for interdiffusion of, e.g., metal contacts.

Despite the in some regard 'additional complications' of organics well-ordered thin films can be grown by OMBD. We hope the improvement of the understanding of the growth mechanisms will further promote the applications of organics.

Moreover, organics with their specific features promise to give rise to fundamentally new growth phenomena such as orientational transitions and new scaling exponents which is an exciting subject in its own right.

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