

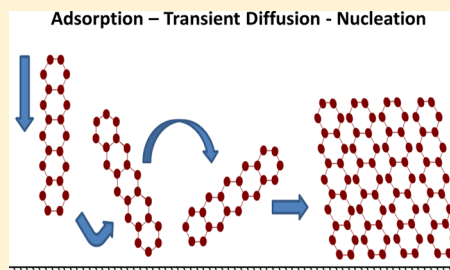
Nucleation of Organic Molecules via a Hot Precursor State: Pentacene on Amorphous Mica

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ABSTRACT: Organic thin films have attracted considerable interest due to their applicability in organic electronics. The classical scenario for thin film nucleation is the diffusion-limited aggregation (DLA). Recently, it has been shown that organic thin film growth is better described by attachment-limited aggregation (ALA). However, in both cases, an unusual relationship between the island density and the substrate temperature was observed. Here, we present an aggregation model that goes beyond the classical DLA or ALA models to explain this behavior. We propose that the (hot) molecules impinging on the surface cannot immediately equilibrate to the substrate temperature but remain in a hot precursor state. In this state, the molecules can migrate considerable distances before attaching to a stable or unstable island. This results in a significantly smaller island density than expected by assuming fast equilibration and random diffusion. We have applied our model to pentacene film growth on amorphous Muscovite mica.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis



In recent years, considerable progress has been made in the understanding of organic film growth. In particular, the initial steps of film formation, nucleation, and aggregation have been at the center of interest because they essentially define the final morphology and hence the physical properties of thin organic films. The driving force for this interest is the potential applicability of organic layers in electronic devices, such as organic field-effect transistors, solar cells, light-emitting devices, sensors, and so forth.^{1,2} So far, it has been assumed that the nucleation and growth of organic films, in particular, of those consisting of rod-like molecules such as pentacene, thiophen, or hexaphenyl, can be described along the existing nucleation models for point-like monomers, such as metal atoms.^{3,4} Recently, however, various experimental results pointed to a somewhat more complex nucleation mechanism for such organic molecules.⁵

The most relevant experimental observables of submonolayer films are the island density and the island size distribution. These quantities depend on the experimental parameters, such as deposition rate and substrate temperature, as well as on system parameters, such as the critical island size, the monomer diffusion energy, and the binding energy of the critical island. By critical island, one understands the largest cluster that is not yet stable. The incorporation of one more monomer results in a stable island that can further grow by the attachment of monomers. Although it is known that this is a simplified scenario,^{6,7} the assumption of a critical island size is nearly exclusively made to characterize the initial layer formation. Furthermore, it is assumed that nucleation and growth are governed by diffusion-limited aggregation (DLA).⁸ On the basis of these assumptions, Venables et al.⁹ have developed a relationship between the island density N and the experimental and system-specific parameters

$$N \propto R^\alpha \exp\left(\frac{iE_d + E_i}{(i+2)kT}\right) \quad (1)$$

where R is the deposition rate, E_d is the activation energy for surface diffusion of the monomers, E_i is the binding energy of the critical island, T is the substrate temperature, k is Boltzmann's constant, i is the critical island size, and the exponent α is $i/(i+2)$. The deposition rate dependence of the island density has been frequently applied to evaluate the critical island size for rod-like organic molecules. Stadlober et al.¹⁰ determined a critical island size i between 3 and 4 for pentacene on various organic and inorganic substrates. A similar result was obtained by Ribič et al.¹¹ for pentacene on polymeric substrates. In our research group, we also determined a critical island size of $i = 2$ and/or 3 for *para*-hexaphenyl on a heavily sputter-amorphized mica surface, depending on the special arrangement of the molecules in the cluster.¹²

Nevertheless, some recent experimental results on the nucleation of *p*-hexaphenyl (6P)⁵ and pentacene (5A) (unpublished results) on sputter-amorphized mica have shown that the concept of DLA is of limited applicability. As pointed out above, the power law scaling of the island density with respect to deposition rate should allow the determination of the critical island size, according to $\ln N \approx \alpha \ln R$, with $\alpha = i/(i+2)$. Accordingly, in this case, the value of α has to be between 1/3 and 1. While this has been found to be applicable for 6P deposited on heavily sputtered mica,¹² for 6P deposited on gently sputtered mica, the slope α turned out to be 1.4, at least in a certain range of the deposition rate.⁵ It was proposed

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that in this case, the nucleation can be better described by attachment-limited aggregation (ALA), as put forward first by Kandel¹³ and worked out later in more detail by Venables and Brune¹⁴

$$N \propto R^\alpha \exp\left(\frac{2[i(E_d + E_b) + E_i]}{(i + 3)kT}\right) \quad (2)$$

In this case, an activation barrier E_b for monomer attachment at the rim of the islands hinders nucleation. Moreover, the meaning of the exponent α is changed to $\alpha = 2i/(i + 3)$; thus, α can vary between 0.5 and 2. This resulted in a critical island size of $i = 7$ for 6P nucleation on gently sputtered mica.⁵ A similar result has recently been obtained for pentacene on the same substrate, where $\alpha = 1.3$ and consequently $i = 6$ (unpublished results). The difference between the nucleation behavior of 6P on heavily sputtered mica in comparison to that for the gently sputtered mica was explained by the increased importance of diffusion limitation on the increasingly roughened mica surface.

Apart from the peculiar island density dependence of the deposition rate, which clearly showed that for rod-like organic molecules, the nucleation process cannot be described by the classical DLA model, another striking feature is frequently observed with respect to the temperature dependence of the island density. According to eqs 1 and 2, for both DLA and ALA, a plot of $\ln N$ versus $1/T$ should yield a straight line; the slope of this line is determined by the activation energies involved. However, there exist several examples in the literature where a clear bend in the relationship $\ln N$ versus $1/T$ was observed. Sassella et al.^{15,16} observed a straight line for the growth of quaterthiophene on silica for substrate temperatures $T > 200$ K but a strong leveling off for lower temperatures. The authors explained this as being due to postdeposition nucleation and growth at low temperatures. Similarly, for α -hexathiophene (6T) grown on a (001) surface of a 6T single crystal, they also reported a leveling off at low substrate temperatures.¹⁷ Ribič et al.¹¹ observed a bend in the $\ln N$ versus $1/T$ representation for pentacene on various substrates at around 330 K. The authors described this phenomenon as being due to possible desorption at higher substrate temperatures. Finally, Yang et al.¹⁸ have studied the thin film growth of *para*-sexiphenyl (6P) on silica, and they also reported a bend at around 330 K in their representation of the mean island area versus $1/T$. The authors ascribed this to a change in the growth mechanism. At low substrate temperature, the impinging molecules should immediately freeze and form a disordered layer. Subsequently, this film should rearrange into an island film; this suggestion is similar to the idea of postdeposition nucleation.¹⁵ While all of the mentioned examples refer to organic molecules, a similar behavior has also been described for metal film growth, copper on Ni(110), showing even two bends in the $\ln N$ versus $1/T$ representation.¹⁹ In that detailed study, the authors describe the first bend as being due to a change from postnucleation at low temperatures (no temperature dependence) to nucleation with a critical island size of $i = 1$ and the second bend to a change of the critical island size from $i = 1$ to 3.

We do not want to evaluate the proposed mechanisms and ponder the pros and cons of the various propositions. Nevertheless, deviations from a straight line in plots of $\ln N$ versus $1/T$ seem to be a quite frequent behavior in organic thin film growth. Indeed, we have also observed such a behavior in our laboratory for *para*-hexaphenyl (6P) on heavily sputtered

mica, where nucleation could be described by DLA,¹² as well as on weakly sputtered mica, where nucleation had to be described by ALA.⁵ Recently, we found a similar behavior for pentacene (5A) on weakly sputtered mica, as depicted in Figure 1. Data from previous work for 6P on mica are included as well.^{5,12}

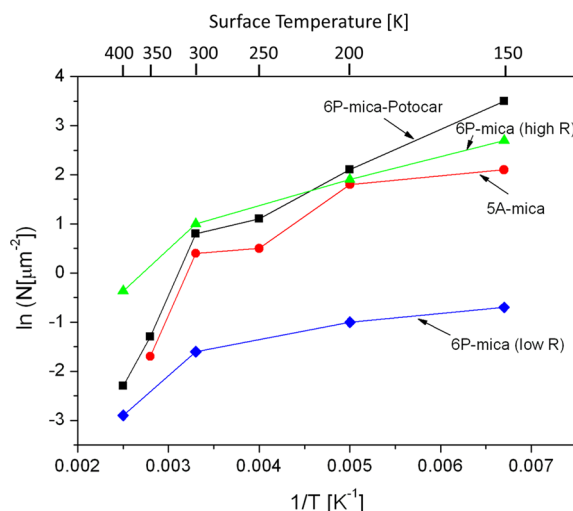


Figure 1. Substrate temperature dependence of the island density for various film/substrate systems. The data “6P-mica-Potocar” were taken from ref 12, and the data “6P-mica (high R)” and “6P-mica (low R)” were deduced from ref 5.

It is obvious that all of the data strongly deviate from linear relationships. We have experimentally verified by thermal desorption spectroscopy that up to 400 K for 6P and up to 350 K for 5A, no significant desorption exists, thus excluding one of the above given explanations for this behavior. We also exclude postdeposition nucleation to be responsible for the decrease of the slope below the rather high temperature of 300 K. In the case of Cu on Ni(100), where an activation energy for diffusion of 0.35 eV was determined, postdeposition nucleation appeared only below 160 K. Because the diffusion energy of large organic molecules on inert substrates is significantly smaller (e.g., 0.02 eV for 6P on 6P(001)),²⁰ postdeposition nucleation could only appear at very low substrate temperatures. A possible reason for the change of the slope could of course be a change of the critical island size with surface temperature. However, for 6P on gently sputtered mica, we have obtained a critical island size of $i = 7 \pm 2$ for substrate temperatures between 150 and 400 K.⁵ No trend to a lower critical island size for lower temperature could be observed. Moreover, the dramatic change of the slope by more than a factor of 7 cannot be explained by a change in the critical island size. Even if it changed from $i = 7$ at 400 K to $i = 1$ at 150 K, this would only lead to a change by less than a factor of 3. The most surprising fact, however, is that the slope in the low-temperature regime of Figure 1 yields unrealistically small activation energies. According to eq 2, the slope β in the plot of $\ln N$ versus $1/T$ for ALA is given by $2[i(E_d + E_b) + E_i]/(i + 3)k$. From Figure 1, we can deduce an average asymptotic slope of $\beta \approx 3600$ K in the high-temperature regime and ~ 500 K in the low-temperature regime. Assuming a simple bond-breaking model for the binding energy of the critical cluster ($E_i = (i - 1)E_c$, with E_c being the binding energy between two 6P molecules) and by making a further simplification of $7(E_d + E_b) + 6E_c \approx 6(E_d + E_b + E_c) = 6E$ (because E_c is much larger than E_d and possibly E_b), we can estimate the sum of all energies

involved, \bar{E} , from the slope β . For the large slope, we obtain $\bar{E} \approx 0.26$ eV, and for the small slope, $\bar{E} \approx 0.036$ eV. In particular, the latter value is ridiculously small, considering the fact that the binding energy E_c between two 6P molecules in a cluster, consisting of seven molecules lying on a 6P(001) plane, has been calculated by molecular dynamics to be about 0.6 eV.¹²

In this Letter, we propose a quite different nucleation scenario that can account for the observed unusual phenomena. We suggest that the impinging organic molecules, which initially possess a kinetic energy according to the Knudsen cell temperature (typically 500 K), cannot immediately dissipate their kinetic energy upon impact on the substrate. Furthermore, excited rotational and vibrational states have to equilibrate. This may lead to a so-called hot precursor state in which the molecules are confined to the surface but have some transient mobility along the surface until they fully accommodate.²¹ This idea was inspired by experimentally^{22,23} and theoretically^{24,25} well-founded similar adsorption processes, for example, for the dissociative adsorption of small molecules or the adsorption of hydrogen atoms.²⁶ An instructive example is the adsorption of Xe on Pt(111),²⁷ where most of the adsorbed Xe atoms were found at step edge sites, even at a surface temperature of 4 K, indicating a transient mobility over several 100 Å at this temperature. Some other examples for adsorption via a hot precursor are oxygen adsorption on Ag(110)²⁸ and water adsorption on Rh(111).²⁹ Furthermore, when the scenario of a hot precursor holds, varying the kinetic energy of the impinging molecules should allow modification of the nucleation and growth. This has indeed been shown by several groups where the kinetic energy of pentacene has been varied by seeding in supersonic molecular beams. An influence on both the film morphology^{30,31} as well as the electronic properties of the pentacene films has been observed.³² Although the existence and importance of transient mobility in precursor states has frequently been questioned in the past, nowadays, this scenario is generally accepted. A comprehensive reference list to this subject can be found in a recent paper by Gao et al.³³

It is quite difficult to describe the microscopic details of the formation and duration of a hot precursor state and the subsequent processes that lead to nucleation. When an impinging molecule encounters the substrate surface, part of its initial kinetic energy (about 86 meV at 500 K) and internal energy (rotation, vibration) will be dissipated, but some part can also be converted into parallel kinetic energy and frustrated rotational motion. Furthermore, the molecule will be accelerated in the attractive potential, and this energy can then also be partially converted into lateral motion. The rotational to lateral kinetic energy conversion will strongly depend on the orientation of the impinging molecule. When the molecule is finally trapped on the surface, it will travel along the surface in a ballistic-like motion, where it can continuously lose energy by inelastic scattering with surface phonons until it fully equilibrates, and the further motion can be described by random hopping. During this hyperthermal sojourn, the molecules can hit other molecules to form unstable or stable clusters or become incorporated into an existing cluster. The clusters may even not be in equilibrium with the surface. Hot molecules hitting the islands may transfer enough energy to break them apart or at least detach some monomers again. A comprehensive description of the processes for molecules in a hot precursor and their contribution in aggregation would require detailed molecular dynamics and kinetic Monte Carlo simulations, which is beyond the scope of this work and has not

been performed on large organic molecules so far, to the best of our knowledge.

For a semiquantitative description of our experimental data, we mimic the increased mobility in the hot precursor state by random diffusion of molecules with an effective temperature larger than the surface temperature. We define an effective temperature

$$T_{\text{eff}}(T_i, T_s, \kappa) = T_i - \kappa \cdot (T_i - T_s) \quad (3)$$

with T_i as the temperature of the impinging molecules (i.e., the Knudsen cell temperature), T_s as the surface temperature, and κ as a coefficient that is related to the energy dissipation during the molecule impact at the surface and the sojourn in the hot precursor. The special ansatz (eq 3) was inspired by the well-known energy accommodation coefficient α^* , which can be measured by molecular beam scattering, $\alpha^* = (T_i - T_{\text{out}})/(T_i - T_s)$.³⁴ In that case, the outgoing (nonaccommodated) scattered molecules can be described by a temperature $T_{\text{out}} = T_i - \alpha^*(T_i - T_s)$. If we now assume that these nonaccommodated molecules cannot leave the surface because their normal component of the momentum is not high enough to overcome the adsorption potential well due to an efficient normal-to-parallel momentum transfer, the molecules may travel temporarily along the surface as hot molecules. We describe the ensemble of hot and thermalized molecules, including the stable and unstable clusters on the surface, by the effective temperature T_{eff} .

In Figure 2, we plot the qualitative relationship between the island density $\ln N$ as a function of $1/T_s$ for various coefficients

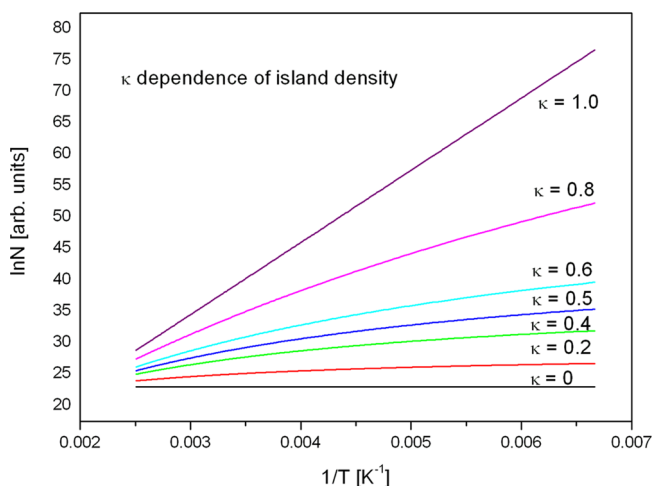


Figure 2. Qualitative dependence of the island density on the surface temperature for various energy dissipation coefficients κ according to eqs 2 and 3. For the calculation, an energy $\hat{E} = 1$ eV and $T_i = 500$ K were used.

κ , according to eqs 2 and 3, $\ln N \approx \hat{E}/kT_{\text{eff}}(T_i, T_s, \kappa)$, with $\hat{E} = 2[i(E_d + E_b) + E_i]/(i + 3)$. One clearly recognizes the curved shape of these relationships, which is most pronounced for an energy dissipation coefficient of about 0.5. Furthermore, one can observe the significant decrease in slope with decreasing κ for the same constant activation energies involved.

In Figure 3, we show quantitative fits to the experimental data for pentacene on the sputter-amorphized mica surface by using the following equation, assuming the ALA nucleation scenario

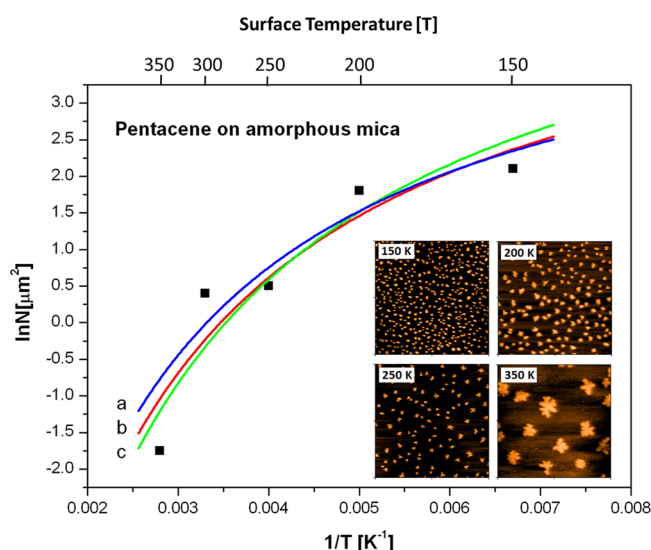


Figure 3. Experimental data points (black squares) for the island density as a function of the surface temperature for pentacene on sputter amorphized mica, together with three fit curves a–c. (a) $\bar{E} = 1.01$ eV, $\kappa = 0.23$; (b) $\bar{E} = 0.99$ eV, $\kappa = 0.25$; (c) $\bar{E} = 0.98$ eV, $\kappa = 0.27$. The inset shows some of the AFM images used for the determination of the island density, $8 \times 8 \mu\text{m}^2$ for 150, 250, and 350 K and $4 \times 4 \mu\text{m}^2$ for 200 K.

$$N[\mu\text{m}^{-2}] = 10^{-8} \cdot N_0 \left(\frac{4R}{\nu_0 N_0} \right)^{2i/i+3} \exp \left(\frac{2[i(E_d + E_b) + (i-1)E_c]}{(i+3)k(T_i - \kappa(T_i - T_s))} \right) \quad (4)$$

with $N_0 = 4 \times 10^{14} \text{ cm}^{-2}$ (density of pentacene molecules in the islands composed of standing molecules, roughly equivalent to the density in a 5A (001) layer), $R = 1 \text{ ML/min}$ ($7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$), $T_i = 500 \text{ K}$ (Knudsen cell temperature), and $i = 6$ (this value was obtained from the deposition rate dependence of the island density, unpublished results). Furthermore, we make use of the before-mentioned simplification $i(E_d + E_b) + (i-1)E_c \approx (i-1)(E_d + E_b + E_c) = (i-1)\bar{E}$. The curvature of the fit is mainly determined by the accommodation coefficient κ . Only values of $\kappa \approx 0.15\text{--}0.3$ lead to a proper curvature. For a quantitative fit, the parameters are not independent from each other. The classical hopping frequencies for surface diffusion are on the order of 10^{13} s^{-1} . Using this frequency, we obtain a best fit with $\bar{E} = 0.99 \text{ eV}$ and $\kappa = 0.25$ (Figure 3). However, because, according to transition-state theory, the rate constant is the product of kT/h and the ratio of the partition functions in the transition state and the adsorbed state, this value can be much larger for large organic molecules. This has not only been shown for desorption³⁵ but also for diffusion of organic molecules. For 6P on sputtered mica, we obtained $\nu_0 = 2 \times 10^{17} \text{ s}^{-1}$.¹² Using such a diffusion frequency, we obtain a best fit with $\bar{E} = 1.49 \text{ eV}$ and $\kappa = 0.19$. Despite the rather broad range of possible energy and frequency factors, the obtained values are much more realistic than those deduced by the classical evaluation, where diffusion of equilibrated molecules is assumed.

In summary, we have described a possible scenario for the unusual temperature dependence of the nucleation of organic molecules. We propose that the impinging molecules, which possess a translational energy according to the evaporation source temperature, enter a transient hot precursor state before equilibrating to the surface temperature. This enables the

molecules to migrate over larger distances along the surface than in the equilibrated state, thus influencing the nucleation and growth considerably. Specifically, for the system pentacene on sputtered Muscovite mica, which has been shown to obey ALA, we observe a strong deviation from a straight line in the $\ln N$ versus $1/T$ plot, indicating the effect of transient mobility in nucleation and aggregation. In particular, for low surface temperatures, the island density is much smaller than expected from classical nucleation theory. It turns out that for a proper description of the experimental results, an energy dissipation coefficient of $\kappa \approx 0.19\text{--}0.25$ has to be assumed. Although several unknown parameters enter the modified Venables equation (diffusion constants and various activation energies), a reasonable value for the sum of all energies involved of about $1\text{--}1.5 \text{ eV}$ could be obtained, whereas the application of the classical nucleation models dramatically failed.

EXPERIMENTAL METHODS

Pentacene was deposited on a Muscovite mica surface by physical vapor deposition from a Knudsen cell in an ultrahigh vacuum chamber. The cell temperature was about 500 K to realize a deposition rate of 1 monolayer/min. The mica samples ($10 \times 10 \times 0.01 \text{ mm}^3$) were attached to a steel plate via tantalum wires. The steel plate was heated resistively, and its temperature was controlled by a Ni–NiCr thermocouple spot-welded to the back of the plate. This allowed controlled heating of the mica sample. With additional LN_2 cooling, the temperature of the mica sample could be varied between 100 and 1000 K. For a quantitative determination of the deposited material, a quartz microbalance was used, which was located next to the mica substrate. The mica substrate was cleaved with adhesive tape prior to installation into the vacuum chamber and subsequently gently sputtered by argon ions. Ten minutes of sputtering with 500 eV Ar^+ ions at an argon pressure of $5 \times 10^{-5} \text{ mbar}$ was sufficient to change the 5A film morphology from needle-like islands, composed of lying molecules, to compact islands composed of standing molecules.⁵ The surface chemical composition was analyzed by Auger electron spectroscopy and X-ray photoelectron spectroscopy. Thermal desorption spectroscopy was applied to determine the thermal stability of the pentacene film and the sticking coefficient. Ex situ atomic force microscopy (Nanosurf, EasyScan2) was used to analyze the film morphology.

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Notes

The authors declare no competing financial interest.

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