Attachment limited versus diffusion limited nucleation of organic molecules: Hexaphenyl on sputter-modified mica

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1. Introduction

The understanding and tailoring of organic thin film growth is a challenging issue in the context of modern organic electronics. Whereas the nucleation and growth of (metal) atoms is well understood [1–3], there is still lack of a comprehensive description for the nucleation and growth of larger (anisotropic) organic molecules. Although experimental evidence exists that in many cases organic film growth can be described sufficiently well with the models developed for single atom nucleation [4–7], there are also indications that substantial differences exist [8,9]. It is obvious, that the specific features of organic molecules (weak molecule–molecule and molecule–substrate interactions, low diffusion energies, diffusion anisotropy, many degrees of freedom, etc.) can lead to a larger variety of growth mechanisms than for point like particles.

In this letter we describe the nucleation and sub-monolayer formation of para-hexaphenyl (6P) on sputter-modified Muscovite mica(001) surfaces as a model system for the interaction of rod-like organic molecules with weakly interacting substrates. The merit of mica as a model substrate is the easy preparation of a rather clean, atomically flat single crystalline surface by just cleaving a mica sheet. It has been shown previously that on a freshly cleaved mica surface 6P forms needle like islands which are composed of standing molecules [12]. Molecular dynamics calculations revealed that also in this case first clusters of lying molecules develop, which then reorient into the upright position at a cluster size of about 10–15 molecules [9]. From the island density as a function of the deposition rate, as well as from island size distributions (ISD) and capture zone distributions (CZD), a critical island size of 2–3 molecules was obtained for deposition at room temperature [9], by applying the nucleation model of diffusion limited aggregation (DLA) [3]. However, the temperature dependence of the island density exhibited some unusual features and it was argued that the anisotropic diffusion probability and/or orientation dependent attachment probability of the monomers at the rim of the islands might be responsible for these features. Here we demonstrate that in addition to the diffusion limitation the attachment limitation governs the nucleation and growth of 6P on mica(001), depending on the surface preparation by ion sputtering. We believe that the findings on this model system are relevant for many similar, more application related organic film/substrate systems, e.g. pentacene on silicon oxide [4,5,13,14], where typically the dielectric substrates are plasma treated prior to deposition of the organic semiconductor [15].

2. Experimental

The mica(001) samples (10×10×~0.01 mm³) were prepared by cleaving them with adhesive tape in air and then attaching them to a steel plate sample holder, which was immediately installed inside a UHV chamber. The sample holder could be heated resistively and cooled by LN₂ to obtain sample temperatures between 150 K and 800 K. Surface characterization was performed by low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS),
Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS), with respect to surface crystallography, surface chemical composition and thermal stability, respectively. The 6P films were deposited by physical vapor deposition (PVD) from a Knudsen cell. A quartz microbalance was used to determine the 6P film thickness quantitatively. For the modification of the mica surface to obtain exclusively layers with standing 6P molecules, the surface was sputtered with 500 eV Ar⁺ ions, using an argon partial pressure of $5 \times 10^{-5}$ mbar.¹ After the in-situ preparation and characterization of the 6P films on mica, the samples were investigated ex-situ by atomic force microscopy (AFM), by applying the tapping mode (Nanosurf, EasyScan2). More details regarding the sample holder, sample preparation and characterization of the samples with surface analytical techniques have been described elsewhere [9,12].

3. Results and discussion

In Fig. 1 three AFM images of sub-monolayer 6P films are shown, where about 0.1 monolayer (ML) were adsorbed on differently sputter-modified mica(001) surfaces, with a deposition rate of 0.1 ML/min at room temperature. Sputtering was performed with the above mentioned parameters, with sputter times of 3 min (a), 10 min (b) and 60 min (c), respectively. We could show that a sputter time of 3 min was sufficient to change the 6P layer growth from needle-like islands, consisting of flat lying molecules, to dendritic islands composed of standing molecules. Also, a LEED analysis showed that after 3 min sputtering the distinct LEED spots of the freshly cleaved mica have already disappeared. However, from XPS and AES we observed that the chemical composition of the surface (silicon, aluminum, oxygen, potassium) was not significantly changed. Only small amounts of initially adsorbed carbon were removed. But even for extended sputtering the chemical composition of the near surface region remained the same, in particular the potassium signal did not change. Thus, one has to assume that in this case a change of the surface geometric structure is responsible for the changed 6P layer growth, rather than a change of the chemical composition.

The aggregation mode and the critical island size can be experimentally determined by the measurement of the island density $N_i$ as a function of the deposition rate $R$. In Fig. 2 we present selected AFM images as obtained for different deposition rates at 200 K, to demonstrate the morphological development of the sub-monolayer 6P films. Similar series of AFM images were obtained for 6P films prepared at 150 K, 300 K and 400 K substrate temperature, respectively, over a wide range of deposition rates. The final coverage was held in the range between 0.1 and 0.3 ML to stay in the aggregation regime. Below this coverage the film growth would be in the nucleation regime where the island density still increases with coverage; above about 0.5 ML the island density starts to decrease due to coalescence. In all cases the mica(001) surface was modified prior to 6P deposition by 10 min Ar⁺ sputtering.

The most frequently applied model to describe nucleation is that for diffusion limited aggregation [16]. According to Venables et al. [3] the island density $N_i$ in the aggregation regime can be described as a function of the deposition rate $R$ by a power law [3]:

$$\frac{N_i}{N_0} = \eta(\theta, i) \left( \frac{4R}{\nu_0 N_0} \right)^{\frac{1}{2}} \exp \left( \frac{iE_d + E_i}{(\nu + 2)kT} \right).$$

Here $N_0$ is the number of adsorption sites per unit area ($4.4 \times 10^{14}$ 6P molecules cm⁻² in the (001) plane), $\eta$ is a weak function of the

¹ In this work a different sputter gun was used than in Ref. 9. In that work the sputter gas was introduced through the sputter gun, whereas in this work the gas was introduced via a separate leak valve. Therefore, in this work the effective ion flux is smaller for comparable equilibrium Ar pressure and sputter time.

![Fig. 1. AFM images (8 μm x 8 μm) of 6P grown on sputter-modified mica(001) surfaces at $T = 300$ K, with various sputter time: (a) 3 min (b) 10 min (c) 60 min, sputter voltage: 500 V, Ar pressure: $5 \times 10^{-5}$ mbar; 6P deposition rate: 0.1 ML/min, coverage: 0.1 ML.](image1)

![Fig. 2. AFM images (8 μm x 8 μm) of 6P grown on sputter-modified mica(001) at 200 K with different deposition rates: (a) 0.14 ML at 0.037 ML/min (b) 0.13 ML at 0.097 ML/min, (c) 0.18 ML at 0.30 ML/min, (d) 0.26 ML at 0.80 ML/min.](image2)
coverage Θ and the critical island size i, with \( \eta \approx 0.2–0.3 \) [3], \( \nu_0 \) the attempt frequency for surface diffusion, \( E_0 \) the activation energy for monomer diffusion, \( E_B \) the binding energy of the critical cluster, and \( k \) the Boltzmann constant. In this model it is assumed that condensation is complete, i.e. no desorption of the monomers is allowed, and the attachment probability at the island edge is unity. According to Eq. (1) the critical island size can be determined from the deposition rate dependence of the island density. The value \( \alpha = i/(i+2) \) can only vary between 1/3 (for \( i = 1 \)) and 1 (for large \( i \)). In Fig. 3 \( \ln(N_x) \) versus \( \ln(R) \) is compiled for four different series of deposition, performed at substrate temperatures of 150 K, 200 K, 300 K, and 400 K, respectively. One can see that two regimes with different slopes \( \alpha \) exist, but within the regimes the slopes are nearly the same for all substrate temperatures. The surprising result is, however, that the average values of \( \alpha \approx 1.4 \pm 0.1 \) for higher deposition rates and \( \alpha \approx 0.7 \pm 0.1 \) for lower deposition rates. Apparently, the experimental data compiled in Fig. 3 for the high deposition rate regime cannot be explained by diffusion limited aggregation, where the slope \( \alpha \) should be smaller than unity.

Kandel [17] and more recently Venables and Brune [18] have considered a scenario where the incorporation of the approaching monomers at the island edge is hindered. Such island edge barriers can exist in surfactant mediated growth, where the island edge atoms have been shown to be more active in order to attach to approaching surfactant molecules [19]. A physically different, but phenomenologically equivalent scenario can even be visualized for the incorporation of the flat lying 6P molecules at the edge of the islands, which are either composed of lying molecules for cluster size smaller than about 15 molecules or of standing molecules in larger islands [7]. Here the attachment probability will depend on the relative orientation between the approaching (lying) molecules and the molecule arrangement at the rim of the island, leading to an effective barrier for attachment. The overall capture number \( \sigma \) of an island depends on both, the diffusion barrier and the attachment barrier. Venables and Brune [18] have shown that the capture numbers add inversely \((1/\sigma = 1/\sigma_B + 1/\sigma_n)\). If the attachment barrier capture number \( \sigma_n \) is negligible compared to the diffusion barrier capture number \( \sigma_B \), the nucleation and growth are diffusion limited and Eq. (1) describes the nucleation process. For the reverse situation, \( \sigma_B \gg \sigma_n \), however, the following relationship was derived by Kandel [17]:

\[
\frac{N_x}{N_0} = \eta (\Theta, i) \left( \frac{4R}{\nu_0} \right)^\frac{1}{\eta} \exp \left( \frac{2[(E_B + E_0) + E_i]}{(i+3)kT} \right).
\] (2)

Here, \( E_B \) is the attachment barrier and \( \eta \) again a weak function of the coverage \( \Theta \) and the critical island size \( i \) [18]. One can see that for such a scenario the slope \( \alpha = 2/(i+3) \) can vary between 0.5 (for \( i = 1 \)) and 2 (for large \( i \)). For the above mentioned slope of \( \alpha = 1.4 \pm 0.1 \) we derive a critical island size of \( 7 \pm 2 \) for 6P nucleation on moderately sputtered mica. For very low deposition rates and/or preferred nucleation at some surface inhomogeneity (heteronucleation) might also play a role in this case. Of course, it would be desirable to identify the critical island size directly by high-resolution AFM. However, since nucleation is a dynamic process it would be very difficult to unambiguously determine the critical island size by this method during deposition.

From the comprehensive data set in Fig. 3 one can also extract the island density as a function of temperature at constant deposition rate. The slope of the straight line in the plot \( \ln(N_x) vs 1/T \) yields the energy term \( \hat{E} = 2[(E_B + E_0) + E_i]/(i+3)k \). The evaluation for deposition rates between 0.1 and 1 ML/min yields \( \hat{E} \approx 0.2 \) eV. Unfortunately, from this evaluation the contribution of the individual energy terms cannot be identified.

4. Conclusions

In conclusion, we have shown that the nucleation of rod-like organic molecules (6P) on a moderately sputtered mica(001) surface is attachment limited. The reason for this behavior is most likely that the attachment probability of the elongated 6P molecules depends on the relative orientation between the approaching (lying) molecules and the molecules at the rim of the islands (either lying in small clusters or standing in larger islands). There exist many unfavorable configurations for molecule incorporation, leading to an effective attachment barrier and hence to an integral attachment probability smaller than unity. A critical size of \( i = 7 \pm 2 \) molecules was determined from the deposition rate dependent island densities, using Kandel’s formalism for attachment limited nucleation. Furthermore, we have shown that the surface roughness, and hence the diffusion probability on the surface, plays a crucial role for the nucleation and aggregation mode. With increasing surface roughness and/or by decreasing the deposition rate, the nucleation process can change from attachment limited to diffusion limited. The scenario of attachment limitation has not been considered so far in organic film growth, but it may play an important role for many practical cases in organic electronics, e.g. for pentacene film formation on silicon oxide.

Acknowledgments

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References