Nucleation and growth of rod-like organic molecules on inert substrates: 6P on mica

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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], 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 [2], there are also indications that substantial differences exist [3]. It is obvious, that the specific features of organic molecules can lead to a larger variety of growth mechanisms than for point like particles.

In this contribution we describe the nucleation and sub-monolayer formation of para-hexaphenyl (6P) on mica surfaces as a model system for the interaction of rod-like organic molecules with weakly interacting substrates. It has been shown that on freshly cleaved mica 6P forms needle like islands which are composed of flat lying molecules (Fig. 1a) [4]. However, a modification of the mica surface by argon ion sputtering changes the film formation drastically: dendritic islands form which are composed of standing molecules (Fig. 1b) [5]. From the island density as a function of the deposition rate a critical island size of 2-3 molecules was obtained, by applying the nucleation model of diffusion limited aggregation (DLA). 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 diffusion the attachment probability governs the nucleation and growth of 6P on mica, depending on the surface preparation by ion sputtering.

The most frequently discussed nucleation mode is the diffusion limited aggregation. According to Venables et al. [6] the island density \( N_x \) in the aggregation regime can be described as a function of the deposition rate \( F \) by a power law: \( N_x \propto (F/D)^\chi \), where \( D \) is the surface diffusion coefficient and \( \chi = i/(i+2) \), with \( i \) being the critical island size. In this case the exponent \( \chi \) can only vary between 0.33 (\( i = 1 \)) and 1 (for large \( i \)). This was indeed fulfilled for 6P deposited on a heavily sputtered mica surface [3]. However, it was found that the 6P island density can be strongly influenced by the sputter dose. Moreover, it was observed that on weakly sputtered mica the deposition rate dependence cannot be explained with the DLA mechanism, because the experimentally observed exponent \( \chi \) was larger than 1.
Kandel [7] and more recently Venables and Brune [8] considered a scenario where the incorporation of the approaching monomers at the island edge is the limiting factor for nucleation, rather than diffusion. In this case the scaling exponent $\chi = 2i/(i+3)$. With this scenario we can well describe the experimental data and from the obtained $\chi = 1.4 \pm 0.1$ we determine a critical island size of $7 \pm 2$.

A second interesting feature of 6P film growth on mica is the frequently observed bimodal island size distribution, both in the case of the freshly cleaved surface (Fig.1a) as well as on the sputter modified surface (Fig. 1b). We studied this phenomenon with AFM and TDS, which allows us to identify a possible wetting layer and its influence on the film formation. In particular, we performed TDS before and after venting the vacuum chamber and re-evacuation. It turns out, that the small 6P islands (clusters) on both, the freshly cleaved and the sputter-modified mica surface, are the result of post-nucleation during the exposure of the 6P covered mica surface to air, caused by the co-adsorption of water.

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Fig.1 AFM images of 6P on freshly cleaved mica (a) and sputter modified mica (b)

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