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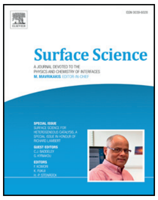

On the nucleation and initial film growth of rod-like organic molecules

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ABSTRACT

In this article, some fundamental topics related to the initial steps of organic film growth are reviewed. General conclusions will be drawn based on experimental results obtained for the film formation of oligophenylene and pentacene molecules on gold and mica substrates. Thin films were prepared via physical vapor deposition under ultrahigh-vacuum conditions and characterized in-situ mainly by thermal desorption spectroscopy, and ex-situ by X-ray diffraction and atomic force microscopy. In this short review article the following topics will be discussed: What are the necessary conditions to form island-like films which are either composed of flat-lying or of standing molecules? Does a wetting layer exist below and in between the islands? What is the reason behind the occasionally observed bimodal island size distribution? Can one describe the nucleation process with the diffusion-limited aggregation model? Do the impinging molecules directly adsorb on the surface or rather via a hot-precursor state? Finally, it will be described how the critical island size can be determined by an independent measurement of the deposition rate dependence of the island density and the capture-zone distribution via a universal relationship.

1. Introduction

Thin films of organic semiconductors have attracted considerable interest in the recent past due to their promising applications in organic electronics. Various organic electronic devices are already on the market, e.g. solar cells, light emitting diodes, displays and radio frequency identification tags, to name just a few. The advantages of organic electronics in comparison to silicon-based technology are manifold. Properties such as low-cost of fabrication, material flexibility, large-scale fabrication by roll-to-roll printing at moderate temperatures and even possibly biocompatibility and biodegradability of the electronic material are scientifically and technologically attractive. Although for many purposes polymers are used, the application of small organic semiconducting molecules becomes increasingly important. In this case, organic thin films are mainly fabricated by physical vapor deposition. While this method weakens some of the above-mentioned advantages, it allows a very precise fabrication and tailoring of the organic films, which is an inevitable prerequisite for detailed investigations of the growth mechanism. However, despite those inherent advantages of physical vapor deposition techniques, many of the fundamental physical processes taking place during adsorption and organic thin film formation are still poorly understood.

The aim of this short review article is to summarize some of the most recent findings regarding the nucleation and growth of films composed of the rod-like organic molecules pentacene ($C_{22}H_{14}$), p-quaterphenyl ($C_{24}H_{18}$) and p-hexaphenyl ($C_{36}H_{26}$) on gold and mica substrates. These molecules are commonly used and increasingly relevant for applications in organic electronics. Pentacene (5A) is the most frequently used material to fabricate organic transistors, due to its high charge carrier mobility [1], while p-hexaphenyl (6P) was one of the first materials used to build blue light emitting diodes [2]. In the author's view, the growth characteristics of these rod-like molecules can be seen as prime examples of organic film growth in general.

The organic molecules were deposited on the substrates in an ultrahigh vacuum chamber by physical vapor deposition from a stainless steel Knudsen cell; the deposited amount was quantitatively measured with a quartz microbalance. The substrates were clipped onto a heatable sample holder which allowed the application of thermal desorption spectroscopy (TDS) to characterize the kinetics and energetics of adsorption and film formation. Additionally, Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were applied to chemically characterize the substrates and/or the thin films. Low-energy electron diffraction (LEED) was performed to study the structure of the monolayer films, while the structure and morphology of thick films were measured ex-situ by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. Details on the experimental procedures can be found in a number of previous publications [3,4,5].

In this article, some frequently discussed issues in the context of the nucleation and growth of films composed of rod-like organic molecules will be addressed: Which parameters define whether the island-like film is composed of lying or upright standing molecules? Is there a wetting layer between and underneath the islands? Can the nucleation and growth be described by the classical diffusion-limited aggregation model? The discussion of these issues is mainly based on experimental work performed in my group at the Graz University of Technology and on theoretical work carried out by Alberto Pimpinelli at the Rice University, Texas.

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2. Organic films composed of lying or upright standing molecules

When rod-like organic molecules are deposited on a substrate surface they will first adsorb in a flat-lying configuration, in which they diffuse along the surface and meet other molecules to form unstable or stable clusters, which further grow with increasing coverage and form islands. It turns out that basically two different island types can be observed, which are either composed of flat-lying molecules or of upright-standing molecules [6,7,8]. When the molecules are strongly bound to the substrate surface, not only the first monolayer is composed of lying molecules, but also the additional molecules in higher layers are incorporated in flat-lying orientation. Since both the diffusion probability as well as the incorporation probability are highly anisotropic, typically needle-like islands are formed in this case. Examples of such layer formation are 4P on Au(111) [9,10], 6P on Au(111) [11,12,13], 6P on KCl(001) [14,15] and 6P on crystalline mica [4,16,17]. In Fig. 1a an optical microscopy (OM) image is shown for a 20 nm thick 4P film deposited on Au(111) at room temperature, showing needle like crystallites of more than 20 μm length [9]. X-ray diffraction reveals that the crystallites are oriented with the 4P(211) plane parallel to the (111) plane of the gold surface. This plane is composed of molecules in a herringbone-like arrangement, where the long axes of the molecules are parallel to this plane and the short axes alternatively parallel or side-tilted. Moreover, XRD pole figures show that the molecules in the crystallites are aligned with respect to the arrangement of the gold atoms, either along the Au[$1\underline{1}0$] or the Au[$11\underline{2}$] direction (epitaxial relationship) [10].

The growth of 6P films on Au(111) shows several similarities with that of 4P, however, a higher substrate temperature is needed to form long needle-like islands. While at 300 K only randomly oriented short crystallites with diameters around 100 nm are observed, films grown at 430 K exhibit needle-like crystallites of up to 10 μm length [13]. The reason for this difference is the smaller diffusivity of the longer oligophenylenes. A large-scale AFM image (Fig. 1b) shows that the needles are macroscopically oriented along distinct directions of the underlying substrate and rotated by 120°, again hinting at epitaxial growth. XRD and pole figure measurements reveal that in this case the 6P($21\underline{3}$) plane is parallel to the Au(111) surface. The arrangement of the molecules in this plane is similar to that for the 4P(211) plane. The azimuthal orientation of the molecules is exclusively along the Au[$1\underline{1}0$] direction [11].

6P deposited on KCl(001) exhibits a similar temperature dependent layer formation as described above. However, the diffusion probability at equivalent temperatures is much higher than on Au(111). While at and below room temperature only small crystallites form, the deposition at 450 K leads to extremely long needles (up to several 100 μm). The AFM image in Fig. 1c shows part of such a long needle which was formed after deposition of 6P at 450 K. The total amount of deposited 6P corresponds to just 1 nm mean film thickness [15]. Cross section measurements on this needle yield a width of about 200 nm and a needle height of about 150 nm. It needs to be mentioned that it was quite difficult to find the needles in the AFM at all, demonstrating the extremely high diffusion length of the 6P molecules on KCl at this temperature. Also noteworthy is the uniform width and height of these needles, which is probably caused by a stabilization due to strain within the needles. A detailed XRD investigation [18] showed that the long axes of the 6P molecules are again parallel to the (001) plane of the substrate, but the short axis is slightly side tilted, more precisely the

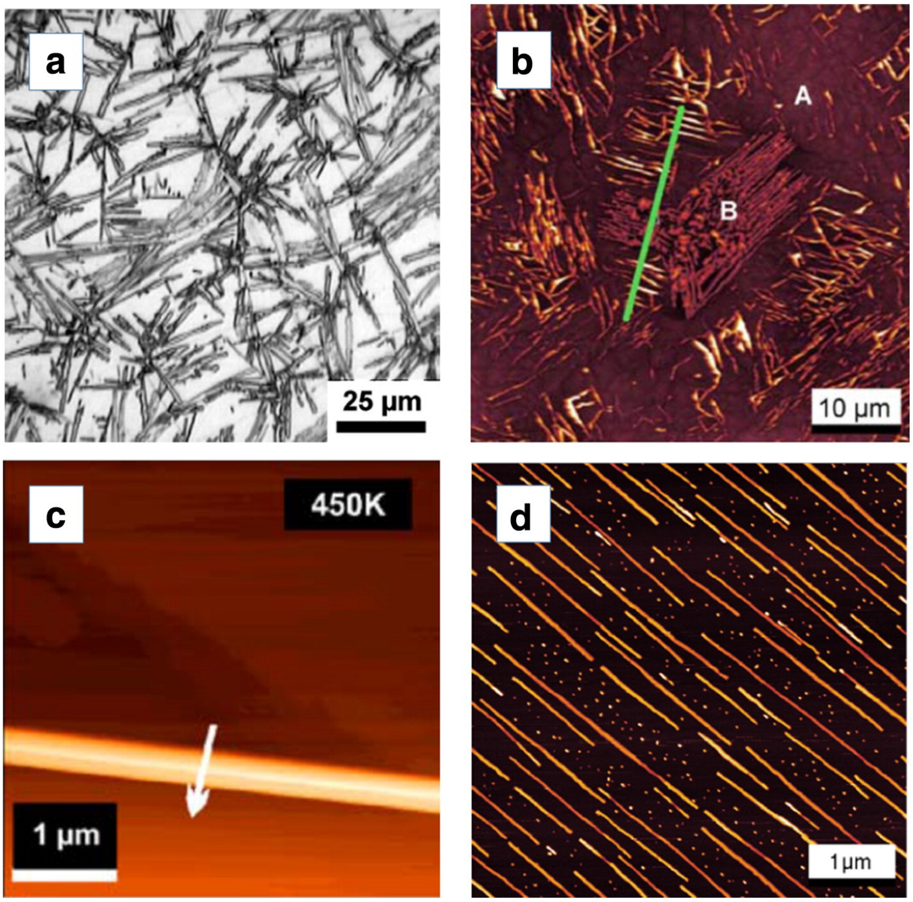

Fig. 1. (a) OM image of 20 nm 4P on Au(111) at 300 K, (b) AFM image of 30 nm 6P on Au(111) at 430 K, (c) AFM image of 1 nm 6P on KCl(001) at 450 K, and (d) AFM image of 1 nm 6P on mica at 300 K.
Reprinted with permission from Refs. [9] (a), [13] (b), [15] (c), and [4] (d).

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