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Epitaxial growth of organic heterostructures: Morphology, structure, and growth mode

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Abstract

For organic molecular materials the definition of the condition of epitaxial growth has been subjected to several misconceptions and a great debate, leading in any case to less restrictive requirements than for inorganic materials. Here, the deposition of oligothiophene films by molecular beam epitaxy on properly grown organic single crystals is discussed and *all-organic* rigorous epitaxy demonstrated for both sub-monolayer and several-monolayer thick films. The possibility of growing all-organic nanostructures directly follows from these results.

Keywords: Molecular beam epitaxy; In situ characterization; Atomic force microscopy; Thin film structures; Semiconductor–semiconductor thin film structures; Surface structure, morphology, roughness, and topography

1. Introduction

In the last decades, the evolution of semiconductor physics and technology, with their wide variety of devices and artificial structures (e.g. superlattices, quantum wells and dots, nanostructures), has lead to a parallel evolution of the growth techniques and the connected concepts. In particular, the condition of epitaxy has evolved from the mere geometrical meaning towards something related with the growth dynamics. Indeed, both the experimental assessment of new physical phenomena and the development of new device geometries requiring a fine control of, e.g. layer thickness, interface and surface quality, order, homogeneity over rather large areas, clearly demonstrated the need for much more than a precise relationship between substrate and overlayer lattices [1]. In particular, an epitaxial system is demonstrated to have technological relevance when it displays over a large scale: (1) exclusively two-dimensional (2D) nucleation of islands on singular surfaces (or step-flow growth on vicinal surfaces); (2) commensurism of islands with the substrate lattice (overlayer and/or substrate lattice distortions may occur to achieve commensurism through pseudomorphic growth); (3) islands with both coherent azimuthal and textural order; (4) island aggregation dominated by coalescence; (5) possibility to grow several monolayers (ML) of the same material without generating growth transitions or instabilities; (6) control of the material dose at the submonolayer level; (7) high purity of the materials.

Recent research on organic molecular materials with possible application as semiconductors in devices and nanostructures [2,3] pushes now towards a concept of epitaxy involving, also for organics, the other aspects of epitaxy which naturally raised for inorganic materials. In addition to the previous points, specific requirements have to be added for *all-organic epitaxy*: (8) use of organic single crystalline substrate; (9) physisorption of molecules on the substrate surface, involving only long range van der Waals interactions.

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Up to now, the attempts made to reach epitaxy with organic materials employed primarily inorganic substrates, possibly passivated [4], and were restricted to the growth of submonolayer films of few molecules self-assembled in small ordered domains [5–9]; only few experiments have been carried out using organic substrates [10–13].

Here, we demonstrate how all-organic epitaxy, utterly fulfilling all the conditions reported above (to be simultaneously verified on a large-scale to obtain true epitaxy) can be successfully accomplished by the use of the organic molecular beam epitaxy (OMBE [3]) technique, providing a high-resolution morphological study of thin molecular films of oligothiophenes grown on high quality organic single crystals. The results of the ex situ characterization by atomic force microscopy (AFM) is also supported by in situ growth monitoring carried out by reflectance anisotropy spectroscopy (RAS).

Both homoepitaxy and heteroepitaxy of α-quaterthiophene (α4T) are considered here, interesting from slightly different points of view. Homoepitaxy, which allows a high control on the quality of surface layers, is also a necessary step for studying the intermolecular interactions within the material leading to film nucleation and growth. On the other hand, heteroepitaxy is studied as the most suitable choice for several applications, where different materials with optimised properties need to be integrated in complex structures.

2. Experiment

To reach the highest sample quality, one of the most interesting and well characterised family of molecular semiconductors, namely oligothiophenes, was chosen for the present work. Commercial α6T was purified by several sublimation cycles and then used for the single crystal growth [14]; α4T was synthesized and purified following a recently optimized procedure [15], then the single crystals to be used as substrates were grown from solution [16] and by vapour phase transport [17].

The deposition of α4T thin films was carried out under ultra-high vacuum (better than 5×10^{-10} Torr) by OMBE, using Knudsen-type effusion cells; deposition temperature was 170 °C and deposition rate 0.3 nm min^{-1}. The film thickness was monitored by a quartz microbalance installed close to the substrate [18]. The substrates were kept at room temperature during film growth.

RAS experiments were carried out in situ during deposition of α4T on α4T in the spectral range 1.5–5.0 eV using a home-made apparatus with two polarizers installed on the OMBE chamber [12,19,20] equipped with a quartz strain-free window. The results are given in terms of the ratio between the difference of the light intensity R_α and R_β reflected by the sample when impinging on it with a beam linearly polarized along two orthogonal directions α and β of the substrate and their average (as a function of photon energy):

$$\Delta R/R = 2\frac{R_\alpha - R_\beta}{R_\alpha + R_\beta}. \quad (1)$$

The directions α and β for the present experiments were nearly aligned (within the experimental uncertainty) with the axes of the crystal substrate at the surface.

AFM images were collected ex situ in tapping™ mode with a Nanoscope IIIa MMAFM (Veeco Instruments) using silicon cantilevers.

3. Results and discussion

As a first substrate, the low temperature polymorph of α4T (α4T/LT) [17] was selected, exhibiting a layered structure with monomolecular layers 15.23 Å-thick parallel to the (0 0 1) plane, which is also the widest growth surface. From the quantitative analysis of AFM images collected after the deposition of sub-monolayer films, nucleation and growth of these layers can be discussed. In Fig. 1a

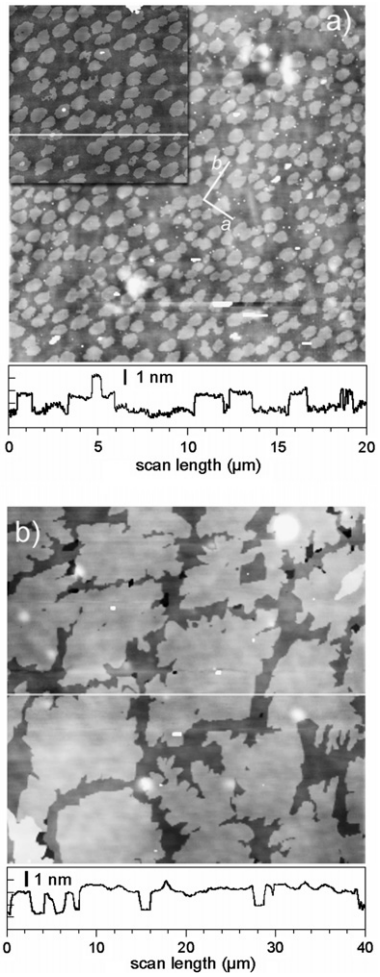

Fig. 1. 40×40 μm^2 AFM images (measured ex situ) of (a) 0.5 ML and (b) 5 ML of α4T grown on α4T/LT(0 0 1). Inset: 20×20 μm^2 AFM image with double resolution collected on the same film of (a). In (a) the orientation of the substrate surface axes is indicated ($a = 6.09$ Å, $b = 7.86$ Å, $\gamma = 90°$); below both images a cross-sectional profile of the AFM signal is reported corresponding to the horizontal white line.