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Tuning the growth mode in organic molecular-beam epitaxy

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The growth process of molecular thin films deposited on an interacting crystalline substrate by organic molecular-beam epitaxy is monitored *in situ* by reflectance anisotropy spectroscopy (RAS). From the RAS signal evolution measured during the early stages of deposition, evidence is found of two opposite growth modes, namely layer-by-layer and island modes, obtained when changing the supersaturation of the vapor phase on the substrate.

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Over the last decade, an increasing interest has been devoted to organic molecular semiconductors and to their applications.[1,2] The study of such materials has thus evolved from their synthesis and chemical properties towards their physical properties in the solid state and, in particular, in thin films. A proper growth technique for obtaining a fine control of the film properties is organic molecular-beam epitaxy (OMBE Ref. 1), the most natural choice when high-quality samples are needed and when the scientific interest is directed to the intrinsic properties of the material. Indeed, in several cases detailed studies of molecular crystals could be successfully carried out only when OMBE samples became available.[3–5] Nonetheless, the potentiality of OMBE has not yet been fully exploited, since the basic physical principles governing organic thin-film growth and crystallization are not well understood and detailed growth models not yet developed, even if some decisive steps have been recently made.[6–10] In this respect, the layer-by-layer epitaxial growth of molecular thin films has not yet been demonstrated, in particular for low molecular weight materials. This would open the way towards the experimental study of organic nanostructures, very promising for their physical properties and applications.[1,6,11] Up to now, the development of research in this field has been limited by the lack of spectroscopies that are (i) nondestructive for organic materials and (ii) able to monitor *in situ* the ultrahigh vacuum (UHV) growth. The latter property is mandatory since molecular solids are commonly affected by desorption and structural rearrangements after deposition.[12–14] On the contrary, so far, nearly all spectroscopies, i.e., probe microscopies and structural techniques, have been applied *ex situ*, just giving an indirect information.

A detailed comprehension of the OMBE process requires the study of the microscopic processes[15] occurring on the substrate surface. For inorganic MBE, the role of kinetics and thermodynamics in governing these phenomena has been extensively studied,[8,15–18] owing to the strong bonds of inorganic systems, which allow the epitaxial growth of the film in conditions near to equilibrium. On the contrary, in the case of organic materials a similar study is still lacking since the low adhesion of the physisorbed material, and the relatively high vapor pressure of the molecular solid, force the deposition to be carried out at drastic off-equilibrium conditions.[9] Nonetheless, we present here an attempt to reach organic epitaxy by using an "inorganic strategy," i.e., by tuning thermodynamic parameters, such as the degree of supersaturation of the vapor phase,[15] and by properly selecting a strongly interacting substrate, such as an organic single crystal. As the necessary nondestructive *in situ* monitoring technique, we recently demonstrated that reflectance anisotropy spectroscopy (RAS) is the best choice for organics, due to its particularly high sensitivity.[19,20] We mention that another optical technique, namely differential reflectance spectroscopy (DRS Ref. 21), has been also successfully used for *in situ* studies on organics.[22] Both RAS and DRS combine spectroscopic information on the optical properties of the growing film with the *real-time* monitoring of their evolution.

We have selected well-characterized materials, such as oligothiophenes,[2] as the molecular sublimants, whose crystal structure and film morphology are known as a function of the growth parameters.

In this Communication, an *in situ* study of quaterthiophene thin films during OMBE growth is reported, as carried out utilizing the *real-time* capabilities of RAS. By a proper choice of substrate and using substrate temperature for the control of thermodynamic conditions, the OMBE process is tuned in order to obtain either a layer-by-layer or an island growth mode.

Quaterthiophene (4T) was synthesized and purified according to a recently optimized procedure.[23] Thin films were grown by OMBE under 5×10^{-10} Torr base pressure on substrates of (010)-oriented potassium acid phthalate (KAP) (Ref. 24) at room temperature (RT) or at 123 K (low temperature, LT). A quartz microbalance installed close to the substrate is used to measure the nominal film thickness. The KAP substrate induces a preferential orientation of the 4T polycrystalline film and the complete in-plane anisotropy of its macroscopic optical response.[25] The structure of the 4T films is the low-temperature monoclinic structure; at RT the crystal in the films is oriented with the $[100]_{4T}$ and $[010]_{4T}$ directions along the $[001]_{KAP}$ and $[100]_{KAP}$ directions of the KAP crystal, respectively;[26] one monolayer (ML) is 15.3-Å thick.

RAS experiments were carried out in the range 1.5–5.0 eV during deposition at near normal incidence using a homemade apparatus with two polarizers.[20,27] The results are given in terms of the ratio between the difference ΔR of the light intensity R_α and R_β reflected by the sample for a beam linearly polarized along two orthogonal directions α and β and their average R as a function of the photon energy,

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

In the present case, the directions α and β are nearly parallel to the $[001]_{\mathrm{KAP}}$ and $[100]_{\mathrm{KAP}}$ directions of the KAP substrate crystal. For a layer of thickness $d \ll \lambda$ (λ being the wavelength of light), $\Delta R/R$ can be expressed in terms of the complex dielectric function anisotropy $\Delta\hat{\varepsilon}_1$ of the growing layer

$$\Delta R/R = \frac{8\pi d}{\lambda}[A\Delta\varepsilon_1'' - B\Delta\varepsilon_1'], \tag{2}$$

where $\Delta\varepsilon_1'$ and $\Delta\varepsilon_1''$ are, respectively, the real and imaginary parts of $\Delta\hat{\varepsilon}_1$ (Refs. 28,29). The coefficients A and B depend[21] upon the substrate dielectric function $\hat{\varepsilon}_s$ and can be computed from experimental optical data.[30] In particular, $A(B)$ depends upon the dispersive (dissipative) part of $\hat{\varepsilon}_s$ and $B = 0$ holds where the substrate is not absorbing. For KAP, at RT B is negligible up to 3.9 eV (Ref. 30). Optical data for KAP at low temperature are not available. However, given the blueshift of the absorption edge when T decreases, B should be null in the same range also at LT. Consequently, in almost the whole photon-energy range of our spectra $\Delta R/R$ is directly proportional to the deposited thickness d times the anisotropy $\Delta\varepsilon''_1$ of the imaginary part of the dielectric function of the layer, that is the layer absorption anisotropy.

In Figs. 1 and 2 we report the RAS spectra in the range from 2.9 to 4.2 eV collected at different growth stages during the deposition of a 10-nm-thick 4T film on KAP(010) at RT and at LT. The spectrum of the bare substrate displays a high-energy sharp increase due to the absorption edge of KAP, shifting with temperature. A complete RAS spectrum was collected every 1 nm nominal thickness of the film, stopping the molecular flux during measurement; then, for further deposition steps the flux was again switched on, then off to collect a new RAS spectrum, and so on. In both sets of curves, a relatively sharp band superimposed on the substrate-related background is observed: its spectral position—which shifts from 3.57 to 3.81 eV in the RT sample (Fig. 1), while it is fixed at 3.57 eV in the LT one (Fig. 2, top panel)—is clearly related to the known excitonic response of crystalline 4T (Ref. 25). First of all, its appearance in the spectra suggests a very strong anisotropy of the optical response of the 4T film along the $[001]_{\mathrm{KAP}}$ and $[100]_{\mathrm{KAP}}$ directions of the KAP substrate; then, its relatively small width is characteristic of the crystal response; finally, its spectral position is close to that of the transition to the upper Davydov component of the exciton bands originating in the crystal from the first molecular excited state of the 4T molecule.[25] In the spectra measured at LT at the very early stages of deposition also a broader and weak band is detected from about 3.1 to 3.8 eV, possibly originating from the 4T nuclei forming immediately after the first molecules reach the substrate.

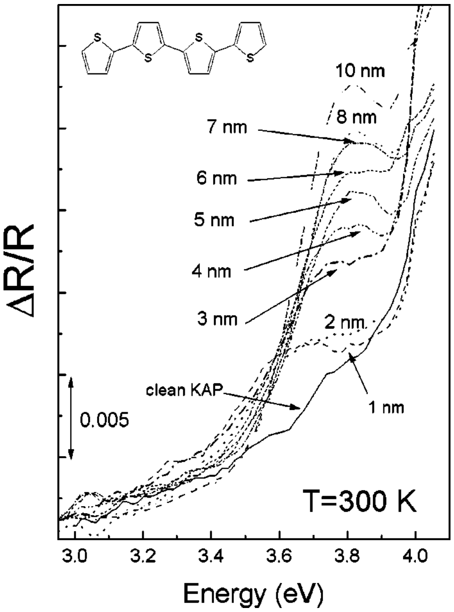

FIG. 1. RAS spectra of a 4T film grown on KAP(010) at 300 K, with thickness ranging from zero (clean KAP) up to 10 nm. Each spectrum has been collected after a single deposition step, corresponding to 1 nm nominal film thickness. At the top, the 4T molecular structure is sketched.

The shift of the exciton peak in the RT experiment is most likely the consequence of some rearrangement of the film

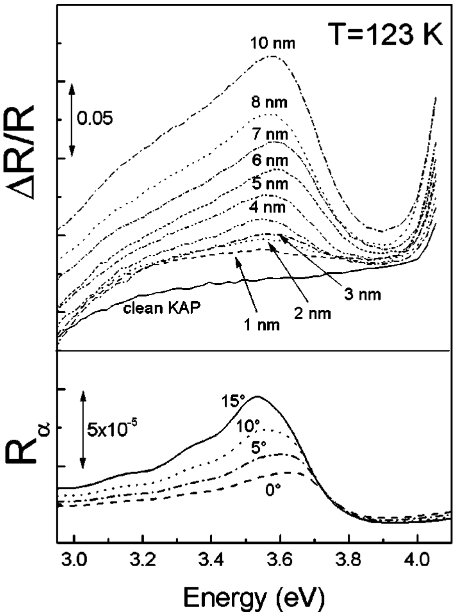

FIG. 2. Top: RAS spectra of a 4T film grown on KAP(010) at 123 K, with thickness ranging from zero (clean KAP) up to 10 nm. Each spectrum has been collected after a single deposition step, corresponding to 1 nm nominal film thickness. Bottom: Polarized reflectivity curves R_α calculated from the dielectric tensor (Ref. 36) for different rotation angles of the crystal around the $[010]_{4\mathrm{T}}$ direction.

structure during growth. The opposite behavior is observed for the LT experiment, where the same peak shows a constant position at lower energy (3.57 eV), matched also by the RT peak for film thickness below 2 nm. Such an energy position of the exciton peak, shifted by about 0.1 eV from the 3.68-eV position commonly observed[25] at normal incidence, allows to extract from RAS worthy information on the structure of the layer grown at the two temperatures.

When a highly anisotropic crystal such as 4T is concerned, the spectral position of the main peaks correlates to the way the dielectric tensor is probed by the light,[31,32] so that the observed spectral shift of the exciton peak may originate from a different orientation of the film surface. The first molecules reaching KAP arrange differently from what is usually observed *ex situ* even at RT, due to the direct interaction with the substrate surface. Indeed, at RT, where thermal energy is high enough, during deposition the 4T crystal undergoes a structural transition, while at LT the configuration of the first MLs is maintained. The interaction of the π orbitals of 4T with the KAP (010) plane, with C-H bonds protruding out of the surface, favors an arrangement of the molecules more parallel to the substrate, as is indeed observed for 4T on Ag(111) (Ref. 33) and justified on a theoretical basis.[34] In the case of 4T this tendency gives rise to the growth of needlelike crystallites which, for higher material doses, coexist with flat islands.[26] Such crystallites are extensively detected in the atomic force microscopy (AFM) images of the surface of RT samples grown in this experiment,[35] while they are absent in the LT samples; this gives a strong support to the conclusions of the present Communication, although AFM had to be carried out *ex situ*.

To check the hypothesis of a slightly modified structure, we have estimated the shift of the main peak calculating the response of a material having the dielectric tensor of 4T (Ref. 36) (i.e., the same unit cell and intermolecular distance), but exposing a high index surface (different from the $(001)_{4T}$ plane of 4T films at RT (Ref. 26), as obtained by rotating the crystal around the $[010]_{4T}$ monoclinic axis (so that the molecules are further tilted towards the substrate). Figure 2, bottom panel, shows the polarized reflectivity spectra R_α (electric field along the $[100]_{4T}$ direction) calculated for the usual 4T arrangement exposing the $(001)_{4T}$ plane (0° spectrum) and after rotating the tensor by 5°, 10°, and 15°. The observed peak shift assesses the tilt of the molecules towards the substrate as responsible for the position in the RAS spectra of the LT sample: the 10° spectrum shows the best match with the 3.57-eV experimental position. Back to the data of Fig. 1, the shift of the main peak with thickness from 3.57 up to 3.81 eV is justified, within the same frame, by a molecular tilt of about 10° towards the substrate [with respect to the usual molecular arrangement in the $(001)_{4T}$ plane] up to about 10° closer to the surface normal. Such a behavior is indeed common for rodlike conjugated molecules, which arrange in metastable structures due to kinetic effects.[37]

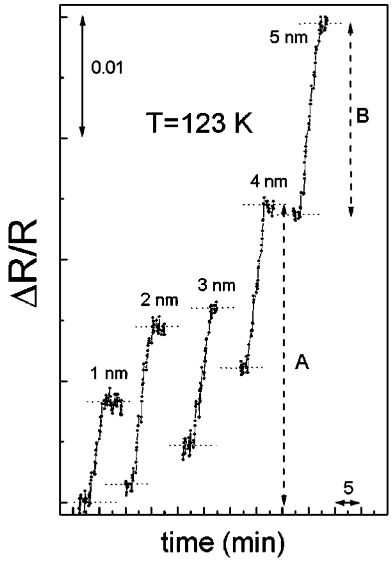

FIG. 3. Evolution of the RAS signal collected at 3.57 eV during deposition of a 4T film on KAP(010) at 123 K. The first five steps of deposition (1 nm - nominal thickness each) are reported. The horizontal dotted lines indicate the initial and the final levels of $\Delta R/R$ for each curve. The signal variations A and B correspond to the deposition of the first complete ML of 4T on KAP and of 2/3 of the second ML onto the first, respectively.

Important consequences come from the above interpretation of RAS results. During the LT experiment, a substantial increment of supersaturation is achieved by decreasing temperature while maintaining the molecular flux constant, with the direct effect of a decrease of the size of the critical nucleus down to a few molecules.[15,16,18] In such an out-of-equilibrium condition, nucleation is actually two-dimensional (2D), even if the necessary condition for a heterogeneous three-dimensional (3D) nucleation is still fulfilled [i.e., the specific energy of adhesion of 4T islands on KAP(010) is significantly lower than the surface energy of the face of 4T crystals in contact with the substrate, whatever the contact plane of 4T crystals on KAP is]. Only 2D aggregates on crystalline surfaces achieve more stable states by changing the equilibrium positions of the molecules to match the lattice parameters of the substrate (pseudomorphic growth): this is the case of 4T at LT, whose growth is actually pseudomorphic. Indeed, the 6% lattice mismatch along $[100]_{4T}$ can be totally compensated by the 10° tilt of the molecules to the substrate plane (while keeping the equilibrium distance among 4T molecules unchanged). This is actually a possibility that only anisotropic van der Waals solids possess, leading to stressed structures with a relatively low loss of cohesion energy, which can be preserved during the deposition at LT up to tens of MLs, without leading to a Stranski-Krastanov transition (the needlelike crystallites are indeed absent in the AFM images). On the contrary, at RT, where supersaturation is relatively low, heterogeneous nucleation of 3D germs of 4T is expected.[16] On KAP, which is a single crystal, the azimuthal order and texture of the growing film are then controlled by the rules of 3D epitaxy and by the energy of the interface (contact plane), respectively. On this basis, the structural rearrangement observed at RT for thickness just above 1 nm can be regarded as a phase transition driven by the increment of the volume-surface ratio in the 3D islands. When nuclei are small enough, surface effects are predominant and the film displays the same molecular arrangement found in the LT sample; on the contrary, for thicknesses above 1 nm, volume effects become predominant and the 4T molecules arrange maximizing intermolecular interactions at the expense of the molecule-substrate interaction.

To complete the picture of nucleation and growth of 4T on KAP, decisive information comes from the time evolution of the RAS signal at the peak (3.57 eV) monitored during deposition, shown in Fig. 3 for the LT deposition. The different curves refer to the successive deposition steps: for each step, the initial and final levels of signal have been indicated by horizontal dotted lines. $\Delta R/R$ always increases linearly with time (at RT a similar behavior has been observed), reflecting a linear increment of the quantity of crystallized material on the substrate surface [see Eq. (2)]. At the beginning of a single deposition stage, the RAS signal has decreased with respect to the end of the previous one, showing that 4T molecules desorb from the substrate in the interval between consecutive depositions. Desorption is indeed a rather common phenomenon for low-weight molecular materials, even at low temperature.[12–14] Only after a nominal deposition of 4 nm (step #4 in Fig. 3) $\Delta R/R$ is unaffected by desorption. Since 2D pseudomorphic growth occurs at LT, such a regime change after step #4 indicates the full coverage of the substrate. The attainment of one effective monolayer then corresponds to a RAS signal variation equal to 0.025 (*A* in Fig. 3).

Two important conclusions can be drawn from Fig. 3: (i) the adhesion energy of 4T layers is lower on the KAP surface than on the 4T crystal surface, as desorption is nearly absent after step #4; (ii) the growth of the LT sample follows a true layer-by-layer mode, as shown from the RAS signal variation *B* measured after step #4 for deposition of 1 nm (about 0.016, see Fig. 3), which scales to 0.024 for one complete ML (~1.5 nm), in agreement with the value measured for *A*. Since desorption affects the anisotropy signal, in principle it also affects the spectra in Figs. 1 and 2, and rigorously the *nominal* thickness that labels each RAS spectrum should be corrected for this effect.

In conclusion, the *in situ* and *real-time* analysis of the growth of 4T films under different conditions, carried out by RAS, is used here to demonstrate that the microscopic processes driving the film growth can be controlled by tuning growth parameters. Indeed, evidence of a change from an island growth mode at RT to a layer-by-layer pseudomorphic growth for the LT experiments is found and interpreted in terms of the formation of a coherent interface between substrate and film, attained by a tilt of the molecules. In addition, a partial desorption at the film surface is clearly observed. This permits a quantitative evaluation of the interactions of the 4T molecules either with the bare KAP or with the film surface of a fully developed 4T layer.

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[29] Formula (2) treats the bulk substrate as isotropic, an assumption that is clearly not satisfied in our case. Nevertheless, in the photon-energy range where the substrate is only birefringent (KAP is transparent up to 3.9 eV), it is possible: (i) to take into account the optical anisotropy of the bulk, for instance, by treating with the Jones method the substrate effect on the light electric field traveling through the material [see R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1980)]; (ii) to use formula 2 (as for an *isotropic* bulk) for the interpretation of the RAS spectrum originating from the layer, since the substrate birefringence has been considered separately.

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