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Abstract
Reflectance anisotropy spectroscopy (RAS) has recently been used to monitor *in situ* and *in real time* the growth of thin organic layers in ultra high vacuum (UHV) (Goletti *et al* 2003 *Appl. Phys. Lett.* **83** 4146). In this paper, after a short discussion of RAS, with particular attention to the application to organics, we present recent results on the deposition of ordered oligothiophene films by organic molecular beam epitaxy (OMBE), namely α-sexithiophene and quaterthiophene films onto potassium acid phthalate substrates.

1. Introduction

The possibility of real time monitoring during growth of materials has often been assessed to be a decisive condition to extract crucial information about process kinetics: it could offer the possibility of intervening in the deposition itself in view of a higher process control, for example for real time correction of possible errors or failures. The opportunities of molecular beam epitaxy (MBE) for growing inorganic semiconductors have been also exploited for the benefits of the *in situ* application of reflected high energy electron diffraction (RHEED) [1]. However, it has been demonstrated that optical spectroscopies, such as reflectance anisotropy spectroscopy (RAS) and ellipsometry (the former now quite commonly used on MBE reactors), represent a real alternative to electronic probes [2, 3]. Information obtained by RAS is in good agreement with the one given by RHEED: characteristic oscillations, related to the number of deposited monolayers, have been measured at well-defined photon energies during growth of III–V and II–VI materials [4–6]. Moreover, optical techniques represent a unique chance of *real time* monitoring when deposition is performed in high pressure (as in metal organic chemical vapour deposition, MOCVD) [7] or even in a liquid environment [8].

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The use of RHEED has not been extended to ultra high vacuum (UHV) deposition of organic materials [9], due to the damage that high-energy electrons could produce in soft matter. As a consequence, optical spectroscopy represents in this case probably the only real, advantageous possibility of following the kinetics of growth for organics. Different techniques have been applied to organic materials: ellipsometry [10], surface differential reflectivity (SDR) [11], RAS [12–16]. RAS offers a more straightforward interpretation of results with respect to ellipsometry, and does not need to modify the state of the surface (often irreversibly), as in SDR, to extract the contribution of the grown layer. RAS allows measuring the optical properties of a sample in real time, without any need for comparison with a reference sample, and the spectrum is meaningful *per se*, expressing the optical anisotropy of a sample along two perpendicular directions. Obviously, the possibilities of RAS are limited to anisotropic materials, however, organic molecules and layers often exhibit large optical anisotropies.

Since its early application to organics, it has been clearly shown that RAS possesses the necessary sensitivity to thickness and even to morphology for use as a monitoring technique [13]. Results obtained on organic layers deposited by the Langmuir–Blodgett (LB) and Langmuir–Schaeffer (LS) methods [15, 16] have proved that a detailed study of optical anisotropy can provide information about both structure and morphology, relating the characteristic spectral lineshape to a particular arrangement of molecules on the substrate [17]. However, LB and LS deposition techniques, capable of producing ordered layers, suffer the intrinsic limit of not being UHV compatible. We have then applied RAS to the growth of organic layers in UHV conditions by OMBE [18], obtaining very comforting results that have proven the high sensitivity of this spectroscopy. In this paper, we will briefly mention these older experiments for sexithiophene (6T), and present new data related to the OMBE deposition of a different oligothiophene molecule, namely quaterthiophene (4T).

2. Technique and apparatus

In a reflectance anisotropy spectrometer, linearly polarized light—alternatively directed along two orthogonal directions (α and β)—impinges on a surface at near normal incidence. Modulation of light polarization is accomplished via the birefringence of the transparent optical head of a piezo-elastic-modulator (PEM), oscillating at the resonance frequency $\nu/2$ [19]. The reflected beam is then collected and focused in a detector, producing a signal analysed by a lock-in amplifier. In this way one measures the variation ΔR of reflected light, modulated at frequency ν. The ratio between ΔR and the mean reflectivity value R expresses the result of the measurement:

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

where R_α (R_β) is the reflectance coefficient of the sample for light polarized along α (β). S is related to the anisotropy of the sample reflectance, nevertheless the experimental result will also contain the possible contribution of the optical apparatus, which must be eliminated or reduced. The weight of this spurious term can be evaluated just by rotating the sample by 90° around the normal to its surface: in this way, only the signal due to the anisotropy of the sample changes sign in consequence of the different geometry, while the contribution coming from optics does not, allowing the isolation of the 'true' sample anisotropy by the difference between the two spectra. However, since UHV manipulators do not always allow azimuthal sample rotation, the optical apparatus and the optical window of the chamber should be 'birefringence-free'. At the moment, low-birefringence quartz viewports are commercially available for the range 0.7–5.5 eV [20]. To perform measurements at lower energies, we have built a low-strain CaF_2 window that introduces a structureless background lower than 0.001 up to 0.3 eV.

When an organic layer of thickness $d \ll \lambda$ (λ being the wavelength of light) is deposited on a substrate, $\Delta R/R$ can be expressed in terms of the complex dielectric function anisotropy $\Delta \hat{\varepsilon}_1$ of the growing layer [21]:

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

where $\Delta \varepsilon_1'$ and $\Delta \varepsilon_1''$ are, respectively, the real and imaginary part of $\Delta \hat{\varepsilon}_1$. The coefficients

$$A = \frac{\varepsilon_s' - 1}{(1 - \varepsilon_s')^2 + \varepsilon_s''^2} \qquad \text{and} \qquad B = \frac{\varepsilon_s''}{(1 - \varepsilon_s')^2 + \varepsilon_s''^2} \tag{3}$$

contain the dependence upon the substrate dielectric function, and can be computed from experimental optical data. In particular, A (B) mainly depends upon the dispersive (dissipative) part of $\hat{\varepsilon}_s$. In general, A and B are different from zero, both contributing to form the $\Delta R/R$ signal; consequently, we have to perform Kramers–Kronig analysis of $\Delta R/R$ spectra to obtain $\Delta \hat{\varepsilon}_1$ [22]. $B = 0$ holds where the substrate is not absorbing: in this simpler case, $\Delta R/R$ is directly proportional to the deposited thickness d times the imaginary anisotropy $\Delta \varepsilon_1''$, which is the layer absorption anisotropy.

Introducing the complex Fresnel coefficients r^α and r^β of the sample for light polarized along α and β, we define the complex quantity

$$\Delta r/r = 2(r^\alpha - r^\beta)/(r^\alpha + r^\beta). \tag{4}$$

If the optical elements of the experimental apparatus are expressed by the Jones matrix formalism [23, 24], one obtains that the real and imaginary parts of $\Delta r/r$ are modulated at different frequencies: ν for the real part, $\nu/2$ for the imaginary part [24]. Consequently, they can be detected separately by a lock-in technique, opportunely choosing the reference frequency. For more details, the reader should consult [24].

In the limit of small anisotropies (an assumption that is usually correct in the case of semiconductors and metal surfaces, but of dubious validity for organic materials) the real part is simply related to the anisotropy of the reflected intensity, and the imaginary part to the phase of the signal:

$$\Delta r/r = \Delta R/2R + i\Delta\theta. \tag{5}$$

Since in organic materials large anisotropy signals are often measured, one could wonder what can be considered 'small'. In [25] an upper limit equal to 0.2 has been quantified by the authors, beyond which formula (5) is no longer correct, since higher order terms should be considered to expand $\Delta r/r$. Nevertheless, we remark that:

(i) *in any case* the modulation of the sample reflectance ΔR is measured by the lock-in tuned at twice the PEM resonance frequency;
(ii) *in any case* the experimental result expressed in terms of $\Delta R/R$ is the meaningful expression of the sample reflectance anisotropy.

$\Delta R/R$ spectra presented in this paper have been measured in the visible–near UV range (250–800 nm, or 1.5–5.5 eV) by using a compact spectrometer consisting of a xenon lamp, a grating monochromator, CaF_2 lenses to collect and focus light, a home-made PEM and a photomultiplier. Optical fibres were used to guide light from the lamp to the monochromator and then to the PEM.

Two different experimental configurations can be adopted: in the first version (2P, originally proposed by Aspnes and co-workers [4, 7]), two polarizers are used, one to define the linear polarization of incoming light, the other (analyser) to analyse the state of polarization of the outcoming beam; in the second apparatus (1P, [26]) only one polarizer is necessary.

The two configurations are completely equivalent when Re $(\Delta r/r)$ or $\Delta R/R$ are concerned. But only with 2P can one measure also the imaginary part of $\Delta r/r$, useful to obtain directly both the real and imaginary part of the sample anisotropic optical functions. The presence of possible errors in the optics (misalignment of polarizers, PEM, sample, not ideal efficiency of the optical elements, etc) introduces correction terms that are of the first order when the 2P configuration is utilized for measurements, and of the second order when the 1P configuration is preferred [24]. From this finding one should conclude that 1P apparatus is less exposed to consequences of experimental mistakes. Nevertheless, it is still convenient to use 2P when the optical alignment obliges one to use mirrors after the sample reflection, or when detector window is birefringent.

The electronic apparatus of our set-up (using a real-time feed-back to maintain a constant photocurrent from the detector) has been recently redesigned and miniaturized to be compatible with a completely transportable system. In the near future, the range of measurements will be extended up to 0.6 eV by changing the monochromator and detector. We have recently developed a prototype to perform RAS experiments in IR up to 4 μm, particularly promising for organics investigation [27].

3. Experimental details

In the present study quaterthiophene (4T) and sexithiophene (6T) have been used as molecular material, the former synthesized and purified according to a recently optimized procedure [28], the latter synthesized according to the standard procedure [29] and purified by sublimation. Thin films were grown in ultra-high vacuum (UHV) by OMBE under 5×10^{-10} Torr base pressure, with deposition temperature and deposition rate equal, respectively, to 290 °C and 3 Å min^{-1} for 6T, and 170 °C and 3 Å min^{-1} for 4T. A quartz microbalance calibrated for 4T or 6T deposition and installed close to the substrate has been used to measure the nominal film thickness.

The choice of substrate is fundamental to obtain a well-ordered layer. As an example, we report in figure 1 two spectra, the former measured at an oxidized Si(001), usually used as a reference for its optical isotropy producing a structureless and nearly flat spectrum in the range 1.5–5.5 eV, and the latter after deposition of a 50 Å thick layer of quaterthiophene. An absolutely negligible variation of the optical anisotropy is detected by RAS, the consequence of a very slight degree of order in the layer. By contrast, if the same amount of material is deposited onto a (010)-oriented single crystal of potassium acid phthalate (KAP), the growth produces a high degree of order, evident in RAS spectra (see below) as well as in atomic force microscope (AFM) images of the sample after growth and in absorption spectra [30]. Similar results hold also for deposition of 6T on KAP. In fact, KAP induces a preferential orientation of the organic polycrystalline film and the in-plane anisotropy (complete in the case of 4T) of its macroscopic optical response. Given our knowledge of the structure being stable at room temperature (RT) and the unit cell orientation in the films of 6T [31] and 4T [32], one monolayer (ML) at RT can be considered 15.3 Å (22 Å) thick for 4T (6T). Finally, in our experiment, directions α and β are nearly parallel to the a and c axes of the KAP substrate crystal lattice [33].

The coefficients A and B, which contain the dependence upon the substrate dielectric function, can be computed from experimental optical data [34]. For KAP, B is approximately null up to 3.9 eV at room temperature. Optical data for KAP at low temperature are not available, however (given the blue-shift of the absorption edge when T decreases) it is very likely that B is null in the same range. Consequently, in about the whole photon energy range of our spectra $\Delta R/R$ is directly proportional to the deposited thickness d times the
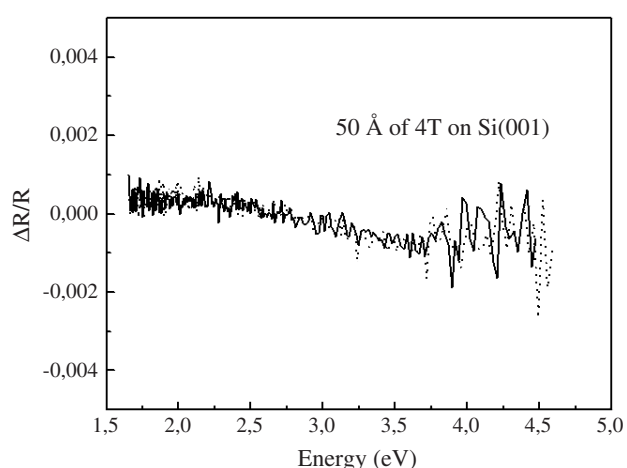
Figure 1. $\Delta R/R$ spectra measured on an oxidized Si(001) surface: (a) before (full curve) and (b) after (dotted curve) deposition of a 50 Å thick layer of 4T in UHV. In this case optical anisotropy has been measured along the [$\bar{1}$10] and [110] directions of the Si surface.
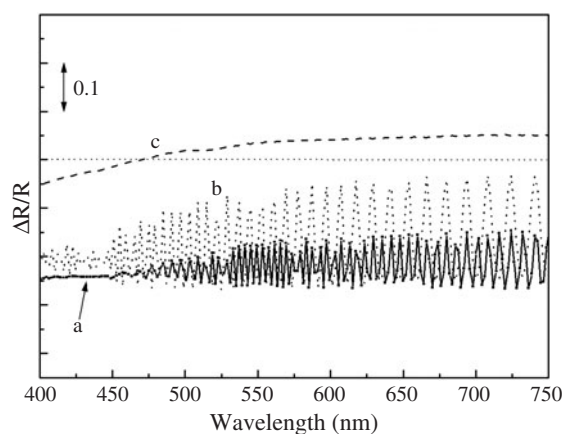
Figure 2. $\Delta R/R$ spectra measured *in air* on a (010) KAP substrate used for the UHV growth of oligothiophene layers: (a) with two polarizers (polarizer + analyser), in reflection (full curve); (b) with two polarizers in transmission (dotted curve); (c) with one polarizer (without analyser), in reflection. The distance between two adjacent maxima (or minima) doubles when passing from spectrum a to spectrum b, as the effective sample thickness halves. In spectrum c, the dominant oscillations due to the KAP birefringence are no longer visible, as the second polarizer has been removed. The dotted horizontal line represents the experimental 'zero'.

imaginary anisotropy $\Delta\varepsilon_1''$. The anisotropic structure of KAP, forcing the molecules to be oriented, generates its optical properties. KAP is transparent in the range 1.55–3.35 eV, with a sharp absorption edge at about 3.55 eV (at room temperature), but is birefringent. The effect of KAP birefringence in $\Delta R/R$ is represented in figure 2 via the strong oscillations visible in the spectrum for $\lambda > 400$ nm [18]. Indeed, in the transparency region, light travels through the whole sample and is then reflected, producing a phase shift $\Delta\Phi$ between the polarized electric fields vibrating along the optical axes a and c of the KAP plate. In its turn, $\Delta\Phi$ changes continuously with wavelength λ, varying the polarization of the outcoming beam with respect
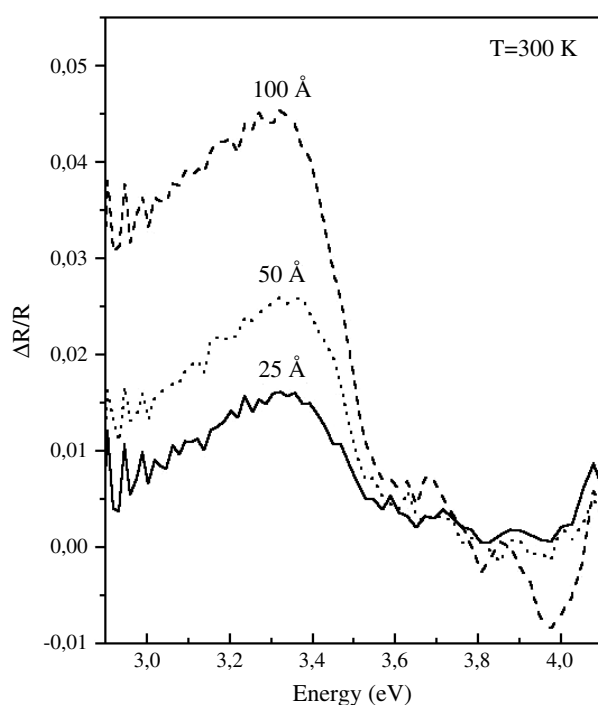
Figure 3. Difference—with respect to the substrate spectrum (not reported)—of experimental $\Delta R/R$ spectra collected in UHV at different growth stages of 6T on (010) KAP: (1) after deposition of 25 Å of 6T (about 1 ML); (2) after deposition of 50 Å of 6T (about 2 ML); (3) after deposition of 100 Å of 6T (about 4 ML). The substrate temperature was 300 K.

to the second polarizer, thus producing the oscillations. It is possible to demonstrate that the distance $\Delta\lambda$ between two adjacent maxima (or minima) depends upon $1/d_{sub}$ (d_{sub} being the substrate thickness). Actually, when transmission spectra are recorded from the same sample, $\Delta\lambda$ doubles as the effective thickness is halved (figure 2, spectra (a) and (b)). As a convincing check, if the second polarizer is eliminated, oscillations disappear (figure 2, spectrum (c)). However, in our OMBE experiments the use of the second polarizer has been necessary to avoid spurious anisotropy due to the optics, in particular for the presence of a plane mirror after the sample to collect efficiently the beam from the UHV chamber to the detector. Finally, we note that the signal oscillations are an unwanted outcome of the experiment, as they partially limit the spectral range where RAS may be used to monitor the film growth. Nonetheless, in the case of several crystalline oligothiophenes, and in particular of 4T and 6T, the most intense structures are observed around 3.2–3.5 eV, where the strong response related to the molecular exciton dominates. In this range, oscillations are strongly damped in $\Delta R/R$ signal.

4. Results and comments

RAS experiments on UHV deposition of sexithiophene layers at room temperature have been the first application of this spectroscopy to study *in situ* the OMBE process, and have been discussed elsewhere [18]. Here we will just mention that a marked anisotropy signal, related to the main exciton transition of the molecule, has been measured at about 3.34 eV, with amplitude increasing nearly proportional to the nominal deposited thickness. To cancel the contribution of the substrate, in figure 3 we have subtracted the RAS spectrum measured at clean KAP from
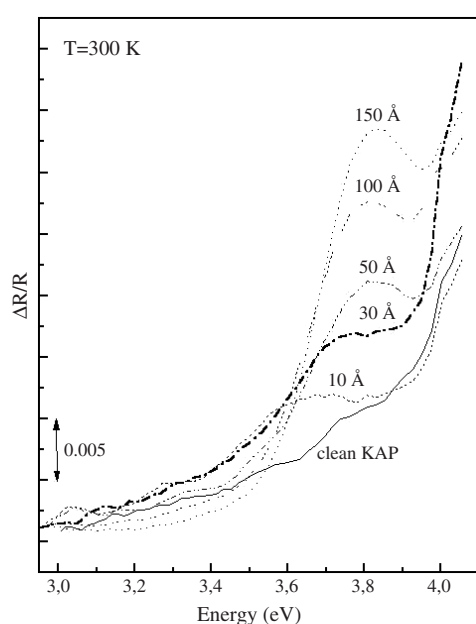
Figure 4. Experimental $\Delta R/R$ spectra measured during OMBE deposition of 4T layers onto a clean (010) KAP substrate at 300 K. During a single deposition stage 10 Å of organic material was deposited. Only a restricted set of spectra has been reported: (1) clean KAP substrate; (2) after growth of a 10 Å thick layer; (3) after growth of a 30 Å thick layer; (4) after growth of a 50 Å thick layer; (5) after growth of a 100 Å thick layer; (6) after growth of a 150 Å thick layer. The complete set of spectra has been reported and discussed in [36].
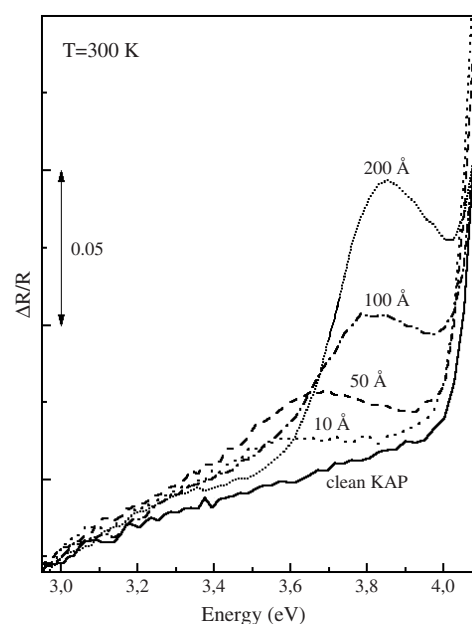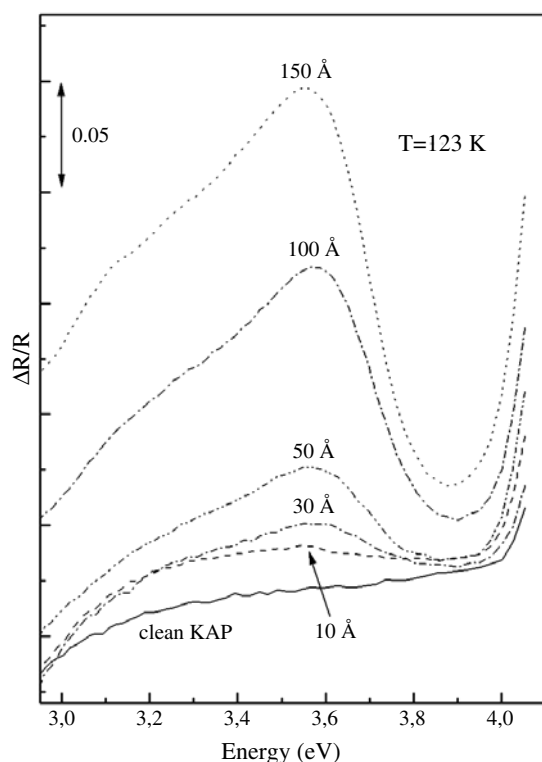
Figure 5. Experimental $\Delta R/R$ spectra measured during OMBE deposition of 4T layers onto a clean (010) KAP substrate at 300 K. At variance with figure 4, after the very first deposition stages, a single bunch of 50 Å of organic material has been deposited. Only a restricted set of spectra has been reported: (1) clean KAP substrate; (2) after growth of a 10 Å thick layer; (3) after growth of a 50 Å thick layer; (4) after growth of a 100 Å thick layer; (5) after growth of a 200 Å thick layer.

spectra taken after deposition of a certain thickness of 6T (25 Å, about 1 ML; 50 Å, 2 ML; 100 Å, 4 ML). The limited thickness range investigated does not allow us to reach conclusions about the growth mode of the system, studying the connection between the signal amplitude and the thickness, although the slight shift of the main peak towards lower energy (about 50 meV) as well as the augmenting broadening of the curve could originate from a structural or morphological rearrangement of the 6T crystalline film, varying the optical properties of the sample.

In a further experiment, we have more carefully studied the evolution of the spectral lineshape with thickness. Moreover, we have deposited the oligothiophene molecules (in this case quaterthiophene, 4T) at two different substrate temperatures, 300 and 123 K (thereafter mentioned as RT and LT, respectively), to take account of possible thermal effects.

In figure 4 we report RAS spectra collected at different growth stages during deposition of a 150 Å thick 4T film on (010) KAP at RT. A complete RAS spectrum was collected every 10 Å nominal thickness of the film, stopping the molecular flux during measurement. However, just a limited set of spectra has been drawn in figure (clean KAP, 10, 30, 50, 100, 150 Å). For the clean substrate, the RAS signal increases sharply at high photon energy due to the absorption edge of KAP. It is apparent that a relatively sharp band superimposed to the substrate-related background is observed to increase with thickness: its spectral position—shifting from 3.57 eV (10 Å) to 3.83 eV (150 Å)—is well related to the known exciton response of crystalline 4T [35].

Figure 6. Experimental $\Delta R/R$ spectra measured during OMBE deposition of 4T layers onto a clean (010) KAP substrate at 123 K. During a single deposition stage 10 Å of organic material was deposited. Only a restricted set of spectra has been reported: (1) clean KAP substrate; (2) after growth of a 10 Å thick layer; (3) after growth of a 30 Å thick layer; (4) after growth of a 50 Å thick layer; (5) after growth of a 100 Å thick layer; (6) after growth of a 150 Å thick layer. The complete set of spectra has been reported and discussed in [36].

As a comment, its appearance in the spectra suggests a clear anisotropy of the optical response of the 4T film along the *a* and *c* directions of the KAP substrate, while the relatively small width is characteristic of the crystal order.

We have performed a second experiment at RT using a larger deposition step, 50 Å (thereafter indicated as *fast deposition*) instead of 10 Å (*slow deposition*). The spectra, covering a slightly larger coverage range (0–200 Å), are shown in figure 5. It is evident that the overall behaviour is similar to the case of the *slow deposition*: a large band appears at about 3.55 eV, then shifts towards higher photon energies with increasing thickness. However, two distinct peculiarities are apparent: the shift of the peak is more gradual than in the *slow* case (after 50 Å it is not yet pinned), and the total anisotropy is larger.

When *slow* deposition has been performed at LT, a very different dependence of the spectra upon layer thickness has been recorded (figure 6). A broad band is detected, centred at about 3.6 eV. This band does not shift with thickness, always peaking at the same position. The anisotropy is very high, witnessing an extended order of the layer. When the final sample (covered with 150 Å) is heated from LT to RT (always in UHV) the spectrum continuously modifies its lineshape and position, reaching 3.83 eV, which is the energy position measured for the peak in the RT deposition (see figures 4 and 5), a very likely consequence of a structural rearrangement of the layer.

The most evident result coming from a comparison of experiments performed at different substrate temperatures is the behaviour of the peak position. In normal incidence reflectivity measurements for the (001) plane of a 4T crystal, the exciton peak appears at 3.68 eV, to be compared with: (i) 3.57 eV, measured at all stages of deposition at LT; (ii) about 3.6 eV, recorded just at the beginning of growth at RT (after deposition of 10 Å), both for *fast* and *slow* deposition; (iii) in about 3.8 eV, measured for the higher coverage regime at RT. Given the anisotropic optical properties of the growing crystal, we interpret the spectral shift of the exciton peak as originated from a different orientation of the molecules at the substrate surface. From *ex situ* measurements, it is known that 4T molecules are arranged with their axis tilted from the normal to the surface plane [32]. The temperature of the substrate and the UHV condition of growth could promote an arrangement of the layer different from what usually observed *ex situ* at RT. This means that at LT the configuration of the first ML should be different from RT; moreover, it is maintained up to further layers (as deduced from the constant position of the peak). We have estimated which is the spectral shift that one should expect for a layer with the same dielectric tensor of 4T (same unit cell and intermolecular distance) but with molecules tilted to assume a configuration more parallel to the substrate surface. This is actually a possibility that only such anisotropic van der Waals solids possess, leading to stressed structures with a relatively low loss of lattice energy, which can be preserved during the deposition at LT up to tens of MLs, without leading to a Stranski–Krastanov growth mode. As a result, the best fit of the experimental 3.57 eV position comes out from an additional rotation of molecules by 12° towards the substrate plane. Within the same scenario the peak at 3.81 eV is interpreted as due to molecules oriented closer to the surface normal, a behaviour that is quite common in a rod-like π-conjugated molecule as 4T, related to a kinetic effect due to the higher T leading to a metastable structure.

The consequences of this interpretation of RAS data are significant for the comprehension of the 4T OMBE growth. Since this topic is discussed extensively elsewhere [36], without going into detail we just report the main conclusions: the growth process of 4T on KAP is described in terms of a layer-by-layer mode when the substrate is at LT, in terms of an island mode at RT. In this respect, the structural rearrangement observed at RT for thickness just above 10 Å 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 at RT the film displays the same molecular arrangement found in the LT sample; by contrast, for thicknesses above 10 Å, volume effects become predominant and the 4T molecules arrange in a way that maximize intermolecular interactions at the expense of the molecule–substrate interaction.

In conclusion, the application of RAS to OMBE deposition of ordered quaterthiophene and sexithiophene layers has proved that this is an excellent spectroscopy for monitoring the UHV growth of organic layers *in situ* and *in real time*, and for studying the kinetics of deposition, i.e. the evolution of the structure, morphology and electronic properties of the layer *during growth*. In particular, the UHV deposition of thin layers of 4T has been studied *in situ* for the first time, showing that growth of 4T is layer-by-layer at 123 K. This result proves that by changing the substrate temperature the growth mode of the organic layer can be tuned, with exciting consequences for the possible development of real organic devices.

References

[1] Herman M A, Richter W and Sitter H 2004 *Epitaxy: Physical Principles and Technical Implementation* (Berlin: Springer)

[2] Chiaradia P and Del Sole R 1999 *Surf. Rev. Lett.* **6** 517 and references therein

[3] McGilp J F 1990 *J. Phys.: Condens. Matter* **2** 7985

[4] Harbison J P, Aspnes D E, Studna A A, Florez L T and Kelly M K 1988 *Appl. Phys. Lett.* **52** 2046

[5] Zhang J, Taylor A G, Lees A K, Fernandez J M, Joyce B A, Raisbeck D, Shukla N and Pemble M E 1996 *Phys. Rev.* B **53** 10107

[6] Hingerl K, Balderas-Navarro R E, Bonanni A and Sifter D 2001 *J. Vac. Sci. Technol.* B 1650

[7] Aspnes D E, Bhat R, Colas E, Keramidas V G, Koza M A and Studna A A 1989 *J. Vac. Sci. Technol.* A **7** 711
Richter W 1993 *Phil. Trans. R. Soc.* A **344** 453

[8] Berkovits V L, Gusev A O, Lantratov V M, L'vova T V, Pushnyi A B, Ulin V P and Paget D 1996 *Phys. Rev.* B **54** R8369

[9] Forrest S R 1997 *Chem. Rev.* **97** 1793

[10] Kampen T U, Paraian A M, Rossow U, Park S, Salvan G, Wagner Th, Friedrich M and Zahn D T 2001 *Phys. Status Solidi* a **188** 1307
Tsankov D, Hinrichs K, Roseler A and Korte E H 2001 *Phys. Status Solidi* a **188** 1319

[11] Nitsche R, Proehl H and Fritz 2003 *NATO Science Series 100: Organic Nanophotonics* ed F Charra, V M Agranovich and F Kajzar (Dordrecht: Kluwer) pp 103–17

[12] Pemble M E, Turner A R, Shukla N, Bitzer T, Frederick B G, Kitching K J and Richardson N V 1995 *J. Chem. Soc. Faraday Trans.* **91** 3627

[13] Frederick B G, Power J R, Cole R J, Perry C C, Chen Q, Haq S, Bertrams Th, Richardson N V and Weightman P 1998 *Phys. Rev. Lett.* **80** 4470

[14] Miller E K, Hingerl K, Brabec C J, Heeger A J and Sariciftci N S 2000 *J. Chem. Phys.* **113** 789

[15] Di Natale C, Goletti C, Della Sala F, Drago M, Chiaradia P, Paolesse R, Lugli P and D'Amico A 2000 *Appl. Phys. Lett.* **77** 3164

[16] Goletti C, Paolesse R, Dalcanale E, Berzina T, Di Natale C, Bussetti G, Chiaradia P, Froiio A, Cristofolini L, Costa M and D'Amico A 2002 *Langmuir* **18** 6881 and references therein

[17] Castillo C, Vázquez-Nava R A and Mendoza Bernardo S 2003 *Phys. Status Solidi* c **0** 2971

[18] Goletti C, Bussetti G, Chiaradia P, Sassella A and Borghesi A 2003 *Appl. Phys. Lett.* **83** 4146

[19] Kemp J C 1969 *J. Opt. Soc. Am.* **59** 950
see also http://www.hindspem.com

[20] Studna A A, Aspnes D E, Florez L T, Wilkens B J, Harbison J P and Ryan R E 1989 *J. Vac. Sci. Technol.* A **7** 3291

[21] Selci S, Ciccacci F, Chiarotti G, Chiaradia P and Cricenti A 1987 *J. Vac. Sci. Technol.* A **5** 327 and references therein

[22] Goletti C, Arciprete F, Almaviva S, Chiaradia P, Esser N and Richter W 2001 *Phys. Rev.* B **64** 193301

[23] Azzam R M A and Bashara N M 1977 *Ellipsometry and Polarized Light* (Amsterdam: North-Holland)

[24] Salvati A and Chiaradia P 2000 *Appl. Opt.* **39** 5820

[25] Acher O and Drevillon B 1992 *Rev. Sci. Instrum.* **63** 5332

[26] Berkovits V I, Kiselev V A and Safarov V I 1989 *Surf. Sci.* **211/212** 489 and references therein

[27] Goletti C, Bussetti G, Arciprete F, Chiaradia P and Chiarotti G 2002 *Phys. Rev.* B **66** 153307

[28] Trabattoni S *et al* 2004 *J. Mater. Chem.* **14** 171

[29] Garnier F, Yassar A, Hajlaoui R, Horowitz G, Deloffre F, Servet B, Ries S and Alnot P 1993 *J. Am. Chem. Soc.* **115** 8716

[30] Sassella A, Borghesi A, Spearman P and Tavazzi S 2002 *Eur. Phys. J.* B **28** 385

[31] Campione M, Borghesi A, Moret M and Sassella A 2003 *J. Mater. Chem.* **13** 1669

[32] Horowitz G, Bachet B, Yassar A, Lang P, Demanze F, Fave J and Garnier F 1995 *Chem. Mater.* **7** 1337

[33] Sassella A *et al* 2003 *Synth. Metals* **138** 125

[34] Eremina T A, Furmanova N G, Lakakhova L F, Okhrimenko T M and Kuznetsov V A 1993 *Crystallogr. Rep.* **38** 554

[35] Sassella A, Borghesi A, Wagner Th and Hilfiker J 2001 *J. Appl. Phys.* **90** 3838

[36] Sassella A, Campione M, Moret M, Borghesi A, Goletti C, Bussetti G and Chiaradia P 2004 *Phys. Rev. Lett.* submitted