Available online at www.sciencedirect.com

SCIENCE DIRECT®

Organic Electronics 5 (2004) 73–81

Organic Electronics

www.elsevier.com/locate/orgel

The application of reflectance anisotropy spectroscopy to organics deposition

C. Goletti [a,*], G. Bussetti [a], P. Chiaradia [a], A. Sassella [b], A. Borghesi [b]

[a] *Dipartimento di Fisica and Unità INFM, Università di Roma "Tor Vergata", Via della ricerca Scientifica 1, I-00133 Roma, Italy*

[b] *Dipartimento di Scienza dei Materiali and Unità INFM, Università di Milano-Bicocca, Via Cozzi 53, I-20125 Milano, Italy*

Received 25 June 2003; received in revised form 7 January 2004; accepted 17 January 2004

Abstract

Reflectance anisotropy spectroscopy (RAS) has been recently used to investigate organic compounds, similarly to what has been already done in the case of inorganic semiconductors and metals. An important development is the application of RAS to monitor *in real time* the growth of thin organic layers in ultra-high vacuum (UHV). In this paper, we discuss the main characteristics of RAS spectroscopy, underlining its peculiar advantages with respect to other techniques. Then, we present recent results obtained by following *in situ* the deposition of an ordered organic film in UHV, namely α-sexithiophene films onto potassium acid phthalate.

PACS: 78.20.−e; 78.66.Qn; 81.15.−z; 81.15.Ef

Keywords: Organic layer growth; Organic molecular beam deposition; Real-time monitoring of growth; Reflectance anisotropy spectroscopy; Oligothiophenes; Langmuir–Blodgett layers

---

1. Introduction

In recent years, a noteworthy research activity has grown about molecular materials, in particular some families of conjugated molecules, polymers and oligomers (e.g. oligo- and poly-thiophene [1,2]) exhibiting semiconducting properties. Their solid phase is suitable for applications in optical and electronic devices [1,3,4] whose performances, however, are not yet competitive with respect to their inorganic counterparts. Promising results have been recently obtained, supporting further research.

Most of the activity is devoted to the determination and control of the solid-state properties of these materials, in turn related to the properties of the constituent molecules, isolated or in solution. Once the relationship between the molecule and the corresponding solid has been established, the solid-state properties could be designed and finely tuned.

A relevant limit about organic materials is represented by the low level control of their structural quality, since deposition is usually achieved by methods rather simple and easy to use, such as spin coating and casting from solution. On the other hand, a technique—namely Langmuir–Blodgett

---

[*] Corresponding author. Tel.: +39-06-72594288; fax: +39-06-2023507.

E-mail address: goletti@roma2.infn.it (C. Goletti).

1566-1199/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.orgel.2004.01.002

(LB) deposition—that allows a high order in the structure of the deposited film, is limited to soluble molecules with proper hydrophilic and hydrophobic groups, and in addition produces just a few molecular layers. Considering that technological applications in semiconductor devices require crystalline materials of different molecular compounds exhibiting a high structural quality and a certain thickness, these techniques are not appropriate for sample preparation. Moreover, the possibility of growing an organic film under high control is a difficult task if there are not experimental techniques available for the characterization of samples *in situ* and *in real time*, with a proper sensitivity down to very thin layers [5].

Organic molecular beam deposition (OMBD [6–8])—developed from molecular beam epitaxy (MBE) used for inorganic semiconductors [9]—has demonstrated to be a growth technique particularly suitable to reach a fine control of thin molecular films in terms of composition, homogeneity, structure, morphology and thickness. In OMBD the molecules are sublimated in ultra-high vacuum (UHV) environment (10^{-10} Torr or better) by heating the source up to a properly selected temperature. The molecular beam (whose density is related to the sublimation temperature) reaches the substrate, where the solid film grows. Different choices of the deposition conditions and of the substrate result in films with very different structural, optical and transport properties [10–14].

The aim of OMBD-based research is to find the best growth conditions for obtaining particular properties of the solid molecular films, and to use such conditions for growing very high quality samples.

Several experimental techniques, originally developed for *in situ* analysis during MBE deposition, have been slightly modified, when possible, for application in OMBD systems [6,9]. As an example, we cite electron diffraction techniques with high-energy beams in reflection (reflected high-energy electrons diffraction, RHEED). RHEED, on the other hand, is at present only rarely used in OMBD for *real-time* monitoring since it often produces damage of the soft organic materials. It is usually applied to check the substrate conditions prior to deposition or to grow test samples [6].

Optical techniques are appropriate to investigate molecular solid films, and offer several advantages with respect to other spectroscopies, avoiding contaminants and damage of the sample, being utilizable in vacuum and on insulating samples, giving the possibility to study buried interfaces and various surface morphologies [15]. Among optical methods, ellipsometry is very powerful and sensitive, giving complete information on the optical properties of materials (isotropic and anisotropic), multilayers, and in general samples whose characteristics vary with thickness [16]. Since about a decade, ellipsometry has been also used for *in situ* and *real time* growth control in MBE systems [17] and is therefore appropriate for OMBD. However, ellipsometric quantities "as measured" are not easily interpreted, and require modeling the sample and its dielectric tensor to extract meaningful information [18,19].

Reflectance anisotropy spectroscopy (RAS) has been originally applied to semiconductor and metal surfaces [20–22], metal–semiconductor interfaces [23], heterojunctions [24], and recently used to study successfully organic layers [25–32]. It is a modulation technique, that measures the reflectance difference between light polarized along two orthogonal directions on the sample surface. It gives no signal on amorphous or randomly oriented microcrystalline samples, while, on the contrary, is very sensitive when applied to systems that, after deposition, display a preferential alignment. Recent RAS results obtained on Langmuir–Blodgett layers have demonstrated that also for a film grown on not ordered substrates (as glass and polycrystalline metals), where an average order is driven by the deposition technique itself or by self-assembly of the molecules, a detailed study of the optical anisotropy can provide information about its structure and morphology [30–32].

The natural evolution of these results is the use of RAS for *real-time* monitoring of the controlled growth of thin molecular films under UHV conditions [26,27], as already demonstrated for inorganic semiconductors deposition [20,33–35]. With respect to ellipsometry, RAS exhibits a noteworthy advantage, since it provides spectra straight related to the sample properties, i.e. the sample optical anisotropy along two orthogonal directions. Given its high sensitivity to thickness, RAS can detect and study the very first molecular layers, whose arrangement on the substrate varies with the deposition conditions, types of molecules and substrate, influencing the subsequent layers. Obviously, the information brought out by RAS must be integrated with data from other techniques (STM, AFM, photo-emission). Significant results should come from the application of reflection absorption infra red spectroscopy (RAIRS) in conjunction with RAS: being sensitive to the vibrational properties of the layer, RAIRS could provide information about the identification and orientation of the deposited molecules, moreover having an experimental geometry fully compatible with RAS acquisition [36].

This effort will certainly help to understand what RAS is able to detect in the structural and electronic properties of the organic layer, and to comprehend the capabilities and limits of this spectroscopy when applied to organics.

2. Reflectance anisotropy spectroscopy

In RAS, the linear polarization of light impinging onto the sample is modulated at the frequency v between two orthogonal directions (α and β). Such a modulation is accomplished via the birefringence of the transparent optical head of a photo-elastic-modulator (PEM), oscillating at the resonance frequency $v/2$ [37]. A lock-in amplifier, measuring the signal modulation ΔR, detects the reflected light. The result of the RAS measurement is expressed by the ratio between ΔR and the mean reflectance R of the sample: $S(\hbar\omega) = \Delta R/R$, where $\hbar\omega$ is the photon energy. The signal S is modulated at frequency v.

If we introduce the complex Fresnel coefficients r^{α} and r^{β} of the sample for light polarized along directions α and β, we define the complex quantity:

$$\Delta r/r = 2(r^{\alpha} - r^{\beta})/(r^{\alpha} + r^{\beta}) \tag{1}$$

The real and imaginary part of $\Delta r/r$ are modulated at different frequency: v for $\mathrm{Re}(\Delta r/r)$, $v/2$ for $\mathrm{Im}(\Delta r/r)$ [38].

In the limit of small anisotropies (as for semiconductors and metal surfaces), the real part is related to the anisotropy of the reflected intensity, and the imaginary part to the phase term of the signal [38]:

$$\begin{aligned}\Delta r/r &= \mathrm{Re}(\Delta r/r) + \mathrm{i}\,\mathrm{Im}(\Delta r/r)\\ &= \Delta R/2R + \mathrm{i}\Delta\theta\end{aligned} \tag{2}$$

Tuning the lock-in amplifier to the correct reference frequency, it is possible to extract $\mathrm{Re}(\Delta r/r)$. If one takes into account possible errors in the optics (due to misalignment of polarizers, PEM, sample, not ideal efficiency of the optical elements, etc.) corrections due to these imperfections are of the first order in $\Delta r/r$ when the two polarizers configuration (2P, polarizer and analyser) is used for measurements, while they enter as a second order term when the one polarizer configuration (1P) is preferred [38].

Actually, 1P and 2P configurations are completely equivalent when $\mathrm{Re}(\Delta r/r)$ is concerned. Under this point of view, 1P allows avoiding a second polarizer (usually costly) and is less exposed to consequences of experimental mistakes. Nevertheless, it is still convenient to use 2P: (i) when the imaginary part of $\Delta r/r$ is necessary to obtain both the real and imaginary part of the anisotropic sample optical functions; (ii) when the optical alignment obliges the use of mirrors after the second polarizer, or when the birefringence of the detector window is not negligible.

We will not enter into further details of the experimental apparatus. We only mention that, while RAS spectra are usually measured in the visible-near UV range (250–800 nm), a prototype has been recently developed to extend the spectral range up to 4 μ, particularly promising for organics investigation [39].

3. The application of reflectance anisotropy spectroscopy to organics

The very first RAS study of organics dates back to 1995, when the adsorption of O_2HCO_2H and $C_6H_5CO_2H$ on Cu(1 1 0) was monitored in UHV by using a HeNe laser-based system operating at fixed wavelength [25]. A few years later, Weightman and coworkers reported a study of the azimuthal dependence of the optical reflectance anisotropy for anthracene and 3-thiophene carboxylate layers deposited in UHV onto Cu(1 1 0) [26,27].

RAS has been also applied to characterize layers of sapphyrin (an aromatic system similar to porphyrin) deposited onto a polycrystalline metal substrate by the LB method [30]. The RAS signal shows an evident anisotropy, increasing with thickness, in coincidence with the main absorption of the molecule (Fig. 1). The line shape of the spectrum is well reproduced by calculations, by using a three layers model [40] with a thin organic layer onto a gold substrate (Fig. 2). The optical properties of the sapphyrin molecule have been evaluated by a semiempirical quantum chemistry approach (INDO/SCI method) [41]. The good agreement between experiment and fit shows that the RAS signal mainly comes from the anisotropy of the sapphyrin molecule itself.

A larger anisotropy has been measured at LB [31] and Langmuir–Schaeffer [32] layers of porphyrins. Experimental RAS spectra display a particular line shape dependence upon the deposited thickness, passing from an appearance similar to the absorption curve (absorption-like), to an evident derivative behaviour (derivative-like). In this case, the origin of the signal has been interpreted as due to the ordered superstructure of the layer after growth, very likely producing a strong interaction between adjacent macrocycles. There is a critical value of the coverage after which the line shape passes from absorption-like to derivative-like appearance (Fig. 3). As tested by atomic force microscope (AFM) data, the measured thickness value of the layer augments, since the molecules—adsorbed on the substrate with a certain angle γ—change their slope: γ increases, then producing a larger interaction between adjacent molecules (Fig. 4). This phenomenological finding, very recently reproduced by calculations [42], is an important confirm of RAS sensitivity to the structural as well to the electric properties of the organic layer.

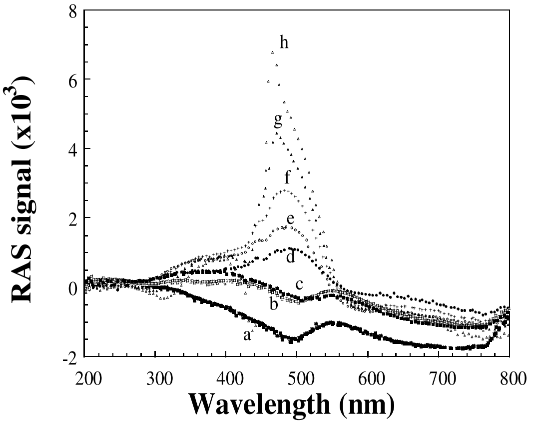

Fig. 1. RAS spectra measured at Langmuir–Blodgett layers of E_2M_8-sapphyrin with thickness *nominally* in the range 0–20 ML: (a) polycrystalline gold; (b) 2 ML; (c) 6 ML; (d) 12 ML; (e) 14 ML; (f) 16 ML; (g) 18 ML; (h) 20 ML. The absolute sign of the RAS signal is arbitrary (for more details, see [30]).

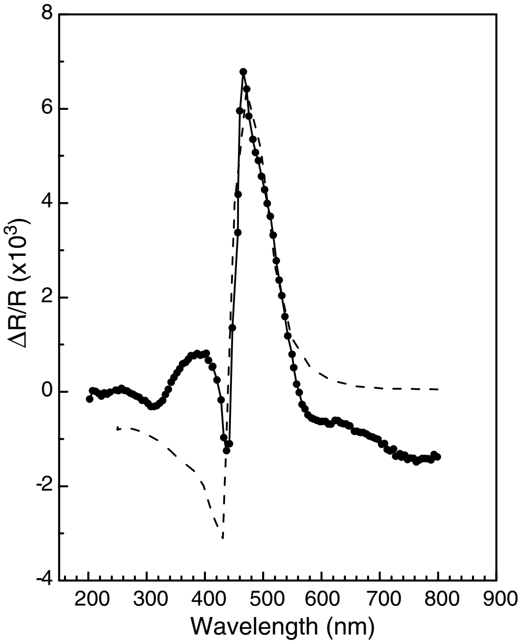

Fig. 2. RAS spectrum measured at 20 *nominal* ML of sapphyrin (filled dots + full line). The lineshape computed by the three-layer model—with parameters values (for the sapphyrin layer) determined by INDO/SCI method—has been also reported (dashed line) (for more details, see [30]).

Two important issues must be considered when organics are studied by RAS:

(1) As mentioned in the previous paragraph, only when the sample anisotropy is *small* expression (2) holds for complex $\Delta r/r$ [43]. This condition is certainly fulfilled in the case of metal and semiconductor surfaces, but it is *not always* true for organics, where particularly large values of

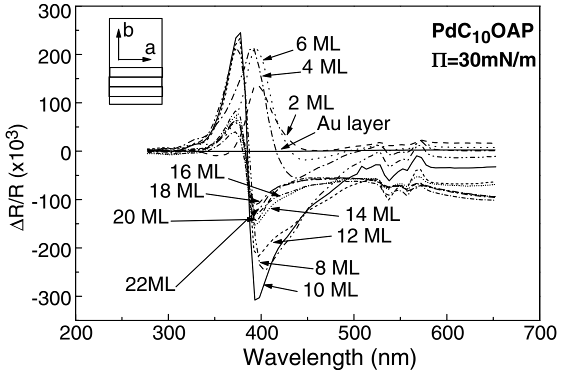

Fig. 3. $\Delta R/R$ spectra measured at Langmuir–Schaeffer layers of PdC$_{10}$OAP porphyrin deposited onto gold ($\Pi = 30$ mN/m). Total coverage ranges from 0 to 22 ML. The absolute sign of the quantity $\Delta R/R = 2(R^a - R^b)/(R^a + R^b)$ is arbitrary. In [32], the vertical axis of the same figure was labelled as "$2 \times \mathrm{Re}(\Delta r/r)$". However, given the high value of the anisotropy, the exact expression of second harmonic RAS signal should be in terms of $\Delta R/R$ (see text). In the inset: *a* and *b* directions (α and β defined in the text) with respect to the substrate. The layers (3 mm large) of different thickness deposited by LS technique have been also reported (the figure has been reproduced from [32]).

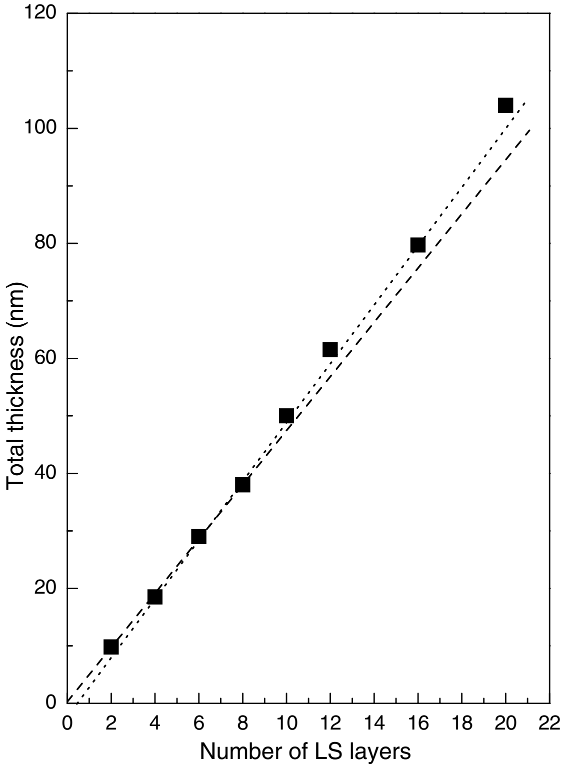

Fig. 4. Dependence of the film thickness—as measured by atomic force microscope (AFM)—on the number of deposited layers for PdC$_{10}$OAP ($\Pi = 30$ mN/m). The dashed and dotted lines are obtained by a linear fit of the data *below* and *above* 8 ML. At this coverage, the RAS spectrum line shape changes abruptly from absorption-like to derivative-like. The change of slope is compatible with a slight variation in the tilt angle of the molecule (for more details see [32]).

anisotropy are sometimes measured. In this case, the signal measured by the lock-in amplifier tuned at twice the PEM resonance frequency is *always* the reflectance variation ΔR. Consequently, experimental results can be *meaningfully* expressed in terms of $\Delta R/R$, that is the anisotropy of the sample reflectance. However, the expression of the signal in terms of the sample Fresnel coefficients is now more complicated, and the real and imaginary parts of $\Delta r/r$ are no more directly obtained from the lock-in.

(2) In organic layers, symmetry directions sometimes are not defined a priori, at variance with crystalline metals and semiconductors. In consequence of that, an azimuthal inspection of the sample optical anisotropy is necessary. It is easy to show that, if the sample is rotated by the angle Φ with respect to the orthogonal axes of RAS, the overall spectrum follows the dependence

$$\Delta R/R = \Delta R/R_{\max} \cos(2\Phi) \qquad (3)$$

(Fig. 5). The angle at which the maximum signal $\Delta R/R_{\max}$ is measured defines how the sample axes must be aligned to obtain the right azimuthal orientation.

4. Reflectance anisotropy spectroscopy and organic molecular beam deposition

With few remarkable exceptions [26,27], up to now the application of RAS to organics has been restricted to deposition techniques (LB, LS, spin coating, etc.) limited by contaminations and a scarce (or null) control of the growth process. In OMBD, that on the contrary is a controlled

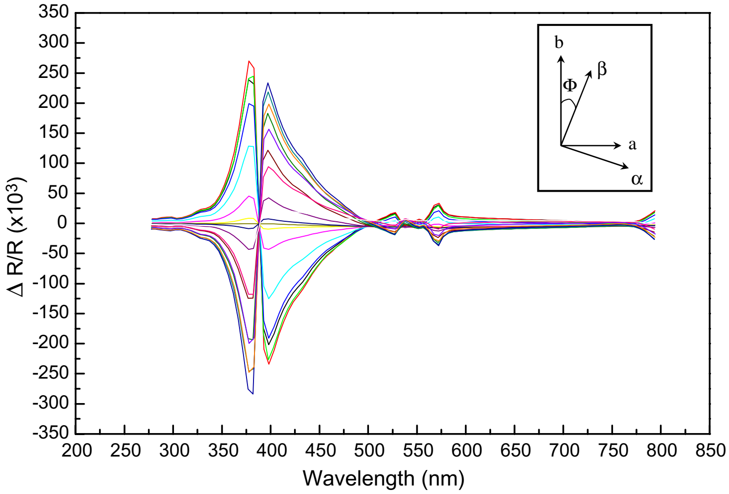

Fig. 5. Azimuthal dependence of $\Delta R/R$ spectra measured at a 10 ML thick layer of $PdC_{10}OAP$ ($\Pi = 30$ mN/m) deposited onto gold by Langmuir–Schaeffer technique. In the experiment, the sample has been rotated with respect to the optical apparatus, held fixed. The azimuthal rotation (by an angle Φ) of α and β axis of RAS with respect to a and b axis of sample is sketched in the inset.

deposition in conditions of excellent vacuum, these limits are absent.

In the following, we will report results recently obtained by coupling a RAS spectrometer to an OMBD chamber to measure optical anisotropy spectra *during growth* [44]. The RAS spectrometer has operated in the range 250–800 nm (1.5–5.0 eV), in the version with two polarizers. Normal-incidence optical access to the sample was obtained by a UHV quartz strain-free window [45], mounted at the bottom of the growth chamber, which introduces a negligible background anisotropy in the whole photon energy range.

Details of preparation of α-sexithiophene (6T) used for deposition are presented in [44]. A quartz microbalance installed close to the substrate has been used to measure the nominal film thickness. The films were grown at about 5×10^{-10} Torr base pressure on (0 1 0)-oriented single crystals of potassium acid phthalate (KAP) [46]. KAP belongs to the orthorombic system, and in the range 1–4 eV is transparent and biaxial [47,48]. The use of polarized light complicates the spectra, and artefacts coming from the substrate birefringence are expected in experimental data.

The role of the substrate deserves further consideration, given its role in ordering the film. In fact, although the films grow as polycrystalline, KAP induces a preferential orientation of the crystalline islands: therefore an in-plane anisotropy of the macroscopic optical response of the 6T films rises [49], similarly as found for α-quaterthiophene (4T), where anisotropy is complete [50]. In comparison, the deposition of 50 Å of 4T performed in the same way but *on an oxidized Si(0 0 1) surface* gives an almost negligible optical anisotropy signal, in consequence of a very likely disordered layer structure. The thickness of a single monolayer (ML) is about 22 Å, i.e. half of the longest unit cell axis, which grows nearly perpendicular to the substrate surface.

As expected, the anisotropy spectrum measured at the clean, freshly cleaved substrate presents a not null offset due to the anisotropic optical properties of KAP. Evident oscillations (due to the KAP birefringence) are superimposed onto this offset signal, slightly modulated by a Fabry-Perot term due to the multiple reflections inside the sample (Fig. 6). KAP rotates the plane of polarization of *outcoming* light with respect to the original polarization plane. When the beam passes through the second polarizer, a not null signal is produced, whose intensity continuously varies with wavelength. For a more detailed discussion, the reader should read [44].

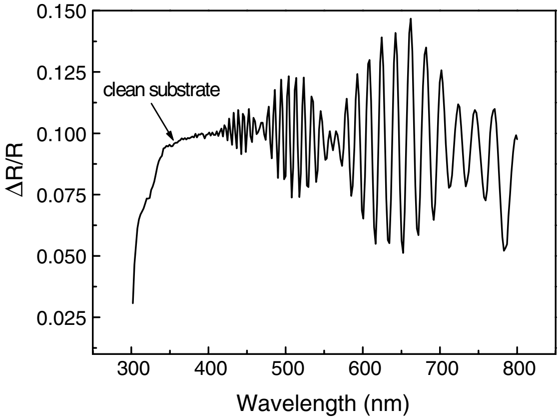

Fig. 6. Experimental spectra $\Delta R/R$ collected in UHV at the clean (0 1 0) KAP substrate before deposition of 6T layers. Please note that the vertical axis in Fig. 1 of [44] has been labelled as "$2\,\mathrm{Re}(\Delta r/r)$". According to [43], the two expressions for the second harmonic RAS signal are equivalent in this range of anisotropy.

We consider this signal as a base line to subtract from the spectra measured at the different coverage values. Moreover, the presence of the oscillations, largely dominant at wavelength higher than 450 nm, limits our considerations to the range 300–450 nm.

In Fig. 7, the difference spectra measured after deposition of 25 Å (curve i), 50 Å (curve ii) and 100 Å (curve iii) (about 1, 2 and 4 ML, respectively) have been reported. A large signal (increasing with coverage) is detected with maximum at 371 nm, where the main reflectivity structure of 6T films is expected. The existence of such a large anisotropy witnesses the average order of the film, which is noticeably maintained with increasing thickness, sign of the crystalline quality of the sample.

Although in this first experiment we have investigated a reduced coverage range, we notice that RAS allows studying details of the line shape variation, in turn related to the evolution of the optical and structural properties of the growing layer. Although a detailed analysis of the data will be presented in a forthcoming paper, we mention that: (i) the peak position slightly shifts with coverage; (ii) the width of the curve at half-maximum increases; (iii) the amplitude presents a nearly linear dependence upon coverage.

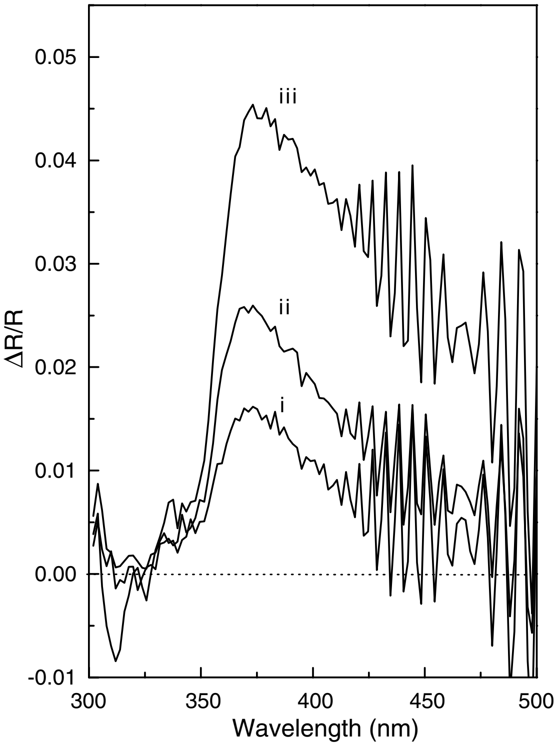

Fig. 7. Difference—with respect to the substrate spectrum reported in Fig. 6—of experimental $\Delta R/R$ spectra collected in UHV at different growth stages of 6T on (0 1 0) KAP: (i) after deposition of 25 Å of 6T (about 1 ML); (ii) after deposition of 50 Å of 6T (about 2 ML); (iii) after deposition of 100 Å of 6T (about 4 ML) (the figure has been reproduced from [44]).

The slight red-shift of the main peak and the augmenting broadening of the curve could originate from a structural or morphological rearrangement of the 6T crystalline film. Fig. 8 highlights the dependence of the amplitude vs the nominal coverage. Actually, a linear behaviour implies a nearly constant sticking coefficient for 6T molecules, irrespective of the fact that they are adsorbed onto the bare KAP substrate or onto the organic film. The overall linearity of the RAS signal vs 6T coverage is also evident in Fig. 9, where the experimental curve relative to the growth of a 50 Å (about 2 ML) thick film on KAP is shown. OMBD growth has been monitored *in real time* measuring the signal evolution at the fixed wavelength $\lambda = 371$ nm, where the maximum sensitivity is expected. The corresponding film

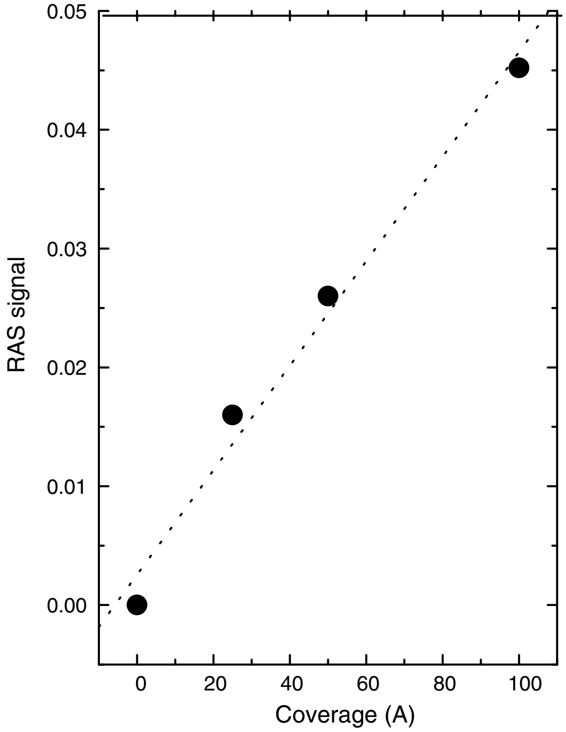

Fig. 8. Amplitude of the RAS signal at about 371 nm (related to the main 6T structure) vs the deposited thickness (from data of Fig. 7). The fit represents a possible linear dependence.

thickness detected by a quartz microbalance is reported for comparison (both data sets have been normalized to their respective maximum value). Abrupt slope changes are observed in both curves when the shutter, which is in front of the 6T source, has been opened and closed to start and finish deposition, respectively (Fig. 9).

From Fig. 9, considering the noise level we estimate that in this experiment RAS is able to detect a deposition of about 4×10^{12} molecules/cm^2, [1] that is 1/50 of the molecules forming the complete monolayer. Such a high sensitivity makes RAS an excellent technique for *in situ* growth monitoring.

We also observe a slight signal variation up to 100 s after the shutter has been closed, likely due to the deposition of residual 6T still present in gas phase in the OMBD chamber, producing an additional thickness close to the microbalance sensitivity. It may nonetheless suggest some optical phenomena related to structural rearrangements, undetectable by the microbalance, as the spectral shift of the main peak observed in Fig. 7 for the thickest layer.

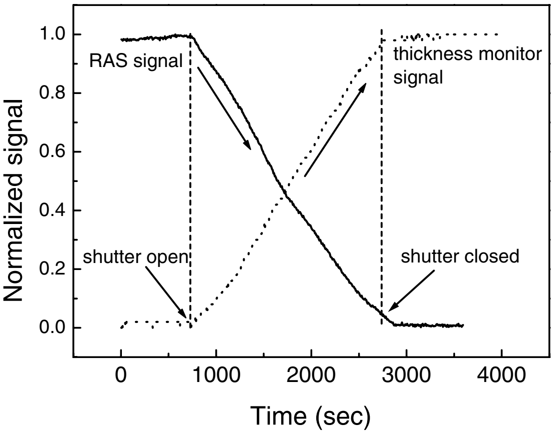

Fig. 9. Experimental $\Delta R/R$ signal at fixed wavelength ($\lambda = 371$ nm) and nominal thickness evolution measured with a quartz microbalance during the UHV growth of a 50 Å (about 2 ML) thick 6T film. Both signals have been normalized with respect to their maximum value; the time of shutter opening and closing is indicated (the figure has been reproduced from [44]).

In conclusion, RAS is certainly a well-suited spectroscopy to monitor the growth of organic layers *in situ* and *in real time*. It will allow studying the kinetics of OMBD deposition, i.e. the evolution of the structure, morphology and electronic properties of the layer *during growth*.

Acknowledgements

We gratefully acknowledge C. Di Natale, R. Paolesse and A. D'Amico for the fruitful scientific collaboration, E. Mazzone for the design of the new RAS electronics (SMART-RAS), S. Trabattoni for purifying the 6T prior to deposition.

References

[1] H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, John Wiley and Sons, Chichester, 1997.

---

[1] The number of 6T molecules forming a complete monolayer has been assumed to be 2.1×10^{14} molecules/cm^2.

[2] D. Fichou (Ed.), Handbook of Oligo- and Poly-Thiophenes, Wiley–VCH, Weinheim, 1999.

[3] S. Forrest, P. Burrows, M. Thompson, IEEE Spectrum 37 (8) (2000), http://www.spectrum.ieee.org/publicfeature/aug00/orgs.html, and references therein.

[4] J.M. Shaw, P.F. Seidler, IBM J. Res. Dev. 45 (2001) 3;
D.B. Mitzi, K. Chondroudis, C.R. Kagan, IBM J. Res. Dev. 45 (2001) 29.

[5] D.E. Hooks, T. Fritz, M. Ward, Adv. Mater. 4 (2001) 227.

[6] S.R. Forrest, Chem. Rev. 97 (1997) 1793.

[7] T.J. Schuerlein et al., Jpn. J. Appl. Phys. 34 (1995) 3837.

[8] R. Tubino et al., Opt. Mater. 9 (1998) 437.

[9] A. Pimpinelli, J. Villain, Physics of Crystal Growth, Cambridge University Press, Cambridge, 1998.

[10] T. Nonaka et al., Thin Solid Films 256 (1995) 262.

[11] A. Sassella et al., Synth. Metals 98 (1998) 83.

[12] A. Borghesi et al., Adv. Mater. 10 (1998) 931.

[13] A. Sassella et al., Synth. Metals 101 (1999) 538.

[14] M.A. Herman, H. Sitter, Molecular Beam Epitaxy: Fundamentals and Current Status, Springer Verlag, Berlin, 1989.

[15] J.F. McGilp, J. Phys.: Condens. Matter 2 (1990) 7985.

[16] R.M.A. Azzam, N.M. Bashara, Ellipsometry and Polarized Light, North Holland, Amsterdam, 1977.

[17] C. Pickering, Thin Solid Films 313–314 (1998) 406.

[18] T.U. Kampen, A.M. Paraian, U. Rossow, S. Park, G. Salvan, Th. Wagner, M. Friedrich, D.T. Zahn, Phys. Stat. Sol. (a) 188 (2001) 1307.

[19] D. Tsankov, K. Hinrichs, A. Roseler, E.H. Korte, Phys. Stat. Sol. (a) 188 (2001) 1319.

[20] D.E. Aspnes, J.P. Harbison, A.A. Studna, L.T. Florez, Phys. Rev. Lett. 59 (1987) 1687.

[21] V.I. Berkovits, V.A. Kiselev, V.I. Safarov, Surf. Sci. 211/212 (1989) 489.

[22] Ph. Hofmann, K.C. Rose, V. Fernandez, A.M. Bradshaw, W. Richter, Phys. Rev. Lett. 75 (1995) 2039.

[23] C. Goletti, C. Springer, U. Resch-Esser, N. Esser, W. Richter, B.O. Fimland, Phys. Rev. B 61 (2000) 1681.

[24] V. Emiliani, A.I. Shkebtii, C. Goletti, A.M. Frisch, B.O. Fimland, N. Esser, W. Richter, Phys. Rev. B 59 (1999) 10657.

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

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

[27] B.G. Frederick, R.J. Cole, J.R. Power, C.C. Perry, Q. Chen, N.V. Richardson, P. Weightman, C. Verdozzi, D.R. Jennison, P.A. Schultz, M.P. Sears, Phys. Rev. B 58 (1998) 10883.

[28] P. Weightman, Phys. Stat. Sol. (a) 188 (2001) 1443, and references therein.

[29] E.K. Miller, K. Hingerl, C.J. Brabec, A.J. Heeger, N.S. Sariciftci, J. Chem. Phys. 113 (2000) 789.

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

[31] C. Goletti, R. Paolesse, C. Di Natale, G. Bussetti, P. Chiaradia, A. Froiio, L. Valli, A. D'Amico, Surf. Sci. 501 (2002) 31.

[32] C. Goletti, R. Paolesse, E. Dalcanale, T. Berzina, C. Di Natale, G. Bussetti, P. Chiaradia, A. Froiio, L. Cristofolini, M. Costa, A. D'Amico, Langmuir 18 (2002) 6881.

[33] I. Kamiya, D.E. Aspnes, L.T. Florez, J. Harbison, Phys. Rev. B 46 (1992) 15894.

[34] D.E. Aspnes, R. Bhat, E. Colas, V.G. Keramidas, M.A. Koza, J. Vac. Sci. Technol. A 7 (1989) 711.

[35] W. Richter, Philos. Trans. R. Soc. London A 344 (1993) 453.

[36] See for example: http://nottingham.ac.uk/~ppzpjm/sect6_3.htm. For a recent application of RAIRS to molecular beam adsorption: S. Schauermann, J. Hoffmann, V. Johànek, J. Hartmann, J. Libuda, Phys. Chem. Chem. Phys. 4 (2002) 3909.

[37] J.C. Kemp, J. Opt. Soc. Am. 59 (1969) 950, http://www.hindspem.com.

[38] A. Salvati, P. Chiaradia, Appl. Opt. 39 (2000) 5820.

[39] C. Goletti, G. Bussetti, F. Arciprete, P. Chiaradia, G. Chiarotti, Phys. Rev. B 66 (2002) 153307.

[40] J.D.E. McIntyre, D.E. Aspnes, Surf. Sci. 6 (1971) 4370.

[41] J.E. Ridley, M.C. Zerner, Theor. Chim. Acta 32 (1973) 111.

[42] C. Castillo, R.A. Vazquez-Nava, B.S. Mendoza, private communication.

[43] The problem of quantifying when an anisotropy signal can be considered *small* has been addressed in O. Acher, B. Drevillon, Rev. Sci. Instrum. 63 (1992) 5332, In this paper the authors define an upper limit equal to about 0.2 for the measured RAS signal. For higher anisotropy values, the authors suggest that a slightly different expression for $\Delta r/r$ should hold.

[44] C. Goletti, G. Bussetti, P. Chiaradia, A. Sassella, A. Borghesi, Appl. Phys. Lett. 83 (2003) 4146.

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

[46] R. Tubino, A. Borghesi, L. Dalla Bella, S. Destri, W. Porzio, A. Sassella, Opt. Mater. 9 (1998) 437.

[47] T.A. Eremina, N.G. Furmanova, L.F. Lakakhova, T.M. Okhrimenko, V.A. Kuznetsov, Crystallogr. Rep. 38 (1993) 554.

[48] A. Sassella, A. Borghesi, Th. Wagner, J. Hilfiker, J. Appl. Phys. 90 (2001) 3838.

[49] S. Tavazzi, D. Besana, A. Borghesi, F. Meinardi, A. Sassella, R. Tubino, Phys. Rev. B 65 (2002) 205403.

[50] A. Sassella, A. Borghesi, F. Meinardi, R. Tubino, M. Gurioli, C. Botta, W. Porzio, G. Barbarella, Phys. Rev. B 62 (2000) 11170;
A. Sassella, D. Besana, A. Borghesi, F. Meinardi, S. Tavazzi, R. Tubino, Synth. Met. 121 (2001) 1419.