

Pseudomorphic growth of organic semiconductor thin films driven by incommensurate epitaxy

A. Sassella,^{1,a)} M. Campione,¹ L. Raimondo,¹ A. Borghesi,¹ G. Bussetti,² S. Cirilli,²
A. Violante,² C. Goletti,² and P. Chiaradia²

¹Dipartimento di Scienza dei Materiali and CNISM, Università degli Studi di Milano-Bicocca,
I-20125 Milano, Italy

²Dipartimento di Fisica and CNISM, Università degli Studi di Roma "Tor Vergata," I-00133 Roma, Italy

(Received 18 December 2008; accepted 24 January 2009; published online 20 February 2009)

A stable pseudomorphic phase of α -quaterthiophene, a well known organic semiconductor, is obtained by growing films with organic molecular beam epitaxy (OMBE) on a single crystal of another organic semiconductor, namely, tetracene. The structural characteristics of the new phase are investigated by monitoring *in situ* the OMBE process by reflectance anisotropy spectroscopy; thus assessing that incommensurate epitaxy is in this case, the driving force for tuning the molecular packing in organic molecular films and in turn, their solid state properties. © 2009 American Institute of Physics. [DOI: 10.1063/1.3081413]

The key factor improving the performances of thin film devices based on organic semiconductors is the achievement of high charge mobility through the control of growth mechanisms aimed at improving the structural quality and morphology of the thin films.¹ The fine tuning of the material properties by a suitable modification of the molecular orientation and packing (crucial for determining the electronic band structure of the solid film and its charge-transport properties)² represents an alternative experimental opportunity. The arrangement of different organic semiconductors in multilayer architectures, including semiconductor junctions, gives further beneficial effects in thin film devices.¹

In this framework, organic molecular beam epitaxy (OMBE) represents the best choice among the growth techniques, assuring high quality films and controlled interfaces in organic heterostructures in view of both fundamental studies and applications.^{3,4} Among the strategies for growing samples with designed properties, one of the most promising is the use of organic substrates⁵⁻⁷ whose effect in tuning the molecular orientation of the overlayer has been already demonstrated. In particular, when organic single crystals are used as substrates, highly oriented organic heterostructures are grown even in the absence of any geometric coincidence between substrate and overlayer (incommensurate epitaxy).^{5,8-13}

In this letter, we investigate the properties of an organic-organic heterostructure by demonstrating the OMBE growth of an epitaxial pseudomorphic phase of the α -quaterthiophene (α -4T) film on tetracene (TEN) single crystals. By means of reflectance anisotropy spectroscopy (RAS), we monitored *in situ* the OMBE process, showing that the α -4T overlayer grows with a distorted lattice structure with respect to the bulk crystal, which results in incommensurate epitaxy. In addition, the full *ex situ* stability of this new phase is demonstrated so that organic-organic epitaxy is definitely assessed as a powerful tool for tuning the properties of the growing films.¹⁴

α -4T was synthesized and purified according to Ref. 15, while commercial TEN was purified by several sublimation

steps before use. TEN single crystals were grown by physical vapor transport.¹⁶ Its crystal structure belongs to the triclinic system, with unit cell parameters $a=6.06$ Å, $b=7.84$ Å, $c=13.01$ Å, $\alpha=77.13^\circ$, $\beta=72.12^\circ$, $\gamma=85.79^\circ$, and two molecules per unit cell.¹⁷ TEN single crystals are thin flakes exposing a wide, clean, molecularly flat (001) surface, and a few mm² in size, which does not require cleavage before use. α -4T thin films were grown by OMBE on TEN(001), at room temperature and at a base pressure $\leq 5 \times 10^{-10}$ Torr with 165 °C source temperature and about 0.3 nm/min deposition rate (as monitored by a calibrated quartz microbalance¹⁸). RAS experiments were carried out at near-normal incidence *in situ* and *ex situ* using a homemade apparatus with two polarizers.^{19,20} The experimental RAS signal is expressed as a function of the photon energy, in terms of

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

where R_α and R_β are the light intensities reflected by the sample for incident light linearly polarized along two orthogonal directions α and β . The TEN crystal substrate was inserted in the OMBE chamber by aligning a_{TEN} parallel to α within few degrees of uncertainty. The crystal axes a_{TEN} and b_{TEN} on the TEN(001) surface were previously identified from the known anisotropy of the TEN substrate by polarized optical microscopy (uncertainty of $\pm 2^\circ$), exploiting its birefringence and dichroism.^{21,22} During the OMBE experiment, RAS spectra have been collected every 1.2 ± 0.1 nm nominal thickness of the deposited film, stopping the molecular flux during the optical measurements.

In Fig. 1, we report the RAS spectrum collected *in situ* on the TEN crystal substrate and all the spectra collected *in situ* at different growth stages, up to 5 nm thickness of the film. Below 3 eV, the TEN spectrum presents the typical spectral features coming from the well known anisotropic optical response of TEN single crystals when oriented as our substrate and analyzed by polarized light.²² In the spectral range between 3 and 4 eV, where TEN is known to be transparent, a featureless background is detected. It originates from the interference due to the crystal finite thickness (as

^{a)}Electronic mail: adele.sassella@unimib.it.

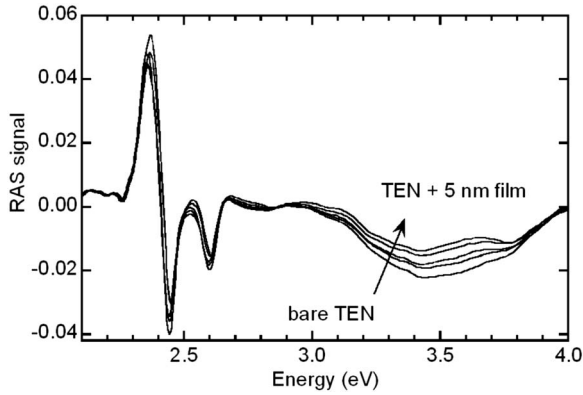


FIG. 1. *In situ* RAS spectra as taken on the TEN(001) face of a 750 nm thick tetracene single crystal and after the deposition of α -4T thin films (each deposition step is about 1.2 nm). The arrow indicates the evolution of the spectra as the thickness of the α -4T thin film increases.

indeed checked by measuring different TEN samples, not shown here). In the case under analysis this phenomenon is strongly limited due to a suitable choice of the TEN crystal substrate so thin that any complete fringes cannot be observed; in this way, after deposition of α -4T the anisotropy²³ of the film can be detected, if any.

All the curves in Fig. 1 exhibit a sort of crossover point at about 2.8 eV. At lower photon energies, only slight intensity changes of the peaks are measured possibly connected to the birefringence of the film, giving a contribution which depends on film thickness. In the higher energy range between 2.8 and 4 eV, a continuous evolution with film thickness is observed. Here, the most striking feature is the arising of a new band from about 3.2 eV up to about 3.8 eV as the α -4T thin film thickness increases; therefore attributable to the optical response of α -4T.¹³ To better analyze this band in Fig. 2(a) we report the RAS difference (Δ RAS) between each RAS spectrum of the films and the RAS spectrum of the bare TEN substrate (all of them reported in Fig. 1). The Δ RAS spectra show a peak at about 3.6 eV whose intensity scales almost linearly with film thickness. The comparison of Δ RAS with the absorbance anisotropy of a crystalline oriented film of α -4T [see Fig. 2(b)] reveals a very good agreement in line shape (the difference in peak position will be discussed below). This is not surprising, as in this photon energy region the α -4T film behaves as a thin absorbing layer onto a thick transparent substrate.

The following two conclusions can be drawn from the data in Figs. 1 and 2:

(1) The “positive” evolution with thickness of the main band is the signature of an oriented growth. The band line shape reflects the anisotropy of the known optical absorption of (001)-oriented single crystalline thin films of α -4T with the structure of the low temperature (α -4T/LT) polymorph having a monoclinic unit cell with parameters $a=6.09$ Å, $b=7.86$ Å, $c=30.48$ Å, and $\beta=91.8^\circ$.^{5,23–25} Indeed, the difference $A_{\parallel a_{\alpha-4T}} - A_{\perp a_{\alpha-4T}}$ between the absorbance for polarized light with the electric field parallel ($\parallel a_{\alpha-4T}$) and perpendicular ($\perp a_{\alpha-4T}$) to the $a_{\alpha-4T}$ axis, reported for such a single crystalline α -4T film in Fig. 2(b), shows a positive band due to the strong absorption feature under $\parallel a_{\alpha-4T}$ polarized light, negligible under $\perp a_{\alpha-4T}$ polarized light;^{24,25} hence, by the comparison between Figs. 2(a) and 2(b), one can deduce that in the heterostructure α -4T/TEN the unit cell axis $a_{\alpha-4T}$ is

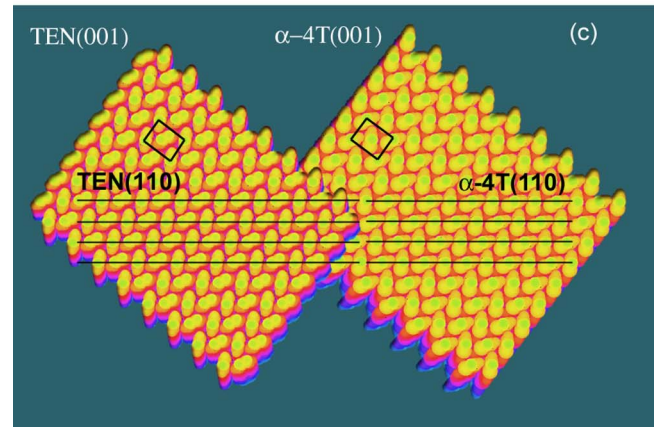
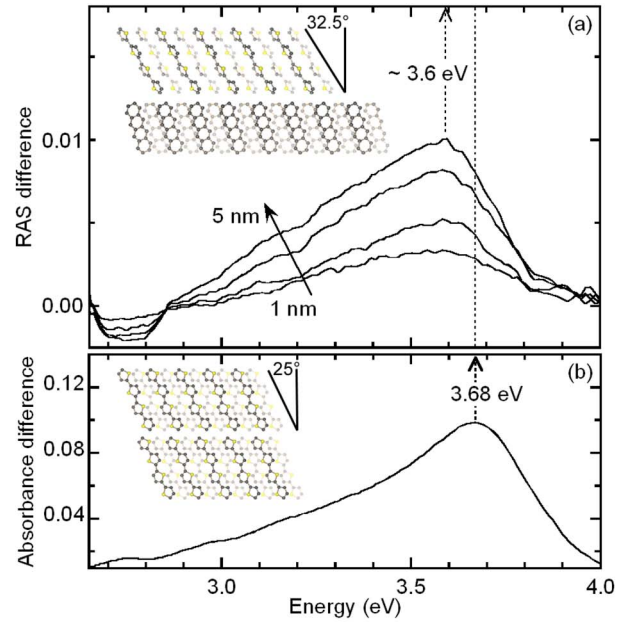


FIG. 2. (Color online) (a) RAS difference (Δ RAS) between the RAS spectra of the α -4T film grown on TEN and the RAS spectrum of the bare TEN substrate, reported in Fig. 1; the continuous arrow indicates the evolution of the signal with the nominal thickness of the film. Inset: sketch of the side view for the molecular arrangement in the new α -4T phase grown on TEN, as deduced by the RAS spectra. (b) Anisotropy $\Delta A_{\text{abs}} = A_{\parallel a_{\alpha-4T}} - A_{\perp a_{\alpha-4T}}$ of the experimental absorbance of a 10-nm-thick α -4T crystalline film with the α -4T/LT structure. Inset: sketch of the molecular arrangement in the structure of α -4T/LT single crystal. In both panels the position of the ΔA_{abs} main peak is indicated with dotted arrows. (c) Spacefill structural model of the TEN(001) and α -4T/LT(001) surfaces (top view) where the surface unit cells are reported (a -short axis and b -long axis), oriented with TEN $[1\bar{1}0] \parallel 4T[110]$, the TEN(110) and α -4T(110) families of lattice planes responsible for surface corrugation (see text) are visualized by black lines.

aligned to a_{TEN} (remind that the α direction of the RAS apparatus is nearly parallel to a_{TEN}). The oriented growth of a crystalline α -4T film on TEN is therefore demonstrated to hold during each growth step.

(2) The position of the band maximum, substantially constant at about 3.6 eV, indicates a pseudomorphic stable growth. The absence of any significant shift up to a thickness of 5 nm suggests the formation of a very stable film from the early to the final growth stages. As for the specific spectral position of this peak, it is shifted with respect to the one at 3.68 eV for the α -4T/LT single crystals and thin films^{24,25} [see Fig. 2(b)]. A spectral shift in this amount (see the dotted arrows) can derive from a different arrangement of the mol-

ecules with respect to the structure of α -4T/LT sketched in the inset of Fig. 2(b) by analogy with the previous results.^{26,27} Indeed, a similar behavior has been already observed for deposition of α -4T on potassium hydrogen phthalate substrates at 123 K where the main RAS peak is shifted toward lower energy by about 0.1 eV. Two concomitant factors could justify such an experimental shift: the expansion (or contraction) of the unit cell parameter with the consequent variation in the intermolecular interactions due to the change in the intermolecular distances and molecular orientation. As extensively discussed in Ref. 27 since the first factor would validate energy shifts one order of magnitude smaller even for cell expansion of up to 6%, only the assumption of a different tilt of the molecules with respect to the substrate surface in a sort of “distorted” structure would easily justify greater energy shifts.²⁸ In particular, the observed new spectral position at 3.57 eV was attributed to a film phase with molecules tilted by additional 7.5° to the surface [see the inset of Fig. 2(a)] with respect to the equilibrium arrangement.^{26,27} Nonetheless, in those samples grown at 123 K, the film structure relaxes toward the α -4T/LT equilibrium structure after the postgrowth annealing at room temperature, revealing the metastable nature of the observed pseudomorphic structure. A different situation holds in the present case: even after months of storage in air at room temperature, RAS spectra collected *ex situ* on the whole heterostructure (not reported here) do not show any significant difference with respect to that recorded *in situ*, demonstrating that the overlayer does not undergo any structural relaxations. In conclusion, the TEN single crystal induces the growth of a stable pseudomorphic phase of α -4T, i.e., a new phase with a slightly distorted structure, satisfying the requirements of epitaxy. This is the most remarkable result worth to be discussed in greater details.

By analyzing the driving forces for organic epitaxy, a comprehensive description of the α -4T/TEN heterostructure can be achieved. If intermolecular distances are kept constant, the 7.5° increment in the molecular tilt (deduced from RAS) gives rise to a variation in the length of the $a_{\alpha-4T}$ axis from 6.09 to about 6.5 Å and of the spacing of the α -4T(002) planes (the ones almost perpendicular to $c_{\alpha-4T}$ axis) from 15.3 to about 14.2 Å. Simultaneously, keeping constant the volume per molecule, the $b_{\alpha-4T}$ -axis is expected to contract from 7.86 to about 7.7 Å. Such a unit cell distortion determines the loss of geometric lattice match between α -4T/LT(001) and TEN(001) so that its role in driving the overlayer orientation is ruled out, as in incommensurate organic epitaxy.^{5,12} Rather, if one assumes this variation in the unit cell parameters, the spacing of the α -4T(110) planes increases from 4.8 to about 5.0 Å, therefore matching the spacing of the TEN(110) planes (4.96 Å) almost perfectly. These families of planes [sketched in Fig. 2(c)] enclose for both crystal rows of nearest-neighbor closed-packed molecules along the α -4T(110) and TEN(110) directions, conferring the characteristic corrugation of the α -4T(001) and TEN(001) surfaces. The coincidence of the corrugation direction and spacing of the (001) surfaces of the two crystals determines a favorable crystallochemical interaction, which is the real driving force for the observed pseudomorphic growth; this also gives the heterostructure full stability. Note that, considering the mentioned distortion of the cell parameters of the overlayer, the angle between $a_{\alpha-4T}$ and a_{TEN} is

about 5°, confirming the above conclusion (1) about alignment. As a final remark, we underline how the present detailed description of the pseudomorphic α -4T phase grown on TEN could only be deduced from a proper interpretation of RAS data, being not possible from a combination of only *ex situ* atomic force microscopy and optical absorption measurements.¹³

In conclusion, we have demonstrated that organic semiconductor thin films displaying a stable pseudomorphic structure can be grown by OMBE applying the strategy of using another organic crystalline semiconductor as substrate; therefore exploiting its orienting effect based on incommensurate epitaxy. This successful strategy can be applied for expanding the tunability of the physical properties of a material with a positive impact on the realization of organic multilayer devices embedding semiconductor junctions.

¹W. Brütting, *Physics of Organic Semiconductors* (Wiley, New York, 2005).

²D. Nabok, P. Puschnig, C. Ambrosch-Draxl, O. Werzer, R. Resel, and D.-M. Smilgies, *Phys. Rev. B* **76**, 235322 (2007).

³S. R. Forrest, *Chem. Rev. (Washington, D.C.)* **97**, 1793 (1997).

⁴M. A. Herman, W. Richter, and H. Sitter, *Epitaxy* (Springer, Berlin, 2004).

⁵M. Campione, A. Sassella, M. Moret, A. Papagni, S. Trabattoni, R. Resel, O. Lengyel, V. Marcon, and G. Raos, *J. Am. Chem. Soc.* **128**, 13378 (2006).

⁶G. Koller, S. Berkebile, J. R. Krenn, F. P. Netzer, M. Oehzelt, T. Haber, R. Resel, and M. G. Ramsey, *Nano Lett.* **6**, 1207 (2006).

⁷D. G. de Oteyza, T. N. Krauss, E. Barrena, S. Sellner, H. Dosch, and J. O. Ossò, *Appl. Phys. Lett.* **90**, 243104 (2007).

⁸M. Campione, S. Caprioli, M. Moret, and A. Sassella, *J. Phys. Chem. C* **111**, 12741 (2007).

⁹A. Sassella, M. Campione, L. Raimondo, S. Tavazzi, A. Borghesi, C. Goletti, G. Bussetti, and P. Chiaradia, *Surf. Sci.* **601**, 2571 (2007).

¹⁰A. Sassella, A. Borghesi, M. Campione, S. Tavazzi, C. Goletti, G. Bussetti, and P. Chiaradia, *Appl. Phys. Lett.* **89**, 261905 (2006).

¹¹X. Zeng, L. Wang, L. Duan, and Y. Qiu, *Cryst. Growth Des.* **8**, 1617 (2008).

¹²A. Sassella, M. Campione, and A. Borghesi, *Riv. Nuovo Cimento* **31**, 457 (2008).

¹³M. Campione, L. Raimondo, and A. Sassella, *J. Phys. Chem. C* **111**, 19009 (2007).

¹⁴T. Minari, S. Mari, T. Nemoto, S. Isoda, K. Tsukagoshi, and Y. Aoyagi, *Appl. Phys. Lett.* **91**, 123501 (2007).

¹⁵S. Trabattoni, S. Laera, R. Mena, A. Papagni, and A. Sassella, *J. Mater. Chem.* **14**, 171 (2004).

¹⁶R. A. Laudise, Ch. Kloc, P. G. Simpkins, and T. Siegrist, *J. Cryst. Growth* **187**, 449 (1998).

¹⁷D. Holmes, S. Kumaraswamy, A. J. Matzger, and K. P. C. Vollhardt, *Chem.-Eur. J.* **5**, 3399 (1999).

¹⁸M. Campione, M. Cartotti, E. Pinotti, A. Sassella, and A. Borghesi, *J. Vac. Sci. Technol. A* **22**, 482 (2004).

¹⁹C. Goletti, G. Bussetti, P. Chiaradia, A. Sassella, and A. Borghesi, *Appl. Phys. Lett.* **83**, 4146 (2003).

²⁰C. Goletti, G. Bussetti, P. Chiaradia, A. Sassella, and A. Borghesi, *J. Phys.: Condens. Matter* **16**, S4393 (2004).

²¹J. Vrijmoeth, R. W. Stok, R. Veldman, W. A. Schoonveld, and T. M. Klapwijk, *J. Appl. Phys.* **83**, 3816 (1998).

²²S. Tavazzi, L. Raimondo, L. Silvestri, P. Spearman, A. Camposo, M. Polo, and D. Pisignano, *J. Chem. Phys.* **128**, 154709 (2008).

²³T. Siegrist, Ch. Kloc, L. A. Laudise, H. E. Katz, and R. C. Haddon, *Adv. Mater. (Weinheim, Ger.)* **10**, 379 (1998).

²⁴A. Sassella, A. Borghesi, P. Spearman, and S. Tavazzi, *Eur. Phys. J. B* **28**, 385 (2002).

²⁵S. Tavazzi, A. Borghesi, M. Laicini, and P. Spearman, *J. Chem. Phys.* **121**, 8542 (2004).

²⁶A. Sassella, M. Campione, M. Moret, A. Borghesi, C. Goletti, G. Bussetti, and P. Chiaradia, *Phys. Rev. B* **71**, 201311(R) (2005).

²⁷M. Campione, A. Borghesi, M. Laicini, A. Sassella, G. Bussetti, C. Goletti, and P. Chiaradia, *J. Chem. Phys.* **127**, 244703 (2007).

²⁸P. Spearman, A. Borghesi, M. Campione, M. Laicini, M. Moret, and S. Tavazzi, *J. Chem. Phys.* **122**, 014706 (2005).