Spectroscopic analyses of molecular packing in pentacene thin films

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Summary. — Pentacene thin films are studied with three different and not invasive techniques to assess their capability to identify the thin-film thickness (in this research from 50 nm to 300 nm). Atomic Force Microscopy can detect the morphology of a surface and therefore the thickness at the edge of a scratch in the layer. X-ray spectroscopy can assess the presence of a bulk-phase and a thin-film phase related to the thickness of a pentacene layer. Finally the photocurrent spectroscopy, carried out on pentacene thin-film transistors, can measure the density of states distribution around the band edge and show the increase of the Davydov splitting related to a particular thickness. This information is extremely useful in the implementation of electronic devices like Organic Thin Film Transistors (OTFT), Organic LEDs and solar cells.

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The employment of organic semiconductors for electronic devices is becoming very important thanks to their low costs of realization and implementation and to the possibility to fabricate very thin, flexible and transparent layers by simple deposition techniques like, for example, solution and spin coating [1]. The most relevant devices fabricated up to date with these materials are solar cells, OLED, Organic Thin-Film Transistors (OTFT) and biological sensors.

To these very good qualities one must add some disadvantages, like the low carrier mobility, if compared to inorganic semiconductors, and the fast degradation of the electric parameters, like threshold voltage, mobility and I_{on}/I_{off} ratio, due to the oxidation in atmosphere.

As far as the carrier mobility is concerned, the organic semiconductor with the highest mobility achieved by now is pentacene [2], a small molecule formed by five benzene

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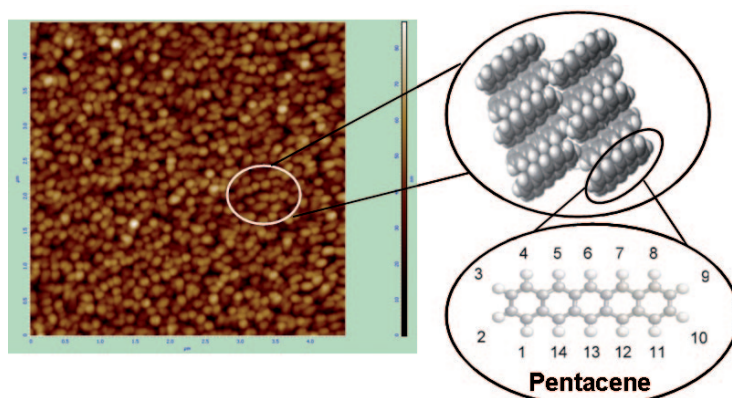
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Fig. 1. – AFM map in contact-mode of a small surface ($4.5\,\mu$m $\times$ $4.5\,\mu$m) of a pentacene layer $300\,$nm thick. In the focus it is shown the typical molecular packing of pentacene, called *herringbone*, and finally the structure of the pentacene molecule ($C_{22}H_{14}$).

rings ($C_{22}H_{14}$). To further improve the mobility value, an exhaustive study about the effects of different molecular packing on different substrates and with different deposition technique is necessary. Every molecule of pentacene is packed to others by π-bonds to form a *herringbone*-like structure, but the packing angles and the separation between the molecules may change according to the kind of substrate, the speed of deposition of the semiconductor and also its thickness [3,4]. To study this complex subject, this paper focuses on the analyses of molecular packing variations due to the film thickness. All the measurements were carried out in air and at room temperature to show the potentiality of these techniques to be used in standard conditions.

Atomic Force Microscopy (AFM) measurements were carried out in contact-mode for a $300\,$nm thick pentacene layer, evaporated on quartz slides. In fig. 1, the 2-dimensional map of a $4.5\,\mu$m $\times 4.5\,\mu$m area is shown. In the inset is represented the molecular packing (*herringbone*) and the structure of the pentacene molecule. AFM, used in contact mode, can also be used to determine the thickness of the layer through a scan on an area crossed by a scratch appositely done to measure the profile of the film. We measured by this technique the thickness of two layers: $300\,$nm and $50\,$nm. In fig. 2 is shown the profile of the first sample crossed by a scratch: this one is about $25\,\mu$m large, and the two lateral barriers are $300\,$nm thick, as expected. In this figure is also drawn, as a suggestion, a distinction between a "thin-film" phase and a "bulk" phase. The first phase is located at the interface with the substrate and usually is more or less $50\,$nm thick. The second phase instead start to dominate after a thickness of 150–$200\,$nm.

As for the change of the molecular packing due to the thickness, it actually varies just by passing from a thin-film phase to a bulk phase. These two phases are still not unequivocally identified, but what is sure is the presence of two diffraction angles in the relative X-ray diffraction (XRD) measurements. As shown in fig. 3, the diffraction peak corresponding to the thin-film phase is located at the angle $\vartheta = 5.73°$ for the plane (00k), when, the lattice spacing is about $1.55\,$nm; the peak related to the bulk phase appears at $\vartheta = 6.10°$, when the lattice spacing is about $1.45\,$nm. The peaks situated at the side of the two main ones, are related to the other planes of the triclinic single crystal structure. The measurements show the passage from a dominant thin-film phase
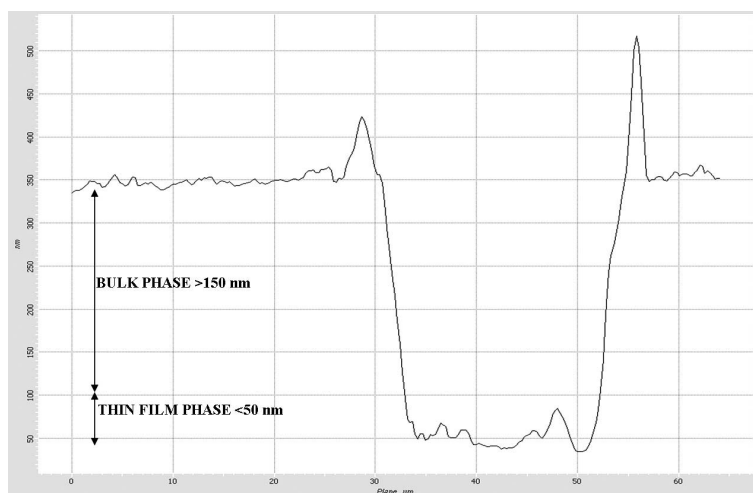
Fig. 2. – Profile of the edges of a scratch in a pentacene layer 300 nm thick, measured by AFM in contact-mode. The separation in thin-film phase and bulk phase is only appended to suggest the proportion of the two parts.

(thickness $=$ 50 nm) to an intermediate phase (thickness $=$ 200 nm) up to a dominant bulk phase (thickness $=$ 300 nm). These measurements are in good agreement with other similar studies [3].

The third technique, the photocurrent spectroscopy (PC), is here proposed as a novel way to measure the thickness of pentacene thin films. This technique can also be carried out on fully operational Organic Thin-Film Transistor (OTFT) with pentacene as an
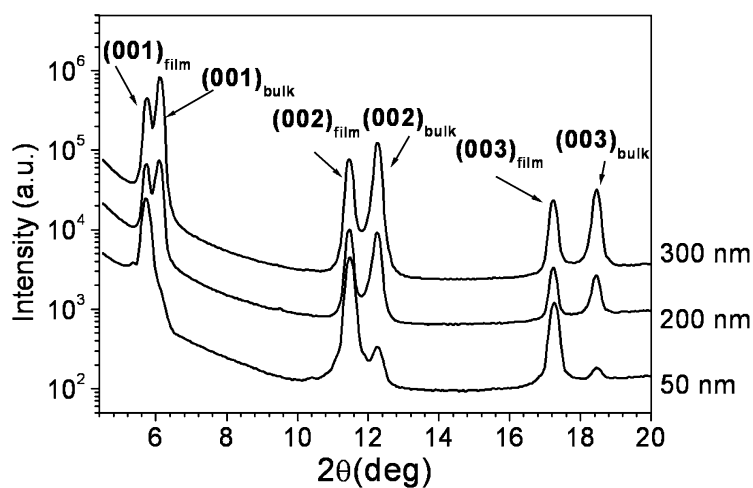

Fig. 3. – X-ray diffraction curves of 50 nm, 200 nm and 300 nm thick pentacene thin films. The two peaks in the middle show the diffraction angle for the plane (00k) for the bulk phase and thin-film phase. The other peaks instead are related to the other planes.
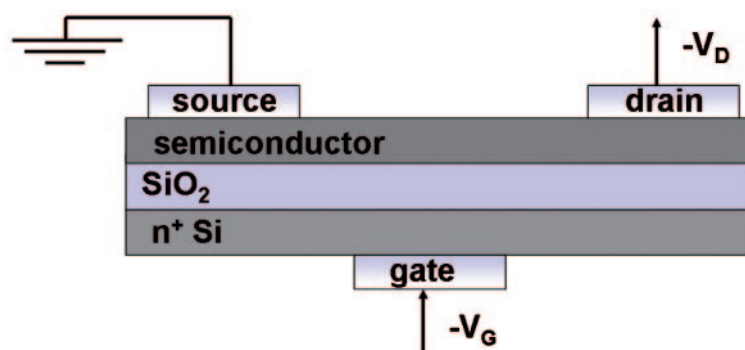
Fig. 4. – Schematic layout of a OTFT device with pentacene active layer.

active layer. All devices have been realized using a bottom contact configuration with gold source and drain electrodes ($W = 5\,\text{mm}$, $L = 50\,\mu\text{m}$, being W and L channel width and length, respectively) patterned by means of usual photolithographic process (fig. 4). Pentacene active layers were deposited by thermal evaporation and film thickness was monitored by a quartz crystal microbalance. Photocurrent spectroscopy is carried out with a QTH lamp coupled to a SPEX monochromator and mechanically chopped at low frequency ($< 20\,\text{Hz}$), and measured through a digital lock-in amplifier (Stanford Research 850). The energy resolution is $0.01\,\text{eV}$ at $2.40\,\text{eV}$. When the energy of the monochromatic light ($h\nu$) reaches the energy of the semiconductor band edge, the electrons make a transition to the conduction band and the measured current shows a peak of intensity, *i.e.* a photocurrent peak. The PC signal must be normalized by the photon flux that is mea-
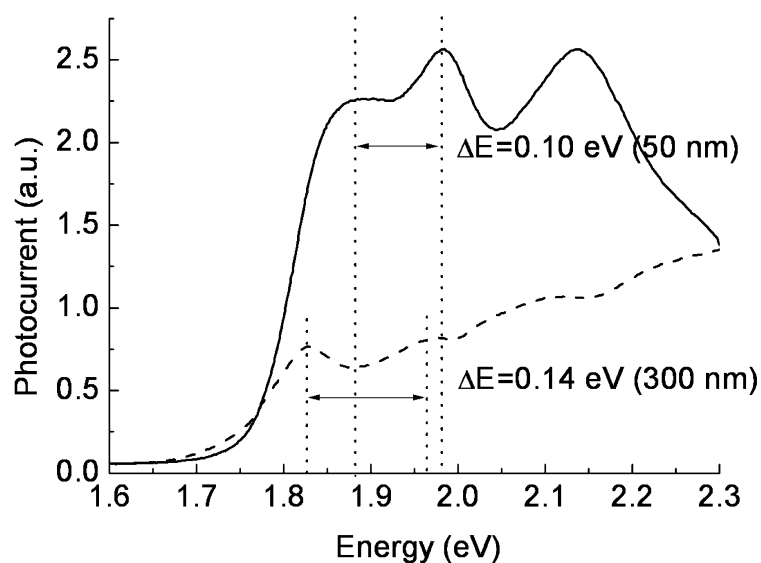

Fig. 5. – Photocurrent spectra of OTFTs with different active pentacene layer thickness: $50\,\text{nm}$ (solid line) and $300\,\text{nm}$ (dashed line), for $V_G = 0\,\text{V}$.

sured with a calibrated Si photodiode. PC analyses are carried out under low-injection conditions (1×10^{13} photons/cm^2 at $\lambda = 450$ nm) and no variations are observed in the PC spectra following exposure to the incident photon beam, as assessed by comparing consecutively acquired spectra. The information achieved by PC is the distribution of the Density Of the States (DOS) of the organic semiconductor around the electronic band edge. OTFTs with pentacene film thicknesses varying from 50 nm to 300 nm have been measured and fig. 5 reports the PC spectra for two OTFTs, 300 nm and 50 nm thick, respectively. The identification of the thickness of the layer can be obtained from the splitting in energy between the first two singlet levels (Davydov splitting) in the DOS distribution [5]. This splitting increases as the film grows thicker. In fact, if we compare the two spectra it can be noticed that, for the 300 nm thick one, the first two peaks are placed at 1.82 eV and 1.96 eV, instead, for the 50 nm thick one, they are placed at 1.88 eV and 1.98 eV. So the Davydov splitting is, respectively, 0.14 eV and 0.10 eV for the two films. This splitting can be correlated to the film thickness because, when the bulk phase increase, the lattice spacing decrease, so the coupling of intermolecular π-electron system becomes more effective. This enhances the Davydov splitting of the first absorption band because a greater energy will be necessary to have an electron transition [6]. Another pregnant consideration is that PC spectroscopy can provide all this information (DOS distribution, molecular packing and thickness of the film) without affecting the electrical properties of the organic thin film transistor, *i.e.* in a non-invasive way [7].

In conclusion the thickness of a pentacene thin film has been measured by three different techniques: AFM, XRD and PC spectroscopy in standard conditions, and they all provided reproducible results. In this way, we have assessed how PC spectroscopy can be used as a reliable and non-invasive tool that can be successfully employed also for the analysis of fully operational electronic devices, such as OTFTs. In this manner, the construction of an organic device, like a OTFT, can be improved and checked with the information about the molecular packing and the film thickness to achieve a better mobility and a better quality of the device.

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