

Raman Identification of Polymorphs in Pentacene Films

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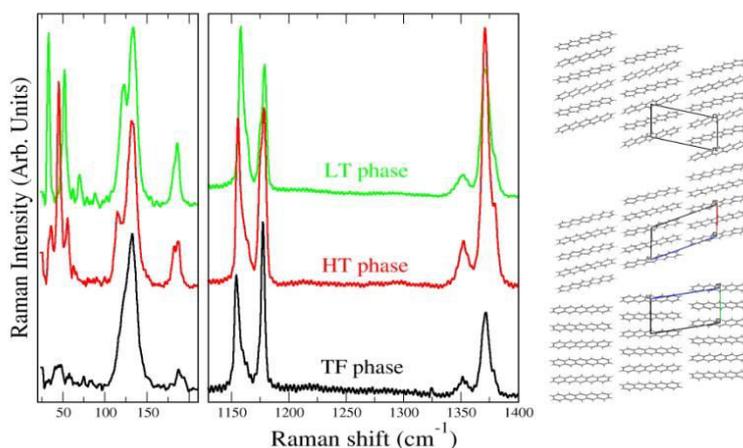
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Over recent years, Pentacene has become the prototype of organic semiconductors, as it exhibits mobility well above $1 \text{ cm}^2(\text{Vs})^{-1}$, thus directly yielding to the fabrication of organic thin-film transistors (OTFT) and other electronic devices [1]. In order to optimize device performance, it is of course necessary to properly characterize the chemical and physical purity of the sample, as impurities and static or dynamic disorder have a decisive role in determining the carrier localization. Pentacene films grown to fabricate operational devices belong either to the TF, or the HT or the LT polymorph, showing different inclination of the Pentacene molecules with respect to the *ab* crystal plane (see right side of the Figure). The TF polymorph grows on SiO_x substrate, and generally evolves to the HT one with the film thickness [2]. The HT polymorph may transform to the LT one under bias stress [3].

In this Communication we present the Raman spectra of Pentacene films grown on Si-SiO_x by Supersonic Molecular Beam Deposition (SuMBD), as a function of layer thickness and of temperature. We are able to obtain the Raman spectra in the low-frequency and high frequency regions, and provide a useful comparison of the spectra of the three polymorphs (left side of the Figure).



Raman spectra (left) and structure (right) of the three Pentacene polymorphs.

We once more demonstrate that Raman micro-spectroscopy is a very efficient and non-destructive method to characterize different polymorphs of organic semiconductors. In addition, the comparison between the spectral region of lattice phonons with that of the intra-molecular vibrations provides useful insights on the degree of crystallinity of Pentacene. Indeed, the fact that intensity of the lattice phonon band around 130 cm^{-1} is of the same order of magnitude as that of intramolecular bands, shows that the TF phase grown by SuMBD method has a high degree of lateral order, i.e., the film grows layer-by-layer up to the highest obtained thickness. However, the interlayer correlation is low, as shown by the weakness of the lowest frequency Raman phonons. From this point of view, the TF phase can be considered as a sort of two-dimensional (2D) phase, i.e., long range order can exist only in the *ab* plane, whereas the HT or LT phases are true 3D phases, even when grown in the form of film. This is confirmed by the fact that a different growth method, low-rate high-vacuum molecular beam deposition, yields 3D nucleation, finally ending in a (disordered) HT polymorph, with all the 3D lattice phonons being clearly visible [2].

References

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