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Letter

Supersonic molecular beams deposition of α-quaterthiophene: Enhanced growth control and devices performances

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ABSTRACT

The alpha-quatertiophene is widely considered an interesting material for the realization of organic electronics and opto-electronics. Compared to other oligothiophenes, the performances of transistors based on this compound are limited by its kind of growth on the typical materials used for device realization. Here we show that via seeded supersonic beams we can lead to a nice improvement of both morphological and electrical properties of the film grown, through a better control of the initial state of the precursor in the vapor phase. Using the high kinetic energy achievable in the supersonic beams, we increase the dimensions of the grains and the coalescence of different islands, limiting the grain boundary formation. As consequence, the performance of the realized field effect transistors is enhanced of one order of magnitude.

Small molecules are widely considered an interesting and viable way to understand the intrinsic properties and the processes involved in charge and energy transport in semiconductor conjugated polymers [1]. These are key issues in the fabrication of improved, reliable, and efficient devices both for electronics and electro-optics [2]. In particular, oligothiophenes are an appealing class of compounds for their high stability to oxidation processes [3] and for their high degree of flexibility in "molecular engineering". On the other hand major difficulties arise from the solid state packing of this class of molecules, where lack of control on structure, morphology and grain boundaries formation reduces the efficiency of the charge transport [4] limiting the performances of the organic devices [5].

The processes that control the thin films formation depend on the delicate balances between molecule–molecule and molecule–surface interactions [6], which regulate the kind of growth (Frank van der Merwe, Volmer-Weber, Stransky-Krastanov) [7]. Nevertheless for the feeble nature of the forces involved in the formation of molecular solids and for the large number of polymorphs and orientations possible in the organics [8,9], it is hard to have a good control on growth. The objective of our work is to improve

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the performances of devices, field effect transistor (FET) in particular, improving the control on the molecular assembling.

Starting from these problematic and knowing the different works that have shown the importance of the state (in terms of translational, rovibrational and momentum) of the molecules in the processes involving their collision and the energy transfer with the surface [10], we have proposed a new approach to grow organic thin films, based on seeded supersonic beams [11]. Supersonic beams give, indeed, the possibility to control the energetic state in terms of kinetic energy (E_k), momentum and internal degree of freedom of the impinging particles, by setting the initial working conditions such as the source nozzle dimensions, the temperature and pressure of the reservoir, etc. Seeding the vapors of the organic semiconductors in a lighter carrier gas (He in our experiments) that defines the conditions of the free jet expansion, makes it possible to control the final state of the seeded molecules [12]. During the supersonic expansion, the internal degrees of freedom of the molecules undergo a strong cooling process while the kinetic energy can be increased, from the few hundreds of meV of an effusive source, up to several eV by varying the degree of seeding [11]. For this reason supersonic molecular beam deposition (SuMBD) allows to overcome some of the difficulties inherent to the available techniques for the growth of films of organic molecules.

Here we show the results achieved in the growth of quaterthiophene ($\alpha - 4T$) on SiO_x/Si for the realization of organic field effect transistors by SuMBD. The $\alpha - 4T$ molecules on this kind of surface typically present a 3D growth that strongly limits the performances in devices [13]. We will see that varying the E_k of the impinging molecules, it is possible to modify the growth of the $\alpha - 4T$, improving its morphology. To verify the importance of E_k, we selected two different regimes of growth: the first one where the seeded $\alpha - 4T$ molecules have an average E_k of 3.0 eV and the second one where their E_k is in the order of 7.5 eV. We have characterized the obtained films by atomic force microscopy to optimize the growth processes and to understand the effect of the kinetic energy of the impinging molecules in the thin film growth. We then used these films to build FETs in top contact configuration. Thus we are able to correlate the films morphology to the devices performances showing that a fine control on the state of the molecules can improve the characteristic of our transistors.

The experimental apparatus and the method used to realize the seeded supersonic beams of $\alpha - 4T$ are described elsewhere [11]. It essentially consists of: two stages/chambers differentially pumped high vacuum apparatus, a hyperthermal source placed in the first chamber, an ultra high vacuum deposition chamber and a time of flight mass spectrometer (ToF-MS) used to verify the purity of the materials, to determine the energetic properties of the seeded molecules, and to determine the molecular flux. The ionization of the molecules/atoms in the beam is obtained with the 4th harmonic of a Nd::YAG laser (266 nm/4.66 eV). The $\alpha - 4T$ was grown on highly doped silicon (n^{++}) wafers covered with 50 nm thermally grown silicon oxide, cleaned in hot (325 K) isopropylic alcohol, treated with ozone for 30 min, and then outgassed at 455 K for 12 h in ultra high vacuum. All the depositions were performed at room temperature (298 K) with a flux of about 0.2 nm/min. XRD spectra was collected in Bragg-Brentano geometry with a Panalitycal X'Pert Pro diffractometer. We used a Cu anode with wavelength of 1.5406 Å. The step size was 0.05° (2Θ) and the average time was 60 s/step. Topographic characterization of the films has been performed by AFM microscopy in air, using a Smena SFC050 scanning head by NT-MDT. Depending on the sample, measurements have been carried out in semi-contact mode AFM (using NSG11 silicon cantilevers by NT-MDT) or in contact mode (using CSG10 Au-coated silicon cantilever by NT-MDT).

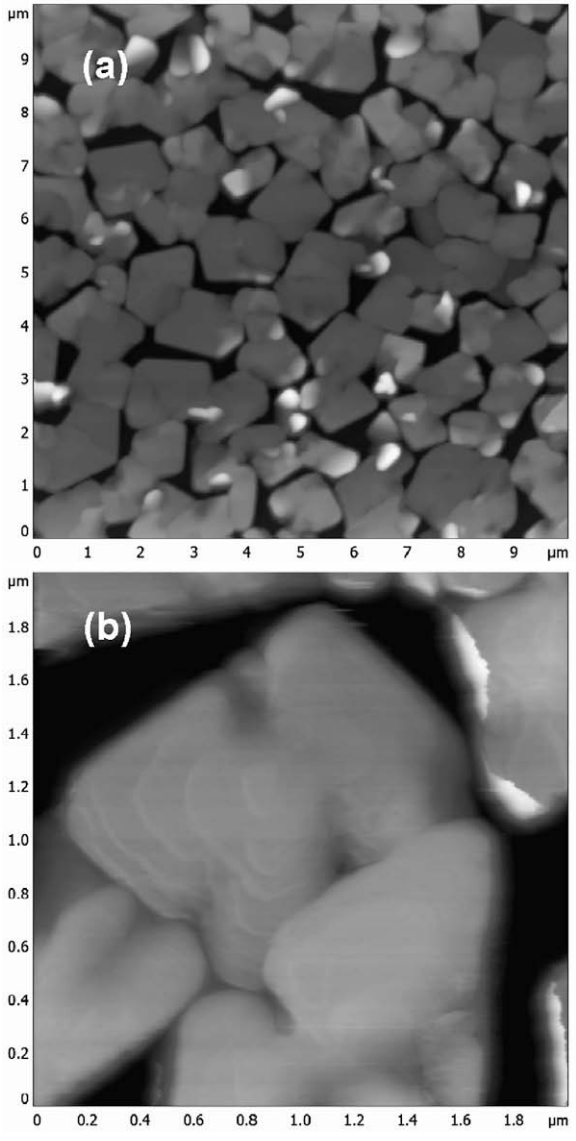

Fig. 1. AFM topographic images of a film grown on SiO_x/Si with impinging molecules having 3.0 eV of E_k. (a) Image $10 \times 10\ \mu m^2$ acquired in semi-contact mode; (b) detail of a grain ($2 \times 2\ \mu m^2$) acquired in contact mode.