SuMBE: Growth by Seeded Supersonic Beams of Organic Materials for Optoelectronic Devices

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Abstract

We have shown that thin film growth of pi-conjugated materials by seeded supersonic molecular beams (SuMBE) is an effective approach to control structure and morphology. These are key features to improve control on energy and charge transport properties and hence for the realization of improved devices including optolectronic applications. Recent results on phthalocyanines, thiophene oligomers and acenes will be discussed showing that control on the precursors, in terms of energy and momentum in particular, is of paramount importance in controlling the final properties of the films including the optical response as well as interfaces. Films showing optical properties comparable to those of the corresponding single crystals and with a controlled morphology have been produced by "tuning" the initial parameters in the beam. The initial kinetic energy, easily varied in the range from a fraction of eV up to tens of eV by changing the seeding of the molecules into an inert carrier gas (i.e. He, Ar, etc.), is shown to be a key parameter. Even the defect type and density as well as the polymorphism can be controlled by this method. In a SuMBE co-deposition scheme we have developed solar cells based on phtalocyanines and fullerenes the performance of which could be optimized by controlling the SuMBE deposition parameters. An outlook of the possible developments will be discussed in view of a new generation of devices.

Introduction

Development of novel optoelectronic and electronic devices made of organic semiconductors, like organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs) organic solar cells require high quality film deposition methods with improved control on chemical, physical, electronic and optical properties. The chemical "engineering" at the molecular level promises an increasingly wide spectrum of opportunities of material functional properties. Often a critical question is to achieve an adequate control on structure and morphology at the solid state needed to fully exploit the molecular properties and to produce "useful" devices. Often a defect free growth of (poly-)crystalline materials with well defined molecular ordering is desired. A strong improvement on the growth from liquid phase has been achieved by vacuum deposition methods (PVD) and in particular by organic molecular beam deposition (OMBD) or organic molecular beam epitaxy (OMBE). For many practical applications OMBD/OMBE has proven to be well appropriate. However, it still faces severe limitations depending on the type of molecule and substrate so that an improved control of the film quality remains desirable to give rise to better performing devices. Factor ruling a key role are the strong anisotropy of the molecular precursors and the often large number of polytypes in the solid phase. We have developed a new approach [1] to tackle such questions, which we called supersonic molecular beam epitaxy (SuMBE). This method uses the expansion of a light carrier gas into vacuum, with organic molecules evaporated (seeded) into the gas stream[2].

Supersonic Beams of Organic Molecules

The supersonic expansion of the light inert gas induces a series of effects on the heavier molecular seeds. First of all a well controllable aerodynamic acceleration is produced by the large number of collisions (typically 100-1000) that the heavier slow molecules experience during the expansion with the much faster, lighter particles, of the carrier gas. As a consequence, by simply changing the carrier gas species and the percentage of seeding one can continuously change the initial kinetic energy of the seeded molecule. Figure 1 shows this effect for a series of π-conjugated molecules of interest in the field (pentacene, oligothiophenes, phthalocianines). An interesting point is that one could span a regime of kinetic energies from tens of meV up to tens of eV. This allows covering the whole range from the typical energies of standard OMBD up to the thresholds of chemical activated processes including absorption, dissociation, surface reactions, etc. (a sort of "hammer chemistry"). An example of this extreme is represented by some of our experiments on the SiC synthesis by supersonic beams of C_{60} [3]. We discuss here an intermediate regime where the characteristics of the beam would give improved control on the growth of the films on different substrates.

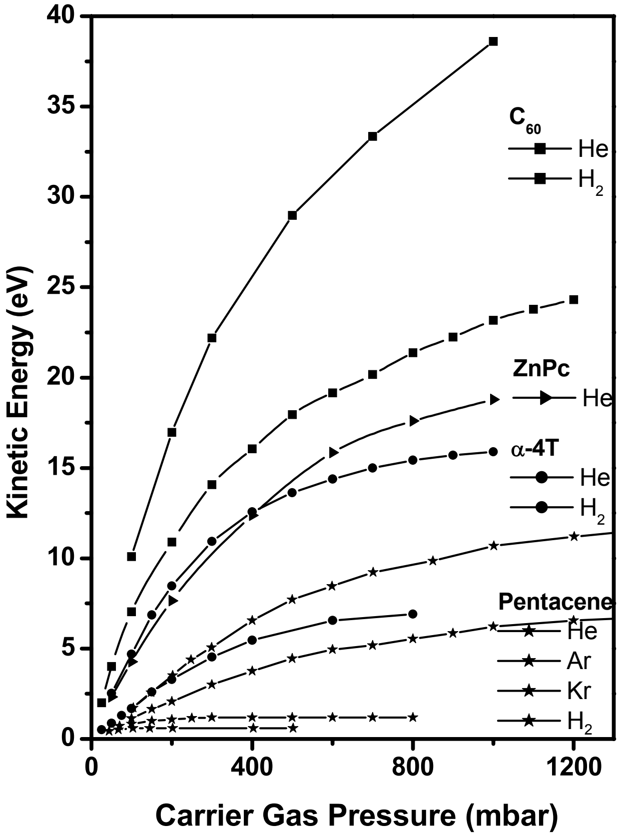

Figure 1. Dependence of the kinetic energy of several p-conjugated molecules seeded in a supersonic beam of a much lighter gas (H2, He, Ar) (see text). The abscissa gives the pressure of the carrier gas into the source; the temperature of the source is kept constant.

Another important effect, occurring to strongly anisotropic molecules when seeded in a supersonic expansion, is the alignment of their backbone along the beam axis. This effect, observed in oligothiophenes[4] and benzene,[5] is driven by the need to show their least cross section to the denser and faster flow of the lighter carrier species. Thus "molecular Frisbees" travelling with a preferred order in the gas stream are achieved. We than used such an energetic controlled beam of ordered organic molecules for film deposition onto solid substrates.

SuMBE Grown Thin Films

First experiments with SuMBE deposition of organic molecules indicated a growth of ordered molecular films. These experiments dealt in particular with oligothiophenes.[6-8] Major relevant properties concern morphology, structure and optical properties. In more recent experiments we explored the properties of pentacene grown on thermally oxided Si (100). Figure 2 shows the different morphology achievable by SuMBE using different initial conditions of the molecules. Using Kr as a carrier gas we could produce a beam of pentacene at kinetic energies similar to the ones produced by a Knudsen cell (typically a few hundreds of meV. Films grown with such beams show the typical morphology shown in Figure 2. The AFM micrograph, obtained in tapping mode, shows grains on the scale of 100 nm where it is hard to recognize any other feature. When higher kinetic energies are used the morphology is strongly affected and an increasing degree of ordering is obtained.

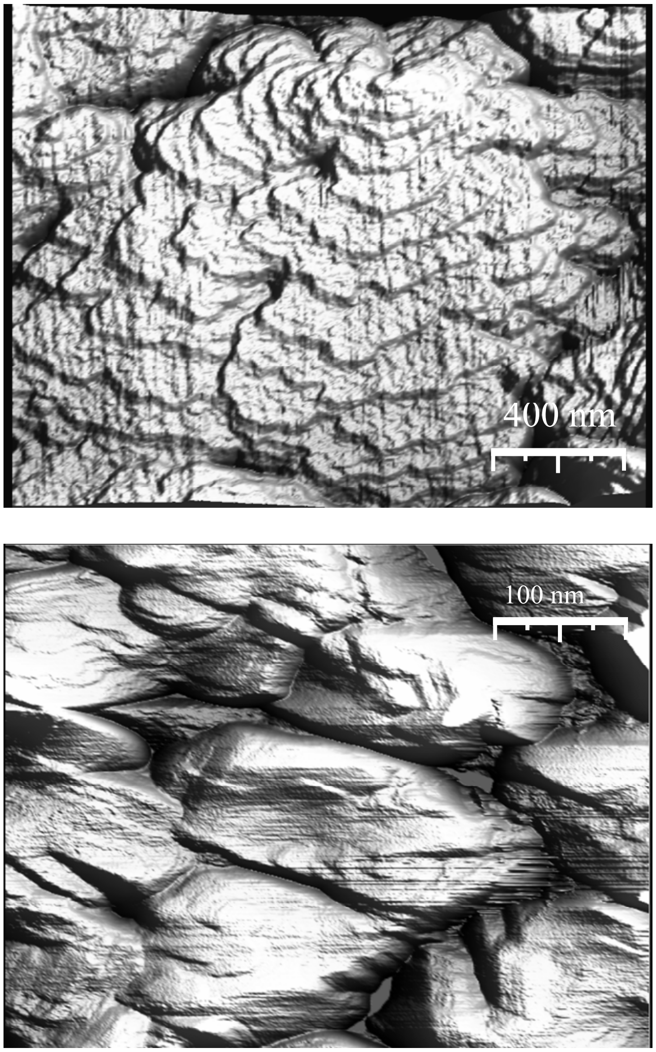

Figure 2. Example of the different morphologies achievable with SuMBE at room temperature. The case of Pentacene on a SiO_2/Si is shown. When a low kinetic energy of about 0.5 eV is used a granular unresolved morphology is observed (bottom micrograph) typical of an OMBE growth in similar conditions. Using higher kinetic energies (~5 eV) a much more ordered layered structure can be produced (top micrograph)

The top AFM micrograph of Figure 2 shows the morphology of a pentacene film grown by supersonic beam with the molecule at a kinetic energy of about 5.5 eV. A very regular terraced structure is observed which is regular over a μm scale. It should be emphasized that such a result could not be achieved in the OMBD configuration unless accompanied by thermal annealing procedures confirming literature data[6]. In collaboration with the group of prof. Scoles, we have also shown that the structure could be nicely controlled by SuMBE studying the conditions of layer by layer growth achievable on a clean Ag(111) and studied by atomic diffraction and X-ray reflectivity.[7]

We have also addressed the question of the optical quality of the samples, several hundreds of nm thick, grown by SuMBE in terms of degree of crystallinity and of density of defects. We used low temperature photoluminescence a sensitive probe of degree of ordering and presence of defects. Figure 3 shows an example of such measurements. The three spectra refer to films grown in very similar conditions (flux, substrate and preparation conditions) but for the kinetic energy of the precursors in the beam. At the highest kinetic energy used (15 eV) the spectrum appears very well resolved and practically all the features observed are interpreted as the vibronic structure and its replicas but for a very small feature labelled “C”. Such a feature becomes increasingly important as the kinetic energy of the beam is decreased down to 11 and 8 eV respectively. Similarly the 00 peak becomes smaller. We could associate such a feature to the presence of defects due to molecules slightly bended with respect to the crystalline phase of the film. It should be noted that spectra as sharp as the once reported in Figure 3 cannot be obtained using any other growth method unless one uses ultra-thin films on strongly orienting substrates and/or, to a certain extent, temperature treatments.

An interesting class of molecules, widely studied for several optoelectronic devices, is represented by phthalocyanines. The different symmetry of these molecules makes their growth quite different than observed for rigid rotor like molecules. In this case we have systematically studied the growth under different conditions in particular for ZnPc and for TiOPc. A variety of different morphologies have been observed varying the beam parameter, the substrate and the growth temperature. A more detailed discussion will be given in a coming paper,[8] here we would like to emphasize that ingle crystals larger than 5 μm X 5 μm several hundreds of nm thick have been obtained. Figure 5 shows an AFM image obtained by growing TiOPc on mica using a supersonic beam of 17eV and a substrate temperature of about 490K.

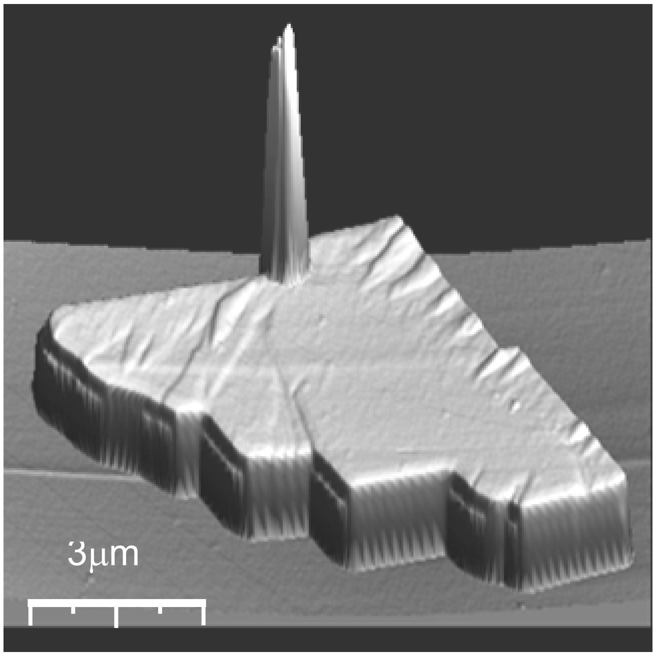

Figure 3. Combining SuMBE with growth at higher temperatures a variety of morphologies could be produced up to large single crystals. Here it is shown an example of TiOPc on mica.

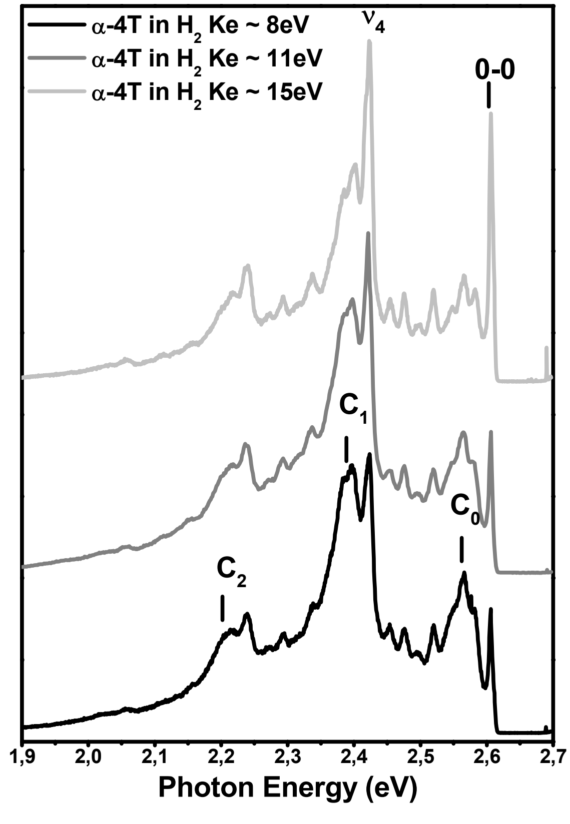

Figure 4. Low temperature (10 K) photo-luminescence from films of quaterthiophene grown using different initial kinetic energies as reported in the top of the figure.The feature labeled “C” refers to defects. The PL data confirm the ability to control features like these.

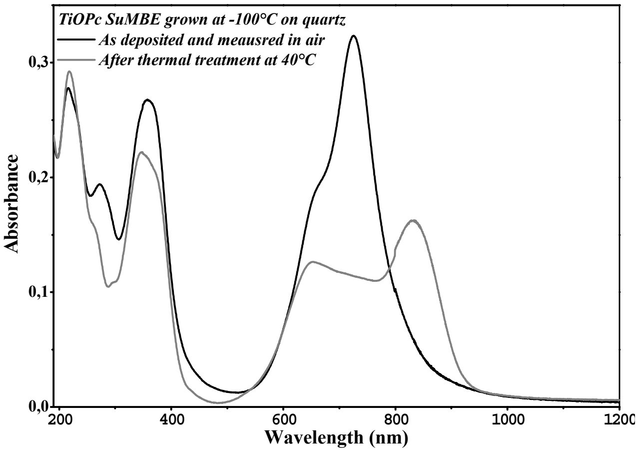

Figure 5. Absorbance of SuMBE grown films with or without heating at 40°C in air. The distinctive signature of phase II of TiOPc is clearly observed for the heat treated sample.

We have also produced films in the pure phase I and phase II polymorphs by combining the control on the kinetic energy of the precursors with different substrate temperatures. An interesting effect has been observed for films grown at temperatures below room and then subjected to a mild temperature treatment (40-50°C in air). Figure 5 shows the absorbance spectra of one of such samples. The spectrum of the film as grown and exposed to ambient air is typical of the TiOPc as obtained by any other standard deposition at room temperature. After a mild treatment at only 40°C, for les than an half hour in ambient air, the spectrum changes completely showing the band at about 830 nm that is a typical signature of the phase II polymorph.[9] After such a procedure the film formed remain very stable in time over a long period. If any further thermal treatment is carried out over temperature range up to 200°C no further modification of the spectra. We ascribe this effect to the formation of nano-micro-precursors induced by the SuMBE growth that allow the formation of a metastable phase that is responsible of the transition to the phase II during the mentioned treatment. This is also indicated by the fact that if the sample grown at -100°C is not treated soon (in bout one hour) after exposure to ambient air, the transformation to phase II is not observable unless very high temperatures are used (larger than 200°C).

Conclusions and Outlook

We have shown that SuMBE is a very valuable growth method that gives rise to umprecedented control on the growth of molecular speies of different types from rigid-rod like such as acenes and oligothiophenes to more symmetric and planar ones such as phthalocianines.

This highly enhanced control on structure and morphology of organic films that is achieved by SuMBE opens a new perspective for the development of devices where energy and charge motilities are key parameters to take care of. We carried out first tests in this direction developing simple solar cells where the active layer is deposited using SuMBE.

Similar studies are under way to develop a new generation of organic thin films transistors and sensors. They could in fact strongly benefit of the enhanced mobilities that the control, by SuMBE growth, on structure and morphology gives rise to.

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Biography

Salvatore Iannotta received his Doctor in Physics at the University of Bologna in 1976 and the Ph.D. in Chemistry at the University of Waterloo–Canada in 1984. Since 1984 he has worked at the Consiglio Nazionale delle Ricerche. He is presently Research Director-responsible of the section of Trento of the Institute of Photonics and Nanotechnology–Italian National Research Council. He is the Italian representative in the "Nanometer Structures" division of the IUVSTA (International Union of Vacuum Science and Technology Associations)." His work has primarily focused on the synthesis and Characterization of Nanostructured and Molecular Materials for Photonics and Microelectronics. He is author of more than eighty papers in refereed journals and invited speaker to more than 20 international conferences.