Organic, Cluster Assembled and Nano-Hybrid Materials produced by Supersonic Beams: Growth and Applications to Prototype Device Development

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ABSTRACT

An approach to the growth of films of π-conjugated organic materials, cluster assembled and nanohybrid materials combining supersonic free jets with a UHV deposition apparatus including surface characterization methods will be discussed. The unique control achievable with supersonic beams on initial kinetic energy, momentum and state of aggregation enables the growth of materials with controlled properties at different length scales. Results obtained with organic semiconductors and oligomers point out the crucial role of kinetic energy in growing organic crystalline films with well controlled morphologies and structures. By means of supersonic beams of clusters, nanocrystalline metal oxide films can be grown without annealing, so that grain size and morphology can be better controlled. In a co-deposition scheme these interesting features are combined in order to obtain a new class of hybrid functional materials with appealing properties for electronics, gas sensing and photovoltaic applications.

Keywords: growth, organic semiconductors, nanophase metal oxides, nanohybrid materials, gas sensors.

1 INTRODUCTION

The ability to synthesize nanostructured thin films with controlled structure and to tailor the needed interfaces is a key to develop new classes of devices. Indeed the properties of organic semiconductors as well as those of nanostructured metal oxides make them appealing for application in many fields, as electronics (Thin Film Transisitors, Organic Light Emitting Diodes), gas sensing (both air and Volatile Organic Compounds analysis) and solar energy conversion, nevertheless control on morphology and properties of thin films with thickness suitable for the use in real prototype devices is still hard to achieve.

As to organic molecules, it has been proved that electronic transport and optical properties depend strongly on molecular orientation and packing. A supersonic molecular beam growth (SuMBE) technique has been developed that ensures a substantial improvement of quality and control of the properties of thin films. Very interesting results have been obtained with molecules such as thiophene-based oligomers, which can be considered the prototypes of π-conjugated systems for studying optical and electrical properties [1], and with pentacene [2]. With regard to metal oxides, the deposition from Supersonic Cluster Beams (SCBD) has proven to be a viable bottom-up approach to the synthesis of films with controlled structure at the nano-level [3]. It will be shown how the appropriate combination of these molecular beam methods opens new perspectives in the intriguing field of hybrid materials in which inorganic structures (metal oxides) are functionalized by means of organic species. The combination of nanophase TiO_2 and metal phthalocyanines will be used as a test case.

2 EXPERIMENTAL

2.1 Supersonic beams of organic molecules and clusters

Supersonic free jets have been in the past largely exploited to prepare molecules in a well defined thermodynamic state for studies with time of flight methods [4]. Indeed molecules or clusters highly diluted in a supersonically expanding carrier gas exhibit a narrow velocity distribution, low divergence and, especially in the case of small molecules, alignment and a substantial relaxation of internal degrees of freedom. Therefore, when depositing species, control on the expansion's parameters gives unprecedented control on the initial state of the precursors.

The production of continuous supersonic beams of organic molecules is performed by means of a source consisting of a quartz tube in which a carrier gas (He, H_2, Ar) is seeded with species sublimated by Joule heating (see Figure1). The mixture then expands into vacuum through a nozzle. Kinetic energy as well as the degree of clustering can be tuned by changing the carrier gas, the nozzle diameter and the seeding parameters (source temperature, gas inlet pressure).

The deposition of clusters is performed via a Pulsed Microplasma Cluster Source (PMCS) [5], which has been developed in collaboration with the group directed by Prof. Milani at the University of Milan (Figure 1). Clusters are produced by quenching of the plasma in a buffer gas after a discharge between two electrodes hosted in a ceramic cavity. Virtually any conducting material can be vaporized, and the contamination of the gas with chemical species can be exploited to modify the nature of the aggregates (for example oxygen is introduced in order to obtain metal oxide clusters). The kinetic energy is in the eV/atom range, thus very interesting for studying cluster-surface interactions and for assembling nanostructured materials. Indeed cluster fragmentation is negligible, and a material preserving memory of its precursors is obtained. Control on the cluster size is attainable acting on the source operating parameters and by means of inertial aerodynamic separation effects: this is very important in order to control the structure and properties of the film, since many properties of these precursors are size-dependent.

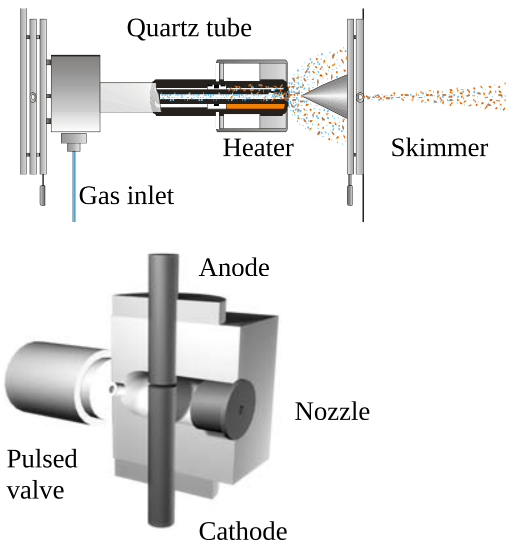

Figure 1: Schemes of the continuous supersonic molecular beam source (top) and of the PMCS (bottom).

2.2 "In situ" characterization and codeposition scheme

To better understand growth and properties of the nanostructures and interfaces we have developed a system with suitable "in situ" characterization tools. In particular this is necessary to link the properties of films and interfaces to the deposition parameters and to the initial state of the precursors, so that we can learn to grow "tailored" materials. In order to produce hybrid nanostructures we have made the apparatus to be operated with up to three different sources running simultaneously and aiming at the same focus point where the substrate is located. Layer by layer growth, blending, doping and direct synthesis of nanostructures of organic, inorganic or hybrid materials can be tailored by the beam properties and parameters. Different devices can be fully assembled and characterized "in situ".

The system can be operated in UHV and is equipped with a fast load lock entry. The deposition chamber is at present equipped with two supersonic sources and an electron beam evaporator, while a Knudsen cell and a third source can be mounted, all facing the sample. Due to the collimation of the beams, precise spots (nearly 1 cm in diameter) are produced on the sample, thus avoiding an extensive use of masks and shields. The sample is held by an x-y-z-θ–ϕ manipulator. The temperature of the substrate can be tuned in the range 120 – 800 K. The deposited films can be characterized in situ at several stages of growth by means of a Jobin-Yvon ellipsometer. A time of flight mass spectrometer (TOF-MS), developed on purpose to characterize both supersonic beams of clusters and organic molecules is available for beam characterization (cluster mass distribution, kinetic energy).

The study of electronic and chemical properties of surfaces and interfaces is performed by means of Auger, X-ray and UV photoemission spectroscopy. Low resolution SEM and LEED investigation of surface structure and morphology is also possible.

3 RESULTS

3.1 Organic thin film growth and prototype devices

With the SuMBE approach we have achieved very promising results in the synthesis of thin films of organic molecules such as pentacene [6] and thiophene-based oligomers [7,8]. As to the latter, both AFM and photoluminescence show a highly ordered structure and good optical response. The key to understand this outcome is in the features of the deposition technique: the kinetic energy (tens of eV) and the alignment that the molecules gain in the beam induce ordering on the surface. A clear evidence of this has been given by experiments on pentacene [9], demonstrating good electronic properties comparable to those of amorphous silicon. AFM characterization of films grown at increasing kinetic energies has shown that larger and larger micrometric crystalline terraces can be produced up to uniform crystalline films, where charges move without meeting grain borders. Such morphology has allowed obtaining OTFT with state of the art field effect mobility.

The deposition of metal phthalocyanines (MPc) is currently under study. In particular TiOPc SuMBE deposition has shown to procure access to different crystalline phases, including the phase II with improved absorption optical properties [10], and CuPc is being studied both for gas sensing (see § 3.4) and photovoltaic application.

3.2 Kinetic activated growth of nanostructures

Features of the SuMBE method can also be exploited to approach the growth of nanostructures difficult to obtain with traditional methods. Silicon carbide (SiC) synthesis on silicon substrates is a clear example of the potential of the technique. This is an attractive field, due to the possible integrations between the two materials, for example for a brand new class of sensors, as well as MEMS based tools for harsh or bio-compatible environments. Some problems arise when SiC is grown heteroepitaxially on a Si substrate, because of the mismatches in lattice and thermal coefficients.

Using a highly collimated supersonic flux of C_{60} the kinetic energy of the fullerene cage can be tuned from 0.5eV up to 70eV, therefore well above the ~0.07eV of the conventional thermal evaporation techniques. We have grown SiC films on Si(111)-7×7 in UHV as a function of the C_{60} kinetic energy, at 800°C and 750°C substrate temperatures, the latter being a value at which carbide formation is not achievable by standard methods using such a precursor [11]. The carbide synthesis can be obtained by the kinetic activation of the process, while the electronic and structural properties of the film can be controlled by monitoring the beam parameters (flux and particles energy). Substrate temperatures ranging from 500°C down to Room Temperature were also explored, performing in situ surface electron spectroscopies (AES, XPS, UPS, LEED). The possibility to grow SiC at room temperature, where no thermal formation of the carbide is possible, is currently under investigation.

3.3 Cluster assembled titania and gas sensing applications

The development of the PMCS has opened new perspectives in the synthesis of cluster-assembled materials by means of the SCBD (supersonic cluster beam deposition) technique. This source is capable of delivering stable and intense cluster beams, so that the production of films several hundreds of nm thick is possible in a few hours. Very interesting results on the synthesis of nanostructured titania have been obtained. Particularly, the XRD, Raman and AFM characterization of as-deposited films show a highly porous structure with the presence of anatase, brookite and rutile crystals with size ≤20 nm (figure 2), and there are indications of an existing correlation between cluster size and crystalline phase [12]. Thus this deposition technique allows one to obtain a nanocrystalline porous film without any thermal annealing procedure, which would produce undesired grain growth and coalescence.

Gas sensing devices that include nanostructured TiO_2 as active medium exhibit performances at the state of the art as to sensitivity to VOC (ethylene and methanol) [12]. Thanks to the high effective area and to effects related to the nanometric grain size, such results are obtained at a temperature well below 300°C. The lowering of operation temperature with respect to sensors produced with more standard techniques yields advantages both in terms of stability and power consumption.

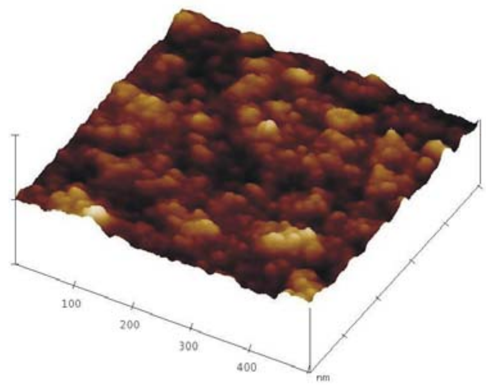

Figure 2 : AFM 500 x 500 nm^2 image of a nanostructured TiO_2 film grown by supersonic cluster beam deposition.

3.4 Hybrid materials: the organic-metal oxide interface and preliminary results in gas sensing

The concept of kinetic activation described in § 3.2 founds a very promising application in the field of the synthesis of hybrid nanostructures. Indeed chemical processes at the organic – inorganic interface can be activated by means of the supersonic beam deposition, as pointed out by photoemission experiments performed on the CuPc/TiO_2 system, whose results are summarized in figure 3. In the bottom XPS spectra the C1s and N1s core level excitations of a CuPc thin film are reported. Depositing nanostructured TiO_2 on the organic film does not produce significant changes, while in the case of the deposition of CuPc on the oxide a shift and a change in the shape of the levels is found, indicating that a chemical interaction takes place. This result confirms the crucial role of kinetic energy in view of the synthesis of a novel hybrid material in which the interaction between the organic and inorganic parts improves the properties of the film. In the codeposition scheme this interaction can be maximized while keeping control on the deposition parameters of both species.

Preliminary results on CuPc/TiO_2 hybrid gas sensors confirm that with the SuMBE/SCBD approach metal oxides can be sensitized by means of organic molecules. Figure 4 shows a SiO_2/Si substrate with Au interdigitated contacts (and Pt heaters on the back) on which a sensing layer has been deposited through a stencil mask. These hybrid sensors under methanol exposure have shown performances improving TiO_2-based devices from the point of view of sensitivity and operation temperature, and CuPc sensors in terms of baseline stability. Such results show that this is really a novel material in which qualities of the two precursor species are combined. The work on hybrid gas sensors is carried out in close collaboration with the group of prof. Siciliano at the Institute for Microelectronics and Microsystems (IMM-CNR) in Lecce.

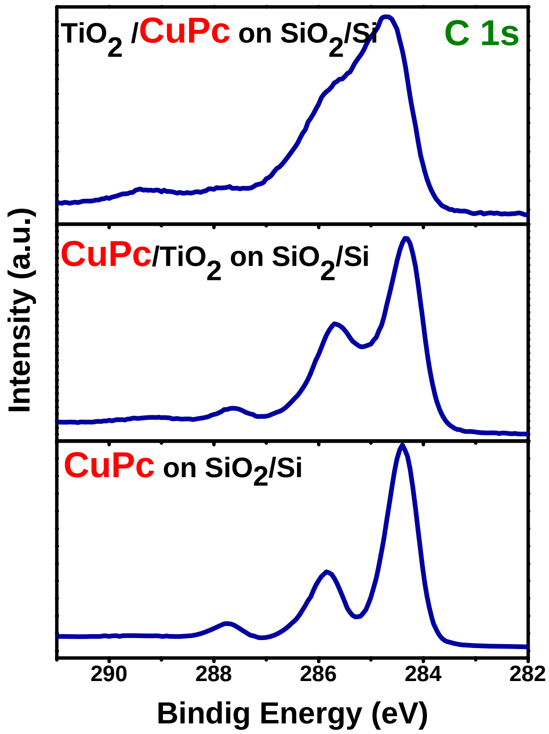

Figure 3 : XPS investigation of the C1s core level in the CuPc/TiO_2 hybrid system.

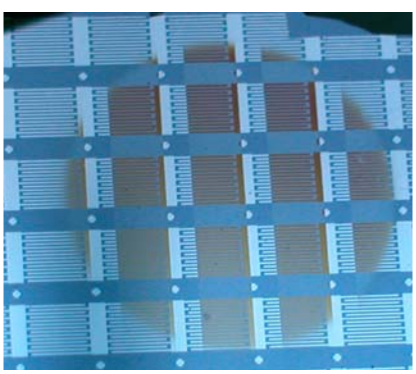

Figure 4 : Silicon substrate with patterns of Au contacts on which a sensing layer spot is clearly visible. A stencil mask has been used to select the sensor area.

4 CONCLUSIONS

The application of supersonic beam deposition methods of organic, inorganic and hybrid nanostructures is very promising. Thanks to the kinetic activation of ordering and chemical processes achievable with these techniques, unprecedented control on film structure and morphology is obtained. Moreover new perspectives in the synthesis of functional nanomaterials are opened by the codeposition scheme. The development of a system enabling in situ characterization of precursors, films and interfaces with several techniques (TOF-MS, ellispometry, electron spectroscopy, LEED) allows us to perform comprehensive studies of these materials. Applications of the deposition technique cover a wide range of applications: interesting results in the preparation of OTFT and gas sensors have been obtained and very promising preliminary results on hybrid sensors have been mentioned. The study of such hybrid systems in which inorganic nanostructures are functionalized by small organic molecules is the main objective of the future activity, together with the production of prototype devices based on these concepts, mainly gas sensors and PV cells.

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