

Structural and morphological phase control by supersonic beams on titanyl phthalocyanine: An investigation on the growth



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ABSTRACT

Titanyl Phthalocyanine (TiOPc) is a cyclic oligomer widely used in organic electronics for its good stability, optical properties and charge mobility. Several polymorphs of TiOPc are known, showing different physical properties and consequently, in particular in the growth of thin films, the full control over the crystal phase formation is critical to effectively tune the conductive properties of the material. As a consequence, the availability of growth techniques allowing a precise control of both the morphology and crystal phase of the obtained films is crucial for the production of devices. In this work the structural properties and polymorphism of titanyl phthalocyanine thin films, grown on silicon substrates, have been systematically studied by synchrotron radiation grazing incidence X-rays diffraction and atomic force microscopy. Films obtained by the use of hyperthermal seeded supersonic beams technique allowed to unveil the key role played by the kinetic energy of the molecules in stabilizing specific polymorphs of TiOPc. The different growth conditions lead to grain dimensions in a range from the nanometric to the micrometric scale, depending on the substrate temperature and on the kinetic energy of the beam, while a high degree of fiber-like crystallographic order is observed in all the analyzed samples. The excellent control over phase selection, grain size and shape together with the production of well oriented high quality crystals makes of the hyperthermal seeded supersonic beams technique a promising tool for the realization of TiOPc thin films with structural and morphologic properties suitable for electronic application.

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1. Introduction

Phthalocyanines (Pc) are oligomer macrocyclic compounds with p type π -conjugated semiconducting behavior. Their peculiar optical and electric properties, including an intense absorption in the visible region, make them optimal candidates for applications in Organic Electronics [1]. In recent years indeed Pc have been successfully applied in the optoelectronics [2], photovoltaics [3],

spintronics [4], and sensing [5] fields. Intense efforts are being devoted to the individuation of the most suitable growth processes to achieve full control of the structural and morphologic properties of the Pc thin films, finally aimed to allow a fine tuning of their electronic and optical properties.

In the case of Titanyl Phthalocyanine [6,7] (TiOPc) a specific interest is related to optoelectronic applications, related to absorption properties in the visible region, extended toward infrared. TiOPc may also be exploited as an active channel in organic field effect transistors (OFET) [8]. In particular, TiOPc was used in unipolar and ambipolar OFET, exhibiting mobility in the range 10^{-5} – 10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ [9]. An exceptionally high mobility of $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was reported for films deposited at high

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temperature on octadecyltrichlorosilane-modified SiO₂/Si substrates [10]. The realization of effective devices, however, relies on the precise control of the structural properties, in particular due to the presence of strong polymorphism, related to the nonplanar and polar structure of the TiOPc molecules. The main stable crystal structures of bulk TiOPc were characterized in the early 80s by means of X-ray diffraction (XRD) by W. Hiller et al. [11] and were identified as phase I (or β), monoclinic, with P2₁/c space group and Z = 4, and phase II (or α), triclinic, with P1 space group and Z = 2), grown as single crystals by chemical vapor deposition [12]. Another polymorph, called phase Y, is sometimes reported being structurally related to phase I, with a different tilting angle of the molecules in the a-b plane [13], and up to date, only polycrystalline films of phase Y have been grown. The different polymorphs show different conductivity, mobility and optical properties. This makes the development of phase-selective growth methods mandatory in order to obtain specific properties in the film and to improve the devices performances [14–16]. The most widely used techniques for the growth of TiOPc films are Langmuir-Blodgett (LB) and spin-coating [17], which, in combination with post-deposition treatments, lead to films of phases I, II, or Y [15]. The phase selection can be achieved by exposing the films to vapors of solvents, such as chlorobenzene or xylene, followed by annealing processes. The best results in terms of phase control can be achieved by Organic Molecular Beam Deposition (OMBD) [18–20]. Typically, OMBD uses an ultrahigh-vacuum apparatus and sublimates a highly purified powder or a melt of the organic source material from a temperature controlled oven or Knudsen cell. The flux of the molecular beam can be controlled mainly by a combination of heater power and mechanical shutters. Substrate temperatures of about 100 °C yield the simultaneous presence of amorphous and crystalline regions (phases I and II). At higher temperatures, the films grow preferentially as phase II [21]. An innovative approach allowing a better control on the growth process, is supersonic molecular beam deposition (SuMBD), based on the expansion of a hypothermal beam, whose kinetic energy is able to stabilize phases which are far from thermodynamic equilibrium. We have previously performed morphological and structural studies of TiOPc thin films realized by SuMBD, in particular on amorphous surface of quartz substrates [22], and on atomically flat surfaces of mica substrates [23]. Our studies showed that the high kinetic energy supplied to the molecules by the supersonic expansion has a crucial ordering effect [24,25], producing larger uniform grains with respect to OMBD. In the present paper we report on a detailed analysis of the TiOPc growth conditions, performed by grazing incidence X-rays diffraction (GIXRD) making use of synchrotron radiation and by atomic force microscopy (AFM). The effects of the different growth parameters on the crystal structure of the films are investigated, allowing to clarify the role of the kinetic energy of the hyperthermal beams in driving polymorphism. In addition, the morphology and crystallites grain size are described as a function of the growth conditions. The effects of SuMBD approach on the accurate control of the crystalline grains size and phase, will be discussed and the ability to improve the crystals size to a quasi-single crystal structural regime, will be analyzed.

2. Experimental section

A homemade supersonic beam deposition apparatus, already described elsewhere [26], was used for the growth of TiOPc thin films. It consists of a differentially pumped supersonic beam and a deposition chamber (Fig. 1). The supersonic beam source is constituted by a quartz tube, closed at the front end, with a 50–130 μ m hole, used as nozzle and placed in a high-vacuum chamber. An inert carrier gas (helium in this experiment) is

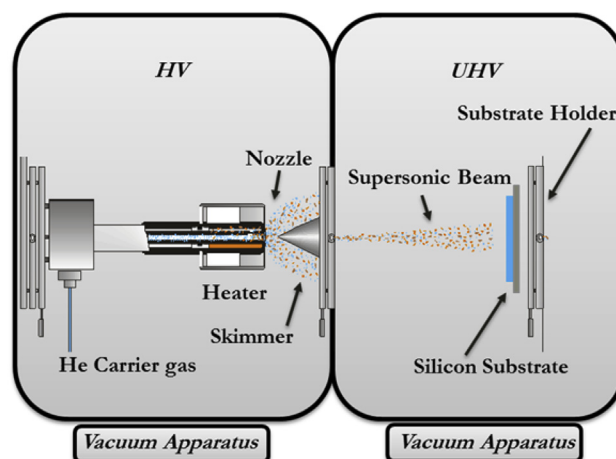


Fig. 1. Schematization of the supersonic molecular beam deposition (SuMBD) system.

supplied to the source at controlled pressure, typically set in the 1000–2000 mbar range. In order to monitor the molecular beam, an in-line time of flight-mass spectrometer (TOF-MS) has been used. The laser multiphoton ionization, has been achieved by the fourth harmonic of a Nd:YAG laser (266 nm), monitors the intensity, purity and stability of the beam. The TiOPc organic material is seeded by Joule heating sublimation into the carrier gas at very low rate. The seeded gas expands through the nozzle into the vacuum chamber, generating a supersonic beam. By changing the working parameters (sublimation temperature, nature and pressure of the carrier gas, nozzle diameter and shape) we are able to finely control the kinetic energy, the momentum, and the cooling of the internal degrees of freedom of the molecules in the beam [27]. By skimming the free jet expansion, it is possible to select the central part of the beam through a sharp-edged conical collimator, which separates the source chamber from the deposition chamber (base pressure 10⁻⁷ mbar). The molecular beam is finally intercepted by the substrate for the deposition of the film. The temperature of the substrate can be controlled in the range from –115 up to 250 °C, with a stability of about 1 °C. The TiOPc films were grown at two different temperatures: 25 °C (RT) and 220 °C on a [100] silicon wafer, cleaned by hot acetone and after isopropyl alcohol. A quartz microbalance measures the deposition rate, which is fixed for all the samples at 0.5 nm/min. The source operating conditions were tuned to keep two different kinetic energy regimes for Phthalocyanine molecules, one referred as “high kinetic energy” (HEk) at 15 eV, and the other “low kinetic energy” (LEk) at 0.1 eV. The duration of the deposition was set to produce films of the same nominal thickness (~60 nm). We used TiOPc powder coming from the same batch (Syntec - Sensient GmbH, Wolfen, Germany) for all the experiments. It was first purified by repeated vacuum gradient sublimation cycles, after which the TOF-MS mass spectra did not show any significant residual contamination.

The structural properties of the film were analyzed by using grazing incidence x-ray diffraction (GIXRD) performed at the Elettra synchrotron radiation facility in Trieste, Italy at the XRD1 beam line. The monochromatic beam energy was set to 8.05 keV. The diffraction patterns were recorded in reflection mode with a 2D detector MarCCD165 (MarResearch) positioned perpendicular to the incident beam at a distance of 130 mm. The sample inclination with respect to the beam was changed from $\omega = 3^\circ$ to $\omega = 9^\circ$ in steps of 1° yielding diffraction images that were simultaneously fitted to increase the pole figure coverage. The images were analyzed by means of the Maud software [28], which makes use of

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