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Comparison of organic thin films deposited by supersonic molecular-beam epitaxy and organic molecular-beam epitaxy: The case of titanyl phthalocyanine

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Abstract

Recently, supersonic molecular-beam epitaxy (SuMBE) was invented as an alternative method for the deposition of organic material, using higher kinetic energies for deposition than conventional organic molecular-beam epitaxy (OMBE). Using titanyl phthalocyanine (TiOPc) as a model substance, we show that the SuMBE deposition results in increased crystal quality of the deposited material. This is induced by the high kinetic energy of the molecular-beam in SuMBE, which leads to increased molecular mobility on the surface, resulting in larger crystal sizes and higher crystal quality. Alternatively, similar films as made by OMBE can be deposited by SuMBE at lower substrate temperatures. This temperature reduction may be of interest for the deposition of stacked organic devices on underlying heat sensitive layers, as they are quite common in organic electronic devices.

Keywords: Molecular-beam epitaxy; Single crystal epitaxy; Semiconducting films; Polycrystalline thin films; Atomic force microscopy

1. Introduction

There is large interest in the deposition of well-defined organic thin films, which can be used in organic electronic devices, such as organic solar cells or organic field effect transistors (OFETs). In some of those applications, a well-controlled crystallinity is desired, e.g., for harvesting charge carriers at heterointerfaces in organic solar cells. Since the exciton diffusion length is a few tens of nanometers, crystal dimensions of the same order of magnitude are desired. Larger crystals are needed in OFETs, since high order within the films can reduce the number of grain boundaries, leading to improved electrical transport properties. One of the standard methods to achieve highly ordered films is organic molecular-beam epitaxy (OMBE). Recently, supersonic molecular-beam epitaxy (SuMBE) was introduced as an alternative method for organic material deposition [1,2]. SuMBE uses a supersonic beam consisting of a molecular vapor sublimed into a much higher density of carrier gases such as H_2 or He.

The setup of a SuMBE source is sketched in Fig. 1. The method allows for the preparation of well-collimated, highly directional beams of organic molecules with controlled kinetic energy from a fraction of eV to several tens of eV, while the kinetic energy of the beam and the thermal energy of the molecules are decoupled. This range is quite interesting since several surface processes can be activated, ranging from physisorption to chemisorption and surface reactions. It should be noted that due the fast and efficient cooling caused by expansion the molecules (down to a few K) the ro-vibrational degrees of freedom are confined producing a molecular-beam with a preferential alignment of

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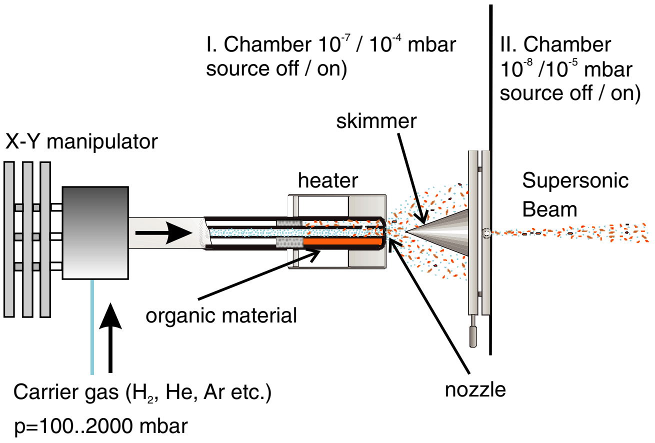

Fig. 1. Setup of the SuMBE source.

the molecular backbone along the beam [3]. The kinetic energy which is dissipated upon arrival on a substrate's surface may explain the different growth modes of SuMBE and OMBE made molecular films which we find.

The method of SuMBE has been described in detail in previous publications [1,4]. Originally, SuMBE was invented for the deposition of inorganic nanocrystalline films. Recently, it was also applied to the deposition of organic molecules, such as quaterthiophene [4–6], pentacene [7], and titanyl phthalocyanine [8]. It could be shown that SuMBE is suitable to deposit organic materials with a high degree of order, and recently even the fabrication of an OFET by SuMBE has been demonstrated [9].

In this paper, we present a direct comparison of OMBE and SuMBE deposited organic films to study the similarities and differences of samples made by both the methods. As a model system, we have chosen titanyl phthalocyanine (TiOPc), a derivative of phthalocyanine (Pc) with a TiO group protruding from the central cavity of the Pc backbone. This molecule is used e.g., as a red-sensitive charge carrier generator in organic solar cells [10]. It forms a number of polymorphs which can be distinguished by their optical absorption, without the need of X-ray measurements [11]. Thin films of different polymorphs of TiOPc can be made by choice of an appropriate substrate temperature, and in case of SuMBE deposition also by the setting of the kinetic energy of the organic material in the molecular beam. The latter, however, was kept constant in the experiments presented here.

2. Experimental

Two vacuum systems were used for the deposition, a home-built SuMBE apparatus and an ultrahigh vacuum OMBE system. The SuMBE source (see Fig. 1) works as follows: a gas stream with typically $p_{\text{gas}} = 100$–2000 mbar is led over a heated quartz vessel, which evaporates the organic material into the gas stream. This seeds the gas stream with organic material. The seeded gas expands through a heated nozzle into a first vacuum chamber, leading to a high-speed acceleration and cooling of both the gas and the organic material. Then, the beam passes a skimmer, which removes the outer, lower energetic part of the beam. A second, high vacuum chamber with another skimmer follows. In a third, ultrahigh vacuum chamber (not shown in Fig. 1), the deposition occurs onto a substrate at variable temperature. For all experiments shown here, the carrier gas was He, at a working pressure inside the source around $p_{\text{He}} = 1600$ mbar. The deposition rate was set to 1 Å/min or slightly below. The OMBE experiments were done in a UHV system with a Knudsen cell evaporator under the control of a quartz microbalance. Film thicknesses and deposition rates were in the same range as in SuMBE, as checked by absorption spectroscopy for the films grown on glass.

TiOPc material from the same batch (Syntec–Sensient GmbH, Wolfen, Germany) was used for all experiments. It was purified in vacuum by repeated gradient sublimation. Substrates were freshly cleaved mica sheets and quartz discs. Both were degassed in UHV at 200 °C for $\geqslant 12$ h before deposition to desorb water and other volatile contaminants from the surface. The UV–Vis–NIR spectra were collected in a Varian Cary 5000 spectrometer (SuMBE samples) and a Shimadzu UV-PC 3100 spectrometer (OMBE samples). AFM images were collected in tapping mode using a multimode AFM (digital instruments). The evaluation of the experimental data was carried out with the scanning probe microscopy freeware WSxM [12].

3. Results and discussion

Fig. 2 shows AFM images of crystalline TiOPc films on mica, which were grown on 220 °C hot mica by the use of SuMBE (a) and OMBE (b). In SuMBE, single crystals grow in a well-shaped manner, with high-quality epitaxy which can be studied by evaluation of the crystal directions (for details see [8]). In contrast, OMBE made crystals are significantly smaller and their shape is less defined. Further, a large number of "bent molecular needles" is found, which is completely absent in SuMBE. Although one finds a few single crystals with shapes as in SuMBE made films, most of the material agglomerates in tiny polycrystals or in unshaped heaps. The influence of the substrate in OMBE grown films is obviously smaller than in SuMBE films: the crystals are oriented more randomly, although some influence of the substrate remains. This can be deduced from the existence of preferred crystal directions on mica. The cross-section (Fig. 2(c)) shows yet another difference: While SuMBE creates regular crystals, the structures made by organic molecular-beam deposition are significantly more irregular and possess a much higher aspect ratio. Further, the surface of the molecular crystals made by SuMBE is molecularly flat and parallel to the substrate, while on the OMBE samples flat areas are rare. Such different crystal morphology may originate in a different molecular arrangement at the interface to the substrate caused by the different preparation methods (e.g., standing or flat