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Device relevant organic films and interfaces: A surface science approach

G. Koller, S. Berkebile, J. Ivanco, F.P. Netzer, M.G. Ramsey *

Institute of Physics, Karl-Franzens-University, A-8010 Graz, Austria

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Abstract

Here the morphology, molecular orientation and electronic structure of in situ prepared *para*-sexiphenyl (6P) and α-sexithiophene (6T) films studied with atomic force microscopy, near edge X-ray absorption fine structure spectroscopy and valence band photoemission are presented. Attention is given to the differences between different organic crystallite orientations and the pitfalls in the interpretation of area averaging surface sensitive techniques that can arise from inhomogeneities in the films, which commonly occur even on single crystal inorganic substrates. The growth of organic–organic heterostructures is then considered for sexithiophene films grown on homogeneous upright (6P(001)) and lying (6P(203)) crystalline films. In both cases, the orientation of the substrate molecules is imposed on the molecules of the second species and thick films of upright-on-upright or lying-on-lying could be produced. The organic substrates are thus shown to be excellent templates for further organic film growth that do not require the stringent UHV conditions of inorganic templates.

Keywords: Organic interfaces; Organic film growth; Oligothiophenes; Oligophenyls; Photoelectron spectroscopy; Near-edge X-ray absorption spectroscopy

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1. Introduction

Driven by the wealth of the possible technological applications conjugated organic materials have been gathering increasing interest worldwide. At present, light emitting and simple electronic devices are on the threshold of being commercially realised, while new applications, such as solar cells and the possibilities of organic lasers are being explored. It is now generally recognised that the interfaces in organic devices are crucial to their performance, however, the basic questions of how and why, and to what extent they can be controlled are still open. To address these issues requires controlled/reproducible investigations and in the last few years there has been increasing activity in this area involving model molecules on single crystal substrates, that is, the surface science approach [1–6]. The fundamental issues that are important are both electronic and geometric: the relative position of electronic levels (band alignment) is a prime determinant of the charge injection ability, molecular orientation and crystallinity control the light emission/absorption and charge transport, while film morphology is generally important to device construction and function. Moreover, different devices, such as field effect transistors (OFETs) or opto-electronic devices, have different requirements as light emission/absorption is polarised parallel to the molecular axis, while charge transport is highest perpendicular to it, as illustrated in the schematic of Fig. 1. Thus, the understanding of organic film growth is important for the full potential of organic electronics to be realised.

Here, we concentrate on the larger single-linked chain like the molecules sexiphenyl and sexithiophene. These were chosen on the one hand because of the understanding of the interactions of their monomer and dimers obtained in the earlier work [2–6], while on the other hand, they are model molecules that are directly device relevant. Sexithiophene (6T) was the active material in the first organic field effect transistor (OFET) with useful characteristics [7], while sexiphenyl (6P) was one of the first blue organic light emitting diodes (OLED) [8]. We have been studying the electronic and geometric structure of films of these

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* Corresponding author. Tel.: +43 316 380 5203; fax: +43 316 380 9816.
E-mail address: michael.ramsey@uni-graz.at (M.G. Ramsey).

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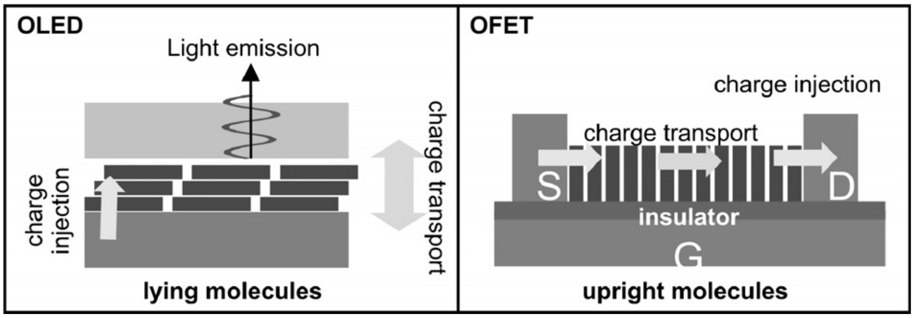

Fig. 1. Schematic of the desired molecular geometry in an OLED and an OFET.

molecules on a variety of different substrates including metals, semiconductors and insulators from the initial stages of formation up to device relevant thicknesses (from 1 to 500 Å). All substrates were based on single crystals, whose surfaces can be prepared in situ in UHV allowing atomic level control of cleanliness and order – a basic prerequisite for reproducible, controlled surface science studies. In this, particular attention has been given to the inorganic substrateś ability to act as templates for orienting the molecules and controlling the crystallite orientation and morphology of the films [9–12]. The thus achieved crystalline organic films of different orientations were used as model substrates for controlled studies of organic on organic heteroepitaxy. Photoemission studies addressing the energy level alignment have been numerous in the literature in the last few years. It is now generally recognised to be controlled by the interface dipole and the ability to inject charge is not an intrinsic function of the contact material per se, but rather a function of the specific interaction of the particular organic with the particular inorganic contact surface [3,5,6,13–15]. Here, we illustrate that the film morphology and the molecular orientation within the organic films can also strongly influence the band alignment as measured by photoemission.

2. Experimental

All films were grown in situ under UHV conditions. Both the *p*-sexiphenyl (Tokyo Chemical Industry Co.) and the α-sexithiophene (Syncom, D.V.) were deposited from thoroughly degassed evaporators such that the pressure in the spectrometer systems remained in the low 10^{-10} mbar range during film growth. Nominal evaporation rates of 2 Å min.^{-1}, as monitored by a quartz microbalance assuming a density of 1.3 g cm^{-3} for 6P and 1.5 g cm^{-3} for 6T, were used. The $TiO_2(110)$ substrates, mounted on sample holders that allowed heating, cooling and azimuthal rotation, were prepared by Argon bombardment and annealing cycles to form the (1×1) surface reconstruction. The ultra-violet valence band photoemission spectra were excited with unpolarised He I radiation and collected either with a Scienta SES 200 analyser (UPS, acceptance angle of 16°) or in a VG-ADES angle resolving spectrometer (ARUPS, acceptance angle of 1°). The Auger yield near edge X-ray absorption (NEXAFS) experiments were performed in the MUSTANG end station attached to the Russian–German bending magnet beamline at the Berlin synchrotron radiation facility BESSY II. AFM measurements were performed ex situ in air, on the in situ prepared and characterised films, with a Digital Instruments Nanoscope IIIa in intermittent (tapping) mode. The films were also monitored during growth with reflectance difference spectroscopy (RDS) and X-ray diffraction (XRD) was performed to assess crystallite orientation.

3. Results and discussion

An aspect that is generally ignored in the studies with area averaged techniques such as photoemission or NEXAFS is the possibility of inhomogeneous organic film growth. Given the propensity of these molecules to crystallize and the extreme differences of the surfaces of different crystallite orientation, the assumption of homogeneity can be misleading. This is illustrated for films of sexiphenyl and sexithiophene grown on $TiO_2(110)$ in Figs. 2 and 3. Fig. 2a shows an AFM image from 35 Å of 6P evaporated at approximately 300 K, while Fig. 2b and c show the UPS spectra of this particular film for normal and off normal emission. Two distinct morphologies are visible on the surface; large rectangular needles ($\sim$1 μm × 100 nm × 10 nm) oriented parallel to the [1 1 0] azimuth and terraced areas with step heights approximately the length of the molecules. As well as these structures are visible to the AFM, there regions between the needles, which will also contribute to surface sensitive spectroscopies. Both NEXAFS (see later) and X-ray diffraction [9–11] show that the long needles are 6P(2 0 3) oriented crystallites, where all the molecules are parallel to the substrate and the [0 0 1] azimuth. The terraced areas, in contrast, can be associated with 6P(0 0 1), where the molecular axes are 17° from the surface normal. Homogeneous surfaces of either of these orientations can be achieved by careful control of the substrate temperature during growth; the 6P(2 0 3) needles grow at $\leqslant RT$, while the near upright 6P(0 0 1) films grow at elevated temperatures (400 K) [10]. As can be seen in the figure the very strong emission features of the substrate are no longer visible in the UPS spectra implying the surface is indeed