White fluorescent nano-fibers prepared by periodic organic hetero-epitaxy

G. Schwabegger\textsuperscript{a}, F. Quochi\textsuperscript{b}, G. Hernandez-Sosa\textsuperscript{a}, T. Djuric\textsuperscript{c}, G. Bongiovanni\textsuperscript{b}, A. Vollmer\textsuperscript{d}, M. Oehzelt\textsuperscript{d}, I. Salzmann\textsuperscript{e}, R. Resel\textsuperscript{e}, N. Koch\textsuperscript{e}, H. Sitter\textsuperscript{a}, C. Simbrunner\textsuperscript{a}

\textsuperscript{a} Institute of Semiconductor and Solid State Physics, Johannes Kepler University, A-4040 Linz, Austria
\textsuperscript{b} Dipartimento di Fisica, Universit\'a di Cagliari, SLACS-INFM/CNR, I-09042 Monserrato (CA), Italy
\textsuperscript{c} Institute of Solid State Physics, Graz University of Technology, Austria
\textsuperscript{d} Helmholtz Zentrum Berlin f"ur Materialien und Energie GmbH, Germany
\textsuperscript{e} Institut f"ur Physik, Humboldt-Universit"at zu Berlin, Germany

ABSTRACT

To preserve the morphological properties of para-hexaphenyl (p-6P) based nano-fibers and simultaneously tune their emission wavelength, periodic organic-organic hetero-epitaxy was utilized. Multilayer structures of p-6P and \(\alpha\)-sexithiophene (6T) have been prepared by hot wall epitaxy and analyzed by scanning force microscopy, fluorescence microscopy, X-ray diffraction and time resolved spectroscopy. We demonstrate that organic hetero-epitaxy can be applied to produce multilayered nano-fibers with high crystallinity, well defined epitaxial relationships along different material phases, molecular azimuthal order, and long-range morphological homogeneity. It is shown, that it is possible to precisely control and tune the highly polarized photoluminescence emission of the nano-fibers from the blue to the green and orange spectral regime by a variation of the 6T concentration. Remarkably, it is possible to prepare nano-fibers emitting white polarized light.

Keywords: para-hexaphenyl, sexi-thiophene, organic hetero-epitaxy, nano-fibers, white polarised emission, lasing

1. INTRODUCTION

In the past decade, small molecular organic semiconductors have been a hot topic in scientific research. Their electronic and optical properties combined with their low cost processability are appealing for flexible optoelectronic and photovoltaic applications.\textsuperscript{1–4} The physical properties of organic semiconductors, in particular the charge transport and optical emission, crucial for the performance of any kind of the previously mentioned devices, depend both on the crystalline arrangement in the solid state and on the molecular structure. Although it has been demonstrated that the molecular properties (e.g. the optical emission) can be tuned by chemical tailoring, the crystalline properties of thin films are more difficult to control. Moreover, the methods used to grow single crystals are not practical for technological applications. An interesting approach to overcome this drawback in order to obtain more desirable macroscopic properties is to produce highly crystalline organic nanostructures by means of self assembly.

When organic molecules are deposited on crystalline substrates, molecule-molecule interactions tend to be stronger than the substrate-molecule interactions during crystal formation. This growth mechanism usually dominates in organic thin film growth and it is referred to in literature as quasi-epitaxy.\textsuperscript{5} Opposite to other bottom-up approaches, where sometimes the preparation steps are costly or not fully compatible with organic semiconductors, epitaxially driven self assembly presents an alternative way to obtain highly ordered and crystalline nanostructures. Furthermore, with the help of vacuum deposition techniques, the growth, composition or doping of organic nanostructures can be accurately controlled to obtain customized optoelectronic properties.

\textsuperscript{Further author information: (Send correspondence to C.S.)}
C.S.: E-mail: clemens.simbrunner@jku.at, Telephone: +43 732 2468 9658
Among the huge variety of organic molecules, thiophenes and phenylenes are promising building blocks for the fabrication of nano-fibers because of their photonic and electronic properties as well as their thermal stability. As a consequence, beside para-phenylene oligomers, also thiophenes, thiophene/phenylene co-oligomers and functionalized para-phenylene molecules have been deposited on muscovite mica (001) to study their epitaxial growth. It has been shown that a proper selection of the molecular species allow to tune the optical properties, and in particular, the spectral emission. Nevertheless, it turned out that simultaneously crystallographic, morphological and structural properties are subject to major changes. As indicated in fig. 1(i) para-hexaphenyl (p-6P) nano-fibers are characterized by a highly parallel fiber formation. Contrary, self-assembled nano-fibers based on thiophenes or thiophene-phenylene oligomers show lower macroscopic anisotropy concerning the orientation of their long needle axes (LNA) and polarised emission. The latter observation roots in the obtained molecular adsorption geometry and a doubling due to the presence of a mirror symmetry plane on the muscovite mica (001) surface.

Consequently, more complex approaches have to be found to achieve efficient tuning of the nano-fibers' optical properties in combination with a conserved polarized emission. Recently, it has been demonstrated that organic-organic heteroepitaxy of nano-fibers can provide a proper method to influence the molecular alignment in a positive and controlled way. In particular, it has been shown that sexi-thiophene (6T) molecules which have been deposited by hot wall epitaxy (HWE) on top of p-6P nano-fiber templates adopt a specified nano- and macroscopic order leading to highly polarized emission in the green and red spectral range. As indicated in fig. 1(ii), intense green fluorescence has been observed for nano-fibers with nominal sub monolayer (ML) coverage of 6T. When resuming the 6T deposition, the nucleation of inhomogenously distributed 6T crystallites on top of the p-6P fiber templates can be observed by the presence of red fluorescent areas (compare fig. 1(iii)).

While p-6P nano-fibers are characterized by a quasi rectangular cross-sectional shape, 6T crystallites nucleated on top are remarkably tilted due to the configuration of their (100) low energy plane. The obtained cross-sectional shape of the nucleated 6T crystallites in combination with optical losses due to self-absorption processes represent a serious drawback for the implementation of waveguiding and the fabrication of self-assembled optical resonators. Based on these considerations it seems highly advantageous to suppress the formation crystalline 6T and to force the predominant formation of a green emitting 6T ML phase.

2. PERIODIC ORGANIC HETERO-EPITAXY

In order to achieve an increased emission of intense green 6T fluorescence and to gain better control on its spectral contribution, the influence of periodic deposition of p-6P/6T on top of p-6P nanofiber templates is analysed. The used growth chamber is equipped with a HWE reactor for p-6P and a separate one for 6T evaporation. To ensure stable growth conditions the muscovite mica substrates, which have been freshly cleaved in air, are continuously heated to 120°C. In a first step, a p-6P template layer is evaporated with a nominal thickness of ≈33 nm. Subsequently, the sample is periodically transfered 10 times (n=10 periods) between the 6T and p-6P...
HWE reactors under high vacuum conditions. During each deposition cycle, a ML coverage (~0.38 nm) of 6T molecules is inserted and subsequently buried by a p-6P spacing layer.

To study the influence of $\Delta d_{p-6P}$ on the spectral response, a sample series is fabricated, were $\Delta d_{p-6P}$ is continuously increased from 16 nm to 325 nm (a graphical sketch of the sample preparation is depicted in fig. 2a). In a first step photoluminescence (PL) was chosen to characterize the fabricated nano-fibers. As indicated in fig. 2b, when optically excited by a He-Cd laser at $\lambda=325$ nm, the PL of all samples is characterized by the presence of two well separated emission bands. While the emission band at higher energies can be attributed to p-6P crystallites (350-500 nm), the sensitized 6T molecules emit at 500-700 nm. In order to obtain a correlation between the 6T PL emission intensity and $\Delta d_{p-6P}$, all emission spectra are normalized to the p-6P (0-1) peak.

Within the presented set of samples all emission spectra are dominated by blue p-6P and green interfacial 6T emission and, importantly, no contributions of crystalline 6T are detected. This observation underlines that the formation of red emitting 6T crystallites is successfully suppressed. Moreover, as indicated in the inset of fig. 2b, the intensity ratio $I_{6T}/I_{p-6P}$ of 6T and p-6P emission scales with $1/\Delta d_{p-6P}$, which underlines a precise control of the spectral response by the chosen growth parameters. By increasing the p-6P spacing layer thickness, the nano-fibers’ fluorescence can be shifted from the green via the white to the blue spectral range, which is demonstrated by fluorescence microscopy images depicted in fig. 2c.

To discuss nano-fibers’ fluorescence properties concerning the fabrication of opto-electronic device structures, it is advantageous to calculate the 1931 Commission Internationale de l’Eclairage (CIE) coordinates from the spectra. The obtained CIE coordinates for the spectral response of a pure p-6P, ML 6T and crystal 6T emissions are indicated in fig. 2d by blue (0.16, 0.07), green (0.42, 0.54) and red (0.55, 0.44) filled squares. Moreover, CIE
coordinates for fluorescent nano-fibers of the discussed sample series are calculated and are plotted in fig. 2d by white filled circles. As demonstrated by a black solid line, the emission colour of p-6P/6T nano-fibers can be shifted on a straight path from the yellow-green to the blue spectral range, simply by increasing the p-6P spacer thickness. Moreover, as indicated by a red cross, representing the daylight simulator D65 coordinates (0.31, 0.33), the obtained emission covers the white spectral range which is of high significance for possible device applications. At this point it should be stressed that a dominant contribution of the ML 6T phase plays an essential role for achieving white luminescence. The latter argument is underlined by a dashed line, which represents the direct pathway between pure p-6P and crystalline 6T emission, and consequently, colour coordinates which can be achieved by a mixture of pure p-6P and 6T.

In a next step, polarisation dependent optics was performed to study the optical anisotropy and consequently the degree of azimuthal molecular order within the p-6P/6T nano-fibers. For polarization-resolved fluorescence spectroscopy organic nano-fibers are excited over a large area of some 100 mm$^2$ at 375 nm by a frequency-doubled Ti:Sapphire oscillator with 82 MHz repetition frequency. The PL emission is analysed by a rotating linear polarizer, wavelength dispersed in a grating spectrometer and detected by a liquid-nitrogen cooled detector. The polarizer is turned stepwise by 5° in an angular range of 360°.

The investigated sample is fabricated by the deposition of $n=25$ periods of 6T, seperated by p-6P spacing layers of $\Delta d_{p-6P}=5.5$ nm. The upper panel of fig. 3 depicts the polarization-wavelength spectrogram of the fluorescence intensity. Due to the strong quenching of blue p-6P emission, its spectral contribution is magnified by a factor of 25. The polarisation angle is defined relative to the LNA of p-6P/6T fibers which is indicated by a view along the nano-fibers’ orientation in the inset of fig. 3. The corresponding height data has been deduced.
Figure 4. a) Geometrical configuration of the probed molecular rotational degrees of freedom for a single sexi-thiophene (6T) molecule on a para-hexaphenyl (p-6P) (11̅1) surface. ϕ_z characterizes the azimuthal adsorption geometry of 6T, ϕ_x/ϕ_y describe the herring bone angle/molecular inclination relative to the substrate surface b) The solid black line represents the energetically most favourable adsorption energy (E_{ad}) versus ϕ_z. A clear minimum at ϕ_z=105° is observed, which corresponds to a parallel alignment of 6T relative to the long molecular axis of p-6P. To demonstrate that the adsorption minimum is independent from the herring bone angle, analogous curves are presented for molecular configurations with fixed ϕ_x={90°, 45°, 15°, 0°}. c) A real space model of the energetically preferable 6T adsorption geometries for the selected herring bone angles; corresponding adsorption energies are listed. d) A top view onto the p-6P stack and adsorbed 6T molecules. The surface unitcell is indicated by a black polygon.

by scanning force microscopy yielding a nano-fiber height of approximately 200 nm.

Strikingly, high optical anisotropy is observed for the entire spectral range. Moreover, all spectral contributions are characterized by an analogous polarisation state. Based on the latter observation and experimental findings obtained by x-ray diffraction pole figure analysis,\textsuperscript{16,18} it can be concluded that 6T molecules adopt the azimuthal orientation of the long molecular axis determined by p-6P molecules in the template fiber. For a detailed analysis, the bottom part of fig. 3 depicts spectra acquired at 0° (solid line) and 90° (dotted line) polarisation angle. The obtained intensity ratios are on the order of 11 which substantiates the parallel molecular arrangement and high azimuthal order of both molecular species within the fabricated nano-fibers.

3. FORCE FIELD SIMULATIONS

Finally, force field simulations are performed to study the molecular adsorption geometry of 6T in more detail. The adsorption of a single 6T molecule on a p-6P (11̅1) template layer is investigated by probing the adsorption energy E_{ad} as a function of three lateral (x,y,z) and angular degrees of freedom. Both structures are assumed to be rigid. The atomic distances are deduced from the p-6P equilibrium bulk structure\textsuperscript{19} and the internal structure of an isolated 6T molecule.\textsuperscript{9} The geometry of the chosen rotational axes (ϕ_x, ϕ_y, ϕ_z) is indicated in fig. 4a. While ϕ_z is representative for the azimuthal adsorption geometry of 6T, ϕ_x/ϕ_y describe the herring bone angle and molecular inclination relative to the substrate surface, respectively. For the presented adsorption data of 6T, the binding energy for each combination of ϕ_z=[-180°, -175°, ..., 180°]; ϕ_y=[-20°, -16°, ..., 20°], ϕ_z=[0°, 5°, ..., 180°] has been optimized concerning the lateral adsorption position (x,y,z), yielding E_{ad}(ϕ_x, ϕ_y, ϕ_z). For the calculation
of the binding energy, force field parameters were taken from the universal force field (UFF)\textsuperscript{20} and a dominant van der Waals interaction is modeled by the implementation of a Lennard-Jones 6-12 type potential.\textsuperscript{9}

In a first step, the optimized adsorption energy versus azimuthal molecular orientation $\varphi_z$ is analysed and presented by a solid black line in fig. 4b. The obtained curve is characterized by a pronounced minimum at an adsorption angle $\varphi_z=105^\circ$. The latter configuration represents a parallel orientation of the 6T molecule relative to the long molecular axis (LMA) of p-6P in the template layer. Consequently, simulations are perfectly consistent with experimental observations based on polarisation dependent optics.

Interestingly, the observed minimum is independent from the chosen herring bone angle $\varphi_x$. The latter statement can be underlined by analysing $E_{ad}(\varphi_z)$ for fixed $\varphi_x={90^\circ, 45^\circ, 15^\circ, 0^\circ}$. The obtained curves are also depicted in fig. 4b and are colour-coded by corresponding symbols. While, edge-on 6T molecules ($\varphi_x=90^\circ$) represent the least favourable configuration ($E_{ad}=-1.89$ eV), force-field simulations yield the best adsorption geometry for approximately flat-on molecules ($\varphi_x=15^\circ$, $E_{ad}=-2.68$ eV). The latter observation can be understood by a maximization of the molecular contact area.

For a better visualization, fig. 4c and fig. 4d depict a real space model of the optimized adsorption geometries for the chosen herring bone configurations. The representation also indicates that the topmost layer of the template crystallite is built up by an alternating stacking of approximately flat-on and edge-on p-6P molecules. At this point it should be stated that simulations are performed for a single 6T molecule and, consequently, reflect only an optimization of the molecule-substrate $E_{mol-sub}$ interaction. Certainly, with an increasing packing density, molecule-molecule interactions between 6T molecules will play a major role and have to be considered by an additional energetical contribution $E_{mol-mol}$. The latter mechanism is also responsible for a frequently observed packing rearrangement from all flat-on to an alternating flat-on/edge-on configuration with an increasing surface coverage.\textsuperscript{21–23} Consequently, the obtained adsorption geometries do not necessarily reflect the molecular arrangement within the p-6P/6T crystal stack. Nevertheless, as all 6T herring bone configurations show common minima at $\varphi_z=105^\circ$, a preferred azimuthal alignment of 6T parallel to the LMA of p-6P can be concluded from the performed simulations.

4. CONCLUSION

The successful fabrication of periodic p-6P/6T nano-fibers grown by hot wall epitaxy is demonstrated. Based on PL measurements, it is shown that the spectral contributions of 6T and p-6P can be precisely controlled by the chosen strategy. In particular, the fluorescence of the fabricated nanofibers can be tuned from the yellow-green via the white to the blue, depending on the chosen thickness of the p-6P spacing layer which separates the 6T monolayers. The contribution of crystallite 6T emission can be successfully suppressed, which represents important progress to cover the white CIE color space. Furthermore, it is shown by polarization-dependent PL measurements that the fabricated nano-fibers are characterized by highly polarised emission across the entire visible spectrum, which can be explained by a parallel arrangement of 6T molecules relative to the LMA of p-6P within the nano-fibers’ template. By performing force-field simulations, the experimentally observed molecular alignment can be understood by a preferred azimuthal adsorption geometry of 6T parallel to p-6P independent of the herring bone stacking angle. The fact that periodical deposition of p-6P/6T molecules yields highly parallel oriented, self-assembled and homogeneously fluorescent nanofibers, whose emission color can be precisely tuned by the chosen p-6P/6T periodicity, certainly suggests the chosen approach for future device applications, for example, white OLEDs.

ACKNOWLEDGMENTS

This work has been financially supported by the Austrian Science Fund (FWF): P25154 and by the federal government of Upper Austria (project ‘Organische Nanostrukturen’).

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