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High oriented epitaxial oligomer/fullerene structures grown by hot wall epitaxy

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Abstract

This work focuses on single layers and bilayers of *p*-sexiphenyl (PSP) and C_{60} grown by Hot Wall Epitaxy (HWE). A detailed study of the growth process was performed on glass, ITO and mica substrates. Sexiphenyl on mica forms a highly ordered anisotropic surface structure which was not observed for the other substrates by atomic force microscopy. Consequently, sexiphenyl layers grown on mica show much higher optical anisotropy (dichroic ratios up to 14 in emission) in comparison with layers grown on glass. The crystallinity of the layers was investigated by X-ray diffraction (XRD), showing clear diffraction peaks for layers grown on mica. Bilayers show a strong quenching of the photoluminescence (PL) due to the ultrafast electron transfer to C_{60}. © 2001 Published by Elsevier Science B.V.

Keywords: Epitaxy; Thin film structures; Fullerene; Oligo-phenylene; Oriented structures

1. Introduction

Organic donor–acceptor systems [1–4], in particular, conjugated oligomer/fullerene bilayers [4] are very interesting for photovoltaic device applications. These materials are thermally stable up to 300–400°C, can be obtained with high purity and can be processed as thin films by high-vacuum deposition techniques. The interest in bilayers with fullerens is due to the well-known photophysical phenomenon, the ultrafast photoinduced charge transfer which occurs in this case at the interface [5]. The interface morphology, molecular packing and structural properties of the donor and acceptor layers are essential for the photovoltaic response of conjugated oligomer/C_{60} bilayer devices.

In contrast to physical vapor deposition [3,6–8] or molecular beam epitaxy [9,10], Hot Wall Epitaxy (HWE) [11] allows growing epitaxial layers close to thermodynamic equilibrium. As a consequence the organic molecules can find the most suitable arrangement before being incorporated into the crystal lattice, resulting in highly ordered structures of the deposited layers. In this report we show that, depending on the growth conditions and the substrate material, anisotropic films of crystalline *p*-sexiphenyl (PSP) with luminescence dichroic ratios up to 14 can be produced by HWE.

2. Experimental details

High purity PSP and C_{60} were purified by three-fold sublimation under a dynamic vacuum of 10^{-6} mbar. The substrates were freshly cleaved (0 0 1)-oriented mica or chemically cleaned glass and ITO coated glass. The vacuum during growth was about 6×10^{-6} mbar. The films were grown at a fixed PSP and C_{60} source temperature of 240 and 400°C, respectively. The substrate temperatures were varied in a range of 50–180°C. Details about the HWE system and growth conditions are given in [11].

The film morphology was imaged using optical microscopy and atomic force microscopy (AFM). The AFM studies were performed using Nanoscope IIIa microscope operated in contact mode in air. The crystalline quality of the PSP films was investigated by a conventional X-ray diffractometer in coupled $\theta/2\theta$ reflection mode. Polarized photoluminescence (PL) spectra were measured on a Hitachi F-4010 fluorescence spectrometer at normal incidence. Low

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temperature luminescence measurements were performed in reflection geometry with a monochromator — photomultiplier setup under high vacuum.

3. Results and discussion

The growth process of PSP strongly depends on the substrate material and substrate temperature. Fig. 1 shows typical AFM images of single layer samples grown on mica, ITO and glass substrates. As depicted in Fig. 1a PSP forms a large scale ordered structure, if the film is grown on crystalline mica. Such large scale ordering was not observed for comparable systems like α-sexithienyl (αT6) on mica [8] or PSP on GaAs [6,9] grown by other techniques. The structure consists of well oriented crystallites looking like very long 'needles' separated by rather flat areas. AFM line profile measurements show that these needles are typically about 16 nm high and 200 nm wide with flat areas of 300–400 nm in between. The length of the needles is up to ≈100 μm resulting in length to width ratio in the order of 500. The needles (crystallites) are strongly anisotropic and

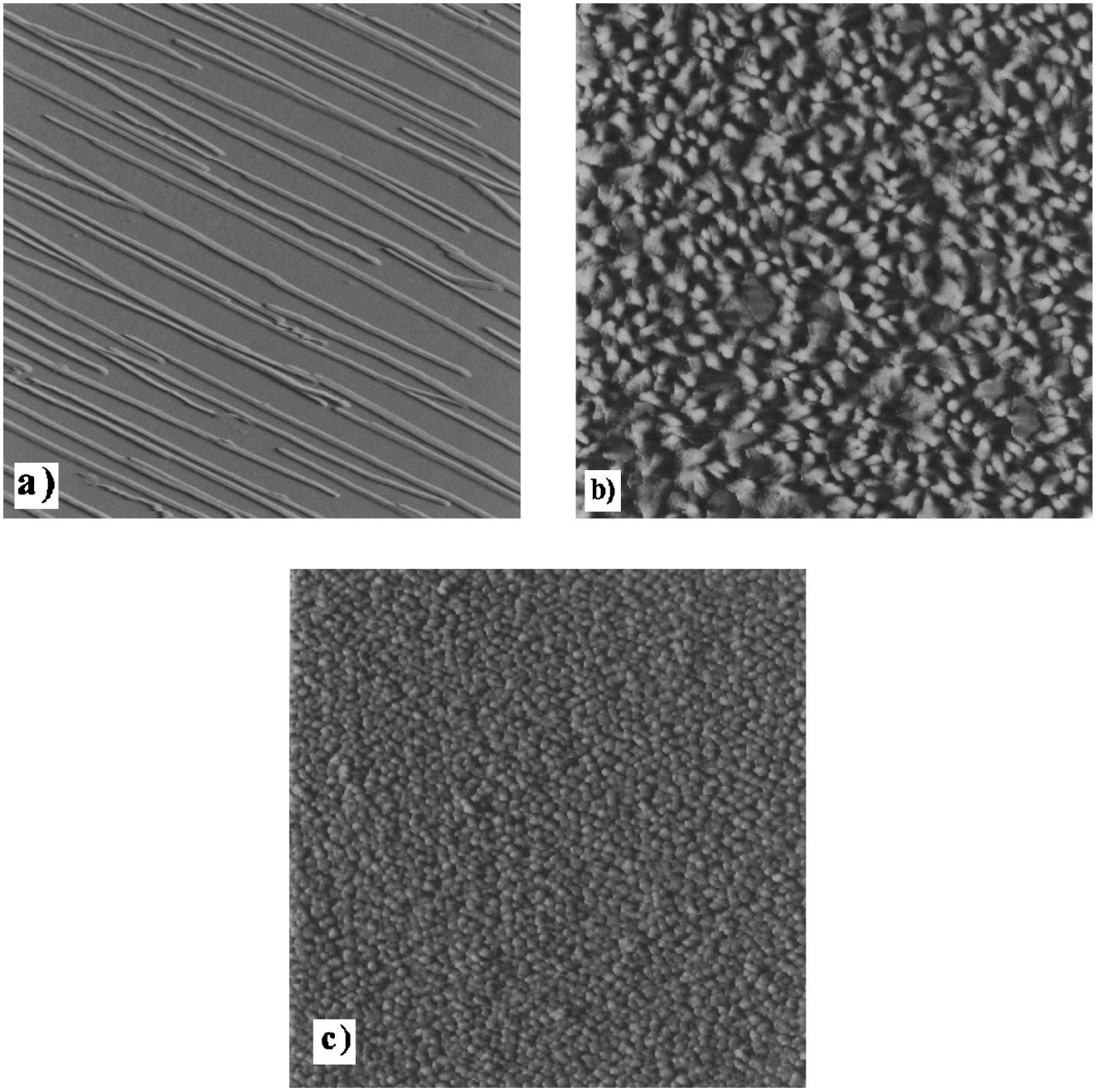
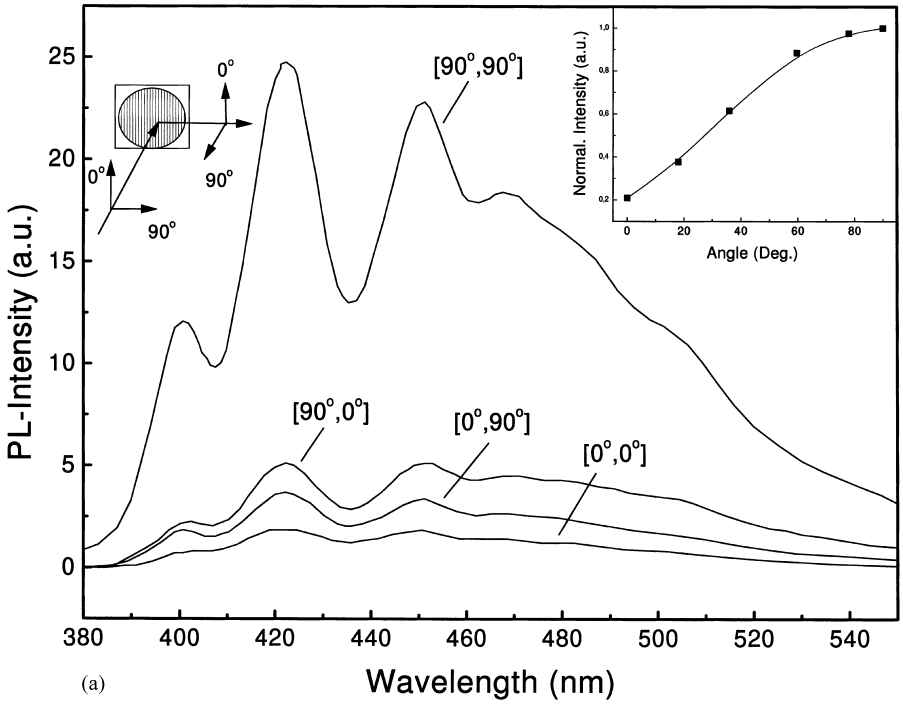


Fig. 1. 10 × 10 μm AFM images (so called 'deflection or error' images of the feed back signal) of PSP films grown on mica (a), ITO (b) and glass (c) substrates at 70–90°C.

their axes align according to one preferential direction predetemined by the crystal lattice of mica. On perfectly cleaved mica this preferential direction is not changed for the whole film surface of 20 mm^2, as found by light-microscope studies. The roughness of the flat area between the needles is determined to 3-4 nm that is comparable to roughness on the surface of the needles (≈3 nm). Cleaved mica typically shows a surface roughness around 0.2–0.3 nm. Therefore, we assume that the PSP films are closed and the areas between the needles are also covered by PSP wetting layer.

The crystalline structure and the orientation of PSP films grown on mica at 90°C was determined by X-ray diffraction (XRD) measurements. Only a (1 1 −1) reflection from the film and (0 0 *l*) reflections from the mica substrate were observed in $\theta/2\theta$ scans. Hence, from the XRD one can conclude that HWE technique yields highly crystalline PSP films oriented on mica along (1 1 −1).



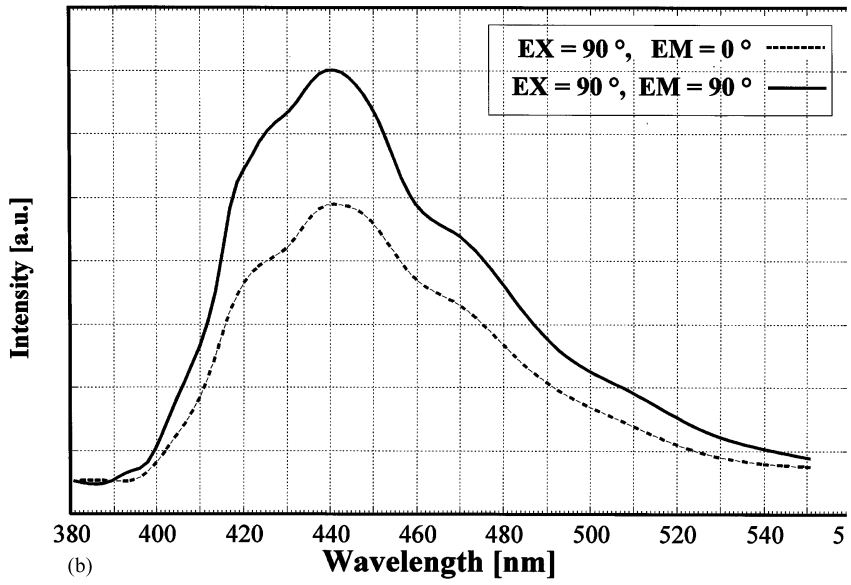


Fig. 2. Polarized PL spectra of PSP films grown on mica (a) and glass (b) excited at 350 nm. The left insert in Fig. 2a shows a schematic representation of the measuring geometry, the right insert shows the angular dependence of the emission for excitation polarized at 90°. The Fig. 2b shows the spectra for excitation polarized at 90°. Measurement temperature is 293 K.

In contrast to PSP on mica no large scale ordered structures could be observed on amorphous substrates as ITO coated glass (Fig. 1b) and glass (Fig. 1c). In both cases the films consist of islands whose sizes increased with growth temperature, which is similar to results obtained for PSP and T6 films grown by physical vapor deposition [6,8]. At a substrate temperature higher than 180°C no film growth was observed. As depicted in Fig. 1c PSP on glass forms a more compact film compared to PSP on ITO. The island sizes on ITO are at least two times higher.

In order to determine the optical anisotropy of highly ordered PSP films on mica we performed PL measurements in a two polarizer geometry, sensitive for the excitation and probe polarization. In Fig. 2a the polarized PL spectra of PSP on mica are shown. For all four permutations of polarizations a well known PL spectrum [12] with three pronounced bands is observed. The PL shows vibronic fine-structure [12]. The maximum of emission is observed if the excitation acts perpendicular to the needles direction. The dichroic ratio for 90°–90° emission compared to 0°–0° is ≈14. The strong emission bands depicted in Fig. 2a have the electric field vector component perpendicular to the film surface. It was shown earlier that the optical absorbance of PSP films depends strongly on the orientation of the sexiphenyl molecules relative to the substrate/incident beam: high optical densities are expected if the electric field vector acts parallel to the chain axis of the molecules [13]. So we can conclude that the PSP molecules are slightly tilted towards the substrate surface with their long axes almost perpendicular to the needles. This is in agreement with our XRD studies presented above and implies a very well ordered stacking of PSP molecules.

Fig. 2b shows typical polarized PL spectra of a PSP film grown on glass. The spectra were taken in the two polarizer geometry depicted in Fig. 2a. A small polarization effect is observed for these disordered films (see Fig. 1c) by changing the polarization of the emission beam. No effect was found for excitation beam (not shown). In agreement with earlier studies [13] we can conclude that the PSP molecules on glass are staying more or less perpendicular to the substrate surface.

Bilayers of C_{60}/PSP were obtained on mica and glass substrates. For the growth of the first C_{60} layer on mica, the optimized parameters given in [11] were used resulting in monocrystalline (1 1 1)-oriented C_{60} films. Using AFM it was found that on C_{60} coated mica PSP grows epitaxially. If the mobility of the molecules is high enough ($T_s > 120$°C), PSP forms oriented islands with sharp edges separated by large voids as depicted in Fig. 3. This observation suggests again that a crystalline substrate favors growth along a preferential direction.

Fig. 4 shows typical PL spectra of C_{60}/PSP bilayers grown on mica. Due to the ultrafast electron transfer to C_{60} [5] a strong quenching of the PL is observed. The quenched PL

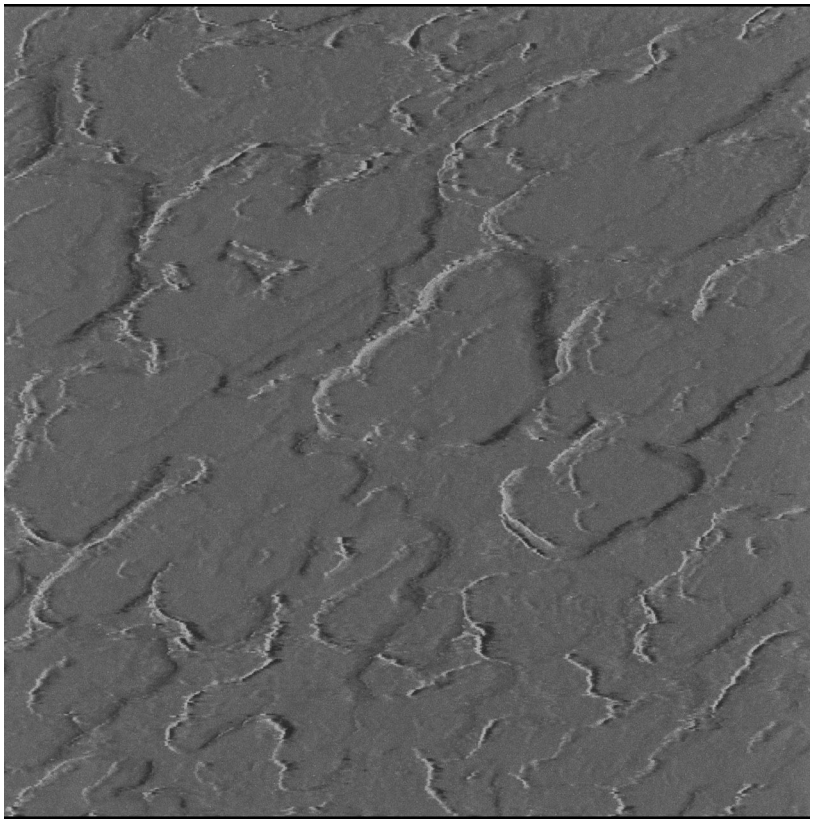


Fig. 3. 5×5 μm AFM images (so called 'deflection or error' images of the feed back signal) of C_{60}/PSP bilayer structure grown on mica at 120°C.

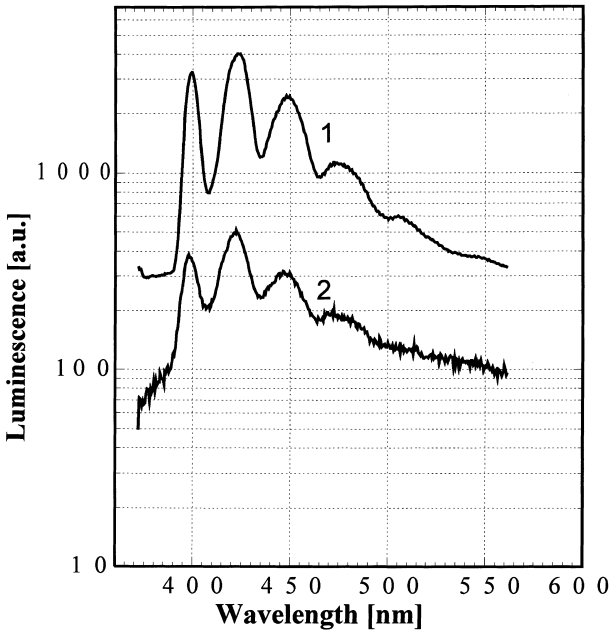


Fig. 4. PL spectra of a PSP film (1) and C_{60}/PSP bilayer structure (2) grown on mica. Measurement temperature is 4 K. Excitation is provided by Ar-laser with 350 nm.

spectra shows no shift or new spectral features indicating that no new radiative states below the π–π^* gap of PSP. The C_{60} luminescence occurs above 690 nm (not shown here) and its shape is very close to that one given in [11] for C_{60} films grown on mica.

4. Conclusions

Single layers of PSP were grown on mica with high optical dichroic ratios up to 14. These layers are crystalline and oriented along (1 1 −1). A self-organization of PSP molecules occurs during HWE growth resulting in 'needle' like structures with a strongly expressed preferential direction, showing a length to width ratio in the order of 500. In contrast to PSP films grown on mica, films grown on glass or ITO consists of disordered islands as found by AFM measurements. C_{60}/PSP bilayers show a strong quenching of the PL due to the ultrafast electron transfer to C_{60}. The potentiality of the HWE technique to grow highly ordered structures, demonstrated in this work, has interesting aspects for optoelectronic devices based on conjugated oligomers.

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