Highly Ordered Crystalline Thin Film Bilayers of para-Hexaphenyl and C$_{60}$ Grown by Hot Wall Epitaxy

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ABSTRACT

This work focuses on single - and bilayers of para - hexaphenyl (PHP) and C$_{60}$ grown by Hot Wall Epitaxy. A detailed study of the growth process was performed on glass, ITO and (001)- oriented cleaved mica substrates. The ordering of the layers was investigated by X-ray diffraction, showing clear diffraction peaks for layers grown on mica. The PHP layers grown on mica show high optical anisotropy (dichroic ratios up to 14 in emission) according to the polarization dependent photoluminescence experiments. The highly ordered structure is also reflected in the surface morphology of the layer as observed by atomic force microscopy. The epitaxial growth on mica is mirrored by the main alignment of the surface structure to the orientation of the mica substrate.

INTRODUCTION

Organic donor-acceptor systems [1-4], in particular, small molecule dyes [3] and small molecule conjugated oligomer/fullerene bi- and multilayers [4] are very interesting for photovoltaic device applications. These materials are thermally stable up to 300-400°C, can be obtained as pure materials and can be processed as thin films in high-vacuum or ultra high-vacuum conditions. On the other hand the interest in bilayers comes from the well known photophysical phenomenon, ultrafast photoinduced charge transfer which occours in this case at the interface [5]. The morphology of the interface, molecular packing and structural properties of the donor and acceptor layers are essential for photovoltaic response of conjugated oligomer/C$_{60}$ bilayer devices.

This work focuses on single - and bilayers of para - hexaphenyl (PHP) and C$_{60}$ grown by Hot Wall epitaxy (HWE). In contrast to the physical vapor deposition [3,6-8] or molecular beam epitaxy [9,10], the HWE allows to grow 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 substrate material, anisotropic films of crystalline PHP with dichroic ratios up to 14 in emission can be produced.

EXPERIMENTAL DETAILS

High purity para-hexaphenyl (PHP) and C$_{60}$ were purified by threefold sublimation under a dynamical vacuum of 1×10^{-6} mbar. The used substrates were freshly cleaved (001)-oriented mica or chemically cleaned glass and ITO coated glass. In the growth

chamber of the HWE system two HWE reactors and one preheating/annealing oven were installed [11]. Each of the reactors consisted of two separately heated ovens for the wall and source zone, which could be kept at different suitable temperatures during growth. The quartz tube with the source material at the bottom was mounted inside the ovens. The substrate was placed close above the tube end and could be heated separately. The sample holder could be moved from one HWE reactor to another one using a computer controlled step-motor, which allows also the growth of multilayer structures. The vacuum during growth was about 6×10^{-6} mbar. The films were grown at a fixed PHP- and C_{60}-source temperature of 240°C and 400°C, respectively. The wall temperature was in the range of 240-260°C for PHP growth and 400-420°C for C_{60}. The substrate temperatures were varied in a 50-180°C range. These growth parameters resulted in a low deposition rate of about 2-3 nm/min.

The film morphology was imaged using optical microscopy and atomic force microscopy (AFM). The AFM was conducted using NanoScope IIIa Microscope operated in contact mode in air. The crystalline quality of the PHP-films was investigated by a conventional X-ray diffractometer in coupled $q/2q$ reflection mode using CuK_{α} radiation. Polarized photoluminescence spectra were measured on a Hitachi F-4010 Fluorescence Spectrometer at normal incidence. All optical measurements were performed at room temperature.

RESULTS AND DISCUSSION

The growth process strongly depends on the substrate material and substrate temperature. Figure 1 shows typical AFM images of monolayer samples of PHP grown on crystalline mica substrates. In contrast to α-sexithienyl (T6) thin films on mica [8] and PHP films on GaAs [6,9] grown by other techniques, a large scale ordered structure (see
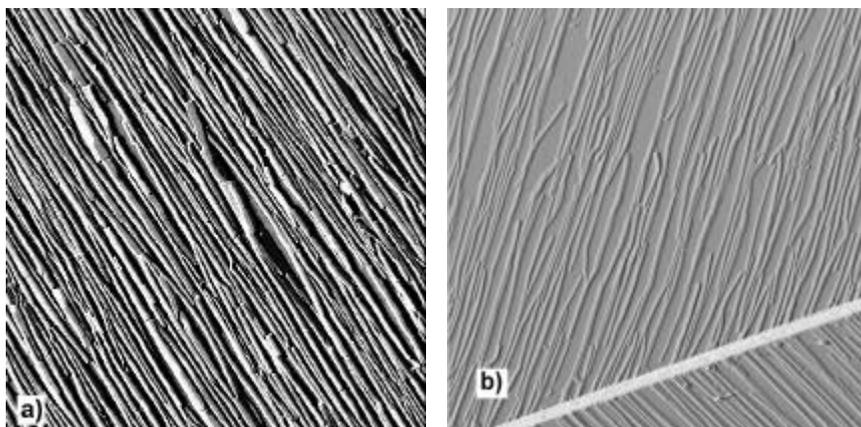

Figure 1. *AFM images (so called "deflection or error" images of the feed back signal) chracterizing the "needles" morphology of PHP films grown on mica at 90°C. a) 20x20 μm image, deposition time-60 minutes; b) 30x30 μm image, deposition time-10 minutes.*

figure 1a) with a strongly expressed preferential direction is observed. This structure consists of large oriented crystallites looking like „needles „ separated by relatively flat areas. AFM line profile measurements show that these „needles„ depicted in figure 1a are typically about 130 nm high and up to 800 nm wide with flat areas of 300-400 nm in between. Needles with a length of up to ≈100 μm were detected. The crystallites are strongly anisotropic and their axes align according to one preferential direction. 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. On terraces, separated by big cleavage steps, the preferential direction of the „needles„ can change by 120° without any other changes in its morphology. A typical example is shown in figure 1b. The roughness of the space between the needles is determined to 3-4 nm that is comparable to the 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 PHP films are closed and the areas between the „needles„ are also covered by a hexaphenyl wetting layer.

The crystalline structure and the orientation of PHP films grown on mica at 90°C was determined by X-ray diffraction (XRD) measurements. Only a (11-1) reflection from the film and (00l) reflections from the mica substrate were observed in $q/2q$ scans. Hence, from the XRD one can conclude that HWE technique yields on mica highly crystalline PHP films oriented along (11-1).

Figure 2 shows typical AFM images of monolayer samples of PHP grown on amorphous substrates as glass (figure 2a) and ITO coated glass (figure 2b). In contrast to PHP on mica no large scale ordered structures could be observed. In both cases the films consist of islands whose sizes increases with growth temperature. This is similar to results obtained for PHP and T6 thin films grown by physical vapor deposition on crystalline substrates as GaAs or mica [6,8]. PHP on glass as depicted in figure 2a forms a very smooth closed film. In comparison to glass the island sizes on ITO are at least two times higher. At substrate temperatures higher than 180°C no film growth was observed.
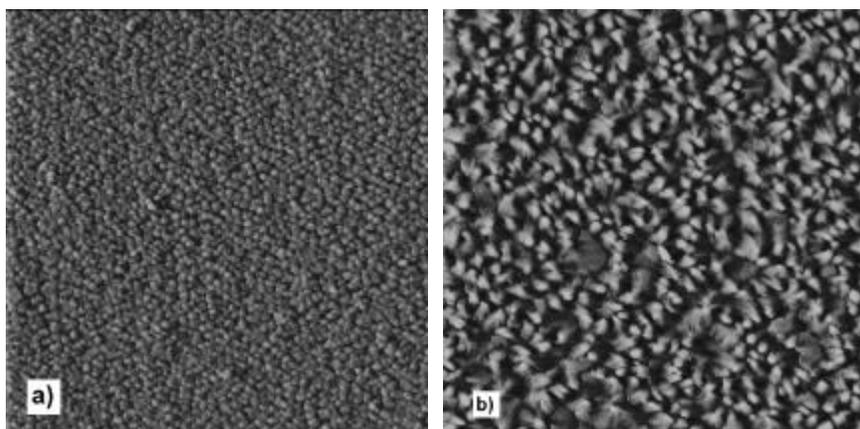

Figure 2. *10 x 10 **m**m AFM images (so called "deflection or error" images of the feed back signal) of PHP films grown at 70°C. Deposition time-60 minutes. a) glass substrate; b) ITO substrate.*

In order to determine the polarization degree of the light emitted from highly ordered PHP films on mica we performed photoluminescence (PL) measurements in a two polarizer geometry for the pump polarization and probe polarization. In figure 3a the polarized PL spectra of a film (its morphology is depicted in figure 1a) are shown. For all four permutations of polarizations a well known PL spectrum (upper spectrum) with three pronounced bands [12] is observed. The PL emission 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 figure 3a have the electric field vector component perpendicular to the film surface. It was shown earlier that the optical absorbancy of PHP films depends strongly on the orientation of the hexaphenyl molecules relative to the substrate/incident beam: high optical densites are expected if electric field vector acts parallel to the chain axis of the molecules [13]. This yields in a polarization effect of the absorbtion and the emission respectively. So we can conclude that the PHP molecules are slightly tilted towards the substrate surface with their long axes almost perpendicular to the „needle„ axis. This is in agreement with our XRD studies presented above and implies a very well ordered stacking of PHP molecules.

Figure 3b shows typical polarized PL spectra of PHP film grown on glass. The spectra were taken again in the two polarizer geometry depicted in figure 3a. Only a small polarization effect can be found for these disordered (see figure 2a) films by changing the polarization of the emission beam as shown in figure 3b. Since no dependence on the polarization of the excitation beam was found, we can conclude that the PHP molecules on glass in contrast to mica are staying more or less perpendicular to the substrate surface [13].

The unique setup with two sources allows the production of bi- and multilayer structures, just by changing the position of the substrate from one oven to another one.
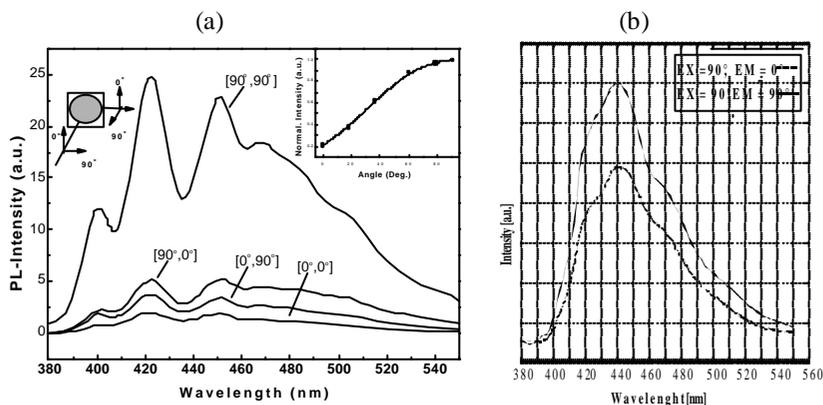
(a)   (b)

Figure 3. *Polarized PL spectra of PHP films grown on mica (a) and glass (b) for excitation at 350 nm. The left insert in figure 3a shows a schematic representation of measuring geometry, the right insert- the angular dependence of the emission for excitation polarized at 90°. The figure 3b shows the spectra for excitation polarized at 90°.*
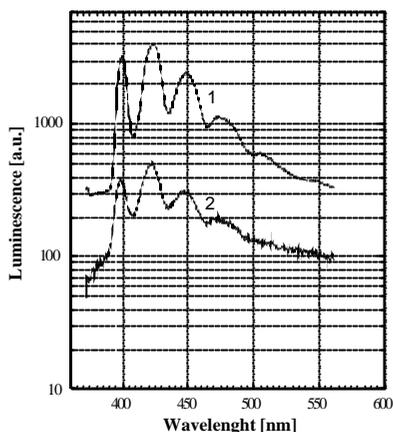
Figure 4. *Luminescence spectra of a PHP film (1) and C_{60}/PHP bilayer structure (2) grown on mica. Measurement temperature is 4 K. Excitation wavelength is 350 nm.*

By this strategy bilayers of C_{60}/PHP 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 perfect mono crystalline (111)-oriented C_{60} films. On such films we studied the growth process of PHP. Using AFM it was found that on C_{60} coated mica PHP grows epitaxialy. If the mobility of the molecules is high enough ($T_s > 120°C$), they are forming oriented islands with sharp edges separated by large voids. This observation suggests again that a crystalline substrates favor growth along preferential directions.

Figure 4 shows typical PL spectra of C_{60}/PHP bilayers grown on mica. Due to the ultrafast electron transfer to C_{60} [5] a strong quenching of the PL is observed. The strong PL of pristine PHP is quenched by one order of magnitude at 4 K. The quenched PL spectrum of the bilayer shows no shift or new spectral resolved species indicating no new radiative states below the π-π^* gap of PHP. The C_{60} luminescence occours above 690 nm and its shape is very close to that one given in [11] for pristine C_{60} films grown on mica.

Bilayers of PHP/C_{60}, sandwiched between ITO and Al electrodes, show a strongly enhanced photovoltaic effect compared to pristine PHP films of similar thickness.

CONCLUSIONS

In summary, single - and bilayers of para - hexaphenyl and C_{60} were grown by Hot Wall Epitaxy. A detailed study of the growth process was performed on glass, ITO and (001)- oriented cleaved mica substrates. Single layers of PHP were grown on mica with high optical dichroic ratios up to 14. These films are crystalline and oriented along (11-1). A self-organization of PHP molecules occurs during HWE growth resulting in „needle" likes structures with a strongly expressed preferential direction, showing a length to height ratio in the order of 1000. According to all optical and XRD data the PHP molecules are basically laying on the mica substrate with a small tilt angle to the surface and with their long axes almost perpendicular to the „needles„ direction. In contrast to mica no large scale ordering are found on glass or ITO. For PHP films grown on glass or ITO the polarized PL indicate a preferential orientation of the chains

perpendicular to the surface. C_{60}/PHP bilayers show a strong quenching of the PL due to the ultrafast electron transfer to C_{60}. The potential of the HWE to grow highly ordered structures, demonstrated in this work, has interesting implications in terms of polarized optoelectronic devices based on conjugated oligomers.

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