

Optoelectronic devices based on para-sexiphenyl films grown by Hot Wall Epitaxy

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Abstract

In this work, we demonstrate the fabrication of hot wall epitaxially grown para-sexiphenyl films for light emitting diodes and PSP/C₆₀ bi-layer structures for photovoltaic cells. Para-sexiphenyl films display blue electroluminescence, which shows a spectrum coinciding with its photoluminescence. Photovoltaic devices are also fabricated and their external quantum and power conversion efficiencies are presented and discussed.

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1. Introduction

Organic multi-layer systems [1–4] consisting of molecular dyes [3–6], conjugated oligomers and fullerenes [4–8] are very interesting for optoelectronic applications. These small molecules are thermally stable up to 300–400 °C, can be obtained as pure materials and can be processed to thin films by deposition in high-vacuum conditions. Furthermore, the interest in bi- and multi-layers of donor/acceptor materials comes from the well known photophysical phenomenon, ultrafast photoinduced charge transfer, which can occur at the interface between donors and acceptors [9]. The morphology of the interface, molecular packing and structural properties of the donor and acceptor layers are therefore essential for photovoltaic response of such structures.

Device structures based on *para-sexiphenyl* (PSP), a six units oligomer of *para-phenylene*, are interesting due to the intense blue luminescence of PSP itself [7,8], and due to the possibility of photoinduced charge transfer to the fullerenes in PSP/C₆₀ bi-layers as shown in [10]. Furthermore, we demonstrated recently that the highly ordered structures of PSP and C₆₀, including multi-layers, can be fabricated by Hot Wall Epitaxy (HWE) [10–12]. Most device applications for organic materials would desire such ordered layers. It

would therefore be interesting to implement the HWE grown films into organic optoelectronic devices.

In this work, we demonstrate the fabrication of hot wall epitaxially grown PSP layers for light emitting diodes as well as PSP/C₆₀ bi-layer structures for photovoltaic cells.

2. Experimental

The optoelectronic devices were fabricated in a sandwich geometry, using ITO coated glass as bottom and LiF (0.6 nm)/Al (60 nm) as evaporated top electrode. On the ITO, a layer of PEDOT:PSS was spin coated from an aqueous solution with a thickness of approximately 100 nm as hole injection layer. After subsequent drying in dynamic vacuum, the active layer of PSP or bi-layers of PSP/C₆₀ were grown by HWE. PSP and C₆₀ were pre-purified by threefold sublimation under a dynamical vacuum of 1×10^{-4} Pa. HWE was used as evaporation technique, which turned out to be very appropriate for Van der Waals Epitaxy [11,12]. The vacuum during growth was about 6×10^{-4} Pa. The films were grown at a fixed PSP and C₆₀ source temperatures of 240 and 400 °C, respectively. The substrate temperature was also fixed at 90 °C for both layers. The wall temperature was in the range of 240–260 °C for PSP growth and 400–420 °C for C₆₀. The thickness of PSP and C₆₀ layers was varied in the range 50–130 nm. Further growth details can also be found in [10–12].

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Current–voltage curves were recorded with a Keithley 2400 source meter. The electroluminescence (EL) was measured with an Avantes spectrometer. A steuernagl solar simulator with 80 mW cm^{-2} was used as illumination source to measure the photovoltaic cells. Photoluminescence was measured with a silicon diode after a monochromator and cut-off filters. The signal was detected with a lock in amplifier. The samples were excited with the mechanically chopped multi-line UV light from an Ar^+ laser. Absorption spectra were recorded with an UV-Vis HP spectrophotometer at normal incidence. Photocurrent spectra were recorded by illumination with monochromatic light from a xenon lamp, a lock-in amplifier was used to detect the current. The lamp spectrum was measured with a calibrated Si diode.

3. Results and discussion

At first, we tested the single layer devices based on PSP for EL. Fig. 1 shows the typical EL spectra obtained from ITO/PEDOT/PSP/LiF/Al structures. Corresponding current (I)–voltage (V) curves show a rectification value of ~ 100 at $\pm 7 \text{ V}$ and an onset for the current injection at $+5 \text{ V}$. The EL shows two peaks at 425 and 450 nm. The onset for EL is between 5 and 6 V and coincides with the onset of current injection. The PL spectrum of PSP show similar features as the EL, but is shifted for $\approx 10 \text{ nm}$ to the blue. These observations are in a good agreement with [7,13]. It is worth mentioning here that the electrical field ($\approx 5 \times 10^5 \text{ V/cm}$) required for the onset of the EL in our single layer devices is comparable with that for optimised multi-layer devices based on PSP [13].

Bi-layer devices of PSP/ C_{60} were tested for their suitability as photovoltaic cells. Fig. 2 shows the photocurrent spectra of such a device. The photocurrent shows a peak maximum in the UV at approximately 350 nm with an external quantum efficiency exceeding 10%. The cut-off towards lower wavelength is caused by the absorption of ITO. In the visible range, the photocurrent spectrum shows a shoulder around 450 nm and a small peak at 620 nm. Both can be attributed to weak absorption bands of C_{60} . Further, the charge generation layer at the PSP/ C_{60} interface limits the short-circuit current.

The I – V characteristics of this device, shown in Fig. 3, demonstrate rectification values of 500 at $\pm 2 \text{ V}$. This is also reflected by the high fill factor of 0.50 for the I – V curve under illumination. The short-circuit current value is low despite the high quantum efficiency in the UV since the mismatch of the absorption to the solar spectrum. The absorption of PSP is known to be strongly dependent on the orientation of the molecule axis relative to the substrate [14], which in turn is determined by the growth technique, deposition conditions and the substrate used. PSP films with the molecular axis perpendicular (standings orientation) to the substrate show a weak absorption below 300 nm, whereas films with the molecular axis parallel (lying orientation) to the substrate absorb strongly in the range between 300 and 400 nm [14]. AFM and absorption measurements of PSP films on PEDOT substrates give hint that films with standing molecules are formed under HWE growth conditions used in this work. Hence, the films grown with “lying molecules” would be needed in order to improve the absorption of the PSP in the near UV and therewith the performance of photovoltaic cells. Further growth and device investigations are necessary to achieve this goal.

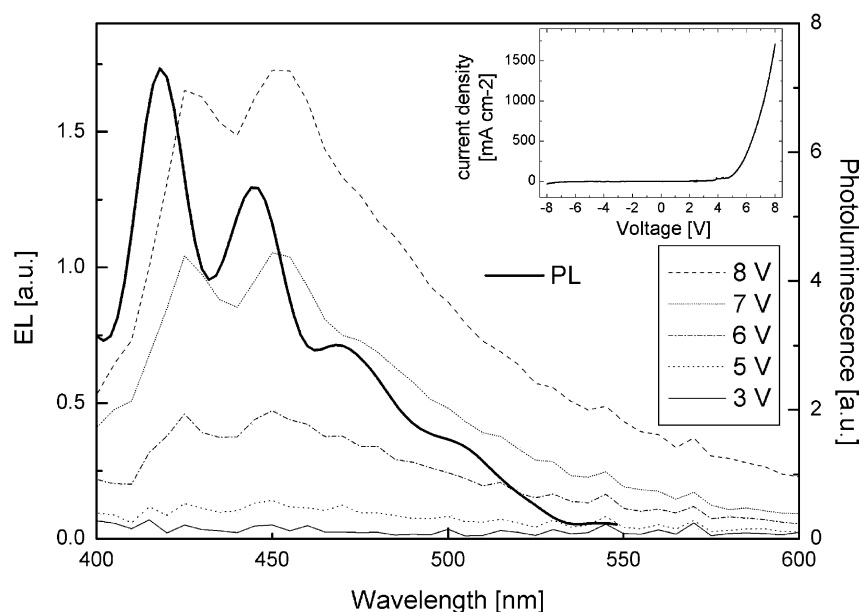


Fig. 1. Electroluminescence of a PSP ($d = 100 \text{ nm}$) single device at different voltage. Inset shows the corresponding current–voltage curve. Full line shows the photoluminescence of a PSP film on mica.

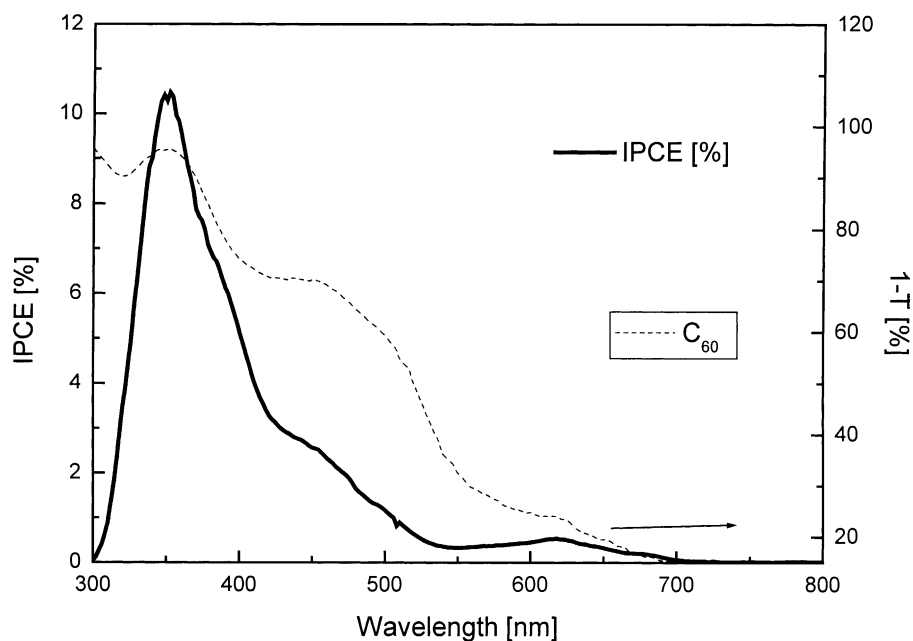


Fig. 2. Photocurrent spectra of a PSP (50 nm)/C₆₀ (100 nm) bi-layer device. Illumination is done through the ITO/PEDOT/PSP side. The absorption spectrum of the C₆₀ layer grown on glass is shown for comparison.

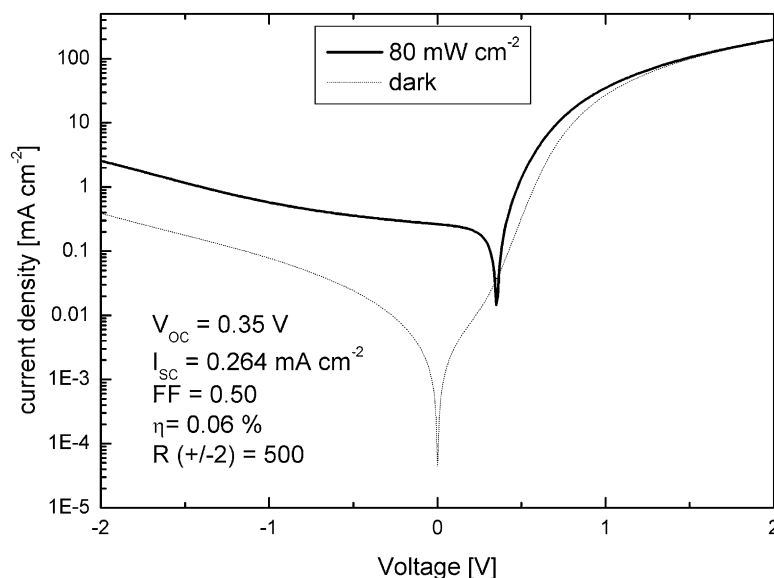


Fig. 3. Current–voltage curve of a PSP (50 nm)/C₆₀ (100 nm) device in the dark (dotted line) and under illumination from a solar simulator.

4. Conclusion

PSP single layer devices grown using HWE display blue EL, which shows a spectrum coinciding with its photoluminescence. The electrical field required for the onset of the EL in these single layer devices was comparable with that for optimised multi-layer device structures grown by common vacuum evaporation techniques. PSP/C₆₀ bi-layer devices show excellent diode behaviour. The quantum efficiency exceeds 10% in the UV. Further optimisation by varying the

active layer thickness, growth conditions and interdiffusion at the interface is needed.

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