Interface engineering to probe exciton energy transfer mechanism in conjugated polymer bilayers

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ABSTRACT

Possible donor/acceptor interaction mechanisms in conjugated polymer bilayers, separated by aluminum dioxide (Al_2O_3) layers, were investigated based on photoluminescence quantum efficiency measurements associated with an energy transfer efficiency model. Al_2O_3 separation layers were produced by atomic layer deposition (ALD) and their thicknesses measured by ellipsometry and confirmed by X-ray reflectivity. Our results for poly[phenylene-vinylene]/Al_2O_3/polyfluorene bilayer systems showed that the exciton energy transfer between donor and acceptor molecules occurs with appreciable efficiency only at distances significantly smaller than the Förster radius.

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1. Introduction

Solid state blends and sequential bilayers of conjugated polymers constitute gain media that enable us to study different donor/acceptor exciton energy transfer (EET) [1] and other phenomena like exciplex formation [2–6] or the formation of aggregated states and their effects on donor/acceptor interactions [7]. In blends, short range interactions are more likely to occur due to the proximity of donor and acceptor molecules, being favored by exciton migration. In sequential bilayers, however, the situation can be quite different due to very distinct conformational states, packing and interdiffusion length conditions of donor and acceptor molecules at the interface between adjacent layers [8]. The mixing of donor and acceptor molecules at the heterojunction interface would mask dipolar interaction mechanisms that could occur differently from the Förster mechanism. Bilayers with different thicknesses of Al_2O_3 layer between donor and acceptor layers were fabricated in order to avoid this mixing, allowing clearer donor–

acceptor interaction studies. The Al_2O_3 layers were grown by atomic layer deposition (ALD). This technique has been used recently and extensively to deposit inorganic oxide layers on top of organic systems such as organic LEDs and transistors, photovoltaic devices and organic solar cells [9–14]. Cyclic chemical vapor deposition (C-CVD) is also another technique for growing Al_2O_3 layers, which effectively prevents diffusion of water vapor into the active organic layers [15].

2. Experimental details, results and discussions

In Fig. 1 we show a schematic representation of the fabrication of the bilayers including the ALD procedure to grow Al_2O_3 separation layers. For the fabrication of donor and acceptor polymer layers we used poly($9,9-$dioctylfluorene$-2,7-$diyl) (PFO) and poly[$2-$methoxy$-5-(2-$ethylhexyloxy)$-1,4-$phenylenevinylene] (MEH-PPV), respectively. The PFO (3.0 mg/ml in toluene) and MEH-PPV (3.0 mg/ml in chloroform) solutions were stirred for over 24 h. The MEH-PPV solution was spread first by spin-coating at 1500 rpm on glass substrates. The MEH-PPV films were heated at 60 °C on a hot-plate for 30 min

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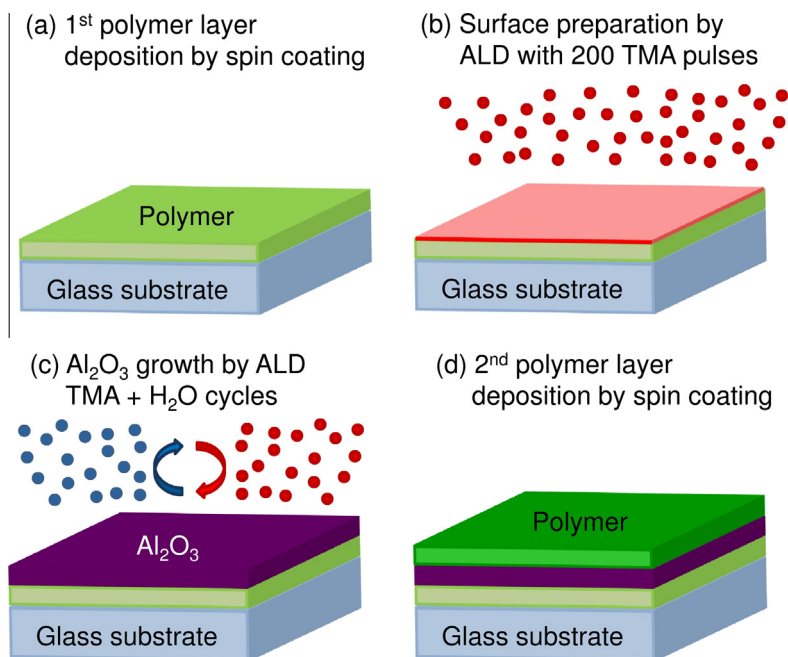 *E-mail address:* cury@fisica.ufmg.br (L.A. Cury).

Fig. 1. Fabrication process of MEH-PPV/Al$_2$O$_3$/PFO bilayers on glass substrates. (a) Deposition of 1st MEH-PPV polymer layer via spin-coating; (b) chemical preparation of the MEH-PPV polymer surface by ALD with 200 pulses of trimethyl aluminum (TMA); (c) growth of Al$_2$O$_3$ layer following the standard thermal ALD using Trimethylaluminium (TMA) and water as precursors; (d) deposition of 2nd PFO polymer layer via spin-coating.

to further remove residual solvent. Al$_2$O$_3$ layers with different numbers of ALD cycles were grown on top of the MEH-PPV films on a Cambridge Savannah 100 ALD reactor. As shown in Fig. 1b, the process begins by saturating the surface with 200 Trimethylaluminium (TMA) pulses with duration of 0.015 s, separated by 40 s of purge time at 50 °C. This initial step modifies the surface chemical termination, making it chemically active for the subsequent ALD deposition procedure. Al$_2$O$_3$ films are then deposited at 50 °C by cycling TMA and H$_2$O inside the reactor chamber (each precursor pulse with 0.015 s duration and 40 s purge time). Following this stage, sketched in Fig. 1c, the thicknesses of Al$_2$O$_3$ and MEH-PPV layers were measured by ellipsometry using a J. A. Woollan Co., Inc. ellipsometer, model M2000. The MEH-PPV layer measured by ellipsometry in all bilayers had a thickness of (59 ± 4) nm while the X-ray reflectivity results, described below, yield an average layer thickness of (52 ± 5) nm. The bilayer structures were completed by spreading the PFO solution on top of the Al$_2$O$_3$ at 1500 rpm, as represented in Fig. 1d. To avoid formation of fluorenone defects, the PFO film was not heated further [16]. The average thickness of the PFO layer measured by ellipsometry was (32 ± 4) nm.

X-ray reflectivity measurements of our system with the first polymer layer covered by the Al$_2$O$_3$ separation layer, as well as for the complete bilayers with separation layers, were performed at the XRD2 beamline of the Brazilian Synchrotron Laboratory (LNLS), with a fixed photon energy of 8 keV. Selected results on samples with the first polymer layer and Al$_2$O$_3$ layers of 20, 40 and 60 ALD cycles are shown in Fig. 2a. In this figure the arrows mark the reflectivity minima corresponding to the Al$_2$O$_3$ thickness

oscillations, while the minima observed at low q_z are related to the thickness fringes due to the first polymer layer thickness. Using this procedure, we obtained identical results for the oxide separation layer thickness in sample series with and without the upper polymer layer. The minima arise from the mass (and consequently electron) density contrast, shown in the inset of Fig. 2a; the layer thicknesses can be directly retrieved as $2\pi/\Delta q_z$, where Δq_z is the distance between neighboring minima. The thicknesses of the Al$_2$O$_3$ layers, measured by ellipsometry and by X-ray reflectivity (shown in Fig. 2b), exhibit similar dependencies on the number of ALD cycles, confirming that the thickness of Al$_2$O$_3$ layers deposited by our procedure is proportional to the number of cycles.

The emission properties of the bilayers were characterized by photoluminescence (PL) at room temperature. It is worth noticing that the emission characteristics of the MEH-PPV after deposition of the Al$_2$O$_3$ layers [step (c) in the fabrication scheme of Fig. 1] do not change, exhibiting the same PL shape as before. For the PL measurements the bilayer films were placed inside an integrating sphere from Labsphere coupled to a ORIEL-Newport monochromator (15 cm) and CCD. Samples were excited using a 375 nm line from a CW diode laser with the incident laser beam crossing the samples from the donor to the acceptor layer. This laser line is absorbed principally by the PFO donor layer, which in turn induces the EET effect toward the acceptor MEH-PPV molecules. The PL spectra in Fig. 3a have been normalized at the pure electronic PFO peak position. The consecutive enhancement of the MEH-PPV acceptor peak (at around 570 nm) due to EET from PFO sites is better seen on a logarithmic scale. The PL measurements