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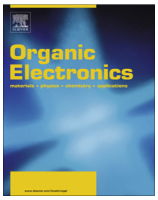

Exciton-induced degradation of organic/electrode interfaces in ultraviolet organic photodetectors

Qi Wang [*], Hany Aziz

Department of Electrical & Computer Engineering, and Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo Ontario N2L 3G1, Canada

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ABSTRACT

We study the degradation mechanisms of ultraviolet (UV) organic photodetectors (OPDs). Contrary to expectations, we determine that the bulk of the organic layers in UV OPDs is stable under prolonged UV irradiation, showing no detectable changes in photophysical characteristics such as photoluminescence yield and exciton lifetime and thus not contributing to the observed degradation behavior of UV OPDs. However, the results show that the organic/electrode interfaces in UV OPDs, including indium tin oxide (ITO)/organic and organic/metal ones, are susceptible to UV irradiation, leading to a deterioration in both charge injection and extraction across the interfaces. The degradation of the organic/electrode interfaces in UV OPDs is essentially induced by UV-generated excitons in their vicinity and may be responsible for nearly 100% of the photo-current loss of UV OPDs. Approaches for improving the photo-stability of organic/electrode interfaces, and thus the lifetime of UV OPDs, are also investigated. We demonstrate that the use of thin (~0.5 nm) interfacial layers such as lithium acetylacetonate at organic/metal interfaces can significantly reduce the interfacial degradation, and the use of appropriate hole transport materials such as N,N′-bis (naphthalen-1-yl)-N,N′-bis(phenyl) benzidine at ITO/organic interfaces can greatly improve the interfacial photo-stability.

1. Introduction

Organic optoelectronic devices have attracted enormous attention in the last two decades. Among these devices, ultraviolet (UV) organic photodetectors (OPDs) are potentially promising in a wide range of civil and military applications, such as chemical and biological analysis, flame detection, optical communications and astronomical studies, because of their unique advantages in manufacturing cost and mechanical flexibility in comparison to the inorganic (e.g., Si-based) counterparts. Despite extensive studies on developing UV OPDs of high sensitivity [1–3], these devices generally suffer relatively short device lifetime [2], which significantly hampers their commercialization. Furthermore, the degradation mechanisms of these devices still remain largely unstudied. Therefore, a clear understanding of the underlying degradation behavior of UV OPDs is required.

A large number of studies on uncovering the degradation mechanisms of organic optoelectronic devices have primarily focused on degradation phenomena occurring in the bulk of organic semiconductor materials [4,5]. Aside from a few studies on degradation behavior of indium tin oxide (ITO)/organic interfaces [6,7], interfacial degradation in these devices, such as at interfaces between electrodes and organic materials, has not been sufficiently explored. Moreover, it remains essentially unknown whether degradation in UV-OPDs occurs more predominantly in the organic layers bulk or at device interfaces.

Electrode contacts, including anode and cathode, are indispensable components of OPDs and other organic optoelectronic devices. They are used for facilitating the conduction of charge carriers across the devices, such as

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[*] Corresponding author. Tel.: +1 (519) 888 4567x34803.
E-mail address: q45wang@uwaterloo.ca (Q. Wang).

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injecting electrons and holes into organic semiconductor layers in the case of electroluminescent devices (i.e., organic light emitting devices) and extracting photo-generated electrons and holes from organic semiconductor layers in the case of photovoltaic and light sensing devices (i.e., organic solar cells and OPDs). Because of their significant roles in affecting device performance, organic/electrode interfaces (i.e., anode/organic and organic/cathode interfaces) have been the focus of a large number of studies [8–14]. Most of the studies have made great efforts to understand the chemical and electronic nature of these interfaces and to come up with methods for enhancing the electrical characteristics of these interfaces. For example, in the studies of organic/cathode interfaces, the formation of organometallic compounds at the organic/cathode interfaces is determined to be responsible for efficient charge carrier injection across the interfaces [8–11], and the use of thin layers (~1 nm) of alkali metal halides at the interfaces can greatly improve both charge injection and extraction [12–14]. Moreover, in the studies of anode/organic interfaces, plasma treatment of anode surfaces and the use of interfacial layers at the interfaces are found to improve device efficiency and stability significantly [15–20].

Despite the considerable amount of work on organic/electrode interfaces in organic optoelectronic devices in general, the effect of irradiation on these interfaces has not been systematically studied, except for the studies by Heil et al. [21] and Lo et al. [7] which showed that irradiation can lead to changes at ITO/organic interfaces, resulting in a deterioration in charge transport across them. Whether similar photo-induced changes may take place at organic/cathode interfaces however remains unclear. More importantly, the role of such photo-induced interfacial degradation in the degradation of OPDs, where exposure to light is obviously more relevant, has yet to be addressed.

We recently determined that organic/electrode interfaces in organic optoelectronic devices are generally susceptible to exciton-induced degradation [22–24]. Prolonged exposure to irradiation in the UV–visible range results in a gradual deterioration in charge carrier conduction across organic/electrode interfaces. Since the degradation of organic/electrode interfaces is found to be highly dependent on the density of excitons created in their vicinity, and also most organic semiconductor materials used in small-molecule based organic optoelectronic devices absorb strongly in the UV region rather than in the visible/infrared regions because of their relatively large bandgap (i.e., ~3 eV), it is natural to wonder whether organic/electrode interfacial degradation plays a critical role in UV OPDs and contributes significantly to the degradation of UV OPDs. Furthermore, it remains unknown if this exciton-induced interfacial degradation in UV OPDs can be effectively reduced. Therefore, a systematical study on exciton-induced degradation of organic/electrode interfaces in UV OPDs is required.

In this study, we investigate the degradation mechanisms of UV OPDs. Contrary to expectations, the bulk of the organic layers in UV OPDs is determined to be very stable under UV irradiation and does not contribute to the observed degradation behavior of UV OPDs. However, the organic/electrode interfaces in UV OPDs are found to be very susceptible to prolonged UV irradiation, leading to a deterioration in both charge injection (i.e., from electrodes to organic layers) and extraction (i.e., from organic layers to electrodes). The degradation of the organic/electrode interfaces in UV OPDs is essentially induced by photo-generated excitons in their vicinity. Approaches for improving the photo-stability of organic/electrode interfaces, and thus the lifetime of UV OPDs, are also studied, where the use of certain interfacial layers at organic/cathode interfaces can significantly reduce the interfacial degradation, and the use of appropriate hole transport materials at anode/organic interfaces can greatly improve the interfacial stability.

2. Experimental section

In this work, UV OPDs containing various organic/electrode interfaces are fabricated and studied. N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl) benzidine (NPB) and 4,4′,4″-Tris(N-3-methylphenyl-N-phenylamino) triphenylamine (m-MTDATA) are used as hole transport materials (HTM), and bis-(2-methyl-8-quinolinate)4-phenylphenolate (BAlq) is used as an electron transport material (ETM). Aluminum (Al) and ITO are used as cathode and anode, respectively. Lithium fluoride (LiF), cesium carbonate (Cs_2CO_3) and lithium acetylacetonate (Li-acac) are used as interfacial layers between ETM and metal cathode. All the samples are fabricated by the vacuum deposition of organic materials and metals at a rate of 1–2 Å/s at a base pressure of $\sim 5 \times 10^{-6}$ Torr on ITO-coated glass substrates. The ITO substrates are cleaned with acetone and isopropanol, respectively, in ultrasound for 20 min. Inductively coupled plasma with an optimized CF_4/O_2 (3:1) gas mixture is used to modify the surface of the ITO substrates. Plasma conditions of CF_4/O_2 gas mixture are: gas pressure 20 Pa; radio frequency power 100 W; treatment time 2 min. Monochromatic illumination from a 200-W Hg-Xe lamp equipped with an Oriel-77200 monochromator is used for irradiation tests. An Edinburgh Instruments FL920 spectrometer is used for time-domain fluorescence lifetime measurements. All tests are carried out in a nitrogen atmosphere.

3. Results and discussion

We first fabricate and test OPDs of the general structure ITO(120 nm)/HTM(20 nm)/HTM:ETM(50 nm,1:1 in volume)/ETM(15 nm)/Al(100 nm), as shown in Fig. 1(a). In these devices, NPB and m-MTDATA are selected as the HTM, respectively, and BAlq is selected as the ETM, due to their widespread use in UV OPDs. The ITO here is treated with CF_4/O_2 plasma [23] before the vacuum deposition of the organic materials and metal. Fig. 1(b) shows the absorption spectra of the organic semiconductor materials used in the devices, obtained from films of ~30 nm thick deposited on a quartz substrate. As Fig. 1(b) shows, both NPB and m-MTDATA absorb significantly in the UV region (i.e., from 300 nm to 400 nm), but absorb little in the