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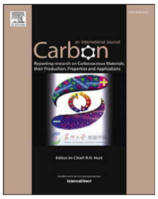

Toward facile broadband high photoresponse of fullerene based phototransistor from the ultraviolet to the near-infrared region

Lili Du [a, 1], Xiao Luo [a, 1], Feiyu Zhao [a], Wenli Lv [a], Jianping Zhang [a], Yingquan Peng [a, b, *], Ying Tang [b], Ying Wang [a]

[a] Institute of Microelectronics, School of Physical Science and Technology, Lanzhou University, South Tianshui Road 222#, Lanzhou 730000, China
[b] College of Optical and Electronic Technology, China Jiliang University, Xueyuan Street 258#, Hangzhou 310018, China

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ABSTRACT

Organic phototransistor (OPT) is a promising organic device with substantial attention due to its photodetection combined with lightweight, flexibility, large-scale yields, and low cost of organic materials. In addition, spectral tunability and long photocarrier lifetime for organic materials make them highly attractive for advanced optoelectronic device applications. Here, we report high-performance broadband photodetection devices fabricated using an all-organic heterojunction of fullerene/chloroaluminum phthalocyanine with a high-efficiency exciton-dissociation-interface and complementary spectral absorption. Operating at room temperature, the prepared OPTs offer broadband ultraviolet–visible–near infrared spectral response, exhibiting ultrahigh photoresponsivity of 94.4 A/W, the highest detectivity ~1.5 × 10^{13} Jones combined with external quantum efficiency of 26,066%, and the ability to measure high-frequency signals. These parameters are comparable or even superior to commercially available silicon carbide, silicon and indium gallium arsenide photodetectors, indicating the possibility of many applications based on broadband detection utilizing our devices. A semi-quantitative calculation and energy level mechanism reasonably explain the ultrahigh performances above. Our results suggest that organic compounds with mutual complementary spectra can be used for constructing photosensitive active layer, in which optimized interfacial electronic structure and morphology help photoexciton dissociation and extend the spectral response range.

1. Introduction

Light detection for ultraviolet (UV) to near infrared (NIR) regimes has a wide range of commercial and scientific applications that include imaging, spectroscopy, communication, biomedical applications, environmental monitoring and defence sensing [1–17]. It is eagerly desirable to have a facile photodetector with a response spectrum covering a broad spectral range from UV to NIR. Today commercially available photodetectors are typically made from silicon carbide (SiC), silicon (Si) and indium gallium arsenide (InGaAs) for detection in UV, visible and NIR regimes, respectively [18–20]. However, these commercial photodetectors have relatively narrow response spectra. For example, silicon photodetectors are only good for the visible/NIR range, while high-end photodetectors made from SiC are generally selected for UV sensing. In addition, some photodetectors based on inorganic narrow band-gap semiconductor materials (such as InGaAs [21]) must be cooled in the operation due to the high density of intrinsic thermal charge carriers, and comparatively complicated process in the actual production and operation means a low yield and high cost. In recent years, the study of broadband photosensitive materials and uncooled detectors has become a hot topic [7,10–14,22]. For example, Armin et al. demonstrated a broadband organic photodiode that has performance metrics comparable or superior to inorganic photodiodes with an active layer comprised of a PCDTBT:PC70BM bulk heterojunction blend, showing a specific detectivity of ~10^{13} Jones [10]. Saran and co-workers reported that the photosensitivity of the fullerene (C_{60}) nanorods could be enhanced 400-fold via an ultralow photodoping mechanism, offering broadband UV-NIR spectral tunability [11]. Very recently,

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* Corresponding author. Institute of Microelectronics, School of Physical Science and Technology, Lanzhou University, South Tianshui Road 222#, Lanzhou 730000, China.
E-mail address: yqpeng@lzu.edu.cn (Y. Peng).
[1] These authors contributed equally to this work.

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Chen et al. presented a highly broadband (from visible to infrared) photodetector based on chemical vapor deposition graphene-silicon heterostructure, and this device shows ultrahigh responsivity (>10^4 A/W) at wavelength of 632 nm [12]. In general, broadband photodetectors consist of photoconductor [13], photodiode [10], and phototransistor [14], achieved by either single material [8] or multi-material compound [9]. Phototransistor is a type of photodetector device consisting of a transistor channel with an optically controlled gate, which converts incident light into electrical signal. Compared to conventional photoconductor or photodiode, the phototransistor is able to detect the light signal more sensitively without serious problems such as noise increment, and they are easily integrated into electronic circuitry because of their complementary metal oxide semiconductor (CMOS) like configuration.

Organic phototransistors (OPTs) have attracted significant attention in the past decades [2,15,23,24]. Because organic active materials can be modified to be either panchromatic [8] or selectively tuned to a specific wavelength from UV to NIR regions, manifesting adjustable band gap. Moreover, high extinction coefficient of the functional organic materials as well as lightweight soft mechanical properties allows for their use in a variety of innovative light-signal detection systems such as large-area imagers and scanners, X-ray detection in bio-medical applications, short-range plastic optical-fiber-based transceivers, position-sensitive detectors, and integrated sensoristics for Lab-on-a-chip [2,15]. In this paper, we reported a facile broadband OPT via a simple fullerene (C_{60})/chloroaluminum phthalocyanine (AlClPc) heterojunction, thereby successfully demonstrating remarkable broad-spectral photoresponse from UV to NIR region. For as-fabricated OPT (Fig. 1), a self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS) was used as induced layer to promote huge needle-like crystalline C_{60}. C_{60} and AlClPc were chosen as N-type and P-type materials to form photo absorber layer due to their complementary spectra in UV-NIR region [25,26]. Meanwhile, C_{60} was also used as carrier transport layer because of its high electron mobility [16]. Significantly, the methodology here exhibits great promise for developing all-organic broadband photodetectors with spectrum response ranging from UV to NIR light.

2. Experimental

2.1. Materials and device fabrication

C_{60} was purchased from Luminescence Technology Co., Ltd., Taiwan, and OTS from Sigma–Aldrich Co. Ltd. America, respectively, and used as received. AlClPc was synthesized and purified according to the procedure reported before [27,28]. Prior to film deposition, the synthesized phthalocyanine was purified further by vacuum sublimation. The configuration of bottom-gate top-contact OPTs and the chemical structure of OTS were presented in Fig. 1. The OPTs were fabricated according to the following procedure. A heavily doped n-type silicon (n^+-Si) wafer with thermally grown SiO_2 ($C_i = 3.37$ nFcm^{-2}) were used as the gate and gate dielectric, respectively. The substrates were cleaned with piranha solution (H_2SO_4: $H_2O_2 = 7$: 3 mixed solution) for 1 h, followed by acetone, ethanol, and deionized water for 10 min each. Subsequently, these substrates above were further treated through vapor deposition of OTS for 2 h [29] and then were rinsed by chlorylene and dried with high-purity nitrogen. Next, 40 nm thick C_{60} films and 40 nm thick AlClPc films were successively deposited onto the substrates using thermal evaporation technique without breaking vacuum. Gold (Au) source and drain electrodes (30 nm) were deposited on the top of the organic films with a fixed channel length (L) and width (W) of 50 μm and 2 mm, respectively. During all the materials deposition, the chamber pressure was kept under high vacuum condition (~1×10^{-3} Pa). For a systematic comparison, in the same way, the C_{60}-based and AlClPc-based OFETs were fabricated simultaneously, and all devices were deposited in the same batch and every type of devices had four samples.

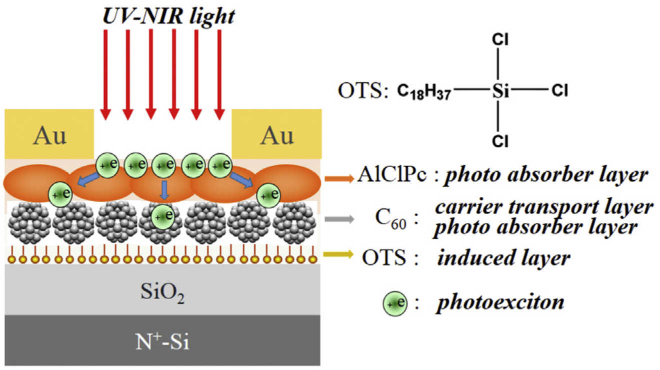

Fig. 1. Schematic configuration and illustration of as-fabricated C_{60}/AlClPc heterojunction phototransistor. The inset is the molecular structure of OTS. (A color version of this figure can be viewed online.)

2.2. Measurements and characterizations

All the measurements were carried out immediately after the devices were taken out of the thermal evaporation chamber, using an organic semiconductor characterization system in the dark and illumination condition. X-ray diffraction (XRD, Rigaku D/max-2400 with Cu Kα radiation) was employed to study the structure of the samples. For optical absorption measurements, 40 nm C_{60}, 40 nm AlClPc, and the films of C_{60}(40 nm)/AlClPc(40 nm) heterojunction were vacuum deposited on cleaned quartz substrates, respectively. TU-1901 spectrometer was used for the measurements of absorption spectra. In order to measure the photo effect, a commercially available violet laser diode (450 nm, 20 mW/cm^2), a red laser diode (650 nm, 125 mW/cm^2) and a NIR laser diode (808 nm, 720 mW/cm^2) were used as light source. The variation of optical power was realized by neutral density filters with various transmittances.

3. Results and discussion

3.1. Absorption property studies

UV–visible spectroscopy is one of the most widely used techniques to study the optical characterization of films. Fig. 2 shows optical absorption spectra of 40 nm AlClPc, 40 nm C_{60}, and C_{60}(40 nm)/AlClPc(40 nm) heterojunction films. Absorption peaks of the C_{60} film are confirmed in the range of ca. 300–550 nm (range I, UV-green). Whereas, the spectra of the AlClPc film contain the Soret and Q bands [25] and the absorption peaks are observed at around 350 and 600–800 nm, corresponding to spectral range II (ca. 300–400 nm, UV) and range III (ca. 550–900 nm, green-NIR), respectively. Two absorption peaks in Q band are clearly observed at around 600–800 nm, which is similar to that of the α-crystalline film reported previously [30]. Significantly, there exist mutual-complementary spectra for C_{60} and AlClPc active materials in terms of range I-III, resulting in a complete cover of UV–Vis–NIR photoabsorption. As expected, the absorption spectrum of C_{60}(40 nm)/AlClPc(40 nm) heterojunction films further corroborates the result of broadband absorption above (see blue line in Fig. 2). This affords the capability of broadband photodetection under the irradiation from UV to NIR light. It is worth noting that the existence of complementary absorption between fullerene or