Solution processed white light photodetector based N, N’-di (2-ethylhexyl)-3,4,9,10-perylene diimide thin film phototransistor

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In this study, a solution-processed n-type photo-sensing organic thin film transistor was investigated using polymeric dielectric under different white light illuminations. N, N’-di (2-ethylhexyl)-3,4,9,10-perylene diimide and divinyl tetramethyl disiloxane-bis (benzo-cyclobutene) were used as a soluble active organic semiconductor and as a dielectric material, respectively. Stable amplification was observed in the visible region without gate bias by the device. The electrical characterization results showed that an n-type phototransistor with a saturated electron mobility of 0.6 × 10−3 cm²/V·s and a threshold voltage of 1.8 V was obtained. The charge carrier density of the channel of the device exhibited photo-induced behaviors that strongly affected the electrical properties of the transistor. The photosensitivity and photoresponsivity values of the device were 63.82 and 24 mA/W, respectively. These findings indicate that perylene diimide is a promising material for use on organic based phototransistors.

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1. Introduction

Organic thin film transistors (OTFTs) are one of the most important evolving topics in semiconductor technology due to their potential use as a lower cost electronic component relative to conventional amorphous silicon transistors. Since the first OTFT was reported, OTFTs have been investigated broadly. In addition, their potential applications, including electrochemical, luminescent, and electronic properties, and chemical properties completely depend on their substitution positions due to their localized LUMO state. The changes in their electronic and chemical properties completely depend on their substitution positions in the bay positions.

Today, most organic devices with high mobility can be created by evaporating small molecules under high vacuum. However, the deposition of small organic molecules by vacuum technology leads to the consumption of the materials and to high production costs due to the necessity of high vacuum technologies for achieving a desired device. This production process limits the production of large area electronic devices, which can easily be produced by solution processing techniques, such as spin coating, drop casting, dipping or inkjet printing. Therefore, the molecular architecture is important for organic electronic applications to produce soluble organic semiconductors for use in industrial production without non-vacuum processes [7].

However, many different soluble materials are used in organic electronic devices to form an active semiconductor layer. In addition, several of these materials are small, p-type, polymeric molecules that are used for solution-processed deposition. These materials are used because of the imperfect solubility of n-type organic molecules in organic solvents. Soluble n-type organic semiconductors have attracted attention for the development of OTFT applications. One of the most promising soluble n-type materials is perylene 3,4,9,10-tetracarboxylic acid diimide (PDI) because its molecular structure can be used to change the substituents on the N atoms in imide or on the bay positions. Substituting functional groups on PDI can create several features, including electrochemical, luminescent, and electronic properties, and can enhance solubility to allow for the construction of organic based electronics [8-10]. In addition to having the lowest unoccupied molecular orbital (LUMO) level, which changes from −4.0 to −4.3 eV, the PDI derivatives have strong electron affinities and are classified as n channel OTFTs. In fact, n-channel PDI derivatives are generally more susceptible to oxidation by moisture and oxygen under ambient conditions due to their localized LUMO state. The changes in their electronic and chemical properties completely depend on their substitution positions on the PDI. An inductive effect was observed when the N atoms of the imide were substituted, whereas substitution in the bay position...
leads to more dramatic planar geometry changes and induces intermolecular charge transport [11]. In the last few years, n-channel OTFTs, which are based on PDI derivatives with high mobility and air stability, have been created by substituting electron accepting moieties, such as per-fluoroalkyl groups-CN, –Cl, –F, and perfluoroaryll, into the N atom or bay positions [12–14].

Photodiodes and photoconductors are two terminal devices that produce photocurrent signals instead of delivering electrical power to a load. Phototransistors are called three terminal devices, in which the third electrode at the channel relative to the two terminal photodiodes. The flowing current through the channel strongly depends on both the photo-induced and gate-induced charge carriers [15]. Therefore, phototransistors have advantages for use in light induced electronic circuits, such as switches, light triggered amplification, detection circuits and highly sensitive image sensors.

Inorganic phototransistors exhibit high responsivity and high charge carrier mobility. However, their applications are limited due to the difficulties of conducting high temperature vacuum processes. Compared to inorganic phototransistors, organic phototransistors have outstanding characteristics of low temperature fabrication, flexibility, and large size applications. Several groups have reported the formation of phototransistors based on polymers or small molecule organic semiconductors, including thiophene, pentacene, and fluorinated copper phthalo-cyanine [16–19]. Although most of the reported organic phototransistors are p-channel, studies regarding n-channel phototransistors on polymeric dielectrics are available and the development of these phototransistors is highly important for improving complementary metal oxide and semiconductor phototransistor technologies in photo-electronic circuits to provide highly stable optical signal processing with photosensitivity [20].

Herein, we prepared a process for creating organic photo-transistors based on the N, N′-di (2-ethylhexyl)-3,4,9,10-perylene diimide (EHPDI) organic semiconductor and the divinyltetramethyldisiloxane-bis (benzo-cyclobutene) (BCB) dielectric with top contact/bottom gate geometry. The soluble BCB dielectric material was used to obtain high dielectric transparency on the indium tin oxide (ITO) to allow light to penetrate through the device from the bottom to the top. The electrical and photo-induced parameters, such as photosensitivity and photoswitching, were analyzed from I–V characteristics in the dark and under different white light illuminations. This technology could be used for optoelectronic circuits with large or flexible areas due to the observed solution processes for both semiconductors and the insulator layer.

2. Experimental

2.1. Materials and instrumentation

The electrical characteristics of the fabricated OTFTs were measured using Keithley 2400 source-meters. The surface morphology of the EHPDI semiconductor deposited on the BCB dielectric was examined in tapping mode using a Q-Scope 250 Scanning Probe Microscope (Ambios Technology) operating at room temperature. The capacitance measurements of the polymeric dielectric layer were conducted using the prepared metal–insulator–metal device structure with an Agilent E4980A LCR meter. The thicknesses of the dielectric and semiconductor were determined by a surface profilometer (Ambios XP-1). To characterize the device under illumination, a solar simulator (KHS equipped with a 750 W Xe lamp) with density filters was used. The incident light intensity was measured using a reference solar cell that was calibrated by Fraunhofer ISE.

2.2. Synthesis of N, N′-di (2-ethylhexyl)-3,4,9,10-perylene diimide

EHPDI was synthesized according to previously reported papers [21,22].

A suspension of perylene-3,4,9,10-tetracarboxylic acid anhydride (2 g, 5.1 mmol) in 100 mL of pyridine was heated at 130 °C for 30 min while vigorously and continuously stirring. Then, 2-ethylhexyl amine (2.5 mL; 15.3 mmol) was added to the reaction flask and was subjected to the same temperature for 24 h under flowing Ar gas. The reaction mixture was cooled to room temperature and poured into 250 mL of a 5% HCl solution. The resulting red precipitates were collected by filtration and were washed with excess water and methanol before drying. The following parameters were obtained: a yield of 97.0%, AT-IR bands at 1693 and 1648 (imide vibrations), 1H NMR (400 MHz CDCl3) with δH 8.63 (d, J = 7.9 Hz, 4H, Perylene-H), 8.53 (d, J = 8.1 Hz, 4H, Perylene-H), 4.11–4.21 (m, 4H, =CH2–N), 1.97–1.20 (m, 2H, –CH2–), 1.35–1.46 (m, 16H, –CH2–), 0.98 (t, 6H, –CH3), and 0.92 (t, 6H, –CH3).

2.3. Fabrication of the organic thin film transistors

The OTFTs were fabricated using a top contact/bottom gate geometry and the chemical structures of the organic layers that were used are shown in Fig. 1. Indium tin oxide coated glass was patterned by etching with diluted HCl to create the bottom gate electrode. Prior to coating with dielectric, the substrate was cleaned by soaking it in ultrasonic baths with distilled water, acetone and iso-propanol. The BCB, which was purchased from Dow Chemicals, was spin coated on the patterned glass substrate at 1500 rpm for 45 s. Next a curing process was conducted at 285 °C in a vacuum oven under an argon atmosphere for 1 h to enforce the cross-linking of the BCB polymer. Finally, the BCB was cooled over night to form a dielectric with a thickness of 2 μm on the ITO glass. The EHPDI was dissolved in 1 mL of the chloroform and chlorobenzene solvent mixture (3:1 v/v) and stirred overnight. To make an EHPDI thin film with a thickness of 60 nm, the spin coat technique was used on the BCB coated substrate at 1500 rpm for 50 s. Al metal electrodes (purity 99.9%) with a thickness of 60 nm were deposited on the EHPDI active layer by using the vacuum evaporator under 2 × 10−6 mbar and a shadow mask with a channel length (L) of 40 μm and a channel width (W) of 2 mm. The electrical characterization of the fabricated device was conducted in an inert gas atmosphere inside the glove box.

3. Results and discussion

The UV–Vis spectra of the EHPDI semiconductor in chloroform and of the film deposited on the glass are shown in Fig. 2. The UV absorption of EHPDI presents three characteristic absorption bands due to the n–n* and n–π* transitions that result from the bonding and antibonding energy levels. The maximum absorption of the EHPDI was 525 nm, which can be attributed to the n–π* transition of the molecule due to the nonbonding electrons of the oxygen atoms. While the onset absorption value of the EHPDI is approximately 555 nm in solution, its
value on the thin film shifts to a longer wavelength of 555 nm to 632 nm. This shift implies that the planar structure of EHPDI has a well-stacked structure that is attributed to π–π interactions.

Fig. 3 depicts an atomic force microscopy (AFM) image of the solution-processed EHPDI film on the BCB layer in two and three dimensions. As previously reported, the BCB film exhibits a very smooth surface [23]. The charge transport layer forms between the insulator and the active layer in one or a few molecular layers that are affected strongly by the rough dielectric surface. Therefore, the insulator surface should be very smooth to enhance the charge carrier at the channel near the dielectric region [24]. As shown in Fig. 3, the EHPDI film was arranged as a string of beads that were side by side in local regions with an average grain size of 240 nm on the BCB coated substrate. The average maximum height and root mean squared roughness values of the semiconductor films were 39.73 nm and 8.93 nm, respectively. These ball-like shapes create a large density of bores and protuberances on the semiconductor surface, as shown in Fig. 3. Although the AFM image of surface does not provide complete information about the semiconductor/dielectric interface, we estimated the interface shape from the surface topography.

Fig. 4(a) shows the output characteristics of the EHPDI thin film transistor that was fabricated on top of the BCB gate-insulator with Al top drain-source contacts in the dark. The change in the drain current \(I_{ds}\) with \(V_{ds}\) linearly confirms that the ohmic contact is well established between the metal and semiconductor. The saturated regime of the transistor was achieved at a higher drain voltage \(V_{ds}\) than the gate voltage, \(V_{gs}\). The calculated electron field-effect mobility \((\mu)\) was obtained from the saturated regime by using the following equation [15]:

\[
\mu = \frac{2L \mu C_i \left( \frac{V_{gs} - V_{th}}{2} \right)^2}{d V_{gs} \left( V_{gs} - V_{th} \right)}
\]

where \(W\) is the width of the channel, \(L\) is the channel length, \(C_i\) is the capacitance per unit area of the insulator that was measured as 1.73 nF/cm² by the LCR meter at 1 kHz, \(\mu\) is the charge carrier mobility (i.e., electron mobility for this device) and \(V_{th}\) is the threshold voltage. The electron mobility and threshold voltage were ~0.6 × 10⁻³ cm² V⁻¹ s⁻¹ and 1.8 V, respectively. The \(I_{on}/I_{off}\) ratio (on-current/off-current) was ~10².

Fig. 4(b) shows the transfer characteristics (\(I_{ds} - V_{gs}\)) of the EHPDI OTFT in the saturation and linear regions is given by the following equations [15]:

\[
\begin{align*}
I_{ds(lin)} &= \frac{W}{L} \mu C_i \left( \frac{V_{gs} - V_{th}}{2} \right)^2, \quad V_{gs} > V_{th} \\
I_{ds(sat)} &= \frac{W}{2L} \mu C_i \left( V_{gs} - V_{th} \right)^2, \quad V_{ds} = \left( V_{gs} - V_{th} \right)
\end{align*}
\]

The saturated electron field-effect mobility \((\mu)\) and the threshold voltages can be determined from the slope of \((I_{ds(sat)})^{1/2}\) versus \(V_{gs}\) in which the intercept of \(V_{gs}\) with the axis is shown in Fig. 4(b), respectively. The electron mobility and threshold voltage were ~0.6 × 10⁻³ cm² V⁻¹ s⁻¹ and 1.8 V, respectively. The \(I_{on}/I_{off}\) ratio (on-current/off-current) was ~10².
The drain current versus the drain voltage curves of the EHPDI thin film transistor under various illumination intensities (from 56.4 mW/cm² to 91.06 mW/cm²) at $V_{gs} = 0$ V are shown in Fig. 5(a). The generation of a photo-induced charge carrier was clearly observed as the drain-source current increased and depended on the illumination intensity without the induced gate. This result indicates that the light behaves as a fourth terminal that optically switches the device on and off in addition to conventional sources, drains and gate terminals. Regarding the penetration of light through the semiconductor, the photon with a higher or equal band gap energy relative to the semiconductor creates a large number of excitons. Subsequently, the excited electrons are dissociated from the semiconductor to the dielectric interface, which causes the conductivity to increase through the channel and drain current. Excess charge carriers cause a shift in the quasi-Fermi level, which induces internal photovoltage [25]. This internal photovoltage creates field effects in organic thin film transistors and behaves as the gate electrode without an applied gate to source the voltage. The induced photovoltage effect can be observed in Fig. 5(b) by evaluating the drain-source current increment, which is the difference between the illuminated ($I_{ds}$) and dark ($I_{dark}$) currents. The output characteristics of the EHPDI thin film transistor depend on different illuminations and exhibit good photosensing properties, which refer to the increasing light intensities for each other. Although the pinch off points ($V_{ds} = V_{gs} - V_{th}$) of the active observed channel were clear in the dark, the linear change in the saturation region under illumination depends on the $V_{ds}$. In addition, the pinch off points shift to higher $V_{ds}$ voltages, as shown in Fig. 5(b). The increment of conductivity in the saturated region is attributed to the photogenerated charge carriers of the channel, in which $V_{ds} > V_{gs} - V_{th}$.

The threshold voltage is an important device parameter for demonstrating how to turn on the channel. The interface states and the charge concentrations in the channel dominate the threshold voltage. The fixed $V_{gs}$ and the change in the threshold-voltage under illumination resulted in drain current increments of $I_{ds}$ to $I_{ds} + \Delta I_{ds}$, which are equal to $I_{ds}$. The drain-source current increment $I_{ds}$ and the threshold voltage shift from positive to negative values are easily observed from the transfer characteristics of the device, as shown in Fig. 6. This increment of the photogenerated charge carriers with light intensity results in a large $I_{ds}$ and a shift in the threshold voltage ($V_{th}$) for reaching the accumulation mode and opening the transistor. The majority of carriers dominate the OTFT operation, in contrast with the c-Si FETs. Therefore, the accumulated regime induces more charge and more conductivity. The threshold voltage for organic thin film transistors in the accumulation regime can be given by Eq. (4) [26].

$$V_{th} = \pm \frac{q n_{0} d}{C_{i}} + V_{FB}$$  \hspace{1cm} (4)

Here, $V_{FB}$ is the flat band potential, $q$ is the elementary charge, $n_{0}$ is the bulk carrier density and the sign of the right-hand side changes with the main carrier type and the numbers of electrons or holes. The charge carrier density ($n_{0}$) is significantly changed near the channel due to the light intensity beside the flat-band voltage ($V_{FB}$) if it is invariant.

The dependency of the threshold voltage and the electron field-effect mobility with respect to light intensity is shown in Fig. 7. The electron mobility shows an increment from $0.6 \times 10^{-3}$ cm²/V·s to $1.2 \times 10^{-3}$ cm²/V·s with a light intensity comparison with threshold voltage. The dependency of mobility on the light intensity is reported in the literature, and is similar for different organic and inorganic semiconductors [27,28]. Changes in the mobility of charge carriers (except for excess charge carriers) result in an increment of conductivity and an accumulation regime. Regarding the increment of electron mobility under illumination, it is assumed that the changes in the illumination intensities cause high temperatures on the surfaces of the device during electrical measurement. Therefore, field-effect mobility is expected to increase as the temperature increases due to the photon-assisted charge transport mechanisms in the organic semiconductor [29].

Although light induced mobile charge carriers are predominant on $V_{ds}$, the interface trapped charge shifts of $V_{th}$ depend on the densities of the negatively charged states [30]. To determine the number of interface states, the sub-threshold swing ($S$), which denotes the sharpness of the onset of field effects, was investigated to calculate another parameter and the mobility and on/off current ratio [31]. The value of $S$ was determined as the inverse slope of the log($I_{ds}$) versus $V_{gs}$ and was below the threshold at 53.6 V decade⁻¹ in the dark, which indicates a large concentration of shallow traps at the channel edge. At the low gate voltage below the threshold, the carrier density exhibited a smaller increase due to the density of states at the semiconductor/insulator interface.

![Fig. 5. Output characteristics of the EHPDI phototransistor under various illumination conditions at (a) $V_{gs} = 0$ V and (b) under various $V_{gs}$.](image)

![Fig. 6. Transfer characteristics of the EHPDI phototransistor relative to the illumination intensity at $V_{ds} = 80$ V.](image)
Thus, the measured sub-threshold swing was large. If the density of the deep bulk states \(N_{ss}\) in the semiconductor and the interface states of \(N_{ss}\) are assumed as independent of energy, the sub-threshold slope facilitates the calculation of these states. The maximum number of interface traps can be calculated by assuming that \(N_{ss} = 0\) and by using the following equation [32,33]:

\[
N_{ss}^{\text{max}} = \left( \frac{qS\log(e)}{kT} - 1 \right) \frac{C_1}{q}
\]  

(5)

where \(N_{ss}^{\text{max}}\) is the maximum number of interface traps, \(k\) is Boltzmann’s constant, \(T\) is the absolute temperature and \(q\) is the electronic charge. The \(N_{ss}^{\text{max}}\) value of the transistor was \(9.57 \times 10^{12}\) (eV)\(^{-1}\) cm\(^{-2}\). In contrast, the metal-oxide dielectric and polymeric dielectric can include mobile ionic impurities that create molecular dipoles that act as traps at the semiconductor/insulator interface. These interface states are attributed to the impurities located near the channel that prevent the efficient dissociation of the photo-generated excitons and their diffusion towards the electrodes.

Two additional important parameters for evaluating the performance of organic thin film phototransistors are photosensitivity (\(P\)), which is defined as the ratio of the photocurrent to the dark current (\(I_{ph}/I_{dark}\)), and the photoresponsivity (\(R\)). These parameters are calculated by using Eqs. (5) and (6), respectively [32].

\[
P = \frac{I_{ph} - I_{dark}}{I_{dark}}
\]  

(6)

\[
R = \frac{I_{ph} - I_{dark}}{P_{in} \cdot A}
\]  

(7)

Here, \(P_{in}\) is the power of the incident light per unit area, \(I_{ph}\) is the drain-source current under illumination, \(I_{dark}\) is the drain-source current in the dark and \(A\) is the effective device area. The photosensitivity and photoresponsivity of the device were obtained by sweeping the gate voltage across different illumination intensities, as shown in Fig. 8. The photosensitivity of the device was 5.44 in the accumulation regime \(V_{gs} = 80\) V and 63.82 in the depletion regime \(V_{gs} = 0\) V at an illumination intensity of 91.06 mW/cm\(^2\). The main factor of the photosensitivity variety depends on turning the device on and off because the photocurrent becomes significantly greater as the illumination intensity increases in the depletion regime (off state) relative to the accumulation regime (on state), as shown in the inset graph in Fig. 8(a).

When the device is in depletion mode (i.e., the off state \(V_{gs} < V_{th}\)), the photocurrent is directly proportional to the incident light power \(P_{in}\). Therefore, the photo-generated charge carriers increase the channel conductivity (i.e., photoconductivity) and the drain-source current, which leads to the high photosensitivity when the device is turned off. When the device is turned on, the electrons that were created by light absorption near the channel flow easily through the channel. Thus, the positive charge carriers of the semiconductor accumulate near the source electrode and dielectric. These accumulated holes induce semiconductor energy levels near the source electrode and decrease the potential barrier between the channel and source. The threshold voltage shift, which is a photovoltaic effect, apparently results from these accumulated charge carriers. In addition, the variations of the produced photocurrents with light intensity become logarithmic, as shown in the inset graph in Fig. 8(a) [34]. Therefore, the increment ratio of the photocurrent is smaller when in the turned-on state rather than the turned-off state and the photosensitivity decreases at higher \(V_{gs}\).

The photoresponsivity of the EHPDI thin film transistor will change the illumination and gate voltages, as shown in Fig. 8(b). The photoresponsivity values, which are a conversion of the optical signal to the electrical signal, were 24.5 mA/W and 8 mA/W in the accumulation and depletion regimes respectively. In contrast with the photosensitivity, the photoresponsivity was greater in the accumulation regime than in the depletion regime because the number of charge carriers was strongly dependent on the intensity compared with the gate voltage. As shown in Fig. 8(b), the photoresponsivity of the device decreases as the light intensity increases because the increment of the photocurrents decreases as the light intensity increases (i.e., saturation of photocurrents at \(V_{gs} > V_{th}\), as shown in the inset of Fig. 8(a) at \(V_{gs} = 80\) V).

Although more charge carriers are enhanced by photo-generation at higher illumination levels, these charge carriers cannot flow through the entire channel. This result potentially occurs due to the charge
transport mechanisms, in which the charges are trapped because they recombine with the interface states and the space charge effects under the source electrodes when a high density of carriers are photogenerated. Other possible mechanisms of the photocurrent saturation can be attributed to exciton–exciton annihilation due to the interactions between enhancement excitons from the high irradiance [32].

4. Conclusions

In summary, we demonstrated the creation of a solution processed organic thin film phototransistor using an EHPDI organic semiconductor on a transparent BCB dielectric layer. The device showed n-channel characteristics with a saturated electron mobility of $0.6 \times 10^{-3} \text{cm}^2/\text{V} \cdot \text{s}$ in the dark or under illumination, the electron mobility under illumination ($1.2 \times 10^{-3} \text{cm}^2/\text{V} \cdot \text{s}$) was two times higher than in the dark and was nearly stable at different illumination intensities. The threshold voltage shifted to the negative regime under illumination due to the photodoping effect, which generates more excitons. The observed photosensitivity of the device was 63.82 in the off-state operating condition. The phototransistor exhibited photoresponsivities in the on and off states of 24 mA/W and 8 mA/W, respectively. The fabricated phototransistor was stable under illumination on the BCB dielectric layer. Our results indicate that this device could be used as a photo-sensor in optoelectronics for large areas and for cost-effective applications.

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References