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Effect of keto defects on the electrical properties of fluorene-based oligomers

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The effect of ketonic defects on electrical properties, i.e., the performance of organic field-effect transistors (OFETs) was examined in fluorene end capped fused bithiophene oligomers (BFTT). The long wavelength emission at 2.1–2.3 eV resulting from the ketonic defects was observed in photoluminescence spectra of BFTT films after UV irradiation in air. In addition, the peak corresponding to the carbonyl stretching mode of the fluorenone moiety at 1721 cm^{-1} was also apparent after UV irradiation for periods longer than 6 h in air. These observations confirm that ketonic defects are present in the fluorene units of BFTT after photo-oxidation. The threshold voltage (V_{th}), i.e., switch-on voltage, of OFETs was increased and field-effect mobility (μ_{FET}) was decreased after the formation of the ketonic defects, since these defects induce the formation of numerous trap sites in the bandgap of the semiconducting conjugated oligomer. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1787939]

Conjugated organic oligomers or polymers based on fluorene units have attracted a great deal of interest for use in applications of organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs).[1–3] Among these, polyfluorenes (PFs), one of the promising materials among blue light-emitting polymers, have been a subject of active study, due to their high stability and color purity.[1] However, the desirable luminescent properties of PFs are severely degraded by the formation of keto defects, which give rise to a low-energy emission band at 2.2–2.3 eV after thermal and photo-oxidation.[4] Therefore, the effects of keto-defect sites on emission properties, i.e., the color purity and stability of OLEDs of PFs, have been intensively studied since the first report was published.[5]

From the standpoint of electrical properties, high performance OFETs have been fabricated using fluorene-based polymers such as poly-9,9′dioctyl-fluorene-co-bithiophene (F8T2), in order to their self-ordering properties by liquid crystalline nature.[2] Conjugated oligomers based on fluorene end-capped thiophenes have also received attention since they showed a high performance for *p*-type active materials with excellent air and UV stability.[3] These stabilities are the result of the relatively lower highest occupied molecular orbitals (HOMO) levels, which allows unwanted oxygen doping to be avoided. Therefore, these compounds could overcome the disadvantage of oligothiophenes, which are some of the most promising materials for use in *p*-type semiconductors but are easily oxidized due to their relatively low band gap and high HOMO levels.[6] Because of their outstanding properties of self-organization and stability, much more research on utilizing fluorene-based conjugated polymers or oligomers is likely in the near future for applications to OFETs. Similar to PF-based OLEDs, keto defects resulting from thermal or photo-oxidation could strongly affect the performance of fluorene-based OFETs as well. In particular, it is expected that keto defects would result in more severe damage to electrical properties since the degradation or change in electroluminescent spectra of PFs is more serious, compared with photoluminescent (PL) spectra after keto-defect formation.[4]

In this letter, we report on the effect of keto-defect sites, in fluorene units, on the performance of OFETs using a *p*-type active material based on a structural combination of fused bithiophene with fluorene (BFTT). OFETs using BFTT as a *p*-channel showed a more rapid degradation of device performances, i.e., a decrease of field effect mobility (μ_{FET}) and an increase of threshold voltage (V_{th}) after UV irradiation in air which results in the formation of keto defects rather than in an inert nitrogen atmosphere. The reason for these degradations will be discussed in this letter.

The chemical structure of BFTT is shown in Fig. 1. BFTT was synthesized using the Suzuki coupling reaction

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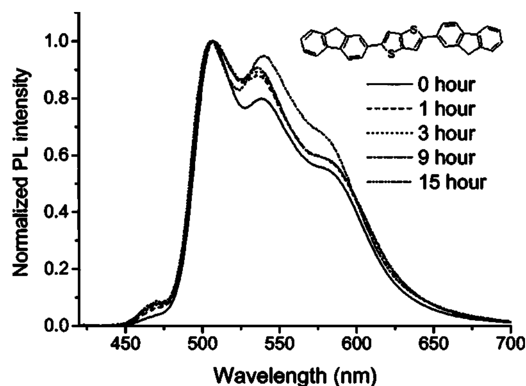

FIG. 1. PL spectra of BFTT films on SiO_2/Si before and after UV irradiation in air. Inset: The chemical structure of BFTT.

between 2,5-dibromothieno[3,2-b]thiophene[7] and the corresponding pinacolato boronic ester-substituted fluorene, analogous to previously described methods.[3,8] A thin film organic semiconducting layer was deposited onto a SiO_2 (300 nm, 10 nF/cm^2) surface of a heavily doped silicon wafer used as the gate electrode. The OFETs were completed by evaporating gold (50 nm thick) through a shadow mask to form source and drain electrodes. A more detailed description of the evaporation process can be found in our previous report.[9] This device had a channel length and width of 20 μm and 5 mm, respectively. The FET characteristics were measured with a KEITHLEY 4200 semiconductor characterization system in air. The stability of the devices with respect to photo-oxidation was measured after UV irradiation at a wavelength of 380 nm using a Hamamatsu LC5 instrument (50 mW/cm^2). PL spectra and IR transmission spectra were measured using a JASCO FP-777 Spectrofluorometer and a PERKIN ELMER system 2000 FTIR, respectively.

Figure 1 shows PL spectra of a BFTT film (300 nm thick) before and after UV irradiation in air. The intensity of PL peaks decreased after UV exposure. Besides this, there are two important changes after UV irradiation. One is that the intensity of the peak at 540 nm (~2.3 eV) and 585 nm (~2.1 eV) increased with UV irradiation time. The other is that the peak at 476 nm was also increased after UV irradiation. It would be expected that the increase in the intensity in the longer wavelength region is induced by the formation of keto defects on fluorene units.[4] The latter change at the shorter wavelength might be the result of the partial loss of conjugation in BFTT after UV irradiation.[3]

Figure 2 shows FTIR transmission spectra of BFTT films (about 300 nm thick) before and after 3, 6, and 15 h of UV irradiation in air and 6 h of UV irradiation in a nitrogen atmosphere (bottom curve), respectively. The carbonyl stretching peak, assigned to photo-oxidized fluorenone defects, at 1721 cm^{-1} was clearly observed after UV irradiation for periods longer than 6 h in air. The intensity of the peak at 1721 cm^{-1} was further increased after UV irradiation for 15 h. A sufficient density of keto-defect sites was formed to permit their detection by our FTIR instrument after 6 h of UV irradiation in air. However, in the case of the sample exposed to UV light in nitrogen, no peak appeared, even after irradiation for 6 h. This also confirms that the structure related with the 1721 cm^{-1} peak can be photo-oxidized keto defects of fluorene. In the case of a 50-nm-thick film, which is the same thickness as was used in the FET device, the

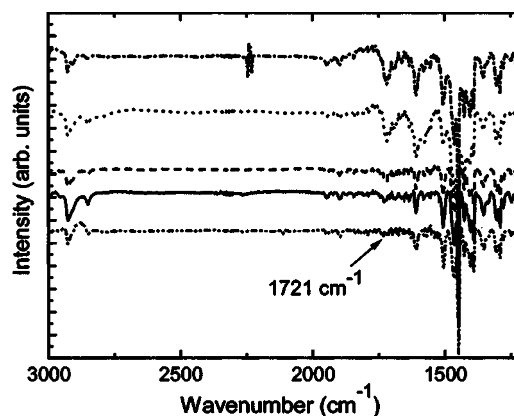

FIG. 2. IR transmission spectra of BFTT films on SiO_2/Si before and after UV irradiation in air and a nitrogen atmosphere. The curves were measured from the pristine BFTT film (solid line) and films irradiated with UV for 3 h (dashed line), 6 h (dotted line), and 15 h (dash-dotted line) in air. The bottom-most curve (dash-dotted-dotted line) was measured from a BFTT film irradiated with UV for 6 h under nitrogen.

1721 cm^{-1} peak could not be detected, probably because the film was too thin to result in a perceptible change.

The BFTT FETs were fabricated in a top contact geometry to investigate the effect of keto defects on the performance of the devices. Figure 3(a) and the inset show the drain current (I_D) versus gate voltage (V_G) or source-drain voltage (V_D) characteristics with various V_G for p-channel FETs deposited at a substrate temperature (T_s) of 150 °C. The film showed a layered morphology with an edge-on orientation at the T_s used, indicating that the longest molecular axis is in almost the same direction as the normal direction of a substrate. The μ_{FET} and V_{th} of the OFETs were obtained

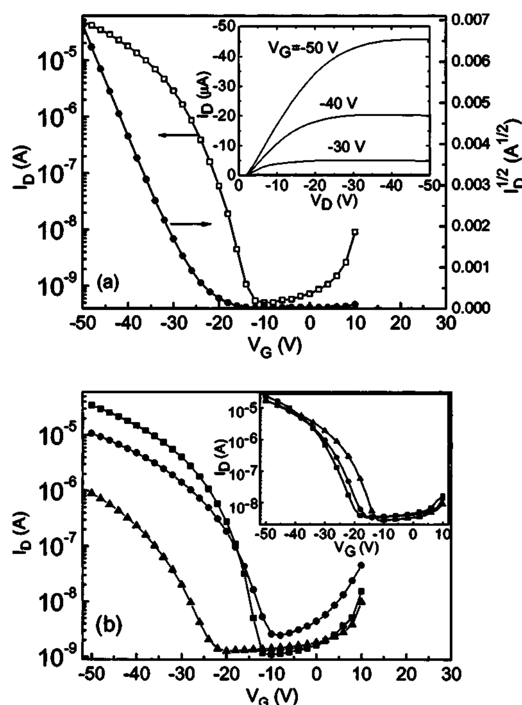

FIG. 3. (a) I_D vs V_G characteristics of BFTT FET measured at V_D=−50 V. Inset: I_D vs V_D characteristics with V_G varying from 0 to −50 V in steps of −10 V. (b) Transfer characteristics of BFTT FETs as a function of UV irradiation time illuminated in air and nitrogen atmosphere (inset) at V_D =−50 V: before UV irradiation (closed squares) and after UV irradiation for 3 h (closed circles) and 6 h (closed triangles).

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TABLE I. BFTT FET characteristics (T_s=150 °C) before and after UV irradiation in air or nitrogen atmosphere.[a]

	Fresh	3 h later	6 h later
Mobility [cm^2 V^{-1} s^{-1}]			
Saturation region	0.053 (0.037)	0.012 (0.023)	2.1×10^{-3} (0.017)
Linear region	0.037 (0.017)	8.9×10^{-3} (0.015)	1.3×10^{-3} (0.011)
V_{th}[V]	−23.4 (−27)	−22.9 (−25.4)	−29.6 (−21.8)
On / off ratio	7.7×10^4 (5.3×10^4)	1.4×10^4 (4.2×10^4)	1400 (4×10^4)

[a]Values in parentheses were measured with BFTT FETs before and after UV irradiation in nitrogen atmosphere.

following the conventional characterization equation for FET, as proposed by Horowitz *et al.* for saturation regimes.[10] The calculated μ_{FET}, the current ratio of the on and off state (I_{on}/I_{off}), and V_{th} obtained by plotting I_D and $I_D^{1/2}$ versus V_G were 0.058 cm^2 V^{-1} s^{-1}, 7.7×10^4, and −25 V, respectively.

Transfer characteristics of typical BFTT FETs as a function of UV irradiation time are shown in Fig. 3(b) (in air) and the inset (for a nitrogen atmosphere). The device irradiated in air showed a more rapid decay of μ_{FET} and I_D than that the one irradiated in a nitrogen atmosphere. An additional distinctive feature is that the V_{th} of the device irradiated in air showed re-rising after 6 h of UV illumination while that for the device irradiated in nitrogen was decreased continuously with UV irradiation time.

More detailed characterizations of FET performances are summarized in Table I. The μ_{FET} and I_{on}/I_{off} of the BFTT device irradiated in air decreased more rapidly than that irradiated in nitrogen with increasing UV irradiation time. The more rapid degradation of μ_{FET} in air can be attributed to both a partial loss of conjugation and the formation of keto defects because the μ_{FET} of OFETs is strongly dependent on the density of the mobile charge carrier.[3,11] This disruption of π-conjugation after UV irradiation is consistent with the increased intensity of the PL peak at 476 nm as shown in Fig. 1. In addition, the faster decrease of I_{on}/I_{off} for the device irradiated in air resulted from both a rapid descent in the on-state current and ascent of the off-state current. However, the change in V_{th} after UV irradiation exhibited a different trend from the two parameters mentioned above. The V_{th} value was similar or slightly decreased after UV irradiation in air for 3 h. On the other hand, the V_{th} increased further to −29.6 V after UV irradiation in air for 6 h. The re-rising in V_{th} is believed to be the contribution by keto-defect formation under UV irradiation [4] since the V_{th} value depends on the density of trap following the multiple trap released model proposed by Horowitz *et al.*[10] A number of traps are generated in the band gap by the formation of keto defects and more charge carriers are necessary to fill the increased trap sites. Therefore, a higher V_G is required to obtain *an effective current flow* in the conduction and valence band region. The increased concentration of trap states as the result of keto defects is also supported by a slightly larger difference in calculated mobility values between the saturation and linear regime for the device measured after UV irradiation for 6 h compared to the unirradiated and irradiated device in air for 3 h.[12] This re-rising in V_{th} was not observed for the device illuminated by UV in nitrogen. Moreover, the fact that the re-rising in V_{th} was clear after a 6 h period of UV irradiation was also consistent with the FTIR results shown in Fig. 2. This also confirms that these effects can be attributed to the formation of keto defects.

In conclusion, the effect of keto defects formed by photo-oxidation on electrical properties was examined with reference to the properties of OFETs, using a fluorene-based conjugated oligomer, BFTT. The formation of keto defects leads to a rapid degradation in the performance of the device, i.e., increasing V_{th} and decreasing μ_{FET} simultaneously, due to the generation of numerous trap sites in the band gap. We therefore conclude that, for OFETs based on fluorene-based oligmers and polymers, it would be desirable to develop methods to reduce these photo-degradation processes and consequently to improve the long-term stability of OFET devices.

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