Title	Ultraviolet light responses in photovoltaic properties of TiO₂ / conducting polymer heterostructure devices
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Citation	Applied Physics Letters. 2004, 85(15), p. 3139-3139
Version Type	VoR
URL	https://hdl.handle.net/11094/75655
rights	
Note	

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Ultraviolet light responses in photovoltaic properties of TiO$_2$/conducting polymer heterostructure devices

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Photovoltaic properties of heterostructure devices of titanium oxide (TiO$_2$) and conducting polymer thin films have been studied. Normal photovoltaic properties were stably observed upon the visible light irradiation of the wavelength range corresponding to the absorption of a conducting polymer, and unique photovoltaic properties were also observed upon the ultraviolet (UV) light irradiation of the wavelength range corresponding to the absorption of TiO$_2$. UV light irradiation caused marked increases in the short-circuit current at the visible-wavelength range and in the open-circuit voltage. These properties have been discussed by considering the enhancement of the built-in field which originates from the hole accumulation caused by the trap levels in the TiO$_2$ layer or TiO$_2$/conducting polymer interface. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1804234]

Conducting polymers with extended π conjugation in their main chains have attracted considerable attention not only from a fundamental viewpoint but also from the viewpoint of their practical application as materials suitable for electronic and optoelectronic devices, such as light-emitting diodes and photovoltaic devices.[1,2] Among various conducting polymers, poly(3-alkylthiophene) (PAT) has unique optical and electrical properties and can be widely used as a soluble and fusible polymer.[3–5]

The photovoltaic device using conducting polymers is attracting considerable attention as one of the promising applications that utilize the advantages peculiar to conducting polymers, such as light weight, flexibility, processability, low cost, and large area. However, because of low electron mobility, the charge carriers, which contribute to the photocurrent, are restricted to those created just near the negative electrode by the optical filter effect of the conducting polymer itself.[6,7] That is, in most cases, indium tin oxide (ITO) is used as a positive electrode and only low-energy photons, which can pass through the conducting polymer layer, can be used for carrier generation near the negative electrode. To solve this problem, the photovoltaic cells using titanium oxide (TiO$_2$) and zinc oxide (ZnO), which are semiconductor oxides and transparent in the visible-wavelength range, were investigated.[7–11] In these cells, the transparent electrode on the light-incident side plays a role as the electron collector. Therefore, the direction of the photocurrent is reversed and the optical filter effect is suppressed, which contribute to the enhancement of the photocurrent. However, detailed studies on the interface between an organic semiconductor, such as a conducting polymer, and a metal or an inorganic semiconductor in organic photovoltaic devices, still remain to be carried out.

In this letter, we report on the photovoltaic properties in heterostructure devices of poly(3-hexylthiophene) (PAT6) and TiO$_2$, demonstrating the enhancements of the short-circuit current in the visible-wavelength range and the open-circuit voltage upon ultraviolet (UV) light irradiation.

TiO$_2$ thin films were fabricated by radio-frequency magnetron sputtering deposition onto the quartz substrates or the ITO-coated quartz substrates with a sheet resistance of 10 $\Omega/\square$. As a conducting polymer, regioregular PAT6 (Aldrich Ltd.) with an alkyl side chain length of six dissolved in toluene was used, which is convenient for spin coating.

Absorption spectra of TiO$_2$ and PAT6 thin films on quartz substrates were measured using a SHIMADZU UV-3150 spectrophotometer.

PAT6 layers of the photovoltaic devices were fabricated by spin coating the conducting polymer solution onto the TiO$_2$ layer, and Au layers, as counter electrodes to the ITO electrodes, were deposited by thermal evaporation through a shadow mask at a pressure of approximately 10^{-4} Pa. The active area of each photovoltaic cell was 1×1 mm^2.

A high-intensity xenon lamp (500 W) in combination with a monochromator was used as an UV-visible light source for photoresponse measurements. The photocurrent action spectra were measured under the short-circuit condition using an electrometer (KEITHLEY 617S). The spectral responses of the cells were corrected by measuring the calibration spectrum of an UV-enhanced Si photodiode placed at the sample position. The intensity of 500-nm-wavelength light was approximately 0.6 mW/cm^2. The current–voltage characteristics were measured using a high-voltage-source measurement unit (KEITHLEY 237).

In the measurements under UV light irradiation, using an ultrahigh-pressure mercury lamp as an UV light source, the photovoltaic devices were irradiated by the light of the UV-wavelength range using the glass filter that was transparent only around the wavelength of 360 nm. This UV light intensity was of the same level as the intensity of the UV visible light source used in the photoresponse measurements. For all photovoltaic cells, an incident light was irradiated from the ITO electrode side, and measurements were carried out in vacuum at room temperature.

Absorption spectra of TiO$_2$ and PAT6 thin films are shown in Fig. 1. The absorption of TiO$_2$ existed mainly in

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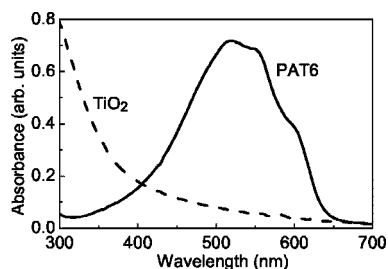
FIG. 1. Absorption spectra of TiO$_2$ and PAT6 thin films.

the UV-wavelength range shorter than 400 nm. On the other hand, the absorption of PAT6 is mainly in the visible-wavelength range, and the absorption edge and the absorption peak are located at 650 nm and 520 nm, respectively.

Figure 2 shows the photocurrent spectra before and after UV light irradiation, that is, wavelength dependences of external quantum efficiency (EQE) of photocurrent before and after UV light irradiation. The structure of the photovoltaic device (ITO/TiO$_2$/PAT6/Au) is shown in the inset of Fig. 2. For visible light irradiation longer than 400 nm in wavelength corresponding to the absorption of PAT6, the photocurrent spectrum with a peak at the wavelength of 510 nm was observed. On the other hand, after the irradiation of UV light shorter than 400 nm corresponding to the absorption of TiO$_2$, the photocurrent increased markedly. This peak intensity of EQE is approximately twofold that before the UV light irradiation, and is mainly observed in the visible-wavelength range corresponding to the absorption of PAT6.

Time response of the short-circuit current upon UV light irradiation is shown in Fig. 3. The sample was irradiated continuously with the monochromatic light of 500 nm wavelength, and additionally with UV light from 10 to 70 min after starting the measurement. Upon UV light irradiation, the short-circuit current increased promptly and then increased gradually towards saturation. Upon shut off of the UV light irradiation of 60-min duration, the current decreased promptly and then decreased gradually, taking 1 h or longer for the current to return to the same level as the original short-circuit current before UV light irradiation.

This photocurrent response can be divided into three components: (i) the photocurrent only by irradiation of light of 500-nm wavelength, (ii) the photocurrent only by UV light irradiation, and (iii) the photocurrent generated gradually by the simultaneous irradiation of light of 500 nm wavelength and UV light. Each component is shown in Fig. 3. That is, the photocurrent components which promptly respond to light irradiation correspond to each single irradia-
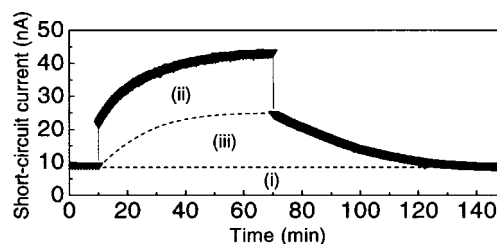
FIG. 3. Time response of the short-circuit current upon UV light irradiation under monochromatic light irradiation of 500-nm wavelength. UV light is irradiated at 10 min and shut off at 70 min. (i), (ii), and (iii) indicate the three photocurrent components.

tion, and the photocurrent component that increases or decreases gradually corresponds to the photocurrent upon irradiation of visible light, which depends on UV light irradiation.

Figure 4(a) shows the time responses of the short-circuit current upon repeated irradiation. As with Fig. 3, the photocurrent component also gradually changed upon on-off repetitions of UV light irradiation under irradiation of light of 500-nm wavelength. The photocurrents responded promptly for each irradiation of the light of 500-nm wavelength or UV light, and were almost constant throughout the irradiation time. Therefore, the above division of photocurrent components seems to be reasonable.

Figure 4(b) shows the time responses of the open-circuit voltage upon repeated irradiation. Upon irradiation of light of 500-nm wavelength, the open-circuit voltage responded promptly and it was almost constant throughout the irradiation time. On the other hand, upon UV light irradiation, the open-circuit voltage responded promptly, but it increased and saturated with irradiation time, unlike the photocurrent response under a condition similar to that shown in Fig. 4(a). Upon on-off repetitions of UV light irradiation under irradiation of light of 500-nm wavelength, an increase the same as that upon UV light irradiation only was observed, and it decreased gradually after the shutoff of the UV light irradiation. The time required for the saturation of the open-circuit voltage under the UV light irradiation was shorter than that required for the saturation of the short-circuit current. However, the time required for the open-circuit voltage to return to the initial value after shutoff of UV light irradiation was longer than that required for the short-circuit current.
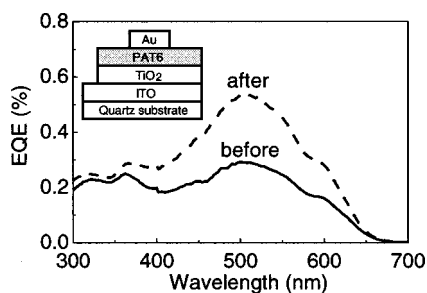

FIG. 2. External quantum efficiency (EQE) of photocurrent spectra of before (solid line) and after (broken line) UV light irradiation. The inset shows the device structure.
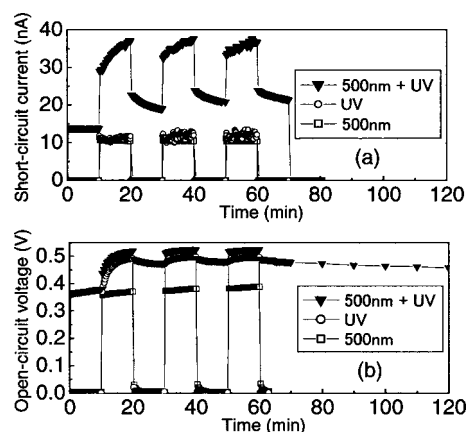

FIG. 4. Time responses of (a) short-circuit current and (b) open-circuit voltage by repeat irradiation.
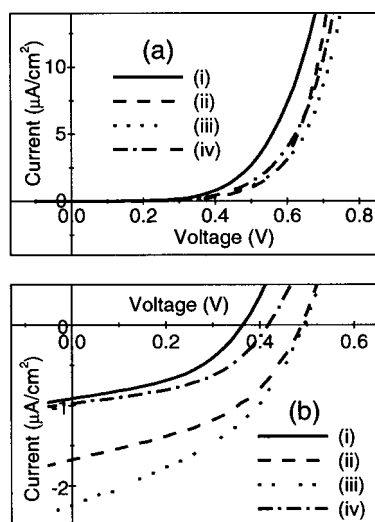
FIG. 5. Current–voltage characteristics of the photovoltaic device at (a) dark and (b) irradiated (500 nm). Four lines indicate (i) before UV light irradiation, (ii) after UV light irradiation of 10-min duration, (iii) after UV light irradiation of 60-min duration, and (iv) at 1 h after shutoff of UV light irradiation.

FIG. 6. TiO_2/PAT6 junction state before (solid line) and after (broken line) UV light irradiation.

The current-voltage characteristics of the photovoltaic device (a) under dark and (b) under irradiation (500 nm) are shown in Fig. 5. Four lines indicate the current–voltage characteristics (i) before UV light irradiation, (ii) after UV light irradiation of 10-min duration, (iii) after UV light irradiation of 60-min duration, and (iv) at 1 h after shutoff of UV light irradiation. The threshold voltages under dark condition shift after UV light irradiation. The changes in the short-circuit current and the open-circuit voltage shown in Figs. 3 and 4 also appear in the current–voltage characteristics shown in Fig. 5(b). The difference between lines (ii) and (iii) in Fig. 5(b) indicates that the saturation of the open-circuit voltage is faster than the saturation of the short-circuit current, and the (iv) line in Fig. 5(b) indicates that the recovery of the open-circuit voltage to the initial value is slow. These changes in the threshold voltages under the dark condition and the open-circuit voltage under irradiated condition caused by UV light should indicate the change in the junction state of the photovoltaic device, and changes in the photocurrent are caused as the result. Such changes of the current–voltage characteristics by absorption of a window layer were also reported in the case of heterojunction devices of inorganic semiconductor, and various models, such as a carrier recombination model by trap levels such as impurity levels, are proposed.[12,13] For example, the changes in the current–voltage characteristics of $ZnO/CdS/CuInSe_2$ solar cell upon blue photon irradiation were consistent with the model based on the low free-electron concentration and the high concentration of deep trap levels in the CdS window layer.

The UV light responses observed in this study might originate from the deep trap levels in the TiO_2 layer or in the TiO_2/conducting polymer interface. When a high concentration of deep trap levels exists in the TiO_2 layer, at equilibrium state, the concentration of electrons in the conduction band must be low because of the trapping of electrons. UV light irradiation corresponding to the band gap of $TiO_2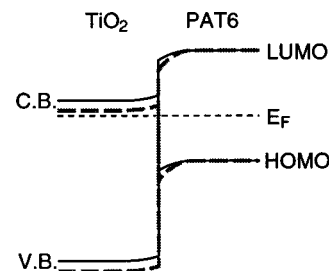$ excites electron-hole pairs in the TiO_2 layer, then holes are trapped at the trap levels, resulting in the increase in the electron concentration in the TiO_2 layer.

Figure 6 shows the presumable changes in the junction state of the TiO_2/conducting polymer before and after UV light irradiation. After UV light irradiation, the Fermi level of TiO_2 seems to approach the conduction band with the increase in the electron concentration in the TiO_2 layer; therefore, the built-in field at the junction interface with PAT6 rises. This rise of the built-in field contributes to that of the open-circuit voltage as a photovoltaic device. The raised built-in field contributes to the increase in the photocurrent in the visible-wavelength range, because the built-in field efficiently dissociates the excitons generated in the PAT6 layer upon irradiation of visible light.

In conclusion, the effects of UV light irradiation on TiO_2/conducting polymer photovoltaic devices, such as increases in the short-circuit current in the visible-wavelength range and increases in open-circuit voltage, were investigated. To explain these changes, we considered the model using the rise of the built-in field which originated from the hole accumulation caused by the trap levels in the TiO_2 layer or the TiO_2/conducting polymer interface.

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