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Very high open-circuit voltage ultraviolet photovoltaic diode with its application in optical encoder field

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We demonstrate a very high voltage based organic photovoltaic (PV) diode by stacking two ultraviolet (UV) sensitized organic PV diodes. It shows an open-circuit voltage (V_{oc}) of 4.34 V under 365 nm UV irradiation with intensity of 2 mW/cm^2. Due to the especially high V_{oc} the PV diode device could be integrated in electronic logic device, as a result a high or a low potential states can be harvested directly under the UV irradiation or not, respectively. The difference between high and low potential states is great and the temporal response is fast, which make it an attractive and promising candidate in application of optical encoder. © *2010 American Institute of Physics*. [doi:10.1063/1.3318438]

The field of organic electronics has gained tremendous interest over the last ten years due to their potential applications in variety of organic electronic and optoelectronic devices, such as field effect transistors,[1] organic light-emitting diodes (OLEDs),[2] photovoltaic (PV) cells,[3,4] memory device,[5] and photodetectors.[6] In these devices the traditional inorganic materials used as active elements are being replaced by organic materials due to their low manufacturing cost, light-weight, and mechanical flexibility compared to inorganic counterparts. Such devices could be advantaged from the many attractive features of organic materials, in particular, the possibility to tailor their synthesis to match specific needs and the ease of processing thin films over large area.

In the organic photodiode (PD) field, most of attention is focused on the photocurrent response. Multilayer donor–acceptor structure and a reverse bias voltage have been employed to harvest more photogenerated carriers and a high signal-to-noise ratio[7] but it also incurs a cockamamie fabricated process. For a PD, a reverse bias also can boost the extracted efficiency of photogenerated carriers and eventually increase in the responsivity.

In this letter, we demonstrate a new tandem structure PD device that is different from above PD based on the aim of increase in photocurrent. It presents tandem PD comprises two ultraviolet (UV) PV diodes. The subunit has a structure of m-MTDATA/TPBi/Bphen, here m-MTDATA, TPBi, and Bphen denote 1,3,5-tris(3-methylphenyl-phenylamino)-triphenyamine, 1,3,5-tris-(N-phenyl-benzimidazol-2-yl) benzene, and monobathophenanthroline, which act as electron donor and acceptor as well exciton blocking layers, respectively. It was found that such a structure device with similar the unit structure exhibited an exclusive UV PV response.[8] Herein, we only pay more attention to its open circuit voltage (V_{oc}) rather than photocurrent response. It is expected that if the V_{oc} is up to a high level of >2.4 V, the PD could be recognized as *on* state in logical switch circuit, that is, a new application field in the PD will be discovered.

Generally, V_{oc} of a PV diode is lower than 1 V, therefore, a V_{oc} over than 2 V could not be achieved in double-unit tandem diode system. In order to get a higher voltage response PD device, a high V_{oc} PV diode must be constructed. And then it was acted as a unit to fabricate a tandem structure PD diode. In our group, PV diode with a V_{oc} of over 2 V has been obtained using the materials of m-MTDATA, TPBi, and Bphen, respectively.[8] The high V_{oc} should be attributed to the large difference between the Fermi levels of the donor and acceptor.[7]

All devices were fabricated on cleaned glass substrates precoated with conducting indium-tin-oxide (ITO) anode with a sheet resistance of 25 Ω/sq, and the substrates were treated by UV ozone in a chamber for 15 min after solvent cleaning. The organic films were thermally evaporated in high vacuum ($<10^{-6}$ Torr) using previously calibrated quartz crystal monitors to determine the deposition rate and the film thickness. The organic layers were deposited at a rate of 2 Å/s. The connection layer between two subunits is Ag/WO_3, which were deposited by a rate of 0.5 Å/s. The evaporating rate of LiF and Al cathode were controlled to be 0.5 and 10 Å/s with the thicknesses of 10 and 2000 Å, respectively. A 365 nm UV light with a power of 2 mW/cm^2 was employed to illuminate both types of diodes. The curves of response times of stacked PV diode were determined by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed neodymium doped yttrium aluminum garnet laser with a THG 355 nm output.

The structure of the tandem device (T-Device) and the thicknesses of each layer are schematically shown in Fig. 1(a). The schematic energy level diagram of subunits (S-Device) used in the T-Device is depicted in Fig. 1(b). Two PV subcells were connected by Ag/WO_3 joint layer which serves as the efficient recombination sites of the carriers generated from the two neighboring subcells.[10]

Figure 2(a) depicts the *I*-*V* characteristic of T-Device with the S-Device. It can be observed that the V_{oc}, J_{SC}, and fill factor (FF) of T-Device and S-Device are 4.34 and 2.23 V, 54.6 and 159.8 $\mu A/cm^2$, 49.6% and 37.4% as well yielding power conversion efficiency (PCE) of 5.87% and 6.65%, respectively. Note that V_{oc} of S-Device is nearly equal to the

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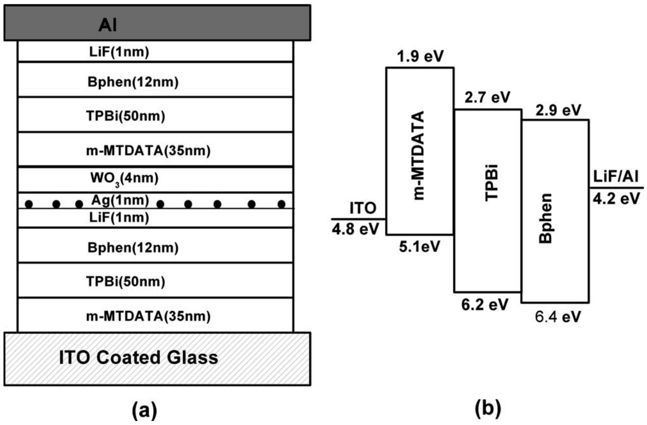

FIG. 1. The structure of the tandem device (a) and its schematic subunit energy-level diagram (b). The HOMO level and the LUMO level which were cited from literatures Refs. 4 and 9.

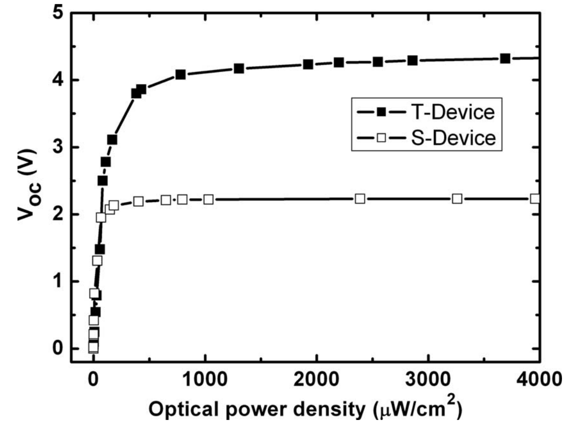

FIG. 3. The dependences of V_{oc} on the incident light intensity for T-Device and S-Device, respectively.

difference of the donor's highest occupied molecular orbital (HOMO) and the acceptor's lowest unoccupied molecular orbital (LUMO), which is accordant with *Tang*'s theory.[3] The V_{oc} of T-Device is nearly twice of the individual cells, which is followed from the alignment Fermi levels of both cells by inserting the thin recombination layer. The tiny difference of 0.12 V implies that the Ag/WO_3 connection layer provides an effective recombination site for generated-carriers coming from adjacent two subunits in T-Device, which leads to the drop of potential in the recombination layer neglected and the connection of both front (nearest the ITO) and back (nearest the cathode) subunit effective. As well known to us, the photocurrent of tandem device is limited by the smaller one. In our T-Device, both front and back subunits are completely same. Photons will be absorbed in front of subunit partly and the incident optical power density in back subunit will be smaller than front one, so the photocurrent will be limited by the back subunit. This results in the lower photocurrent and PCE of T-Device than those of S-Device. In spite of their spectrum response lying in UV zone, an enough high V_{oc} means that it presents a tremendous potential application in optical encoder field, which will be described in detail later.

In electronic logic circuit, a logic level is generally represented by a voltage or current, which depends on the type of electronic logic mode used. Each logic gate requires power so that it uses source and sink currents to realize the correct output voltage. It is well known that the voltage levels that is lower than 0.6 V and higher than 2.4 V are identified with low and high levels in logic circuit, respectively.[11] Due to its high V_{oc} over 4 V, our T-device could be integrated directly into a novel PV system so as to the conventional conversion circuit and power will be no-longer needed. The great difference between high and low potentials makes the translation form "open" and "close" states optical signal to "high" and "low" states electronic signal easily to be distinguished. This implies that the optical signals of "open" and "close" states could be directly transformed into corresponding electronic signals of "on" and "off" states, even into the electrical logical signals "1" and "0," respectively. Therefore, a potential and attractive application in optical encoder field could be achieved. As shown in Fig. 2(b), an optical encoder consists of a rotating disk, a light source and a PD. The disk that is mounted around the rotating shaft has coded patterns of opaque and transparent sectors. As the disk rotates, these patterns would interrupt the UV light illumination onto the PD, so a digital or pulse signal output was harvested. The output signals in optical encoder present only two discrete values, i.e., a low and a high values in optical encoder system. These values are usually named as 0 or 1, or "false" and "true," respectively. A high or a low electrical signal will be harvested when the PD works under presence or absence of UV illumination in optical encoder. In general case, the electrical signal denotes the current signal and then it is transformed into a rectangle-wave signal by the posterior circuit.[12] Herein, a high or low state can directly be harvested when the UV illumination locates at *open* and *close* state, respectively.

Because the T-Device can directly transform the optical signal into high voltage level, the relationship between V_{oc} and the incident optical power density would be a key parameter for the detection. Figure 3 shows the relation of V_{oc} as a function of the incident power intensity under illumination of a 365 nm UV light for T-Device and S-Device, respectively. It can be seen that the V_{oc} rapidly increases with the illumination intensity. The low voltage level (0.6 V) and high voltage level (2.4 V) were harvested as the UV illumination intensities are 23 and 80 $\mu W/cm^2$, respectively, and when the intensity up to 781 $\mu W/cm^2$ the V_{oc} reached to 4 V.

Finally, we investigated the temporal response of the detector. Figure 4 shows typical temporal response curves of the detector which was measured under an irradiation of 355 nm laser chopped at 10 Hz. It can seen that T-Device per-

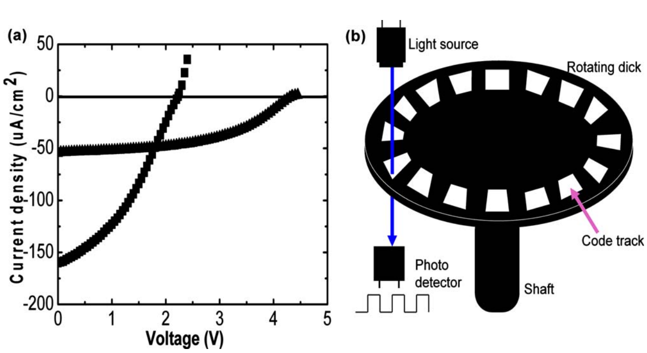

FIG. 2. (Color online) (a) *I-V* characteristics of the T-Device and its subunit (S-Device) under 365 nm irradiation at an incident optical power density of 2.0 mW/cm^2. (b) Schematically working mechanism of optical encoder.

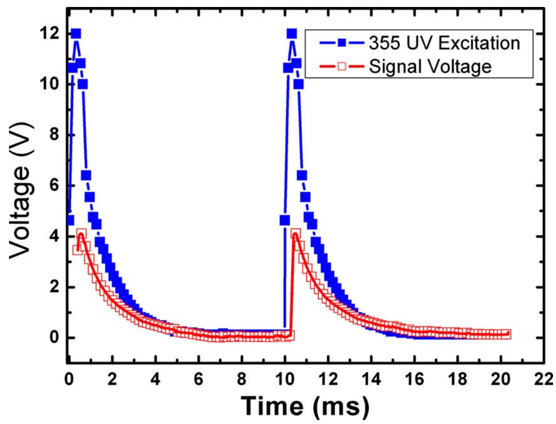

FIG. 4. (Color online) Temporal response of two detectors under irradiations of 355 nm pulse laser.

forms a fast temporal response curves that is well fitted to monoexponential curves, whose time constant is deduced to be 1.5 ms. The long tails in curves can be due to the discharge effect of the capacitance, and it could be shortened if the area of the device ($10\ \mathrm{mm}^2$) will be decreased. Because of the Gaussian line shape of the excited light source (Fig. 4), the charging process of the PD cannot be distinguished in our oscilloscope. But according to the report of other organic PD (Ref. 13) or OLEDs (Ref. 14) the response time of this type of device should lie at magnitude with nanosecond level, which is very advantageous for the application of such a photodetector.

In conclusion, we presented a high V_{oc} UV organic PD by directly stacking two unit PV diodes. The V_{oc} was doubled and the photogenerated current was decreased due to the increase in the series resistance. Owing to the high V_{oc} difference and the quick response time of our T-device, it could be integrated directly into a novel PD system so as to the conventional conversion circuit and power will be nolonger needed. Furthermore, the high V_{oc} makes it promising in integrating the PV device into silicon logic circuit directly.

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