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Visible-blind ultraviolet sensitive photodiode with high responsivity and long term stability

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A high responsivity organic visible-blind ultraviolet photodiode is achieved using aluminum (III) bis(2-methyl-8-quinolinato)4-phenylphenolate (BAlq) and 4,4′,4″-tri-(2-methylphenyl phenylamino) triphenylaine (m-MTDATA) as the electron acceptor and donor, respectively. Under 365 nm illumination with an intensity of 1.2 mW/cm^2, the photodiode behaves a maximum photoresponse of 514 mA/W at −7 V, which is markedly higher than previous reports in our group by Su *et al.* [Appl. Phys. Lett. **93**, 103309 (2008)] and inorganic counterparts based on GaN (150 mA/W) and Si (120 mA/W), respectively. The operational time of the unsealed photodiode is larger than 1000 min when the photocurrent decreases to 67% of its original intensity in air environment. Harvest of so high performance photodiode is mainly attributed to the larger band offsets at m-MTDATA/BAlq heterojunction and skillful device design, etc. The improvement mechanisms are also augured in detail. © *2010 American Institute of Physics*.
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Ultraviolet (UV) visible-blind (VB) photodetectors (PDs) have drawn particular attention due to their potential applications in UV curing monitors, sterilization monitors, and so on for avoiding the interference of visible light waveband in the incident light.[1–4] A reported UV PD diode using tris-(8-hydroxyquinoline) aluminum (Alq) and N,N′-diphenyl-N,N′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) as the acceptor (A) and donor (D) materials, respectively offers a low responsivity (30 mA/W) and is not VB,[3] which may be resulted from the lower energy level offsets at the heterojunction (HJ) interface and stronger energy transfer from TPD to Alq. Our group has reported another UV PD which behaves a higher photoresponse of 380 mA/W at −8 V.[4] The enhancement in the responsivity may mainly be result of larger energy level offset (0.9 eV) between 4,4′,4″-tri-(2-methylphenyl phenylamino) triphenylaine (m-MTDATA) and tris-(8-hydroxyquinoline) gallium (Gaq) comparing with that (0.7 eV) of TPD/Alq counterpart.[5]

At a D/A interface, it is necessary that the donor material has a low ionization potential (IP) which forms a HJ with an acceptor material with a high electron affinity. Depending on the energy level alignment of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of D- and A-materials, the dissociation of the strongly bound excitons can become energetically favorable at such an interface, leading to a free electron polaron in the acceptor and a free hole polaron in the donor. It has been recognized that energy level offsets at HJs are essential to the operation of organic detectors because of the fundamental nature of the photogeneration process in organic materials. On the basis of the argument on principle of designing a PD, in this letter larger band-edge offsets between D/A interface must be first accounted for enhancing the photoresponse. m-MTDATA will still be used as the donor material due to its lower IP (1.9 eV) and higher hole mobility of 3×10^{-5} $cm^2/V\,s$.[6,7] We will use another A-material, aluminum (III)bis(2-methyl-8-quinolinato)4-phenylphenolate (BAlq) with lower LUMO and higher HOMO level,[8] as well as larger electron mobility and higher UV absorption under our determination. These properties of BAlq would be in favor of demonstrating a VB-UV PD that exhibits much higher responsivity. As a result, the optimized PD provides a maximum photoresponse of 514 mA/W at −7 V under illumination of 365 nm UV light with an intensity of 1.2 mW/cm^2. Besides the photocurrent response spectrum almost covers UV waveband from 300 to 400 nm. The dark current is very small and the detectivity is 1.6×10^{12} $cm\,Hz^{1/2}/W$ at −7 V. In addition, the operation lifetime of the unsealed PD diode is larger than 1000 min when the current decreases to 67% of the original intensity under ambient conditions.

The fabrication and main measurement of all PDs were carried out by using the method reported in our group.[4] The measurements of electron mobilities of the BAlq and Gaq were actualized using transient electroluminescence.[9] All the measurements were carried out at room temperature under ambient conditions.

Figure 1 indicates the absorption spectra of 45 nm thick pristine films of m-MTDATA, BAlq, and Gaq, as well as 90 nm thick 1:1 ratio blend films of m-MTDATA:BAlq and m-MTDATA:Gaq on quartz substrates, respectively. The absorption intensity at visible waveband longer than 400 nm is

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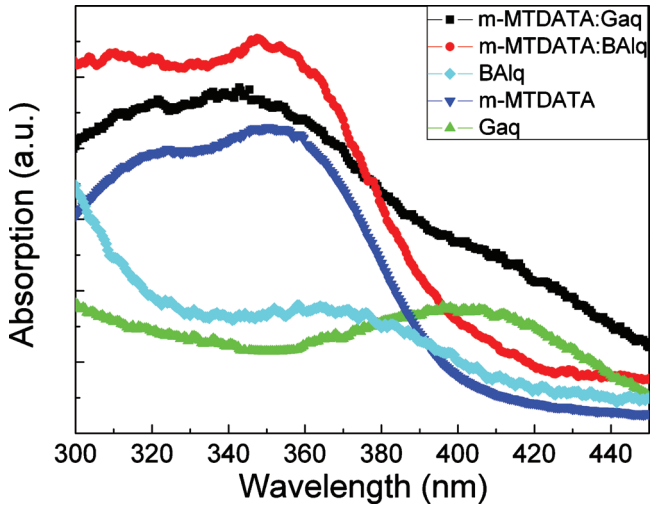

FIG. 1. (Color) Absorption spectra of 45 nm thick pristine films of m-MTDATA, BAlq, and Gaq, as well as 90 nm thick 1:1 blend films of m-MTDATA:BAlq and m-MTDATA:Gaq on quartz substrates, respectively.

much less for m-MTDATA:BAlq than for m-MTDATA:Gaq blend film. We believe that this plays an important role in achieving VB photoresponse.

The optimized PD structure is a hybrid planar-mixed HJ (PMHJ) structure, which is indium tin oxide (ITO)/m-MTDATA (15 nm)/m-MTDATA:BAlq (1:1,50 nm)/BAlq (25 nm)/LiF (1 nm)/Al (100 nm). Figure 2(a) depicts the photocurrent spectral response of the PD at zero bias. Compared with that of the m-MTDATA:Gaq photodiode,[4] the photocurrent response at the visible spectral region is markedly decreased. Note that the photocurrent response almost mainly focuses on neat UV wavebands from 300 to 400 nm and the incident UV radiation shorter than 300 nm is cut down by the ITO glass substrate. Thus the VB photoresponse is harvested thanks to presence of very low absorption intensity in visible wavebands of BAlq. Figure 2(b) illustrates plot of the current density as a function of positive and reverse biases for the diode under illumination of 365 nm UV light and in darkness. We can see that the photocurrent and dark current densities are 616.4 and 0.32 $\mu A/cm^2$ at -7 V, respectively. The photocurrent is about 1.9×10^3 times of the dark current. For our device, the saturated voltage is -7.5 V and at about -9 V the device was broken.

It is well known that reverse bias is an external field applied on the photodiode and the electrical field direction is identical with that of the built-in field between two electrodes, so a gradual rising of photocurrent density with the reverse bias occurs, as depicted in the inset of Fig. 2(b). It can be seen that the photocurrents increase almost linearly with the irradiation intensity from 0.05 to 4 mW/cm^2. The shot noise from the dark current being the major contribution to the noise, we obtain a detectivity of 1.6×10^{12} cm $Hz^{1/2}/W$ at -7 V for 365 nm illumination for our diode,[10–12] which is comparable to inorganic PDs. For instance, a common silicon PD like the Hamamatsu S2551 and $Al_xGa_{1-x}N$-based p-i-n photodiodes behave specific detectivities of 1.5×10^{13} cm $Hz^{1/2}/W$ and 2.0×10^{14} cm $Hz^{1/2}/W$,[13] respectively. Achievement of very high quantum yield of 175% at the response of 514 mA/W seems to be due to an avalanche mechanism.[14] The more detail understanding is under investigation.

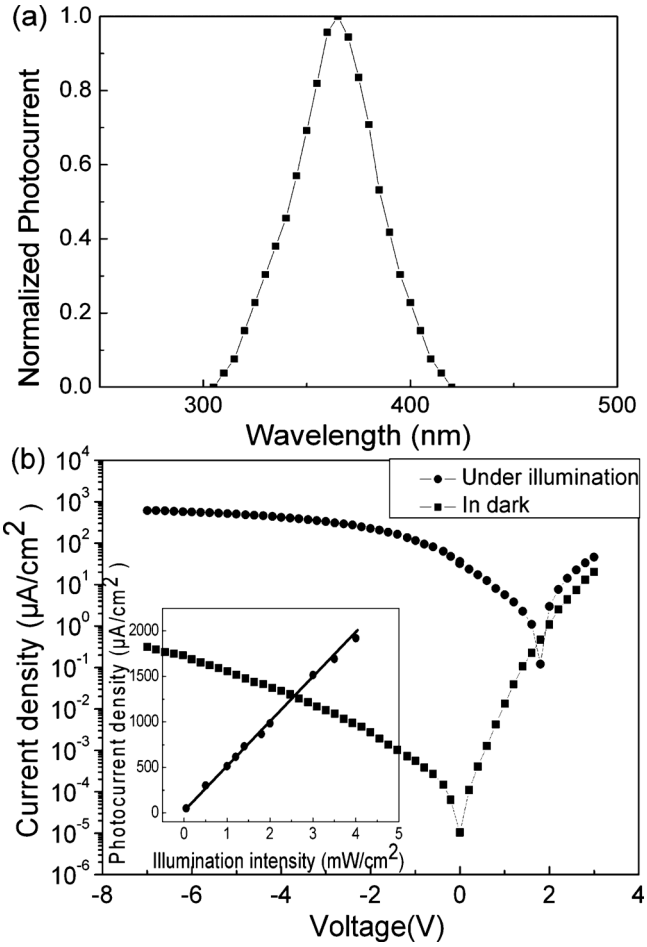

FIG. 2. (a) Photocurrent spectral response of the hybrid PMHJ PD at zero bias. (b) Photocurrent and dark current densities vs bias voltage of the PD shown in logarithm. The inset is the relation between photocurrent density vs illumination intensity of 365 nm UV light.

In terms of the hybrid PMHJ structure,[15] we achieved active region which consists of m-MTDATA donor layer/hole transport layer (15 nm), a mixed m-MTDATA:BAlq layer with 1:1 weight ratio (50 nm) and BAlq acceptor layer/electron transport layer (25 nm). The schematic energy-level diagram of the hybrid PMHJ device is shown in Fig. 3. In such a photodiode structure the efficient exciton dissociation and charge-carrier generation occurs throughout the blend layer as well as at the interfaces between the mixed and two

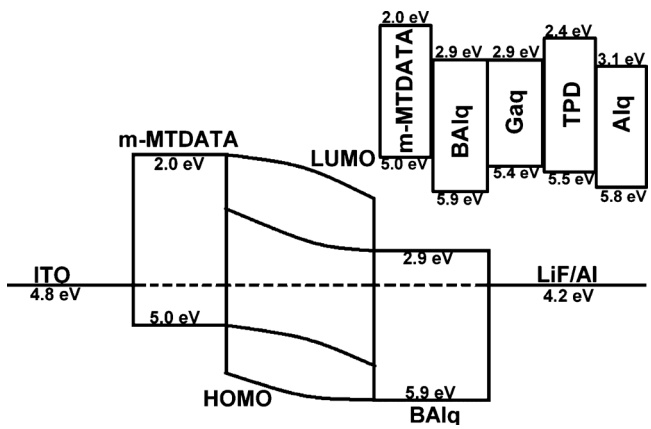

FIG. 3. Schematic energy-level diagram of the hybrid PMHJ PD. Inset: LUMO and HOMO levels of m-MTDATA/BAlq, m-MTDATA/Gaq, and TPD/Alq.

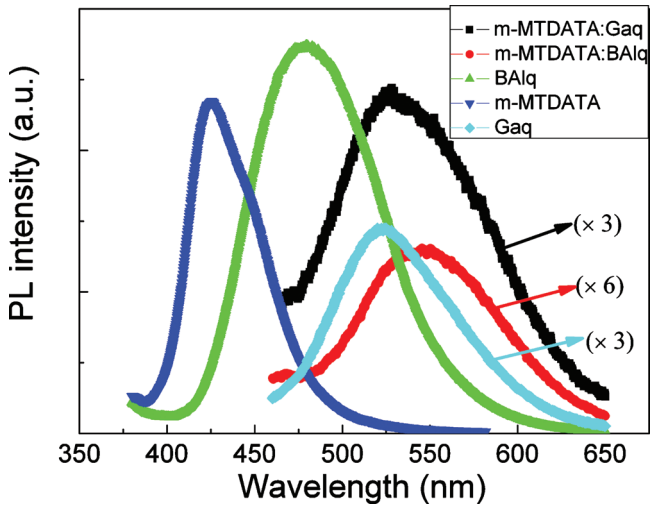

FIG. 4. (Color) PL spectra of 40 nm thick neat films of m-MTDATA, BAlq, and Gaq as well as 90 nm thick m-MTDATA:BAlq and m-MTDATA:Gaq blend films with 1:1 ratio by weight under the excitation of 365 nm UV light on quartz substrates, respectively.

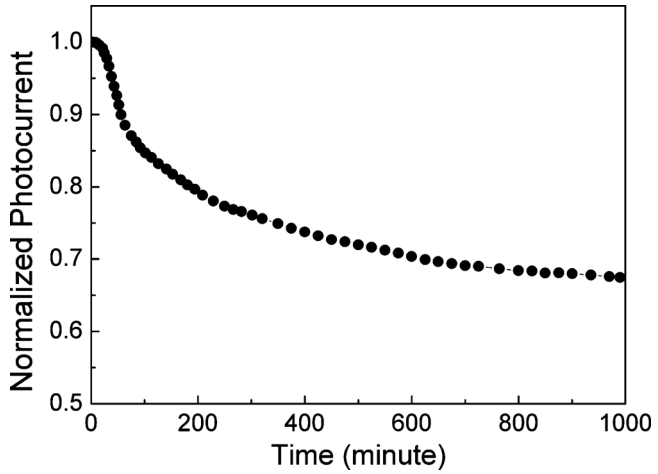

FIG. 5. The dependences of photocurrent on operating time for the hybrid PMHJ PD under constant illumination of 365 nm UV light with an intensity of 1.2 mW/cm^2 at −7 V.

adjacent homogeneous layers. Thus excitons possess higher probability reaching a nearby D/A interface prior to recombination. Using the charge transport layers, a higher efficiency for extraction of photogenerated charges from and through the blend layer is obtained. Besides the electron mobilities of BAlq and Gaq films are 2.92×10^{-6} and 2.11×10^{-6} $cm^2/V\,s$ at 1.4×10^6 V/cm in terms of determination in our laboratory, respectively, that is, it is larger for the former than for the latter. The higher electron mobility would be in favor of balancing carrier transport. On the other hand the HOMO level is higher for BAlq than for Gaq, as indicated in the insert of Fig. 3, which could offer higher possibility of dissociation of photogenerated excitons. Thus lower responsivity of TPD/Alq photodiode partly is due to presence of less level offsets between LUMO and HOMO levels at the D/A interface.

On the other hand, the increase in photoresponse could also be resulted from lower exciplex emission of m-MTDATA:BAlq comparing with m-MTDATA:Gaq film,[16,17] as depicted in Fig. 4. For TPD:Alq blend there is no exciplex emission, the photoresponse is also poor due to the energy transfer from TPD to Alq.[3] The detailed effecting factors on photoresponse with different D:A combinations will be studied in the future.

Finally the dependences of photocurrent on operating time of the PDs is shown in Fig. 5 to understand the degradation of the organic photodiodes.[13,18–20] From Fig. 5 it can be seen that the operational time of the PD working under room temperature and air environment is larger than 1000 min as the current falls to 67% of its original value. If the photodiode could be enveloped to isolate from air the lifetime would be markedly enlarged.

In conclusion, we demonstrated a very high responsivity of an organic VB-UV PD using BAlq and m-MTDATA as the electron A and D, respectively. At −7 V the hybrid PMHJ photodiode offers a maximum photo-response of 514 mA/W. The achievement of so high responsivity is attributed to the excellent alignment levels of the LUMO and HOMO level for exciton dissociation at DA interfaces, higher electron mobility and stronger 365 nm UV absorption of BAlq, etc. It is expected that selection and/or synthesis of the D and A-materials with more appropriate energy level offsets at the D/A HJs, much larger UV absorptions and larger carrier mobility would be a promising route for achieving much higher responsivity UV-VB PDs. The obtained result would be beneficial to the selection and synthesis of D and A materials and configuration design of PD diodes.

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