



High response organic visible-blind ultraviolet detector

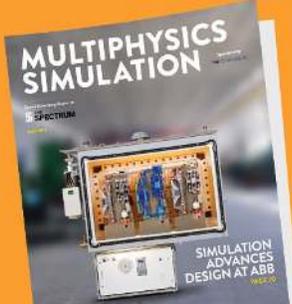
Debdutta Ray and K. L. Narasimhan

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High response organic visible-blind ultraviolet detector

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The authors demonstrate a high efficiency visible-blind ultraviolet organic photodetector with a response of 30 mA/W. The active layer is a blend of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) and tris(8-hydroxyquinoline) aluminum (Alq₃). The authors show that the spontaneous as well as the electric field induced carrier generation efficiencies in the blend are enhanced over its constituents. The spontaneous carrier generation efficiency measured from total carrier collection measurements is 30% in the blend. The photoluminescence of the blend shows an efficient energy transfer from the TPD to Alq₃ molecule. The mobility-lifetime ($\mu\tau$) product in the blend is 2.2×10^{-12} cm²/V. The $\mu\tau$ product is weakly dependent on temperature.

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In recent years, there has been a great deal of interest in solar cells and photodetectors¹⁻⁴ based on organic semiconductors. This has led to an increased understanding and interest in the photophysics of these materials. Excitations in organic semiconductors are predominantly excitonic in nature. Free carrier generation can take place by exciton dissociation. This occurs at various interfaces such as the semiconductor-electrode interface,⁵ interface between two different organic layers,¹⁻³ at impurities or in the presence of external electric fields.⁶ The use of blends in organic photovoltaic devices has led to enhanced free carrier generation efficiencies and has been demonstrated in various solar cell architectures.^{7,8}

Visible-blind ultraviolet (VBUV) photodetectors find application in diverse areas ranging from studies of combustion flames, ultraviolet (UV) curing monitors and sterilization monitors, etc. In this letter, we report on the photoconductivity of a blend of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) and tris(8-hydroxyquinoline) aluminum (Alq₃) and demonstrate a VBUV detector with a peak response of 30 mA/W. The blend was made by coevaporating TPD and Alq₃ on prepatterned indium tin oxide (ITO) coated glass substrates in vacuum at a pressure of 5×10^{-7} Torr. The composition was controlled using three quartz crystal monitors and independently confirmed from optical absorption measurements. The blend composition reported here is TPD:Alq₃=1:1. The device configuration is ITO/blend/semitransparent Al/LiF. The top LiF helped in film encapsulation. Alq₃ was purified using train sublimation. TPD was used as purchased from Aldrich. The photocurrent (PC) is defined as $J_{PC} = J_{\text{light}} - J_{\text{dark}}$.⁹ For PC measurements the incident light on the sample was chopped at 11 Hz using a mechanical chopper.⁹ The incident light intensity was 1.4 mW/cm² at 360 nm. The photocurrent was measured using a lock-in amplifier.

Figure 1 shows the optical absorption spectrum of the blend. As expected, it is a superposition of the absorption spectra of TPD and Alq₃. The inset in Fig. 1 shows the photoluminescence (PL) spectrum of the blend. Also shown

for comparison is the PL spectrum of a bilayer sample where a 500 Å thick TPD film was deposited followed by a 500 Å thick Alq₃ film. As expected, the bilayer film exhibits PL from both TPD (405 and 420 nm) and Alq₃ (520 nm). In contrast, the PL observed from the blend is only due to Alq₃. Figure 1 also shows the PL excitation spectrum of the blend. In this experiment the emission wavelength was chosen to be at 520 nm corresponding to the emission from Alq₃. The excitation spectrum closely follows the absorption spectrum of the blend. Thus, there is an efficient energy transfer from TPD to Alq₃ in agreement with the PL excitation data.

Figure 2 is a plot of the PC as a function of reverse bias for a 400 Å thick (blend) film. The sample was excited at 360 nm (3.44 eV). This energy corresponds to an absorption peak in TPD. The PC increases linearly below -2 V and saturates at around -9 V. In reverse bias, the PC is the sum of the collection length of the carriers and can be written as,⁹⁻¹¹

$$J_{PC} = \eta I e (l_P + l_N) = \eta I e F (\mu_P \tau_P + \mu_N \tau_N), \quad (1)$$

where η is the free carrier generation efficiency, I is the number of photons absorbed per unit volume, F is the electric field, μ and τ are the mobility and the carrier trapping time, respectively, and l is the carrier collection length ($l = \mu\tau F$). The suffix $N(P)$ refers to electrons(holes). When the

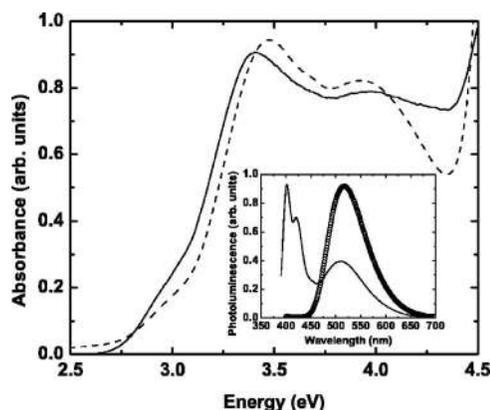


FIG. 1. Plot of the absorption (---) and photoluminescence excitation (solid line) spectrum of the blend. The inset is a plot of the photoluminescence spectra for a bilayer device (—) and blend (○).

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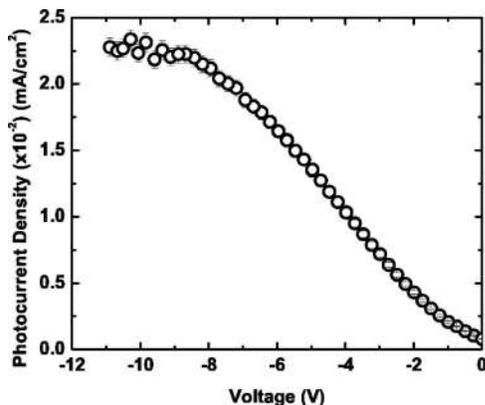


FIG. 2. Plot of the photocurrent density as a function of voltage for a 400 Å thick film when excited at 3.44 eV (360 nm).

collection length is greater than the thickness (L) of the sample (when all the carriers are collected), the photocurrent saturates and is given by, $J_{\text{sat}} = \eta e L$. From the saturated PC, we estimate η to be 38% for the blend. The measured value of η can be written as,⁹ $\eta = \eta(0) + \eta(F)$, where $\eta(F)$ is the exciton dissociation efficiency due to the electric field and $\eta(0)$ is the spontaneous zero field carrier generation efficiency. $\eta(F)$ can be determined from PL quenching measurements and is given by $\eta(F) = [\text{PL}(0) - \text{PL}(F)] / \text{PL}(0)$, where $\text{PL}(0)$ is the zero field PL intensity and $\text{PL}(F)$ the PL at an electric field F . The value of $\eta(F)$ at the highest electric field of 2×10^6 V/cm is around 8%. Hence, we estimate the spontaneous carrier generation efficiency $\eta(0)$ to be at least 30% at 360 nm illumination. This is in contrast with $\eta(0)$ for TPD and Alq₃ which is around 0.1% and 10%, respectively.^{9,10} The free carrier generation rate is significantly enhanced in the blend. Using Eq. (1), we estimate the $\mu\tau$ product for the blend to be 2.2×10^{-12} cm²/V from the linear region of the PC-voltage characteristic in Fig. 2.

We now briefly comment on the magnitude of the field dependent carrier generation efficiency. The PL quenching efficiency $\eta(F)$ is around 0.4% and 1% for neat TPD and Alq₃ films, respectively, at an electric field of 2×10^6 V/cm.^{9,10} In contrast, $\eta(F)$ (8%) is much larger in the blend. A possible explanation for the increased value of $\eta(F)$ in the blend over that observed in neat films of Alq₃ and TPD is as follows. The highest occupied molecular orbital energy discontinuity between Alq₃ and TPD is about 0.3–0.4 eV. In the blend the excitons on Alq₃ in the presence of an applied electric field can dissociate by tunneling of the hole on Alq₃ to a neighboring TPD molecule resulting in a larger value of $\eta(F)$.

Figure 3 shows the spectral response of a 800 Å thick device in reverse bias (–15 V) when illuminated through Al. We note in passing that the dark current is around 2 nA/cm² at –15 V (reverse) bias. The absorption spectrum of the device is also plotted for comparison. The spectral response follows the absorption profile and is *sympatric* with absorption. The photoresponse of the device is roughly constant at 30 mA/W in the UV and falls off sharply at 3 eV (410 nm) by nearly three orders of magnitude. This compares favorably with the response of GaN (150 mA/W) and SiC (120 mA/W) based VBUV detector.^{12,13} Preliminary measurements suggest that the response time is of the order of

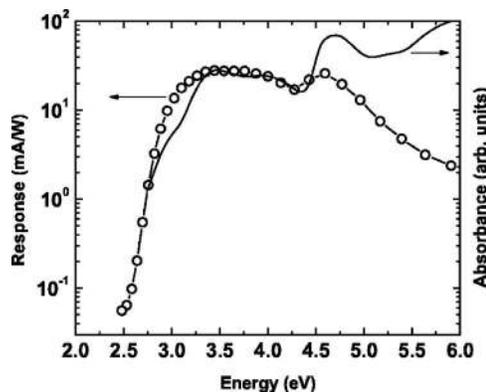


FIG. 3. Plot of photocurrent response as a function of incident photon energy (–○–) for a 800 Å thick film. The absorbance (—) is also plotted for comparison.

milliseconds and is limited by the amplifiers used in the experiment.

Figure 4 shows the PC as a function of voltage measured at different temperatures for a 550 Å thick device. The temperature dependence of the PC near saturation (section A) is due to change of η with temperature and to the $\eta\mu\tau$ product in the linear regime (section B). The thermal activation energy for η is 40 and 65 meV for the $\eta\mu\tau$ product. The difference between these two activation energies gives the activation energy of $\mu\tau$ (25 meV). This suggests that the trapping time depends on carrier mobility in these materials.

In conclusion, we have demonstrated a visible-blind UV detector with a response of 30 mA/W based on a TPD/Alq₃ blend. This device compares very favorably with its inorganic counterparts based on GaN and SiC. Alq₃ molecule in proximity to a TPD molecule helps in increasing the spontaneous carrier generation efficiency in the blend and also aids in electron collection. The quantum efficiency for spontaneous free carrier generation has been measured from total collection measurements to be 30% in the blend. The field dependent generation of carriers is also enhanced in the blend compared to its individual constituents. The $\mu\tau$ product depends weakly on temperature. This suggests that the magnitude of the mobility strongly influences the trapping times in these materials.

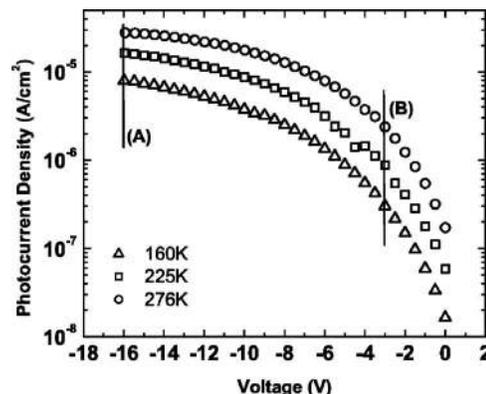


FIG. 4. Plot of photocurrent density (excited at 3.44 eV), of a 550 Å thick device, as a function of voltage measured at different temperatures; 160 K (Δ), 225 K (□), and 276 K (○). The temperature dependence of photocurrent is a due to η near saturation (section A) and is due to $\eta\mu\tau$ at low voltage (section B).

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