

Spectral resolution of states relevant to photoinduced charge transfer in modified pentacene/ZnO field-effect transistors

Josef W. Spalenka,¹ Ehren M. Mannebach,² Dominick J. Bindl,¹ Michael S. Arnold,^{1,2} and Paul G. Evans^{1,2,a)}

¹Materials Science Program, University of Wisconsin, Madison, Wisconsin 53706, USA

²Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin 53706, USA

(Received 3 October 2011; accepted 20 October 2011; published online 9 November 2011)

Pentacene field-effect transistors incorporating ZnO quantum dots can be used as a sensitive probe of the optical properties of a buried donor-acceptor interface. Photoinduced charge transfer between pentacene and ZnO in these devices varies with incident photon energy and reveals which energies will contribute most to charge transfer in other structures. A subsequent slow return to the dark state following the end of illumination arises from near-interface traps. Charge transfer has a sharp onset at 1.7 eV and peaks at 1.82 and 2.1 eV due to transitions associated with excitons, features absent in pentacene FETs without ZnO. © 2011 American Institute of Physics. [doi:10.1063/1.3660225]

Interfaces between organic and inorganic semiconductors are at the core of emerging technologies such as quantum-dot sensitized and dye-sensitized solar cells (DSSCs),^{1,2} nanocrystal-based electroluminescent devices,³ and thin-film field-effect transistor (FET) photosensors.⁴ In each of these cases charge separation or recombination at donor-acceptor interfaces provides the functionality of the devices.⁵ Quantum-dot sensitized solar cells (QDSCs) have the advantage over all-organic solar cells of having generally higher electron mobility in the inorganic component and tunable absorption through control of the nanoparticle diameter.^{6,7} Device efficiency for QDSCs, however, has yet to match that of DSSC or entirely organic solar cells, in part because structures optimizing the charge separation process have not yet been developed.⁸ Fundamental studies of interfacial charge transfer in working devices are essential to closing the gap of QDSCs with other photovoltaic technologies.

The problem of understanding photoinduced charge transfer at buried interfaces is complicated by the mismatch between the characteristic length scales of optical and excitonic phenomena. The exciton diffusion length in organic semiconductors is on the order of several nm, which is two orders of magnitude smaller than the optical absorption length for most wavelengths in the visible spectrum.^{9,10} The volume of pentacene participating in charge separation is small because only excitons generated within approximately 7 nm of the pentacene/ZnO interface contribute to photoinduced charge transfer. It is challenging to determine the optical properties of this near-interface layer, especially in three-dimensional nanocomposites. The interfaces in composites are at varying depths with respect to the surface and the spectrum of light reaching the critical exciton-diffusion region is distorted by the overlying material.

The charge-sensitivity of FETs provides a mechanism to allow the optical and transport properties of the charge-separation region to be probed. Interface properties such as the density of interface trap states in pentacene FETs can be

determined by making electrical measurements while illuminating the channel with a range of photon energies.¹¹ Trap states are progressively filled at higher photon energies and the transistor threshold voltage shifts in response to the trapped charge.¹¹ FET-based measurements show that variations in the electronic properties of chemically attached interlayers between the organic and inorganic phases can dramatically change the rate of interface charge transfer.¹² In this letter, we use dependence of the rate of charge transfer on photon energy to determine the origin of charge transfer and to discriminate against charge transfer to defects in the pentacene film. We find that a large fraction of the total charge transferred resides in long-lifetime trap states, and minimizing the concentration of these states could be a key factor in improving efficiency. Photoluminescence quenching and photoconductivity, in comparison, provide measurements of properties that are averaged over the thickness of the entire device rather than providing interface specificity.¹³

The organic-inorganic FET devices used in this study (inset in Fig. 1(b)) consist of a bottom-contact pentacene FET, forming a channel with a length of 30 μm and a width of 1000 μm , with a dispersed layer of ZnO nanoparticles at the gate dielectric interface. The ZnO nanoparticles were grown via sol-gel synthesis and deposited onto the electrodes of a back-gated FET.¹² The gate oxide thickness is 200 nm, and pentacene thickness is 50 nm. The ZnO quantum dots accept excited electrons from the illuminated pentacene layers. Electrons trapped on the ZnO nanoparticles shift the threshold voltage in FET transfer curves to more positive gate voltages with respect to the source voltage. The magnitude of the threshold voltage shift is proportional to the concentration of charges trapped at the pentacene/gate dielectric interface. After removing as-grown pentacene devices from vacuum and exposing to ambient air and light, the threshold voltage shifts by as much as +15 V. This shift is likely due to photoinduced oxygen doping, as previously observed in pentacene FETs.¹⁴

Spectrally resolved transistor measurements were made by scanning the photon energy of the illumination of the

^{a)}Electronic mail: evans@engr.wisc.edu.

channel of the FETs. At each wavelength, the gate voltage was swept from +60 to -60 V with the drain held at -30 V and the source grounded. The photon energy was scanned from 1.4–4.1 eV using a grating monochromator and a quartz tungsten halogen lamp. The pentacene/ZnO FET devices have memory effects in which charges remain trapped for time scales of seconds or more, resulting in slightly hysteretic electrical properties. Acceptor defects are inherent in vacuum-deposited pentacene films,¹⁵ and these states are not associated with exciton dissociation at the pentacene-ZnO interface. Measurements during illumination were compared with those at fixed time after the end of illumination to allow us to separate effects related to charge transfer to these long-lived trap states. At each wavelength point an after-illumination gate voltage scan was acquired after the light had been off for 5 s. The electrical data has not been normalized to account for the spectral intensity distribution of the tungsten halogen lamp, which exhibits a broad intensity maximum centered at 2.2 eV.

A comparison of the photoelectrical properties of illuminated pentacene devices with and without ZnO QD acceptors is shown in Figs. 1(a) and 1(c). Corresponding electrical measurements acquired 5 s after the end of illumination are shown in Figs. 1(b) and 1(d). The difference in during- and after-illumination electrical properties is quantified by defining a quantity, V_{onset} , which we use as a proxy for the threshold voltage, V_{TH} , and extract from the FET transfer curves. V_{onset} is defined as the voltage at which the source drain current reaches 10 nA. The relationship between V_{onset} , V_{TH} , ΔV_{onset} , and ΔV_{TH} is shown graphically in Fig. 2(a). Because the FET transfer curves have the same shape at low currents, changes in these quantities, given by ΔV_{onset} and ΔV_{TH} , are equivalent. The variation of V_{onset} with photon energy for devices with ZnO at the

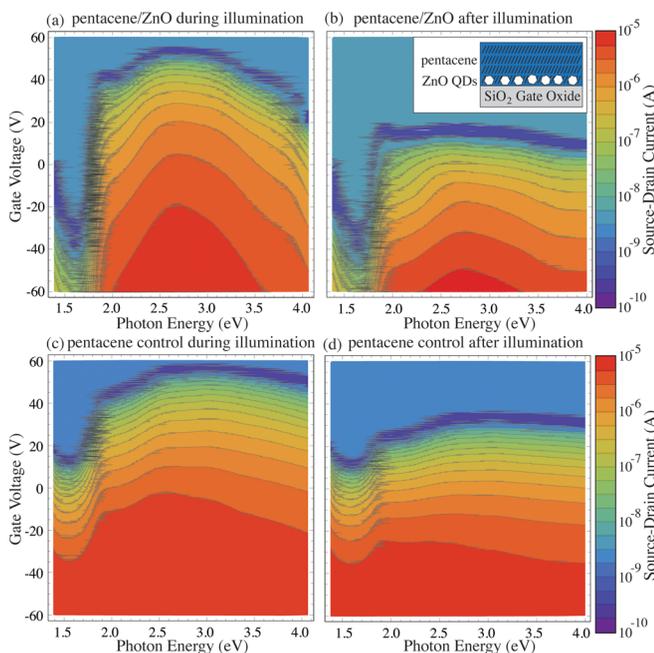


FIG. 1. (Color online) Source-drain current as a function of illumination photon energy and applied gate voltage for a pentacene FET with ZnO at the gate interface during illumination (a), 5 s after illumination (b), for a pentacene control device with no ZnO during illumination (c), 5 s after illumination (d). (inset) The channel of FET device incorporating ZnO nanoparticles at pentacene/SiO₂ gate dielectric interface.

gate interface is shown in Fig. 2(b). The threshold voltage during illumination varies by more than 98 V across the range of photon energies. At energies above the onset of pentacene absorption near 1.7 eV, V_{onset} rapidly increases and reaches a maximum of 48.7 V at a photon energy of 2.67 eV.

The transistor characteristics after the end of illumination, including V_{onset} s, also have a significant dependence on the photon energy, as shown in Fig. 2(b). Photoexcited electrons fill trap states located at the ZnO/pentacene interface at photon energies above 1.7 eV. A fraction of the trapped charges occupy these states for times longer than the duration of the measurement. In the absence of long-lifetime trapped charges, we would expect V_{onset} to return to the dark value after illumination and to be independent of the wavelength of the preceding illumination. The strong wavelength dependence of the after-illumination measurements is a clear indication of the long-timescale of trap dynamics at this interface. The area density of charges, n , transferred to trap states can be calculated from the threshold voltage shift using the relationship $n = (C_i/q)\Delta V_T$.¹⁶ Here, C_i is the capacitance per unit area of the gate dielectric, q is the elementary charge, and ΔV_T is the shift in threshold voltage between measurements before and after illumination. The total charge transferred to the trap states is sufficient to shift the V_{TH} from, -33 V, its value before the experiment to $+49$ V, a shift corresponding to a charge density of $8.5 \times 10^{12} \text{ cm}^{-2}$.

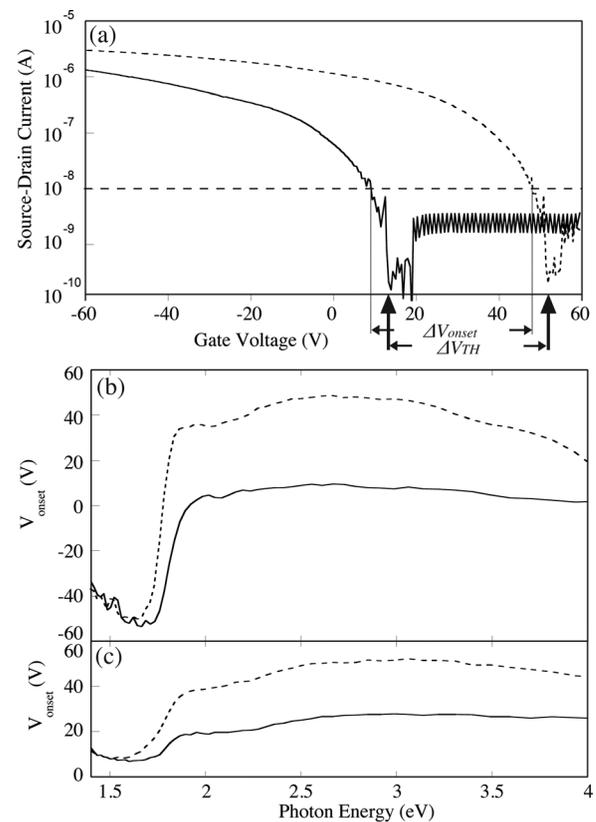


FIG. 2. (a) Current-voltage characteristics for 2.7 eV illumination (dashed curve) and 5 s after illumination (solid line) for the pentacene-ZnO FET device from Figs. 1(a) and 1(b). V_{onset} , V_{TH} , ΔV_{onset} , and ΔV_{TH} are graphically defined. (b) V_{onset} as a function of illuminating photon energy for the pentacene-ZnO FET (dashed line) and 5 s after illumination (solid line). (c) V_{onset} as a function of photon energy for a pentacene control device (dashed line) and 5 s after illumination (solid line).

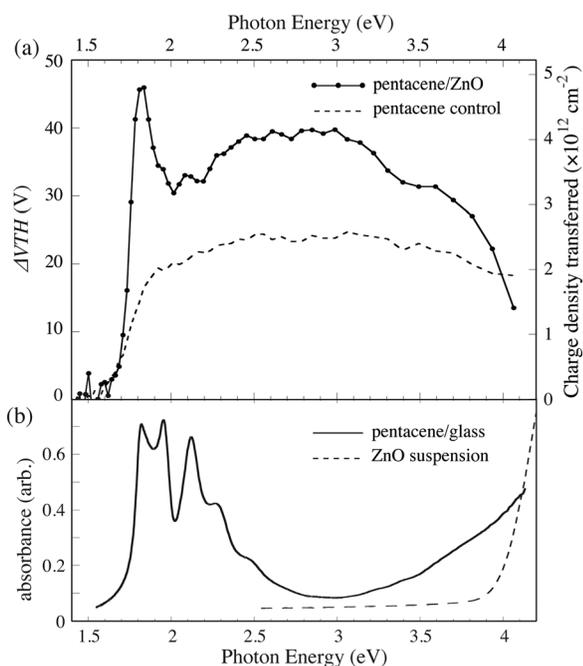


FIG. 3. (a) Threshold voltage shift as a function of incident photon energy for pentacene-ZnO FET (solid line) and pentacene control device (dashed line). (b) Absorbance over the same photon energy range for a pentacene film of comparable thickness on a glass slide (solid line) and for ZnO nanoparticle solution in ethanol prior to spin-coating (dashed line).

Spectrally resolved charge transfer measurements for a control device fabricated without ZnO QDs are shown in Fig. 2(c). Without ZnO, V_{onset} varies within a narrow range between 0 and 10 V for photon energies higher than the pentacene absorption threshold at 1.7 eV. Taken together, the low threshold voltage and small variation with wavelength after illumination show that there are few long-lifetime traps in the control sample and that the long-lifetime states apparent in Fig. 2(b) arise from the ZnO QDs. The origin of the variation in the threshold voltage at photon energies below 1.7 eV is unclear but may be due to the delayed recovery of the device after being illuminated by room light.

The concentration of charges transferred from pentacene to the mobile or short-lived trapped states on the ZnO QDs can be inferred from the shift in threshold voltage between the measurements during and after illumination. This difference eliminates the effect arising from charge transfer to long-lived trap states. The maximum concentration of charge transferred to mobile states or short-lived traps is $5 \times 10^{12} \text{ cm}^{-2}$.

The dependence of the charge transferred to mobile states can be used to determine what species is responsible for transferring charge to the ZnO QDs. Figure 3(a) shows concentrations of charge transferred to mobile or short-lived trap states for a device with ZnO and for a control device without ZnO. Absorption spectra of a pentacene thin film on a glass substrate and ZnO QDs in ethanol suspension are shown in Fig. 3(b). Maxima in the transferred charge appear at photon energies that match the optical absorption of pentacene thin films and are far from the onset of absorption in the

ZnO QDs. Comparing the electrical measurements and absorption spectra shows that charge transfer arises from photons absorbed in pentacene and that the contribution due to direct absorption in ZnO is small. The charge transfer has maxima at photon energies of 1.81, 1.95, and 2.09 eV, corresponding to strong exciton peaks present in the absorption spectra at 1.82 and 2.1 eV, also in agreement with previous measurements of the pentacene optical absorption.¹⁷ We note that the magnitudes of the peaks in the spectrum of transferred charges in Fig. 3(a) would be even higher if the absorption of the illumination at these photon energies by the overlying pentacene were taken into account.

Devices without ZnO nanoparticles do not show maxima in the threshold voltage shift corresponding to the strong exciton absorption features in the pentacene spectrum at 1.82 and 2.1 eV. Pentacene excitons in devices without ZnO do not have a favorable pathway for dissociation and trapping of the electron and consequently do not affect the electrical data.

Although high energy photons ($>2.7 \text{ eV}$) have only a fraction of the intensity incident on the surface compared to lower energy photons, their contribution to photoinduced charge transfer was surprisingly high because they penetrate relatively deeper into the film. A large fraction of the total charge transferred was found to reside in long-lifetime trap states likely due to disorder in the pentacene film in interface region near the ZnO.

This work was supported by the University of Wisconsin Materials Research Science and Engineering Center, NSF Grant No. DMR-0520527.

- ¹E. Martinez-Ferrero, J. Albero, and E. Palomares, *Phys. Chem. Lett.* **1**, 3039 (2010).
- ²B. A. Gregg, *J. Phys. Chem. B* **107**, 4688 (2003).
- ³S. Coe, W. K. Woo, M. Bawendi, and V. Bulovic, *Nature* **420**, 800 (2002).
- ⁴T. Zukawa, S. Naka, H. Okada, and H. Onnagawa, *J. Appl. Phys.* **91**, 1171 (2002).
- ⁵N. Koch, *Chem. Phys. Chem.* **8**, 1438 (2007).
- ⁶P. V. Kamat, *J. Phys. Chem. C* **112**, 18737 (2008).
- ⁷A. Kongkanand, K. Tvrđy, K. Takechi, M. Kuno, and P. V. Kamat, *J. Am. Chem. Soc.* **130**, 4007 (2008).
- ⁸S. Giménez, T. Lana-Villarreal, R. Gómez, S. Agouram, V. Muñoz-Sanjosé, I. Mora-Seró, *J. Appl. Phys.* **108**, 064310 (2010).
- ⁹B. Park, P. Paoprasert, P. Gopalan, T. F. Kuech, and P. G. Evans, *Appl. Phys. Lett.* **94**, 073302 (2009).
- ¹⁰D. Faltermeier, B. Gompf, M. Dressel, A. K. Tripathi, and J. Pflaum, *Phys. Rev. B* **74**, 125416 (2006).
- ¹¹K. Lee, M. S. Oh, S.-J. Mun, K. H. Lee, T. W. Ha, J. H. Kim, S.-H. Ko Park, C.-S. Hwang, B. H. Lee, M. M. Sung, and S. Im, *Adv. Mater.* **22**, 3260 (2010).
- ¹²J. W. Spalenka, P. Paoprasert, R. Franking, R. J. Hamers, P. Gopalan, and P. G. Evans, *Appl. Phys. Lett.* **98**, 103303 (2011).
- ¹³N. C. Greenham, X. G. Peng, and A. P. Alivisatos, *Phys. Rev. B* **54**, 17628 (1996).
- ¹⁴S. Ogawa, T. Najjo, Y. Kimura, H. Ishii, and M. Niwano, *Appl. Phys. Lett.* **86**, 252104 (2005).
- ¹⁵G. Gu, M. G. Kane, and S.-C. Mau, *J. Appl. Phys.* **101**, 014504 (2007).
- ¹⁶S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices* (Wiley, New Jersey, 2007).
- ¹⁷J. Lee, S. S. Kim, K. Kim, J. H. Kim, and S. Im, *Appl. Phys. Lett.* **84**, 1701 (2004).