Dynamics of photoinduced charge transfer between pentacene and a C$_{60}$-terminated self-assembled monolayer

Byoungnam Park,[a] Peerasak Paoprasert, Padma Gopalan, T. F. Kuech, and Paul G. Evans[b]

University of Wisconsin, Madison, Wisconsin 53706, USA

A C$_{60}$-terminated self-assembled monolayer can be used to place molecular acceptor states at the interface between the semiconductor and gate insulator of an organic field effect transistor. The time dependence of the photoinduced charge transfer between pentacene and C$_{60}$ has a fast component with a characteristic time of 1.9 s and slower component with a time constant of 32 and 48 s at the beginning and end of a transient increase in illumination, respectively. Variation in the threshold voltage shift with the thickness of the pentacene results from the competing length scales for light absorption and exciton diffusion. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3080667]

Opportunities in organic electronics have become available by placing self-assembled monolayers (SAMs) with well-defined electronic properties at the gate insulator/semiconductor interface of field effect transistors (FETs). These monolayers modify device properties via static or reconfigurable molecular dipole moments as well as by providing electronic states at the interface.[1–3] A C$_{60}$ functional group attached to a SAM, for example, has an electron acceptor state that can participate in photoinduced charge transfer.[2] Devices incorporating SAMs also enable studies of the fundamental electronic properties of molecules at interfaces and of electronic defects in organic semiconductors. Here we use an organic FET to probe the dynamics of photoinduced charge transfer between pentacene and fullerene acceptors attached to the interface. An analogous charge transfer process between the C$_{60}$ derivative [6,6]-phenyl-C$_{61}$-butyric acid methyl ester and the polymer semiconductor poly(3-hexylthiophene) is a crucial step in organic photovoltaic devices.[4] Understanding charge transfer in photovoltaic structures has been difficult because the relevant interfaces are buried within bulk blends and thus not available to conventional electronic and structural probes.

Pentacene FETs were fabricated on SiO$_2$ gate insulators on which C$_{60}$ molecules were attached to an amine-terminated SAM [Fig. 1(a)] using methods that were previously described.[2] Connections to the FETs allowed electrical measurements to be made during the pentacene deposition without exposing completed devices to the atmosphere.[5] The FETs were characterized in the linear regime of transistor operation in which the drain current $I_{D,\mathrm{lin}}$ is proportional to the drain-source voltage V_D. The drain current can be expressed in terms of the mobility of holes μ, the capacitance per unit area of the gate insulator C_i, and the width and length of the channel Z and L, respectively,[6]

$$I_{D,\mathrm{lin}} = \frac{Z}{L}\mu C_i (V_G - V_T) V_D. \tag{1}$$

For large interface charge densities, the threshold voltage V_T is determined by the charge per unit area Q_i trapped at the semiconductor/gate insulator interface with $V_T = -Q_i/C_i$.

The electronic energy levels associated with a C$_{60}$-terminated SAM at a pentacene/SiO$_2$ interface are not known. Based on the pentacene-C$_{60}$ interface, however, we expect that the C$_{60}$ molecules lead to an acceptor state within the pentacene energy gap.[7] The C$_{60}$ lowest unoccupied molecular orbital (LUMO) is reported to be 0.6 eV below the above the pentacene LUMO at interfaces between C$_{60}$ thin
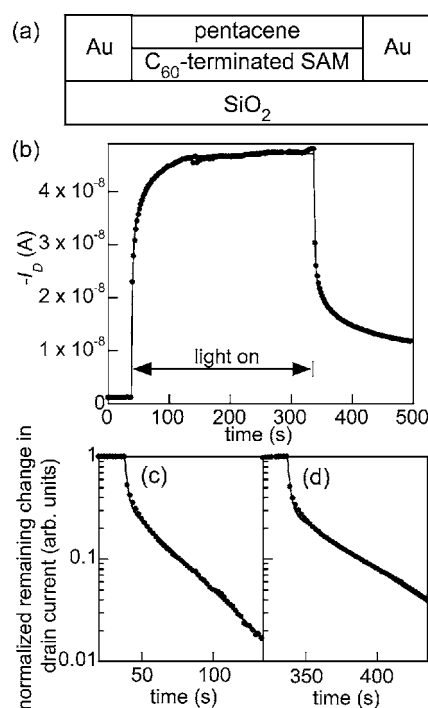

FIG. 1. (a) Schematic cross section of a pentacene transistor with Au source and drain electrodes and a SiO$_2$ gate insulator functionalized with a C$_{60}$-terminated SAM. (b) Drain current as a function of time with illumination by 650 nm light at an intensity of 3 mW cm^{-2} between 40 and 340 s. [(c) and (d)] Logarithmic plots of the drain current and the fit of a sum of two exponential decays at the beginning and end of illumination.

[a]Present address: Georgia Institute of Technology, School of Chemical and Biomolecular Engineering, 311 Ferst Drive, N.W., Atlanta, GA 30332-0100.

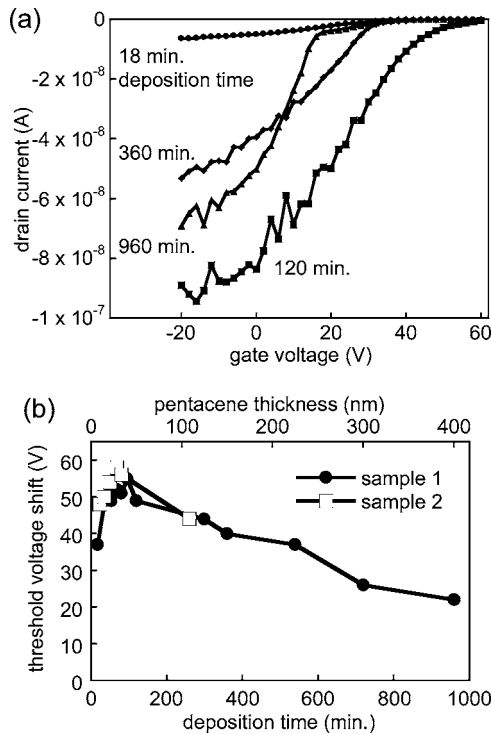[b]Electronic mail: evans@engr.wisc.edu.

FIG. 2. (a) Drain current as a function of gate voltage for illuminated pentacene transistors at several times during the deposition of pentacene, measured with $V_D = -5$ V. (b) The threshold voltage shift resulting from illumination for two samples, measured during the pentacene deposition using a series of gate voltage scans from positive to negative gate voltages, beginning at 60 V.

FIG. 3. (a) The flux of carriers out of the C_{60} states, assuming constant lifetime of 1.9 s. A fit of the model for the flux of excitons to the interface is shown as the solid line using a surface recombination velocity of 29 cm s^{-1} at the pentacene/C_{60} interface.

films and pentacene.[8] Electrons can be transferred from the pentacene to the C_{60} when the pentacene is illuminated.[2]

The movement of charges into and out of the electronic states associated with C_{60} molecules can be observed via the time dependence of the electrical properties of the pentacene FETs. Figure 1(b) shows the drain current as a function of time measured with $V_D = -3$ V and $V_G = 0$. Illumination with light from a 650 nm laser diode at an intensity of 3 mW cm^{-2} began at $t = 40$ s and ceased at $t = 340$ s. All electrical measurements were conducted with the sample at room temperature. The drain current increases by nearly a factor of 50 when the FET is illuminated. Devices without C_{60} have threshold voltages of the order of 0–10 V and do not exhibit these large shifts upon illumination.[2] Charges in the acceptor states on C_{60} molecules change the threshold voltage, which in turn changes the drain current, and the same time constant is thus associated with both the change in the drain current and the change in the total charge on the C_{60} groups.

The observed current in Fig. 1(b) has been fit with a sum of two exponential decays. Logarithmic plots of the data and the fit in Figs. 1(c) and 1(d) show that there at least two exponential time constants associated with the change in the charge in the C_{60} acceptors. The initial faster component has a time constant of 1.9 ± 0.1 s for both the rising and falling edges of the current transient in Fig. 2. The subsequent slower decay has time constants of 32 ± 1 and 47 ± 2 s at the beginning and end of illumination, respectively. These time constants are many orders of magnitude longer than the characteristic times for the recombination of photogenerated excitons in pentacene, 850 ps, indicating that the observed current transient does not arise from photoconductivity in
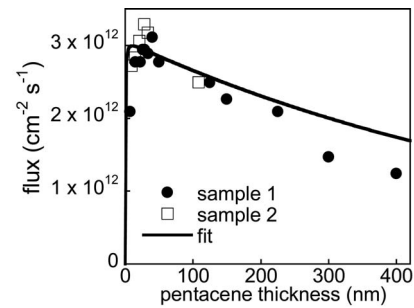
pentacene.[9] The magnitude of these time constants is instead consistent with trap emission rates of 0.1–10 Hz observed in deep level transient spectroscopy experiments in pentacene thin films[10] and in the electrically driven filling and emptying of traps in organic transistors.[11]

The magnitude of the photoinduced charge transfer depends on the thickness of the pentacene layers. Electrical characteristics of a pentacene FET on a C_{60}-terminated gate insulator are shown in Fig. 2(a) at several times during the deposition of a thick pentacene layer. The photoinduced shift in the threshold voltage shift changes with the pentacene thickness as a result of the different length scales for optical absorption and exciton diffusion. The magnitude of the threshold voltage shift as a function of the thickness of the pentacene layer is shown in Fig. 2(b). The thickness axis in Fig. 2 is based on a deposition rate of 0.42 nm min^{-1}, measured using atomic force microscopy and assuming that each completed molecular layer has a thickness of 1.5 nm. Results are shown in Fig. 2(b) for two samples for which the threshold voltage was measured in the linear regime using gate voltage scans from 60 to −20 V. The direction of the scan is important because the gate electric field applied at the beginning of the scan facilitated the initial charge transfer into the C_{60} states.[2]

The optical and excitonic properties of pentacene thin films are available in the literature. Ultrafast experiments give a diffusion constant D of 5×10^{-4} cm^2 s^{-1} and a lifetime τ of 850 ps for excitons in pentacene.[9,12] These result in an exciton diffusion length of 7 nm, far shorter than the optical absorption length α for 650 nm light incident along the surface normal of a *c*-axis oriented pentacene film, 700 nm.[13] Earlier measurements of the optical absorption length vary significantly, however, ranging from 300 nm to 1.7 μm.[14,15] Because of the comparatively short diffusion length, the flux of excitons to the C_{60}-functionalized interface arises from excitons generated by optical absorption within 10–20 nm of the interface. This results in a maximum in the flux of excitons to the interface when the pentacene thickness matches the exciton diffusion length. At larger thicknesses, the flux to the interface gradually decreases because optical absorption reduces the intensity of the light reaching the region near the interface.

In steady state, the escape of carriers out of the states associated with C_{60} is balanced by the rate at which electrons are captured. The number of carriers captured per unit area can be approximated as $\sigma_n v_{th} N_t n$ with a capture cross section σ_n, volume concentration n, and thermal velocity v_{th} of ex-

citons and an area concentration of C_{60} states N_t.[6] The concentration of carriers available to be transferred from the pentacene to the isolated traps can be found by solving the carrier transport problem arising from the absorption of light and the diffusion and recombination of excitons.[16] The product $\sigma_n v_{th} N_t$ is as a surface recombination velocity boundary condition in this calculation.

We have generalized the result in Ref. 16 by allowing the pentacene layer to have different surface recombination velocities, S_0 and S_ℓ, at its two surfaces. The steady state exciton concentration n in the pentacene layer is given by[16]

$$n = Be^{-\beta x} + Ce^{\beta x} + \frac{I\alpha}{D}\frac{1}{\alpha^2 + \beta^2}e^{-\alpha x}. \tag{2}$$

Here $\beta = 1/\sqrt{D\tau}$ is the reciprocal of the exciton diffusion length and x is the depth measured from the top pentacene surface. The semiconductor-gate insulator interface at $x = \ell$. The constants B and C are

$$B = \frac{I\alpha}{D}\frac{1}{\beta^2 - \alpha^2}\frac{-(S_\ell - \alpha D)(\beta D - S_0)e^{-\alpha\ell} + (S_0 + \alpha D)(\beta D + S_\ell)e^{\beta\ell}}{(\beta D - S_0)(\beta D - S_\ell)e^{-\beta\ell} - (\beta D + S_0)(\beta D + S_\ell)e^{\beta\ell}},$$

$$C = \frac{I\alpha}{D}\frac{1}{\beta^2 - \alpha^2}\frac{-(S_\ell - \alpha D)(\beta D + S_0)e^{-\alpha\ell} + (S_0 + \alpha D)(\beta D - S_\ell)e^{\beta\ell}}{(\beta D - S_0)(\beta D - S_\ell)e^{-\beta\ell} - (\beta D + S_0)(\beta D + S_\ell)e^{\beta\ell}}. \tag{3}$$

The illumination I is the number of photons per unit area per unit time incident on the device.

The flux of carriers out of the states associated with C_{60} is given by the ratio of the number of trapped charges per unit area and the faster component of the characteristic times for emission, 1.9 s. In steady state, the flux out of the traps is balanced by the rate of capture of electrons from excitons in the pentacene, $n(\ell)S_\ell$. The solid lines in Fig. 3 are a fit of the experimental flux with $n(l)S_l$, giving $S_\ell = 29$ cm s^{-1}. For film thicknesses greater than the exciton diffusion length, the flux of carriers to the functionalized pentacene/SiO$_2$ interface is unaffected by exciton recombination at the free surface, and we have thus neglected surface recombination at the free pentacene surface by taking $S_0 = 0$ for the fits. The fit of the model in Fig. 3 can be qualitatively improved at large pentacene film thicknesses without changing the other parameters by using a shorter optical absorption length from 400 to 500 nm, consistent with some of the available optical measurements in pentacene thin films.[14]

The magnitude of the threshold voltage shifts, 50–100 V, corresponds to 10^{13} charges per cm^2. A surface recombination velocity of approximately 30 cm s^{-1} obtained from the fit in Fig. 3 gives an effective cross section for carrier capture at C_{60} of 5×10^{-19} cm^2. This cross section for charge transfer is relatively small in comparison with structures, such as inorganic semiconductors in which there are covalent linkages between the semiconductors and acceptor states, but consistent with estimates of cross sections for other traps in organic semiconductors.[11] In fullerene-polymer mixtures, however, intermolecular charge transfer results in a dramatic quenching of the polymer photoluminescence, and the time constants for charge transfer can be as short as the radiative lifetimes.[17] Similarly, charge transfer in covalently linked systems and between states within single molecules can be highly efficient, with transition times on the scale of picoseconds.[18] There is an opportunity for improvement of orders of magnitude in the timescale and efficiency with which charge is transferred the at the C_{60}-pentacene interface.

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