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Containing a Fast-track Communication

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Mobility-independent doping in crystalline rubrene field-effect transistors

Fast-track communication

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Abstract

We report doping effects in an organic semiconductor, crystalline rubrene. Oxygen-related states are introduced (removed) by annealing in oxygen (vacuum), at an elevated temperature. Room temperature stability is found in the resulting effects: (1) about two orders of magnitude increase in carrier density at equilibrium, (2) significant modification of threshold voltages, and (3) an unchanged field-effect mobility in the on-current state. Density of states data are modeled as tunneling from the valence band in the channel region into deep-level acceptors in the adjacent region. These oxygen acceptors are the likely dopant species. © 2007 Elsevier Ltd. All rights reserved.

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There has been increasing interest in organic semiconductors owing to their potential for cost-effective electronic devices for nontraditional applications. In order to enhance the performance of such devices, it is important to understand the fundamental energy and charge transport mechanisms, and in particular, to control the chemical and structural properties that affect transport processes and dopant levels. It is well known that introducing impurities into polymeric systems can increase the conductivity, σ , significantly, concomitant with the introduction of a high density of hopping states [1,2]. While such a level of control is important for making passive devices such as resistors, it is of limited use for active devices where independent control of carrier concentration, n, and mobility, μ , is desired. Since $\sigma = n\mu$, such control would be the natural result of changing σ while leaving μ unchanged. The effect of impurities has also been studied in single crystals where μ values are typically higher than in polymers. In crystals, however, the main effect of added impurities has

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been to degrade μ [3,4]. Beyond the technological significance of accurately assigning changes in σ to changes in either *n* or μ , there is a scientific significance. Fundamental to our understanding of transport in organics – whether delocalized, hopping, or polaron mediated – is our ability to attribute changes in σ to either changes in *n* via chemical doping, or μ via structural disorder. Given the above considerations, the precise role of impurities for charge transport in crystalline organic semiconductors is still unclear.

In this letter, we report the systematic enhancement of n in the organic semiconductor rubrene through oxygen annealing at 380 K as measured by changes in σ , while observing no change in μ in a field-effect transistor (FET). We also observe an oxygen-related signature in the localized density of states (DOS), extracted from gate modulation of activation energies in the FET. These changes in n and DOS are reversible by oxygen and vacuum treatment, and they are stable at room temperature. A tunneling analysis allows these signatures to be associated with deep-level acceptors previously seen in photoluminescence experiments. The combination of changes in n and a chemical origin demonstrates the first example of a μ -independent doping effect in an organic crystal.

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Fig. 1. Typical output characteristics of a rubrene FET device. The inset shows a schematic of the FET devices used in this study; W is the channel width and L is the channel length. The right hand side of the device is not covered by dielectric, exposing the dielectric/rubrene interface to the processing environment; O^* denotes an energetic oxygen species. The lower panel illustrates the process scheme for oxidation or vacuum annealing, and measurement of transconductance as discussed in the text.

The rubrene starting material (Aldrich) for crystallization is first sublimed in a stream of Ar and/or H₂ gas to remove possible impurities. Crystals are grown by horizontal physical vapor transport assisted by Ar gas flow. The source temperature is kept in the range 553-593 K, and crystals nucleate spontaneously along a 30 cm zone with temperature steadily decreasing to ambient temperature at the end of furnace. The sublimed crystals are subsequently used as starting material for iterative crystal growth as described above. For FET measurement, source and drain contacts are painted with a water-based solution of colloidal graphite. The gate insulating layer consists of a 3–4 μ m parylene N thin film, the thickness of which is determined with a profilometer. On the top of the parylene layer, a gate electrode is painted with colloidal graphite between source and drain. In order to assist the diffusion of oxygen into the channel region, which is otherwise impeded by the gate insulating material parylene, we cleave the FETs on one edge at a distance 1-2 mm from the FET structure, as shown in the inset of upper panel of Fig. 1. After fabrication of the devices, output curves of the FETs are measured in order to confirm transistor behavior. The upper panel of Fig. 1 shows typical output curves of an FET measured at room temperature in air.

In the present work on rubrene FETs, two different processes are considered: oxidation and vacuum annealing. In order to examine the effect of the material processing on FETs, the temperature-dependent source-drain current, I_{ds} , is measured at different gate bias, V_{gs} . The lower panel of Fig. 1 illustrates the sequence of elevated temperature processing and measurement steps. After mounting the device in a conventional (MMR) probe station, the chamber is then backfilled with 1 atm of oxygen gas at room temperature. The sample is then heated to 380 K and kept at this temperature in oxygen for a process time, τ_{ox} . After the heat treatment, the sample is cooled to 300 K, and the chamber evacuated to 10 mTorr. To extract the



Fig. 2. The effects of oxidation and vacuum annealing processes. The upper panels show characteristics of transfer curves of FET at $V_{\rm ds} = -40$ V at 300 K during the oxidation process. The lower panels show characteristics of transfer curves of FET at $V_{\rm ds} = -40$ V at 300 K during the vacuum annealing process. Right panels show the effects of the processing on currents at $V_{\rm gs} = 0$ V.

activation energy, E_a , I_{ds} is measured with varying V_{gs} at 280, 290 and 300 K. All measurements are performed in vacuum regardless of process conditions. In order to remove extrinsic oxygen from the FET, the above procedure is used with the chamber under a vacuum of 10 mTorr instead of backfilled with oxygen, a so-called vacuum annealing process. The sample temperature for vacuum annealing is also 380 K, but the process time, τ_{vac} , is 2 h for all the vacuum annealing steps.

In order to investigate the effect of elevated temperature processing on transport behavior, FET transfer curves are measured. Data are taken at saturation, $V_{ds} = -40$ V, to minimize the effect of contact potentials [5]. In this situation, the source-drain current varies as $I_{\rm ds,sat} \propto \mu_{\rm eff} (V_{\rm gs} - V_{\rm th})^2$, where $V_{\rm th}$ is the threshold voltage. The upper panel of the left column of Fig. 2 presents a series of FET transfer curves measured on a single device at 300 K with two oxidation steps. Similar results are obtained on other devices. After 10 h of oxidation, the transfer curve is shifted dramatically. Additional oxidation processing for 17 h causes the curve to move further in the same direction. It is important to note that the curves are shifted without change of the slope, showing that the annealing process has little effect on the FET mobility. The lower panel of the left column of Fig. 2 shows the effect of vacuum annealing process on FET transport behavior. In this case, $I_{\rm ds}$ versus $V_{\rm gs}$ is also measured at 300 K after the 27 h oxidation process. In contrast to oxidation, the elevated vacuum process makes transfer curves move backward to restore the initial oxidation state of the FET. The data show that, as is observed for oxidation, vacuum annealing does not affect field-effect mobilities whereas it significantly alters threshold voltages. We note that the oxidation process is reversible in that the injection or removal of oxygen in the rubrene crystals is controlled by the partial pressure of oxygen in the environment. In order to evaluate equilibrium state of rubrene, off-currents, $I_{\rm ds}$ ($V_{\rm gs} = 0$ V), are measured. In the right panels of Fig. 2, the transfer curves are replotted on a logarithmic scale. The



Fig. 3. Characteristic FET parameters versus oxidation and vacuum annealing time at 380 K. Open symbols show field-effect mobilities. Solid symbols represent threshold voltages. The inset shows carrier densities calculated from the conductance between source and drain electrodes at $V_{\rm gs} = 0$ V.

oxidation process enhances the off-current significantly up to about two orders of magnitude, and the current at $V_{gs} = -60$ V is increased by 41% after 27 h of oxidation. Conversely, vacuum annealing reduces the off-current by a factor of twenty and lowers the on-current by 24%. In the on-state, the current of an FET is governed not only by V_{gs} but also by the materials parameters μ_{eff} , *n*, and V_{th} . Of these parameters, V_{th} is perhaps the most important to control by doping since its magnitude will determine the lowest operating voltage of the device. Below we compare the dependence of these material parameters on processing time.

The data in Fig. 3 show the functional dependence of the materials-governed device properties on process times. One sees that a higher concentration of introduced oxygen reduces V_{th} , presumably by inducing more holes in the valence band. A lower concentration of the dopant species restores $V_{\rm th}$ by removing the added holes without affecting μ_{eff} , i.e. the transport mechanism itself. This observed insensitivity of μ with increased σ implies that the carrier density, $n = \sigma/\mu$, increases with oxygen treatment, as shown in the inset of Fig. 3 for data obtained from I_{ds} at $V_{gs} = 0$ V.¹ The oxygen effect is thus analogous to p-type doping in FETs of inorganic semiconductors where a similar decrease of threshold voltage with increased dopant density leaves μ_{eff} unchanged [6]. This is consistent with previous work which showed the conductivity in rubrene increased on exposure to oxygen [7,8]. The shift of $V_{\rm th}$ bears some similarity to that observed by Podzorov et al. [9] wherein V_{th} was found to increase upon exposure to x-rays. In that work, however, the shift was associated with creation of deep-level traps, not with a known dopant species as in our case.

The DOS is also correlated with oxidation and vacuum annealing process and provides added insight into the doping



Fig. 4. DOS measurement and a schematic diagram for DOS peaks and the movement of the peak position. The left panel shows DOS signatures of vacuum annealing processes. The inset illustrates stability of the created states during vacuum annealing process at 300 K. The right panel shows the result of the tunneling effect for different dopant concentrations using the model discussed in the text. The inset schematically depicts the tunneling model showing charge transfer assisted by tunneling from the channel region (1) to its adjacent region (2) as higher gate bias is applied.

mechanism. In order to extract the DOS versus Fermi energy, F, from E_a , the temperature-dependent I_{ds} is measured at different V_{gs} , and a previously reported analysis is used [10]. The stability of oxygen-related states is examined by repeating the E_a measurement every 30 min for two hours after the first 10 h oxidation leaving the specimen in vacuum at 300 K. The inset of left panel of Fig. 4 shows that there is an oxygenrelated peak in the DOS whose center is located at 0.31 eV, superimposed upon a background DOS, and the peak position and intensity remain unchanged, meaning that the oxidation effect lasts significantly longer at room temperature or below. In addition, the transfer characteristics in vacuum at 300 K are also stable except for minor changes in off-currents. These changes can be affected by relatively rapid diffusion of oxygen along the parylene-rubrene interface but are not significant for typical device operation. The left panel of Fig. 4 shows the effect of vacuum processing. It is worthwhile to note that, while the background DOS is unchanged, the oxygen-related signatures are blue-shifted with the annealing time. The former implies that the material processing does not cause the variation of interfacial energy barriers. If that were the case, then such an injection barrier would enter as a constant term in the E_a measurement, leading to an overall shift of the DOS, which is not observed. On the other hand, the movement of peak position with vacuum treatment can be related to a change in Fermi energy with oxygen concentration as we discuss below.

In order to explain the moving peak we consider a twolayer model: the channel (1) and its adjacent region (2), with charge transfer assisted by tunneling from the channel valence band to ionized dopants in the adjacent region. As shown schematically in the inset of right panel of Fig. 4, the valence band bends upward with negative voltages applied to the gate (curves a-c in Fig. 4), and the quasi-Fermi energy in the channel region is largely modulated by V_{gs} . In contrast, the Fermi level in the adjacent region is determined by the charge neutrality

¹ We note that an assumption of a constant channel depth has been made, so that the order of magnitude change in n shown in Fig. 3 is a lower bound on the actual carrier density obtainable by accurately accounting for enhanced screening in a higher conductivity region.

condition [11] including extrinsic properties such as a dopant population that is partially ionized. Here we consider dopants with a specific energy level ($E_{Acc} = 0.25 \text{ eV}$) corresponding to that observed in our photoluminescence experiment [8]. As the valence band in the channel approaches the dopant level with changing gate bias, a relatively strong electric field induces the holes in the channel to tunnel into the neighboring region, thus filling the ionized dopant states. Tunneling is thus enhanced when the valence band energy in region 1 passes the acceptor level in region 2. In this situation, the first derivative of F with respect to V_{gs} is reduced in a narrow energy region, which causes such a peak in the DOS spectra [10]. In addition, the band bending causing the enhanced tunneling is effectively fixed, as denoted by curve b in the inset. Thus, as the dopant level changes with process condition, here illustrated with vacuum annealing, the bulk Fermi level moves to mid-gap (curves *I–III* in Fig. 4), causing the blue-shift of the quasi-DOS peak having respectively $F_I - F_{III}$ with respect to the Fermi levels in region 2.

We now derive a quantitative description for the DOS based on the above tunneling model. It is important to note that $V_{\rm gs}$ has two components: $V_{\rm gs} = V_{\rm gs,1} + V_{\rm gs,2}$, where $V_{\rm gs,1}$ is the voltage that increases the channel valence band energy thus inducing holes in the channel, and $V_{\rm gs,2}$ is the voltage that compensates for the transfer of charge from region 1 to region 2 through tunneling. Since the amount of transferred charge is proportional to the number of unpaired acceptors, $V_{\rm gs,2}$ can be described by:

$$V_{\rm gs,2} = \frac{qd}{C} \frac{N_{\rm Acc}}{1 + \exp\left((E_{\rm Acc} - F)/kT\right)} \left(1 - T_t\right) T_t,$$
 (1)

where q is charge, d is channel depth, C is the gate capacitance per unit area, N_{Acc} is the acceptor concentration, E_{Acc} is the acceptor energy level, and T_t is the tunneling probability. The tunneling probability for a triangular potential barrier [11] is

$$T_t \approx \exp\left(-4\sqrt{2m^*}E_{\rm Acc}^{3/2}/3q\hbar\xi\right),\tag{2}$$

where m^* is the effective mass of holes, and ξ is the electric field. Inserting $V_{gs} = V_{gs,1} + V_{gs,2}$ into the channel DOS equation previously reported [10], the measured DOS can be rewritten in terms of the superposition of the channel DOS profile and the quasi-DOS peak:

$$N_{\text{gap}}(F) = N_{\text{gap},1}(F) + dV_{g,2}/dF,$$
 (3)

where $N_{\text{gap}}(F)$ is the overall DOS and $N_{\text{gap},1}(F)$ is the channel DOS, the same expression as Eq. (5) in the previous report [10] with V_{gs} replaced by $V_{\text{gs},1}$. The right panel of Fig. 4 shows the result of Eq. (3) for different dopant concentrations in region 1, where we assume that $m^* = 0.18m_0$, where m_0 is the electron rest mass [12], the gap between the channel and the adjacent region is 8 Å, and $N_{\text{gap},1}(F) = 2 \times 10^{21} \exp(-40F) +$

 $2 \times 10^{17} \exp(-2F)$. We note that the m^* value used in the model is in the range of values found in oligomeric thin films and its low value is a possible indication of disorder in the tunnel region [13]. The model clearly reproduces the variation of both quasi-DOS peak position and height as the dopant concentration in region 2 is varied. While a microscopic description of the two regions and the tunnel barrier is still to be determined, region 2 is likely either homogeneous with high dopant concentration or compositionally heterogeneous. This analysis shows that the quasi-DOS peaks are possibly related to the 0.25 eV acceptor level induced by oxygen incorporation [8]. These deep acceptors are most likely the cause of hole doping in the channel region.

In conclusion, we have reported the first measurements of oxygen-related doping effects in single crystal rubrene. We show that by varying the annealing time it is possible to control carrier densities while leaving the mobility unchanged. This is, in essence, doping. The carrier density changes are reversible via a complementary annealing procedure, and the resulting conductivity changes are stable at room temperature. This is, to our knowledge, the first demonstration of a controllable doping effect (as opposed to a change in conductivity) in an organic semiconductor, and should enable a new class of studies aimed at exploring and controlling organic semiconductors for practical applications.

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