

Charge trapping in polymer transistors probed by terahertz spectroscopy and scanning probe potentiometry

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Terahertz time-domain spectroscopy and scanning probe potentiometry were used to investigate charge trapping in polymer field-effect transistors fabricated on a silicon gate. The hole density in the transistor channel was determined from the reduction in the transmitted terahertz radiation under an applied gate voltage. Prolonged device operation creates an exponential decay in the differential terahertz transmission, compatible with an increase in the density of trapped holes in the polymer channel. Taken in combination with scanning probe potentiometry measurements, these results indicate that device degradation is largely a consequence of hole trapping, rather than of changes to the mobility of free holes in the polymer. © 2006 American Institute of Physics.

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The promise of printable, flexible electronic devices and displays has fuelled the development of the polymer field-effect transistor (pFET) over the past decade. However, the long-term performance of state-of-the-art pFETs is limited by degradation mechanisms that cause the threshold voltage to increase in magnitude.^{1–6} The principal effect is thought to be charge carrier trapping either in the organic semiconductor or at the semiconductor/insulator interface, which screens the applied gate voltage. In many structures the effect of contact resistance on device degradation needs to be considered, and can make the reliable extraction of the trapped-charge density solely from *I-V* characteristics a difficult task.⁷ It is therefore desirable to use a noncontact technique, such as spectroscopy or potentiometry, to investigate charge trapping in pFETs. In this letter, we report on a noncontact study of the degradation mechanisms in polymer FETs, performed using a charge modulation technique based on terahertz time-domain spectroscopy^{8,9} (TDS). Terahertz radiation interacts strongly with charge carriers in a material, with a fractional transmission change $\Delta T/T$ (on injection or photoexcitation of charges) proportional to the complex conductivity of the thin film.¹⁰ We demonstrate that this approach permits us to monitor the density of trapped holes in the accumulation layer by coupling the low-mobility holes to higher-mobility electrons in the silicon gate. Correlation of these findings with scanning probe potentiometry measurements allows us to assess separately the contributions to transistor degradation arising from changes in the contact resistance, field-effect mobility, and trapped-carrier density.

A schematic diagram of the bottom-gate, bottom-contact polymer transistors fabricated for this study is shown in Fig. 1. The semiconducting polymer poly[(9,9-dioctylfluorene-2,7-diyl)-co-(bithiophene)] (F8T2) was deposited through

spin casting from solution (in a layer of 100 nm thick) onto an interdigitated gold array (channel length of 40 μm , finger width of 50 μm , and total channel width of 45 μm). The gate electrode comprised a lightly *n*-doped silicon wafer ($2.5 \times 10^{15} \text{ cm}^{-3}$) with a total thickness of 0.62 mm, and a 200 nm thick SiO_2 gate dielectric. The transistors exhibited *p*-type conduction upon application of a negative gate voltage and a source-drain bias.

We used a terahertz time-domain spectrometer similar to the one described in Ref. 8 to measure the terahertz radiation transmitted through the transistors. To create charge-modulation effects, an ac square wave bias voltage V_g was applied to the gate, typically $V_g = 0 \leftrightarrow -30 \text{ V}$ at 40 Hz.¹¹ A lock-in amplifier was used to measure the change ΔT (resulting from the V_g modulation) in the terahertz electric field T transmitted through the transistors [Fig. 1(b)]. The terahertz beam and transistor were kept in a vacuum of 1 mbar to minimize terahertz absorption from atmospheric water vapor. In order to obtain good transmission (25%) through the device it was necessary to orient the transistor with the fingers of the interdigitated array at 90° to the plane of polarization of the incident terahertz electric field. However, in this geometry the interdigitated array diffracts the incident terahertz radiation at wavelengths close to the repeat period of the array ($\lambda = 90 \mu\text{m}$ in silicon, corresponding to 0.98 THz in vacuum). This results in a first diffraction minimum in $\Delta T/T$ near 1 THz [see Figs. 1(c) and 1(d)] and further reductions at higher frequencies. We have therefore limited our data analysis to the unaffected free spectral range up to $\sim 1 \text{ THz}$.

Figures 1(b) and 1(c) display the measured change in terahertz electric field ΔT under the application of a bias $V_g = 0 \leftrightarrow -30 \text{ V}$, which is approximately 250 times smaller than the size of the electric field T transmitted through the transistor. No transmission changes were observed after the F8T2 layer was chemically removed, or for devices fabricated without the polymer layer. Figure 1(d) shows that on

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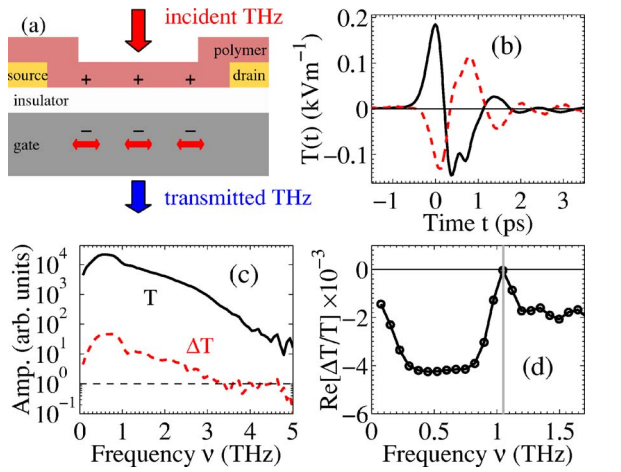


FIG. 1. (Color online) (a) Schematic diagram of the transistor sample geometry for terahertz TDS. Application of a negative gate voltage gives rise to holes in the accumulation layer in the polymer and highly mobile electrons in the silicon gate. (b) Measured terahertz electric field $T(t)$ after transmission through transistor (solid line) and change in transmitted terahertz electric field $\Delta T(t)$ (dashed line, multiplied by 100) upon application of a gate voltage $V_g=0 \leftrightarrow -30$ V. Both are given as a function of electro-optic sampling delay time t . (c) Amplitude spectra of the transmitted radiation $T(\nu)$, and change in transmitted amplitude $\Delta T(\nu)=T(V_g=-30 \text{ V})-T(V_g=0 \text{ V})$ obtained from the time-domain data in (b) through Fourier transformation. (d) Change in transmission $\Delta T/T$ as a function of frequency. The artefact close to 1 THz is a result of diffraction from the interdigitated array formed by the electrodes, as explained in the text.

the application of a gate bias the transistor transmits less terahertz radiation (negative $\Delta T/T$), indicating the creation of a partially reflective layer through changes in the charge carrier density. A negative V_g induces both a hole accumulation layer on the polymer/insulator boundary, and an electron accumulation layer of equal surface carrier density on the insulator/gate boundary [Fig. 1(a)]. The observed transmission change of terahertz radiation with applied gate bias arises primarily from the electrons in the silicon, as the mobility of holes in the accumulation layer ($\mu=7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, estimated from the current in the saturation regime) is more than five orders of magnitude lower than the electron mobility in the silicon gate ($\sim 1400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This interpretation is confirmed by the lack of a transmission change found for an all-polymer transistor (on a quartz substrate) within the experimental noise floor limit of $\Delta T/T < 1 \times 10^{-5}$. For silicon-gate polymer transistors the electron layer in the gate therefore acts as an indirect, but sensitive probe of the hole density in the polymer by coupling it to higher mobility electrons in the silicon.

$\Delta T/T$ increases linearly with the applied gate voltage [Fig. 2(a)], in accordance with an increase of charge density in the channel. We have modeled these data using standard thin-film transmission coefficients. The accumulation layer in the silicon gate was assumed to have a constant electron concentration N_e over a thickness δ_e at each gate voltage. The parameters used were in good accord with those obtained from an analytical solution of Poisson's equation at the SiO_2/Si boundary. The Drude-Lorentz model was used to calculate the dielectric function of the electron layer, with scattering rate $\Gamma=1.5 \times 10^{12} \text{ s}^{-1}$.

Excellent agreement with the experimentally measured $\Delta T/T$ is obtained for an electron accumulation layer density of $N_e^{\text{off}}=2.5 \times 10^{15} \text{ cm}^{-3}$ in the "off" ($V_g=0 \text{ V}$) state and $N_e^{\text{on}}=4.0 \times 10^{18} \text{ cm}^{-3}$ in the "on" ($V_g=-30 \text{ V}$) state when

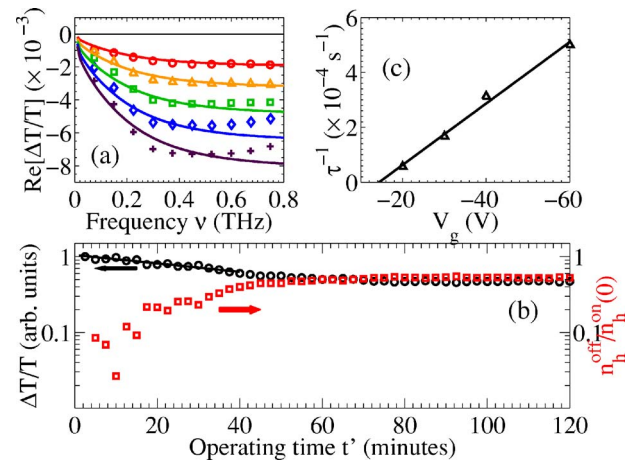


FIG. 2. (Color online) (a) Measured differential transmission signal $\Delta T/T$ for a range of gate voltage modulations $0 \leftrightarrow V_g$ with $V_g = -10 \text{ V}$ (circles), -20 V (triangles), -30 V (squares), -40 V (diamonds), and -50 V (crosses). The solid lines are fits to the data based on a Drude-Lorentz thin-film model as described in the text, with $\Delta T/T \propto V_g \propto n_h$. (b) When $V_g = 0 \leftrightarrow -30 \text{ V}$ is applied for times t' (half the measurement time, owing to the 50% V_g duty cycle) the differential transmission (circles) decays initially exponentially (straight line). The time constant $\tau = (7.1 \pm 2.4) \times 10^3 \text{ s}$ of this decay was determined by averaging fits for three nominally identical transistors, over the first 40 min. The trapped charge density remaining in the channel during the off period $n_h^{\text{off}}(t')/n_h^{\text{on}}(0)$ [squares, extracted from the modeled fits to $\Delta T/T$, with charge density $n_h^{\text{on}}(0) = 3.2 \times 10^{12} \text{ cm}^{-3}$ when on] saturates at large t' . (c) Hole trapping rate $1/\tau$ obtained from exponential fits to $\Delta T/T$ during application of $0 \leftrightarrow -V_g$ for 30 min.

$\delta_e = 8 \text{ nm}$, as shown in Fig. 2(a). The plasma frequency in the off (on) state is 0.2 THz (8.8 THz). Assuming that the sheet charge density in the polymer (n_h) is the same as that in the gate (n_e), the hole accumulation layer charge density for a pristine transistor in the on state N_h^{on} can be calculated from $N_h^{\text{on}} = N_e^{\text{on}} \delta_e / \delta_h$, where δ_h and δ_e are the thickness of the hole and the electron accumulation layer, respectively. Taking $\delta_h = 1 \text{ nm}$ as a reasonable approximation we obtain $N_h^{\text{on}} = 3.2 \times 10^{19} \text{ cm}^{-3}$ at $V_g = 0 \leftrightarrow -30 \text{ V}$, in good agreement with typical values found in the literature.¹⁴ Using identical parameter values to those determined above for $V_g = -30 \text{ V}$, but scaling n_e and δ_e linearly with gate voltage, results in model curves closely matching the measured $\Delta T/T$ over the entire range of applied V_g [Fig. 2(a)].

The sensitivity of our technique to the hole density in the transistor channel makes it an ideal tool to investigate the mechanisms governing degradation of these devices under prolonged application of a gate bias voltage. Measurements of $\Delta T/T$ as a function of biasing time [given in Fig. 2(b)] show an exponential decrease for approximately the first hour, after which the values gradually saturate. We attribute these changes to an increase in density of trapped holes at the polymer/insulator interface with time, resulting in a larger hole density n_h^{off} in the off state (and therefore also an increased n_e^{off} , since trapped holes remain in the channel and contribute to the signal). Figure 2(b) displays n_h^{off} as a function of operating time, as extracted from the data using the model described above under the assumption that all other parameters are unaffected by degradation. The hole density for the off state increases considerably within the first hour, but then saturates at a value of approximately half that of the initial value in the on state $n_h^{\text{on}}(0)$.

The exponential nature of the initial decay of the $\Delta T/T$ signal indicates that the hole trapping rate in the polymer is a

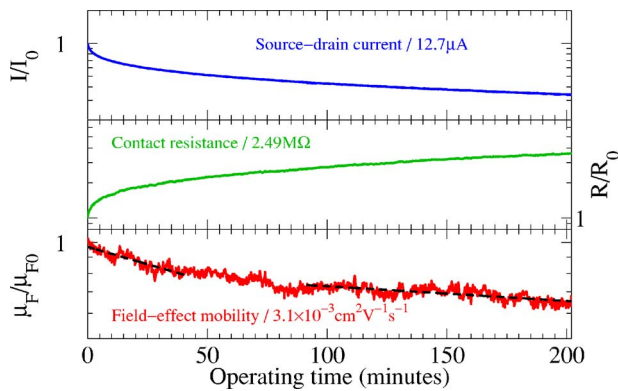


FIG. 3. (Color online) Source current (top), source contact resistance (middle), and field-effect mobility μ_F (bottom) of a $2\ \mu\text{m}$ channel length F8T2/300 nm SiO₂/Si pFET as a function of operating time, normalized to their initial values, and shown on a semilogarithmic plot. The curves were extracted from scanning Kelvin-probe microscopy measurements across the transistor channel. A constant gate voltage bias of $V_g = -40\ \text{V}$ was applied to produce an initial sheet charge density $n_h = 2.9 \times 10^{12}\ \text{cm}^{-2}$ comparable to that in the terahertz experiments. The dotted lines are exponential fits to μ_F at early and late operating times, with time constants $\tau = 1.2 \times 10^4\ \text{s}$ and $\tau = 5.6 \times 10^4\ \text{s}$, respectively.

linear function of the carrier density (i.e., $dn/dt = -n/\tau$) and therefore incompatible with the bipolaronic trapping mechanism ($dn/dt \propto n^2$) that has recently been proposed as a contributor to device degradation on time scales below 1 s.^{3,4} Figure 2(c) demonstrates that the initial trapping rate $1/\tau$, extracted from exponential fits to the initial decay, is proportional to the applied gate voltage. This linear rise in $1/\tau$ suggests that the trapping cross section or the trap density (or both) increases with gate bias, as suggested recently.⁴ We find that the decrease in $\Delta T/T$ is temporarily reversible under illumination, but only for photon energies above the polymer band gap, confirming that the degradation mechanism is largely associated with changes in the polymer.¹³ Similar device recovery is also found after leaving the device with $V_g = 0\ \text{V}$ in the dark, as observed previously.² The modulation period used was too short to obtain significant carrier detrapping during the off state.

Finally, we compare the insights gained about polymer transistor degradation from terahertz TDS techniques with those that may be obtained from more established techniques based on noncontact potentiometry.^{15,16} For this purpose, we have conducted scanning Kelvin-probe microscopy (SKPM) measurements,¹³ which can track the electrostatic potential in the accumulation layer with a high spatial resolution ($<100\ \text{nm}$). The F8T2 transistors investigated were similar to those examined using terahertz TDS apart from a reduced channel length ($2\ \mu\text{m}$), limited by the range of the SKPM tip. Figure 3 displays the resulting source-drain current I , contact resistance R , and channel field-effect mobility $\mu_F = \mu_h n_h$ as a function of operating time of the F8T2 transistor. It can be seen that the early nonexponential decay of I is caused by a rapid initial increase of the contact resistance with operating time. The field-effect mobility, on the other hand, shows an initial exponential decay ($\tau = 1.2 \times 10^4\ \text{s}$) comparable to that obtained from terahertz TDS ($\tau = 7.1 \times 10^3\ \text{s}$) before it tends to saturate at longer operating times. These results demonstrate the difficulty in extracting meaningful information about the dynamics of carrier trapping in pFETs from I - V characteristics, which are significantly influenced by changes in contact resistance.⁷ The observed decay

of the field-effect mobility may be caused by a decrease in either the hole mobility or density in the channel. The combined terahertz TDS and SKPM measurements therefore suggest that the changes in field-effect mobility with transistor operation time are dominated by a reduction in the density of mobile carriers, rather than a decrease in general mobility of all charges in the channel.

In conclusion, we have investigated the mechanisms for degradation of polymer-based FETs using a combination of terahertz spectroscopy and noncontact potentiometry. The observed terahertz transmission change under a gate bias was attributed to the layer of high-mobility electrons that forms in the silicon gate as mirror charges to the lower-mobility hole accumulation layer in the polymer. During the on state of the transistor, the plasma frequency of the electron layer is shifted upwards in frequency, permitting highly sensitive, noncontact probes of the accumulated charge density through terahertz TDS. Our measurements demonstrate an initial monoexponential decrease of the terahertz differential transmission signal with biasing time, in agreement with an increase of trapped charge density in the polymer present also during the off state. Complementary SKPM measurements show that the contact resistance strongly influences the source-drain current at early device operation times ($<40\ \text{min}$). I - V curves taken on their own therefore do not provide direct access to the charge-trapping dynamics in pFETs. By being sensitive only to electrons in the silicon gate, the terahertz TDS measurements are not influenced by the hole mobility in the polymer. From the results of both terahertz TDS and SKPM techniques we infer that an increase in trapped-charge density, rather than a decrease in single-carrier mobility, is responsible for the decline in field-effect mobility with operation time.

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