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Bipolaron mechanism for bias-stress effects in polymer transistors

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The slow formation of hole bipolarons is proposed to explain the bias-stress effect that is observed in some polymer thin-film transistors (TFT). The primary evidence is the observation that holes are removed from the channel at a rate proportional to the square of their concentration. As bound hole pairs form, they deplete the TFT channel of mobile holes, which reduces the TFT current and causes a threshold voltage shift. The slow rate of bipolaron formation is attributed to the mutual Coulomb repulsion of the holes. Contrasting stress effects in different polymers are related to the magnitude of the bipolaron binding energy. Present experiments cannot distinguish whether the bipolarons are intrinsic, or associated with disorder, interfaces, or impurities.

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I. INTRODUCTION

The bias-stress effect is a common property of thin-film transistors (TFT) and is reported in some polymer transistors.[1,2] The characteristic feature is a slow decrease in the on current when the transistor is turned on for an extended time. Equivalently, it is described by a slow shift in the threshold voltage. The effect occurs because mobile carriers are trapped or otherwise removed from the channel, reducing the channel conductance. The effect is usually reversible, but sometimes a high-temperature anneal is required to recover the unstressed state. The time scale for both stress and recovery can be anything from seconds to days or longer.

There are several mechanisms that can cause the bias-stress effect. In any particular situation, the origin might be trapping in states within the gate dielectric, at the semiconductor/dielectric interface or in the semiconductor itself, or an extrinsic effect such as slow ion migration or electrochemical degradation. Slow trapping in the dielectric is often by tunneling, where the exponential dependence of the tunneling probability on distance provides the long time scale. Normal trapping in a semiconductor, with a typical capture cross section of order 10^{-16} cm^2, is generally too fast to account for stress effects, because equilibrium between the free and trapped carriers is established by the time the channel is fully populated.[3] A slow, carrier-induced metastable structural change can occur in the semiconductor, and leads to a corresponding increase in trap density. This form of bias-stress effect is well documented in hydrogenated amorphous silicon.[4]

There are reports of organic TFT's with and without bias-stress effects.[1,2,5] Many studies determine its presence by whether measurement of the transfer characteristic gives a different result when repeated twice. However, as discussed below, a consistent repeated characteristic is not a sufficient condition for the absence of the bias-stress effect. We propose a model for the bias stress effect, based on studies of two polymeric TFT's that have significantly different characteristics. Section II describes the devices and measurements. Section III develops the evidence for a bipolaron mechanism to account for the stress effects, and the properties of the bipolarons are discussed further in Sec. IV.

II. EXPERIMENTAL MEASUREMENTS

Measurements of the bias-stress effect were performed on two *p*-type polymer semiconductors, which when taken together offer some insight into the stress mechanism. Poly(9-9′-dioctyl-fluorene-co-bithiophene) (F8T2) is obtained from Dow Chemicals and has also been studied by other groups.[5] The other material is a regioregular polythiophene ($\mathrm{PT_{RR}}$), synthesized by Xerox Research Center of Canada from a monomer with symmetrical alkyl side chains, thus conferring regioregularilty on the polymer.[6] X-ray diffraction data exhibit sharp peaks, from which it is evident that $\mathrm{PT_{RR}}$ has a (100)-oriented lamellar structure, similar to the structure observed from x-ray measurements in regioregular poly(3-hexylthiophene), P3HT.[7] TFT's formed with $\mathrm{PT_{RR}}$ have field-effect mobilities comparable to those formed with P3HT, but the material is more stable in air.[6] Sirringhaus *et al.* have shown a correlation between regioregularity, lamellar orientation, and high TFT mobility in P3HT.[7]

Bottom gate TFT's were fabricated with alternative structures, all of which gave comparable results. The gate dielectric was either 100 nm of silicon thermal oxide (capacitance 30 nF/cm^2) or plasma-enhanced chemical vapor deposited (PECVD) silicon oxide or nitride (capacitance 20 nF/cm^2). The semiconductor was deposited by spin coating, usually on a self-assembled monolayer (SAM) of organic trichlorosilanes. SAM materials include OTS, OTS8, BTS, and FTS (respectively, octadecyl-, octyl-, benzyl-, and tridecafluoro-1,1,2,2-tetrahydrooctyl-trichlorosilane).[8] The semiconductor thickness was 30–50 nm. Evaporated gold source-drain contacts were deposited in either the staggered or coplanar configuration. In some devices the contacts were made by lithography and in others by jet-printed masks, and the results are not sensitive to the method of fabrication or to the details of the device geometry. The TFT's had channel lengths of 10–100 μm, with width-to-length ratios in the range 5–50 and were conventional device structures with rectangular gate, source, and drain contacts. Both pulsed and quasistatic TFT measurements were made to obtain the transfer characteristics and the time dependence of the on-current. The TFT mobility is in the range 10^{-3}–10^{-2} cm^2/V s in F8T2 and 10^{-2}–10^{-1} cm^2/V s in $\mathrm{PT_{RR}}$.[6,8] All the measure-

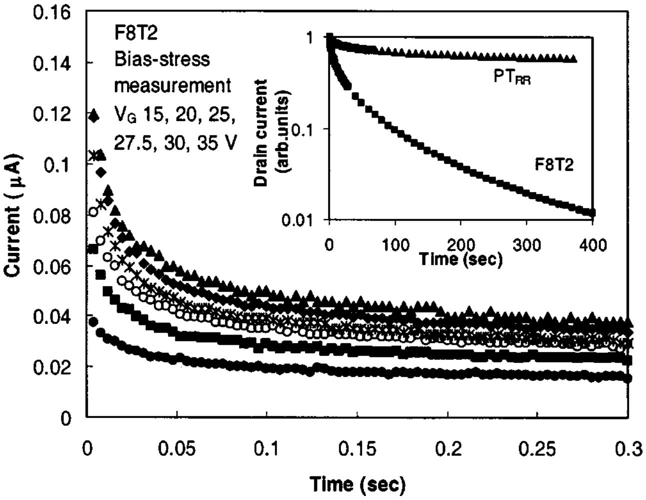

FIG. 1. Time dependence of the drain current of an F8T2 TFT after a gate voltage is applied, measured at various gate voltages as shown. The normalized longer time decay of the drain current for both F8T2 and PT_{RR} is shown in the insert.

ments were made in air and in the dark, and the samples were stored in nitrogen when not in use, to minimize environmental effects.

Figures 1 and 2 show examples of the on current of TFT's made from both polymer semiconductors as a function of time, after switching on the devices to different gate voltages in the linear regime (drain voltage<gate voltage). These data extend for ~1 s and over this period the current in F8T2 decays by 20–60 % and in PT_{RR} by 5–30 %. The decay is initially rapid and then slows, and is more pronounced at higher gate voltage. More details of this gate voltage dependence are described below. The transient effects arising from the TFT capacitance and carrier transit times occur at shorter times than these data. A notable difference between the semiconductors is that the F8T2 TFT current continues to decay over an extended time, while the PT_{RR} current stabilizes relatively quickly. A comparison of the long time decay of the drain current is given in the insert to Fig. 1.

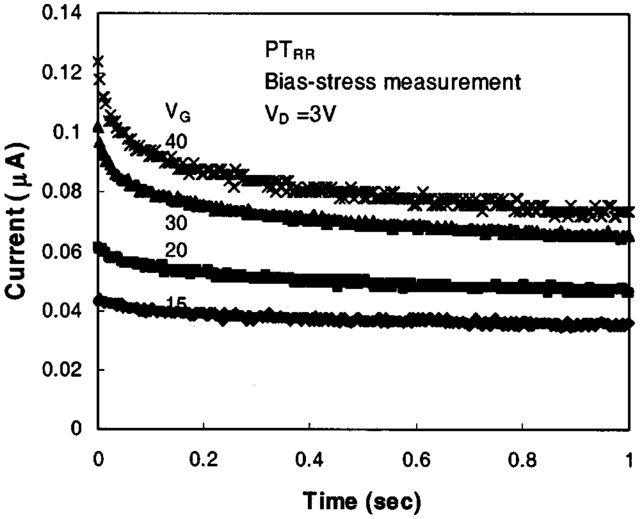

FIG. 2. Time dependence of the drain current of a PT_{RR} TFT after a gate voltage is applied, measured at various gate voltages as shown.

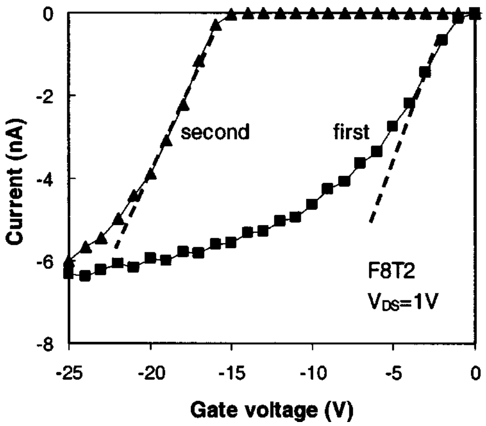

FIG. 3. Repeated quasistatic measurement of the transfer function of an F8T2 TFT, showing strong bias-stress effect. The maximum gate voltage in the measurement is -25 V. The dashed lines indicate the form of the transfer characteristics when measured with a pulsed gate voltage (Ref. 9).

Figures 3 and 4 show quasistatic measurements of the transfer characteristics. The measurement is performed by setting the gate voltage to a positive voltage (usually 10 V) and then decreasing it in 1-V increments of 2-s duration, ending at -20 or -25 V. Each set of data takes about 1 min to acquire and the second measurement is made under the same conditions as the first, but after a short time interval. In F8T2 (Fig. 3), where the stress effects are more pronounced, the classic behavior is observed of a voltage shift in the onset of the current. The transfer characteristics are also strongly curved. However, pulsed measurements of the transfer characteristic give straight lines with a threshold voltage shift after stress.[9] Evidently the curvature in the transfer data in Fig. 3 is a result of the stress effect in progress during the measurements. The pulsed data indicate that the mobility is essentially unchanged and that the stress effect indeed corresponds to the removal of conducting holes from the channel. Figure 4 shows that there is virtually no threshold voltage

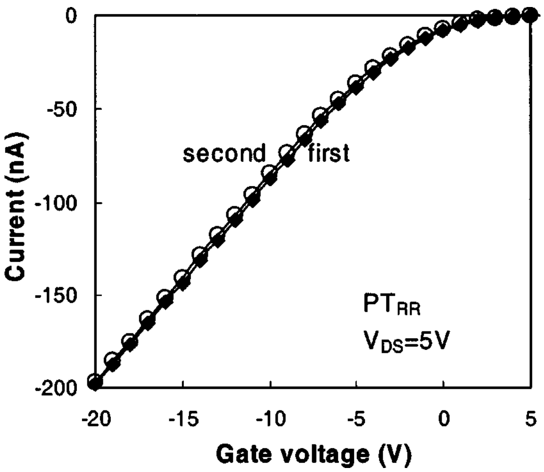

FIG. 4. Repeated quasistatic measurement of the transfer function of a PT_{RR} TFT, showing negligible bias stress effect.

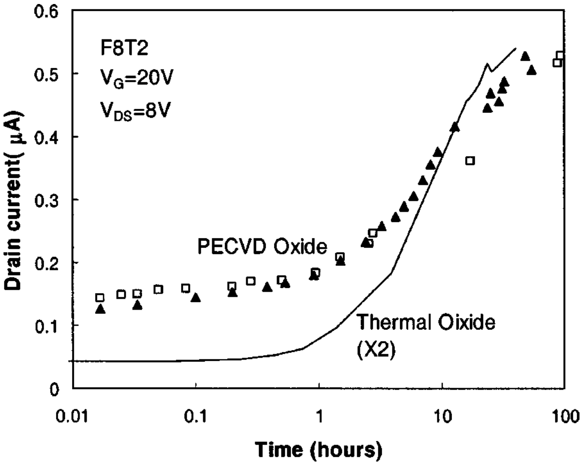

FIG. 5. Time dependence of the recovery in the dark of the drain current in F8T2 TFTs with thermal oxide (line) and PECVD oxide (points) gate dielectric, after a 20-V bias stress is applied. Two sets of PECVD oxide data from the same PECVD sample are shown.

shift in repeated measurements of $\mathrm{PT_{RR}}$. Since current decay is evident in Fig. 2, this result implies that the stress is reversed in a matter of a few seconds at room temperature. More details of the bias-stress measurements in F8T2 are described in Ref. 9.

For both polymers, a similar stress effect is observed in TFT's with different gate dielectrics, when comparing silicon thermal oxide and PECVD oxide. Furthermore, the TFT's are made either with or without a SAM between the dielectric and the semiconductor, and the stress effect occurs in either case. We have tried several SAM's[8] and while there are some variations in the stress, the similarities are substantial.

The recovery of F8T2 after bias stress is shown in more detail in Fig. 5 for TFT's made with the PECVD oxide and thermal oxide dielectrics. The recovery is measured after applying a 20-V gate stress bias for about 1 min, and then leaving the sample in the dark for an extended time, measuring the current briefly to avoid further stress. The device takes about 2 days to recover completely at room temperature. Devices made with both dielectrics exhibit similar recovery kinetics.

Another significant observation is that the stress effect in F8T2 is rapidly reversed by exposure to band-gap light.[9] Only a brief exposure is required so that the process is evidently efficient, and apparently requires fewer carriers to complete than the stressing process. The stressing and illumination cycles appear to be completely repeatable, as we have cycled some samples many times.

Evidence for a bipolaron model

The data strongly suggest that the primary stress effect is associated with electronic states in the semiconductor, rather than in the dielectric or the SAM. The evidence is the insensitivity of results to different dielectrics and different SAM's. Silicon thermal oxide is an excellent dielectric known to have few trapping states, and so should not give a significant stress effect, while PECVD oxide has many more trapping states. Further evidence that associates the stress effect with the polymer is that the same dielectric/SAM combination gives different results for the two semiconductors. The stress is large and stable in F8T2 and smaller and rapidly reversed in $\mathrm{PT_{RR}}$.

The reversal of the stress by illumination in F8T2 suggests that the stress effect corresponds to the trapping of carriers in states for which the occupancy is readily changed by a recombination transition. This result seems inconsistent with a metastable structural change, which usually requires annealing to reverse. Furthermore, the illumination effect is not consistent with ion migration or electrochemical degradation as the origin of the stress effect.

Our conclusion, therefore, is that the primary stress effect occurs in the polymer semiconductor, and the mechanism is slow trapping of holes into a deep electronic state. Slow trapping implies a state with a very small capture cross section, and we suggest that the obvious candidate is the formation of bipolarons, or paired hole states. This model is attractive because (a) bipolarons are known to form in some thiophenes, (b) the repulsion between the two holes should give a very small capture cross section for bipolaron formation, and (c) the bipolaron is a tightly bound state that is either nonconducting or of very low mobility and hence removes mobile holes from the channel. Bipolarons have been studied in detail in thiophene oligomers[10] and also in various polymers,[11] but are generally considered not to occur in regioregular polythiophenes.[12,13] Indeed, rapid formation of stable bipolarons is incompatible with high-mobility TFT's, but the idea that they might form very slowly has apparently not been considered.

The key test for the bipolaron model is the expected concentration dependence of the formation kinetics. The reaction in which two holes, h, form a bipolaron, $(hh)_{\mathrm{BP}}$,

$$h+h\rightarrow(hh)_{\mathrm{BP}}, \tag{1}$$

leads to a rate equation for the hole concentration, N_h,

$$dN_h/dt=-kN_h^2+bN_{\mathrm{BP}}, \tag{2}$$

where the second term on the right is the breakup of bipolarons of concentration N_{BP}, and k and b are rate constants.

The predicted N_h^2 behavior was tested by measuring dN_h/dt as a function of time at fixed V_G, and separately as a function of V_G at fixed measurement time. Most of the measurements and the largest values of dN_h/dt are at quite high gate voltages (20–50 V). The hole concentration is obtained from the linear TFT drain current, I_D, according to,

$$I_D/V_D=(W/L)C_G\mu(V_G-V_T)=(W/L)\mu N_h/d, \tag{3}$$

where W/L is the geometry factor, C_G is the gate capacitance, μ is the mobility, and d is the effective width of the accumulation layer. Both types of plots are obtained from the data in Figs. 1 and 2 and other similar measurements, and the plots of dN_h/dt vs N_h^2 are shown in Figs. 6 and 7 for F8T2. The hole concentration is calculated from Eq. (3) with the measured mobility and an estimated d of 1 nm. Similar results are obtained for $\mathrm{PT_{RR}}$ from the data in Fig. 2. We also

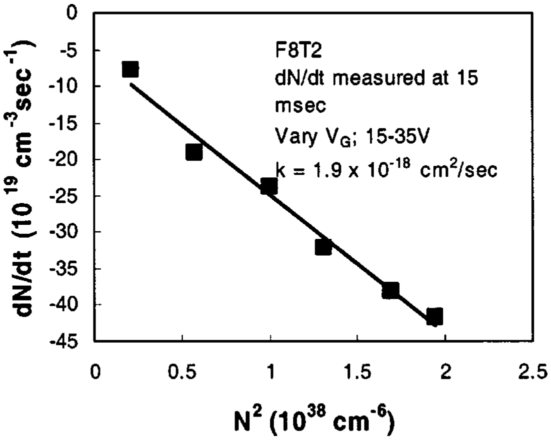

FIG. 6. The rate of decrease of the hole concentration, dN_h/dT, plotted versus the square of the hole concentration N_h^2 in F8T2, measured at constant time and varying gate voltage.

obtained measurements of dN_h/dt from shorter pulsed measurements with times of $\sim 10^{-3}$ s, and these are shown in Fig. 8.

All of the data show the predicted dependence of dN_h/dt on N_h^2 within experimental uncertainty. Comparison of Figs. 6 and 7 shows that both the slope and intercept are slightly different for the two plots. Part of the explanation is the assumption of a fixed accumulation layer depth to obtain the hole concentration. The hole concentration actually varies rapidly with depth into the channel, and the depth varies with gate voltage. The data in Fig. 7 show the same slope for two different gate voltages but a different intercept, which may be due to the different accumulation layer depth. We also assume a constant effective mobility according to Eq. (3) to obtain N_h. This approach ignores shallow trapping and other effects that could modify the actual value of N_h. A precise evaluation of the rate constants needs to take these factors into account.

The two data sets give rate constants of 1.9×10^{-18} and 2.7×10^{-18} cm^3/s for F8T2 and a smaller value of $\sim 1.3\times 10^{-18}$ cm^3/s for PT$_{RR}$. Note that the rate constants for the two materials only differ by a factor 2 even though the stress effect is very different.

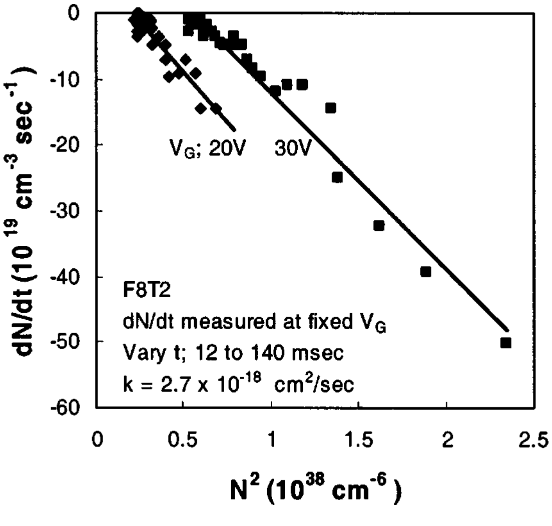

FIG. 7. The rate of decrease of the hole concentration, dN_h/dT, plotted versus the square of the hole concentration N_h^2 in F8T2, measured at constant gate voltage and varying time.

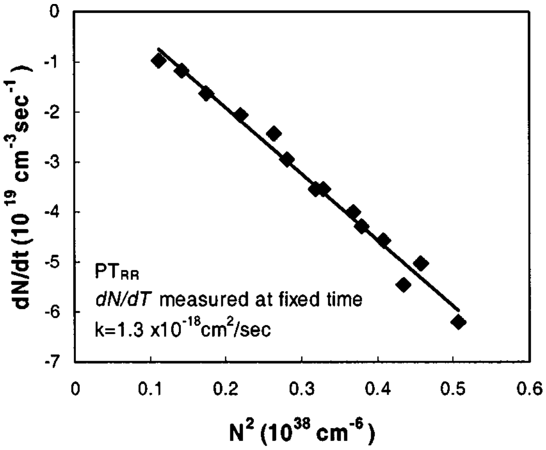

FIG. 8. The rate of decrease of the hole concentration, dN_h/dT, plotted versus the square of the hole concentration N_h^2 in PT$_{RR}$ measured at constant time and varying gate voltage.

III. DISCUSSION

The observed dependence of dN_h/dt on N_h^2 provides strong evidence that the bias stress effect is the result of the interaction of pairs of holes, and hence supports the bipolaron model. Various aspects of the model are discussed next.

A. Trapping cross sections

The data provide an estimate of the capture cross section for bipolaron formation. According to the standard trapping model, which describes the capture of a scattering mobile carrier, the rate constant is the product of the capture cross section σ and the effective thermal velocity v_T. The trapping time τ is given by

$$\tau^{-1}=N_h\sigma v_T=kN_h. \tag{4}$$

The thermal velocity of mobile carriers is $v_T=(3kT/m_h)^{1/2}$, where m_h is the hole mass, which is normally of order 10^7 cm/s although the effective mass is not known. However, the small values of the measured mobility strongly suggest that holes spend a substantial portion of their time in shallow traps, with a corresponding reduction in the effective thermal velocity. Given the lack of detailed knowledge about the transport, we can only estimate that the free-carrier mobility is ~ 1 cm^2/V s, as found in single-crystal organic molecular solids,[14] and hence that trapping reduces the mobility and effective velocity by a factor ~ 100. The capture cross section is therefore of order 10^{-23} cm^2, which is about 7 orders of magnitude smaller than typical values for neutral traps. A small cross section is consistent with a repulsive interaction between the holes. The subsequent discussion does not depend on a precise value for the cross section.

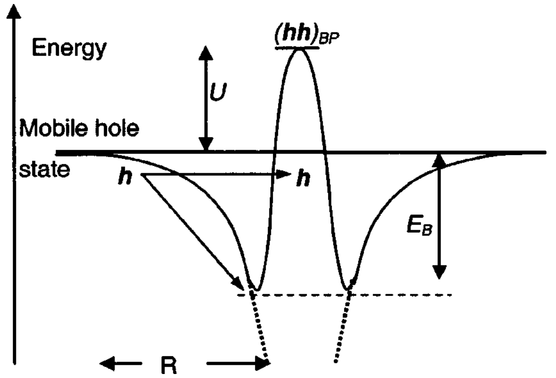

FIG. 9. Model illustrating the Coulomb potential barrier to the formation of a bipolaron, and two alternative capture mechanisms.

For the purposes of this discussion, the cross section may be approximated by the product of a typical neutral trap cross section of 10^{-16} cm^{-2}, and a factor, P_B ($\sim 10^{-7}$), which is the probability of overcoming the repulsion. We therefore associate P_B with the Coulomb barrier, E_B, between the holes. As illustrated in Fig. 9, the two plausible mechanisms for the capture of the pair of holes are thermal excitation over the barrier, or tunneling through the barrier, which have probability

$$P_B = \exp(-E_B/kT), \quad \text{thermal activation} \tag{5}$$

$$= \exp(-2R/R_0), \quad \text{tunneling} \tag{6}$$

where R_0 is the extent of the hole wave function and R is the separation. The estimate of P_B corresponds to a barrier height of about 0.4 eV or to R/R_0 of ~ 8.

A Coulomb barrier of ~ 0.4 eV corresponds to a separation between the two holes of about 0.9 nm (assuming a dielectric constant of 4), which is consistent with there being a significant interaction between holes if the hole wave function has an extent of $R_0 \sim 0.5$ nm. For the tunneling model, the same wave function extent leads to a tunneling distance of 4 nm, at which distance the Coulomb barrier is about 0.05 eV. Again, this seems a reasonable value for the tunneling distance since the thermal and disorder energy should easily allow the holes to approach this close. It is hard to distinguish between the two models, but careful measurements of the temperature dependence of the bias stress could resolve it, since the tunneling mechanism is almost independent of temperature. Preliminary measurements find only a weak temperature dependence at lower temperatures, favoring the tunneling model. In practice, a combination of tunneling and thermal excitation probably occurs. Detailed theoretical calculations are needed to give better estimates of the capture rates, particularly for the tunneling mechanism.

B. The bipolaron binding energy

According to the bipolaron model, the difference in the recovery rate of the bias stress between F8T2 and PT$_{\mathrm{RR}}$ is explained by a different binding energy of the bipolaron. A large binding energy gives a stable state with slow recovery in the dark, while a smaller binding energy allows fast recovery by thermal activation, and rapid stabilization of the stress effect. The equilibrium bipolaron concentration for the reaction in Eq. (1) is given by

$$N_{\mathrm{BP}} N_V = N_h^2 \exp(U/kT), \tag{7}$$

$$N_h + 2N_{\mathrm{BP}} = N_0, \tag{8}$$

where U is the formation energy of the reaction, N_0 is the initial (i.e., unstressed) hole concentration as determined by the gate voltage, and N_V is the effective concentration of available hole states (the highest occupied molecular orbital level). As previous authors have noted,[15] when the formation energy is large, most holes form bipolarons, but when U is small, the large entropy of the holes limits bipolaron formation. When U is small, Eqs. (7) and (8) approximate to

$$N_{\mathrm{BP}} = (N_0^2/N_V)\exp(U/kT) \sim 10^{13}\exp(U/kT), \tag{9}$$

using the values $N_0 = 10^{17}$ cm^{-3} and $N_V = 10^{21}$ cm^{-3}. U needs to be larger than about 0.2 eV for a significant bipolaron concentration at room temperature. There is essentially complete conversion of holes to bipolarons when $U > 0.5$ eV. A relatively small difference in formation energy therefore can account for the different properties of F8T2 and PT$_{\mathrm{RR}}$.

The bipolaron formation energy is also related to the stability of the stress effect. Detailed balance relates the rate at which bipolarons dissociate into a pair of holes and the bipolaron formation rate. Setting $dN_h/dt = 0$ in Eq. (2), and using Eq. (7), gives

$$b = kN_V \exp(-U/kT) \equiv \omega_B \exp(-U/kT), \tag{10}$$

where ω_B is the attempt-to-escape frequency for bipolaron dissociation, and is $\sim 10^3$ s^{-1} using the measured rate constant k and the above estimate for N_V. Note that ω_B is a factor $\sim 10^9$ lower than typical values for an attempt frequency, similar to the factor reducing the capture cross-section. Using an estimate from Fig. 5 of 1 day for the recovery time in F8T2, b is 10^{-5} s^{-1} and the bipolaron formation energy is $kT\ln(\omega_B/10^{-5})$ ~ 0.52 eV, which is consistent with the observation of a large stress effect. These values illustrate that according to the bipolaron model, the magnitude of the bias stress effect is correlated with the recovery time—large stress effects are stable for an extended time and weak stress effects recover more rapidly.

C. Stress recovery by illumination

The data showing a rapid reversal of the stress by illumination in F8T2 are readily explained by the capture of electrons, through the recombination process

$$(hh)_{\mathrm{BP}} + e \rightarrow h. \tag{11}$$

Since the bipolaron state has a double positive charge, the electron is strongly attracted and hence recombines rapidly. Band-gap absorbed light creates both free carriers and excitons, and it is also possible that the excitons reverse the bipolarons directly. The effects of illumination are discussed in more detail elsewhere.[9]

D. Bipolaron structure and disorder effects

There is an extensive literature on the formation and properties of bipolarons in polymers and organic small molecules.[11] Of particular relevance is the identification of bipolarons in oligothiophenes (*n*T) in solution.[10] Bipolarons are clearly observed in 6T and 9T but in 12T the doubly charged state more closely resembles two separate hole polarons, suggesting an effect of conjugation length in the formation of bipolarons. This work also found a second form of bipolaron that resulted from the dimerization of oligothiphenes. The role of bipolarons in polythiophene, and the influence of structural order, is less certain. There is a clear difference in the hole polaron states between regioregular and regiorandom PT as determined by induced absorption measurements.[12,13] The regioregular form has smaller polaron binding energies, which is attributed to delocalization of the holes arising from the π-π stacking in the two-dimensional structure of the ordered lamellae. Bipolarons are not identified in the induced absorption spectra of $\mathrm{PT}_{\mathrm{RR}}$ and there is some disagreement as to the identification of the induced optical transitions.

The Vardeny group observes the coexistence of the different energy polaron states corresponding to the ordered phase and the disordered phase in their studies of regioregular polythiophene.[13] This result suggests that bipolaron formation may be favored at certain sites in the polymer, and certainly one would expect the disorder of the polymer structure to lead to a distribution in the formation energies. It is possible that the bipolarons do not form in highly ordered regions of the polymer, but only at the boundaries between ordered domains, or at the dielectric interface. Bipolarons may even require an impurity such as oxygen to be stabilized. It is suggested that polymer chains can be modeled as short oligomers separated by conjugation defects.[15] Chains in the disordered or interface regions may have shorter effective conjugation lengths and so have a greater tendency to bind bipolarons, based on the length effect in oligomer solutions.[10] Hence, the bias-stress effect may depend critically on the nature of the sample preparation. The disorder may also give a distribution to the rate constant for the formation of bipolarons, which could contribute to the differences in Figs. 6 and 7, to the time dependence of the current as in Figs. 1 and 2 and also to the recovery rate in Fig. 5. A much better understanding of the polymer structure is needed to resolve these questions.

There is also insufficient information to give a structural interpretation of the difference between $\mathrm{PT}_{\mathrm{RR}}$ and F8T2, as several alternative explanations are possible. F8T2 is a copolymer comprising fluorene and bi-thiophene units. The pair of thiophene rings may act like a short oligomer and favor bipolaron formation. Localization of holes on the thiophene may depend on the relative ionization potentials although these are rather similar for the two materials.[16] It is also possible that the difference is related to the degree of disorder in the two materials, and that more ordered polyfluorenes might exhibit smaller bias-stress effects.

E. Implication for TFT's

The main implication for TFT's of the bipolaron model is that the stress effect is a property of the semiconductor, and those materials that form stable bipolarons are less suitable for TFT's. Since the rate of bipolaron formation increases rapidly with hole concentration, operation at low gate fields greatly reduces the stress effects, which may partly explain some of the differences in published data. Materials with small bipolaron formation energies recover rapidly, which also reduces the adverse effects of bias stress. Hence if bipolarons prove to be the correct bias-stress mechanism, then TFT materials need to be found in which the formation energy is small enough to eliminate bipolarons or at least make their equilibrium concentration reasonably low, as we propose is the case for $\mathrm{PT}_{\mathrm{RR}}$. A study of bipolaron formation could therefore help the search for suitable TFT materials. Conversely, studies of the bias-stress effect may provide considerable insight into the properties of bipolarons.

Polymer semiconductors with stable bipolarons should have minimal equilibrium free hole concentration, because the available holes will pair. Hence these TFT's should turn on at a gate voltage close to 0 V in their rested state. The presence of bipolarons may therefore complicate the interpretation of the measured threshold voltage.

It is interesting to consider whether the bias-stress effects in pentacene can also be explained by the bipolaron model. We have observed that the bias stress effect is independent of the dielectric and the SAM, and therefore also appears to be a property of the semiconductor.[17] However, sufficiently detailed stress measurements have not yet been performed.

IV. SUMMARY

Studies of the bias-stress effects kinetics show that mobile holes are removed from the channel at a rate proportional to the square of their concentration. We conclude that trapped hole pairs—bipolarons—are the primary stress mechanism. The rate of bipolaron formation is very slow, because of the strong Coulomb repulsion of holes. The bipolaron binding energy determines whether the stress effect is large and stable, as we find in F8T2, or small and transient, as in $\mathrm{PT}_{\mathrm{RR}}$. Details of the bipolaron structure are not clear, but it seem probable that structural disorder is important in stabilizing the bipolarons.

The bipolaron is an example of a negative correlation energy (negative U) state, since the pair has lower energy than the isolated holes. The negative U is made possible by a local structural distortion of the polymer. However, the structural relaxation immediately reverts when the carriers are removed, unlike a metastable structural change that can remain after the carrier is released, as is found in *a*-Si:H.[18] It is interesting to note that negative U states are present in many different classes of disordered materials, and profoundly affect their properties. In chalcogenide glasses, they occur at coordination defects, and in *a*-Si:H they are manifested as the formation of defects during the deposition of doped material.

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[3] A trap density of at least 10^{16}–10^{17} cm^{-3} is needed to trap enough carriers to have a significant stress effect, for which Eq. (4) gives a trapping time of $\sim 10^{-6}$ s. for a capture cross section of 10^{-16} cm^2.

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