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Chemical impurity effects on transport in polymer transistors

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Exposure of unencapsulated bottom gate polythiophene thin film transistors (TFTs) to several organic and inorganic volatile chemicals induces large changes in the TFT properties. Various neutral molecules cause the mobility of the TFT to decrease and enhance the bias stress effect, with the changes being reversible upon annealing. The effect on the mobility and stress are characteristically different for each compound and are attributed to different preferred locations in the host. Some molecules cause electronic doping of the semiconductor with corresponding changes in threshold voltage. In the case of the donor, ammonia, a gate-induced incorporation rate is observed. The distribution of acceptor energies of the recently found ozone acceptor is analyzed.

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I. INTRODUCTION

The long-term stability of organic semiconductors with respect to electrical stress and chemical contamination is one of the main concerns for their applications in thin film transistor (TFT) arrays. Organic TFTs are known to be sensitive to volatile chemical impurities, since they are studied as chemical sensors.[1–6] Impurity molecules generally reduce the TFT current, but most studies do not determine whether this is due to a change in mobility, threshold voltage, or any other TFT attribute. It is of interest to understand the physical mechanisms, either to control them in TFT backplanes or exploit them in sensors. Recently we have shown that polythiophene TFTs are stable over an extended period when held in clean dry air or dry nitrogen,[7] but that the presence of water vapor enhances bias stress instability.[8] We have also characterized the change in threshold voltage resulting from a pulsed gate bias stress extending over periods of up to 5 months under conditions similar to those experienced in a TFT backplane.[7] Here we report the effects of exposure to various volatile chemicals on both the TFT characteristics and the bias stress effect.

Some compounds act as electronic dopants and consequently cause a large change in bulk conductivity or a shift in the TFT threshold voltage. For example, iodine and other halogens are known to be electron donors in several polymers.[9] Jarret *et al.* studied acceptor doping of polythiophene TFTs with an oxidizing agent and found that the field effect mobility increased with dopant concentration.[10] It is commonly observed that exposure to ambient air induces acceptor states.[11] Originally these were attributed to oxygen doping. However, our studies have shown that the polythiophenes are rather stable in oxygen,[7] and instead we show elsewhere that ozone is the likely source of the p-type doping.[12] We report further analysis of the doping effect and also describe the n-type doping effects of ammonia. The contrasting properties of donors and acceptors provide information about the electronic transport and density of states distribution in the TFTs.

II. MEASUREMENTS

The TFTs are fabricated with the polymer semiconductor PQT-12,[13] using a plasma-enhanced chemical-vapor deposition (PECVD) gate dielectric and in the bottom gate, bottom electrode configuration, as described elsewhere.[7] The gate dielectric is silicon nitride with a silicon oxide capping layer that allows adhesion of the octyltrichlorosilane (OTS-8) self-assembled monolayer that modifies the surface energy and promotes ordering in the polymer. The polymer is spin-coated to a thickness of about 50 nm. There is no encapsulation so that the PQT-12 forms the top layer of the device. Devices studied have channel lengths from 5 to 50 μm but the results did not show strong dependence on the length. After preparation, the samples are annealed at 120 °C in dry nitrogen for 20 min to promote development of the ordered polycrystalline structure. Between measurements the samples are annealed at 100 °C for about 10 min to reverse the effects of the chemical exposure.

Samples are mounted in a dark chamber in flowing dry nitrogen or dry air—measurements under these conditions provide the control data. Exposure to a specific chemical is made by switching to a flow of nitrogen which has passed over the volatile liquid of interest held at room temperature in a small container. The exposure is stopped by switching back to pure N_2. TFT characteristics are measured both during and after exposure, using pulsed gate and drain voltages for the higher gate voltages and dc measurements for the low current region near threshold. Bias stress measurements are made using a pulsed gate voltage with a specific duty cycle, which was usually $1/200$, as described elsewhere.[7] These conditions were chosen to allow comparison with unexposed samples which have been studied in some detail. Pulsed measurements allow the current to be monitored without inducing additional bias-stress. All the stress measurements are made with negative gate bias, so that the p-channel TFTs are in accumulation, and all the measured currents are negative. Plots with a logarithmic current scale show absolute values of the current.

The concentration of molecules in the carrier gas was not measured, but some measurements of the uptake of organic compounds are reported using a quartz crystal monitor (QCM). For these measurements, a polythiophene film is deposited on the quartz crystal which has a gold surface with a hydrophobic self-assembled monolayer formed from hexadecanethiol. The frequency change directly gives the mass uptake in the film.

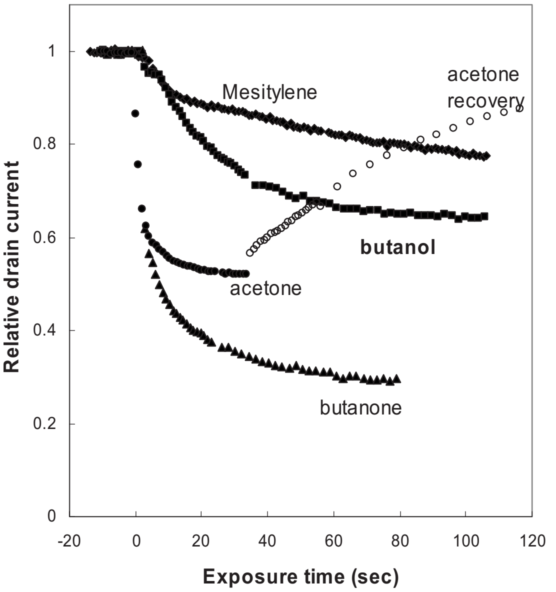

FIG. 1. Change in drain current upon exposure of a TFT to vapor from several solvents, and recovery data for acetone when the vapor exposure is terminated. Each data point represents a single pulsed measurement with $V_G=-25$ V and $V_{DS}=-5$ V, made at approximately 1 s intervals.

A. Organic solvents and related compounds

Figure 1 shows the result of exposing a TFT at room temperature to some of the organic solvents. The current is monitored using a 30 ms gate voltage pulse with a repetition time of about 1 s. With exposure to acetone, butanone, isopropanol, and heptane, the drain current drops rapidly within the first few seconds and then stabilizes within 30 s. Butanol and mesitylene have a slower response, and these compounds also have a substantially lower vapor pressure. The vapor pressures of the various solvents are shown in Table I. After the exposure is ended, the drain current increases slowly, and the recovery of acetone is illustrated in Fig. 1. We determined that at least for acetone, the recovery rate is inversely proportional to the gas flow rate, and hence is primarily determined by the time it takes to vent the impurities from the chamber. Therefore for the higher vapor pressure organics, the time constant to diffuse in or out of the sample is not limiting, and is no more than a few seconds. There was a slower response for the lower vapor pressure solvents, suggesting slower diffusion in the film. The recovery of the current is generally not complete, at least within about 1 h and particularly if the exposure was for an extended time. However, in each case almost complete recovery to the initial state is observed after annealing to 100 °C. The same sample has been cycled many times with different impurities, and only after numerous exposures is there a significant irreversible decrease in the current in the annealed and unexposed state.

TABLE I. Room temperature vapor pressure (mm Hg) of the various solvents studied.

Acetone	Butanone	Propanol	Heptane	Butanol	Mesitylene
202	77.7	35.26	39.2	4.87	2

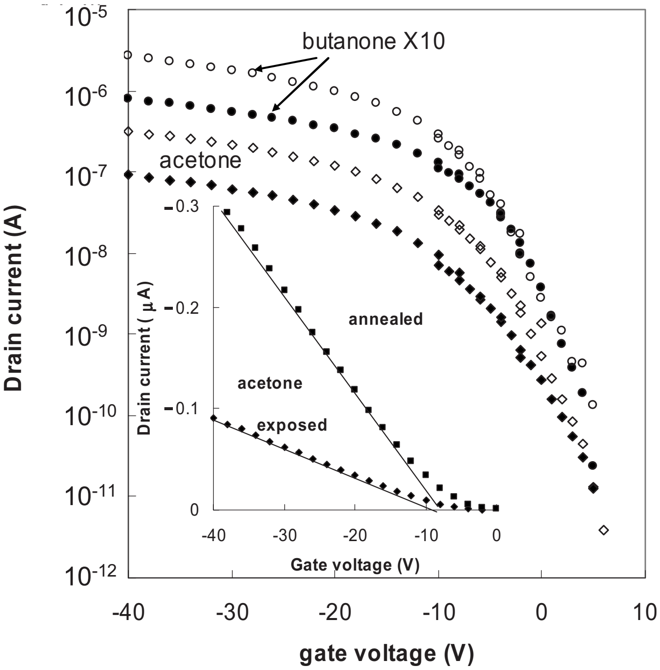

FIG. 2. TFT transfer characteristics (linear regime, $V_{DS}=-5$ V) for exposure to acetone and butanone compared to the annealed state, showing the decrease in mobility with no change in the threshold or onset voltage. Open data points are for the annealed state and the closed data points are measured during exposure. The inset shows the transfer data for acetone on a linear scale, showing a drop in mobility but no change in threshold.

Figure 2 shows the TFT transfer characteristics in the linear regime during exposure to acetone and butanone, compared to the annealed state. There is no significant change in the onset voltage and the inset to Fig. 2 shows that the decrease in drain current is evidently due to a reduction in mobility, with minimal change in threshold voltage. Measurement of the output characteristics show no sign of additional contact resistance, indicating that the changes occur throughout the channel. The results were qualitatively similar for the other organic solvents, with a drop in current corresponding almost entirely to a reduction in mobility with little or no change in onset or threshold, partial reversibility at room temperature, and complete reversibility after annealing. The magnitude of the reduction in current varied quite substantially and is generally, though not exactly, correlated with vapor pressure (see Fig. 1). The absence of a significant change in the onset voltage indicates that there is no significant doping effect with these molecules. The location of the onset voltage is rather arbitrary because it depends on the current at which it is measured, but comparison of different samples allows us to identify shifts with an accuracy of about 1 V.

Figure 3 shows examples of the mass uptake measurements for some solvents, using the QCM method. There is an abrupt increase in mass within the first 100 s of exposure, after which the concentration in the film stabilizes. The mass

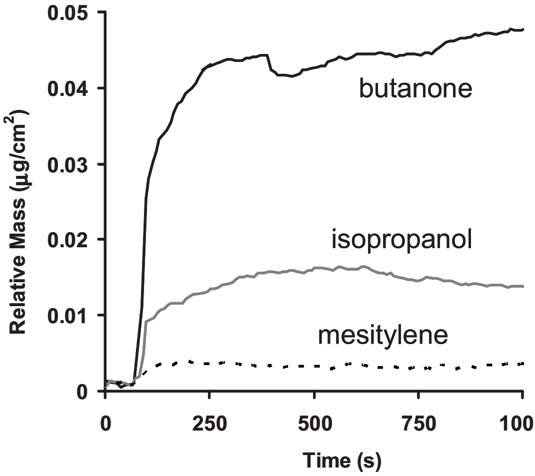

FIG. 3. Quartz crystal monitor data showing the mass uptake of butanone, isopropanol, and mesitylene into PQT-12 as a function of time after exposure.

uptake correlates with the vapor pressure, which determines the concentration in the gas flow. The similarity between the uptake measurements and the change in drain current shown in Fig. 1 indicates that the drain current is responding to the amount of solvent in the film. A mass uptake of 0.04 μg/cm^2 corresponds to about 1% by weight in the film. Previous measurements of water uptake in similar films also found about 1% weight gain for exposure for relative humidity (RH) levels around 50%.[8]

Exposure of the TFTs to water vapor shows comparable effects with a drop in mobility and a small change in threshold voltage, in agreement with previous measurements.[8] The rate of change of drain current is comparable to the low vapor pressure solvents, suggesting a diffusion limited process, and the rate of recovery at room temperature is also slow, but the effects are reversible by annealing. Long exposure to high humidity (i.e., $>90\%$ RH) causes the TFTs to fail under operation after about 1 day of low duty cycle operation, with visible damage to the film. The probable cause is electrochemical effects at the contacts, since unbiased control samples did not fail during the same exposure. Devices in lower humidity ($<60\%$ RH) do not fail even after several days of bias stress, and recover on annealing to 100 °C.

B. Bias stress effects

Bias stress measurements made with various impurities are shown in Fig. 4 and are compared to data for the annealed state in dry N_2. These bias stress data are obtained with a -30 V gate voltage pulse of 30 ms duration with a repetition time of 1 s and the data for all the impurities in Fig. 4 were measured on the same sample which was annealed between exposures. The measurements were performed after exposing the sample to the vapor for an extended time (at least twice the measurement time) without any gate voltage applied. In every case studied, the decreasing current shows that there is an enhancement in the bias stress effect upon exposure to molecular impurities, compared to the annealed samples in dry air or nitrogen. Figure 4 also indicates the relative change in drain current due to the exposure but before the stress measurement has begun. It is apparent that a large mobility change is not associated with a larger bias stress, and indeed the two effects seem to be anticorrelated. The largest increase in the stress effect occurs with water vapor exposure, while the change in the mobility is relatively small compared to the other compounds.

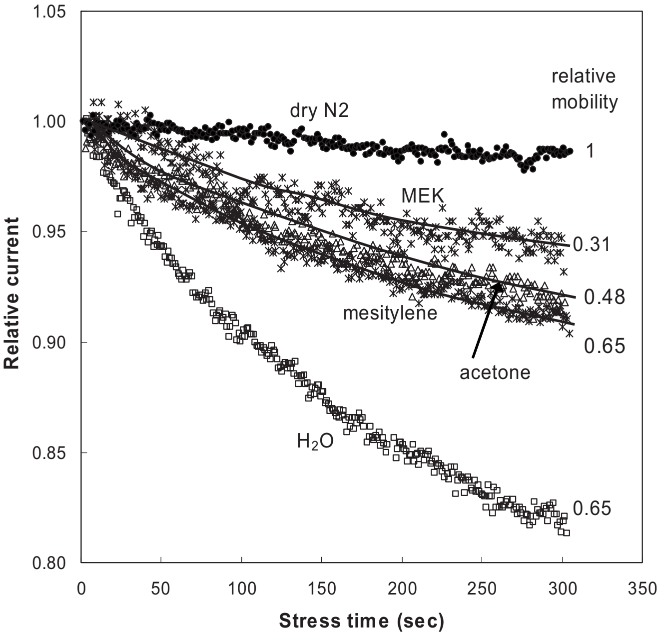

FIG. 4. Relative change in drain current due to the bias stress effect for steady state exposure to the compounds indicated. Stress is performed at a gate voltage of -30 V, applied for 30 ms with a 1 s repetition rate. The drain current at the start of the bias stress, relative to the unexposed state, is indicated.

More detailed measurements of the bias stress during exposures extending for a few days were performed using a pulsed gate voltage with a duty cycle of 1/200, which are the same conditions as in a recent study of stress.[7] The samples were exposed to the vapor for about 1 day before the measurement to ensure that the sample had equilibrated in the vapor. After each stressing period the TFT characteristics were measured and the threshold voltage, V_T, and mobility was separately extracted. The measurements confirm that the stress effect is primarily a shift in the threshold voltage. Figure 5 shows examples of the time dependence of the V_T shift, ΔV_T, comparing chemical exposure with the unexposed annealed state of the same sample. As shown in the previous studies of TFTs in dry air or nitrogen, ΔV_T increases as a power law with time (approximately $t^{0.4}$) and eventually stabilizes to a constant value, due to a dynamic equilibrium with a recovery mechanism.[7]

The data in Fig. 5 confirms that impurities greatly increase the rate of change of ΔV_T, consistent with the data in Fig. 4. The largest increase is found for water vapor, for which the rate is increased by about a factor of 200, while acetone increases the rate by about five times. The enhanced $\Delta V_T(t)$ follows approximately the same power law time dependence as the unexposed samples. It is notable that despite the greatly increased rate of V_T shift, the stabilized V_T shift

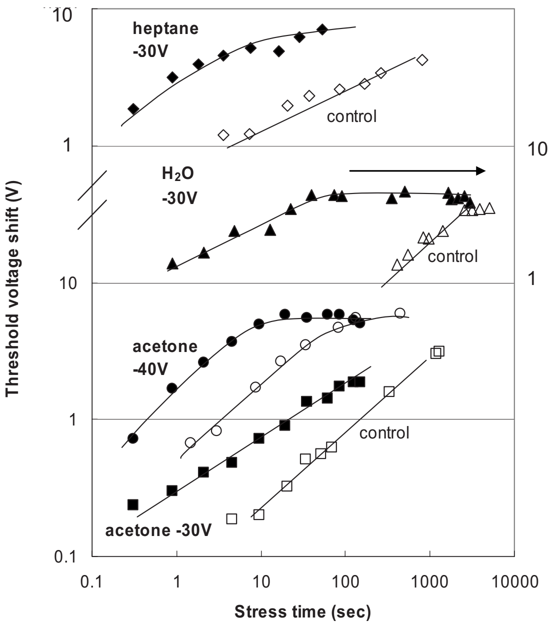

FIG. 5. The threshold voltage shift induced by a gate bias for TFTs exposed to the chemicals indicated, and compared to the annealed and unexposed controls (open data points). The gate voltage is −30 or −40 V as indicated and the duty cycle is 1/200. The total elapsed time is therefore 200 times the stress time, so that stress time of 1000 s corresponds to a measurement extending for about 2 days.

after about 1 day of stress is almost the same as in the unexposed samples. The implication is that the recovery rate is also enhanced by the impurities, and this result is directly confirmed by measurement of the recovery of ΔV_T, after the stress is removed. Figure 6 shows the recovery of the bias stress for TFTs exposed to water vapor compared to the same device in clean dry air (CDA). The time constant is 6 h with water vapor compared to 85 h for the unexposed samples. The starting value of the threshold shift in CDA is lower than with water vapor, in part because the sample had not quite reached the stabilized stress state. The recovery data therefore show that the molecular impurities accelerate both the hole trapping and the recovery, but apparently do not greatly change the steady state density of trapped holes.

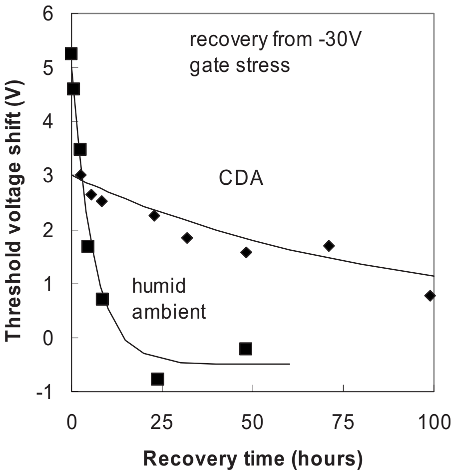

FIG. 6. Recovery of threshold voltage shift after bias stress is terminated, comparing the recovery of samples exposed to water vapor (humid ambient air) compared to the same sample stressed in clean dry air (CDA). The solid lines correspond to an exponential decay with a time constant of 6 and 85 h, respectively.

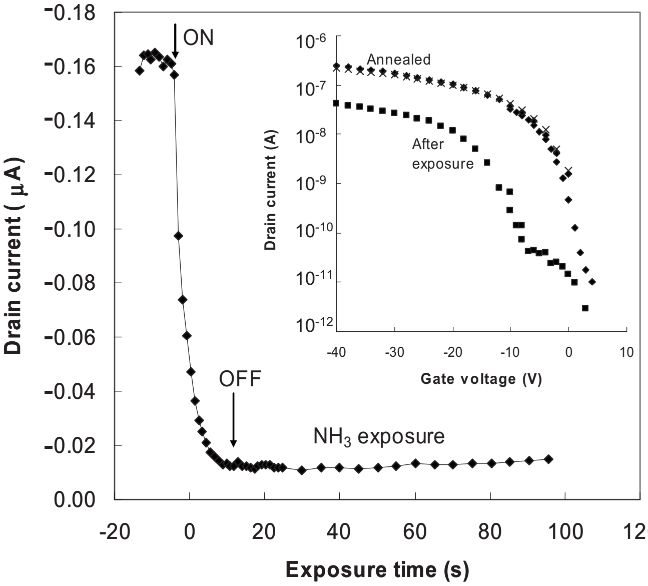

FIG. 7. Change in the drain current due to exposure to NH_3/H_2O vapor (household ammonia). There is a large drop in current and very little recovery after exposure is terminated. The inset shows the transfer characteristics, which exhibit a threshold voltage shift to negative voltages and a marked reduction in mobility.

The response of the TFT to exposure is controlled by two rate constants—the rate at which impurity molecules diffuse into the sample and the stress induced rate of change of the threshold voltage. Since we monitor the exposure effects by applying a gate bias, we need to be sure that stress effects are not affecting the exposure measurement. Comparison of Figs. 1 and 4 shows that the two rates can usually be clearly distinguished, even though there is some overlap in the time scales. For example, exposure to acetone causes the current to drop 40% in 2 to 3 s, while the stress effect changes the current by 10% in 5 min. Only in the case of water vapor is there some ambiguity because the response to the exposure is relatively slow and the bias stress rate is fast. However, we have exposed the samples in the absence of the gate field and found that the change in current upon the first application of a gate bias is consistent with the changes seen while the current is monitored during exposure.

C. Donor and acceptor molecules

Exposure to some molecules causes an obvious doping effect evident from a shift in the threshold voltage, and both donors and acceptors have been studied. The donor studied is ammonia, which has also been studied for possible use in polymer chemical sensors.[14] The change in drain current resulting from exposure of a TFT to ammonia (NH_3) in a water solution (household ammonia) is shown in Fig. 7. The de-

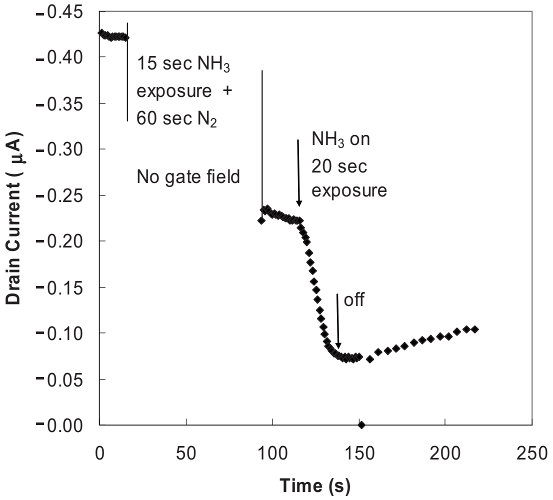

FIG. 8. Measurements of the drain current comparing exposure to ammonia with and without a gate field. Data points correspond to the application of a pulsed gate field.

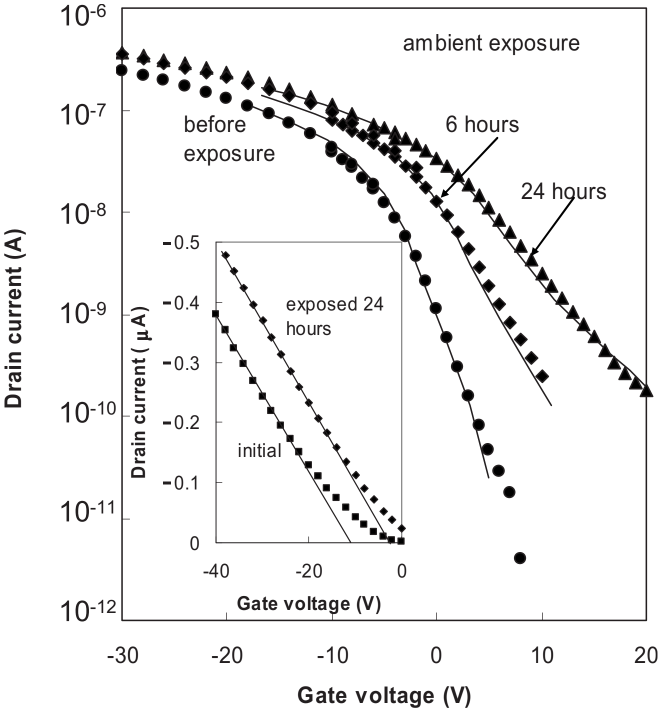

FIG. 9. Measurements of the TFT characteristics showing the changes that occur upon exposure to ambient air for up to 1 day. The increase in subthreshold slope is evident and the inset shows the threshold voltage shift of about 7 V. Solid lines are fits to a model for the acceptor distribution discussed in the text.

crease in current is >90% after only 5 s exposure, and there is little recovery after the NH_3 exposure is stopped. The TFT characteristics in the inset of Fig. 7 show that along with a large drop in mobility there is also a substantial negative onset voltage shift of 5–10 V, but the subthreshold slope does not change significantly. Clearly NH_3 dopes the material with electron donors, presumably by forming a positive ion which might be NH_4^+, since there is water vapor present to contribute the extra H.

Unlike the molecular impurities described in Sec. II B, the response to NH_3 exposure depends on the presence of a gate voltage, as shown in Fig. 8. In the first part of the measurement, the sample is exposed to the vapor for 15 s, and then to dry nitrogen for 60 s without application of a gate bias. The TFT current is then monitored with pulsed measurements, which shows that the exposure without the gate voltage results a reduction in current of about 40%. The sample is then exposed to ammonia for a further 20 s with the pulsed gate field on, and there is a further reduction in current by a factor of 3. Hence the change in mobility and threshold are much less when the exposure is performed without a gate voltage. Gate-induced incorporation was only observed with the ammonia donor and we discuss below how it might be related to the formation of charged donor states.

Continued exposure to NH_3 for several minutes during measurement of the characteristics caused the TFTs to stop conducting. The on-current dropped to less than 1 nA, which prevented performing stress measurements during exposure. Annealing to 100 °C reverses the effects indicating that the NH_3 does not react strongly with the polymer.

The acceptor studied is a contaminant of ambient air, which has been widely noted to affect TFT characteristics and usually has been attributed to oxygen.[11,15] However, our previous studies showed that at least for PQT-12, these changes are not observed when the sample is held in either clean dry air (CDA) or humidified CDA.[7] It is therefore attributed to a contaminant of air, and recently we show that it is most probably ozone.[12] The present data are equivalent to those described in the ozone studies, and the purpose of repeating them here is to estimate the acceptor binding energy, which is discussed in Sec. III B.

Figure 9 shows that exposure of an annealed sample to the ambient air in the dark results in a threshold voltage shift to positive voltage by about 7 V and also a substantial broadening of the subthreshold, so that the onset voltage shifts by about 20 V. Figure 10 shows that the threshold voltage shift takes about 24 h to stabilize, and that there is partial recovery when the exposure is stopped. The changes occur slowly, which is consistent with the very low ozone concentration in the air. Annealing to 100 °C reverses the effects. Evidently the impurity creates an electron acceptor comprising a negative ion and an excess mobile hole. The mobility does not decrease, and in fact a small increase (∼10%) is observed, which is interesting since the ambient has relative humidity of about 30%, which by itself reduces the mobility.

D. Acetic acid

Measurements were also made on TFTs exposed to glacial acetic acid vapor, the only acid tested in this study. As with other compounds, the TFT drain current decreased abruptly upon exposure to the vapor, dropping to less than 20% of the initial value. Figure 11 shows an example of the transfer and output characteristics for an exposed sample with a channel length of 5 μm. Both the transfer and the output data showed clear signs of a large contact resistance, rather than a uniform drop in mobility. There is obvious current crowding in the

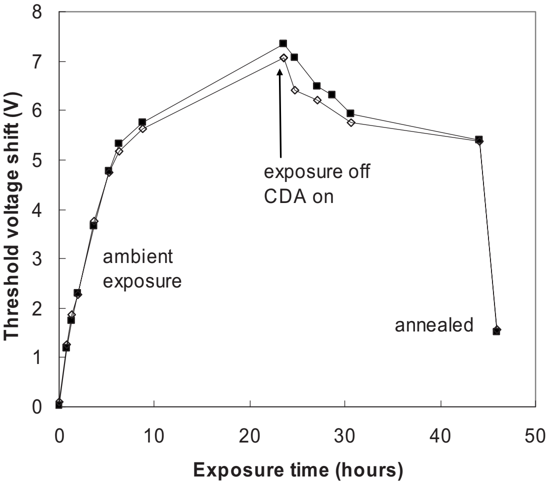

FIG. 10. The time dependence of the threshold voltage shift for two samples upon exposure to ambient, showing an increasing V_T shift for up to 24 h exposure, with some recovery when the sample is held in CDA for a few hours, followed by a more complete recovery after a thermal anneal.

output characteristics, which is not present in the unexposed sample. The transfer characteristics show little change in current up to a gate voltage of 10–15 V, but then the current saturates and is evidently limited by a large series resistance. It seems likely that the acetic acid preferentially interacts with the metal contacts to give the large series resistance, and this might be an electrochemical effect. However, the TFT characteristics recover on annealing to 100 °C, so any chemical change that occurs at the contact must be reversible.

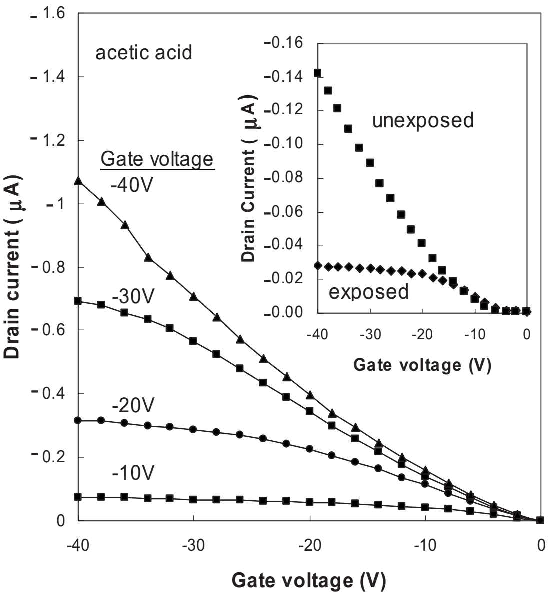

FIG. 11. Measurements of the output characteristics of a TFT exposed to glacial acetic acid, showing clear signs of current crowding. The inset shows the transfer characteristics measured at $V_{DS}=-5$ V, which indicates a large series resistance as a result of exposure.

III. DISCUSSION

A. Nondoping compounds

The QCM measurements show that the mass uptake of the solvents into PQT-12 is broadly correlated with the solvent vapor pressure, which should be proportional to the solvent concentration in the gas stream. Hence the film does not show particular selectivity to any solvent, and the uptake in the film seems to stabilize at an amount that is roughly proportional to the concentration in the vapor, and is approximately 1% by mass. The changes in drain current are also roughly in proportion to the vapor pressure, suggesting that the effects are in proportion to the concentration of solvent in the film.

The various organic solvents have different chemical characteristics. Acetone, isopropanol, butanol, and butanone are polar molecules, while heptane and mesitylene are nonpolar. Also, isopropanol and butanol are alcohols with hydrogen that may dissociate. There is no obvious correlation between the magnitude of the drain current changes and any of these chemical characteristics. We conclude that the polar nature of the molecule or dissociation of H cannot be the sole mechanism by which the mobility is reduced by the exposure. Furthermore, the observation that the impurity effects are all reversed by annealing leads us to conclude that molecules do not form a strong chemical bond to the polymer. A simple estimate that the typical rate of release from a bound state is of the order $10^{12} \exp(-E_B/\mathrm{kT})$ s^{-1} suggests that the binding energy, E_B, cannot be larger than about 0.7 eV. We therefore propose that the effects are primarily due to the physical presence of the molecules, rather than their chemical or electrical properties. An obvious mechanism is that the molecules cause local disordering of the neighboring polymer structure and may also cause uniform swelling of the material.

It is well-established that the mobility of polythiophene semiconductors is sensitive to the ordering of the material,[16] and so the association of reduced mobility with increased disorder is not a surprise, particularly considering that the concentration of the impurities is about 1% by weight. Factors that control the mobility of polymer TFTs are the conjugation of the polymer chains and the π-π interaction between chains, which determine the intrachain and interchain mobility, along with the grain boundary structure of the polycrystalline material.[17] Large well-ordered grains are associated with high mobility, in part because there is less disordered grain boundary material. The compounds absorbed into the TFT could affect any of these factors, and without specific information about their location in the film, we cannot identify the mechanism.

Bias stress is also associated with disordered materials and is caused by slow hole trapping.[18,19] The traps are not apparent in the normal TFT characteristics because they interact only very slowly with the mobile holes and do not modify the mobility. The slow rate of trapping is attributed to a barrier between the mobile holes and the trap state, and could be an energy barrier or physical separation that involves tunneling.[17] The steady state threshold voltage shift that is observed after hours to days of stress reflects a dynamic equilibrium between trapping and de-trapping. The observation that impurities accelerate the V_T shift but do not change the steady state V_T shift, implies that the molecules influence the stress kinetics but not necessarily the actual trap sites, as the following analysis indicates.

The rate of change of the conduction hole concentration, n_H, can be expressed as

$$\frac{dn_H}{dt} = -n_H P_T + N_T P_R, \tag{1}$$

where N_T is the concentration of trapped holes and P_T and P_R are the capture and release rates into stress-inducing trap holes states. The V_T shift is proportional to N_T. In steady state when the stress-induced V_T shift stabilizes,

$$\Delta V_T(\text{stabilized}) \propto N_T(\text{steady state}) = n_{HO}[1 + P_R/P_T]^{-1}, \tag{2}$$

where n_{HO} is the unstressed conduction hole concentration. Our measurements show that impurities increase the trapping rate P_T, with the change for water vapor being about a factor of 100. The nearly constant value of the stabilized V_T shift implies that the ratio P_R/P_T is approximately constant even though the individual values of P_T and P_R may vary by orders of magnitude. The actual stress kinetics are nonlinear, but this simple linear rate model captures the essential properties. Mechanisms that affect the rate of capture and release proportionately are likely to involve an intermediate state.

A further interesting observation is that all the impurities influence both the mobility and the bias stress, but in generally opposite ways. Those that have the largest effect on the mobility (e.g., butanone) have a small effect on the stress, and water vapor is an example of the opposite situation. Electronic states that reduce the mobility are characteristically different from those that provide the bias stress V_T shift, and so we expect that the different effects are associated with the preferred locations of the impurities. Since the molecules are mobile, each can reach its lowest energy configuration and presumably therefore occupy specific locations within the polymer matrix. Hence molecules that reside near the hole traps may enhance the bias stress effects while those that reside close to critical hole conduction pathways will have the most effect on the mobility.

It is difficult to identify the mechanism of the impurity effect without more detailed knowledge of the transport and stress mechanisms. However, two mechanisms seem plausible. We have proposed previously that bipolaron formation is responsible for at least part of the stress effect, and that the Coulomb repulsion of holes explains the slow rate of formation.[20] Impurity states could catalyze the formation and release of bipolarons by providing an intermediate state to capture a pair of holes. Alternatively the stress might be due to holes tunneling to distant trapping sites either in the semiconductor or possibly in the dielectric interface. Again, an intermediate state could lead to the same increase of the rate of both trapping and release. The physical location of the impurity site can determine its relative effect on the hole mobility and the rate of bias stress.

The striking sensitivity of the bias stress effect to impurity molecules leads to the possibility that bias stress effects in unexposed samples is due to residual impurities, particularly water vapor or the solvent from which the film was deposited. Stress effects are observed in samples held in a dry environment for months, but it is possible that residual water vapor or solvent remain. Since an H_2O concentration in the film of about 1% enhances the rate of V_T shift by a factor of ~100, a residual concentration of order 100 ppm could account for the stress in annealed and unexposed samples.

B. Donor and acceptor states

The magnitude of the threshold voltage shifts (~5–10 V) for both the donor and acceptor, coupled with the TFT gate capacitance of about 20 nF/cm^2, leads to an active dopant concentration of about 10^{12} cm^{-2}. This concentration corresponds to an average separation in the plane of ~10 nm, which is comparable to the crystallite size in PQT-12. This concentration is about 1000 times less than the 1% incorporation rate of the neutral molecules discussed above. Either a much smaller concentration of the dopant is incorporated, or the doping efficiency is low and most molecules are neutral and inactive.

The difference in the shape of the TFT characteristics for the donor and acceptor doping are readily understood. The negative acceptor core will give rise to bound hole states near the valence band (highest occupied molecular orbital level). Depending on the binding energy, these states slow the movement of the Fermi energy and hence can easily broaden the subthreshold region of the transfer characteristics as is observed in Fig. 9. The donor (NH_3) is expected to form bound electron states near the conduction band (lowest unoccupied molecular orbital level), but these are too high in energy within the band gap to affect the subthreshold slope of a hole conduction TFT, which is also consistent with the observations.

The data in Fig. 8 shows that a negative gate bias induces the formation of ammonia donors. We consider the reaction of ammonia with a free hole and possibly with an additional hydrogen to form the ammonia donor ion,

$$NH_3 + h + (H) \rightarrow NH_4{}^+. \tag{3}$$

This reaction implies that the concentration of donors is enhanced by the presence of holes, consistent with the observations. The reversibility of the doping effect with a low temperature anneal suggests the possibility of an equilibrium reaction, in which case the donor concentration, N_D, is given by the law of mass action,

$$N_D = kN_M n_H = kN_M \beta (V_G - V_{T0} - \Delta V_T), \tag{4}$$

where k is the reaction rate constant, N_M is the neutral ammonia concentration, V_{T0} is the undoped threshold voltage, and β is the gate capacitance divided by the electronic charge. Since $\Delta V_T = N_D/\beta$, Eq. (4) can be solved to give the equilibrium values, which are

$$\Delta V_T = \frac{V_G - V_{T0}}{(1 + 1/kN_M)}; \quad N_D = \frac{\beta(V_G - V_{T0})}{(1 + 1/kN_M)}. \qquad (5)$$

The doping continues until holes are depleted by the threshold shift, and the equilibrium values depend on the product of the reaction rate constant k, and the ammonia concentration. Only a small fraction of the ammonia is converted to donors when k is small. Acceptor concentrations may be similarly enhanced by a positive gate bias, but we have not investigated this effect.

The acceptors introduced by exposure to the ambient do not significantly change the mobility. Given that we believe the acceptor is ozone, which is present in air in concentrations of ~50 parts per billion, the likely explanation is that the concentration is sufficiently low in the film that there is no disordering effect to reduce the mobility. The acceptors themselves are neutral when occupied and so should not have a large Coulomb interaction effect on the mobility when the TFT is turned on. In contrast the ammonia donor causes a large drop in mobility. Donors are positive when the TFT is turned on and one possibility is that potential fluctuations from the positive charges within the channel could account for the drop in mobility. However, the bias stress effect in undoped TFTs induces a similar density of trapped positive holes, which evidently do not affect the mobility in the same way. It therefore seems more likely that the mobility decrease is again due to a physical disordering effect of the impurity. Partly this might be due to the water vapor incorporated with the ammonia, but we have shown that water vapor by itself does not cause a large mobility change. The most likely explanation is that much of the ammonia is incorporated as neutral NH_3 and only a small fraction as a donor, as discussed above.

The approximate energy of acceptors can be deduced from the TFT characteristics shown in Fig. 9. A shallow acceptor with binding energy no larger than a few kT from the band edge causes a shift in the threshold voltage but essentially no change in the subthreshold because the gate voltage dependence of the Fermi energy is dominated by the band edge density of states. A deep acceptor with binding energy more than 0.3 to 0.4 eV has virtually no effect on the characteristics because the Fermi energy is already closer to the band edge when the TFT turns on. The observation of a V_T shift and a broadened subthreshold region therefore indicates that the acceptors must be distributed from the band edge to a binding energy of about 0.3 eV.

We have developed a simple model for the TFT characteristics to estimate the acceptor distribution. The model is described in more detail in Ref. 17 and is based on an analysis of the transport which uses a two-dimensional density of states appropriate for transport in a single molecular layer of the polymer.[17] We assume that the acceptors do not introduce a new conduction path (i.e., hopping conduction) and that mobile hole states start ~0.15 eV above the band edge, due to the presence of localized nonconducting states at the band edge. The model also includes some donorlike fixed charge to adjust the threshold voltage of the undoped state. The TFT characteristics are calculated with a distribution of acceptors, and one example of a satisfactory fit to the data is indicated in Fig. 9. This model has a narrow acceptor level at the band edge, which provides most of the threshold voltage shift, and a second band from 0.25 to 0.35 eV above the conducing hole states to fit the subthreshold slope. The density of states is shown in Fig. 12 and has 25% of the acceptors at the band edge and 75% in the deeper states. The three fits to the data in Fig. 9 use the same distribution but with different concentrations of acceptors, and all the other parameters of the model are kept the same.

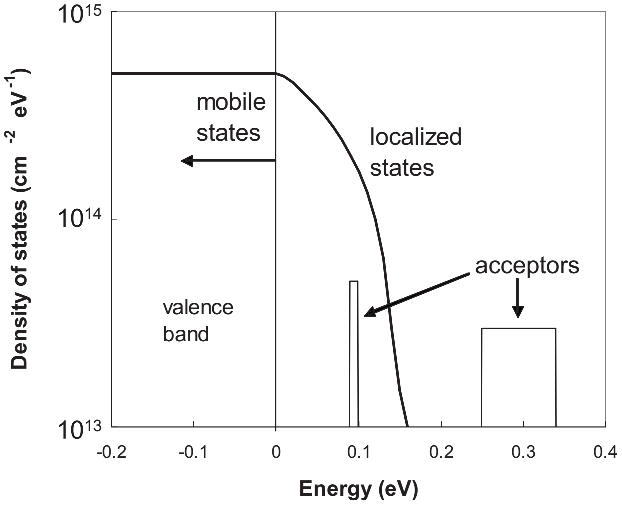

FIG. 12. Density of states (DOS) model used to calculate the effects of acceptors on the transport. Mobile states start at $E=0$ and have the constant DOS of a two-dimensional conducting sheet. The band edge localized states and acceptor levels are indicated.

The fit to the TFT characteristics is rather insensitive to the exact distribution of acceptor states so long as it extends over the energy range from 0 to 0.3 eV. A single narrow distribution of acceptors by itself does not provide a good fit. The possible explanations for a broad distribution of acceptors include different locations of the acceptor core with respect to the polymer, different binding energies due to polymer disorder, and an intrinsically broad distribution of acceptor binding energies. Also, we cannot exclude that the acceptor distribution continues to larger binding energy, since deeper acceptors have no effect of the TFT characteristics. As reported elsewhere, first principles calculations of the ozone acceptor states found that the acceptor level is about 0.3 eV, which is in good agreement with the results of the numerical calculations.[12]

IV. CONCLUSIONS

Polythiophene thin film transistors are sensitive to exposure of various volatile organic and inorganic compounds. Many solvents are rapidly absorbed into the films in concentrations of order 1%. Most solvents do not dope the polythiophene but cause a reduction in mobility and a substantial increase in the rate at which a threshold voltage shift is induced by a gate bias stress. We tentatively attribute the reduction in mobility to a physical disordering effect on the polymer. The bias stress change seems to have a different origin, and has the characteristic property that the stressing rate changes greatly but the steady state V_T shift is much less affected.

Some compounds can be found that dope the semiconductor and we have studied the donor ammonia and an acceptor in ambient air which is probably ozone. Ammonia has the property that the uptake of donors in the film is controlled by the gate. For the ozone acceptor, the TFT characteristics allow an estimate of the hole binding energy distribution, and the results are consistent with a previously calculated value of 0.3 eV.

The implication of these results for TFT devices is clear. Semiconducting polymer materials need to be free of molecular impurities at least to a fraction of a percent level in order to achieve their maximum mobility. Devices need sufficient passivation to prevent the incorporation of volatile compounds for the duration of their useful lifetime. Since high mobility polymers usually require a high degree of structural order, it is possible that the high performance materials will be more susceptible to impurities than lower mobility materials. Such a comparison would make for an interesting study.

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