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Effects of order and disorder on field-effect mobilities measured in conjugated polymer thin-film transistors

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The morphology of conjugated polymer thin films has been controlled by exploiting the processes giving rise to solvatochromism in the initial polymer solutions from which the polymer films were deposited by spin coating. The material used was the substituted polythiophene, 3[2(S2-methylbutoxy)ethyl]-polythiophene. Starting with polymer dissolved in “good” solvent, various quantities of “bad” solvent when added lead to the reorganization of the solubilizing side chains attached to the conjugated polymer backbone. Ordering of these side chains increases with addition of bad solvent decreasing the flexibility of the backbone, yielding more rigid rodlike polymer chains. This in turn causes aggregation and finally precipitation. It is found that this molecular order can be transferred from solution to solid film during the spinning process, ascertained from optical spectroscopy. With these films acting as the active layer in a field-effect transistor structure, the mobility of the carriers injected into the films can be measured. It is found that as the molecular order and aggregation increases, carrier mobility decreases from \(-10^{5}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) to \(\approx 10^{8}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in films displaying the highest degree of molecular order. This is ascribed to the increased interchain separation in the ordered systems along with effects due to macroscopic aggregate grain boundaries.

I. INTRODUCTION

Recently, there has been a substantial interest in the use of conjugated polymers as the active semiconductor in field-effect transistors (FET).\(^1,2\) From a technological viewpoint these materials offer a considerable advantage over inorganic semiconductors in their ease of processing. Spin coating, for example, can be used to produce high-quality thin polymer films. From a purely scientific viewpoint, the behavior of a polymer within a FET can provide useful information about the material, such as the charge carrier mobility.\(^3\) The effect of order and disorder in the polymer film upon the carrier conductivity can be extracted from a study of the FET device characteristics. A typical device structure is shown in Fig. 2 and was operated in accumulation mode. To obtain values for carrier mobility and polymer conductivity the operation of the thin-film transistors was modeled using the equation\(^4\)

\[
I_{DS} = \frac{\mu WC_l}{L} \left( (V_G - V_D)V_{DS} - \frac{V_{DS}^2}{2} \right) + I_0,
\]

where \(I_{DS}\) is the source-drain current, \(\mu\) the effective carrier mobility, \(W\) the source-drain channel width, \(L\) the source-drain channel length, \(C_l\) the gate capacitance/unit area, \(V_{DS}\) the source-drain bias voltage, \(V_G\) the gate bias voltage, \(V_D\) the offset voltage, and \(I_0\) the ohmic current.

The first term in this expression represents the gate-voltage-modulated source-drain current caused by the formation of an accumulation layer in the polymer, at the polymer-insulator interface, in the negative-gate-bias regimes. The second term represents ohmic conduction through the bulk of the polymer layer due to its intrinsic conductivity. This is proportional to \(V_{DS}\), but independent of \(V_G\).

For the case where \(|V_G| > |V_{DS}|\) the source-drain current varies linearly with \(V_G\). Therefore, a plot of \(I_{DS}\) vs \(V_G\) results in a straight line with gradient \(M\), where

\[
M = \frac{\mu WC_l V_{DS}}{L}.
\]
from which the effective carrier mobility can be extracted since all other parameters are known. Mobility measurements were thus made from devices operating in the $|V_D| > |V_D|$, “linear” regime.

II. EXPERIMENT

To obtain PMBET with various degrees of chain order, we have exploited the well-known technique used in the field of polydiacetylenes (PDA) of adding quantities of nonsolvent to solutions of PDA in good solvent. In the case of PDAs such as 9BCMU, this would be chloroform (good solvent) and hexane (bad solvent). In the case of PMBET, the solvent used is THF, and the nonsolvent added to it is methanol.

Throughout this work, a typical set of solutions was studied. The ratios of solvent to nonsolvent used are given in Table I. All samples were first made up by dissolving 0.02 g of PMBET in 4 ml THF. After all the polymer had dissolved, the varying quantities of methanol, nonsolvent, were added. In solution a solvatochromic effect was observed. Progressive methanol addition caused the originally orange-red solution to become dark orange, red, and then dark red. When the ratio of methanol:THF exceeded 4:10 a red precipitate was formed. From these solutions, films of PMBET could be spun, using a photoresist spinner at 1000 rpm onto the FET structures, as shown in Fig. 2, and glass substrates. The solvatochromic effects observed in the initial spinning solutions are "transferred" to the resultant films; however, the red shifts are enhanced in the solid state. These effects were quantified by UV/vis spectroscopy.

Typical conditions employed throughout to obtain mobilities and conductivities from the FETs were $V_D$, fixed between $-1$ and $-5$ V and $V_T$ scanned from $-20$ to $-10$ V.

All measurements were made using devices with dimensions $W$ = 20 mm and $L$ = 10 $\mu$m. Readings taken at several values of $V_D$ enable repeated measurements of $\mu$. The polymer conductivity was measured using the $I_D$ vs $V_D$ characteristics when $V_D$ = 0 V. The film thickness was estimated at $\sim$100 $\AA$ by comparison of the absolute absorption of samples to the absorption coefficient of PMBET. All electrical measurements were made using a Hewlett-Packard HP 4140B pA meter/voltage source.

III. RESULTS

A. UV-vis spectroscopy

The absorption spectrum of a PMBET film spun from pure THF solution (sample 1) shows a main peak at 546 nm with a shoulder at around 600 nm (Fig. 3). PMBET films spun from solutions with increasing methanol content show this main peak to shift to longer wavelengths, 552 nm for sample 2 and 564 nm for sample 3. The peak absorbance decreases in intensity. A new peak emerges from the shoulder at 600 nm and also shifts toward longer wavelengths as the methanol content of the spinning solution is increased. For sample 3 the new peak is seen at 610 nm, while for films spun from sample solutions 4 and 5 it is at 628 nm. It was noticed that the films spun from methanol treated solutions were scattering. This scattering was greater for films spun from the solutions with higher methanol content. This could also be the cause of increased absorption in the UV, e.g., the onset of absorption around 300 nm.
This shoulder and new peaks which are clearly evident in the subsequent spectra are ascribed to vibronic bands. In all cases the lowest energy band is the \( \sigma-\pi^* \) transition with the first vibronic side band being 190 meV higher in energy (in all cases). This is very consistent with the electronic transition being strongly coupled to the \( \sigma-\pi^* \) stretch of the polymer backbone. Typically for most thiophenes the \( \pi-\pi^* \) stretch occurs at \( \sim 1500 \text{ cm}^{-1} \) or 185 meV. This energy separation is independent (in within a few meV) of chromic shift. These results from spun films are consistent with those reported by Rughooputh et al.\(^7\) in solutions of polyalkylthiophenes.

**B. FET characterization**

As previously stated, all mobility measurements were performed with devices operating in the \( |V_G|>|V_{DS}| \) regime, and accumulation mode\(^8\) with \( V_{DS} \) scanned so as to give a set of measurements from which mobility can then be calculated. A typical set of results for a PMBET film is shown in Fig. 4. As predicted by theory, each \( V_G \) line is linear allowing accurate values of mobility to be determined. For each film sample (1–5) such measurements were made, the mobilities calculated from them are shown in Table II. Sample 5 displayed no measurable modulation of the source-drain current with applied gate voltage. Along with this mobility data, the sample conductivities estimated from \( I_{DS} \) vs \( V_{DS} \) measurements at \( V_G = 0 \text{ V} \) are also given, the measured conductivity of sample 3 appears somewhat low; this we ascribe to an overestimate of the film thickness. A correlation between methanol content and measured mobility is found. In all cases, increased methanol content in the spinning solutions yields lower carrier mobility and bulk conductivity.

**IV. DISCUSSION**

From the optical-absorption measurements, it can be seen that generally as poor solvent is added to the spinning solutions, the absorption of the subsequent films red shifts, with increased UV absorption being observed along with increased film scattering. The observed shift in absorption toward longer wavelengths is interpreted as an increase in the effective intrachain conjugation length. This arises because the average length of rigid rod along the polymer chain increases as the concentration of methanol (nonsolvent) in the solution is increased. Similar effects are well documented in the side-chain polydiacetylenes. In this case the addition of hexane to solutions of BCMU PDA derivatives\(^6\) causes solvatochromic shifts. Here chains occur as random wormlike coils in good solvent, addition of poor solvent causes the individual chains to collapse down on themselves via intramolecular interactions such that sections of the chain form into rigid rods.\(^7\) These more rigid chains readily aggregate, even in dilute solution. The driving force for this collapse is not hydrogen bonding\(^10\) but an intramolecular attraction. In the BCMUs it is still not clear whether the aggregates are amorphous or fringed micelles which have partial crystallinity.

The appearance of the films, becoming progressively more cloudy as the nonsolvent content of the spinning solution increases, suggests an increase in the crystalline fraction of the films or that aggregation of the polymer chains occurs in solution prior to spinning. This explains why we observe the scattering trail on the low-energy side of the \( \pi-\pi^* \) transition of the polymer. Further evidence for this comes from the gain in oscillator strength of the \( \sigma-\pi^* \) transition. This is very consistent with the electronic transition being strongly coupled to the \( \sigma-\pi^* \) stretch of the polymer backbone. Typically for most thiophenes the \( \pi-\pi^* \) stretch occurs at \( \sim 1500 \text{ cm}^{-1} \) or 185 meV. This energy separation is independent (in within a few meV) of chromic shift. These results from spun films are consistent with those reported by Rughooputh et al.\(^7\) in solutions of polyalkylthiophenes.

**TABLE II.** Measured field-effect mobilities and polymer film conductivities. For film preparation conditions see Table I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (( \text{s cm}^{-1} ))</th>
<th>Mobility (( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7x10^{-5}</td>
<td>4.0x10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>7.3x10^{-6}</td>
<td>1.5x10^{-6}</td>
</tr>
<tr>
<td>3</td>
<td>6.1x10^{-8}</td>
<td>1.5x10^{-8}</td>
</tr>
<tr>
<td>4</td>
<td>3.0x10^{-8}</td>
<td>1.5x10^{-8}</td>
</tr>
<tr>
<td>5</td>
<td>9.5x10^{-9}</td>
<td>unmeasurable</td>
</tr>
</tbody>
</table>
falls (markedly) as nonsolvent is added to the spinning solution, but at the same time effective conjugation length of each chain within the film increases. Within the more ordered regions of the film the conjugated backbone will be more rigid. This rigidity will decrease the degree of freedom of the side groups, causing them to order. This ordering of the side groups will on average increase the interchain separation of the conjugated backbones, thus reducing the hopping probability between chains reducing the carrier mobility and hence conductivity. These results are in good agreement with those of Paloheimo et al. who have quantitatively shown that increasing the size of the substituent on the thiophene backbone, thus increasing chainchain separation, also leads to a decrease in carrier field-effect mobility.

On comparing our values of mobility with those quoted by Horowitz et al. for various thiophene systems, nothing untoward is seen. The value of $4 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ obtained for PMBET films cast from a purely good solvent is high for a substituted polymer, but not unduly so. Thus, the observed effects on mobility must be caused by the effects of either order or aggregation or both. Recent work in the field of oligomeric thiophenes has shown that interchain transport is all important. Compared to $\alpha$ substitution, $\beta$ substitution drastically reduced carrier mobility, due in part to loss of crystallinity and because the adjacent, facing thiophene rings are much further apart, although it is observed that a $\beta$-substituted dodeca thiophene has a mobility of $5 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$, a value approaching that which we have measured for PMBET. From these findings we deduce that in the pristining films of PMBET, there is a fair degree of order between the more closely spaced chains, as the optical spectrum of such a film displays vibronic structure, hence interchain transport is high with a concomitant high carrier mobility. As nonsolvent is added to the spinning solution chain rigidity and increased conjugation ensues, corresponding to increased order within the film, aggregation occurs, as deduced from increased scattering. The mobilities within such films falls; however, this we ascribe to the effects of increased chain separation on a microscopic scale and to the effects of grain boundaries on the macroscopic scale. These boundaries between the individual aggregate particles disrupts bulk mobility, which is measured in our experiment, although within a particle the mobility may well be higher.

V. SUMMARY

We have used a metal-insulator-semiconductor FET structure to measure charge-carrier mobility and conductivities of PMBET films, spun from solvent:nonsolvent mixtures. Optical characterization of films spun from solutions containing varying ratios of THF methanol (nonsolvent) shows clear vibronic structure on the $n\rightarrow n^*$ transition. Solvatochromic shifts are maintained in the spun films due to the rapid evaporation of the solvent from the (thin) films during the spinning process. This rapid evaporation locks in chain structure. As the nonsolvent content of the spinning solution is increased, films show increased conjugation, i.e., red shift of the visible absorption. This we ascribe to increased rigidity, and hence longer conjugation lengths along the polymer chain. Accompanying this, films appear more scattering, this we ascribe to aggregation within the solutions, and the films produced from them.

This latter observation is very important when considering the measured carrier mobilities in the films. As nonsolvent content increases the mobility in the films spun from these solutions decreases. This can be ascribed to effects on both the microscopic and macroscopic scale. On the microscopic scale, increased chain rigidity will cause the side groups to order increasing interchain separation and hence reduce the interchain hopping probability. The presence of macroscopic grain boundaries associated with the aggregation particles in the films affects the bulk mobility within the films. These results should be kept in mind when considering devices made with high-mobility oligomers, as again grain boundaries may be limiting the maximum attainable carrier mobilities and thus, ultimate device performance. Experiments such as microwave electrical conductivity will help to differentiate between these effects, and are underway at present.