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Giant anisotropy of carrier mobility in electroluminescent conjugated polymer

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The horizontal and vertical hole mobility of amorphous spin-coated electroluminescent conjugated films are studied. It is found that the horizontal mobility is about four orders of magnitude larger than the vertical mobility. The horizontal mobility increases daily with the aging of the polymer solution from which the film is spun. Low temperature and photoluminescence study reveal that the giant mobility anisotropy is a result of the alignment of the aggregates, formed during aging, by the centrifugal force of the spin. © 2006 American Institute of Physics.

In most of the conjugated polymers device structures a thin polymer film is formed by spin coating. The polymer chains are amorphous in such films. The carrier motion in the typical sandwich light-emitting diode structure is vertical to the film, with mobility as low as $10^{-10}$ m$^2$/V s. The model for vertical carrier transport has been established. Surprisingly, there are very few studies on the carrier transport horizontally to spin-coated amorphous conjugated polymer films, which is of equal fundamental importance. Because of the horizontal centrifugal force during the spin, the morphology of the resulting film can hardly be isotropic. In fact, optical measurement revealed that the polymer chains are mostly aligned along the substrate. In addition, the relation between morphology and mobility anisotropy and the way to control the mobility are by themselves outstanding open questions. In this work we found that the horizontal mobility is indeed larger than the vertical mobility for as much as four orders of magnitude; $10^{-6}$ m$^2$/V s is reached at the field of $5 \times 10^7$ V/m. This is the largest mobility ever reported for amorphous polymer films. Such value is close to the mobility of self-assembled ordered structure of nonemissive polymers. We discovered that the ultimate horizontal mobility in the film is actually determined by the evolution of the chain morphology in the parent solution which leads to aggregates. Spin coating transfers such aggregates into the film. The centrifugal force is shown to be required to align the aggregates into the large hopping domains, which consequently cause the giant anisotropy.

We obtain the hole mobility by fitting the space-charge-limited current (SCLC). The SCLC current-voltage relation is $J=(9/8)\varepsilon \mu (E)V^2/L^3$. $J$ is the current density, $L$ is the distance between the electrodes, $E$ is the average electric field, $\mu$ is the mobility, $\varepsilon$ is the vacuum permittivity and $k$ is the dimensionless dielectric constant. By fitting the experimentally measured $J$ vs $V$ relation with the expression above one obtains the field-dependent mobility $\mu(E)$. The SCLC method can be applied for both vertical mobility $\mu_v$ and horizontal mobility $\mu_h$. $\mu_v$ can also be measured by the characteristics of field-effect transistors (FETs). The saturation drain current $I_d$ is given by $I_d = W \mu_c C_{ox} (V_g - V_t)^2/2L$, where $W$ is the channel width and $L$ the channel length, $C_{ox}$ is the capacitance of the gate insulator, $V_g$ is the gate voltage and $V_t$ the threshold voltage. At saturation the drain voltage $V_{ds}$ is $V_g - V_t$, so the average electric field $E$ in the channel is $V_{ds}/L$. From $I_d$ vs $V$ relation at saturation we obtain the field-dependent horizontal mobility $\mu_h(E)$.

In addition to $E$, the mobility may also depend on the carrier density $n$ if $n$ is close to the degenerate regime. For a consistent study of mobility anisotropy, one needs to estimate $n$ and make sure that we are far away from degeneracy for both vertical and horizontal transport. Consider the typical electroluminescent conjugated polymers poly (2-methoxy-5 (2′-ethyl-hexyloxy) -1,4-phenylene vinylene) (MEH-PPV) where the chains are packed in the locally ordered structure with cell volume for each monomer equal to $15 \times 3.56 \times 6.65 \times 335 \AA^3$. The monomer density $n_0 = 1/355 \AA^{-3} = 2.8 \times 10^{21}$ cm$^{-3}$, which is the effective density of states. In SCLC the carrier density $n(x)$ is $(1/e)\sqrt[3]{e/\mu x}$, where $x$ is the distance from the injection electrode. Averaging $n(x)$ from $x = 0$ to $x = L$, the mean carrier density is given by $n = (2/3) eE/\varepsilon L$. The dielectric constants are $\kappa_0 = 3$ in horizontal direction and $\kappa_2 = 2.4$ for vertical direction. For vertical transport we take $L = 0.1 \mu$m and maximal field $E = 8 \times 10^7$ V/m. The resulting $n_v = 7.2 \times 10^{16}$ cm$^{-3}$. For horizontal transport we take $L = 3 \mu$m and maximal field $E = 8 \times 10^7$ V/m. The resulting $n_h = 3 \times 10^{13}$ cm$^{-3}$. Both $n_v$ and $n_h$ are 5–6 orders of magnitude smaller than $n_0$, so the SCLC transport is safely in the non-degenerate regime and the carrier mobility should not depend significantly on the carrier density. On the other hand, for FET the nondegenerate condition does not hold so well. In FET the surface charge density $\sigma$ of the accumulation layer is related to the gate voltage by $\sigma = C_{ox} V_g$, where $C_{ox} = \varepsilon_{ox}/d$; $d$ is the insulator thickness. The vertical surface electric field $E_v$ is given by $E_v = (\varepsilon_{ox}/\varepsilon_0 k) E_{ox} = (C_{ox}/\varepsilon_{0} k_0) V_g$. The value of vertical distribution $l$ of the holes in the accumulation layer is roughly $l = k_0 T/(\varepsilon E_v)$, where $k_0$ is the Boltzmann constant and $T$ is the temperature. The FET hole density $n_f$ is therefore $n_f = V_{ds}^2 k_0^2 \varepsilon_0/(k_0 T k_{e0} d^2)$. For SiO$_2$, $k_{e0} = 3.9$; $d$ is taken as the...
The vertical mobility $\mu_v$ (V) and horizontal mobility $\mu_h$ (HA, HB, FET) of MEH-PPV are shown as functions of averaged electric field $E$. The number of days indicates the time of solution aging at room temperature (20°C). Data HA and HB are obtained by SCLC fitting. The channel length $L$ is 3 μm for HA and 2.5 μm for HB. $\mu_v$ does not depend on aging; $\mu_h$ increases with the aging time. In general, $\mu_h$ is much larger than $\mu_v$.

The very low carrier density for SCLC, on the other hand, is not used as the main method for our experiments below. Let us focus on the optimal condition which form locally crystalline regions.10

Despite being amorphous, $\mu_h$ reaches as high as $10^{-6}$ m$^2$/V·s at field around 5 × 10$^7$ V/m. Because the carrier density in the horizontal SCLC is even smaller than the vertical SCLC, the much higher horizontal mobility cannot come from the difference in carrier density as proposed earlier. Interestingly, the highest FET mobility (open square in Fig. 1) is close to the SCLC mobility (open triangle). This implies $\mu_h$ does not depend on the carrier density $n$ significantly even for $n$ around 10$^{20}$ cm$^{-3}$. The only possibility for $\mu_h \gg \mu_v$ is therefore the intrinsic anisotropy in the morphology of the polymer chains.

In order to understand the origin of the anisotropy, we measure the mobility at different temperatures. Figure 2 shows the temperature dependence of $\mu_h$ and $\mu_v$. Both mobilities follow the Poole–Frenkel form $\mu = \mu^* e^{-\Delta k_B T}$, which is typical for hopping transport. $\beta = 1/k_B T / \gamma < 1$ is similar for $\mu_h$ and $\mu_v$ as seen in the slopes of the plots. The energy barrier $\Delta$ for hopping is obtained by plotting the extrapolated zero-field mobility $\mu_0$ vs $1/T$. The slope is also similar for $\mu_h$ and $\mu_v$ as shown in the inset; $\gamma$ lies between $10^{-3}$ and $2 \times 10^{-3}$ eV. The only major difference between horizontal and vertical transport is $\mu^*$, which accounts for the $10^4$ difference in the mobility. Both $\Delta$ and $\gamma$ reflect the energy barrier for hopping between sites. For vertical transport the sites correspond to conjugation segments with various conjugation length and therefore various on-site energies. $\Delta$ is roughly the variance of the energy distribution. Similar $\gamma$ and $\Delta$ imply the energy disorder among hopping sites in the horizontal direction is of the same origin. On the other hand, $\mu^*$ reflects the real-space distance for each hopping. The much larger horizontal $\mu^*$ suggests that the effective hopping site is much larger than just one conjugation segment. Somehow the segments arrange in such a morphology that ordered domains, i.e., the “sites,” are formed horizontally and the holes move easily inside the domains and hop across the energy barriers only when they reach the boundary of the domains. We suspect that the domains consist of polymer chain aggregates, which form locally crystalline regions.10

For MEH-PPV film spun from chloroform solution $\mu_h$ is found to increase with the concentration. This is the first sign that aggregate is critical to the mobility. Based on 0.38 wt% chloroform solution, many process conditions are tested to control the mobility. Surprisingly, the single most important condition for $\mu_h$ is not anything that one does to the film itself, e.g. baking and annealing. Instead it is the “aging” of the parent solution that matters most. By aging we mean the process condition that matters most. By aging we mean the time interval between the dissolution of MEH-PPV and the spin. In Fig. 1 we show how the mobility depends on the aging time at room temperature (20°C). The mobility increases daily and saturates only after as long as ten days. This is true for both SCLC (data A and B) and FET. The formation of aggregates or whatever morphology features responsible for the giant anisotropy must have already taken place in the solution. PL spectra for various aging time confirm this picture. There are two peaks in the photolumines-
The 620 nm shoulder is the highest in the drop cast film significantly. In Fig. 5 we show film PL with different speed. The peak grows by days in solution the high is lower for low-temperature aging. This is expected because virtually no effect. The inset of Fig. 4 shows that the mobility of field-effect transistor based on electroluminescent amorphous polymers with morphology control.

In conclusion, we show that there is a giant mobility anisotropy in polymer film resulting from the slow aggregate formation in the parent solution. Our work opens the possibility of field-effect transistor based on electroluminescent amorphous polymers with morphology control.

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The solution and film PL spectra at fixed two days of aging with various aging temperatures are shown. LT is 5 °C, RT is 20 °C, and HT is 40 °C. There are more aggregates as the temperature increases. Accordingly, horizontal mobility also increases with aging temperature as shown in inset.

The solution undergoes a constant evolution in its microscopic morphology. We also discovered that the slow aggregate formation can be made much faster by slightly increasing the aging temperature to 40 °C. At 40 °C the aggregate formation reaches saturation in two days, about five times faster than 20 °C. We show in Fig. 4 the solution PL after two-day aging with various aging temperatures. At high temperature (40 °C) the 580 nm peak for isolated chain becomes almost invisible. On the other hand, at low temperature (5 °C) the spectra is almost the same as just dissolved. The solution PL feature is translated to film as shown in Fig. 4. At low temperature the chain motion is frozen and the aging has virtually no effect. The inset of Fig. 4 shows that the mobility is lower for low-temperature aging. This is expected because the high \( \mu_h \) requires a large amount of aggregates. Finally, we found that \( \mu_h \) also depends on the spin speed significantly. In Fig. 5 we show film PL with different speed. The 620 nm shoulder is the highest in the drop cast film (zero spin speed) and decreases with the spin speed. Apparently the centrifugal force tends to destroy the aggregate as reported before. One would expect that the drop cast film, with most aggregates, gives the maximal \( \mu_h \). The answer is the opposite as shown in Fig. 5. Drop cast film has the lowest mobility, while 2000 rpm gives the highest. This proves that the mobility is determined by two competing factors. Aggregates are needed in the first place to form the large hopping domains. High spin speed destroys the aggregates and could lower the mobility. Nevertheless, the centrifugal force of the spin is required after all to align the aggregates in some anisotropic manner. Despite having the highest amount of aggregates, the drop cast film lacks the alignment so its \( \mu_h \) is the lowest. In fact, it is close to \( \mu_n \), further indicating the isotropic morphology without the spin.

References: