Charge Injection and Transport in Organic Nanofibers

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Abstract. We investigate the carrier injection and transport in individual para-hexaphenylene nanofibers by electrical transport measurements at different temperatures. The injected current shows much weaker temperature dependence than what would be anticipated from a simplistic model that considers the injection barrier height equal to the difference between the metal electrode work function and the HOMO energy level of the organic semiconductor. Semi-quantitative modeling suggests that the weak temperature dependence is due to injection into a distribution of states rather than into a single energy level. This disorder induced energy level broadening could be caused by the electrode deposition process.

1. Introduction

Self-assembled para-hexaphenylene (p6P) nanofibers display a range of appealing features that point towards their potential application in future nanophotonic and optoelectronic systems. Their photoluminescence output is in the blue range of the spectrum and is highly polarized [1], thus indicating a high degree of crystallinity. A similar nanofiber electroluminescence spectrum is expected from thin-film measurements [2]. In addition, these sub-wavelength nanofiber structures show waveguiding capabilities [3]. We have recently shown how electrical contacts to nanofibers can be made based on a shadow masked evaporation technique [4], and how mechanical manipulation allows the generation of artificial structures [5].

However, the details of carrier injection and transport in these nanofibers are not completely understood. Recently we showed that the current-voltage (I-V) characteristics of gold contacted nanofiber devices appear to be limited by hole injection from the gold electrode to the p6P nanofiber [6].

2. Experimental

The crystalline p6P nanofibers are made by hetero-epitaxial growth on a heated muscovite mica substrate under high vacuum conditions, where the oligomers self-assemble into fiber-like structures [7]. These nanofibers have a typical height of a few ten nanometers, a width of a few hundred nanometers, and an as-grown length of several 100 micrometers. The molecular structure and the nanofiber crystal structure are shown in figure 1.
The nanofiber devices are fabricated by dispersing nanofibers in a suitable liquid and spreading a small amount of the dispersion on an elevated silicon dioxide structure. After evaporation of the liquid, contacts are attached to each end of an individual nanofiber by electron-beam evaporation of the required electrode material using a special shadow mask method as described in [4]. Figure 1c shows an SEM image of an individual nanofiber contacted with two metal electrodes.

After sample preparation, the sample is mounted in a small compartment with electrical feedtroughs where the temperature can be controlled either by lowering the sample into a nitrogen cryostat or by heating it with an attached resistor through Joule heating. The electrical characterization is carried out by slowly sweeping the bias voltage while simultaneously recording the resulting current via a custom-made, Labview-based measurement set-up employing a National Instruments data acquisition card and a Stanford Research current preamplifier.

3. Results and Discussion

Figure 2a shows $I$-$V$ characteristics of an individual nanofiber measured at three different temperatures. As expected for the injection-limited case, the current decreases with decreasing temperature. Figure 2b shows the current at a bias voltage of 3 volts versus reciprocal temperature. The injected current has a clear temperature dependence at higher temperatures and stabilizes below ~ 200 K.

Figure 2. a) $I$-$V$ characteristics measured at three different temperatures (open symbols). The filled symbols show model calculations as described in the text with $(\phi, \sigma) = (0.7 \text{ eV}, 0.13 \text{ eV})$ b) The current measured at a bias voltage of 3 volts versus reciprocal temperature (open squares). The filled symbols show model calculations with different model parameters. Due to the finite sweeping speed, the device structure causes a capacitive off-set of the order of 1 pA or less. This off-set has been subtracted here.
Several theoretical approaches have been used in the interpretation of carrier injection into organic semiconductors [8] including thermionic emission across the interface barrier or a tunneling process. In contrast to conventional inorganic semiconductors, injection in this case occurs into a localized state which must be taken into account. A model based on thermally assisted tunneling into localized states has been developed [9]. This model considers carrier injection from a metal electrode into a localized state which requires a consideration of the energetic structure of the metal/semiconductor interface. Here, we look at the injection of holes from a gold contact into the HOMO level of p6P. The externally applied field $F$ together with the Coulomb interaction with the image charge give rise to an energy barrier $U(x)$

$$U(x) = \phi - \frac{q^2}{16\pi\varepsilon_0 \varepsilon_r} - qFx,$$  

measured with respect to the metal Fermi level. $\phi$ is the energy difference between the Fermi level of the gold electrode and the HOMO level of p6P (neglecting a possible interface dipole layer), $q$ is the elementary charge, and $\varepsilon_0\varepsilon_r$ is the dielectric constant. In the ideal case, the interface should be sharp and the energy levels in the organic semiconductor should remain well-defined all the way towards the interface. In a practical device, however, the deposition of metal contacts on top of the organic material can create some disorder in the region close to the interface [10]. A possible model for the density of states close to the interface is a Gaussian energy distribution $g(E)$ characterized by an energy width $\sigma[9]$

$$g(E) = \frac{N_0}{\sqrt{2\pi}\sigma} \exp\left(-\frac{E^2}{2\sigma^2}\right),$$  

with $N_0$ being the density of traps. A schematic of the energy levels associated with the injection process is shown in figure 3.

In the model by Arkhipov and co-workers [9], the injected current is found by considering injection into the distribution of states in the organic semiconductor followed by either the return of the carrier to the electrode or its diffusive escape into the bulk. The injected current $I_{inj}$ is therefore found as a product of the tunneling probability $\exp(-2\gamma x_0)$ (i.e. the probability of the carrier reaching the position $x_0$ in the first jump), and the escape probability $w_{esc}(x_0)$

$$I_{inj} \propto \int_{-\infty}^{\infty} dx_0 \exp(-2\gamma x_0) w_{esc}(x_0) \int_{x_0}^{\infty} dE \text{Bol}(E) g[U(x_0) - E],$$  

where $\gamma$ is the inverse localization radius and $\text{Bol}(E)$ is a Boltzmann factor

$$\text{Bol}(E) = \begin{cases} \exp(-E/k_B T), & E > 0 \\ 1, & E < 0. \end{cases}$$
The escape probability \( w_{\text{esc}}(x_0) \) is determined by

\[
\begin{align*}
\int_{a}^{\infty} dx \exp & \left[ \frac{-q}{k_BT} \left( Fx + \frac{q}{16\pi\varepsilon_0\varepsilon_r x} \right) \right] , \\
\int_{a}^{\infty} dx \exp & \left[ \frac{-q}{k_BT} \left( Fx + \frac{q}{16\pi\varepsilon_0\varepsilon_r x} \right) \right] ,
\end{align*}
\]

with the thermal energy \( k_BT \) and the distance \( a \) from the electrode to the first site in the semiconductor.

This model has been used to investigate the temperature dependence of the carrier injection. Considering \( \phi \) to be equal to the difference between the gold Fermi level (\( \sim 5.1 \) eV) and the HOMO level of p6P (\( \sim 6.0 \) eV) [11] and considering injection into a single energy level, the current will be strongly dependent on temperature as shown with the full squares in figure 2b. Apparently the actual temperature dependence is weaker than this prediction. A possible explanation for this deviation could be a barrier lowering due to an interface dipole layer [12]. Photocurrent spectroscopy studies of the interface between gold and p6P have shown a significant vacuum layer shift [13]. However, these studies were carried out at ultra-high vacuum conditions. Recently it has been argued that more realistic device fabrication conditions can cause water molecules to be integrated in the interface and cancel the interface dipole [14]. Photoelectron spectroscopy studies of the interface between gold and p6P have shown a significant vacuum layer shift [13]. However, these studies were carried out at ultra-high vacuum conditions. Recently it has been argued that more realistic device fabrication conditions can cause water molecules to be integrated in the interface and cancel the interface dipole [14]. Thus, the results from [13] do presumably not apply here. Since the barrier is unknown, we have tried to model the injection current assuming different values of barrier height: 0.9 eV, 0.7 eV, and 0.5 eV. We have then modified the width of the energy distribution \( \sigma \) until a reasonable agreement between injected current and temperature (in the interval above \( \sim 200 \) K) was observed. These three model predictions are shown in figure 2b (with \( \varepsilon_r = 1.9 \) [3], \( N_0 = 1.7 \times 10^{21} \) cm\(^{-3} \), \( \gamma = (3 \text{ Å})^{-1} \), and \( a = 5.6 \) Å).

The model describes a dependence of the injected current on temperature that is weaker when the carriers are injected into a distribution of states rather than a single energy level: the wider the distribution, the weaker the temperature dependence. Qualitatively, this could explain part of the observed temperature dependence: that the organic layer close to the interface has a disorder induced level broadening that causes more carriers to be injected at lower temperatures. This disorder could be created during the electrode deposition where hot gold atoms or clusters collide against the organic material. It has been shown that this process can cause a less ‘sharp’ interface [13]. However, since neither the exact barrier height nor the width of the energy distribution is known, we cannot make an exact estimate. All three model calculations give very similar results that only deviate slightly at low temperatures where the model is not appropriate at all. Figure 2a includes the calculated \( I-V \) characteristics at three different temperatures together with the measured \( I-V \) curves. In these model calculations \( (\phi, \sigma) = (0.7 \) eV, 0.13 eV \) have been used. A decent agreement is observed at high temperatures although the model predicts the current to increase steeper than observed. At low temperatures the model significantly underestimates the injected current as is also evident from figure 2b. A similar temperature dependence has also been observed experimentally on p6P films [15] even with the temperature dependence reversing sign at low temperatures. It thus appears that some additional factor is in play causing a high current injection even at low temperatures.

It should be noted that in our device geometry the exact electric field distribution is not obvious at all. For simplicity we have assumed here that the electric field was equal to the applied voltage divided by gap distance. However, strictly speaking this only applies to a geometry relating that of a parallel-plate capacitor. For a more accurate determination of the field, a simulation of the field distribution in this device architecture is necessary, and this may influence the agreement between the model and the measured data.

4. Conclusion and Outlook

We have measured the temperature dependence of the injected current from a gold electrode into a p6P nanofiber. The injection current shows a weaker temperature dependence than what would be
anticipated from a simple estimation of barrier height based on the electrode work function and p6P energy levels. A theoretical model [9] that considers charge injection as carrier hopping into a localized state followed by a diffusive escape into the bulk shows that this weak temperature dependence can be explained if one considers injection into a distribution of states rather than a single energy level. This rather simple model is partly in agreement with the measured data, in particular at temperatures above ~200 K, and suggests that some disorder related level broadening is present in the organic material near the electrode interface. Modeling this by a Gaussian distribution of states suggests an energy width $\sigma$ of ~0.1 eV.

The result implies that although the organic nanofiber is near-perfect crystalline, an increased-disorder region exists near the electrode interface. This could for instance be due to the load during electrode deposition where hot gold atoms or clusters collide with the organic material. In that case, creating a good contact to organic nanofibers may be far from straight-forward, requiring a high degree of control of the electrode deposition process. Decreasing the metal evaporation rate could be one method of obtaining a better interface. Another option could be to attach the electrodes by some other means than vaporization, e.g. by prefabricating the electrodes on a carrier substrate and placing the organic crystal on top as demonstrated with macroscopic tetracene crystals [16]. This method should also be possible for the p6P nanofibers either by dispersing these on a prefabricated electrode array or by a more controlled positioning through mechanical manipulation [17]. It should be pointed out, that a well-defined interface with ‘good’ contacts for some applications may not be the optimal situation since level broadening increases injection [10].

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