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Electrical characterization of pn-junctions of PPV and silicon

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Abstract

Poly(phenylene vinylene) (PPV) grown via the precursor route, deposited on top of heavily doped n-type silicon, was studied using electrical measurement techniques. The results are compared to PPV grown via deposition of soluble derivative (MEH-PPV). The two types are very similar. They have comparable free carrier densities and both show minority-carrier effects. The activation energy found via the loss tangent is 0.13 eV. The effect of exposure to oxygen is visible in the capacitance and the current.

Keywords: Semiconductor/semiconductor interfaces, Poly(phenylene vinylene), Electrical measurements.

1. Introduction

Poly(p-phenylene vinylene), PPV, is one of the leading semiconducting polymers when it comes to optical applications. Two routes are very common for polymer deposition. Either the entire polymer is made soluble by adding suitable side chains to the backbone, as in MEH-PPV, or the precursor polymer can be converted in a heating stage. This is done in the precursor-route PPV. In the current study we compare the electrical characteristics of the two different PPV materials.

2. Experimental

The PPV was prepared via the standard tetrahydrothiophenium-based precursor route. Thin films of precursor were deposited onto the silicon substrates (0.5 Ωcm) by spin coating. The conversion reaction was performed under vacuum (ca. $5 \cdot 10^{-5}$ mbar), for 12 hours at about 180°C. The final film thickness is about 100 nm. The device structures were completed by thermal evaporation of gold electrodes (2 mm diameter) at a base pressure of roughly $4 \cdot 10^{-5}$ mbar. The samples were then mounted in the cryostat. The temperature was measured with a standard Pt100 resistor and was controlled with an Oxford ITC 601 temperature controller. The AC measurements were performed with a Fluke PM6306 RCL bridge and the DC (current) measurements were done with a Keithley 487 which also served as the bias source. Between manufacturing and measuring, the exposure of the samples to air was kept at a minimum.

3. Results and discussion

The devices display almost saturating reverse currents, rectification ratios higher than 10^5 at 1 V, low ideality factors of 1.3, and cut-off frequencies well above 1 MHz at room temperature. These are excellent characteristics for polymer-based diodes.

Figure 1 shows IV curves of a typical device at various temperatures. At large forward bias, starting from 0.7 V, the current is limited by the bulk series resistance. From the temperature dependence of the current at +1 V we find an activation energy of 70 meV. At smaller biases, a small shoulder is visible. Such a behavior is very similar to the DC characteristics of MEH-PPV and can be attributed to the presence of minority-carrier currents [1,2].

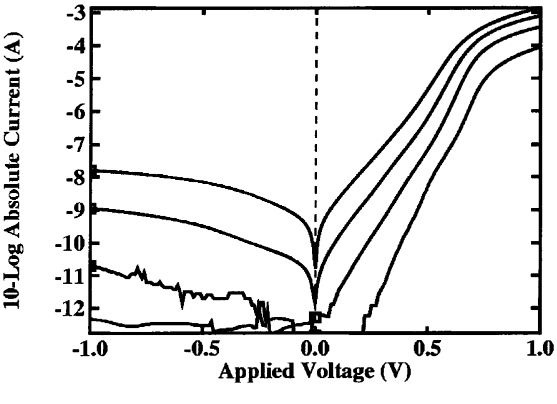

Fig. 1. IV curves for Si/PPV pn-junctions at 285 K (top), 240 K, 194 K and 129 K (bottom).

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Also in the capacitance-voltage measurements the PPV and MEH-PPV behave rather similar. A huge inductance (or negative capacitance) peak is observed in forward bias, see Figure 2, where a so-called Mott-Schottky plot is shown ($1/C^2$ vs. V). We have assigned such peaks to the effects of injected minority-carriers [1]. The difference between PPV and MEH-PPV is that for the latter this peak is at somewhat lower biases, possible due to a slightly different interface layer thickness.

From the slope in the same figure it can be estimated that the free-carrier concentration is about $1 \cdot 10^{16}$ cm^{-3}. This is comparable to the MEH-PPV ($7 \cdot 10^{15}$ cm^{-3}).

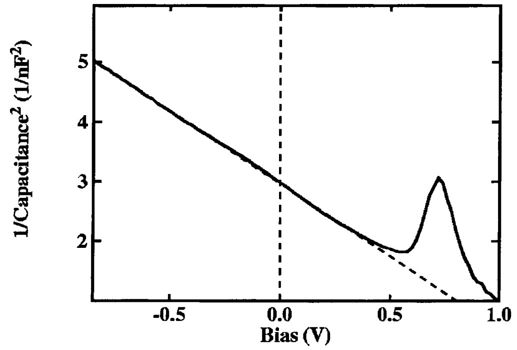

Fig. 2. Mott-Schottky plots at a temperature of 155 K and a probing frequency of 1 kHz. The slope indicates a free-carrier concentration of $1 \cdot 10^{16}$ cm^{-3}. The peak is due to inductive effects of minority-carrier currents.

The loss-tangent ($\tan \delta = G/\omega C$) has a pronounced maximum that depends on the conductivity of the bulk [3]. It is at 38.2 kHz at 132 K and moves beyond 1 MHz at room temperature. An Arrhenius plot of the position of this maximum revealed the activation energy for this process, see Figure 3. For temperatures below 150 K it is weakly activated, while at higher temperatures it is thermally activated with $E_A = 0.13$ eV. This compares very well to the 0.12 eV found for MEH-PPV [1,4].

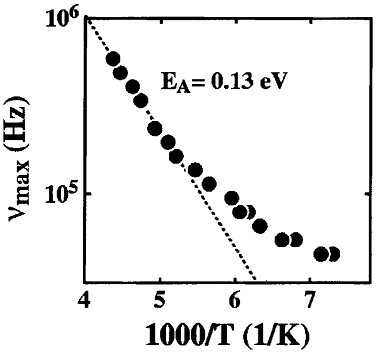

Fig. 3. Arrhenius plot of the frequency of the maxiumum of the loss tangent $G/\omega C$. The activation energy for bulk conductance is 0.13 eV at higher temperatures.

Finally, we studied the effect of exposure of the sample to oxygen. Figure 4 shows how the capacitance slowly decreases over time upon exposure to ogygen (τ = 2.5 h). A decrease in capacitance indicates an expansion of the depletion width and this, in turn, indicates a *decrease* in free carrier density and hence a decrease in acceptor concentration. On the other hand, the IV curves show a slight enhancement of the forward-bias current, indicating an *increase* in carrier-density. The reason for this decrepancy is not well understood at the moment.

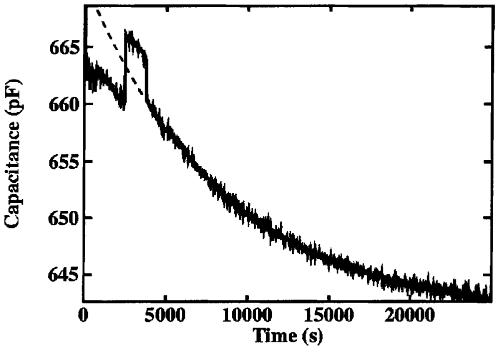

Fig. 4. The change of capacitance during exposure to oxygen follows an exponential curve with $\tau = 2.5$ h (dashed line). The steps at the beginning of the scan are instrumental artifacts.

4. Conclusions

Soluble MEH-PPV and PPV grown via the precursor route behave rather similar in pn-junctions with silicon. This includes the presence of minority-carrier currents and an activation energy of 0.13 eV for the bulk activation process. No DLTS (deep-level transient-spectroscopy) measurements were possible. The effects of persistent exposure to oxygen are a reduction in capacitance and an increase in forward bias current.

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