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Dominic D. Schroepfer, P. Paul Ruden, Yu Xia, C. Daniel Frisbie, and Sean E. Shaheen

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Hydrostatic pressure effects on poly(3-hexylthiophene) thin film transistors

Dominic D. Schroeffer^{a)} and P. Paul Ruden

Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota 55455, USA

Yu Xia and C. Daniel Frisbie

Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, Minnesota 55455, USA

Sean E. Shaheen

Department of Physics and Astronomy, University of Denver, Denver, Colorado, 80208, USA

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Poly(3-hexylthiophene) thin-film transistors are subjected to hydrostatic pressure up to 1 GPa. The charge carrier mobility and threshold voltage are extracted from I_d - V_{gs} curves. These parameters change linearly with pressure and retrace upon gradual pressure release. The mobility increases from 0.001 to 0.004 $\text{cm}^2/\text{V s}$, and the threshold voltage falls from 36 to 2 V over the full pressure range. As a result, the current rises with increasing pressure up to 600 MPa and then falls as pressure is increased further. The increase in the mobility is attributed to enhanced π -orbital overlap under compression. The change in threshold voltage is interpreted as a modulation of trapped charge density. © 2008 American Institute of Physics. [DOI: 10.1063/1.2830330]

Organic semiconductors are emerging as viable materials for extending semiconductor technology to large area and flexible circuits. Among the organic semiconductors, poly(3-hexylthiophene) (P3HT) and similar polymers are particularly promising materials due to their solution processibility and favorable transport characteristics, which approach those of amorphous silicon. To date, the best P3HT-based thin film transistors (TFTs) have had field-effect mobilities on the order of 0.1 $\text{cm}^2/\text{V s}$ and on/off ratios of up to 10^8 .^{1,2} These results are for devices fabricated on silicon wafers with thermal oxide gate insulators, but devices on flexible polymer substrates have been fabricated with only slightly lower performance.³⁻⁶ It has been shown that these TFTs are suitable for display driving circuits, opening the avenue to an all organic display.⁶⁻⁸

However, there is still considerable variation in organic semiconductor device performance depending on details of the fabrication process. For many solution-cast semiconductors, charge carrier mobilities are on the order of 10^{-5} $\text{cm}^2/\text{V s}$ or less, but for well-prepared P3HT films, the mobility is orders of magnitude larger. This increase is largely attributed to the self-alignment of the molecules that allows charge transport between the molecular chains via π -orbital overlap.^{9,10} The characteristics of P3HT devices depend on the deposition conditions: the solution composition, the substrate, and postprocessing steps such as annealing.^{1-3,11} Few of these dependences are well understood.

In molecular crystals of organic semiconductors, the use of pressure to decrease the inter-molecular spacing has been used successfully to increase the mobility.¹²⁻¹⁶ In this work, hydrostatic pressure was applied to P3HT transistors using a compressor (Unipress model U11/GC10) connected to a gas cell. The pressure transducing gas was ultrapure carrier-grade argon. Electrical measurements were made *in situ* with an HP4145B semiconductor parameter analyzer. The pres-

sure was monitored with a manganin pressure gauge in the compressor and the temperature was monitored with a copper/constantan type T thermocouple located in the pressure cell. The pressure was changed slowly enough to allow the ambient atmosphere to keep temperature changes to less than 0.5 °C.

Transistors used for the experiment had top source and drain contacts and a bottom gate. The active layers were made from P3HT purchased from Rieke metals and used without further purification. The P3HT was dissolved in an *o*-dichlorobenzene solution at a concentration of 20 mg/mL and deposited on a SiO_2/Si substrate by the slow dry technique described by Li *et al.* with 600 rpm spin coat deposition.¹⁷ The wet film was allowed to dry in a Petri dish for 30 min and then annealed at 80 °C for 10 min under nitrogen, yielding approximately a 100 nm thick P3HT film covering the entire surface. The wafer was cut into die sized to fit into the pressure cell. Gold was evaporated through a shadow mask to form the source and drain contacts with a channel 20 μm long and 200 μm wide. The heavily doped silicon wafer was the gate with the 300 nm of oxide serving as the gate insulator.

I_d - V_{gs} transfer curves were taken with $V_{ds} = -7.5$ V and V_{gs} swept from -40 to +40 V during the pressure cycle. Ex-

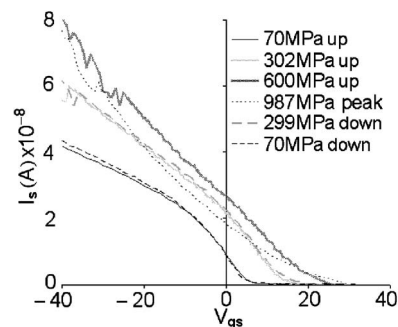


FIG. 1. I_d - V_{gs} curves measured over the pressure range. The pressure increasing and pressure decreasing curves nearly coincide.

^{a)}Electronic mail: schr0647@umn.edu.

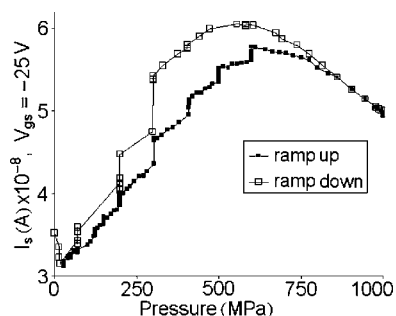


FIG. 2. Drain currents measured at $V_{gs} = -25$ V and $V_{ds} = -7.5$ V vs pressure. When allowed to relax, the retrace is satisfactory. The curve peaks are around 600 MPa.

ample curves are shown in Fig. 1. To monitor the changes of the output current with pressure, the current at $V_{gs} = -25$ V was plotted versus pressure in Fig. 2. The -25 V gate bias was used to ensure operation in the linear regime yet avoids the high noise seen at high gate voltages in some curves. In Fig. 2, steps in the data indicate where the system dwelt at pressure for extended periods of time, showing that relaxation occurred on a time scale comparable to the duration of the experiment. The devices were deemed to have relaxed to the ambient stress once the currents being recorded for consecutive measurements in Fig. 1 changed by less than 1% over 30 min. Then the ramp continued to the next dwell point. During the pressure vent part of the cycle, the relaxation of the devices took much longer, up to 24 h, and so larger steps were taken during the vent. Given enough time at a given pressure point for the devices to relax, the experiments showed satisfactory retraceability, indicating that no persistent damage affecting the transistor properties was incurred.

The linear mobility versus pressure extracted from the data in Fig. 2 at the end of the dwell periods show a 300% increase with pressure and are plotted in Fig. 3. The initial values for these devices are fairly low, but for spin coating deposition, a relatively low mobility is expected.^{11,18} The trend is clearly a linear increase with pressure. If this were the only parameter changing, the current versus pressure curve should increase monotonically throughout the entire pressure range, but as can be seen in Fig. 2, at high pressures, the current drops. The increasing trend in the mobility is consistent with a decrease in the intermolecular distance. With decreasing distance, the π -orbital overlap increases, facilitating charge transfer between the molecules. Considering the exponential dependence of orbital overlap on intermolecular distance would suggest an exponential trend. Compressibility data for crystalline tetracene show a volume re-

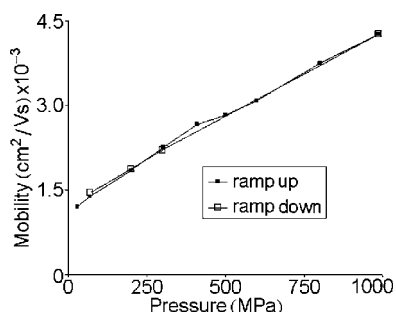


FIG. 3. Linear mobility extracted from the transfer curves vs pressure.

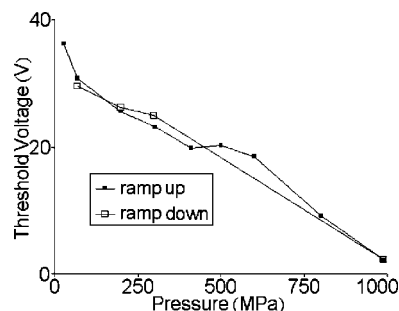


FIG. 4. Threshold voltage extrapolated from the transfer curves vs pressure.

duction of nearly 10% /GPa, which translates to more than 3% /GPa change in the site spacing.¹⁹ The bulk compressibility of P3HT is not expected to differ greatly from tetracene, so some exponential behavior might be seen. However, it is likely that the silicon substrate limits the compression of the active material, which consists of only the first few molecular layers adjacent to the oxide.^{20,21} Taking the lower compressibility of silicon into account, the resulting compression is less than 1% /GPa, leaving nominally exponential plots looking linear.

The threshold voltage for the linear region is plotted versus pressure in Fig. 4. Like the mobility plot, the trend is roughly linear and shows little hysteresis. The trend is toward negative threshold voltages, which for the p -channel TFT means that the devices become harder to turn on as pressure increases. This effect is the main reason why the current in Fig. 2 decreases in the high pressure region. Through the pressure cycle, the mobility and the threshold voltage affect the current in opposing ways; the mobility is dominant at low pressure (where $|V_{gs} - V_T|$ is relatively large) and the threshold is dominant high pressure (where the mobility is large). The likely reason for the threshold shift is a change in the fixed (trapped) charge in the material or at the oxide/P3HT interface, with the trend in the threshold indicating an increase of fixed positive space charge. While care is taken to minimize impurities in the devices, the probable cause of fixed space charge is likely to be impurities that remain. As pressure increases, the electronic band structure of the P3HT active layer changes. The data presented here suggest that the relevant impurity levels shift in such a way as to become more positively charged with increasing pressure.

In summary, subjecting P3HT in a TFT device to high pressure results in a linear increase in carrier mobility and a shift of the threshold voltage in the negative direction. A mobility increase throughout the entire range of pressures used here is expected with a decrease in the intermolecular distances, creating greater π -orbital overlap. The good retraceability indicates that the device remains within its elastic limits. The threshold voltage shift in the negative direction suggests that there are impurities that become increasingly positively charged as the pressure increases. To explore further the phenomena demonstrated here, the addition of temperature variations in combination with pressure is planned.

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