Annealing Study of Diode Parameters of P3HT:PCBM Organic Photovoltaic Devices

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Motivation

Our IGERT Program is focused on obtaining hydrogen from sunlight. This work is on using organic (carbon based) photovoltaics (PV) to generate electricity from sunlight which can then be used to make hydrogen. Organic PV provides a viable, low cost alternative to traditional silicon PV; Polyera corp recently announced a 9.1% power conversion efficiency OPV device. While the pace of development is fast, much of the basic physics is falling behind. This work is on the diode parameters and resistances of a poly 3-hexylthiophene (P3HT)/Phenyl-C61-butyric acid methyl ester (PCBM) device.

Introduction

- We performed an annealing study to improve our understanding of the mechanics of OPVs
- We focused on the well characterized P3HT:PCBM bulk heterojunction device. Upon annealing, the performance of these devices goes up (Fig 4). This increase has been widely studied and is attributed to P3HT crystallization and P3HT and PCBM phase separation
- To better characterize this increase, we applied a simple lumped circuit model:

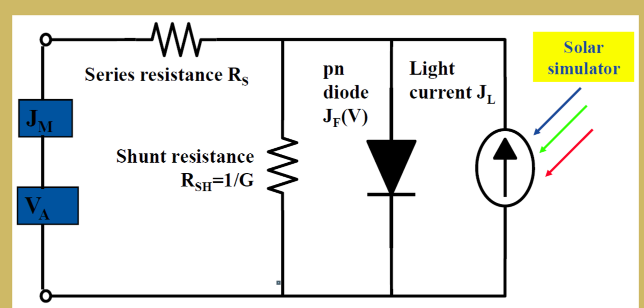

Figure 1: Lumped circuit model documenting usual loss mechanisms

- The current in a solar cell can be characterized by the corrected diode equation plus the solar current:

$$J(V) = J_0\left\{\exp\left(q\frac{V-RJ}{Ak_BT}-1\right)\right\} + GV - J_L(V)$$

J: Current
Jo: Dark Saturation Current
q: Charge
V: Voltage
R: Series Resistance
A: Diode Ideality Factor
k: Boltzmann's Constant
T: Temperature
G: Shunt Conductance
J_L: Photocurrent

- Once J_L and J_d have been corrected for series and shunt losses, the voltage dependent collection function which describes the probability of collecting a carrier at the electrode can be found using:

$$\eta(V_j) = \frac{Jl-Jd}{Jsc}$$

- Which can be fit using the equation

$$\eta(V_j) = \frac{L_c}{D}\left(1-\frac{V_j}{V_{fb}}\right)\left\{1-\exp\left(\frac{-D}{L_c}\left(1-\frac{V_j}{V_{fb}}\right)^{-1}\right)\right\}$$

- L_c: Collection Length, D: Device Thickness, V_{fb}: Flatband Potential

$$\frac{L_c}{D} = \frac{\mu\tau V_{fb}}{D^2} = \frac{\tau_R}{\tau_d}$$

- Solving for μτ leads to the limiting carrier lifetime mobility product

Experimental

- We used commercially available 10-15Ω ITO on a soda lime glass substrate with ~93% transparency
- 20 nm layer of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was spin coated on top of the ITO
- Next, an approximately 175 nm mixture of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) in a 1:0.8 ratio dissolved in chlorobenzene was spin coated on the PEDOT:PSS
- An 80nm layer of Al was thermally evaporated on top of the active layer.
- All devices were then annealed for 20 minutes.

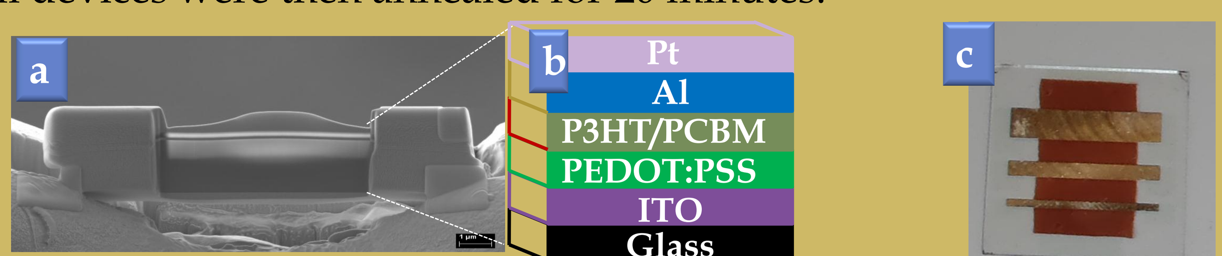

Figure 2:a) Cross-section of a P3HT:PCBM bulk heterjunction device b) Breakdown of each layer c) Top view of finished device

Results

- All devices were tested for JV characteristics using a 100 mW/cm2 solar simulator with an AM 1.5 filter. The JV curves were found with a Keithley 2400 multimeter.

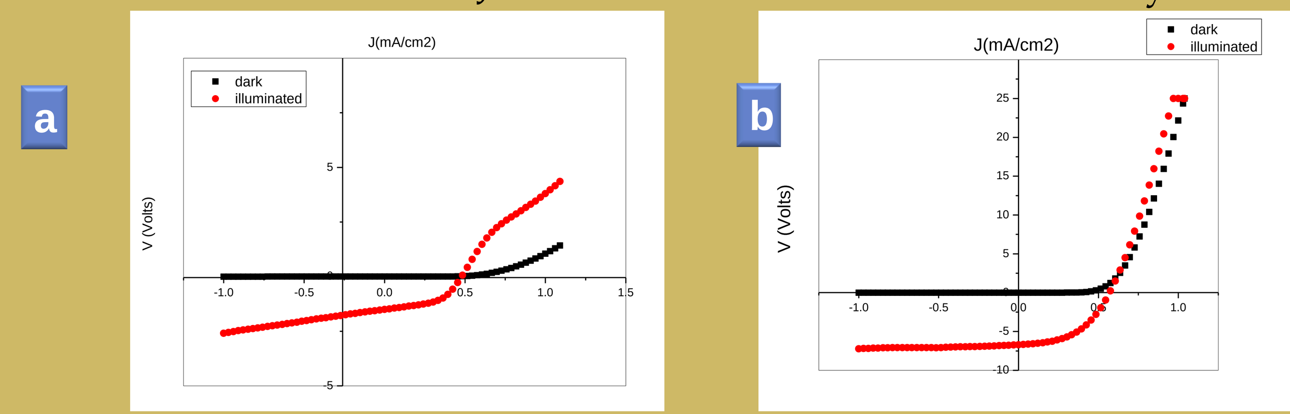

Figure 3: JV curve of an OPV device in the dark (black square) and under illumination (red diamond) a) unannealed, showing "S curve" behavior, which remains until annealing at 80° C. b) device annealed at 160 ° C shows much better diode and solar cell behavior.

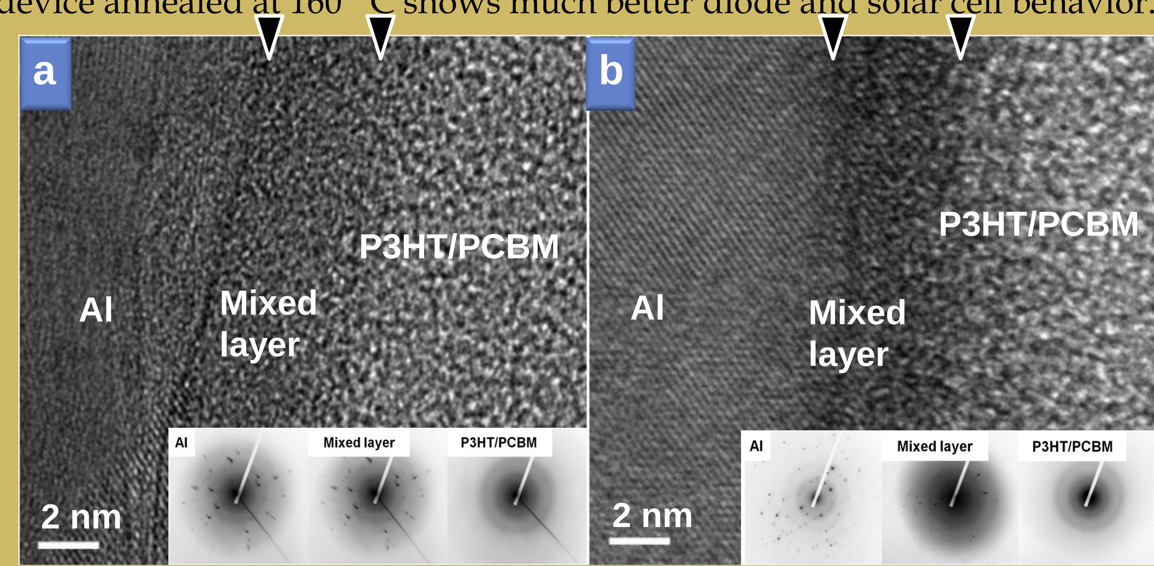

Figure 4: Transmission electron microscopy of the Al/Organic interface of a) an unannealed device and b) a device annealed at 120° C. Notice the lines of regular atomic spacing in the annealed device, an indication of crystalline Al. The white boxes at the bottom are electron diffraction patterns. Dots correspond to crystallinity while a ring indicates amorphous (non-crystalline) material. Once again, the annealed device shows better crystallinity than the unannealed device. The cleaner rings in the P3HT/PCBM layer also indicate crystallinity, confirmed through other studies.

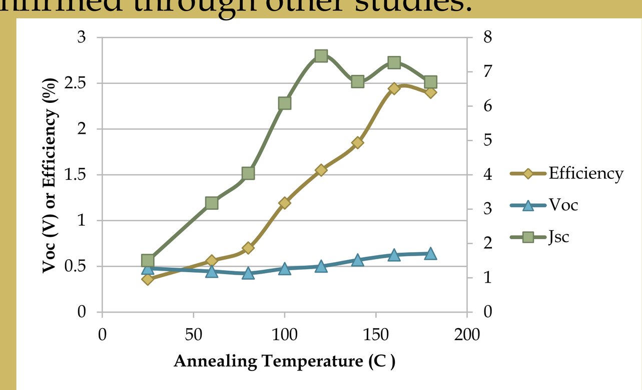

Figure 5: Basic cell parameters extracted from the JV curve. Jsc (mA) corresponds to the right axis. The increase in efficiency can mostly be attributed to an increase in Jsc, partially due to the crystallization of P3HT.

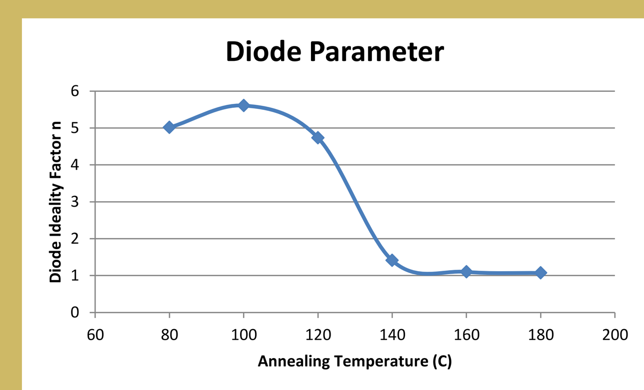

Figure 6: The diode ideality factor decreases as the annealing temperature increases. The lag in the first sample is considered experimental error.

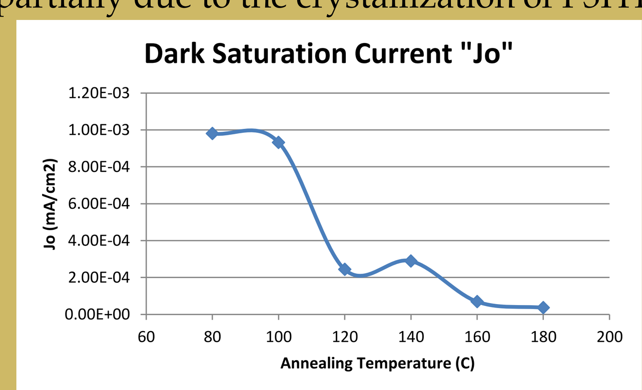

Figure 7: The order of magnitude decrease in Jo suggests a large shift in the material performance. This is due to the crystallization of the P3HT creating cleaner P3HT/PCBM interfaces.

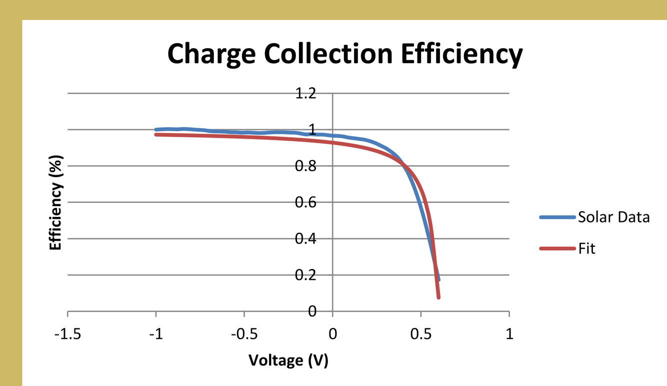

Figure 8: The probability of collecting a carrier at the electrode drops significantly near the flat band potential. The difference between the data and the fit seems significant but is only a 3% difference and leads to an adjusted R-squared value of over .99.

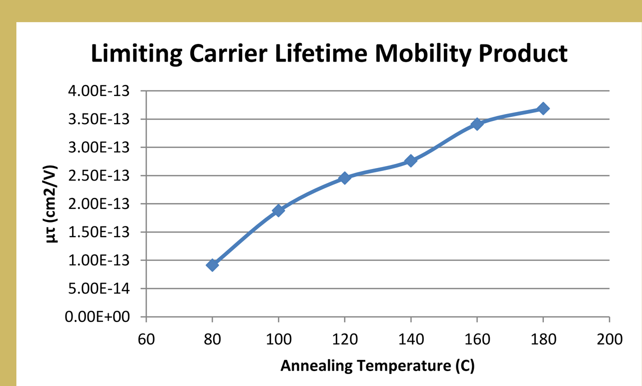

Figure 9: The limiting carrier (electron) lifetime mobility product increases significantly with annealing.

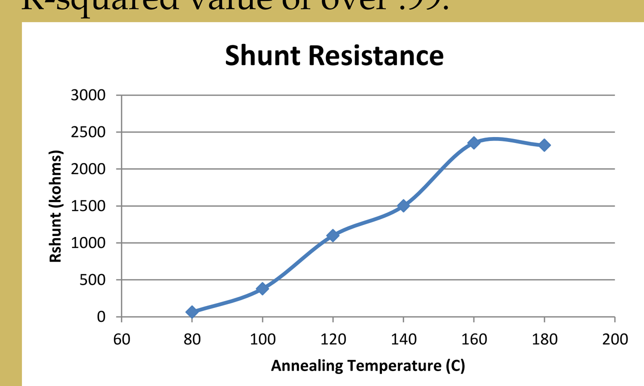

Figure 10: The shunt resistance also increases significantly, which is beneficial to device performance.

Conclusions

- Device parameters across the board responded favorably to annealing. This suggests that annealing is doing more for device performance than just crystallizing the P3HT
- The material properties of the basic diode, produced at the interface of the P3HT and the PCBM improve. This is evident from figures 6 and 7.
- The diode parameter, a measure of recombination of solar generated free electrons with atoms missing an electron, shows a drastic decrease in recombination
- A diode parameter of 1 suggests that recombination is limited by the minority carriers, while above that suggests that recombination is due to both carriers and very widespread throughout the device
- The dark shunt current Jo is a measure of material performance, also showing good results
- The benefits of an increased μτ are obvious and most likely due to crystallization of the P3HT leading to higher mobility, which is well documented. The interesting part of measuring μτ in this manner is that it actually gives in-situ solar parameters. μτ is generally measured in PV through ex-situ measurements such as TOF or CELIV
- The increase of the shunt resistance in Figure 10 is attributed to a decrease in the microscopic conducting pathways, such as a fiber of P3HT connecting the top and bottom electrode

Take Aways

- Organic photovoltaics are developing quickly and costs are coming down
- JV curve analysis can be applied to OPV to give some powerful information which may be able to help increase new polymer's power conversion efficiency
- P3HT/PCBM OPV systems respond very favorably to annealing, as can be seen from the decrease in diode parameter, decrease in Jo, and increase in μτ , which can all be attributed to crystallization of P3HT
- The increase in shunt resistance also makes a better device, and this can be attributed to phase separation
- OPV will most likely never control the PV market, but it will fill a niche and be a part of a renewable energy future

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References

1 B. Ali, R. Murray, S. Hegedus, S. Shah, Journal of Applied Physics, Submitted

2 S. S. Hegedus, Prog. Photovolt. Res. Appl. **5**, 151 (1997)

3 S.S. Hegedus and W. N. Shafarman, Prog. Photovolt. Res. Appl. **12**, 155 (2004)

4 S. S. Hegedus, D. Desai and C. Thompson. Prog. Photovolt. Res. Appl. **15**, 587 (2007)

5 Mayer, A. et al, Appl. Phys. Lett. 85, 6272 (2004)

6 Rujisamphan, N., Deng, F., Murray, R., Ni, C. and Shah, S. "Focused ion beam assisted investigations of Al interface in polythiophene:fullerene solar cells", Nature Materials, Submitted April 2012