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p-n Junction Diodes Fabricated Using Poly (3-hexylthiophene-2,5-dyil) Thin Films And Nanofibers

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Abstract

Poly (3-hexylthiophene-2,5-dyil) (P3HT) is a *p*-type semiconducting polymer which is commonly used in electronic devices. A *p-n* junction diode is an essential electronic device found in all power supplies that are used to charge cellular telephones. Using an *n*-doped silicon substrate together with films or nanofibers of P3HT, we fabricated and characterized *p-n* junction diodes. P3HT films were prepared via drop casting a 2 wt % P3HT solution in chloroform, while P3HT nanofibers were fabricated using the electrospinning technique. The diodes were electrically characterized in air and in vacuum, with and without ultraviolet (UV) exposure. The diodes fabricated using films had a higher rectification ratio and lower turn on voltage compared to those fabricated using nanofibers. Exposure to UV resulted in a higher rectification ratio, and the changes were not reversible. The diode made from the P3HT film was also successfully tested as a half wave rectifier, and the rectification efficiency was 14%. These diodes therefore have the potential to be used as a rectifier and a UV sensor, rendering them multifunctional.

Keywords: P3HT, p-n junction diodes, UV, rectifiers

1. Introduction

The field of organic electronics has largely concentrated on investigating conducting polymers as the active material in basic electronic components like diodes and transistors. A diode is an essential electronic device found in all power supplies and is used to charge cellular telephones. It is a two terminal device that allows current to flow in one direction while preventing it in the other. It is therefore useful in converting alternating current (AC) into direct current (DC) i.e. rectification. This is the current that powers most hand held electronic devices. It is therefore important to study this device and to fabricate it using cheap organic materials. Organic conducting polymers have made it possible to design reliable and inexpensive devices under ordinary laboratory conditions due to their stability and easy of synthesis[1]. Regio-regular poly(3-hexylthiophene) (P3HT) is a commercially available *p*-type semiconducting polymer that is commonly used in electronic devices and sensors[2]. It is used in organic electronics primarily because of its regular end-to-end arrangement of side chains, which allows efficient π-π stacking of the conjugated backbones[3]. Figure 1 shows the chemical structure of this polymer. In this paper, using an *n*-doped silicon substrate together with thin films or nanofibers of P3HT, we fabricated and characterized *p-n* junction diodes. We then compared the operation of the diodes fabricated with P3HT thin films to those fabricated using P3HT nanofibers. The diodes have a rectification ratio of a few hundred and a turn on voltage in the range 0.5V-0.6V and are able to rectify low frequency signals. Some diodes are also seen to be sensitive to ultraviolet radiation. The diodes fabricated using P3HT thin films have higher currents due to their lower bulk resistance. The ability to rectify AC signals and also detect UV radiation is unique to our diodes and makes these devices multifunctional enhancing their use in commercial applications.

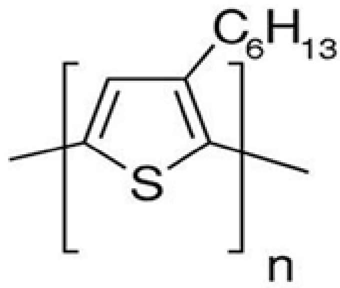

Figure 1. Chemical Structure of Regio-Regular P3HT

2. Experimental Process

The diode construction begins with a heavily *n*-doped substrate that has several lightly *n*-doped layers epitaxially grown over it. Above this lightly doped layered substrate, a 200nm thick SiO_2 layer is thermally grown. Gold (Au) electrodes are pattering over the oxide surface at regular intervals using a thermal evaporator. A window is then etched into the SiO_2 layer away from the Au electrodes in order to expose the lightly *n*-doped Si surface below it as shown in Figure 2(a). A thin film or electrospun fiber of P3HT is then placed as shown in Figure 2(b) over the substrate that makes contact with the Au electrode and the exposed lightly *n*-doped Si layers. The diode is formed at the interface that the polymer makes with the lightly *n*-doped Si. The thin P3HT film was fabricated via drop casting using 2 wt % solution of P3HT in chloroform ($CHCl_3$).

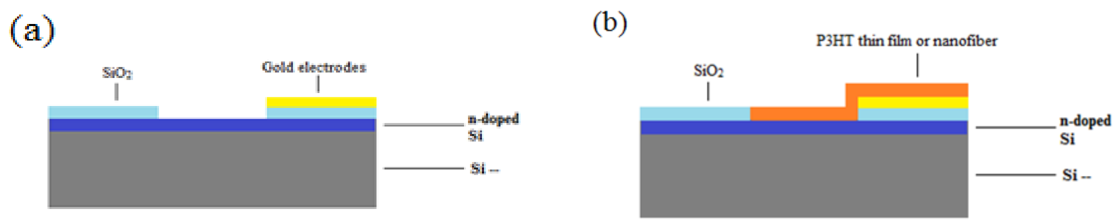

Figure 2 (a) Schematic of a heavily *n*-doped substrate, with an etched window to expose a lightly *n*-doped Si surface. In this way, the P3HT film or nanofiber can be placed as shown in (b), and the diode is formed.

On other hand, P3HT nanofibers were fabricated using the electrospinning technique. Figure 3 shows the basic set-up of the electrospinning apparatus. The P3HT solution with a small amount of polyethylene oxide (PEO) is placed in the hypodermic needle that is then placed on a syringe pump. PEO is a non-conducting polymer, and is added to make the 2wt% P3HT/$CHCl_3$ solution viscous and usable in the electrospinning apparatus. The needle is connected to a high voltage power supply. As the pump slowly pushes out the solution, voltage of about 15 kV is applied to the needle. At this voltage, the electric force on the drop that forms at the needle tip overcomes the surface tension and a jet is issued forward toward the grounded cathode. As the solvent evaporates, fine fibers of the polymer are seen to deposit on the cathode. Single fibers are captured on the substrate shown in Figure 2(a) by passing it quickly in a downward sweeping action in the space between the syringe tip and the collector. In this way fibers are seen to stick to the substrate, some of which make contacts to the electrodes as shown in the schematic of Figure 2(b).

Electrical contacts to the device were made using Au wire and silver epoxy. These contacts are made to the Au electrode and the heavily doped Si substrate and constitute the two terminals of the diode. Figure 4 shows an image of the real devices, with a visible SiO_2 layer, Au electrodes, and electrical contacts. Figure 4(a) is the thin film diode fabricated via drop casting, and Figure 4(b), the nanofiber diode. The current-voltage response of the device was measured using a Keithley 6517B electrometer in air and in vacuum and at room temperature. No change was seen in the data taken in air or vacuum. Ultraviolet (UV) illumination was provided by a UVP model UVGL-25 source, a SRS model DS335 synthesized function generator was used for ac signal excitation and that was recorded on an Agilent Technologies model DSO-X 2012A digital storage oscilloscope.

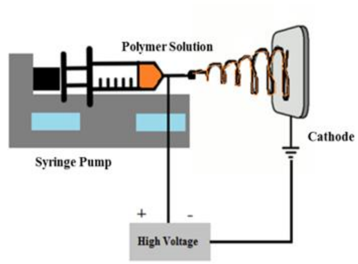

Figure 3. Electrospinning Setup

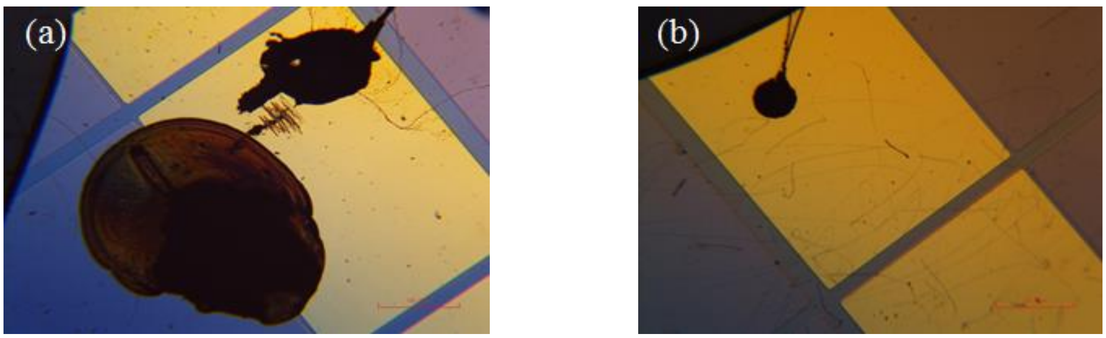

Figure 4. Images of the devices, (a) thin film diode fabricated via drop casting, and (b) nanofiber diode.

3. Results

The plot of the current (I) as a function of the voltage (V) of a P3HT film diode is shown in Figure 5(a), and that for the P3HT nanofiber diode is shown in Figure 5(b). The P3HT film has a lower bulk resistance than the fiber and hence the currents are higher for the film. The graphs shown represent data taken with and without the diode exposed to UV. As seen in Figures 4, the diode conducts current in the first quadrant of the I-V plot and blocks it in the third quadrant as is expected for a diode. In Figure 5(a), when a voltage is applied on the thin film diode, before UV light exposure, the current reached 14 μA at 1V, while the current when the applied voltage was - 1V is 0.07 μA. The rectification ratio, which is defined as the ratio of the current at 1V to the current at -1V, was 198. After UV exposure, when a voltage is applied, the current reaches 14 μA again at 1V. The operation of the diode fabricated from a film therefore has no UV effect in the ON state. The current in the OFF state however was 0.03 μA. Therefore the diode rectification ratio doubled after UV exposure. These results are seen in Table 1. The diode fabricated using a film was less sensitive to UV because the P3HT drop deposited was very thick, so the H_2O cannot be removed completely by the UV[4]. In the nanofiber diode, Figure 5(b), when a voltage is applied, before UV exposure, the current reached 1.6 μA at 1V. It has a rectification ratio of 120. After UV exposure, current decreased to 0.5 μA at 1V, and also the rectification ratio decreased to 59. The nanofiber diode was more sensitive however, because the UV can penetrate the polymer chain and affect charge transport.

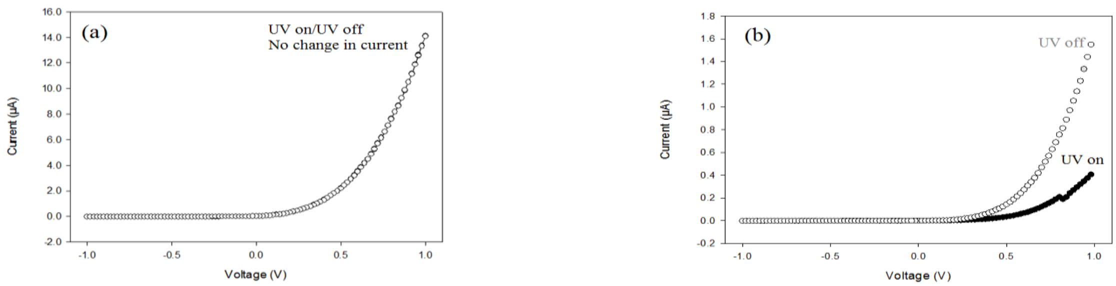

Figure 5. The plot of the current (I) as a function of the voltage (V) of a P3HT film diode is shown in Figure 5(a), and for the P3HT nanofiber diode is shown in Figure 5(b). The graphs shown represent data taken with and without the diode exposed to UV.

A common use of a diode in electronic circuits is for rectification. A rectifier is an electronic circuit that converts an alternating current (AC) signal to direct current (DC), as in power adapters for electronic devices. Figure 6 shows the results of this diode used as a half wave rectifier. The external electrical connections were made to the diode and an AC, 5V peak to peak signal with a frequency of 10 Hz was applied to the diode and a 10 kΩ resistor in series as shown in the inset to Figure 6[5]**.** As can be seen in Figure 6, the output waveform is clipped during the negative cycles and only the positive waveform is allowed to pass through the diode i.e. the diode conducts a current only during the positive cycles of the input signal. The rectification efficiency, defined as the ratio of the DC output power to the input AC power, was ~14%.

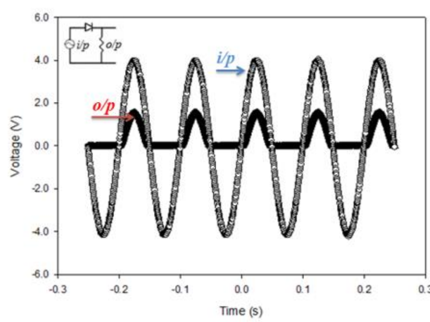

Figure 6. Digital oscilloscope traces of half wave rectification using the p-n junction diode connected in series with a resistor. The input voltage is a 10 Hz, 5V peak to peak wave and the output voltage shows that the negative signal is eliminated. Inset: Circuit diagram using the diode as a half wave rectifier.

To analyze the diode performance, we calculate the ideality parameter (*n*), using the formula:

$$n = \frac{q}{kT}\left(\frac{\partial V}{\partial lnJ}\right) \tag{1}$$

where *q* is the charge of the electron, *k* is the Boltzmann's constant, *T* is the room temperature (300 K), *V* is the voltage applied across the terminals of the diode and J is the current density (current/area) of the P3HT thin film or nanofiber. The ideality parameter (*n*) for an ideal diode is 1 and typical diodes have n > 1. In the thin film diode before UV, *n* has a value of 10.33, and after UV, *n* was 12.25. In the nanofiber diode before UV, *n* was 5.57, after UV, *n* was 8.50.

We believed that these values are high because of humidity and laboratory conditions are not optimal. The turn on voltage was obtained by extrapolating the current in the linear portion of the I-V curve in Figure 5(a) and (b) under forward bias to the voltage axis at zero current. In both diodes, the turn on voltages were not drastically affected in the presence of UV light. It is supposed that as the ideality parameter factor increase, turn on voltage should increase. But in reality this is not the case. The device with a high ideality factor would typically have a lower turn on voltage[6]. The diodes fabricated using films had a higher rectification ratio and lower turn on voltage compared to those fabricated using nanofibers. Also, after UV exposure, changes in both diodes were not reversible. This implies that the devices are UV sensitive, so can be used as a UV sensor. Table 1 below gives a summary of the diode parameters.

Table 1. Summary of Diode Parameters

	No UV presence			UV presence		
	I_{on}/I_{off}	V_{on} (V)	*n*	I_{on}/I_{off}	V_{on} (V)	*n*
Thin Film	198	0.54	10.33	391	0.58	12.25
Nanofiber	120	0.66	5.57	59	0.64	8.50

4. Conclusions

We successfully fabricated diodes using P3HT and *n*-doped Si. The thin film diodes had a higher rectification ratio and lower turn on voltage compare to those fabricated using nanofibers due to their lower bulk resistance. The nanofiber based diodes were more sensitive to UV exposure, because it can penetrate the polymer chain and affect its conductivity. Also, exposure to UV resulted in a higher rectification ratio and the changes were not reversible. The thin film diode was successfully tested as a half wave rectifier, with a rectification efficiency of ~14% at low frequency. The advantage of our device is that it is multifunctional, i.e. it can be used to change AC to DC and it can also be used as a UV light sensor making it more versatile compared to diodes that can only perform rectification.

5. Acknowledgements

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6. References

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