

**AC 2010-292: A NANOTECHNOLOGY APPLICATION FOR PHYSICS
LABORATORY COURSES**

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A Nanotechnology Application for Physics Laboratory Courses

Abstract

Including current research topics into the curriculum is one strategy to engage students in physics courses. We are piloting some innovative laboratory experiments that incorporate aspects of nanotechnology into photovoltaic solar energy conversion devices.

Students produce working devices using conjugated organic polymers. The fullerene, C_{60} , is used as a nanoscale particle and is suspended in the organic polymer solution. The photoactive thin organic films are spin-coated onto glass substrates. The substrates contain a transparent conductive oxide on the surface that acts as an electric contact. The other electric contact is formed by depositing an appropriate metal onto the organic film.

The experimental techniques and equipment used are of broad interest to the engineering and physics communities. The activities are suitable for undergraduate laboratory courses at a variety of levels. The paper will describe the experiments and include some preliminary results.

Introduction

The paper is written so that faculty unfamiliar with photovoltaic devices, and in particular thin film organic polymer solar cells, can incorporate this novel laboratory activity into various physics and/or engineering courses. We believe the laboratory activity provides a valuable context for teaching and learning in the areas of nanotechnology, photovoltaics, elementary and advanced topics in direct current circuits, thin films and the interaction of light and matter. We believe that the device fabrication and subsequent analysis is appropriate for a variety of courses including second semester general physics laboratory courses (typically electricity, magnetism and optics) as well as advanced courses in physics, engineering or both.

First, we present a brief introduction of the physics of thin film organic solar cells incorporating the fullerene, C_{60} . The section is not meant to be a comprehensive review but an introduction to the topic so the uninitiated can successfully, with the aid of the references, explain the topic in sufficient detail. Second, we describe the device fabrication techniques so the processes can be reproduced. Some of the trials and tribulations of the fabrication process are briefly discussed. A brief outline of solar cell characterization is presented along with a student exercise in current-voltage measurement interpretation. We include a section describing an estimate of the photovoltaic conversion efficiency of a typical student-fabricated device. Next, we describe how the activity has been incorporated into an upper level solid state device physics course and also into second semester general physics laboratory courses. We believe it could also be used in an appropriate upper level electrical or chemical engineering course. Subsequently, we describe some future plans for the activity which, along with some other curricula, may culminate in the introduction of a stand-alone nanotechnology course and possibly a minor in nanotechnology.

Device Physics of a Thin Film Organic Solar Cell Incorporating the Fullerene, C₆₀

Shown below in Figure 1 is a schematic representation of a thin film polymer solar cell¹ incorporating the fullerene C₆₀. Commercial glass substrates coated with indium tin oxide (ITO) with a sheet resistance of about 10Ω/□ are used to form the anodes. The fullerene, C₆₀, is suspended, in a measured ratio, into the conjugated polymer MEH:PPV, Poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylenevinylene]. The device structure is completed by depositing the cathode. The cathode is formed by the selective deposition of Wood's metal (Bi_{0.50}Pb_{0.25}Cd_{0.125}Sn_{0.125}) onto the polymer. Since Wood's metal melts at around 80°C it is fairly easy to deposit the cathode.

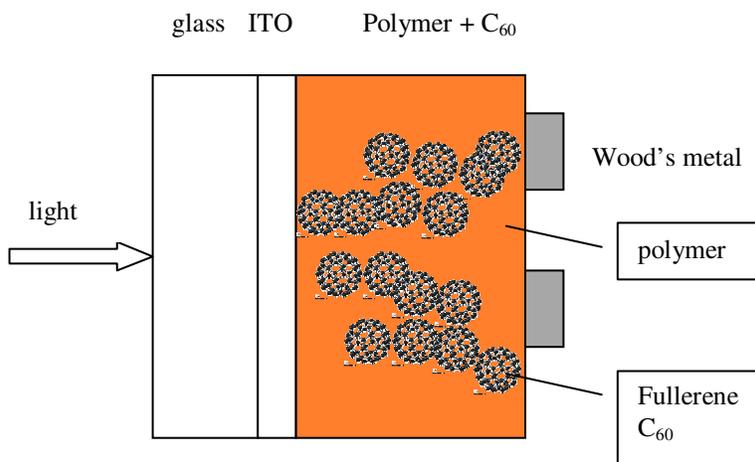


Figure 1. Structure of the thin organic film polymer solar cell with the fullerene C₆₀ suspended. The structure is, of course, not drawn anywhere near to scale.

Conjugated polymers are long chain, high molecular weight compounds with alternating single and double bonds. This particular conjugated polymer is photosensitive. The absorption of a photon can excite an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The energy difference between the LUMO and the HOMO is about the same as the energy of a visible light photon, making the material suitable for photovoltaic device operation. The electron affinity of the fullerene is quite high so if the electron manages to diffuse to the fullerene chain it has a high probability of remaining there. Once on the fullerene chain, the electron becomes mobile and is able to be transported along the chain. On the other hand, hole transport along the conjugated polymer seems to take place via a hopping mechanism.² Charge separation occurs mainly as a result of the difference in work function between the ITO and the Wood's metal. The electrons accumulate at the interface of the Wood's metal while the holes accumulate on the ITO surface. The result, as with the semiconductor pn junction, is the generation of an emf.

The problem with organic devices at present is that there is no strong mechanism to separate the charges, electrons and holes have essentially the same probability to diffuse in either direction. In addition, the polymer has a low dielectric constant, 3-4, compared to about 11.5 for silicon. This leads to electron-hole exciton formation with relatively high binding energies. One strategy to improve performance is to control the morphology upon which the polymer is deposited.³

Thin Film Organic Solar Cell Device Fabrication

We purchased the ITO coated glass slides with a sheet resistance of about $10\Omega/\square$, the MEH:PPV Poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylenevinylene] polymer and the fullerene, C_{60} , from Aldrich for less than \$800. We had chloroform, toluene, hot plates, Erlenmeyer flasks, magnetic stirrers and pipettes on hand.

The device fabrication was performed following the method described by Maldonado⁴, et.al. We dissolved 29.4mg of polymer in 10ml of chloroform and allowed the mixture to stir overnight in a sealed container. The MEH:PPV is not very soluble and we found that magnetic stirring in an Erlenmeyer flask with low heat was desirable. Concurrently, we mixed 0.60mg of C_{60} with 1.0ml of toluene and allowed it to stir overnight in a separate sealed container. It is probably desirable to mix stock solutions of these mixtures to save time. A couple of hours before the experiments were to be performed, the solutions were mixed and about 50% of the solvent was allowed to evaporate. The evaporation process can be sped up by the use of standard rotary evaporation. The weight percent of polymer to fullerene was 98:2.

The ITO coated glass slides are about 25 x 75 x 1 mm, conveniently the same size as standard microscope slides. We used a glass scribe to cut the ITO coated glass into 25mm squares. The devices were produced by spin coating thin polymer films onto the ITO coated slides. The slide was placed on a computer fan with double-sided sticky tape, ITO side up, brought up to speed, and coated with several drops of polymer solution with a glass pipette and rubber bulb. We cut the bottom off of a gallon milk jug to make a splatter shield, as the process can be quite messy when the polymer hits the fan. The apparatus is shown in Figure 2.

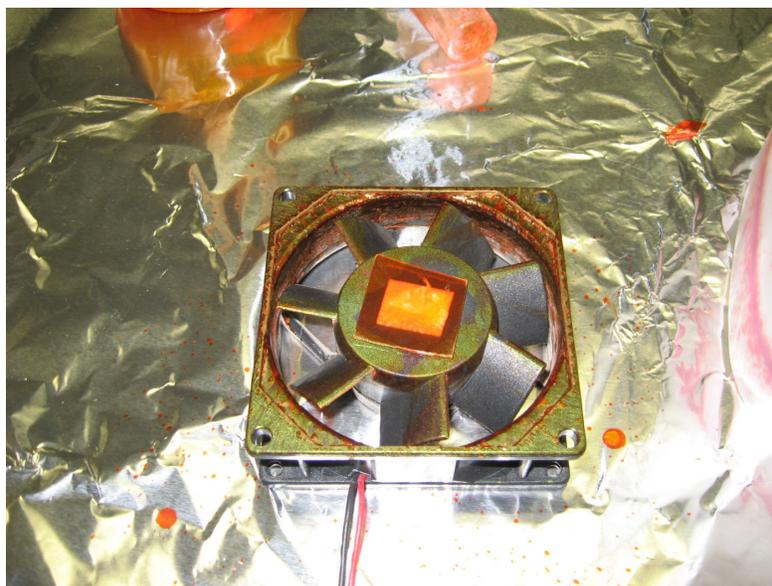


Figure 2. Polymer coated ITO glass substrate attached to the computer fan.

To complete the device structure the cathode must be applied. As stated previously, we have been using Wood's metal due to the low melting point. At the beginning of the laboratory session, we melt several hundred grams of Wood's metal in 150 ml beakers on temperature

controlled hot plates set at about 100°C. We use these beakers because they are tall and thin allowing sufficient immersion of the pipettes. For our purposes, three hot plates were adequate. Students use the glass pipettes like eye-droppers to deposit a droplet of molten metal onto the thin organic film. The droplet freezes quickly and the cathode is formed. Some students put their index finger over the end of the pipette, while others prefer to use a rubber bulb. This seems to be the most difficult part of the fabrication process. If one waits too long to release the metal, it freezes inside the pipette. The pipette can often be salvaged by immersing it back into the molten alloy. We find that it is necessary to have students practice this activity on plain glass microscope slides beforehand. The students use a glass scribe and cut the microscope slides into three 25 mm squares. As an interesting aside, we (re)discovered that Wood's metal expands upon freezing. When we turn off the hot plates and allow the molten metal to freeze, all of the pyrex beakers crack.

Unfortunately, our laboratory does not possess the equipment necessary to generate a complete current-voltage characteristic of a working device, the currents are too small. We have recently purchased for a Keithley 2400 source meter with the GPIB (general purpose instrument bus) capability to facilitate such measurements. At the present time we can only measure the V_{oc} and the I_{sc} of a device. The devices are tested by placing them over a light source and measuring the V_{oc} . It has been our experience that many devices exhibit open-circuit voltages of between 200-300 mV. The measurement process is shown in Figure 3. The light source we used was a ray-tracing box common in many introductory laboratories.



Figure 3. Measuring the V_{oc} of a thin film polymer solar cell incorporating the fullerene C_{60} .

Experimental Results

We wish to estimate the efficiency of one of our working devices. As stated above, since we cannot measure the current-voltage characteristic we need to make some approximations which will be discussed below. In addition, we lack the ability to accurately measure the solar radiation

at the location of the solar cell. Instead, we used an optical pyrometer located on the roof of an adjacent building.

Suppose one has a photovoltaic device with what one generally considers the worst current-voltage characteristic possible, a straight line (It is possible to have a worse characteristic, but this is a pathological condition and will not be considered here.) Let the current-voltage characteristic be represented by,

$$I(V) = mV + I_{sc},$$

where I is the current, V is the voltage, m is the slope and I_{sc} the short-circuit current. The power is given by $P = IV$ so,

$$P = mV^2 + I_{sc}V.$$

The maximum power, P_{max} , is determined by the condition,

$$dP/dV = 2mV + I_{sc} = 0,$$

or,

$$V_{max} = -I_{sc} / 2m.$$

The current at the maximum power point is given by

$$I_{max} = m V_{max} + I_{sc} = m (-I_{sc} / 2m) + I_{sc} = I_{sc} / 2.$$

Therefore,

$$P_{max} = I_{max} V_{max} = (I_{sc} / 2) (-I_{sc} / 2m) = -I_{sc}^2 / 4m.$$

The V_{oc} is given by,

$$0 = mV_{oc} + I_{sc},$$

so that,

$$V_{oc} = -I_{sc} / m.$$

Therefore, under the worst case scenario of a linear current-voltage characteristic, the fill factor, ff , is given by,

$$ff = P_{max} / I_{sc}V_{oc} = (-I_{sc}^2 / 4m) / (I_{sc} \times -I_{sc} / m) = 0.25.$$

Our results under outdoor illumination of approximately 80mW/cm^2 were: $I_{sc} = 0.2\mu\text{A}$, $V_{oc} = 0.28\text{V}$, and $ff = 0.25$. This corresponds to a maximum power of, $P_{max} = 1.4 \times 10^{-5}\text{mW}$. We measured the Wood's metal cathode area to be 0.07cm^2 . The cathode surface area defines the active area of the photovoltaic device. We estimate the device efficiency to be $2.5 \times 10^{-4}\%$. While this number is quite low, we hold an optimistic view and regard this experiment as one where large gains are possible.

Upper Level Physics Course Activities

Last year, for the first time, we introduced this activity into a junior level physics course. The course, Solid State Device Physics (PHY 3680) is taught once a year and is required for all electrical and computer engineering students and is an elective course for other science and

engineering majors. The course covers standard topics such as crystal structure, energy band theory, electron and hole transport, and their application to structures such as the pn diode, and bipolar (BJT) and field-effect (FET) transistors. A brief discussion of photovoltaic devices is included in the section on the pn diode.

During the summer of 2009 we decided to reduce the BJT content and spend two 75 minute periods fabricating devices in the laboratory. We found that the 150 minutes, allotted over two class sessions, was enough for each student to produce at least one working solar cell and perform electrical measurements. The measurements were performed with a Keithley digital multi-meter for voltage measurement and a Keithley pico-ammeter for short-circuit current measurements.

Students responded favorably to this hands-on activity and indicated that it was the highlight of the course. This summer we plan to expand the activity with a homework assignment that includes current-voltage characteristic analysis along with problems related to the concept of sheet resistance and the necessity for current carrying grids. The derivation of the 0.25 fill factor, presented earlier, should be a suitable problem for upper level physics or engineering students. To understand solar cell operation and device optimization it is important for students to investigate the relationship between sheet resistance and resistivity. Many students are surprised to find that the sheet resistance (Ω/\square) is a useful quantity because it is independent of the size of the square. Topics including optical absorption and anti-reflection coating are appropriate at this level. With the acquisition of the Keithley 2400 source-meter we intend to have students measure and characterize the full current-voltage characteristics of their devices. We are also purchasing equipment to measure the total spectral irradiance. In the future we plan to acquire a spectrometer to allow students to measure both the incident light spectrum as well as the absorption in the thin organ film.

Second Semester General Physics Course Activities

In the fall of 2009 the solar cell fabrication laboratory was introduced into two of our second semester general physics laboratory courses; one of which is algebra based (PHY 1330) while the other is the laboratory associated with the calculus based course (PHY 1630). The activity and all measurements were performed during a single three hour laboratory session. Students had adequate time to fabricate and perform device measurements.

By producing working devices students are exposed to several important concepts typically covered during a second semester general physics course such as: the *two-endedness*⁵ of an electrical component, emf, voltage, current, power, current-density, resistance, and the proper use of electrical meters. They view these concepts in the context of a working solar cell incorporating nanoscale components. In addition, they observe a fundamental interaction between light and matter in specific material structures; namely the conversion of light energy into electrical energy in a thin film nanoscopic structure. Topics such as radiance and light intensity can be reinforced in the laboratory by making appropriate measurements.

Like a voltaic cell, a photovoltaic cell generates an emf. The power it delivers to the load depends on the illumination and the external circuit conditions. To illustrate this behavior to

students, they were shown a realistic current-voltage characteristic and asked to identify important device performance parameters. It is critical to note that while the characteristic was realistic, it was generated by an equation to facilitate computation. The characteristic is shown below in Figure 4.

The current-voltage characteristic shown in Figure 4 was generated using the standard solar cell equation⁶

$$I(V) = I_0 e^{\beta V} + I_L,$$

where $I_0 = 10^{-10} \text{A}$, $\beta = 9.05 \text{V}^{-1}$, and $I_L = 4 \text{A}$. The parameters were selected to facilitate computation. The graph in Figure 4 does not represent data from a real device; however the parameters are realistic for a high efficiency, multi-junction solar cell operating under a concentration of 30 suns. Another advantage of simulating the data is that it can be readily changed for different student groups. A simple spreadsheet facilitates the calculation of all important parameters.

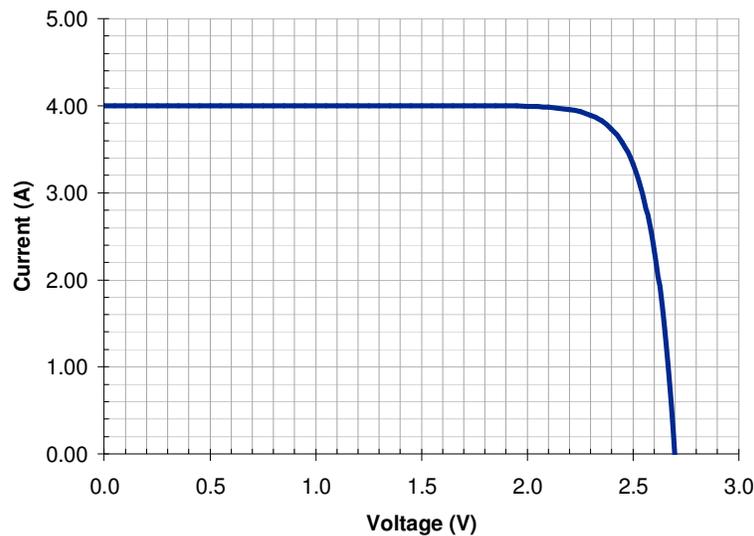


Figure 4. Simulated current-voltage characteristic used to ascertain device performance parameters. It is assumed that the illumination is 30 suns.

The most significant figure of merit for a solar cell is the conversion efficiency defined by the ratio P_{max} / P_{in} . Other electrical parameters are useful in the characterization such as I_{sc} , V_{oc} , I_{max} , V_{max} and the fill factor, ff . The short-circuit current, I_{sc} , is the current when the terminals are shorted, while the open-circuit voltage, V_{oc} , is the voltage when the terminals are open. I_{max} and V_{max} correspond to the current and voltage at the maximum power point. The fill factor, ff , is defined by

$$ff = \frac{V_{max} I_{max}}{V_{oc} I_{sc}}.$$

The device parameters for the graph shown in Figure 4 are given in Table 1. Students were asked to calculate the relevant parameters. The results were that 25 of 27 (93%) students were able to correctly identify all of the parameters except for the fill factor. Two students incorrectly

wrote down the fill factor as being numbers between 2 and 3. It is completely unclear where those numbers came from. Of course not all students found the exact same values for I_{max} and V_{max} but this is to be expected since they must select points off of the graph.

P_{in} (W)	P_{max} (w)	V_{max} (V)	I_{max} (A)	Fill factor	I_{sc} (A)	V_{oc} (A)	Efficiency (%)
50	9.00	2.35	3.83	0.833	4.00	2.70	18.0

Table 1. Device performance from simulated current-voltage characteristic in Figure 4.

Conclusions

We have adopted an innovative laboratory experiment that incorporates aspects of nanotechnology into photovoltaic solar energy conversion devices. We believe that this activity can provide a valuable context to incorporate state-of-the-art research topics in nanotechnology into the undergraduate curriculum. The activity is interdisciplinary in the sense that concepts from physics, chemistry, and engineering are introduced. We performed this activity in two types of physics courses; several sections of a second semester general physics laboratory and also a junior level course for electrical and computer engineers, Solid State Device Physics (PHY 3680). The student responses were overwhelmingly positive and it was apparent that they were enthusiastic about participating in a project involving state-of-the-art research. Even without having access to expensive fabrication equipment, students were able to produce a working photovoltaic cell. The devices incorporate important aspects of nanotechnology such as long chain conjugated polymers and the fullerene, C_{60} . The laboratory equipment is inexpensive and the experiment can be readily replicated at other facilities. We believe that this experiment can become one of the foundational topics to be incorporated into a broader, more interdisciplinary course in nanotechnology.

Bibliography

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- ⁵ To understand the difficulty students have in this area, see for example, Arons, A.B., *Teaching Introductory Physics*, John Wiley & Sons, New York, NY, 1997.
- ⁶ See for example, Donald A. Neamen, *Semiconductor Physics & Devices Basic Principles*, 2nd, Irwin, McGraw-Hill, Boston, 1997, pg. 285.