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A Simple Organic Solar Cell

Gordon Patrick Whyburn

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This experiment attempted to create an organic solar cell using a simple spin coating technique. This was to be done using ZnPc and C₆₀ dissolved in chloroform. However no working solar cell was made. This was probably due to problems with dissolving the solutes in chloroform which led to aggregation and incomplete coverage of the slides during the spinning process. This problem with spinning also caused problems with data collection which slowed the process down. Despite this with further testing and a different solvent it may still be possible to make a working solar cell using the proposed materials and technique.

Chapter 1

Introduction

1.1 Motivation

Finding renewable sources of energy is becoming an increasingly important component of scientific research. Mounting interest over the past few decades can be attributed to two major problems facing the world today. The first is the rapid growth in the demand for energy associated with the development of many third world countries, such as China and India. Their large populations coupled with rising per capita energy demands is leading to a sky rocketing demand for global energy. Greater competition for existing sources of energy has strained the world's supply and demand balance and has increased the prices of traditional sources of energy such as oil, coal, and natural gas (13).

What many believe is a more important motivation for finding renewable energy sources is protection of the environment. With mounting evidence that carbon released into the atmosphere through the burning of hydrocarbons is causing global warming and potentially catastrophic climate change, the need for finding alternative energy sources that do not release carbon is critical. While the possibility of climate change and the possible effects from such change remain debatable, it is widely agreed that the pollution from the burning of fossil fuels has caused other problems as well. These include the destruction of the upper ozone layer, critical for protecting the earth from deadly solar radiation, as well as other environmental problems such as air pollution and habitat loss. These and other externalities from the use of carbon-based fuels have a substantial negative effect on the quality of life of both current and future generations (13, 10).

Many possible sources of environmentally-friendly renewable energy exist, including wind, geothermal, and even tidal energies. While each offers a way to reduce dependence on nonrenewable sources, none can offer enough energy to satisfy the $4.6 \cdot 10^{20}$ joules the world currently uses annually. The one source of renewable energy that has the potential to completely replace nonrenewable sources is solar energy. In about one hour the sun delivers enough energy to earth to meet global energy demands for one year (13,15).

Capturing solar energy can be accomplished in several ways. Research is being conducted in areas such as using sunlight to heat water or to run heat engines that generate electricity. Other research efforts are exploring the development of artificial photosynthesis in order to directly create fuel from sunlight much like plants. This paper, however, focuses on the use of photovoltaic cells or solar cells, devices that turn sunlight directly into electrical energy. They are made from semiconductors, typically silicon; their current efficiencies are around 30% in a laboratory using multiple junctions and more expensive materials such as Gallium arsenide but is only about 18% for solar cells in general use. (12, 15)

1.2 Solar Cells

A major problem with solar cells today is that they are not as cost efficient as conventional sources of energy. To overcome the financial hurdles, research is being undertaken to both raise the efficiency of solar cells and identify and commercialize the use of lower cost materials. While silicon works well in solar cell applications, it requires a considerable amount of energy in its fabrication into crystalline wafers; the cost of silicon wafers has led many researchers to search for different materials to use as the basic semiconductors in solar cells. For this reason, interest in the use of thin film (around 100nm thick films) organic materials has been growing. The current boom in nanoscale science has given researchers new fabrication techniques, new materials, and new methods of probing materials that allow unprecedented control over the structure and dynamics of solar cells, and the opportunity to greatly enhance their efficiencies (15). Thus, in addition to being very inexpensive relative to silicon, organic thin films offer many avenues in which efficiency can be increased. Currently efficiencies of up to 5% have been reported; however with strict control over the morphology through use of emerging technologies in nanoscale science, efficiencies are expected to rise over the next decade eventually resulting in solar cells that are economically viable (15).

While they operate under the same principles as conventional silicon solar cells, organic solar

cells have a number of differences. Organic semiconductors have a stronger absorption coefficient and therefore require far less material to absorb the light. However organic thin films only absorb at the lower end of the spectrum, visible light (rather than a larger spectrum of light that would enable more energy to be captured by the solar cell). They are also very poor charge carriers, which leads to small diffusion lengths that cause problems with charge carriers being trapped or reabsorbed. Another major problem is that organic thin films have large band gaps, on the order of 2 eV, and layers must be very thin in order for the light to retain enough energy to create charge separation. This constraint, however, helps overcome the problem of charge carriers as the thickness will be on the same order of magnitude as the diffusion length (9, 10). It is widely believed that the chemical flexibility of organic systems is enough to compensate for these problems and good efficiencies between 10-15% are still possible.

1.3 Experiment

The experiment discussed in this paper is one designed to identify and build an inexpensive and simple method for creating an effective organic solar cell. The experiment attempts to improve on a previous study done by Taima et al (5). This research used a system of Zinc Phthalocyanine (ZnPc) and Buckminster Fullerene (C_{60}) (figure 1.1) and analyzed the effect of adding an active region of a 1:1 mixture of C_{60} : ZnPc. Without changing the thickness of the cell, they found that adding the mixed active layer increased the efficiency of the solar cell up to about the thickness of the diffusion length, after which point further thicknesses led to a drop off of efficiency. The experiment eventually obtained a power conversion efficiency of 1.5% (5).

Both ZnPc and C_{60} are commonly used materials for thin film solar cells, and as such are relatively cheap and easy to obtain. Both materials have relatively long diffusion lengths compared with other polymers being $30\text{nm} \pm 10$ for ZnPc and $40\text{nm} \pm 5$ for C_{60} (4). An exciton is a bound pair of an excited electron and positive hole. These longer diffusion lengths allow for the acceptor materials to be larger and act as a spacer moving active layer, the layer absorbing the light and creating charges, further into the cell. This structure has the effect of putting the active layer in a region of higher optical field intensity. Materials such as C_{60} with a large index of refraction have an active layer that does not need to be very thick, as the position of the maximum optical field intensity is at $1/(4n)$ from when the light enters the material. With careful control of layer thickness this property could allow for the active region to be both thick and placed in an area of maximum

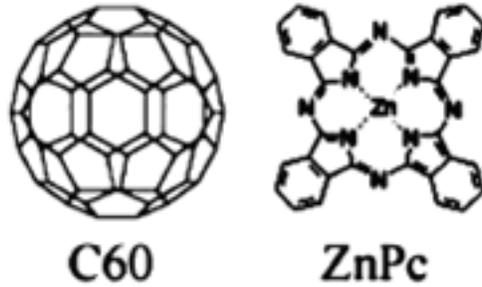


Figure 1.1: Zinc Phthalocyanine (ZnPc) and Buckminster Fullerene (C_{60})

optical field intensity, increasing the overall efficiency of the cell (4).

In addition the spectral absorbances of the two materials do not overlap very much, with ZnPc being most absorbent at extremes and C_{60} being absorbent through most of the middle of the visible spectrum (figure 1.2). This combination allows for a wider range of the spectrum to be converted into energy, increasing the absorbance efficiency. Another way to increase efficiency is to have a material that absorbs in the blue end of the spectrum on the side of the metal film to increase excitation generation near the DA interface (4). This can be done easily by putting the ZnPc on the metal film side.

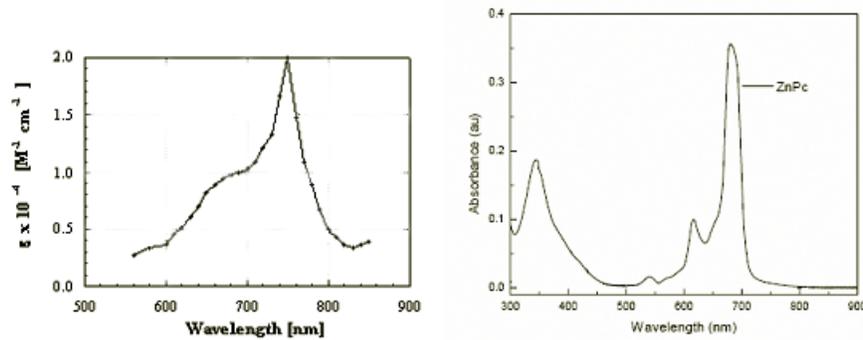


Figure 1.2: Left: Absorbance Spectrum of C_{60} Right: Absorbance Spectrum of ZnPc (4)

In an experiment similar to Taima et al, Sullivan et al (2) used the same set up, with the exception of using CuPc instead of ZnPc and found that by adding active layers of varying ratios and creating

something similar to a gradient (figure 1.3), efficiency was improved; a power conversion efficiency of 1.17% was obtained, close to that of Taima et al. This result was attributed an increase in charge transport efficiency from charges driven to the appropriate electrode by the gradient (2).

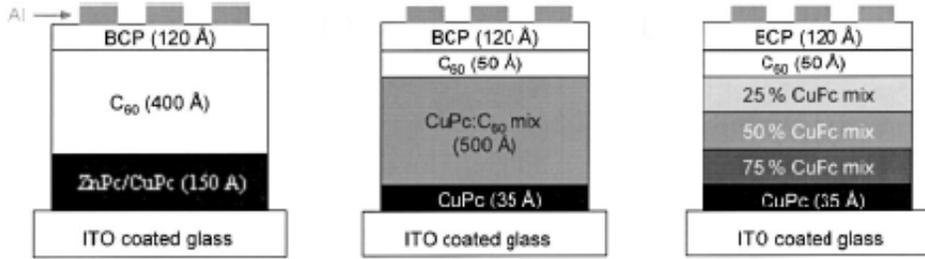


Figure 1.3: Left: Solar cell with only no mixed region. Center: Solar cell with a 1:1 mixed region. Right: Solar cell with regions of different ratios. Moving from left to right it was found the designs were found to have greater efficiencies (2,5)

This finding follows the theory that creating a gradient charge separation should greatly improve efficiency as the excitations will not have to travel as far before they enter a region that will keep them from recombining. A gradient may also help with charge transport as it will help keep charges from becoming stuck at some point in the cell. Improvements in both of these areas should proportionally increase the cells' overall efficiency and therefore are important areas for potential improvement (1, 2).

To increase the efficiency of a solar cell made from ZnPc and C_{60} , therefore, requires the creation of a mixed active layer to improve excitation creation and the formation of a gradient to help with charge separation and charge transport. While Sullivan et al's method could be used to meet both these goals, some problems remain. Because there is no control over the internal structure of the mixed layer, the process relies on random chance to create a clear path for the excitations to move through the active region. What most likely happens is that there are islands of one material surrounded by another. This causes problems when the excitations enter these regions and have no way to continue moving to an electrode; they become trapped and eventually recombine (9).

To fix this problem it would be ideal to create a diffuse heterojunction or a bilayer of two different materials that can diffuse into each other. If the heterojunction can be made in such way that the ratio of D/A material is not constant and a gradient is formed, and uninterrupted paths to the electrodes remain, the problems encountered in previous experiments would be significantly

reduced. To create such an ordered system imprinting with lithography would have to be used which can be rather complicated and could end up being expensive (figure 1.4).

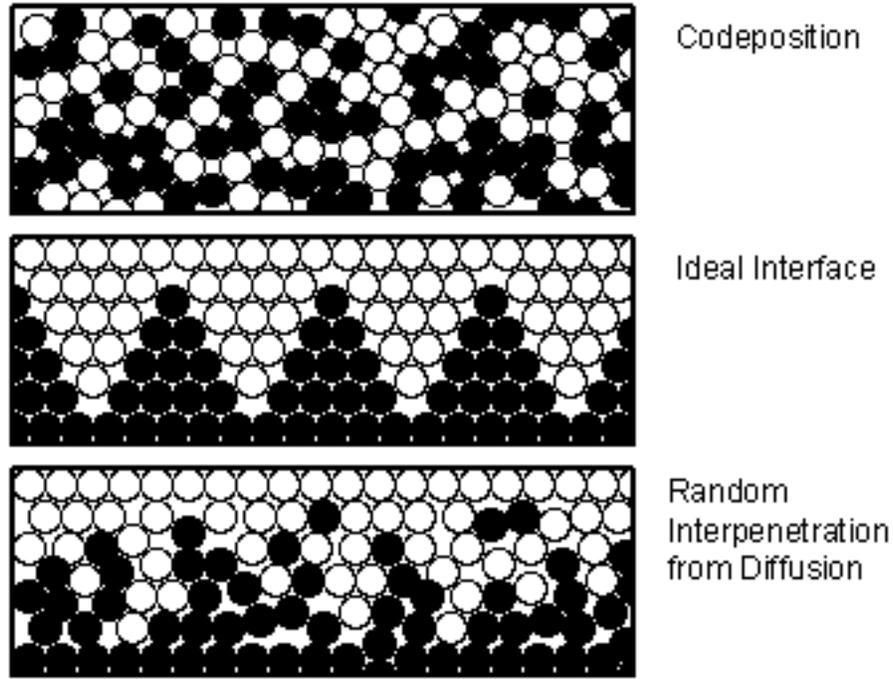


Figure 1.4: Diagrams of different morphologies of the active region of a solar cell

Instead we attempt to create this system, albeit less ordered, using the inexpensive and easy technique of spin coating. It is possible that if one of the materials is spun onto the other using a solvent that dissolves both materials, they will diffuse into each other, creating a gradient and still leaving uninterrupted paths. Some control over the depth of the diffusion could be obtained through use of different solvents and different spin speeds. If these controls are sufficiently precise it even may be possible to have the two layers diffuse to the exactly or nearly to the diffusion length of the excitations and maximize the efficiency of the system. If this technique works it should improve on the efficiency of the cells made by Taima et al and create an inexpensive and relatively effective solar cell.

Chapter 2

Theory

2.1 Solar Cells

Organic solar cells follow most of the same steps and processes of inorganic photo voltaic cells. Both create electric current and voltage from light by going through four steps (figure 2.1). The first is absorption of light normally by a semiconductor, this will generate an exciton, or a hole and electron pair bound together by a weak binding energy (16). Next the exciton will diffuse around the material until it reaches a region where the third step, charge separation or quenching can occur, this will normally be at the donor acceptor (DA) interface. In quenching the electron and the hole are fully separated from each other as the electron will enter a lower energy state in the acceptor material. From here the hole and electron must travel to their respective electrodes in what is called charge transport (9).

While the steps may seem easy there are numerous problems that cause losses in efficiency at each step. Organic semiconductors normally have a high band gap and therefore only absorb light at lower wavelengths, and even at lower wavelengths many only have a small effective range of absorbance, which results in fewer excitons being generated. Once the excitons are generated they diffuse around the material, but if they do not find an acceptor they will quickly recombine. This means that any exciton created further from the DA interface then its diffusion length will not contribute to the overall efficiency (9) .

If the exciton does manage to split there is still a chance that the electron will find itself entering the donor region again and finding a hole and recombining anyway. This can be caused by the DA

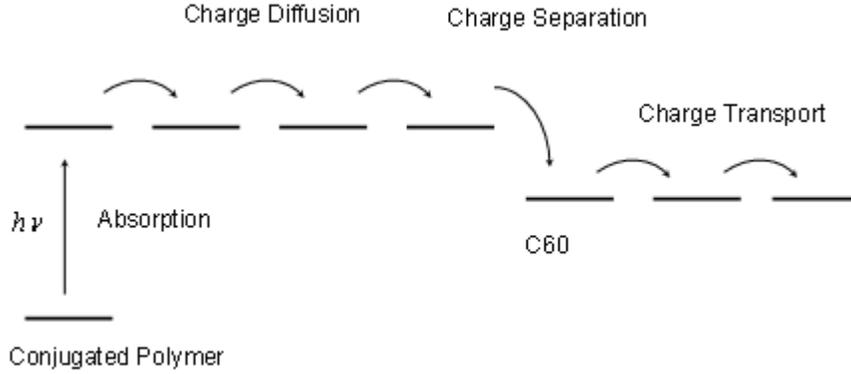


Figure 2.1: Diagram of charge generation in a solar cell

interface being too intermingled, so although the exciton can easily reach the acceptor material it will also be easy for it to be drawn back into the donor material. Another common problem is that the acceptor material does not have an uninterrupted path to the electrode and the electron will be unable to make the journey ending up trapped and eventually recombining. Currently organic solar cells suffer from many of these problems more than their inorganic counter parts which accounts for the much lower overall efficiencies (9.).

The overall efficiency of a solar cell is called the external quantum efficiency given by the number of electrons gathered by the electrode over the number of photons hitting the cell.

$$\eta_{EQE} = \frac{J/q}{\frac{1}{2}c\epsilon_0 * |E_0^+|^2}, \quad (2.1)$$

this result is directly proportional the efficiency of each step, therefore

$$\eta_{EQE} = \phi_A * \eta_{ED} * \eta_{CT} * \eta_{CC}, \quad (2.2)$$

were η_A is the efficiency of the absorbance η_{ED} is the efficiency of the diffusion to the DA interface, η_{CT} is the efficiency of charge transport, and η_{CC} is the efficiency of the charge collection (4). From this we see that any increase in any of these areas will have a directly proportional increase in the overall efficiency.

In many systems η_{CT} and η_{CC} are typically near 100%, assuming that the charges do not become

trapped or recombine after the exciton is separated (4), and so the equation can be simplified to some extent by saying.

$$\eta_{EQE} \approx \eta_A * \eta_{ED}, \quad (2.3)$$

So when making a solar cell it is important to try and improve these areas. Improvement in the efficiency of absorbance can be done in two main ways, picking materials with good absorbance spectrums and making the cell thicker, although there are other techniques such as creating a system that allows for the light to make multiple passes through the cell. Efficiency of diffusion to the DA interface can be improved by using materials with larger diffusion lengths and also by making the active region smaller which directly competing with the need to make the cell thicker to increase the absorbance efficiency (4). While it may be possible to find materials with both good absorbance and large diffusion lengths in order to maximize the efficiency the thickness of the cells layers should be calculated before hand. Work has been done that has found that increasing the thickness of the active region of a solar cell will increase the overall efficiency until it is as thick as the diffusion length of the material before falling off (5,2).

Mathematical modeling has also been done backing up these experimental results using a simple drift-diffusion model Martin et al found that for a heterjunction system that there is an optimal thickness for a mixed active region. This was due to give and take between charge generation at the DA interface and recombination. They found increasing surface area does increase efficiency if thickness is not changed but increasing the thickness of the mixed layer will peak and drop off. Where this peak is will change from device to device based on materials used, the morphology of the mixed region, and conditions but is believed to always be around that of diffusion length of the material, agreeing with experimental results (1).

From this we see that in order to get the best efficiency out of a solar cell particular care must be taken in picking the materials such that they have good absorbance over as broad a range as possible and still have long diffusion lengths. It is also important to try and control the thicknesses of the different parts of the solar cell such that the maximum field intensity is in the active region of the cell and that the active region is about as long as the diffusion length of the materials it is made of. While it is also important to increase the surface area of the DA interface it is important to not that it is possible to go too far and lose efficiency due to reabsorbance of electrons that had already been quenched.

2.2 Ellipsometer

Ellipsometry is an optical technique that uses reflection of polarized light to study a material's optical properties. The basic principle behind it is that when light is reflected off the surface of a material it will undergo a phase shift (δ) and change in amplitude (r). Both δ and r depend on the properties of the material, among other things the angle of incidence (θ), the refractive index (n), the extinction coefficient (k), the thickness of the material (t), and the polarization of the incident beam.

The angle of incidence is defined in the case as the angle between the normal and the incident beam, which is different from some other techniques. The refractive index is a measure of the speed of light in the material and is defined as

$$n = \frac{c_{vac}}{v_{mat}}, \quad (2.4)$$

Where c_{vac} is the speed of light in a vacuum, commonly said to be $3 * 10^8 m/s$, and v_{mat} is the speed of light in the material. The extinction coefficient is a measure of the penetration depth, d_p of the light into the material and is given by

$$d_p = \frac{\lambda}{4\pi * k}, \quad (2.5)$$

Where λ is the wavelength of light in a vacuum. Light can be linearly polarized in two ways, if it is polarized parallel to the plane of incidence it is called p-polarized light if it is polarized perpendicular to the plane of incidence it is called s-polarized light. Phase shifts and amplitude changes are different for the two different polarizations.

It is not possible to find the absolute values of δ and r from ellipsometry however it is possible to find $\delta_p - \delta_s$ and r_p/r_s . These values are called ellipsometric parameters and are defined as

$$\Delta = \delta_p - \delta_s, \quad (2.6)$$

and

$$\tan\psi = \frac{r_p}{r_s}, \quad (2.7)$$

An ellipsometer's basic set up can be found in figure 2.2. Laser light is sent through a polarizer then reflected off a thin film through an analyzer and then measured by a light detector.

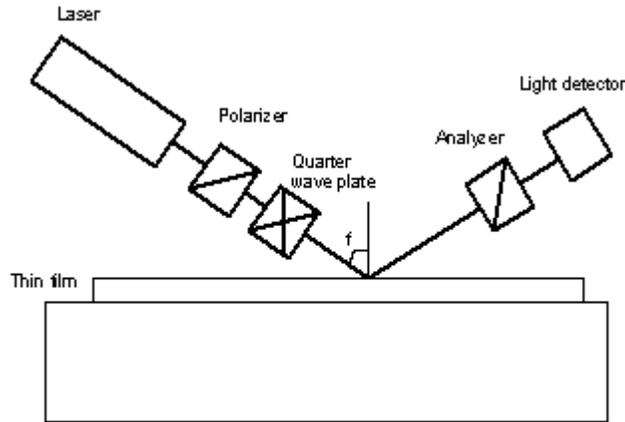


Figure 2.2: Diagram of charge generation in a solar cell

The way a measurement is taken by finding the minimum signal on the light detector by rotating the polarizer and analyzer. The first step is to rotate the analyzer slowly in the range 0 to 90 degrees and find the minimum reading. Next rotate the polarizer within the range 315 to 135 degrees until you get a new and lower meter reading. Repeat these first two steps until the meter has been minimized (the numbers may vary for different ellipsometers these are the one used for a Gaertner Scientific *Waferskan_{TM}* L115B).

Once this has been done the values of the angles are recorded as A_1 for the analyzer and P_1 for the polarizer. To obtain the second set of drum readings A_2 and P_2 add 90 degrees to P_1 and subtract A_1 from 180. From these new values once again minimize the meter reading until you get A_2 and P_2 as they will not be exactly at the calculated values. From here Δ and ψ can be found using the following equations

$$\Delta = 360 - (P_1 + P_2) \quad (2.8)$$

$$\psi = \frac{180 - (A_2 - A_1)}{2} \quad (2.9)$$

If $(P_1 + P_2)$ is greater then or equal to 360 degrees subtract 360 degrees from it before using the equation.

For our purposes we used the software that came with the ellipsometer to calculate the thickness. Since the index of refraction and angle of incidence are known we simply plugged in all known values along with ψ and Δ and had it calculate the value of t . (17)

Chapter 3

Experimental Method

3.1 Materials

99.5% pure buckminster fullerene C_{60} was bought from MTR ltd. From Sigma-Aldrich we obtained 97% pure zinc phthalocyanine (ZnPc), at 632.15nm it has a refractive index of about 1.63 and an extinction coefficient around 4 (17). From Aldrich we also received 96% pure 2,9-dimethyl-4,7-diphenyl-1,10phenanthroline (BCP), and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (Pedot:PSS). The ITO slides were obtained from the physics department and were left from a previous thesis on OLEDs done by M Talkinson.

3.2 Equipment

The Ellipsometer used was a *Waferskan_{TM}* Ellipsometer L115B purchased from Gaertner Scientific Corporation. It was used manually as described in the theory section and has a He/Ne laser with a wavelength of 632.15 nm. Preliminary testing using the manual method found a thickness of 953Å on a 1000Å standard sample, which was an acceptable range of accuracy for our purposes. The spinner was a model WS-400B-6nPP/Lite purchased from Laurell Technologies Corporation. The evaporation system was custom built by David Tanenbaum it is capable of a vacuum under 10^{-6} torr and uses a high current power supply to vaporize the material by heating a Tungsten boat containing the material, see figure 3.1. The AFM was a Dimension 3000 bought from Digital Instruments, all measurements were done using tapping mode using TSPA7 Atimony doped silicon tips bought from

Veeco.

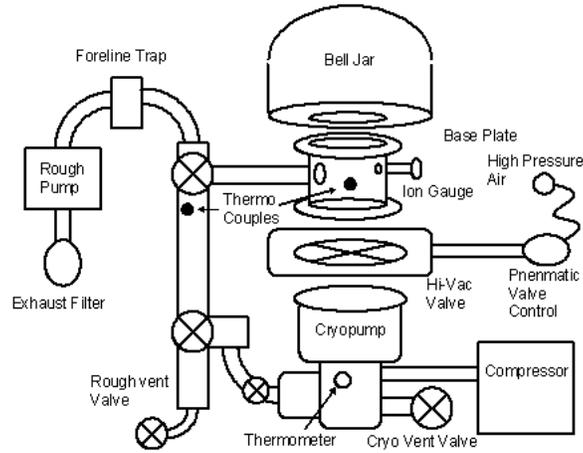


Figure 3.1: Schematic of Evaporator

3.3 Objective

Our preliminary goal is to create a working solar cell as a proof of concept and from there we could try to improve it with any remaining time. The structure we were are trying to get (figure 3.2) will ideally have about 50nm of ZnPc covered by a 50nm layer of C_{60} with the intermingling layer in between not changing the thickness. Between this region and the aluminum electrode it has been shown that adding between 5 and 12nm of BCP will improve efficiency by acting as an exciton blocker, keeping the wrong charges from reaching the electrode, and protect the cell from the hot aluminum (2,5). The thickness of the aluminum electrode does not matter so much but should be between 100 and 200nm. A Pedot:PSS layer is also often used as it can act as an exciton blocking layer and may help in conduction (2,5). This structure would be ideal but it is unlikely that we will obtain it on the first trial and as we are simply trying to get a working solar cell and will not overly concern ourselves with exact thickness.

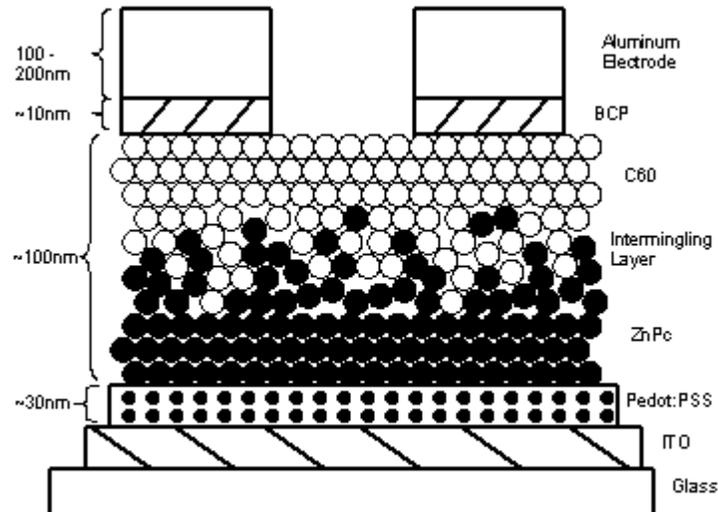


Figure 3.2: Diagram of an Ideal Solar Cell made using this Method

3.4 Preparation of Samples

All solute samples were weighed out beforehand had and the solvent was measured using a one milliliter pipet. Before spinning all samples were put in a sonicator for a minimum of five minutes. All slides were ITO covered glass and were cleaned while on the spinner using ethanol and acetone. The solutions were pipetted onto slide before spinning commenced, except were otherwise stated. Spinning commenced as soon after placing the sample on the slide as possible.

3.5 ZnPc

Spinning ZnPc was done by dissolving it in chloroform as previous work has had success doing this (7). That experiment used a concentration of 12mg/ml at 2000 rpm and so we started are testing around these values. As a preliminary test we measured the thickness of the ITO using the ellipsometer. Using an index of refraction of 1.7 we got a value of 160.3nm, for all subsequent testing with the ellipsometer we had it calculate the thickness values with a 160nm layer with an n of 1.7 and a substrate with an n value 1.52 (glass) underneath it.

The first experiment was a test to find the difference in concentration and film thickness. This

was done with five samples ranging between concentrations of 15 mg/mL and 4 mg/mL. The speed was set at 2000 rpm and left for 30 seconds for each sample, the glass slides appeared to be tinted blue so we believed we had a film on the slide. We found a very small relationship between concentration and thickness, a little over 4\AA per mg/mL of ZnPc (figure 3.3).

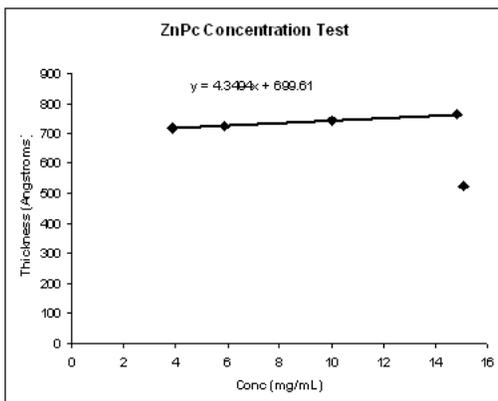


Figure 3.3: Graph of ZnPc Spun at 2000 rpm at different concentration

Using what was left of the 10 mg/mL sample we conducted a speed test taking samples at 2000, 3000, and 4000 rpm for 30 sec. This resulted in no meaningful correlation as you can see in figure 3.4. We did find that our results were not consistent between the concentration test at this concentration and the speed test at 2000 rpm with it changing from 742\AA to 665\AA .

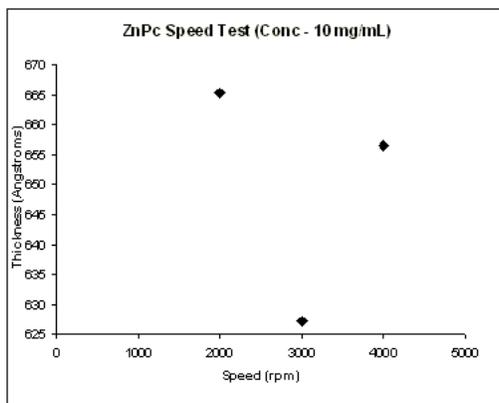


Figure 3.4: Graph of ZnPc solution with a concentration of 10 mg/mL spun at different speeds

Because we wanted more control over the thickness of the ZnPc layer we decided to see if varying the amount of solution put on the slide before spinning would affect any change. Although we doubted that this was the case we decided to test it anyway and using a pipet added between .1 and .05 mL onto the slide and then spun it at 2000 rpm for 30 sec, the ZnPc had a concentration of 9.5 mg/mL. This also gave no meaningful correlation, figure 3.5. We made two slides using the same concentration and found that they agreed well with each other, only being different by 30Å however none of rest seemed to vary more then we expected.

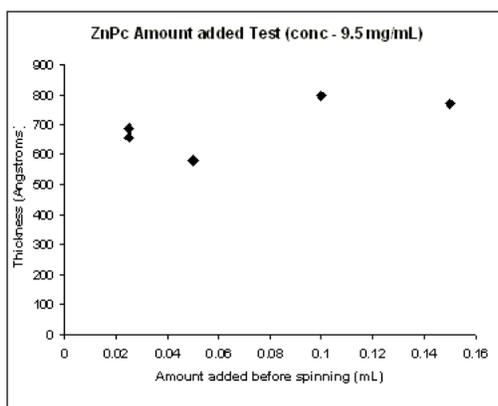


Figure 3.5: Graph of ZnPc solution with a concentration of 9.5 mg/mL spun at 2000 rpm with different amounts of solution added before spinning

Next we tried using a different ellipsometer used by the chemistry department, it was also made by Gaertner Scientific but used two He/Ne lasers with 543.5nm and 632.8nm wavelengths. This test gave very inconsistent results varying widely even on the same blank slide and often not giving any results at all. From talking with researchers who had used it we found that instrument has trouble measuring films on glass substrates and so we could not take any of the data from this test.

At this point we decided that the thicknesses we were getting between 60 and 70nm was good enough for the time being and moved on.

3.6 Pedot:PSS

As we had still not received our C_{60} we moved onto spinning Pedot. The Pedot we bought was not diluted so we did it ourselves. Because the thickness of the Pedot layer did not matter much

beyond being in the correct order of magnitude we simply mixed it until the solution was opaque and everything appeared to have dissolved.

Our first test we wanted to see which solvent worked better ethanol or water. For this test we made two batches of Pedot solution using ethanol for one and water for the other, we also made a solution of ZnPc with a concentration of 13mg/mL. We spun all the samples at 2000 rpm for 30 seconds. Our result was about 140nm for the Pedot mixed in water and we could not get a reading from the Pedot mixed in Etoh, the ZnPc layer was about 120nm nearly double what we had been getting earlier. This led us to question the accuracy of either the spinning or the ellipsometer. To see how stable the ellipsometer was we measured the next day and again 12 days later, after spring break (figure 3.6).

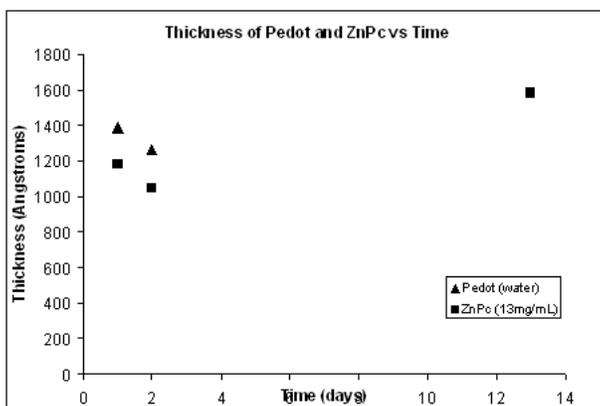


Figure 3.6: Graph of Film Thicknesses of Pedot:PSS and ZnPc with a concentration of 13 mg/mL at different times

We found that the thickness did change with time but seemed to be consistent on any given day, though we did not have enough samples to be sure of this. On the last day we could not get a reading for the Pedot mixed in water either. This lead us to believe that we cannot trust the thickness measurement to a great extent and estimated that it may vary by as much as 30nm.

We next spun a new solution of ZnPc (conc 11.4 mg/mL) onto the Pedot slides we had made, both the water mixed and Etoh mixed. This was done by having the slides already spinning at 2000 rpm and pipetting the ZnPc solution onto the slide in one long smooth jet. We also had a control of just ZnPc on a clean glass slide at 2000 rpm, and because we had extra we also ran ZnPc samples at 3000 rpm and 4000 rpm, however the 3000 rpm sample fell and broke during transport.

From our results on this test we saw no significant difference between the ZnPc slide and the ZnPc plus Pedot slides leading us to believe that the ZnPc had washed off the Pedot. We next tested a clean glass slide and found that it had nearly the same ψ and Δ values as the runs we had just done, around 278 for Δ and 2 for ψ . We tested the clean glass slide four more times and got an error of about two for both ψ and Δ and an average value of about 278 and 0. From this we found that all values of ψ and Δ were in or nearly within that error (figure 3.7). We concluded from this that there was nothing on the slides although we believed that there was a slight blue tint.

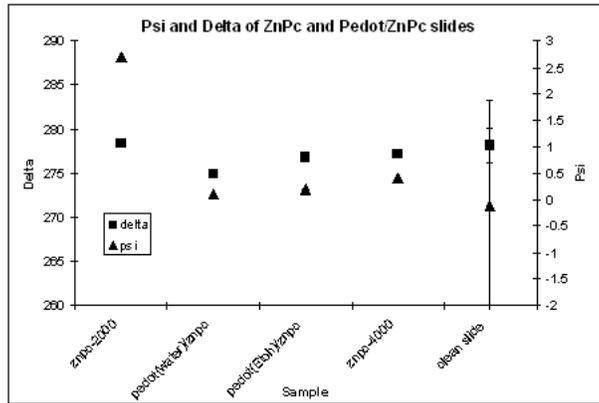


Figure 3.7: Graph of Psi and Delta for ZnPc spun onto Pedot

We planned on repeating the test using water only as it seemed to work better, however found that the after spinning Pedot onto a slide that there was no significant change in ψ or Δ . We tried it again using ethanol but got the same result (figure 3.8).

Looking back at our previous results we found that the ZnPc tests had for the majority of sample the same ψ and Δ values as the clean glass, but since we did have some differences and we could see the blue film on the slides we attributed this the fact that ZnPc and ITO have a similar n value at 632nm wavelength (1.63 and 1.7). One thing that was interesting though was that our first Pedot runs had different values up until the spring break. We have no way of accounting for these differences but theorize that they may have result from poor use of the ellipsometer and that more practice with the it has led to more consistent results.

We next attempted to try a range of speeds in our Pedot test and see if we could get a different result. Using water as the solvent we ranged our speed from 500 to 4000 rpm but found no significant changes in ψ or Δ from that of a clean slide (figure 3.9).

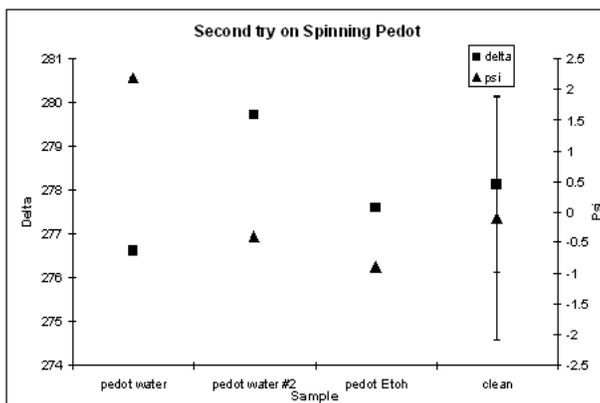


Figure 3.8: Graph of Psi and Delta of Pedot spun at 2000 rpm

Next we tried varying acceleration and speed and found that at around 500 rpm with a slow acceleration (between 1 and 5) it spread over the slide thickly, however it was very uneven and streaky and there were large particles of Pedot in certain areas. Using a higher acceleration (around 15) helped with the streaks but the large particles remained. We found relatively good success of getting rid of the particles and evening out the streaks by adding a second step of high speed, around 3000 rpm, as long as the acceleration was relatively low (around 5). All samples were inspected visually then cleaned and reused until we found a visually acceptable spread. We decided on a spinning process of going to 600 rpm with an acceleration of 1 for 10 seconds followed by going to 3000 rpm with an acceleration of 5 for 10 seconds. This did not let the Pedot dry and eliminated all of the large particles and spread the Pedot relatively evenly.

Testing a sample we still ended up with a somewhat different ψ and Δ (-2.2 and 86.9). Using this Pedot slide we spun some ZnPc (conc 12.2 mg/mL) onto the Pedot slide. We could see no visual difference other than a slight blue tint but under ellipsometer we found that it had now had a ψ and Δ similar to clean glass again (1.6 and 281.2). We tried spinning the Pedot again but this time ended up with a ψ and δ of -.7 and 276.2. We tried one last attempt and got a ψ and δ of -.02 and 277.9.

By this point our C_{60} had arrived and we decided to give up on using Pedot for the time being. Also at this time another group was using the evaporator so we decided to try and make a cell with them but we had not had a chance to do any tests with the C_{60} . We spun a solution of ZnPc (conc 12.2 mg/mL) at 2000 rpm then let it dry for 15 minutes. We followed this by adding the solution

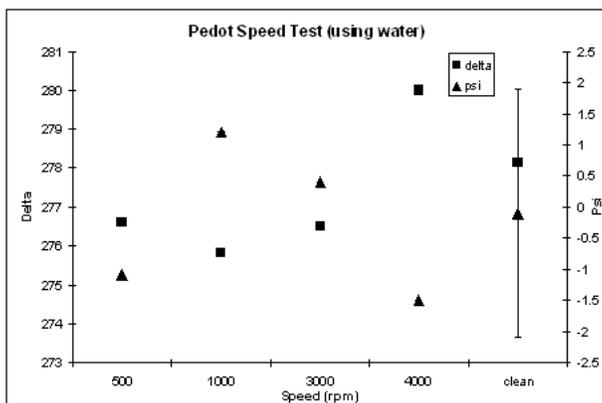


Figure 3.9: Graph of Psi and Delta of Pedot spun at varied speeds

of C_{60} in chloroform (conc 13 mg/mL) while the slide was spinning at 2000 rpm (figure 3.10). The ellipsometer gave a reading -1.2 and 277.1 for ψ and Δ which was not encouraging.

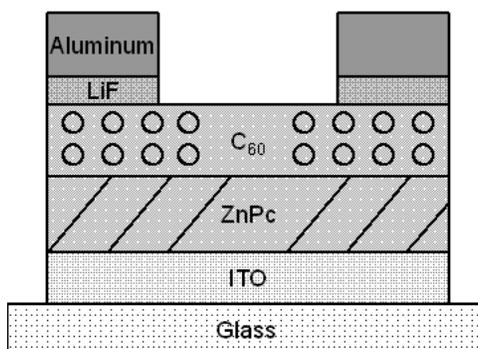


Figure 3.10: Schematic of first Solar Cell Architecture

3.7 First Solar Cell

The evaporation was done at vacuum of around 10^{-6} , we did not know exactly as the pressure gauge was not working at the time. We evaporated a layer of 63\AA of LiF (the other group used AlF instead of BCP but they work under the same principle) and an Aluminum layer of 1075\AA according to the sensor. The cells were left to cool for one day before taking them out and preliminary tests using

an overhead projector did not give any voltage, which we expected.

Using the AFM to look at the height of the electrode we found that electrodes apparently slope up so we could not get a good measurement of the height by comparing it to the non-evaporated portion of the cell. Instead we found a scratch made during the testing process. We found that it had a height of 160nm which was more than the sensor indicated but may have been caused, in part, by the scratch going into the ITO (figure 3.11). In any case the electrode was in the correct thickness range and near enough to the sensor that it can be considered reliable.

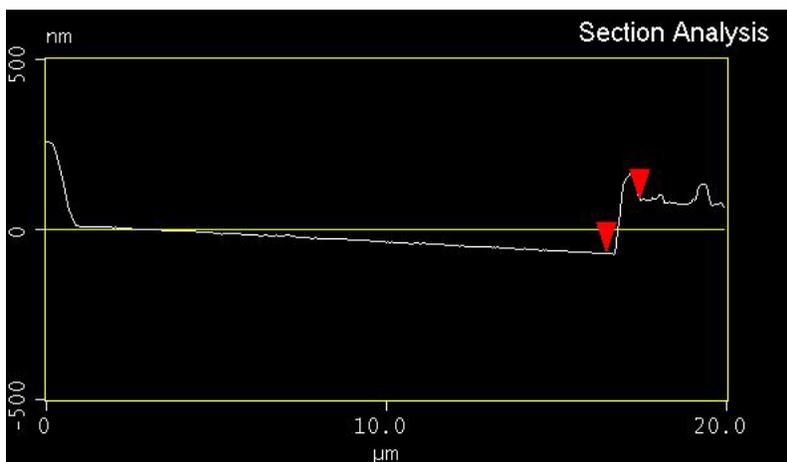


Figure 3.11: AFM height data of a scratch in an Aluminum electrode of the first Solar Cell

3.8 C_{60}

Following the creation of our first solar cell we began testing of the C_{60} . We decided to use chloroform as the solvent since we had extra and it was relatively safe compared to what we were originally going to use, toluene. One problem with chloroform was that C_{60} is not very soluble in it. We got around this by sonicating for long periods of time however there was still some noticeable aggregation. A benefit of it not being very soluble in chloroform was that by spinning it before we spin ZnPc it would be far less likely that it would wash the C_{60} off. This would also give us the advantage of having the blue absorbing region deeper in the cell which could increase the efficiency. A draw back of this is that we would not want to use the BCP layer as it may block the wrong charge carriers.

Our first test was to look at thickness versus concentration. We looked at concentrations between

10 and 30 mg/mL and spun at 2000 rpm for 30 sec. From visual inspection the slide did not look like any of C_{60} had stayed on and the ellipsometer data all matched that of clean glass (figure 3.12).

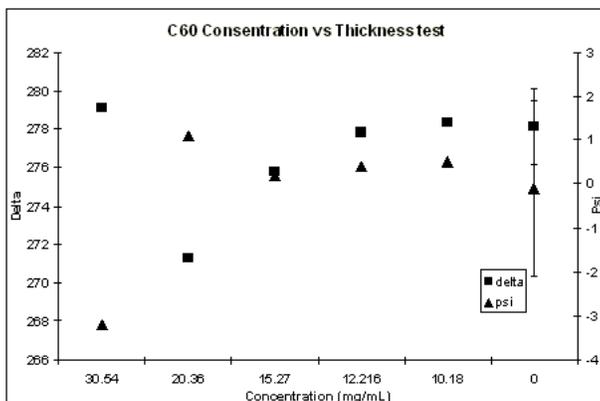


Figure 3.12: Graph of Psi and Delta of C_{60} spun at 2000 rpm with varied concentrations

We decided to raise the concentration and try a speed test with lower speeds. Using a concentration of 101.8 mg/mL (we used such a high concentration to try and guarantee that some would be left on the slide) and sonicated it for 75 minutes before spinning we got it to stick for speeds between 500 and 1100 rpm. We also found a large amount of the solution, nearly covering the slide, had to be placed on for there to be complete coverage. Visually we could see a dark stain from the C_{60} on the slide. It was not streaky which was good however the density left on the slide seemed to change a little from region to region and there were visible specs of aggregated C_{60} though not a large number of them. Also the most opaque of the slides was the sample spun at 500 rpm which was expected, however the least opaque sample was spun at 700 rpm and the samples spun at 900 rpm and 1100 were had nearly the same opaqueness which we did not expect. We attributed this to differences in the amount of solution added before spinning. The results from the ellipsometer once again all matched that of clean glass (figure 3.13).

3.9 AFM

Since we could see the film on the slide we knew something was there and used the AFM to look at it and to try and get a thickness reading from it. We used the samples spun at 900 rpm and 1100 rpm as they looked the most uniform, we also made a new sample of ZnPc with a concentration of

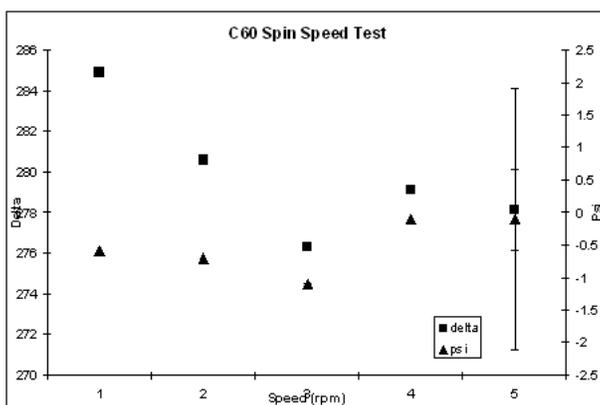


Figure 3.13: Graph of Psi and Delta of C_{60} spun at different speeds with a concentration of 101.8 mg/mL

17.4 mg/mL spun at 1000 rpm. We chose a higher concentration than normal and a lower spin rate than normal to increase the likelihood we would find something on the slide.

Looking at the C_{60} samples we found that we could not get a good height reading because the C_{60} had all aggregated into clumps that were too rough for the AFM to get a good reading on (figure 3.16). From this we decided that this was the problem with the ellipsometer, namely since there was not a complete and even film the ellipsometer only gave us data on the ITO underneath the C_{60} . The ZnPc also turned out to not have complete coverage however it looked more like puddles of blue ZnPc under the microscope instead of being clumped. Getting a reading on one of these puddles using the AFM proved difficult as it was hard to distinguish from the ITO as it rose very slowly from the ITO (figure 3.14). We got a reading of around 50 nm although it was inconsistent. The clean glass sample was very flat and clean (figure 3.15) so we were able to be sure that the roughness on ZnPc slide was ZnPc and not just inconsistency in the ITO.

3.10 Solar Cells

At this point we only had a few days left so we decided to make a solar cell with what we had. We hoped that a large C_{60} clump would be covered by enough ZnPc to act as a small solar cell even if it was only on a small part of the slide. For this to work there would also have to be an electrode in contact with it. It was unlikely that this would happen or even if it did happen it would probably

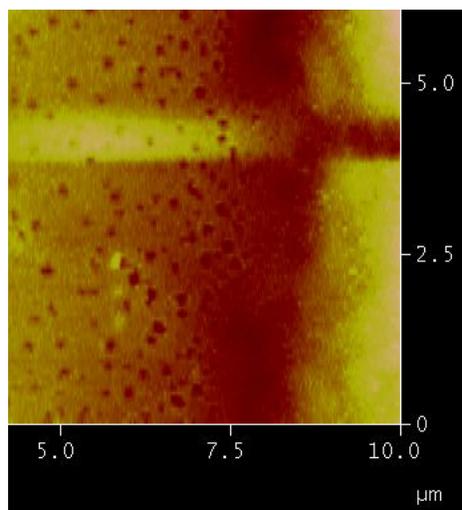


Figure 3.14: AFM image of ZnPc spun onto an ITO covered glass slide, the ZnPc is on the right of the picture

be such a small current that it would not be measured.

We made two cells using the same construction (figure 3.17), we made a solution of 106.8 mg/mL C_{60} in chloroform and a solution of 15.6 mg/mL ZnPc in chloroform. We then sonicated both solutions for about one hour. The C_{60} was spun at 300 rpm for 30 seconds. The cells were then allowed to dry for 15 minutes. We could clearly see the C_{60} on the slide. The ZnPc was pipetted onto the slides while they were spinning at 1000 rpm. The C_{60} layer looked unchanged but there was a blue tint to the slide indicating at least some of the ZnPc had stuck.

The evaporation of Aluminum was done at $2.2 \cdot 10^{-6} \text{ torr}$. The aluminum was deposited at a varying rate between .5 and 5 $\text{\AA}/\text{s}$ up to 506 \AA according to the sensor. After cooling the last step was to wash a small strip on each of the cells using acetone and cotton swab so that we could place a probe directly on the ITO to get a good reading. At all times during the creation process we attempted to keep the cells in either safe light or in the dark to help prevent oxidation.

Dark testing of the cells revealed that the electrodes had a resistance of about 1 Ω per mm and the resistance of the whole circuit was around 20 Ω for each of the electrodes. We got a dark voltage and dark current of zero which was expected. Preliminary testing to see if could generate a current or voltage was done using an overhead projector and a high precision multi-meter and soft tip probes. In the dark the solar cells were placed, one at a time, onto the projector with the glass

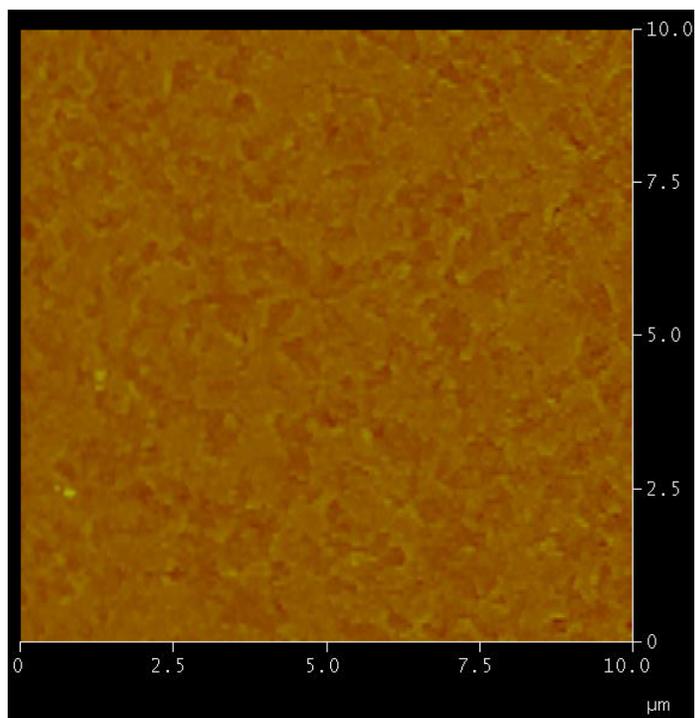


Figure 3.15: AFM image of a clean ITO covered glass slide

down. We then took the probes and placed one on the clean strip and another on an electrode and looked at the voltage and current for each electrode, one after another. Upon testing we found no electrode that gave any current or voltage leading to the conclusion that neither of the cells worked.

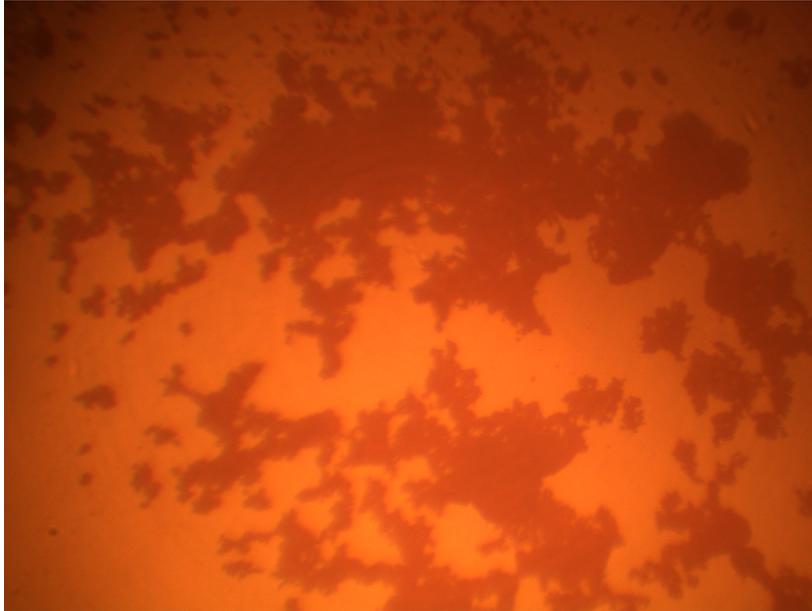


Figure 3.16: Light Microscope Image of C_{60} spun onto an ITO covered glass slide

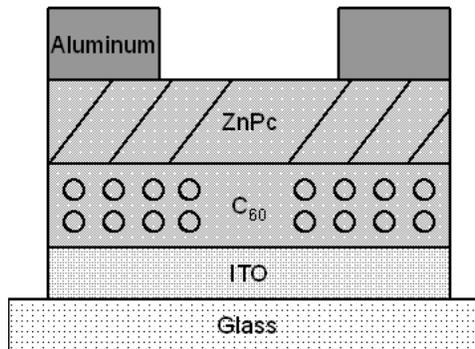


Figure 3.17: Schematic of the second and third Solar Cell Architecture

Chapter 4

Analysis

Problems with aggregation during the spinning process are most likely the reason for the problems we faced during this experiment. Because the films never spread over the whole surface of ITO slides the ellipsometer simply gave the reading of the ITO and not of the film on top of it. Despite this for the first half of the experiment we were getting some results that were different from the ITO, and we even got a linear correlation for one of our tests. This can mean one of two possible things. The first is that the ellipsometer was picking up the thin film of ZnPc and the film was spread consistently enough for there to actually be a linear correlation but as the experiment continued the ellipsometer began to malfunction in some way and was no longer able to pick up the thin film. The second is that the first test was a fluke and the only reason any deviations from the ψ and Δ of the ITO was inexperience with using the manual method and the somewhat large error values caused from doing the tests manually. Also getting a reading of ZnPc was further complicated by the similar n values of ZnPc and ITO which could have lead to problems in identifying the correct thickness. Since the Ellipsometer worked reasonable well with the calibration sample both during the beginning and the end we believe it was more likely the latter explanation.

As a result of not getting good coverage for either of our materials we cannot say definitively if this method would work or not. Therefore it is still possible that with more work a solar cell could be created using these materials and method.

Chapter 5

Future Work

Future work on this project would have to begin with an in depth study of the ellipsometer. Getting the automatic mode to work would greatly increase the speed at which test could be done, but is not necessary. More important would be looking at how the readings vary with time, both day to day and by how long the ellipsometer has been on during the same day. Study of a calibrated sample on a glass slide may also be wise as the glass may in some way interfere with the measurement. Beyond this further experiment would also have to make greater use of the AFM and/or a light microscope to check the spread of the thin films and make sure it is not aggregating.

Beyond changes in equipment more work would have to be done on picking solvents. Chloroform was clearly not ideal for either of the materials as neither completely dissolved into it. Failing finding a better solvent for each material researching a better way of dissolving it then sonication may be an option. In addition more study into both higher and lower concentrations and spin speed may reveal something new. We believe that making one of these cells is still within the realm of possibility however it will take a lot of work.

There are other possibilities for work using the same materials and design. One could use evaporation as was done in previous research and try to improve on some aspect of their design, such as adding in more layers. Another possibility would be to use lithography and masks to get more precise control on the morphology. Another possibility would be to evaporate the first thin film then spin the second onto the top of it and have them diffuse into eachother, as we tried to do in this experiment

Chapter 6

Conclusion

Problems with dissolving the materials and aggregation before, during, and after spinning caused data collection problems throughout this experiment. This along with this possible equipment problems led to problems in data collection and wasted time before the real problem, the poor spinning and aggregations, was discovered. Because of this no functioning solar cells were created. However it is possible with different solvents and better data collection that the problems with spinning can be overcome and a working solar cell can be made.

Chapter 7

Acknowledgments

We would like to thank Professor David Tanenaum for his help in setting up the experiment as well as help with the equipment and problems encountered along the way. We would also like to thank Ian Frank for his help in using the AFM and Lewis Johnson for help with the evaporation process as well as sharing important information and papers on organic solar cells. And last but not least we would like to thank Glen Flohr for help with some of the equipment.

Chapter 8

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