

## Solar Energy-Nano-style

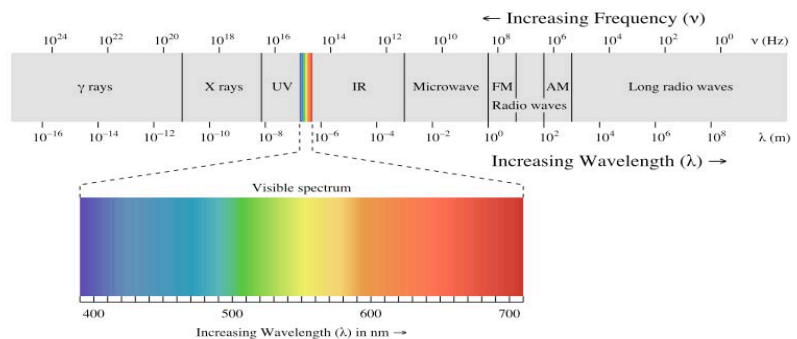
### BACKGROUND

Solar energy is abundant energy resource and has received much attention in the last two decades. Solar cells utilize the photovoltaic effect which converts light energy into electrical energy. Light is composed of photons. The photons are described as being small packets of energy in the form of both waves and particles. The characteristic energy is described by the formula below.

$$E = hf = \frac{hc}{\lambda}$$

Where  $h$  = Planck's constant,  $f$  = wave frequency,  $c$  = speed of light and  $\lambda$  = wave length. This wave length is associated with the energy spectrum; more specifically for solar energy, ultra-violet to infrared spectrum. Figure 1 below is an example of the energy (light) spectrum with corresponding wave lengths. Interesting enough, solar energy thrives on photons associated with the Visible light spectrum.

At these wavelengths, the energies associated closely match the energy required to excite an electron in the semiconducting material. Thus the incoming light energy does not overpower the semiconductor with excess energy. Typical solar cells have maximum efficiencies that lie within 350-700nm wave lengths. This energy contribution coupled with large intensities of light (sunny days,)



increases the amount of current produced which maximizes overall cell efficiency. However, in practice, there are typically material limitations that have adverse effects on solar cell performance.

Traditional solar cells are manufactured using polycrystalline silicon semiconductors. Pure Silicon material, by itself, is not very useful, but becomes a very powerful semiconductor when alloyed with small amounts of impurity elements. The specific doping impurity defines the semiconductor type: n-type (electron source) or p-type (hole source). The junction of these semiconductor types is what creates a separation between the negative and positive charges resulting in a net potential difference and electron flux. However, tradition semiconductors are costly to manufacture due to the stringent chemistry specifications required to maximize semiconductor efficiency and methods for meeting those requirements. One example is application of zone refining to control impurity level. This method consists of large furnace equipment and a tremendous amount of time to produce useful chemistries. Additionally, chemical vapor deposition is used to add additional dopants which also require large equipment and time.

For a solar cell to work as an anti-reflecting coating and a series of layers composing of n/p –type semiconductors must be used to transmit photons, excite electrons and flow electrons to create a current. For a traditional solar cell, each layer facilitates this process in one step. Overall efficiencies for these types of materials may range from 5% to 33% efficient. Silicon based solar panels perform in the 10% to 25% range and exhibit relatively large open-circuit voltage and current. This efficiency range is a drastic improvement from earlier solar cells (order of 1%), but still is relatively low when compared to other energy conversion methods. These lower efficiencies have been, among others, attributed to

reflective losses and narrow wave length operation range. Certainly improvements in material properties could improve these losses and boost efficiency.

In the past decade research has been conducted on a different solar cell that divides the photon absorption and charge separation processes into two steps. These cells are based on a combination of photovoltaic effect physics and electrochemistry; more commonly known as photoelectrochemical solar cells. These cells incorporate nanostructured semiconductor layer with a light absorbing dye sensitizer and a regenerating iodide/triiodide electrolyte. Currently, dye sensitized solar cells approach efficiencies of 11% and produce equivalent open circuit voltage and current to traditional silicon solar cells, at a fraction of the cost. So why all of a sudden does one want to use nanostructured materials?

Nanomaterials offer a unique combination of properties that traditional “micro” materials do not. Because the bulk scale is closer to the atomic size scale, new physics apply to all optical, mechanical, electrical, chemical and thermal properties. In the case of photoelectrochemical cells, the volume to surface area ratio is far smaller than conventional materials yielding enhanced light absorption and electron transfer than similar micromaterials. These changes are directly associated with the increase in surface area per volume, but also due to more particles present in a given volume. Another advantage is more economical method for synthesizing nanoparticles and suspensions. A series of solvents and evaporation steps are typically used to synthesize nanoparticles and ultimately create a suspension. Eventually these suspensions can be sintered by methods consistent with tape casting. In the end, process time and equipment needs are reduced.

Photoelectrochemical solar cell efficiency relies on three main components: light absorbing die sensitizer, electron transfer and electron regeneration. As the name suggests, light absorbing dye sensitizer absorbs photons to excite electrons and create holes. The electrons are excited and transferred into the conduction band of the nanoparticle semiconductor. Electron transfer to and through the nanoparticle semiconductor is near 100% efficient thus boosting the overall cell efficiency. Electrons are transferred through a conductive path to a counter electrode. Oxidation of iodide to triiodide takes place at the photosensitized nanoparticle film/dye sensitizer interface supplying the necessary electrons to newly created (positive charge) holes. Electron flow to a counter electrode (metal or carbon) supplies the necessary electrons to reduce the triiodide to iodide. This cycle is regenerative and important to the cell efficiency.

To achieve a high efficiency the following must be met. First: light absorbing dye must produce excited electrons and holes over a wide light spectrum. Meaning, the cell is using the majority of light energy supplied by source thus boosting current. Secondly, the nanoparticle layer needs to maximize the dye/semiconductor surface area to achieve near 100% electron transfer. Third, the oxidation and reduction electrolyte reaction rates proceed at a rate equal to or greater than electron excitation. A rate less than electron excitation rate will result in an oversupply of electrons and holes to the cell causing recombination to occur decreasing current.

Within each of these topics there are numerous ideas and innovations to improving these types of cells. In order to run we must walk and by that I am challenging you to build your own photoelectrochemical solar cell. While building your cell, make sure to follow all instructions and complete the attached handouts. Good luck and may the light be with you!!!

## MATERIALS

- 1) 2 -Fluorine doped tin oxide glass slides (F-SnO<sub>2</sub>)
  - 2) 0.127g Iodine (I<sub>2</sub>)
  - 3) 0.83g Potassium Iodine (KI)
  - 4) 10 ml ethylene glycol
  - 5) Dish Washing detergent (surfactant)
  - 6) Colloidal Titanium Dioxide Powder (TiO<sub>2</sub>)
    - a. 2ml 2,4-Pentanedione (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>)
    - b. 100ml Anhydrous Isopropanol
    - c. 6.04ml Titanium Isopropoxide (Ti[(CH<sub>3</sub>)<sub>2</sub>CHO]<sub>4</sub>)
    - d. 2.88ml Distilled Water
  - 7) Nitric or Acetic acid
  - 8) Blackberries, raspberries
  - 9) 2ml de-ionized water
  - 10) Ethanol
  - 11) Filter paper
  - 12) Masking Tape
  - 13) Tweezers
  - 14) Binder Clips
  - 15) Multimeter
  - 16) Glassware (beakers, stirring rods etc.)
  - 17) Mortar/Pestle
  - 18) Hot Air Gun
  - 19) Bunsen Burner
  - 20) Tissue Paper
  - 21) Alligator clips with connecting wires
  - 22) 1 LED
  - 23) 1 Incandescent light bulb/lamp
  - 24) Fluorescent lighting
  - 25) 1 Sunny Day
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## PROCEDURE

### *Nanotitanium dioxide suspension*

- 1) Measure out 6 grams of titanium dioxide.
- 2) Add 9ml of nitric or acetic acid to titanium dioxide in a mortar and pestle.
- 3) Grind for 30 minutes to create a lump free paste.
- 4) Add 1 drop of dish washing detergent (surfactant).
- 5) Set suspension aside for 15 minutes to equilibrate.

### *Dye sensitizer preparation*

- 1) Crush 5-6 fresh berries in a mortar and pestle with 2ml of de-ionized water.
- 2) Filter dye, collect and set aside.

### ***Photoelectrochemical solar cell preparation***

- 1) Using a multimeter, determine the conductive side of each glass slide.
- 2) Mask off one of the glass slides, conductive side up, with masking tape 1-2 mm on three sides.
- 3) After the nanotitanium dioxide suspension has equilibrated, place a 2-3 drops of nanotitanium dioxide paste and distribute across the unmasked area with a glass rod.
- 4) Let slide dry for one minute.
- 5) After slide has dried for one minute, remove the tape and place under a hot air gun.
- 6) Heat the slide, using the hot air gun, for 30 minutes to sinter the paste.
- 7) Allow the heat sintered slide to cool to room temperature.
- 8) Once the slide has cooled, place slide face down (Nano layer down) in the filtered dye sensitizer for 5 minutes. This will allow the dye to be absorbed into the Nano pores.
- 9) While the first slide is soaking, take the second glass slide and heat the conductive side over an open flame.
- 10) Move the slide back and forth for a few seconds to create a carbon catalyst layer.
- 11) Remove from flame and allow slide to cool.
- 12) Remove the first slide from the dye and quickly rinse with ethanol to remove water. Dry the rinsed slide with tissue paper or paper towel.
- 13) In a quick manner, place the two slides together (paste and carbon layer facing each other) in an offset manner.
- 14) Attach two binder clips to the two ends (not the offset sides) to hold the slides together.
- 15) Add one drop of the electrolyte solution between the slides. The electrolyte will stain the entire inside of slides by capillary action.

**You have now completed your photoelectrochemical solar cell. ENJOY!!!**

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### **DATA COLLECTION: Solar cell testing**

#### Fluorescent Light (standard school lighting)

- 1) Connect one alligator clip and wire assembly to each glass slide. Make sure the negative (black) wire is connected to the Nano layer glass slide and positive (red) wire to the opposite glass slide.
- 2) Measure the open circuit cell voltage by applying the corresponding colored probes to the correct wires. Make sure the multimeter is on the voltage setting. Record your results in the summary table.
- 3) Connect each wire to the correct terminal on the LED bulb. Record your observations when the wires are connected.
- 4) Set multimeter to measure current and connect probes to the corresponding wire colors (one probe on each side of the LED. Measure the current produced from your solar cell and record value in the summary table.

#### Incandescent Lighting (Desk lamp)

- 1) Turn off classroom lighting and turn on incandescent lighting.
- 2) Position lighting directly over head of your solar cell approximately 8-12 inches away. Record this distance in the summary table.
- 3) Complete Fluorescent Light steps 1-4 recording the necessary data and observations on the summary page.

- 4) Now move the incandescent light angle approximately  $30^\circ$  from vertical to the right or left. Maintain the same distance.
- 5) Complete Fluorescent Light steps 1-4 recording the necessary data and observations on the summary page.
- 6) Move the incandescent light an additional  $30^\circ$  from the previous position. Maintain the same distance.
- 7) Complete Fluorescent Light steps 1-4 recording the necessary data and observations on the summary page.

Sun Light (Outdoors):

- 1) Complete Fluorescent Lighting steps 1-4 and record all necessary data and observations on the summary table.
- 2) Record the relative position of the sun when testing outside (i.e. degree offset from vertical).

Data Analysis:

Using a graphing calculator plot the following:

- 1) Open cell voltage as a function of lighting type. For incandescent lighting comparisons plot only the vertical data point.
- 2) Current as a function of lighting type. For incandescent lighting comparison plot only the vertical data point.
- 3) Incandescent lighting open cell potential and current as a function of lighting position.
- 4) Use each graph to answer the questions below.

| <b>TABLE 1: Data Collection</b> |   |                                       |                             |
|---------------------------------|---|---------------------------------------|-----------------------------|
| <b>Lighting Type</b>            | <b>Position Angle<br/>(Vertical = 0°)</b> | <b>Open Circuit Potential<br/>(V)</b> | <b>Cell Current<br/>(A)</b> |
| Fluorescent                     |   |                                       |                             |
| Observations:                   |   |                                       |                             |
| Incandescent                    | <b>0</b>                                  |                                       |                             |
|                                 | <b>30</b>                                 |                                       |                             |
|                                 | <b>60</b>                                 |                                       |                             |
| Observations:                   |   |                                       |                             |
| Sun Light                       |   |                                       |                             |
| Observations:                   |   |                                       |                             |

### **DATA ANALYSIS AND SUMMARY**

**Data Analysis Questions:**

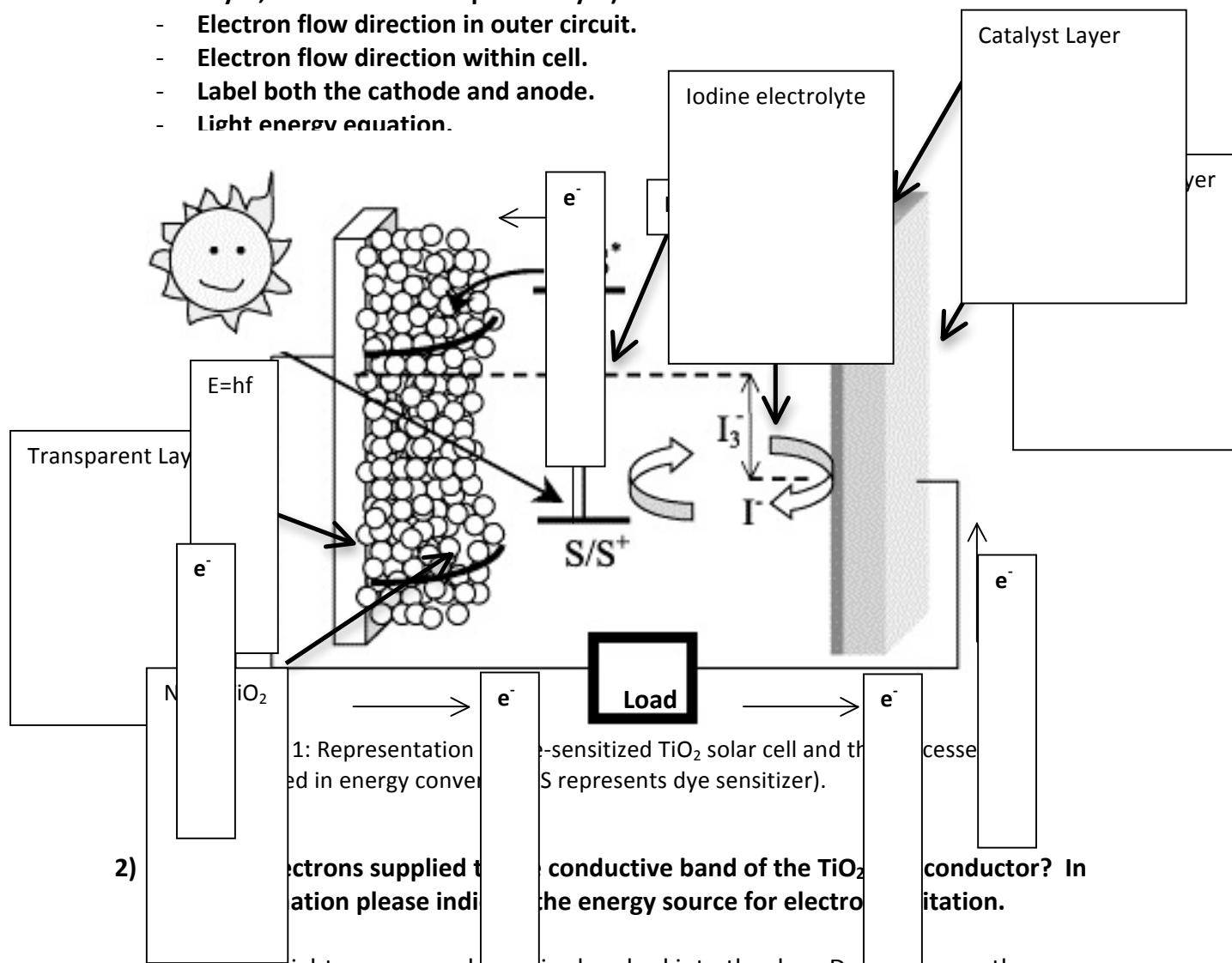
- 1) **What effect does the lighting type have on the open cell potential?**
  
- 2) **What effect does the lighting type have on the current? Is this change related to the cell potential?**
  
- 3) **What effect does the lighting angle have on both current and voltage? How does this factor into the efficiency of the solar cell?**

**PROBLEM SET**

**NOTE: Read the background information to assist you in answering the questions below!**

**1) Indicate the following information on the figure provided below<sup>1</sup>:**

- **Solar cell components (e.g. TiO<sub>2</sub> Nanoparticles, Dye Sensitizer, Electrolyte, Catalyst Layer, Conductive-Transparent layer).**
- **Electron flow direction in outer circuit.**
- **Electron flow direction within cell.**
- **Label both the cathode and anode.**
- **Light energy equation.**



**2)**

1: Representation of a dye-sensitized TiO<sub>2</sub> solar cell and the process of energy conversion (S represents dye sensitizer).

2: Electrons supplied to the conductive band of the TiO<sub>2</sub> nanoparticles. The energy source for electron excitation.

3: Process of electron recombination.

4: Is the dye a conductor? In what way?

- Light energy or photon is absorbed into the dye. Depending on the wavelength and thus associated energy, an electron will be excited out of its standard state into a high energy state.

<sup>1</sup> C. Longo, M. A. De Paoli, "Dye-sensitized solar cells: a successful combination of materials," J. Braz. Chem. Soc., **14** [6] (2003).

- The electron is able to conduct through the conductive band because its energy matches that of the Nano semiconductor conductive band. Effectively a charge separation occurs and an electron flow begins to the conductive slide.
- The light absorbing dye is then left with positively charged holes which wait for an additional electron to recombine and lower the system energy.

**3) After the electrons are excited what is left behind in the dye sensitizer? What charge does this have?**

- **Answer**

- The light absorbing dye is then left with positively charged holes which wait for an additional electron to recombine and lower the system energy.

**4) This solar cell is unique because of its regenerative process. What type of chemical reaction is taking place in the electrolyte? Write and balance the net ionic half reactions for this process. What is the overall reaction?**

- **Answer:**

- Oxidation-Reduction Reactions (REDOX)
- Oxidation Reaction (Anode)



- Reduction Reaction (Cathode)



- Overall reaction is zero

**5) Explain the technical and economic advantage(s) of using Nano particles for a semiconductor as opposed to a polycrystalline silicon semiconductor.**

- **Answer: Technical**

- Increased surface area to volume ratio.
- Increased contact with dye sensitizer to increase excited electron transfer.
- Increased electron conduction through conductive band than equivalent bulk material.
- More light absorbed through nanoparticle film than equivalent bulk material.

- **Answer: Economical**

- Material synthesis does not require the processing equipment and time than conventional solar cells for near equivalent efficiencies. Hence lower costs.
- Raw materials are cheaper. FTO conductive glass is much cheaper than ITO conductive glass. Nano TiO<sub>2</sub> synthesis is much cheaper than conventional solar cells.
- Tape casting method, overall, is much cheaper than zone refining method.



**6) What effect does a high volume fraction of TiO<sub>2</sub> film porosity have on cell efficiency?**

- **Answer:**

- Increase volume fraction film porosity decreases total surface area. Maximizing the surface area of the Nano film is critical to maximum electron transfer efficiency.
- Additionally, film continuity allows for maximum electron conduction through film to conductive slides.

**7) How does surface area effect cell efficiency?**

- **Answer:**

- Decrease in surface area decreases electron transfer from dye sensitizer. This decrease in electron transfer is simply a decrease in current. Hence cell efficiency decreases.
- Maximize surface area of nanoparticle film/dye sensitizer interface, maximize current and cell efficiency.

**8) Based on your explanations above, microstructure plays a role in cell efficiency. You have explained the role of porosity on cell efficiency, but not the size of porosity. Using the data below how does pore-size distribution (average pore diameter) effect cell efficiency? *HINT: think of the dye sensitizer regeneration (reduction) kinetics compared to electron excitation kinetics.***

| <b>TABLE 1: Photovoltaic Properties of Two Electrodes with Same Surface Area but Different Porosity-Size Distribution.<sup>2</sup></b> |  |                            |                       |
|--|--|----------------------------|-----------------------|
| <b>Light Intensity</b>   | <b>Current Density (mA/cm<sup>2</sup>)</b> | <b>V<sub>oc</sub> (mV)</b> | <b>Efficiency (%)</b> |
| <b>Average Pore Size = 4 nm</b>  |  |                            |                       |
| <b>1/10 Sun</b>  | <b>1.4</b>                                 | <b>550</b>                 | <b>4.72</b>           |
| <b>1 Sun</b>   | <b>9.2</b>                                 | <b>620</b>                 | <b>3.35</b>           |
| <b>Average Pore Size = 20 nm</b>   |  |                            |                       |
| <b>1/10 Sun</b>  | <b>1.3</b>                                 | <b>560</b>                 | <b>4.9</b>            |
| <b>1 Sun</b>   | <b>12.1</b>                                | <b>630</b>                 | <b>5</b>              |

- **Answer:**

- Average pore size limits the reaction rates of the electrolyte. Remember two reactions must take place: Electron excitation-conduction, electrolyte regeneration of dye sensitizer. The slower of these two reactions will be rate limiting.

<sup>2</sup> C.J. Barbé *et al.*, "Nanocrystalline Titanium Oxide Electrodes for Photovoltaic Applications," J. Am. Ceram. Soc., **80** [12] 3157-71 (1997).

- Based on light intensity, small average pore size shows a decrease in efficiency with increase in light intensity. This is explained by the reduction reaction of electrolyte is too slow to keep up with a bombardment of excited electrons into and through the nanoparticle film. With increase in light intensity means more photons available for exciting electrons. For the electrolyte to regenerate the dye sensitizer it must be in contact with the dye. Small pores do not allow enough space or limited contact that would slow this transport process down.
- However, with large average pores there is sufficient contact between the dye sensitizer and electrolyte allowing for dye regeneration to take place at the same rate as excitation. The data shows no change in efficiency with increase light intensity.

**Bonus:**

**Why are Boron and Phosphorous used as an impurity in silicon semiconductors? What type of semiconductors do they create? Hint: your explanation should include a discussion about valence electrons and chemical bonding.**

- **Answer:**

- Boron is a part of group IIIA elements which all contain three valence electrons.
- Phosphorous belongs to group VA elements which all contain 5 valence electrons.
- Semiconductors are primarily made of silicon (Group IVA, 4 valence  $e^-$ ) or Germanium and are unique because of the bonding. Silicon has four covalent bonds sharing each valence electron combining to make 8 electrons. This bond is strong, but is interesting in that there are no available electrons to flow or create a current. Silicon in this state would be considered an insulator.
- With the small addition of Boron to the bonded silicon the boron (3 valence  $e^-$ ) creates one bond pair that is not complete. Meaning a hole (positive charge) is left behind as the neighboring silicon atoms are sharing additional electrons. (Keep in mind the amount of Boron is significantly small).
- With small phosphorous additions, silicon/phosphorous bonds form creating four covalent bonds. However, the extra valence electron from the phosphorous remains in the crystal structure. These few extra electrons are the source for electrical conduction in semiconductors.
- Boron doped silicon semiconductors are typically p-type
- Phosphorous doped silicon semiconductors are typically n-type