Characterization of InGaN based Photovoltaic Devices

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ABSTRACT

As our global energy reserves such as fossil fuels, nuclear, and geo-thermal dwindle—and our global energy expenditure exponentially increases at unprecedented rates—it is increasingly apparent that renewable energy solutions must be utilized. Because of its sheer abundance, solar can play a dominate role in our renewable energy armament if a solution can be found to reduce costs and increase efficiency. A new method for making InGaN-based photovoltaic (PV) cells promises to dramatically increase their efficiency by using tunable bandgap materials that can capture light from the entire solar spectrum. This unique property sets InGaN apart from current single and multi-junction PV materials. However, growing high quality InGaN is challenging because conventional techniques use high substrate temperatures ($\sim$1100°C). To make high-quality InGaN materials, their growth temperatures must be substantially reduced because In-rich InGaN decomposes above $\sim$700°C. To fabricate PV devices, challenges with p-type doping of InGaN must also be solved. Our efforts towards solving these problems involves installing, calibrating, and using a Mg evaporator on the Energetic Neutral Atom Beam Lithography & Epitaxy (ENABLE) system for p-type doping of InGaN during growth. Optical and electrical characterization of InGaN samples show, for the first time, successful p-type doping. The results are an important step in making prototype high-efficiency InGaN-based PV devices that could have dramatic impact on future solar energy production.

INTRODUCTION

The reliance on energy continues to grow as more technologies become adopted and utilized. To maintain this dependence on technology a source of energy that is abundant, efficiently generated, and environmentally friendly must be found.

In the United States (U.S.), energy is primarily harnessed from coal, natural gas, and crude oil. And of the energy sources that are considered to be renewable only make up ~10% of the total energy produced. A more specific break down from Energy Information Administration can be seen in Figure 1 (Ene09).
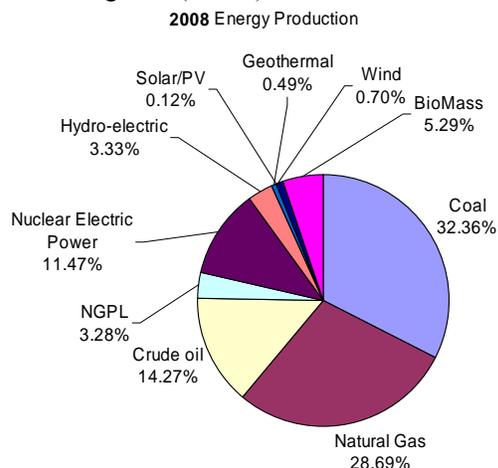

2008 Energy Production

Figure 1: Energy breakdown for the U.S in 2008 from the Energy Information Administration

As of today, solar energy provides only a trivial amount of energy in the U.S, but it has the potential of playing a substantial role in our growing energy needs because the sun is the oldest and most abundant energy source available. However, it is important to note that long term energy solutions will likely involve a combination of solar, wind, and other renewable sources.

Photovoltaic (PV) cells take advantage of the sun, by converting photons into electrical energy. However the current PV technologies only are able to harness photons with certain energies (e.g. energies near the bandgap of the active PV material), leaving a vast quantity of untapped energy in the reaming photons spanning the solar spectrum. If a material that can harness the entire range of the solar spectrum can be found and produced relatively economically, then the resulting global impact would be pervasive—impacting low cost environmentally friendly energy supply and portable energy in rural areas lacking reliable electrical infrastructure.

A new technological advancement developed at Los Alamos National Laboratory by Dr. Mark Hoffbauer for growing thin films using Energetic

Neutral Atom Beam Lithography and Epitaxy (ENABLE) allows the growth of high-quality In-rich InGaN (Indium Gallium Nitride) without the problems of other thin-film growth technologies. InGaN possesses unique optical and electrical properties that can be integrated into light emitting diodes (LEDs), solid state technologies, and photovoltaic cells. These materials are direct badgap semiconductors which allows them to more efficiency absorb photons and generate charge carriers (electron-hole pairs) for efficiently converting sunlight into electrical current. For this reason, direct bandgap semiconductors require substantially less material then indirect bandgap semiconductors.

The near-term goal of this project is to grow tunable bandgap p- and n-type InGaN that can be used for making efficient photovoltaic devices. However certain challenges exist that limit the ability of PV device quality In-rich InGaN to be grown using conventional Molecular Beam Epitaxy (MBE) (Hoffbauer, 2009).

Please refer to the background section for more information on how solar cells work and what PV materials and technologies are currently being used.

SIGNIFICANCE OF InGaN

As mentioned before; InGaN is a direct badgap semiconductor meaning the crystal lattices of the valance and covalent bands are similar with respect to their electron positions.

The uniqueness of InGaN becomes apparent when you vary the In to Ga ratio in the chemical makeup of the material (ie $In_{1-x}Ga_xN$, where $x \leq 0 \leq 1$)). For all In/Ga compositions, InGaN retains its semiconductor properties, which is generally not the case with any other material. This tunable bandgap property allows one to vary the optical and electronic properties that are directly related to how photons are absorbed to generate charge carriers.

By varying the composition of InGaN, efficient PV devices can potentially be fabricated for harnessing the entire solar spectrum. This concept is shown in Figure 2.
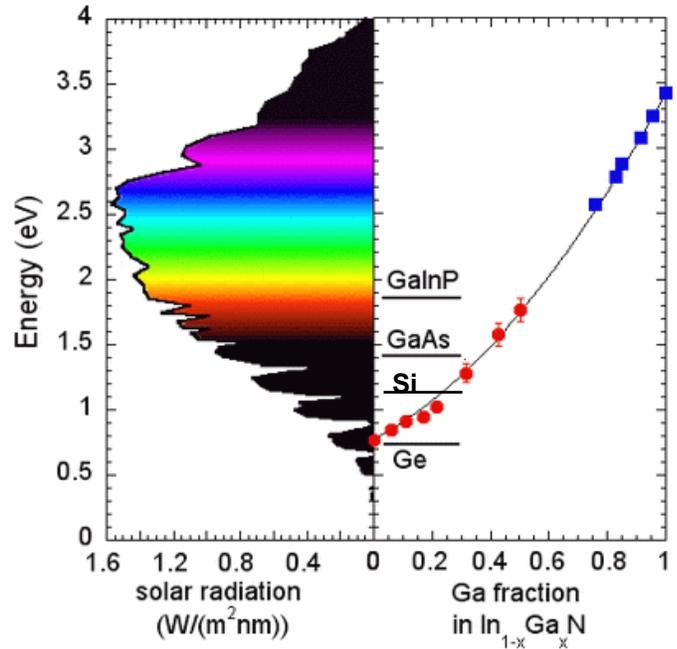

Figure 2: The solar spectrum shows the range of photons energies available from the sun . The right shows current solar cells and which photons they are able to absoub. Note that varing the composition of InGaN shows that it can harnness the entire solar specturm.

On the left of Figure 2 shows the entire solar spectrum., which shows the range of energies available in form of photons emitted from the sun. Current technologies only harness very small ranges of photons to make charge carriers. However, if the varying compositions of InGaN can be successfully grown and doped both p- and n-type for making active p-n junctions, PV cells can be made for harnessing photons having a variety of energies, yielding PVs with theoretical efficiencies of ~30%, >40% and >50% for a single, graded, or multi-junction cells respectfully. Potential PV device structures are shown below. (Mark, 2009)
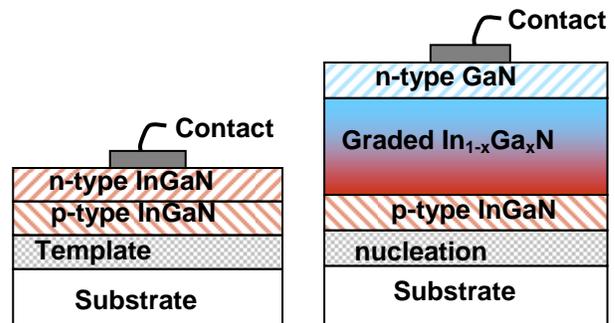

Figure 3: Potential layering of single junction (left) and graded InGaN (left) for PV devices.
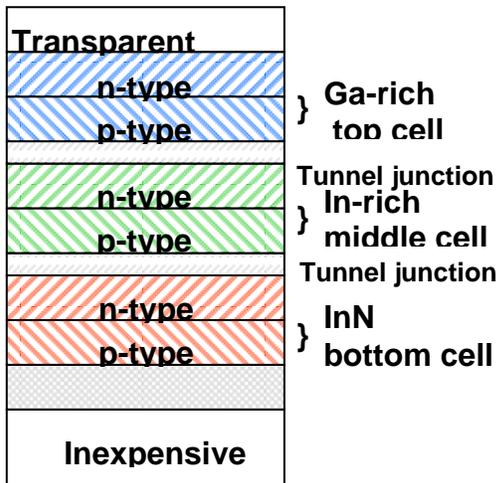
Figure 4: multi-junction PV device for InGaN

To be able to harness the entire solar spectrum it is important to be able to grow p- and n-type InGaN. Currently InGaN is intrinsically an n-type material because it has excess nitrogen (N).

One immediate challenge is to grow p-type material. The most promising element to add to InGaN to make it p-type is magnesium (Mg) because it acts as a hole donor in the material. (Mark, 2009)

GROWING THIN FILMS

When growing thin film materials, two components are utilized. One, being a vacuum chamber and the second being high temperatures. A vacuum is used to provide a clean environment that eliminates impurities and allows various materials to be evaporatively deposited onto substrates. Impurities vary depending on what type of material is being grown, but for InGaN moisture from the air (water), oxygen, and hydrocarbons (e.g. oil from our skin) are dominant. To deal with these impurities, the vacuum chambers are thoroughly cleaned using solvents, and only oil-free turbopumps are used. Once the vacuum system is pumped out, a bakeout or outgassing is performed where the entire camber is heated to ~120°C to release any trapped gases.

Molecular Beam Epixay

The basic method used for growing thin films is Molecular Beam Epitaxy (MBE). This method utilizes deposition sources that evaporate elemental materials by heating them to temperatures where the materials have a high vapor pressure. Usually, this means the materials must be heated past their melting points to allow evaporation of individual atoms of the elements, for example Ga, In, and Mg.

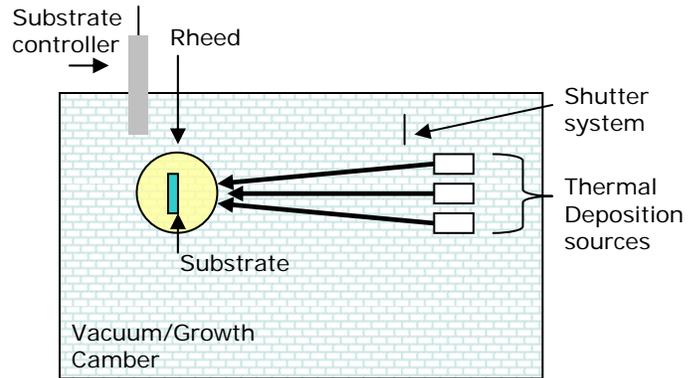The schematic below shows the components of a basic MBE system.

Figure 5: Typical Molecular beam Epitaxy system for growing films

The centers of the deposition sources are position to face the substrate to maximize the delivery of each material to the substrate. Each evaporation source is equipped with a shutter for accurately stopping the delivery of material to the substrate, which cannot be achieved quickly by reducing the temperature of the evaporation sources. Some MBE systems utilize RHEED (Reflection High-Energy Electron Diffraction) to allow real time monitoring of the crystalline growth of the thin film. Also note that the substrate must be heated to help facilitate crystalline growth of the desire thin film material.

Using conventional MBE to grow InGaN is very difficult because nitrogen (N_2) is hard to dissociate using a thermal deposition source because of the strong triple bond ($N\equiv N$). Traditionally, ammonia (NH_3) is used. However dissociating ammonia to make atomic N introduces hydrogen (H), an impurity for InGaN growth.

Another problem exists is that InGaN, once formed, decomposes at temperatures above ~700°C. Unfortunately, the substrate temperature required to successfully grow crystalline InGaN is around 1100°C. This growth/decomposition dilemma makes InGaN difficult to grow using MBE. Because of this situation, it is exceedingly difficult to grow high-quality In-rich InGaN with of >20% In content

Energetic Neutral Atom Beam Lithography and Epitaxy

To overcome the disadvantages of MBE, Energetic Neutral Atom Beam Lithography and Epitaxy (ENABLE) was developed. This system uses a similar process to MBE, except it deposits energetic N atoms onto the substrate surface to grow the desired nitride thin film using a high power CO_2 laser. The laser is used to form a high density plasma that breaks the triple bonds of N_2 gas to form N atoms with high kinetic energies (1 to 5 eV). The N atoms are sent though a nozzle and a series of collimators that direct the them towards the substrate. The schematic below shows a detailed assembly of the ENABLE apparatus.
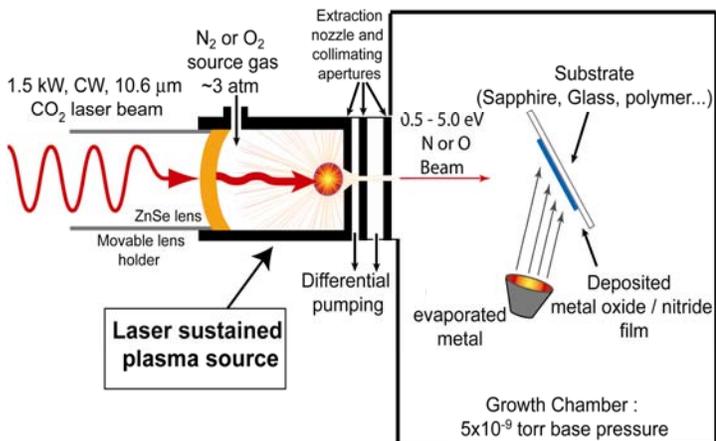

Figure 6: Schematic of the ENABLE system. The laser plasma produces nitrogen atoms with high kinetic energies, effectively reducing the temperature needed for the substrate.

The high kinetic energy of the N atoms are used to overcome activation barriers for reactions with In and Ga to form InGaN on the substrate (typically sapphire). Other schemes for making active N atoms provide kinetic energies of, 0.5 eV.

The high kinetic energies of the N atoms allow for lower substrate growth temperatures, typically 500 to 700°C, because the energetic N atoms overcome the activation barriers to form InGaN, and directly avoiding the InGaN decomposition that occurs above ~700°C. For conventional MBE, the substrate temperatures are in the 800 to1100°C range (Mark, 2009).

Magnesium dopant source

To deposit magnesium into InGaN to make p-type material, a thermal deposition source is used. A Veeco ultra high vacuum (UHV) thermal evaporator source shown below was recently installed and being used.

Figure 7: Thermal deposition source from Vecco that is currently being used for Magnesium to grow, p-type GaN and InGaN

Mg has a melting point of ~650°C but has a high vapor pressure above ~300°C. Thus, the Mg deposition source need to be operated at a minimum temperature of ~300°C. There is one power vacuum feed though that heats the source and a thermocouple that accurately monitors the temperature of the source to make sure that the temperature is well regulated and reproducible.

The Mg evaporation cell was calibrated by measuring the Mg concentration in GaN films using a combination of photoluminescence (PL) that provides an optical signature, and electrical measurements that determine the p- and n-type carrier concentrations in the electrically active films. These results are then correlated to the Mg evaporator temperature, providing a calibration curve for subsequent doping of InGaN films.

RESULTS

The ENABLE system has been used to successfully grow GaN, InGaN, and InGaN of varying composition. Successful p-type doping of GaN has recently been demonstrated (details below) and p-type doping of InGaN is the next challenge to be investigated.

The new Veeco evaporation source for Mg is being calibrated for the optimal temperature that will result in a high concentration of Mg in the films leading to p-type material.

To calibrate the Mg evaporator source numerous films have to be grown at different evaporator temperatures and their optical signatures for Mg dopant concentration measured using PL.

Electrical transport measurements are then used to determine the electron-hole concentrations.

Below is a representation of the optical signature of GaN (Figure 8), and GaN and Mg (Figure 9). The first figure shows what the GaN bandgap would likely resemble before Mg is added.
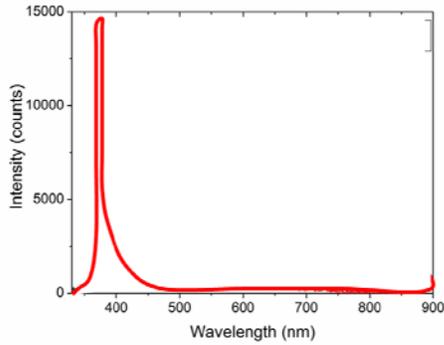

Figure 8: The optical signature of pure GaN

Once the Mg is added to the GaN, other peaks appear. These peaks are called the Mg acceptor bands. Figure 9 shows the optical signature of GaN doped with Mg using ENABLE. The longer wavelength peaks around 400 nm are a clear indication that the sample has varying amounts of Mg in it.
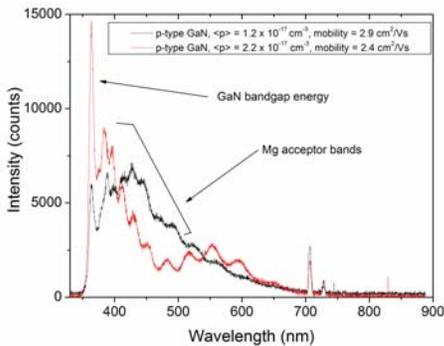

Figure 9: Bandedge and Mg acceptor bands for GaN doped with Mg

So far, four p-type GaN films have been grown and analyzed: ENB-46, 47 and 48 and 49. Using the photoluminescence to obtain the optical signatures, an estimate of the band edge intensity and Mg acceptor intensity can be determined. The Figure 10 shows how the band edge and Mg acceptors vary with increased Mg source temperature/doping. Once the band edge and Mg have been quenched (reduced to zero), the band edge optical signature for increased Mg does not change. This figure is extremely useful in

determining the relative Mg concentration with increases or decreases in the temperature of the Mg source when growing a film.
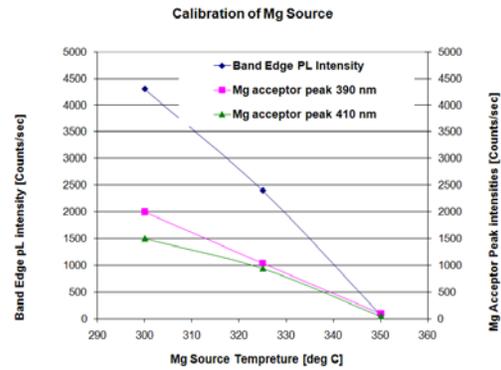

Figure 10: A decrease in bandedge and Mg acceptor peaks as more Mg is evaporated onto the film.

The electrical measurements of carrier concentrations determine the absolute temperature of the Mg source needed for growing p-type material. Results for the electrical characterization are shown in Figure 11**Error! Reference source not found.**. Note that the circles correspond to electron concentrations, and square for ENB-49 corresponds to the hole concentration.

The films grown near 300°C have electron concentrations caused by the GaN having a an excess concentration of nitrogen and not enough Mg has been incorporated into the film to make it p-type. As the magnesium source temperature is increased, more incorporation of Mg occurs in the film; first equalizing the extra electrons from N, before a p-type GaN electrical signature appears.
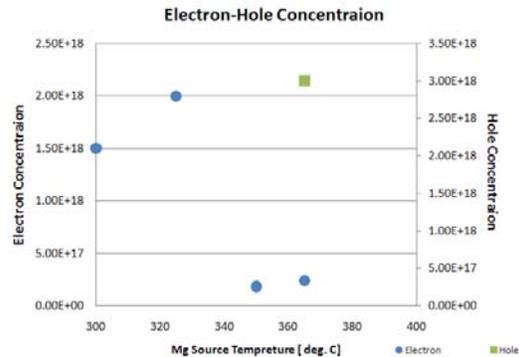

Figure 11: Electron-hole concentration in GaN using new Mg dopant source

The minimum temperature needed to arrive at a p-type material is determined by analyzing the electron concentration data in Figure 11. The

electron concentration for 46, 47, and 48 and 49 are generally decreasing with increase Mg temperature, reaching a zero electron concentration at ~360°C. This indicates that Mg is successfully being doped into the material. Since ENB-49 (hole) indicates that there is a hole concentration, we can conclude that the minimum temperature needed for P-type GaN material is 360°C.

To determine the optimum hole concentration that can yield p-type material, more samples will need to be create using increased Mg source temperatures exceeding 400°C.

CONCLUSION

It has been argued that developing InGaN based photovoltaic cell can make a substantial difference is how energy is produced. Solar cells in general require an n-type material and a p-type material. While InGaN in intrinsically n-type, challenges lie in growing p-type InGaN using Mg as the dopant material. Currently ENABLE has successfully grown, GaN, InN, InGaN,, and Mg doped GaN. The next step is to grown Mg doped p-type InGaN that can then be used to make a prototype InGaN based solar cell.
to attempt to build a prototype of a InGaN based solar cell.

BACKGROUND

Photovoltaic Basics
To understand why InGaN can potentially revolutionize the solar industry it is important to understand how solar cells work.

The basics of all eleterical devices originate from semiconducting materials which are in groups IV, V, and VI of the periodic table of elements. The most commonly used semiconductor is Silicon (Si) shown below.
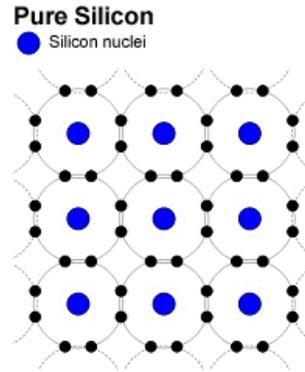

Figure 12: Intrinsic semiconductor Silicon

The above figure shows a pure or an intrinsic semiconductor. Having a pure semiconductor is not very beneficial for PV because there are no free electrons to move around and generate electricity. To introduce these electrons the material will need to be doped by introducing impurities from a higher or lower group, meaning that you'll be introducing an electron or a hole in the material.

In the example of Si, if Boron (group III) is dope into intrinsic Si an extra electron will be introduced and the Si will be a p-type material, or we can dope Phosphorus (group V) into Si, leaving a hole in the surrounding valance shells of the Si atoms, producing an n-type material. Below are figures illustrating the differences.
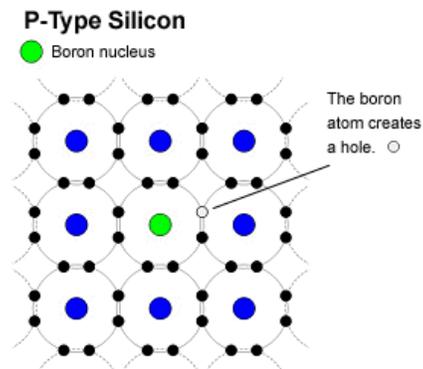

Figure 13: Adding Boron to Silicon will leave a hole in the surrounding Si valance shells.

N-Type Silicon

● Phosphorous nucleus

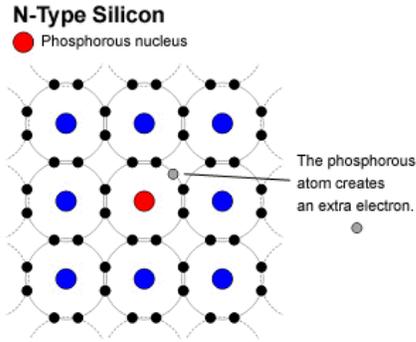The phosphorous atom creates an extra electron.

Figure 14: Adding Phosphorous to Silicon will leave a and extra electron in the surrounding Si valance shells.

When the p and n-type materials are brought together and allowed to reach equilibrium an electric filed is created. The electric field essentially is a dipole that allows the electrons to flow from the p-type material to the n-type material, but not from the n-type to the p-type.
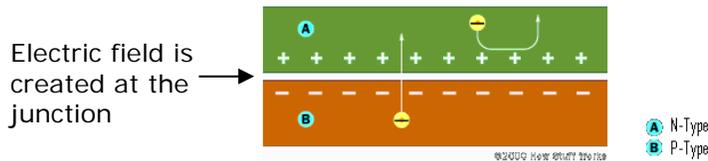
Electric field is created at the junction →

A N-Type
B P-Type

Figure 15: A diode is created when the p and n-type material are brought together

electrons need to be able to flow in a complete circuit; meaning that the negative electrons in the n-type material need to be able to return to the holes in the p-type material. To accomplish this, a load is placed connecting the two materials together.

So as photons are absorbed into to the materials, electrons are released from the p-type material. As they leave the p-type material to go to the n-type they leave behind a hole, this is refereed to as the electron-hole pair. If they are close enough to the electric field then they will be able to travel to the n-type material and though the load and back to fill one of the holes left behind. As more photons are absorbed more electron-hole pairs are created to increase the flow of electrons or current (Aldous).
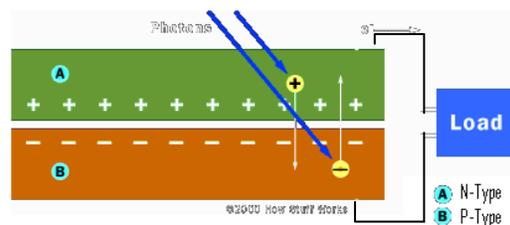

Load

A N-Type
B P-Type

Figure 16: As photon are released, electron hole pairs are created and electrons are able to flow to generate an electrical current

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