# Chapter 1

# Introduction

## 1.1 Energy and Climate Change

The modern world, with its lighted cities, heated homes, millions of cars, trucks, boats, planes, and even Ipods and cell phones, uses far more energy per capita than the world of our ancestors. It is difficult to fathom the magnitude of energy that we, as a planet, are consuming all the time. In 2006, our global civilization consumed 472.3 quadrillion ($10^{15}$) BTUs,[1] which converts to an average power of 15.8 Terawatts (TW), or 15.8 x $10^{12}$ W. With our current global population of approximately 6.5 billion people, that is 2,430 W each, equivalent to constantly running about 40 incandescent, 60 W light bulbs for every single person on the planet. Of course, the per capita consumption is far higher in the developed world, with the typical U. S. consumer using more than 4 times the global average. However, as the rest of the world continues to develop, the per capita consumption will climb even higher.

The energy needs of the planet are projected to continue growing in the foreseeable future, largely due to population growth and the rapid economic development of countries such as China and India. The Energy Information Administration (EIA) of the U. S. Department of Energy predicts that the mean global energy consumption will rise

44% from its 2006 value to an average rate of 22.7 TW by 2030 (Figure 1.1).[2] These numbers are a cause for alarm, not only because it will be a challenge to supply energy on this scale, but because the large majority of our energy (~ 86%)[1] is currently generated by burning fossil fuels (Figure 1.2). In addition to questions about the long-term sustainability of this dependence on non-renewable fuels, there are serious concerns about the consequences of the combustion of so much carbon.

The burning of fossil fuels creates $CO_2$, a known greenhouse gas that contributes to the phenomenon of global warming. While there is still ongoing debate in the media about the validity and consequences of the global warming theory, the scientific community as a whole is largely in agreement that it is real and happening. This is strongly supported by the Intergovernmental Panel on Climate Change's Fourth Assessment Report released in 2007.[3] The clearest evidence that the planet is warming includes global temperature data and worldwide observations of the shrinking of sea ice, the retreating of glaciers, the rising of ocean levels, the bleaching of coral reefs, and the increases in strong storms and floods. On its present course, unabated climate change could have severely adverse effects on ecosystems, submerge coastal cities through sea level rise, and lead to more water shortages and droughts.

There are reasons beyond the threat of climate change to strive for energy production that is less reliant on fossil fuels. Burning coal and petroleum releases gases into the atmosphere that cause pollution and lead to smog and acid rain. Mining and drilling for fossil fuels can devastate the local environment, and oil spills can cause harm to ecosystems from which they can take decades to recover. A dependence on fossil fuels also causes many nations to be dependent on others that are rich in these natural resources, resulting in geopolitical tensions. Lastly, a growing demand for a dwindling supply of resources is clearly an unsustainable energy plan for the long-term future. These issues, along with the grave and uncertain threat of climate change, are strong motivators to replace fossil fuels with carbon-free energy sources.

In the coming decades, carbon-free energy alternatives will need to be implemented on a massive scale to avert the climate change crisis by stabilizing $CO_2$ levels at reasonable target values. The technical analyses of Hoffert et al. indicate that 10 – 30 TW of carbon-free primary power technology will need to be in place by 2050 to meet modest $CO_2$ stabilization goals.[4, 5] Thus, the majority or even the entirety of our global energy consumption will need to be supplied by the middle of this century by sources that do not emit carbon. While they are worth exploring to help ease this transition, the concepts of "clean" coal and carbon sequestration are unlikely to be able to meet this challenge in a sustainable fashion.[6-9] Nuclear fission technology is well-established and has the potential to play a partial role in meeting the "terawatt challenge." However, in addition to serious concerns about nuclear waste, nuclear weapons proliferation, long plant start-up times, and a strong "not-in-my-backyard" sentiment among the general public, energy from fission may be limited on this scale by the abundance of suitable nuclear fuel.[6, 10, 11] Nuclear fusion is a promising long-term carbon-free power source, but it has enormous technical challenges to overcome. Researchers have yet to demonstrate a fusion reactor that generates more energy output than its required energy input, and advancing the technology requires decades-long, exorbitantly expensive, multinational projects such as the International Thermonuclear Experimental Reactor

(ITER).[12] Nuclear fusion is therefore extremely unlikely to provide a significant fraction of the world's energy needs by the middle of this century.[11] To implement at least 10 TW of carbon-free energy by 2050, we will need to turn to renewable energy sources.

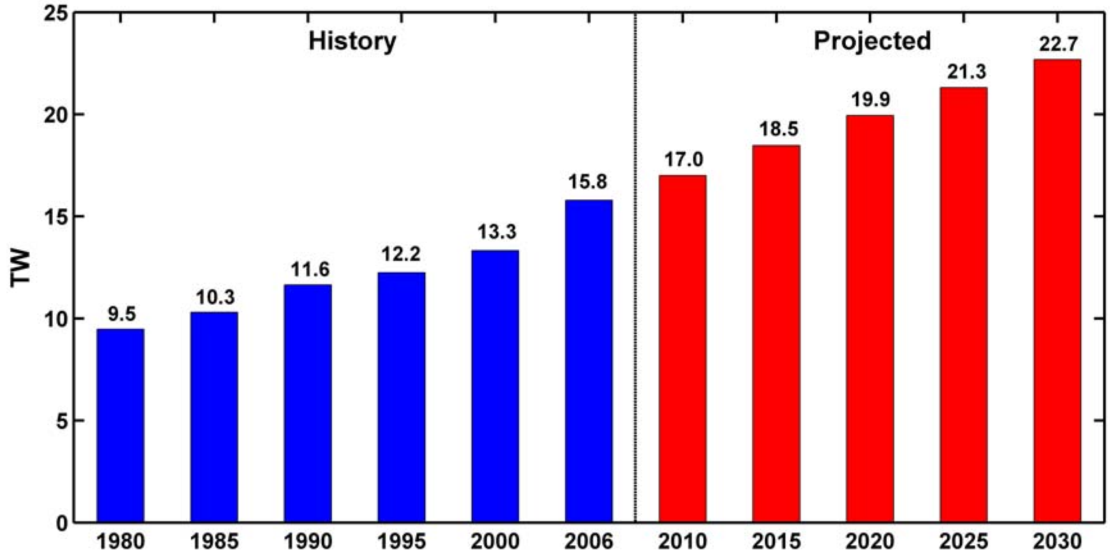

**Figure 1.1. Mean global energy consumption, 1980 – 2030.** Total average annual energy used by humankind, in TW ($10^{12}$ W). Historical data for the recent past is displayed in blue, and projections up to the year 2030 are shown in red. Projections are based on the EIA's International Energy Outlook 2009.[2]

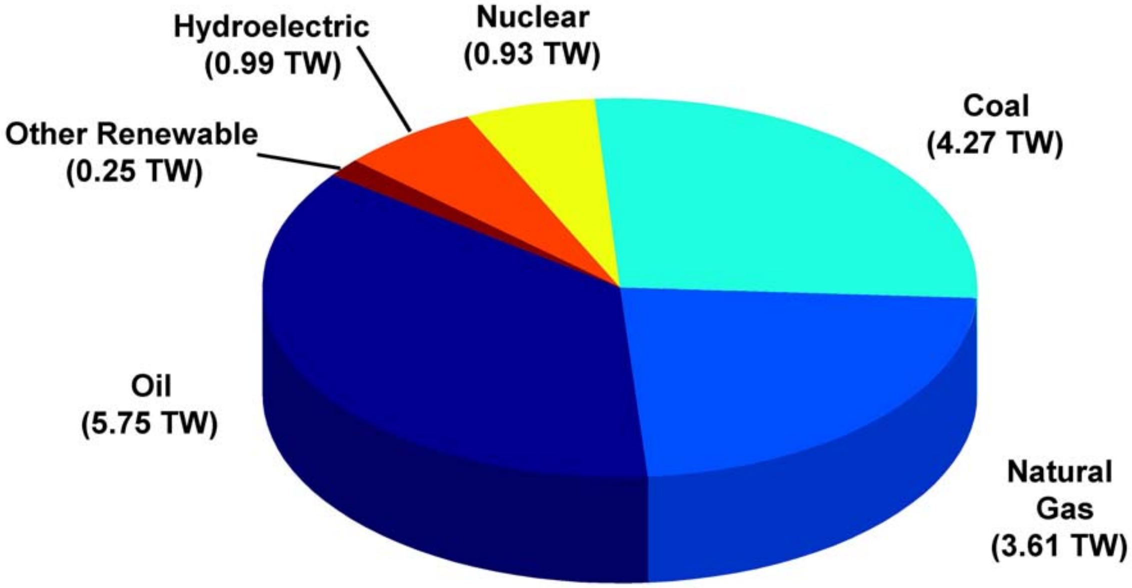

**Figure 1.2. Mean global energy consumption by source, 2006.** A breakdown, in TW ($10^{12}$ W), of how humankind generated the energy it consumed in 2006. "Other Renewable" includes geothermal, solar, wind, and wood and waste. The total average power used by the world in 2006 was 15.8 TW, with ~ 86% generated by the combustion of fossil fuels. Numbers are converted from data provided by the EIA.[1]

## 1.2 Renewable Energy Options

Mankind has developed a number of ways to harness energy from the ongoing natural processes of our environment. These renewable sources include hydroelectricity, biomass, wind, geothermal, ocean, and solar energy. Together these resources provide a hope of meeting the terawatt challenge with carbon-free or carbon-neutral primary energy sources.

A comparison between the practical potential for power generation between these resources highlights which can be key technologies for meeting the world's future energy needs (Figure 1.3).[13, 14] Hydroelectricity is by far the most commonly used renewable energy for electricity generation at present. The World Energy Assessment concludes that there is technical potential for ~ 1.6 TW of hydroelectricity, which does not impose restrictions for economic or environmental considerations.[13] As such, it is an overestimate of the practical limit. Considering that 0.99 TW of hydroelectricity was consumed in 2006 (Figure 1.2),[1] there is little room for this industry to contribute more towards the 10 TW carbon-free energy goal. Biomass for electricity generation and transportation fuel can be produced carbon-neutrally, but the low power density of photosynthesis (~ 0.6 W $m^{-2}$) is a limitation. More than 10% of the Earth's land surface, an area approximately equivalent to all agricultural land, would be needed to get 10 TW from biomass.[6] This would create competition for water supplies, drive up global food prices, and contribute to deforestation and habitat destruction. An optimistic estimate for the potential power generation of biomass is 7 TW.[14] There is theoretically potential for 50 TW of wind energy if the entire suitable land area of the Earth were used. However, a more reasonable limit of 4% land area utilization gives a practical potential of 2 TW of wind power.[13] Geothermal energy has enormous potential but is widely dispersed, and the technological ability to utilize it, rather than its available quantity, will determine how much it can contribute. One estimation for the total continental geothermal energy potential is 11.6 TW.[14] There is also a great deal of energy theoretically available from the ocean in the form of tides, waves, ocean thermal, and salt gradient energy. However, these energy resources are very diffuse and therefore difficult to collect, and the technology for harvesting energy from the ocean is not considered mature enough yet for commercialization.[13]

The most abundant renewable resource by far is supplied by the sun. There is an average 1.2 x $10^5$ TW of solar energy striking the surface of the Earth,[11, 13, 14] which means that in only 69 min, the sun hits our planet with enough energy to run human society at our 2006 rate (15.8 TW) for an entire year. With the conservative restrictions of a 10% conversion efficiency and land-based sites only, there is a practical potential for 60 TW of solar energy.[13, 14] This is nearly four times the 2006 global energy consumption and represents a greater practical potential than the combination of hydroelectricity, biomass, wind, and geothermal energy (Figure 1.3). Our current energy needs could be met by covering just 0.1% of the Earth's surface with 10% efficient photovoltaics. Although there are issues with the solar resource, such as its regional variance and intermittency due to time, season, and weather conditions, its vast abundance in comparison to the other renewable options makes it clear that solar will need to play a leading role in the global energy portfolio to produce > 10 TW of carbon-free primary energy by 2050.

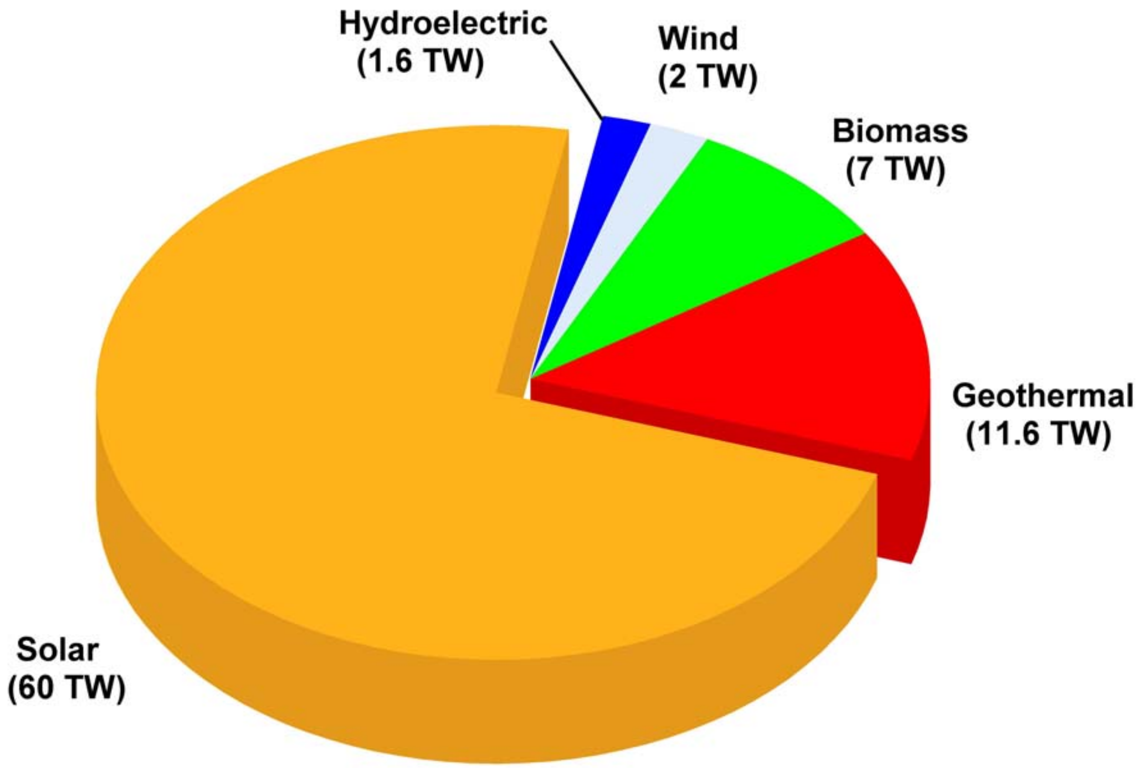

**Figure 1.3. Global practical potential of renewable resources.** Estimates of the technical, annual average power, in TW, available from various terrestrial renewable energy sources.[13, 14] The solar energy number assumes 10% energy conversion efficiency.

## 1.3 Cost of Photovoltaics

Considering the enormous abundance of the solar resource, why are we not using solar energy on a massive scale already? Sunlight falls freely on everyone, and the photovoltaic concept has been around for a long time. Becquerel discovered the photovoltaic effect in 1839,[15] and in the 170 years since that time it has only grown to comprise ~ 0.1% (or 16 GW) of the global energy consumption.[16]

Economics is the main factor limiting the implementation of photovoltaics (PV). The core problem is that solar cells cannot yet provide electricity to the consumer as cheaply as fossil fuels can. The production cost of solar photovoltaics at present is US$ 0.25 – 0.30 per kWh, compared to US$ ~ 0.03 – 0.05 per kWh for fossil fuel based utility-scale electrical power generation.[17-19] Although government subsidies and cost savings from scaling up can help this price comparison, changes in photovoltaic manufacturing are needed to drive the cost per kWh down so that it can be competitive with existing utilities.

With approximately 90% of the market share,[19-22] crystalline and polycrystalline silicon solar cells set the benchmark for photovoltaic prices. Estimates for the least expensive current retail module prices are ~ US$ 3 per peak watt ($W_p$), with average retail module prices closer to US$ 4.50/$W_p$.[20, 23] Although estimates vary substantially,[20, 24] one breakdown of the production of multicrystalline silicon solar module costs assigns 48% of the cost to materials, 13% to cell processing, 9% to module assembly, and 30% to the "balance of systems" (Figure 1.4).[22] Within the materials category, the feedstock costs refer to the expense of electronic grade polysilicon used for crystal growth, which itself is typically produced by purifying silicon dioxides (sand) to metallurgical grade silicon which is then further purified by the Siemens process to electronic grade. In this process, for each mole of Si converted to electronic grade polysilicon, 3 – 4 moles are converted to the byproduct $SiCl_4$.[25] The ingot growth expenses involve polysilicon sorting and etching, crystallization, and ingot shaping and sizing.[24] The crystallization step, through a process such as the Czochralski growth technique or block-casting, is expensive because it is energy intensive, must strictly exclude impurities, and sacrifices a large crucible for each ingot produced.[21] Wafering refers to the costs associated with cutting the Si boules into wafers and then cleaning and polishing them. The cutting process is particularly expensive because it uses wire saws to slice the boule, with each wire consuming ~ 180 μm of silicon lost as waste and requiring the etching of another 25 μm to remove the damaged surface.[24] In all, the wire sawing process wastes up to 35% of the material as "kerf losses."[21] The cell processing costs include chemical etches, diffusion doping, antireflection coating, front and rear contact printing, and cell testing.[24] Module assembly involves connecting the cells together reliably in a circuit, encapsulation of the cells, framing the unit, and testing the module.[20, 24] The balance of systems refers to the inverter, grid connection, and installation fee that are necessary for a fully installed system.

Although photovoltaic electricity costs have been gradually declining (from over US\$ 60/$W_p$ in 1976 to ~ US\$ 4/$W_p$ in 2009), significant changes will be needed to continue the cost curve to the target US\$ 1/$W_p$ that is required to achieve grid parity so that PV can compete with large-scale utilities.[23, 26, 27] Because materials expenses are approximately half of the cost of a solar module, the ability to make solar cells out of much cheaper materials with fewer purification and wafering requirements would subtract substantially from the final price of photovoltaic electricity. Several thin film solar technologies, such as amorphous Si, CdTe, and $CuInSe_2$, are striving for this goal but have not reached it yet.[21] While promising, these technologies have had limitations including low module efficiency, toxicity, and materials scarcity issues.

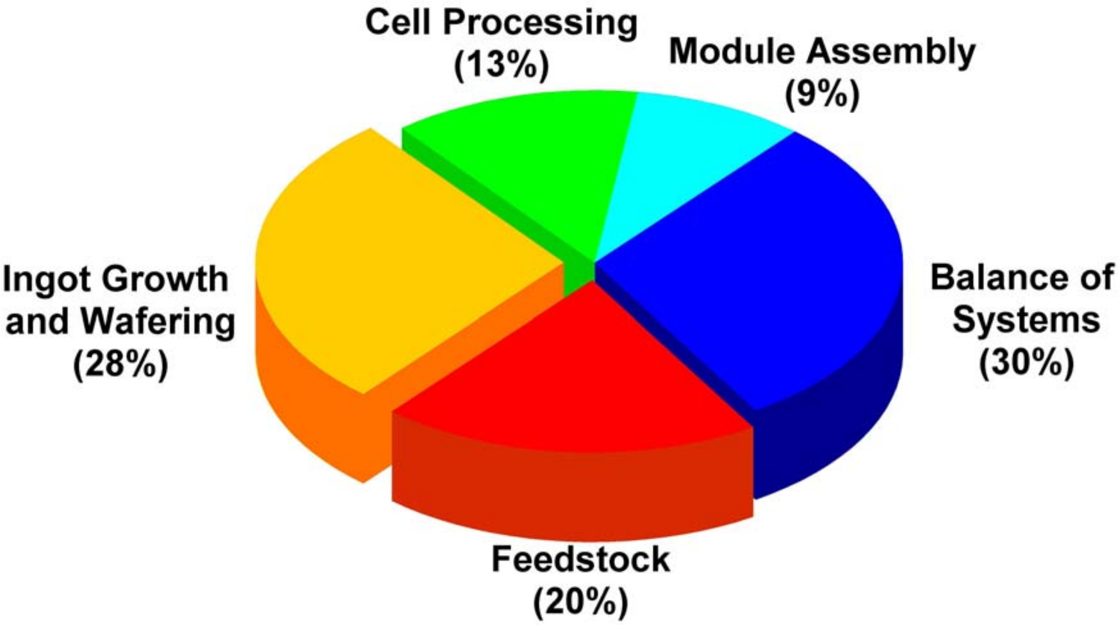

**Figure 1.4. Cost breakdown of crystalline silicon solar PV modules.** Percentages of the total module cost attributed to specific manufacturing processes.[22] Feedstock, ingot growth, and wafering together constitute the materials cost and total 48%.

## 1.4 The Radial Junction Concept

Solar cell materials are costly because they must be able to satisfy the physics necessary to produce photovoltaic electricity. In a cell, a photon of sufficient energy will create an electron-hole pair that is then separated by a built-in electric field near the junction.[28, 29] The charge-carriers that are effectively separated through the junction are collected and sent to the front and back contacts as useful electric current. The minority-carriers (holes for n-type, electrons for p-type) move across the junction, and must therefore be able to diffuse from the point of their generation to within the electric field without recombining in order to produce current.

Solar-quality semiconductor materials are expensive to manufacture primarily because they must be both pure and highly crystalline to minimize the recombination of photogenerated electron-hole pairs. Impurities and grain boundaries act as trap centers where charge-carriers can wait until encountering a carrier of opposite sign, recombining and wasting the energy as heat rather than current. Inexpensive semiconductor materials that are candidates for solar cells generally have a high impurity level and/or defect density, which causes them to have a low minority-carrier diffusion length ($L_n$ for p-type, $L_p$ for n-type).[30]

In a traditional, planar junction solar cell, $L_{n/p}$ must be greater than the optical absorption depth in order to efficiently collect the photogenerated charge-carriers (Figure 1.5). If $L_{n/p} < 1/\alpha$ (an average "optical thickness," related to the absorption constant $\alpha(\lambda)$ integrated over all wavelengths $\lambda$), the solar cell will be carrier-collection limited in the base region. Also, the thickness of the cell, $L$, must be $> 1/\alpha$ to absorb most of the incident light. Defining $1/\alpha$ to be the thickness of material required to absorb 90% of the incoming photons, Si has an optical thickness of $\sim$ 125 μm. Thus efficient, planar junction Si solar cells must have both $L$ and $L_{n/p} > 125$ μm. The same reasoning applies for other semiconductors and sets the lower limit for an acceptable minority-carrier diffusion length in an efficient solar cell. The effective optical thickness, and therefore the necessary $L$ and $L_{n/p}$, can be lowered by using light-trapping techniques (i.e., antireflection coatings, back side reflectors, etc.). However, considering the limitations of the ability of light-trapping to decrease the required thickness,[31, 32] materials with minority-carrier diffusion lengths significantly less than their optical thicknesses cannot be made into high efficiency planar junction solar cells.

By switching to a different cell geometry, however, it may be possible to avoid this restriction. An answer might be found in redesigning the junction architecture to promote the separation of photon absorption and charge-carrier collection into orthogonal spatial directions. Using an array of high aspect-ratio cylindrical pillars with radial junctions, optimal light absorption could occur along the lengthier axial dimension, while charge-carrier extraction would take place over the much shorter radial dimension (Figure 1.6). This structure makes it possible to separately optimize the design for both ideal optical absorption and carrier collection by tuning the wire length and diameter independently. If inexpensive, low-diffusion-length semiconductor materials can be fabricated as a wire array structure in a cost-effective process, they could potentially produce efficient solar cells much more cheaply than the high-diffusion-length planar alternatives.

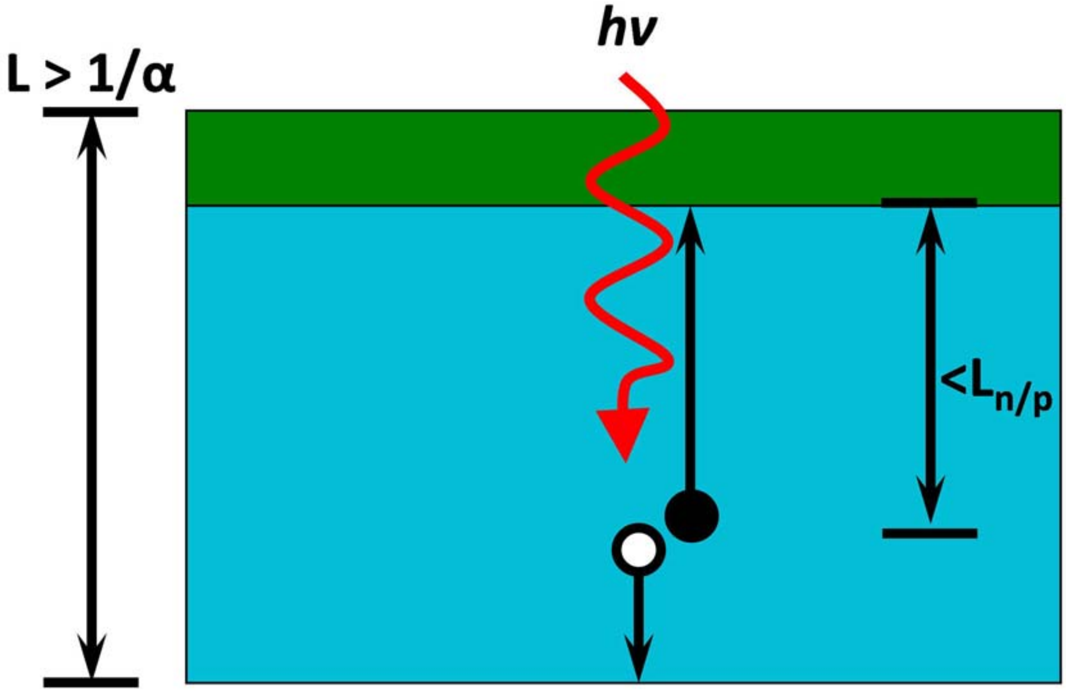

**Figure 1.5. Planar junction solar cell architecture.** The semiconductor slab thickness, *L*, must be greater than the optical thickness, 1/α, to absorb most of the light. The minority-carrier diffusion length, $L_{n/p}$ ($L_n$ for p-type, $L_p$ for n-type), must also be greater than 1/α or the device will be carrier-collection limited toward the base of the cell.

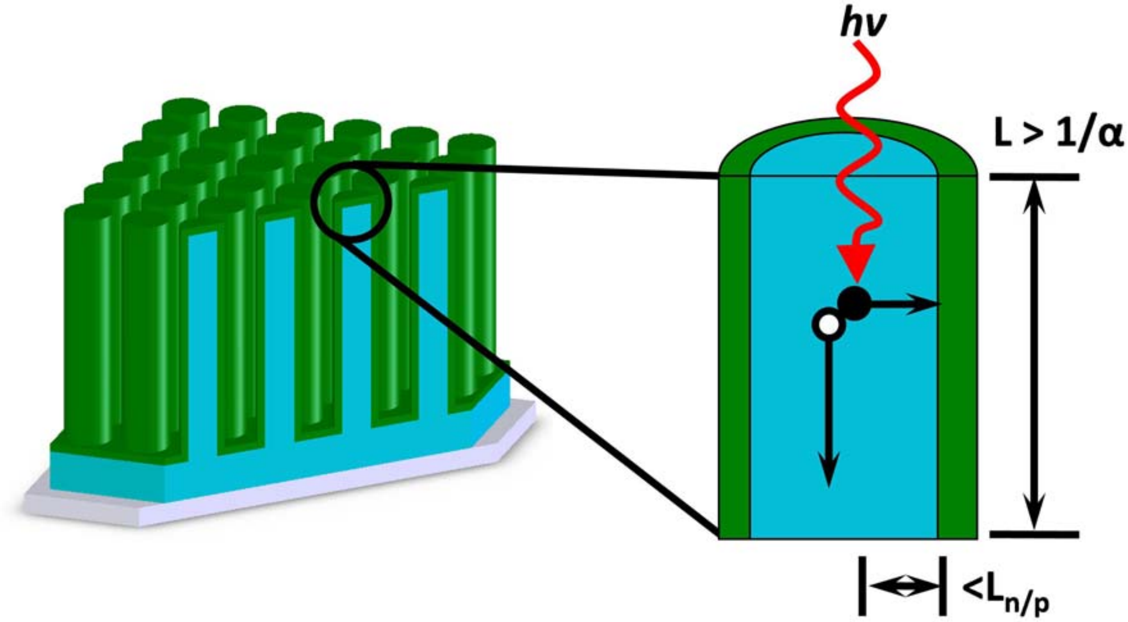

**Figure 1.6. Radial junction solar cell architecture.** The idealized radial junction cell consists of a densely packed array of wires of uniform dimension (image credit: M.D. Kelzenberg). The semiconductor wire length, *L*, should be greater than the optical thickness, 1/α, to absorb most of the light, but the minority-carrier diffusion length, $L_{n/p}$ ($L_n$ for p-type, $L_p$ for n-type), need only be comparable to the wire radius for the device to collect most of its photogenerated charge-carriers.

## 1.5 Modeling of a Radial Junction

At the outset of this project, a theoretical study was conducted by Kayes et al. to model the behavior of an inorganic radial p-n junction solar cell and compare it to a planar cell.[33] The model assumed an abrupt junction with the depletion layer approximation, included the effects of surface recombination and Shockley-Read-Hall recombination from a single-trap level at midgap, used only light normally incident on the top face of the semiconductor rod, and took carrier transport to be purely radial. A single cylinder with a radial junction was investigated, so that the model neglected the complicated optical effects that would result from light passing through arrays of wires of varying packing density and arrangement. The simulation used both Si and GaAs rods. The key findings of the study were that optimal cells had a radius approximately equal to the minority-carrier diffusion length in the core of the rod, doping levels must be high enough that such short radii rods are not fully depleted, the short-circuit current ($J_{sc}$) was basically independent of radius if the radius was less than the diffusion length, open-circuit voltage ($V_{oc}$) decreased with decreasing rod radius, and an increasing depletion-region trap density profoundly decreased the ($V_{oc}$) at diffusion lengths less than ~ 5 μm. The study concluded that radial junctions offered large gains in efficiency over planar junctions if the material was carrier-collection limited in planar form and if the depletion-region recombination rate was relatively low. With higher depletion-region recombination, only modest efficiency gains were possible. For Si, regardless of depletion-region trap density, efficiencies of ~ 15% were predicted with minority-carrier diffusion lengths of 5 – 10 μm, several percent better than the planar equivalent.

This work was eventually followed by additional modeling by Kelzenberg et al. with the benefit of minority-carrier diffusion length estimates for Si wires grown by a chemical vapor deposition method.[34] This model employed the Sentaurus Device simulator software, which simultaneously solves the electron and hole continuity equations and the Poisson equation within the device. A Si p-n junction on a single wire was modeled with most of the same assumptions used in Kayes' work, with the notable exception that carrier transport was allowed to occur in both the axial and radial directions. All the same general trends were confirmed, although this work concludes that a radius equal to half the minority-carrier diffusion length is optimal. Simulated current-voltage curves based on an experimentally measured diffusion length of 10 μm led to a wire cell efficiency of 17%, compared to 13% for a planar cell.

## 1.6 Routes to Wire Array Fabrication

While it will be critical to produce wire array cells that perform as well in experiment as they do in theory, it is equally essential that they be fabricated with a cost-effective method that reduces the materials and processing costs of solar cell manufacturing. If wire array fabrication is as expensive as the production of pure, crystalline planar materials, there is little reason to pursue this technology. Fortunately, a number of approaches have been developed to promote the one-dimensional growth of materials, several of which hold promise as potentially inexpensive routes to manufacture wire arrays.[35-37]

Perhaps the cheapest method is the utilization of solution-based chemistry to induce one-dimensional growth. One possible way to do this is to introduce capping agents that change the free energy of different crystal planes and favor one plane in particular.[35] With this approach, colloids in solution have been grown into nanowires and tetrapod structures.[38] Through the control of interfacial surface tension and a thermodynamic understanding of the nucleation and growth, metal oxide materials can be "purpose-built" from solution into nanowire array structures.[39, 40] Another inexpensive, scalable technique is to use nanocrystals dispersed on a substrate in a hydrothermal solution process to seed the growth of nanowires. This method has been demonstrated to efficiently produce large-area arrays of dense ZnO wires.[41] In general, solution-based wire growth methods are limited in their application for solar cell fabrication by either the disassembled, substrate-free nature of the wires produced or by the restricted types of semiconductors that can be shaped with a particular technique.

Physical or chemical vapor deposition techniques can produce semiconductor wire arrays as well. The most widely used approach, the vapor-liquid-solid (VLS) mechanism, uses a solid catalyst droplet that liquefies upon absorption of a vaporous species until it becomes supersaturated and deposits a solid wire by growth in a particular crystal direction (see Section 3.3.2).[42] The VLS mechanism can produce aligned, highly crystalline wire arrays of a range of semiconductors, but uses potentially expensive gas phase precursors, catalysts, and substrates. The possible need for high growth temperatures and low pressures can also add to the expense of wire growth with this approach.

A straightforward route to the production of one-dimensional structures of practically any material is to use template-directed synthesis.[35] In this method, the material is deposited within the template so that its morphology is shaped by the scaffold surrounding it. The template is usually sacrificial and can be removed by a chemical etch after nanowire deposition. Research groups have demonstrated templates through the use of porous materials, biological macromolecules, surfactants, block copolymers, and nanostructures produced by another method. Porous anodic aluminum oxide membranes are particularly common templates for nanowire synthesis (see Section 2.1).[43, 44] The drawbacks of this approach include the additional processing and complexity of using a template as well as the potential for surface contamination after template removal.

## 1.7 Previous Work Related to Wire Array Solar Cells

Ideas similar to the radial junction wire array solar cell have been investigated to test the concept of decoupling the directions of carrier collection and optical absorption. The first, the vertical multijunction solar cell, etched grooves into a planar base to form a vertical junction that increased the probability of minority-carriers reaching the collecting junction.[45] Later, a parallel multijunction solar cell was explored in which thin, horizontal, interpenetrating n- and p-type layers were alternately laid on top of each other.[46] While both of these designs were demonstrated with impressive efficiencies,[47, 48] research was eventually halted on them, likely because they were not cost-effective to produce. There was even one early published example of Si wires as photoconverters,[49] but it was a preliminary report and the serious study of wire array solar cells was not pursued.

Many of the fundamental properties of semiconductor nanowires are well established, however.[35, 36] The properties of single wires of semiconductors, including their carrier mobilities and lifetimes,[50] their resistivities,[51] methods to passivate their surfaces,[52] and their preparation as core-shell structures,[53] have been reported in detail. The photoluminescence,[54] reflectivity,[55] quantum-confinement effects,[56] and electrical properties[57] of arrays of semiconductor nanowires have been reported. However, comparatively little work has been performed on the use of such nanowire arrays as absorber layers in solar cells. Nanowire arrays have been used in dye-sensitized solar cells.[58-60] In these studies, the presence of $TiO_2$[59] or ZnO[60] nanowires provides a direct path for dye-sensitized, injected majority-carriers to reach the back contact, instead of exploiting the nanowires for their ability to facilitate collection of minority-carriers in the radial direction. Improved minority-carrier collection has been demonstrated, however, in photoetching processes using porous electrodes. Vanmaekelbergh and Kelly observed improved photocurrent quantum efficiencies in their studies comparing planar and nanoporous photoelectrodes of SiC and GaP.[61, 62] Thus, the theory that a nanowire geometry can be effective in overcoming minority-carrier collection length limitations in a semiconducting absorber phase, as compared to the properties of that same material in a planar solar cell structure, remains of significant interest. The work presented herein continues in this context. The objective of this thesis was to develop cost-effective methods for the fabrication of semiconductor wire array solar cells and to test and improve their photovoltaic performance relative to analogous planar solar cells.