

Photovoltaics: Progress in Materials and Technology

Philip Griffin (pgriffi5@utk.edu)

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Prof. Elbio Dagotto
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Department of Physics
University of Tennessee - Knoxville

Abstract

The historical background of photovoltaics technology has proved to be both beneficial, in the case of production capability, and detrimental, in the case of public supported research of new technology, to the prospect of widespread use of solar energy as a terrestrial source of electricity. In this review, the historical background, the fundamental physics, the present day technological possibilities, and the economic viability of the technology of photovoltaics are discussed.

Introduction

Since the observation of the photovoltaic effect by A. E. Becquerel in 1839, the opportunity to exploit the sun's radiant energy on Earth has been available to mankind [1]. Throughout the 19th and first half of the 20th century, however, it was neither technologically feasible nor economically viable to convert any of the sun's radiant energy into electricity for human use. During this time, the seemingly endless bounty of fossil fuels for electricity generation and the ignorance of man to the harmful bi-products of the burning of these fossil fuels created an economic and psychological barrier in society that completely halted progress in photovoltaic technology development.

It wasn't until mankind's desire to explore space in the 1950s that the opportunity of photovoltaic technological development began to emerge. With thoughts to power spacecraft during extended periods of time away from Earth and fossil fuel reserves, scientists and engineers began looking at photovoltaics as a reliable and consistent way to provide remote electricity to these space missions. Under this prerogative, the first practical photovoltaic "solar" cell was developed at Bell Laboratories in 1954, with an initial conversion efficiency of 6% [2, 4]. As the space program progressed, silicon solar cells became the ubiquitous power source for use on most satellites.

Throughout the development process of photovoltaic technology for space applications, researchers never really considered this technology viable for mass power production on Earth. Oil and coal fossil fuels were incredibly cheap when compared with electricity production costs of silicon solar cells. It wasn't until the awareness of the environmental harm caused by fossil fuels and, more likely, the energy crisis of the early 1970s in industrialized nations that public and governmental support of photovoltaic energy began to increase significantly [2].

Since then, the photovoltaics industry has grown rapidly. Aided by the production and facility investments made by semiconductor and microelectronics companies for related applications in other consumer technologies, the photovoltaic industry has grown at least 30% year over year for the last decade [3]. As more technological advances are made and economic incentives are put in place for companies to invest capital in this fast paced industry, the overall cost of solar power production will decrease enough to make it an economically viable alternative to energy production via fossil fuels.

Physics of solar cells

Most of the present photovoltaic technology takes advantage in one way or another of the inherent physics of semiconductor materials. The most commonly used material in the industry today is silicon, and certainly it is the most reliable and efficient material employed in power systems [4].

semiconductors

Semiconducting materials in use today (e.g. silicon) are crystalline materials with electronic properties characterized by the band theory of solids. The band structure of a simple semiconductor consists of a valence band, where all the electronic states are completely occupied, and a conduction band, which is (at $T = 0$ K) completely unoccupied [5]. These bands are separated by a forbidden region or gap where no electron can energetically exist. The size of the band gap in semiconductors is small when compared to that of band gap insulators, and there is a finite probability, when the temperature is increased above absolute zero, to thermally excite electrons from the valence band to the conduction band. These conduction electrons are called *intrinsic carriers* [2]. Another way to excite an electron from the valence band to the conduction band, referred to as optical absorption, is through the subjugation of the material to an electromagnetic field. This process occurs when a solar cell is illuminated with light of frequencies very near to the corresponding band gap energy. When photons with energy less than or much greater than the band gap energy are incident on the material, this energy is lost to the creation of phonons [5].

As an electron moves from the valence band to the conduction band through any of the above mechanisms, a vacancy is left behind in the valence band, creating an *electron-hole pair* [1]. In the crystal lattice the conduction electron is free to propagate, and the created vacancy in the valence band can also propagate through the crystal lattice. The conduction electron is a negative charge carrier and the hole is an effectively positive charge carrier [5]. These two distinct types of charge carriers, while mobile and effectively free in the material, are of opposite charge and will have a coulombic affinity to recombine inside the semiconductor material. While electron-hole pairs are constantly being created when a semiconductor is illuminated with light (of energy near the band gap energy), a current in general will not flow through an external circuit connected to the material. The pathway of recombination within the semiconductor itself is much more energetically favorable than for the charge carriers to flow through the circuit. Thus, to apply the photovoltaic effect to

the production of electricity, it is necessary to develop a device that forces the charge carriers to recombine via the external circuit.

doping a semiconductor

A pure semiconductor is said to be *doped* when impurity atoms are added to the crystal in relatively small quantities and randomly replace atoms in the pure crystal lattice. In the case of silicon (with electronic configuration $[\text{Ne}]3s^23p^2$) there are four tetrahedral covalent bonds that must be completed to form the crystal lattice. If one atom in the silicon lattice is replaced with an impurity atom that has one less valence electron than Si, there will exist a deficit of one electron in the lattice [6]. This hole, when thermally excited into the valence band will propagate randomly throughout the lattice (under equilibrium conditions) and will act as a positive charge carrier. When a pure semiconductor is doped in this manner, it is said to be doped with *acceptors* [6].

Conversely, one atom in the silicon lattice can also be replaced with an impurity atom with one more valence electron than Si. When this process occurs, there is an excess of one electron in the lattice. This extra electron is easily thermally excited to the conduction band of the solid, thus acting as a negative charge carrier and propagating randomly through the crystal lattice. When the pure semiconductor is doped in this manner, it is said to be doped with *donors* [6].

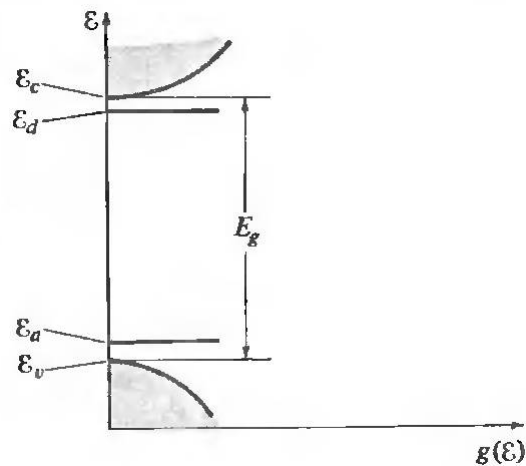


Figure 1: Energy levels in an elementary semiconductor doped with donor and acceptor atoms. While the band gap is large, the energies of the donor and acceptor atoms are within a thermal range of the band gap edges [6].

p-n junction

When a semiconductor doped with acceptor impurities (p-type semiconductor) is fused with a material doped with donor impurities (n-type semiconductor), a device called a p-n junction is formed. This device is usually formed by taking a p-type semiconductor and, from one side, diffusing donor impurities into the material [2]. The interface between the p and n regions of the material is quite small, with thickness on the order of a micron [5]. Far from the junction, the p side is filled with fixed, (-) ionized acceptor impurities and freely moving holes, while the n side is filled with fixed, (+) ionized donor impurities and freely moving electrons. These free (and oppositely charged carriers) diffuse near the interface such that the free electrons migrate to the p-type region and the free holes migrate to the n-type region to equalize the ionized impurities. Thus, near the interface there is a dearth of charge carriers [2].

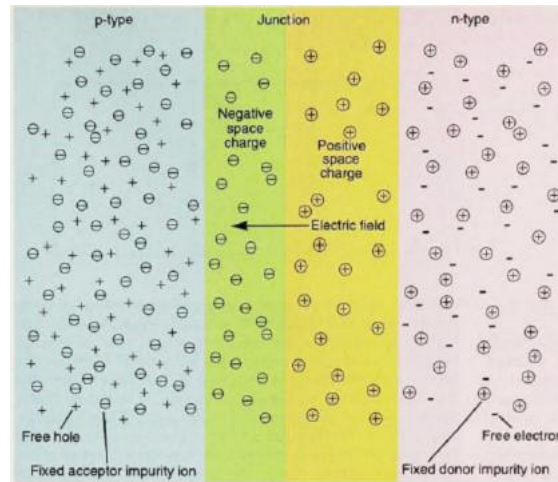


Figure 2: Pictorial schematic of the p-n junction [2].

On the p side of the interface, there exists now an excess of negative charge (due to the diffusing electrons) and, likewise, on the n side of the interface there is an excess of positive charge. This charge distribution creates an electric field near the junction interface that creates a barrier to the natural recombination affinity of the free electrons and holes on either side of the material. Without some kind of external potential to overcome this internal electric field, no current will flow across the junction interface [2]. The only way for these free carriers to recombine would be via a pathway between the p and n sides of the material that is external to the p-n junction. This is the basic

mechanism behind the power production of a solar cell.

Solar Cell Materials

The main focus of product development and materials engineering today remains on the proven technologies of inorganic semiconductors. The stalwart of this segment of the industry is monocrystalline Si, with proven consistency and relatively high efficiency [4]. Recently, research has been highly active in the area of thin film solar cells. The most widely exploited material in thin film production is silicon, however, recent research efforts have been shifting toward the development of CdTe (cadmium telluride) and CIS (copper indium diselenide or disulphide) technology [10]. Efforts have also been made to develop more exotic devices such as organic based solar cells and quantum-dot based solar cells. The most promising and practical developments for power production will remain in the further engineering of the Si, CdTe and CIS technology [10].

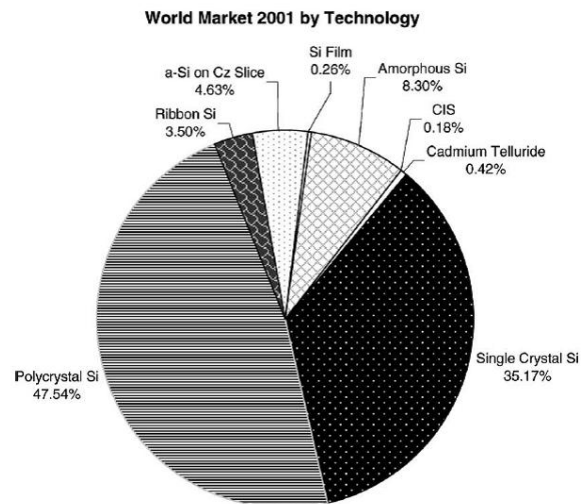


Figure 3: The dominant materials in solar cell technology as of 2001 were mainly manufactured with silicon [4].

monocrystalline silicon wafers

As previously stated, the most reliable and efficient material in use today for solar energy applications is monocrystalline bulk silicon wafers. The production of this bulk material follows the manufacturing process already present in the semiconductor industry, thus it is possible to manufacture

reasonably economical solar cells. In R&D applications, monocrystalline silicon is commonly grown by the floating zone technique, which produces large cylindrical rods of highly pure bulk silicon [4]. Another cheaper method of growth is by the Czochralski method, which inherently introduces more contaminants. Both methods produce a large bulk crystal that is then sawed into thinner, usable wafers. This process tends to waste about half of the grown crystal. Float zone crystal growth has produced record efficient solar cells, while Czochralski crystals usually have a lower efficiency[4]. In power modules, float zone technology has proven 10-16% efficiency, and in laboratory settings it has achieved nearly 25% efficiency [10, 7]. The benefits of silicon technology lie largely in the already established manufacturing capabilities developed by the microelectronics industry and also the long term sustainability and benignness of using silicon as the base material [8].

thin films

amorphous silicon

The desire to reduce material costs is the main motivation behind the development of thin film solar technology. Wafer production accounts for nearly 50% of the entire cost of manufacturing a solar panel, so to reduce the price of material production would greatly increase the economic viability of solar energy [10]. The only way to reduce material production costs is to use less material and find a different process for making solar cells. The development of amorphous (a-Si) and polycrystalline (p-Si) silicon thin films technology was undertaken to accomplish this goal.

Amorphous silicon technology has been implemented in consumer applications such as digital calculators and wristwatches since the early 1980s [10]. With such old technology it is reasonable to wonder why it has not been applied to mass power production. The two main reasons behind this are that a-Si solar cell modules have an average stable efficiency of about 6% and the material is prone to light induced degradation, the Staebler-Wronski effect, which is a main cause of this low stable efficiency [3].

The light induced degradation is thought to be caused by the following process. When silicon thin films are deposited onto a substrate via vapor deposition, the silicon atoms do not form a crystalline structure. Rather, they form an amorphous structure where, periodically, one of the four tetrahedral bonds are left unshared by another silicon atom, a dangling bond [12]. Occupying this available bond (instead of Si) are hydrogen atoms, absorbed into the structure during deposition.

When light illuminates the a-Si:H film, hydrogen atoms are thought to be freed from the a-Si network, leaving behind unfilled silicon bonds [12]. This unfilled bond will effectively trap previously available charge carriers. This process continues with the continuation of illumination of the a-Si:H, and the overall number of free carriers effectively decreases in time to a lower stable level.

polycrystalline silicon

In an effort to reduce the manufacturing costs and wastes associated with the production of single crystal silicon solar cells, researchers have developed the polycrystalline silicon solar cell. The thickness of the active layer in these cells are approximately 10-100 microns [7]. Principally, the physics of the polycrystalline silicon (p-Si) solar cell are identical to the physics of bulk crystalline Si cells. The essential difference lies in the fact that the electron-hole pairs, having been created by the impinging solar radiation, now have a larger probability to recombine at the many boundaries of the small crystallites within the n- or p- type layer of the p-Si cell [7].

In bulk crystalline solar cells, the electron hole pairs are separated by the intrinsic electric field between the n- and p-type layers and can only recombine by flowing through an external circuit. While this effect is substantial and can lead to a decrease in the efficiency of the cell, the cheaper manufacturing process for p-Si technology offsets this loss. In order to make this technology economically feasible, p-Si commercial modules must reach a conversion efficiency of 15% [9]. The best measured efficiency of a 20 cell module of p-Si deposited on glass was realized in 2007 with an efficiency of 10.4% [3].

cadmium telluride

Recently, industrial research efforts have been directed toward the development of cadmium telluride (CdTe) thin film technology. CdTe is considered to be an ideal candidate for thin film solar applications because its band gap is very near to the optimum for solar energy conversion efficiency [4]. Thus, this material has the theoretical ability to convert a greater amount of incoming solar energy into charge carriers when compared with silicon. In addition, the electronic properties of CdTe are much less affected by defects and crystallite boundaries in the material, allowing for cheaper, more economical processing methods [4]. The most common of these growth methods of the CdTe films is by a process known as closed space sublimation. Other methods of production include chemical

vapor deposition, electrochemical deposition, and screen printing [11].

In laboratory settings CdTe solar cells have proven efficiencies of 16% for single cells, while commercial module products have achieved roughly 10% [3]. The highest power output from large area (1 m^2) monolithic thin-film devices has been realized with CdTe solar technology [4]. And while production of CdTe is beginning to be commercially realized by some companies, others, including BP Solar and Matsushita, have abandoned this technology altogether [10]. They cite as a reason for this decision the environmental hazards related to the toxicity of the cadmium needed for this type of solar cell. It has also been noted that tellurium is a relatively scarce element, and even if the majority of the tellurium available on Earth were used for solar cells, production levels would be limited to at most a few GW per year [3]. Never the less, if the environmental concerns can be addressed, CdTe thin film technology will be an important segment of the world's solar energy production capacity.

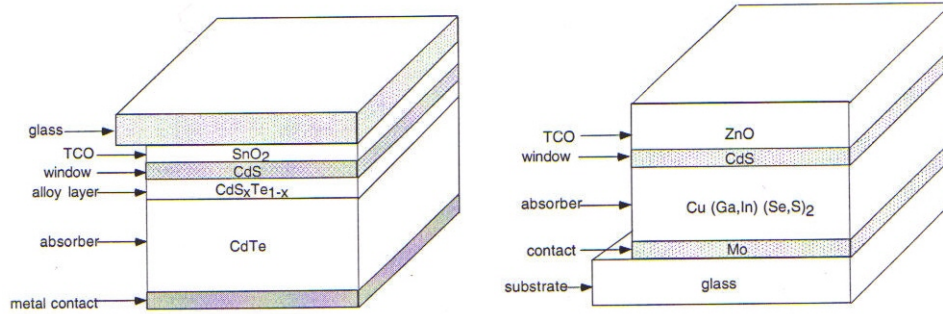


Figure 4: *The basic structure of the CdTe (left) and CIS (right) thin film solar cells are nearly identical. They both incorporate an n-type CdS layer junctioned with a p-type CdTe or CIS layer [10].*

copper indium diselenide

Copper indium diselenide (CIS) solar cells are produced in very similar ways to CdTe cells. Production involves the deposition of a thin layer of the photo-absorber (in this case CuInSe_2) between electrode contacts on a glass substrate. In the laboratory, individual CIS solar cells have achieved energy conversion efficiencies of nearly 20% [10]. While this efficiency level is economically feasible for mass production, other factors have kept CIS technology as only a minor (if not negligible) part of the production effort. Small amounts of cadmium are also used for the production of this technology, but most importantly, CIS production requires indium in relatively similar amounts as copper

is needed. The problem with this is that all of the known reserves of indium on Earth would only produce a few GW of CIS modules in total [3].

Conclusion

The technologies and means of production in the solar energy sector are largely dominated by those associated with some form of silicon. In addition to this widely proven means of production, materials such as cadmium telluride and copper indium diselenide are being increasingly studied as a material to be used in the production of thin film solar cells. More recent academic research efforts have been focused on the use of organic materials and dye sensitized solar cells as a method of energy production, however the efficiencies of this technology are not comparable to those of the inorganic semiconductors mentioned above [1]. It is evident that for the recent future, traditional semiconductor technology will proliferate in the solar energy sector because of its relatively high efficiency and industrially viable manufacturing techniques.

As of 2008, the percentage of the total energy produced in the US by photovoltaics was .07% [13]. As of 2007, the total amount of PV shipments in the US was at 518 MW [13]. However, production of photovoltaics has increased for the past ten years at a year over year rate of roughly 30%. Clearly, as the costs of traditional energy production via fossil fuels becomes increasingly more expensive, the photovoltaic industry will play an ever increasing role in the production of energy in the US and throughout the world.

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