Solar Cell Materials

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1 Introduction

In the current energy crisis, the search for a viable alternative to hydrocarbons has taken many paths: nuclear, wind, solar, etc. Solar cells provide an attractive form of limitless alternative energy. The placement of solar cells can be unobtrusive and provide not only a source of thermal energy, but electricity. However, the development and implementation of effective photovoltaic cells is hindered by two primary components: cost and efficiency.

Research into cheaper and more efficient solar cells has been underway for several decades. From the development of thin-film solar cells with efficiencies greater than 10% in the 1970s to the most recent developments in new photovoltaic materials achieving greater than 24% efficiency (see Figure 1) [1]. Unfortunately, the cost of electricity from current solar cells is about one order of magnitude higher than commercial prices. However, several of the recent developments hold a promising future for the field [1]. We begin by looking at the development of solar cells in general, and the new technologies available.

2 Solar Cell Technology

The basic mechanism behind a solar cell is based on the photoelectric effect and semiconductor physics. A photon with energy greater than the bandgap energy ($h\nu > E_{gap}$) incident on a semiconductor can excite electrons from the valence band to the conduction band, allowing for current flow. The maximum current density is then given by the flux of photons with this energy. Excess energy is lost to thermalization ($h\nu - E_{gap}$). The excitation of the electron to the conduction

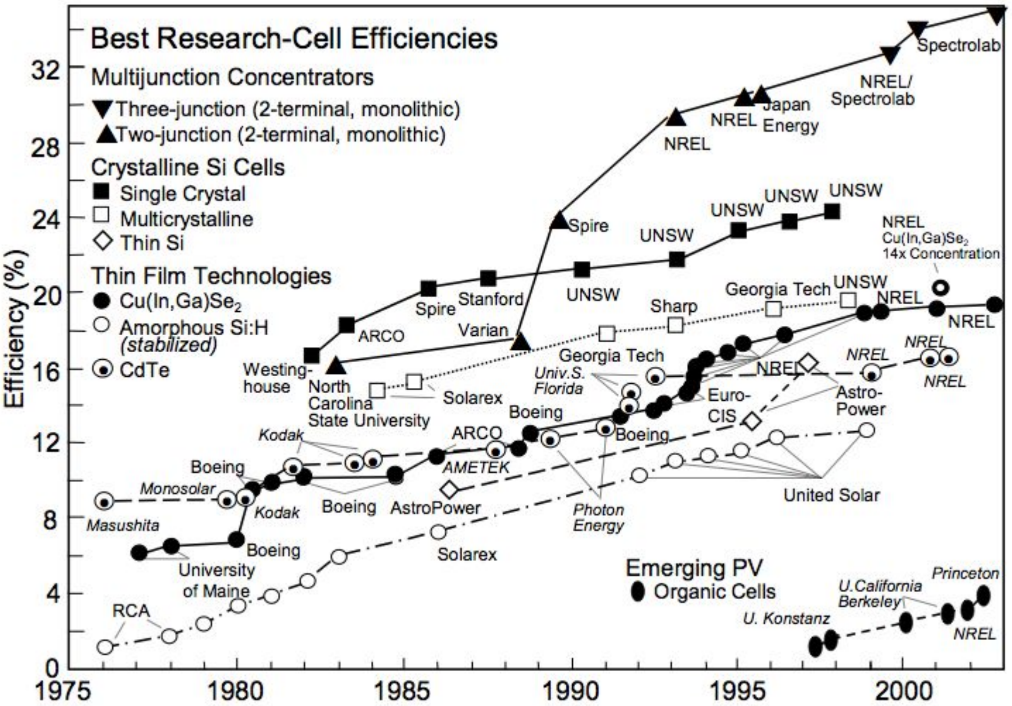

Figure 1: Photovoltaic efficiencies from various materials over the years [1].

band results in a hole in the valence band [2]. In the case of organic polymer solar cells, the electron and its corresponding hole exist in a bound state due to Coulomb attraction. This state, known as an exciton, has a lower energy than an unbound electron and hole [2].

In its simplest form, a solar cell is a large-area p-n junction. Energy from incident light creates the electron-hole pairs (or excitons in the case of organic semiconductors) described above. The electron-hole pairs separate at the junction, with electrons (holes) diffusing across the depletion zone to the p-type (n-type) region, where they become thermally free and generate a current [3]. This simple, but effective model illustrates two important factors in the production of solar cells regarding their efficiency and cost.

It is obvious that the current generated from light incident on a p-n junction is directly dependent on both the mobility of the carriers in the material and the exposed surface area of the junction. For these reasons, semiconductor materials with greater charge mobility and costs low enough to produce at a large scale are needed.

2.1 Silicon: Crystalline and Amorphous [4]

More than 80% of solar cells currently produced are crystalline silicon solar cells,. Nearly all of the other 20% are developed as amorphous silicon solar cells [4]. Silicon wafers have long been the primary base for assembly.

Crystalline silicon solar cells at the commercial level have achieved efficiencies of as much as 16%, whereas experimental developments have achieved efficiencies of more than 24% [4]. These solar cells have proven to be robust in their stability and reliability, even when exposed to harsh conditions over several years.

However, the use of crystalline silicon has several financial disadvantages. The complex processing steps and need for large amounts of high purity silicon stock have driven the cost of these solar cells up [4]. For wafer-based cells, the wafer sizes are limited, and it therefore becomes necessary for them to be externally assembled and connected to obtain larger surface areas. Two plans for improving the cost/efficiency of wafer-based solar cells are the addition of an epitaxial layer or doped amorphous silicon on the wafer surface [4].

The deposition of an high-quality epitaxial layer with appropriate uniformity has been shown to result in efficiencies greater than 19%, but has been difficult and costly to implement commercially [4]. However, the deposition of the doped amorphous silicon for the purpose of forming a heterojunction has produced similar efficiencies, while also simplifying the processing [4].

Recent interest has shifted from wafer-based silicon solar cells to thin-film crystalline silicon. The film thickness are typically $< 10\mu m$ [4]. Low temperature depositions from the gas phase allow for the use of cheap substrates (glass, or aluminum for example). With the addition of hydrogen in the growing crystalline layer, efficient grain-boundary passivation can be achieved giving desired layer properties with grain sizes $< 1\mu m$ [4]. The current method of choice for such depositions is plasma-enhanced chemical vapor deposition (PECVD), which can allow for deposition temperatures as low as 220 ℃. Unfortunately, the best efficiencies achieved are just below 10% [4].

Crystalline solar cells are not the only option. In the 1970s, hydrogenated amorphous silicon (a-Si:H) was introduced as a potential material for semiconductor devices [4]. Since then, it has become the first thin-film material to enter large-scale production for solar cells. The higher visible spectrum optical absorption over crystalline silicon allows for film thicknesses much less than $1\mu m$ [4].

a-Si:H solar cells are ordinarily created with a p-i-n structure in order to reduce recombination loses [4]. Deposition is usually done via PECVD onto various substrates. A common substrate used is TCO coated glass (e.g. $Sn0_2$), with the TCO acting as the front contact [4]. Opaque substrates (stainless steel or polymer), however, are available in flexible foils, making roll-to-roll deposition processes possible (a fast production method easily implemented commercially). However, deposition costs and times ($\sim 1\mathring{A}/hour$) for roll-to-roll deposition and TCO substrate have kept amorphous silicon cells from being significantly more cost effective than crystalline silicon solar cells at the current time. Furthermore, a-Si:H solar cells have only achieved an efficiency of 13% in the laboratory and 8% commercially and suffer from light-induced degradation (Staebler-Wrongski effect) [4]. This degradation reduces efficiency after $\sim$ 1000 hours of operation [4].

Currently, a-Si:H are one of the best candidates for the future of solar cells, due largely to their ability to be produced on cheaper substrates and integrated onto roofs and structures. While low in efficiency compared to crystalline silicon solar cells and stability issues, it is likely that production cost for a-Si:H solar cells will continue to drop in the future [4].

2.2 Other Thin-film Materials: CIS Related, CdTe and Dye Sensitized

Copper-Indium:Diselenide (CIS) and Copper-Indium:Gallium-Diselenide (CIGS) are direct-gap polycrystalline p-type semiconductors with high optical absorption

[4]. That is, the minimum of the conduction band has the same wave-vector as the maximum of the valence band [4]. CIS and CIGS are used in heterojunctions with n-type layers (commonly CdS or ZnO) [5].

CIS and CIGS have a remarkably high efficiency for polycrystalline thin films, at 18.8% in the laboratory. The high efficiency is due to the effective bandgap between 1.1 to 1.2 eV [4]. The addition of Gallium in CIGS increases the bandgap and the performance tune by increasing the open-circuit voltage.

CIS and CIGS solar cells also show good stability and reliability, except in considerable heat and humidity. While commercial production of these solar cells is projected to be significantly cheaper than for wafer-based crystalline silicon solar cells, it is very likely that full scale production will experience difficulties with the availability and price of Indium [4].

Another thin-film material similar to CIS and CIGS is CdTe. CdTe also has a direct bandgap and high optical absorption, but a bandgap energy of 1.45 eV [4]. This results in higher current densities and higher open-circuit voltages than with CIS/CIGS. Typical efficiencies are 16% in the laboratory and 9% commercially [4]. Another benefit of CdTe solar cells is the significant enhancement of carrier multiplication from CdTe nanocrystals. Carrier multiplication is the process by which inelastic scattering of charge carriers and valence electrons creates additional electron-hole pairs (charge carriers). With sufficient enough carrier multiplication, energy lost by photons with energy in excess of the bandgap due to thermalization could be collected [6]. Nanocrystals in photovoltaics is discussed further in the following section.

CdTe is a binary compound, and thus easier to produce solar cells with than CIS/CIGS. Typically, a heterojunction is created on a TCO coated glass substrate using n-type CdS and p-type CdTe.

Obtaining a uniform deposition of CdS is a critical issue in the production of both CIS/CIGS and CdTe solar cells, particularly since stability and efficiency are dependent on the n-p junction. However, a greater hurtle is the use the Cadmium, particularly in CdTe solar cells. While CdTe and CdS are stable, their production from the hazardous material Cd introduces hazards that require strict regulation [4].

The final thin-film we will briefly discuss are dye-sensitized photovoltaic solar cells. Dye-sensitized solar cells were first designed by Michael Gratzel of Ecole polytechnique federale de Lausanne and are unique in that conduction involves only injected electrons, not excitons or correlated electron-hole pairs [7]. Such solar cells have a multilayer structure that separate the processes of light absorption and charge carrier transport, reducing recombination (see Figure 2.2) [8]. Electrolytic dye molecules on a thin surface of gold film absorb incident photons. Electrons from the dye are excited to the conduction band of the gold film. The gold film is deposited onto a TiO_2 layer. The gold-TiO_2 junction creates a Schottky barrier. The excited electrons from the dye must have enough energy to penetrate the Schottky barrier to the conduction band of the TiO_2, generating current through the device [8].

Dye-sensitized solar cells currently achieve an efficiency of about 10% in the laboratory [8]. However, the electrolytic dye can lead to stability issues, particularly outside of prescribed temperature ranges, and additional costs for integrating into series connected systems [4, 8].

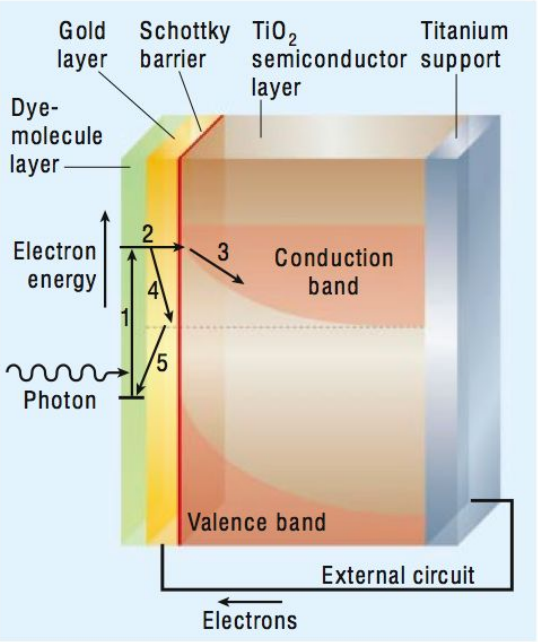

Figure 2: Dye-sensitized solar cell schematic [8]

2.3 Organic Polymers

Inorganic materials are not the only option available for solar cells, however. Around 20 years ago, it was discovered that organic materials could be used in making photovoltaics. However, it was not until the 1990s that a conducting organic polymer solar cells were shown to have an efficiency of 2.9% [2]. Recently developments in the science have resulted in laboratory results of organic solar cells reaching efficiencies as high as 5% [2].

Organic photovoltaics are based on the illumination of a donor and acceptor species. This illumination leads to the separation of excitons, much like in inorganic semiconductors. Organic solar cells are constructed out of various organic polymers, usually embedded with fullerene (acting as the acceptor) [2]. A current polymer being researched is poly 3-hexylthiophene (P3HT) [9].

However, the details of their performance introduce issues. One issue is the correlation between the separation of the bound electron-hole exciton, the primary difference between organic and inorganic solar cells [2]. Excitons experience stronger correlation in organic polymers. The bound state formed by the electron-hole pair makes the charge separation a consideration in efficiencies [2]. Furthermore, there is much research left to be done in the construction of these polymers so as to broaden the light harvesting in the spectrum of visible light, and to deal with nonlinear optical properties [2].

Despite its infancy and low efficiencies, organic solar cells offer a very attractive alternative to inorganic thin-films. The organic polymers used in production allow for solar cells to be made cheaply while still being lightweight and flexible. Additionally, it is easy to extend to large-area modules [2].

2.4 Nano-Scale Materials

Interest has been taken in the use of nanocrystals as an option for effective and inexpensive solar cells. It is believed that the size and shape control of the nanocrystals will allow for the customization of bandgap through absorption of light across the whole spectrum. Furthermore, the 3D confinement leads to greater impact ionization and results in multiple charge carrier creation from a single photon [10]. The confinement increases the density of states along the band edge in a given dimension [11]. With this property, and control of the inter-crystal spacing, the nanocrystals can be thought of as artificial atoms that allow for the tuning of discrete electronic states via size regulation [12]. This control allows for the spectrum of absorption to be tuned at will [2].

Nanocrystalline solar cells consist of large arrays of quantum dots. Current work with PbSe quantum dot solar cell arrays has shown the generation of two to three charge carriers (commonly excitons due to the use of organic polymers with nano-scale photovoltaics) per absorbed photon [13]. Such arrays are cheaper to manufacture than other photovoltaic options because of the ability to process them from solution. However, the efficiency is only around 2.5% compared to the theoretical efficiency of 44% [13]. Harnessing the multiple exciton generation will doubtlessly boost the efficiency. Additionally, the transport of electrons across the array to the circuit electrodes is hindered by the organic chemical coatings used to maintain the stability of the quantum dots [13].

While the intrinsic carrier mobility of the organic coatings reduce the efficiency of nano-scale solar cells, hybrid materials show a promising future as cheap alternatives to conventional inorganic solar cells. One such option is hybrid nanorod-polymer solar cells (see Figure 2.3).

Solution phase synthesis at low temperature (below 300°C) of CdSe nanocrystals allows for the formation of nanorods [9]. The inorganic rods can be combined with a conjugated polymer, P3HT. This gives a high surface area charge transfer junction. CdSe acts as the electron transport medium, whereas the P3HT acts as the hole transport medium. P3HT has the highest field effect hole mobility currently found in a polymer, at $0.1cm^2V^{-1}s^{-1}$ [9]. The absorption spectrum of CdSe and P3HT complement each other, giving a fairly broad visible range of absorption.

P3HT is particularly attractive in that it can be easily cast from a room-temperature solution [9]. Unfortunately, the surface chemistry behind embedding

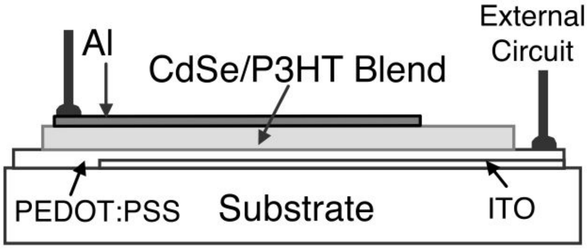

Figure 3: Hybrid nanorod-polymer solar cell schematic [9]

CdSe nano-rods in the P3HT film is very complex due to the nanocrystals limiting the solubility of the polymer. Once again, the polymer also inhibits electron hoping among the crystals and results in a low efficiency (currently reported at 1.7%, with an open-circuit voltage of 0.7 V) [9]. However, altering the aspect ratio of the rods can help in tailoring the length scale and direction of the electron transport. Through further investigation in this tailoring, it is hoped that higher efficiencies can be reached, thus providing a cheap and effective solar cell [9].

3 Conclusion

The sun delivers more energy to the Earth in one hour than is used in a year from all currently available sources, however only 0.1% of the world's energy is derived from it [2]. There are several options available in the production of solar cells. However, it seems unlikely that photovoltaic technology carry the bulk of the world's energy needs in the near future. While thin-films show a great deal of promise, the 24% efficiencies of silicon solar cells has yet to be bested [1]. Unfortunately, silicon solar cell production remain too costly at the commercial level.

Nanocrystalline hybrid arrays show a promising future for cheaper and more efficient solar cells, despite the infancy of the field. The DOE remains optimistic regarding the future of nano-scale materials in photovoltaics. While organic polymers offer a similar (or better) option in terms of cost, nanocrystalline quantum dots provide a tunable absorption spectrum and they promise harnessing of multiple exciton generation [2]. Fabrication at the nano-scale provides a remarkable increase in the precision and level of control that can be obtained over solar cell development. This ability to experiment with, understand, and thus simulate the behaviour of photovoltaics at such a fundamental level bring the field into a new and lucrative realm [2].

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