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Earth Abundant Thin Film Technology for Next Generation Photovoltaic Modules

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EARTH ABUNDANT THIN FILM TECHNOLOGY FOR NEXT GENERATION
PHOTOVOLTAIC MODULES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Electrical Engineering.

by
Githin Francis Alapatt
December 2014

Accepted by:
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Mica Grujicic

ABSTRACT

With a cumulative generation capacity of over 100 GW, Photovoltaics (PV) technology is uniquely poised to become increasingly popular in the coming decades. Although, several breakthroughs have propelled PV technology, it accounts for only less than 1% of the energy produced worldwide. This aspect of the PV technology is primarily due to the somewhat high cost per watt, which is dependent on the efficiency of the PV cells as well as the cost of manufacturing and installing them. Currently, the efficiency of the PV conversion process is limited to about 25% for commercial terrestrial cells; improving this efficiency can increase the penetration of PV worldwide rapidly. A critical review of all possibilities pursued in the public domain reveals serious shortcomings and manufacturing issues. To make PV generated power a reality in every home, a Multi-Junction Multi-Terminal (MJMT) PV architecture can be employed combining silicon and another earth abundant material. However, forming electronic grade thin films of earth abundant materials is a non-trivial challenge; without solving this, it is impossible to increase the overall PV efficiency.

Deposition of Copper (I) Oxide, an earth abundant semiconducting material, was conducted using an optimized Photo assisted Chemical Vapor Deposition process. X-Ray Diffraction, Ellipsometry, Transmission Electron Microscopy, and Profilometry revealed that the films composed of Cu_2O of about 90 nm thickness and the grain size was as large as 600 nm. This result shows an improvement in material properties over previously grown thin films of Cu_2O . Measurement of I-V characteristics of a diode structure composed of the Cu_2O indicates an increase in On/Off ratio to 17,000 from the previous

best value of 800. These results suggest that the electronic quality of the thin films deposited using our optimized process to be better than the results reported elsewhere. Using this optimized thin film forming technique, it is now possible to create a complete MJMT structure to improve the terrestrial commercial PV efficiency.

DEDICATION

I dedicate this thesis to my family for their unrelenting support.

ACKNOWLEDGMENTS

I would like to express sincere gratitude to Dr. Rajendra Singh, my advisor, for his guidance throughout my time at Clemson. His guidance has helped me see the world through a new perspective. I am forever indebted to Dr. Kelvin Poole, who spent countless hours teaching me to build and repair vacuum systems. I am also thankful to Dr. Rod Harrell for helping me to start my research career in electronics. I am also grateful to Dr. Mica Grujicic and Dr. Keith Corzine for serving on my PhD committee. Thanks also go to Dr. James Harriss for helping with training and lab organization and to Dr. Akhlesh Lakhtakia at Penn State for his contribution towards a publication.

ECE technical staff, Mr. David Moline, Mr. John Hicks, and Mr. Robert Teague have been very helpful during my time at Clemson and I sincerely appreciate their help. Several collaborators at Clemson also were very helpful – especially Mr. Aby Thyparambil for his help with ellipsometry, Dr. Colin McMillen for helping with XRD, Mr. Omar Mohiuddin and Mr. Amir Asif for their help in the lab, and Dr. Nishant Gupta for help with the setup of the CVD system. Thanks also go to Dr. Jagdish Narayan and Mr. Fan Wu at NC State University for assistance with the TEM. I am also thankful to my many friends at Clemson.

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CHAPTER ONE

INTRODUCTION

Although the earliest patents on silicon solar cells, granted during the 1940s [1, 2], indicated that the devices had very low efficiencies ($< 1\%$), hopes of higher efficiencies continued to fuel research. In 1954, Chapin and co-workers reported 6%-efficient silicon solar cell [3]. Using the now obsolete International Electrochemical Commission (IEC) 60904-3: Ed 1 spectrum, Zhao and co-workers in 1999 [4] reported a silicon solar cell with 24.7% efficiency. Re-evaluating this same solar cell using the IEC 60904-3: Ed 2 spectrum, Green [5] in 2009 revised the efficiency to 25% [5]

The development of silicon photovoltaic (PV) devices with efficiency $> 20\%$ and related improvements in power electronics and module manufacturing led to predictions that PV electricity can be billed to consumers at the rate of \$0.10/kWh [6]. That prediction has been recently vindicated [7]. The global Photovoltaics (PV) cumulative capacity has grown to 102 GW in 2012 and in the Business-as-Usual scenario, the cumulative capacity is expected to touch 288 GW in 2017. With a policy driven approach, the cumulative capacity is expected to be as large as 422 GW in the same time frame [8].

For sustained global economic growth in this century, PV electricity generation is highly attractive because solar energy is essentially unlimited and PV systems provide electricity without any undesirable impact on the environment [9]. The cumulative installed solar PV electricity generation capacity is expected to double from about 100 GW in 2012 to 200 GW in 2015 [10]. The average selling price of PV panels has dropped

to \$0.65 per peak watt (Wp) [11]. Dominated by the second most terrestrially abundant element—namely, silicon [12]—PV energy generation is firmly moving to the terawatt scale [13].

The magnitude of the current globally installed solar PV capacity, the continually lowering cost of installed PV systems, and the continually diminishing cost of PV generated electricity are the three factors that have established that PV technology is no longer only purely a research area, but it is a very important means to generate green electricity for meeting the needs of rich and poor all over the world [14]. Since huge investments have already been made in the processing of silicon and the functioning of the associated supply chain, only a truly disruptive technology can replace the well-established silicon-based PV technology. It is very important to understand the nature of innovations that will continue to reduce the cost of PV modules and other components of PV systems, similar to the cost-reduction history of silicon-based low-power electronics that has played and continues to play a vital role in enabling the information revolution.

For further cost reduction, design concepts for new manufacturable devices need to be developed beyond the current generation of bulk and thin-film solar cells. Several concepts—such as multiple exciton generation (MEG), carrier multiplication, hot-carrier extraction, intermediate-band solar cells, nanostructured solar cells, etc.—have been proposed to replace the extant solar cells. These cells, which can be possibly made from engineered materials and nano-structures are often called “third generation PV cells” [15], with the materials themselves being referred to as “next generation materials”, “smart materials” or “intelligent materials”. In reality, despite the semantics and the buzz,

there has been no improvement in the efficiency of a solar cell using the so called “smart materials”. Of course, with better engineering, conventional bulk and thin film solar cells have become more reliable and their cost has decreased over the years, and their efficiencies have also increased by a small percentage. However, this increase in efficiency cannot be attributed to any nano-structured – smart material. This raises the interesting first question – during the last 10 years, why has there been no significant increase in the “third – generation” solar cell efficiency even with the introduction of “smart materials”? The second most important question one would like to know is if there are any fundamental barriers that cannot be surmounted by any technological advancement.

Another concept that has been touted to improve PV devices is Self-assembly, and it has been claimed as the new method to manufacture nanomaterial based devices [16-18]. It is widely known that this process can result in extremely small particles, however, the variation in size and shape of particles formed is still quite large [19-23]. Despite years of research, there seems to be no method to produce structures in a pre-defined manner using self-assembly. Self-assembly is a process that has been looked upon as a possible method for manufacturing for decades and there has not even been a single success story. Although self-assembly based techniques may be useful in making low-tech products and for bio-applications, this technique cannot be applied to semiconductor manufacturing.

An extensive literature search led to the idea that none of the aforementioned concepts can deliver a commercially viable module with efficiency over 25%, the current silicon based cell's maximum efficiency. The only practical device with efficiency over 25% is the Multi-junction cell. However, this device is not cost effective because of the materials and processing techniques involved. Another idea, the Multi-Junction Multi-Terminal (MJMT) devices has the potential to decrease the cost of the simple multifunction cells by removing the current constraint and opening up the possibility of using earth abundant materials in the cell. The next task is to find a suitable earth abundant material and to be able to deposit high quality thin films of this material in a method that can be integrated with existing cell production techniques.

In Chapter 2, details of concepts proposed to improve the PV efficiency beyond the existing level are explored. Fundamental limitations of manufacturing such modules are discussed. In addition, effect of variability of the cell on the module's efficiency is explored and results from simulation are shown. Chapter 3 includes the issues with self-assembly when applied to semiconductor manufacturing. Issues related to variability, yield, and throughput are discussed here. In chapter 4, the present state of the PV industry is explored and all commercial technologies are examined with special importance given to best cell efficiency vs. module efficiency. Four kinds of high efficiency silicon PV cell design are explored and the MJMT architecture is detailed. Results from simulation showing the best efficiency possible with a two junction MJMT device is shown. Chapter 5 includes experimental results from depositing and characterizing Cu_2O . A model to explain the current conduction mechanism in forward and reverse bias is presented here.

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CHAPTER TWO

FUNDAMENTAL ISSUES IN MANUFACTURING PHOTOVOLTAIC MODULES BEYOND THE CURRENT GENERATION OF MATERIALS

This chapter is based on the publication - G.F. Alapatt, R. Singh and K.F. Poole, "Fundamental Issues in Manufacturing Photo voltaic Modules Beyond the Current Generation of Materials", *Special Issue on Intelligent Materials for Solar Cells, Advances in OptoElectronics*, Vol. 2012, Article ID 782150, 2012

2.1 Introduction

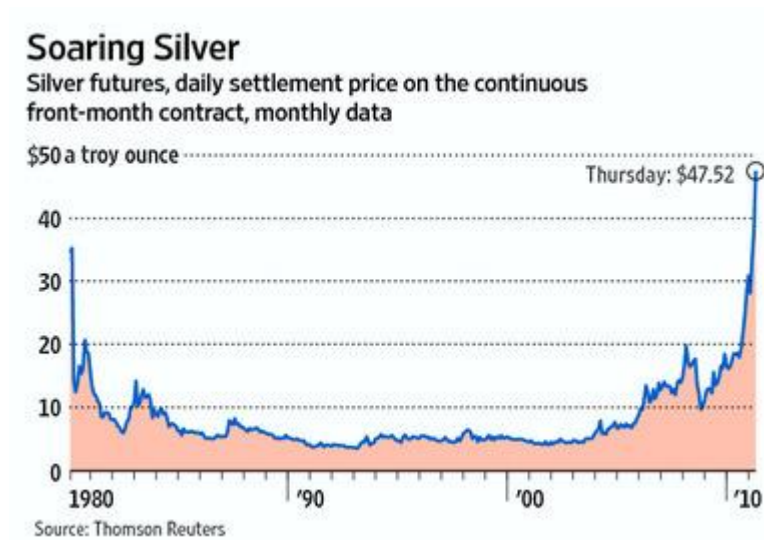
Starting with providing power to the first communication satellite, Telstar, in 1962, photovoltaic (PV) systems have evolved to a market size of about 16 GW in 2010. Current commercial PV market is based on bulk solar cells (Si and III-V compound semiconductors) and thin film solar cells based on a-Si, CdTe and CuInGaSe₂, while the devices are based on p-n homo and hetero junctions and tandem junction solar cells. In the case of III-V compound semiconductor based concentration solar cells, one sun efficiency of 35.8 % has been achieved [1]. Being an active area of research, new materials and structures are constantly being investigated in the hope of getting efficiencies higher than the typical bulk silicon solar cell efficiency of about 20 %. Solar cells, which can possibly be made from engineered materials and nano-structures are often called "third generation PV cells" [2], with the materials themselves being referred to as "next generation materials", "smart materials" or "intelligent materials". In reality, despite the semantics and the buzz, there has been no improvement in the efficiency of a solar cell using the so called "smart materials". Of course, with better engineering, conventional bulk and thin film solar cells have become more reliable and their cost has decreased over the years, and their efficiencies have also increased by a small percentage.

However, this increase in efficiency cannot be attributed to any nano-structured – smart material. This raises the interesting first question – during the last 10 years, why has there been no significant increase in the “third – generation” solar cell efficiency even with the introduction of “smart materials”? The second most important question one would like to know is if there are any fundamental barriers that cannot be surmounted by any technological advancement. The objective of this chapter is to examine the “third-generation” solar cells from the manufacturing point of view and answer the two questions raised previously.

2.2 Manufacturing Requirements of Photovoltaic Modules

Irrespective of the type of materials used in the manufacturing of PV modules, the following key criterion are used in selecting an appropriate technology: (i) no material supply constraint, (ii) low cost of ownership, (iii) low production cost, (iv) prospects of further cost reduction, and (v) green manufacturing with no environmental safety and health issues. Even for silicon (dominant photovoltaic material) the question of supply chain is very important. Silver is used in the manufacturing of bulk silicon solar cells and is being replaced with copper [3]. As shown in Fig. 2.1 [3], silver’s prices have increased significantly in the last 5 years. Due to the use of silver by the film, battery and the electronic industry, the supply chain of silver also affects the PV industry. [3]. Such trends will happen often in the future, and the manufacturing technology should be able to withstand the swings of the market trends. In previous publications we have discussed

the detailed economic requirements of manufacturing photovoltaic materials and PV systems and the interested reader is referred to references [4-6].



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Figure 2.1: Prices of Silver in the last 40 years [3].

2.3 Next Generation Materials

Next generation materials for solar cells include any material or material structure that is currently not being mass produced to manufacture solar cells. This term also refers to organic materials and dyes that are used to fabricate organic solar cells and dye sensitized solar cells. In addition, this term also includes nanostructure materials processed using unproven solar cell manufacturing technologies such as self-assembly. These topics are explained in this section.

2.3.1 Organic and Dye Sensitized Solar Cells

These cells are often processed in a liquid form, with the hope of making them cheaper than current commercial solar cells. Reasonable efficiencies have been achieved using organic materials such as PCBM (Phenyl-C61-butyric acid methyl ester). According to Ref. [7], the best values of efficiency of organic solar cell and organic sub-module are 8.3% (device area = 1.031 cm²) and 3.5 % (aperture area = 308.4 cm²) respectively. This lower efficiency is a direct result of the lower electron mobility, poor contact to electrodes and defects in the material. Apart from these problems, organic solar cells have reliability issues and are degraded when exposed to sunlight and air [8 9].

According to Ref. [7], in case of dye-sensitized solar cells, the device and sub-module efficiencies are 10.9 % (device area = 1.008 cm²) and 9.9 % (aperture area = 17.11 cm²) respectively [7]. Dye sensitized cells share many advantages and disadvantages of the organic solar cells. Some of the similarities are hope of low cost for processing, low efficiency, high concentration of defects, and reliability problems. In both type of solar cells, low carrier mobility because of structural inhomogeneities and the lack of an ordered structure is the fundamental problem. Without any fundamental breakthrough of inventing new organic and dye sensitized photovoltaic materials, these solar cells will not play a significant role in large scale utilization of PV for power generation. However, these solar cells have the advantage of being flexible and light, and can provide power for a niche market consisting of short-lifetime products such as clothing, bags, and temporary shelters etc.

2.3.2 Nano-structured Materials

Using nanomaterials, many concepts have been proposed to increase solar cell efficiency. Examples include multiple electron generation (MEG), carrier multiplication (CM), hot carrier extraction, and intermediate band solar cell. These concepts rely on the performance of nano-materials for obtaining high-efficiency. Quantum dots, a particular nano-structure, have been proposed to increase the solar cell efficiency. To understand nanostructure based solar cells, fundamentals of nano-structures are presented in the next section.

2.4 Fundamentals of Nanostructures

Properties of materials are different when the material's dimensions are only a few nanometers. Such properties can be used to bring enhancements to the solar energy conversion efficiency, if such materials can be successfully manufactured. Currently, commercial solar cells are made from bulk or thin film materials, or a combination of materials, without taking in to consideration properties such as quantum confinement that are associated with a dimension of less than about 10 nm. In the past few decades, there have been proposals of harnessing quantum confinement related properties of materials to yield devices such as high-efficiency solar cells and faster transistors. Many of the proposed concepts capitalize on using the properties which arise from the quantization of energy, momentum and density of states in materials at very small dimensions. For instance, a spherical particle with diameter of about 5 nm will exhibit remarkably different properties than a spherical particle of the same material with a diameter of 1

mm. As early as 1976, Buffat and Borel [10] showed that the melting point of gold particles decreases by about 100 degrees Kelvin as its diameter is made less than 100 nm. Such properties can be generalized and it is observed that all material properties will undergo changes as the material dimension becomes less than a few nanometers [11]. This concept is illustrated in Fig. 2.2

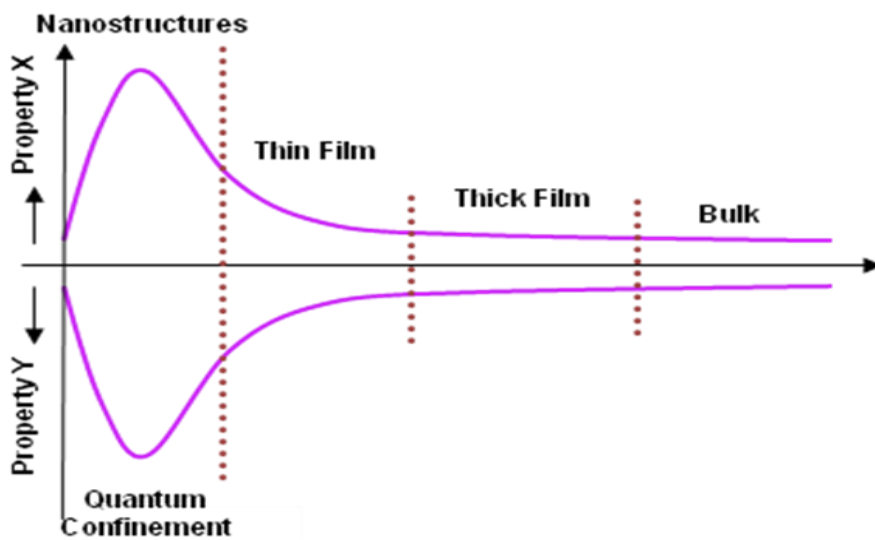


Fig. 2.2. Change of properties with dimension ranging from one atom to bulk dimension.

[11]

The next generation materials that exhibit immensely different properties when compared to regular PV materials can be broadly classified into four categories: 1 D, 2 D, 3 D and 0 D. The first classification, 1 D, refers to structures that have only one dimension significantly larger than the other two dimensions. Examples of such a structure include chains or bundles of molecules or polymers. 2 D nano-structures have

two dimensions that are significantly larger than the third nano-dimension; examples of such a structure are films of nano-materials that are only a few nanometers in thickness, but may have much larger widths and lengths. 3 D nano-structures include honeycomb like structures or a matrix of particles formed by the aggregation of nano-particles. In such a structure, none of the dimensions may be in the nano range. Finally, in a 0 D structure, all the dimensions are only nanometers wide and consequently it has none of its dimensions that are larger than a few nanometers [12]. In all these classes, quantum confinement brings about a change in the material properties. The quantization happens in different dimensions in all the classes of materials. To illustrate this point, in the 0 D structure, all dimensions are only a few nanometers wide and the density of states in that structure is quantized in all three dimensions; while in the 2 D structure, only 1 dimension is on the nano-scale range and thus the density of states is quantized only in one dimension. Fig. 2.3 [13] shows the energy states due to quantization in these structures.

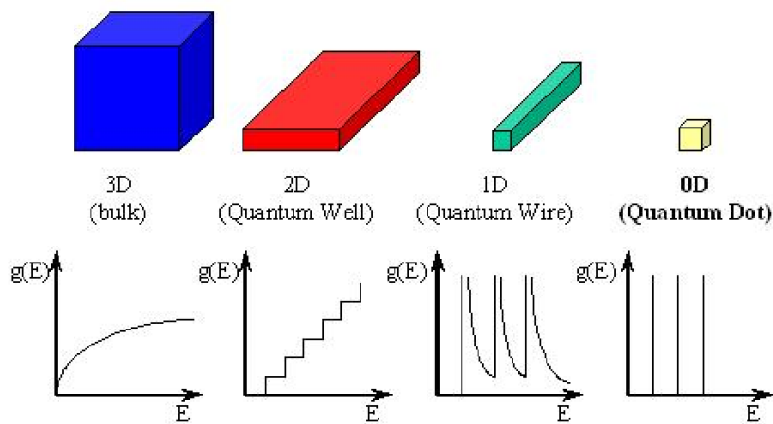


Fig 2.3: Quantization of properties with scaling of dimensions [13].

As stated earlier the interesting, and sometimes useful properties of nano-structured devices arise due to the quantum confinement effect. This has been understood for many years, however, obtaining experimental results to compare with the theoretical model is difficult because of defects and the presence of large densities of surface states.. One should have a good control and understanding of the defects and surface states to be able to make use of nano-structured materials. This is the reason why researchers have been able to find interesting properties in an isolated nano-structure, but, not always in a device made from the nano-structure. There have been numerous attempts to use nano-materials (fabricated by non-lithography techniques) in a variety of applications such as transistors, metallic interconnects, dielectrics and diodes. Even though many principles remain the same across a wide range of applications, this chapter will focus specifically on the application of nano-materials to create the active material of a solar cell. The term “active” is used specifically to differentiate the actual solar cell material that converts light energy into electrical energy from other parts of a solar cell such as electrodes, anti-reflection coatings and interconnects.

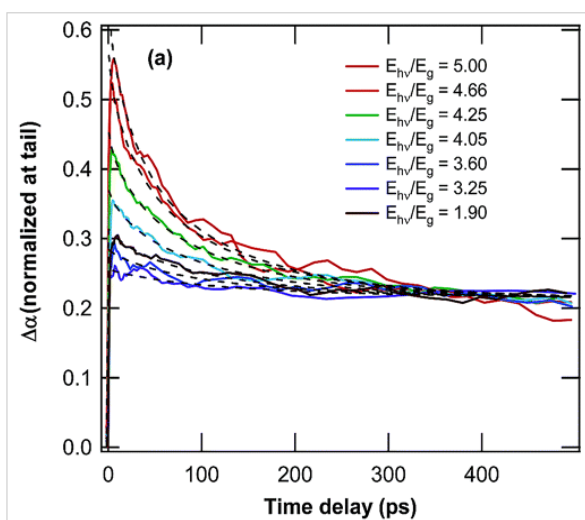
In 1961, Shockley and Queisser calculated the theoretical limit of solar energy to electrical energy conversion for a single junction silicon solar cell as 33% [14]. Until now, this limit has not been exceeded experimentally, the highest efficiency reported in silicon solar cells being only 25% [7]. There have been numerous articles on the possibility of obtaining efficiencies much higher than 33% in single junction solar cells

by using techniques such as MEG, intermediate band solar cell (IBSC), and hot carrier solar cells [15-19]. The earliest of these concepts, the IBSC, was proposed in 1960 by Wolf [20], while the concept of extracting electron hole pairs of energy higher than the band gap of the material was proposed in 1982 [21]. To fabricate such high efficiency solar cells, researchers often propose using nanosystems such as nano-dots, nano-wires, nano-crystals (NC), and carbon nano tubes [19, 21-24] . Since the 1960s, numerous experiments were performed to fabricate such high efficiency cells and none of them was successful. This failure to obtain a higher efficiency even with many years of research points us towards the fundamental flaw of such proposed concepts.

The fundamental flaw in the MEG concept is that the indirect measurement of photoluminescence and related experimental work relates only to local generation of photo carriers and has no relevance to the transport of generated photo carriers over the barrier of the junction. Research towards obtaining a high efficiency solar cell does not end with the observation of the generation of electron hole pairs (EHPs); these created EHPs must also be able to move to the electrodes without interacting significantly with their surroundings. The transport involves carrier-phonon and carrier-lattice interactions, which are minimum in pure structures such as an ultra-pure crystalline silicon solar cell. Only an electrical measurement involving measurement of short circuit current and open circuit voltage reveals how efficiently a cell can convert the photo energy to electrical energy. Unless this test is performed, one cannot speculate about the efficiency. From a manufacturing point of view, this test must be performed on a sufficient number of large area samples to account for process variability and defects.

2.5 Quantum Dots

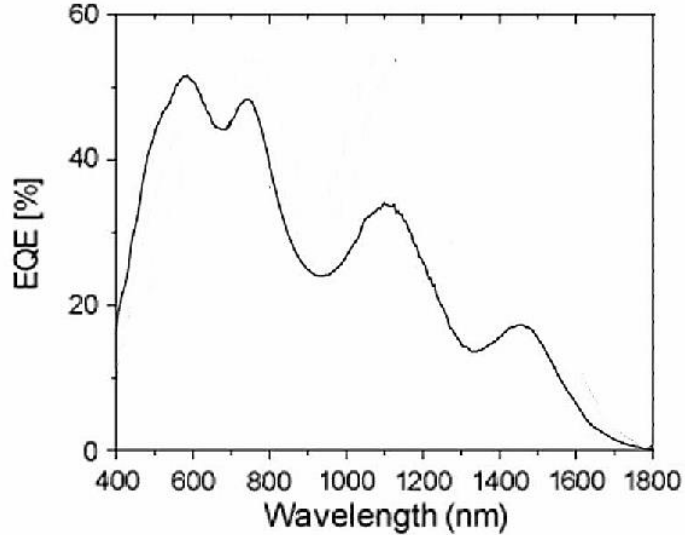
Quantum dots are “0” D particles, in which the band structure is dependent on the particle size because of quantization effects. In theory, the band gap can be controlled by varying the particle size and one can engineer an optimal band gap for high-efficiency solar energy collection. In addition, other methods such as multiple exciton generation (MEG) and hot carrier capture processes have been postulated to increase the solar energy conversion efficiency. Quantum dot proof of concepts for use as solar cells are generally based on transient absorption spectroscopy experiments, in which, the number of carriers generated are counted using light sources and detectors. Fig. 2.4 [25] shows a typical decay curve, which shows that carriers were generated at zero picoseconds (ps) and that the carrier population decayed over a time of 400 ps. This does show that carriers were generated, but these high energy carriers were not transported spatially across a barrier. The transport process across the barrier must take place before these high energy carriers can be used for generating electricity. To date there is no experimental data in quantum dots that shows the high energy carrier transport across the barrier takes place in a quantum dot.



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Fig 2.4. Transient spectroscopy signal decay curve [25]

In an experiment performed in 2009 researchers fabricated a quantum dot photo detector, which is very similar to the fabrication of a solar cell. As shown in Fig. 2.5 external quantum efficiency (EQE) was measured and the number varied between 15 – 52% as the incident wavelength was varied between 400 and 1800 nm [26]. This is the realistic quantum efficiency with which the incident photon is able to generate measurable carriers in a colloid of quantum dots. Some of the photo generated carriers have recombined in quantum dots and the number of collected carriers per incident photon is less than 100% for all wavelengths.



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Fig. 2.5. External Quantum Efficiency versus wavelength of quantum dot photo detector [26]

2.6 Processing Of Nanostructures

To manufacture a nano-structured device in a commercially viable fashion, two technologies are currently under consideration. The first one is the standard top-down approach and the other is bottom-up approach. The most important requirement of the processing technology is the variability the process creates in the critical dimension of the nano-structure. Uniformity of the critical dimension inside the device should be maximum for a process to be considered suitable. Fig. 2.6 shows two Gaussian distributions and their full width at half mean (FWHM). Distribution A is the desired case with a small value for FWHM, however, because of process variations, the resulting distribution of the manufactured critical dimensions looks like Distribution B. This

variation is difficult to optimize and this arises because of the manufacturing process. From this perspective, the above mentioned manufacturing techniques are examined in this section.

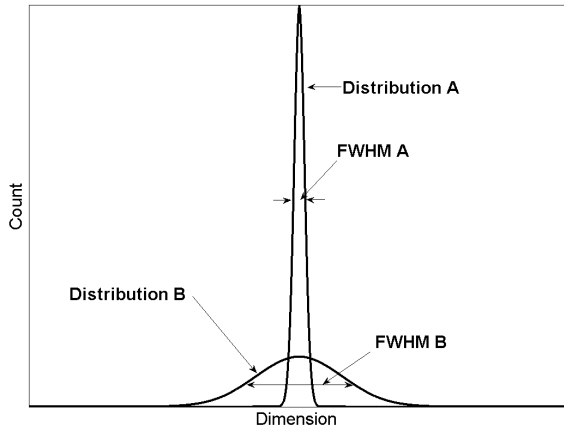


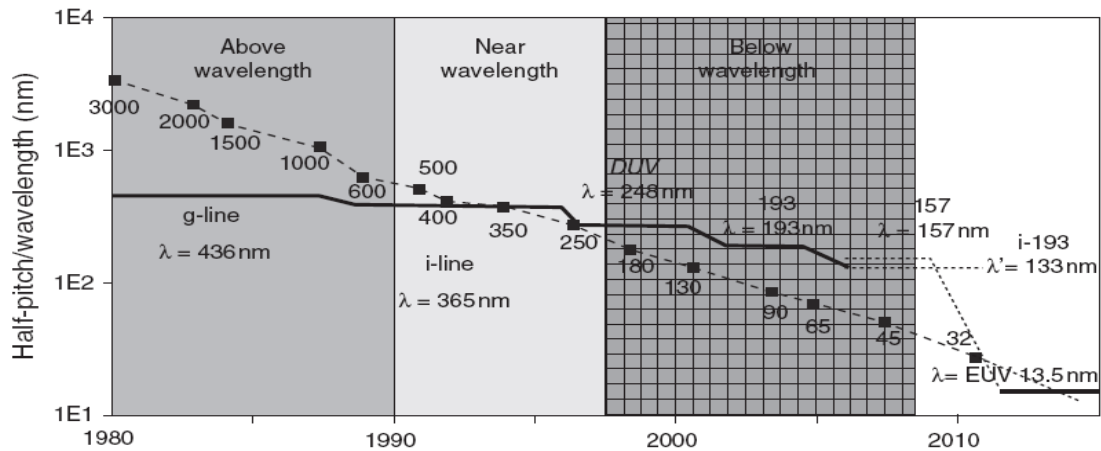
Fig. 2.6: Gaussian distributions of the critical dimension.

2.6.1 Top-Down Approach

Lithography has been the standard technique for transferring patterns during IC manufacturing since its beginning. The minimum feature size, quantified as half-pitch has been steadily decreasing since the 1980s. Invention of better light sources and improved methods of exposure have driven this change. As of now, the half-pitch distance is 22 nm and the light source used has a wavelength of 193 nm, which is about nine times the half pitch distance [27]. Further decrease in the light source wavelength to 13.5 nm using an extreme ultra violet (EUV) source, has the possibility to decrease the half-pitch to the range of a few nanometers. Such a trend is shown in Fig. 2.7. [28]. With lithography,

patterns of half-pitch distance less than 10 nm have been created over a decade ago [29]. Two methods are commonly used to do the top-down lithography – one is selective epitaxy, which is growing material on the required areas; and the other one is selective etching, which is growing material over a large area and etching out the unnecessary portions to create required structures. Both these methods have been used successfully to create nano-structures.

Apart from surface patterning abilities, manufacturing will require profiling abilities along the vertical axis. The deep reactive ion etching (DRIE) process is currently able to make vertical profiles with aspect ratios greater than 50. Thus, the traditional semiconductor industry based manufacturing technology can make nano-dimensional structures for research purposes. However, issues relating to non-homogeneity and process control will determine if these devices can be successfully manufactured on a large scale without defect related problems. Recently, a defect on one of Intel's chip was discovered and analysts predict that this defect is going to cost Intel about \$1 Billion [30]. Defects such as these will determine how successful a nanostructure based product will be. In addition, the high cost of lithography equipment used in the IC industry will require major cost reduction, if ever this approach is used by the photovoltaic industry.



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Fig. 2.7: Trend in Lithography [28]

2.6.2 Bottom-Up Approach

The bottom up approach involves devices using an atom-by-atom, approach and is called self-assembly. In our opinion the meanings of “Self Assembly” have been taken wrongly. A true self assembly process involves programmed cell death or apoptosis [31]. The so called “self-assembly” is actually selective chemistry. The atoms or molecules are forced by chemical, mechanical, or electrical means to assemble in a particular fashion. Researchers have often compared this method to the method employed in the development of an animal or a plant. To demonstrate the fundamental problems associated with “Self Assembly” we consider the growth of carbon nano tubes (CNTs). Scanning tunneling microscope (STM) is used to select multi-wall CNTs of desired length and diameter [32]. Even with the use of STM, only multi-wall CNTs of radius 21 ± 3 nm can be obtained [32]. These results are not comparable to the lithography results

in terms of variability. In a previous publication [33] we have investigated the basic nature of bio-driven systems and showed that due to their fundamental nature of low growth rates as well as their high defect densities, it is highly unlikely that such systems can be used in semiconductor manufacturing.

In other fields, such as quantum dot lasers, researchers have shown that lithography based fabrication processes give much better process control and results in structures with better homogeneity than a process using self-assembly [34]. In a controlled experiment involving etching of silicon to form a 3D wire structure to find better photovoltaic properties, researchers found that the maximum efficiency obtained was only 7%. [35]. These are very recent experiments that prove high efficiency is simply not possible using bottom-up techniques.

2.7 Examination Of Published Results

In Table 2.1 we have included efficiencies that were reported in literature on solar cells that employ the proposed concepts. In some experiments, complicated fabrication methods were used and data from transient spectroscopy or electroluminescence experiments are reported, but neither the I-V data nor the overall efficiency are mentioned. This trend leads the reader away from the reality by talking only about the carrier generation mechanisms. Unless these generated carriers can be separated and collected, there is no solar cell action. As we predicted in 2009 [5], a recently published paper [36] also indicated that a carrier multiplication (CM) process (a process thought to

enhance solar cell efficiency) does not take place and the results suggest no improvement in the CM process in nano-materials in comparison to bulk materials [36].

Table 2.1: Summary of Experimental Results

Cell Type	Efficiency	Ref.
GaAsNi IBSC	0.18%	[37]
GaAs QD IBSC	No data	[38]
Si cell with Quantum dots	5.7-10.6%	[39]
Excitonic PbSe NC	3.4%	[40]
Colloidal PbS QD	6.0 %	[41]
PbS NC	4%	[42]
SL GaAs Hot Carrier	10.9% - 11.2%	[43]
MQW GaAs Hot Carrier	7.1%	[43]
IBSC QD GaAs	9.3%	[44]
Organic Solar Cell	8.30%	[7]
Dye-Sensitized solar cell	10.90%	[7]
QD: Quantum Dots; SL: Super Lattice; NC: Nano Crystal.		

Thus, as can be observed from Table 2.1, none of the proposed concepts results in an efficiency increase in the process of converting photo energy to electrical energy when

compared to the bulk material solar cell. There is no high efficiency observed in any solar cell as predicted by various theoretical and experimental works.

2.8 On the Issue of Process Variations and Defects in Next Generation Solar Cells

The PV industry shares many similarities with the integrated circuit (IC) and light emitting diode (LED) industries. However, there is one important factor that is different. In an IC, one can increase redundancy to account for devices lost because of defects. This is routinely done in the memory industry and results in increased yield and lower fabrication cost. However, this generates an overhead of allocating chip space for memory cells that do not add to the total memory locations and extra logic to detect and replace the faulty devices [45]. In the case of solar cells, until now, every cell that is built is connected and contributes to the final output power. A defect in any of the cells will result in the deterioration of power output from every cell connected to the cell with defects. The same principle applies to cells that have a lower output voltage or a lower output current due to parametric variations. When connected in series, the cell with the lowest output current will become a bottleneck for the whole module, and when connected in parallel, the cell with the lowest output voltage will control the module voltage. Thus, defects are very unforgiving in solar cells and solar cell designs using nano-materials cannot function unless the defect issue is first solved. A similar approach of including redundant cells in a module can be used; however, the overheads will be somewhat expensive because of the lost real-estate.

To illustrate the above mentioned point, a hypothetical case is presented. In Fig. 2.8, individual cells ($m \times n$ matrix) are connected in series and parallel to fabricate the resultant solar module. V and J are the voltage and current at the maximum power point. Cells in each row are connected in series and each row is finally connected in parallel with each other. Thus, each row produces a voltage, V_1 , which is the sum of individual voltages, i.e. $V_{11}+V_{12}+\dots+V_{1n}$, and a current, which is the minimum current in that row, say J (min). When such rows are connected in parallel, the resulting voltage will be the lowest of the total voltages in each row, $V(\text{min})$ and the minimum currents of each row will add up to give the final current $J(\text{total})$. The maximum obtainable current and voltage is thus reduced due to series and parallel connections.

$V_{11},$	$V_{12},$	$V_{13},$	\vdots	$V_{1n-1},$	$V_{1n},$
J_{11}	J_{12}	J_{13}	\cdot	J_{1n-1}	J_{1n}
$V_{21},$	$V_{22},$	$V_{23},$	\cdot	$V_{2n-1},$	$V_{2n},$
J_{21}	J_{22}	J_{23}	\cdot	J_{2n-1}	J_{2n}
$V_{31},$	$V_{32},$	$V_{33},$	\cdot	V_{3n-1}	$V_{3n},$
J_{31}	J_{32}	J_{33}	\cdot	J_{3n-1}	J_{3n}
\approx	$\dots\dots$	$\dots\dots$	\cdot	$\dots\dots$	$\dots\dots$
$V_{m-11},$	$V_{m-12},$	$V_{m-13},$	\cdot	$V_{m-1n-1},$	$V_{m-1n},$
J_{m-11}	J_{m-12}	J_{m-13}	\cdot	J_{m-1n-1}	J_{m-1n}
$V_{m1},$	$V_{m2},$	$V_{m3},$	\cdot	$V_{mn-1},$	$V_{mn},$
J_{m1}	J_{m2}	J_{m3}	\cdot	J_{mn-1}	J_{mn}

Fig. 2.8: An $m \times n$ array of nanostructured cells connected to form a solar cell.

In the case of single crystal Si solar cells, open circuit voltage, short circuit current density and efficiency show a Gaussian distribution [46]. Along the line of observed distribution in Si solar cells, very simple calculations were performed. The mean value of the current at the peak power point was assumed to be 25 mA and that of the voltage was assumed to be 0.5V. Calculations were done with the 3 sigma variation in voltage and current to be 10%, 20%, 40% and 80%. 100 such cells were assumed to be connected as 4 blocks in parallel, with each block consisting of 25 cells in series. This arrangement generates about 90 mA and 12 V, which results in a 1.1 W output power. Random normal data between the 3 sigma points on each side of the mean were generated using the function '*normrnd()*' on GNU Octave for both voltage and current [47]. From the analysis of this data, we come to the conclusion that as the variability in process parameters increases, a significant portion of the power generated is lost in the process of joining cells in series and parallel. On the other hand, individually adding up the power generated in each cell without considering the effect of connections results in only minor loss of power even when variability is high. Practically, to meet certain voltage and current requirements, some sort of connection between cells is required and this will always result in significant power loss if variability is high. In Fig. 2.7, the results of the above analysis are plotted. As can be observed, there is about 55% decrease in output power as the process variability is increased from 10% to 80%.

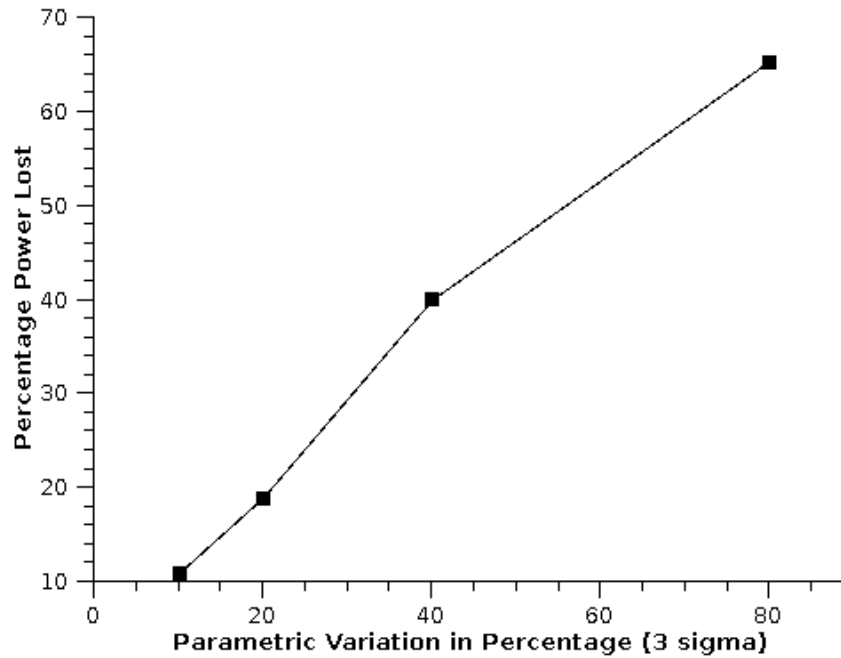


Fig. 2.9 Percentage of power loss as a function of parametric variation

These calculations were performed without considering the effect of reliability and testing issues. When these issues are included, the percentage power lost will be even higher. Other factors such as losses arising due to the interconnects are also ignored to get the final result. In reality, one can expect to see more power losses than shown in Fig. 2.9.

To generalize, also as mentioned in a previous section, the reduction of FWHM is crucial for obtaining the minimum possible variation of critical dimension of the nanostructure based photovoltaic device. The relationship between FWHM and solar cell

efficiency is graphically shown in Fig. 2.10; a very good control on the process will result in devices with consistent properties, and will result in a higher overall cell efficiency.

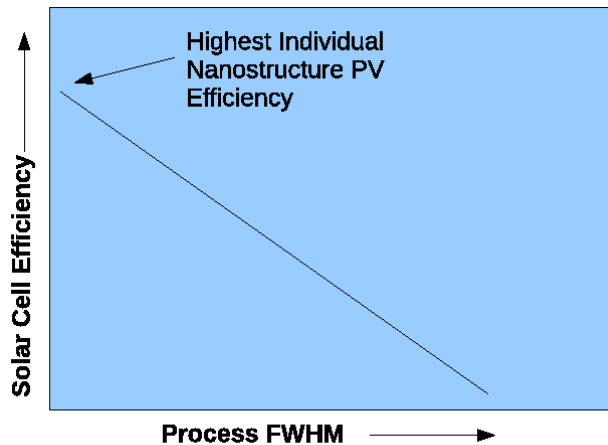


Fig. 2.10: Relationship between FWHM and nanostructure based solar cell efficiency.

2.9 Discussions

In the light of the evidences mentioned above, the bottom-up approach will not result in useful nano-structures because of lack of control on variability and homogeneity. Quantum physics indeed predicts that the band-gap of a material will change as a result of quantization. And, if properly controlled, a structure can be built with materials with varying band gaps. Such a structure can in theory boost the efficiency of a solar cell because the cell will be capable of collecting photons across the complete solar spectrum. This knowledge is not new, and has been around for many years. The problem in making such a structure is that a process to create such a structure with the required precision does not exist

If a nano-structured device needs to be manufactured, one is forced to resort to lithography techniques. Extreme ultra violet (EUV) based lithography has the potential of reaching sub-10 nm resolution. E-beam and ion-beam lithography are proven technologies to create devices in the range of a few nanometers [48]. Tightest process control can be achieved using e-beam lithography and researchers are making nano structures with reasonable control regularly. However, this is an expensive and time consuming process and is not suitable for the production of solar cells on a large scale.

In addition, the simple statistical process control (SPC) based approach in a processing tool should be replaced with the advance process control (APC) based approach. APC is fundamentally different from SPC, because APC relies on a dynamic model based approach to reduce process variability by conducting *in-situ* measurements during the run-time. Real-time analysis of such measured data can detect variations in processing conditions that can result in excess variability. This data is used to automatically perform corrective actions to keeps the process continuously optimized for the desired results. It should be noted that APC is the current technique used to manufacture many parts of the latest generation of ICs by the semiconductor industry [49]. Unless there is a very tight process control, there is no hope of getting a good efficiency in new generation solar cells. A target for the desired process variability is 10% at three standard deviations, which is also the standard followed by the IC industry.

The *in-situ* measurements for the APC should be highly precise, because the performance of the manufactured device depends on how accurately the process can be controlled; the input to this control is simply the *in-situ* measurements. New

measurement techniques that use quantum effects have been discussed [50]. These measurement schemes are still in their infancy, and further research needs to be conducted in this area to create the extremely precise measurement technique. However, this method of using APC along with ultra-low-cost nano-dimension lithography is the better option than the bottom-up based approach. Equipment that will meet the requirements of the photovoltaic industry for manufacturing nanostructure based solar cells do not exist and need to be invented.

From a market standpoint, one of the barriers for extraordinary growth of the PV industry, similar to that of the mobile phone industry, is that investors are constantly being bombarded with vague claims from researchers that their work will lead to high efficiency PV cells. This makes the investors cautious in investing in a current manufacturing technology that may be obsolete soon [51]. As an example, the publication of a paper on multiple exciton generation (MEG) in colloidal silicon nanocrystals [52], motivated the author of [53] to claim that silicon nanocrystals-based solar cells can generate two electrons from one photon, and that single junction PV cell efficiency can be as high as 40%. The fact is that the authors of [52] never fabricated a PV device and MEG phenomena reported in nanocrystals or quantum dots have no direct relevance to the operation of the PV cell [5].

2.10 Conclusions

In this chapter we have presented the potential of manufacturing photovoltaic devices beyond the current generation of bulk and thin film semiconductors. Based on the

theoretical and experimental results presented, it is obvious that the current processing techniques are unable to capitalize on the advantageous features of nanostructures. New processing methods need to be invented that can provide better dimensional control than existing self-assembly technique. At the same time, the cost of ownership for the new equipment must be lower than that of the tools used presently in the manufacturing of solar cells. Concepts proposed to be used in photovoltaic devices such as multiple exciton generations, carrier multiplication, hot carrier extraction, and intermediate band solar cells have fundamental flaws. Inaccurate assumptions used in the operations of above mentioned solar cells do not give due importance to transport of photo generated minority carriers, which is an extremely important process in the operation of a solar cell. In addition, there is no experimental evidence that such “third-generation” devices can perform better than devices based on the current generation of photovoltaic devices. As of now, continuous improvements in bulk and thin film solar cell manufacturing processes are driving costs down and increasing reliability, making solar cells a viable option for power generation.

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CHAPTER THREE

FUNDAMENTAL PROBLEMS OF NANO SELF-ASSEMBLY FOR
MANUFACTURING SEMICONDUCTOR PRODUCTS

This chapter is based on the publication - G.F. Alapatt, R. Singh, N. Gupta, and K.F. Poole, "Fundamental Problems of Nano Self-Assembly for Manufacturing Semiconductor Products", *Emerging Materials Research*, vol. 1, no. S1, pp. 71-76, 2012

3.1 Introduction

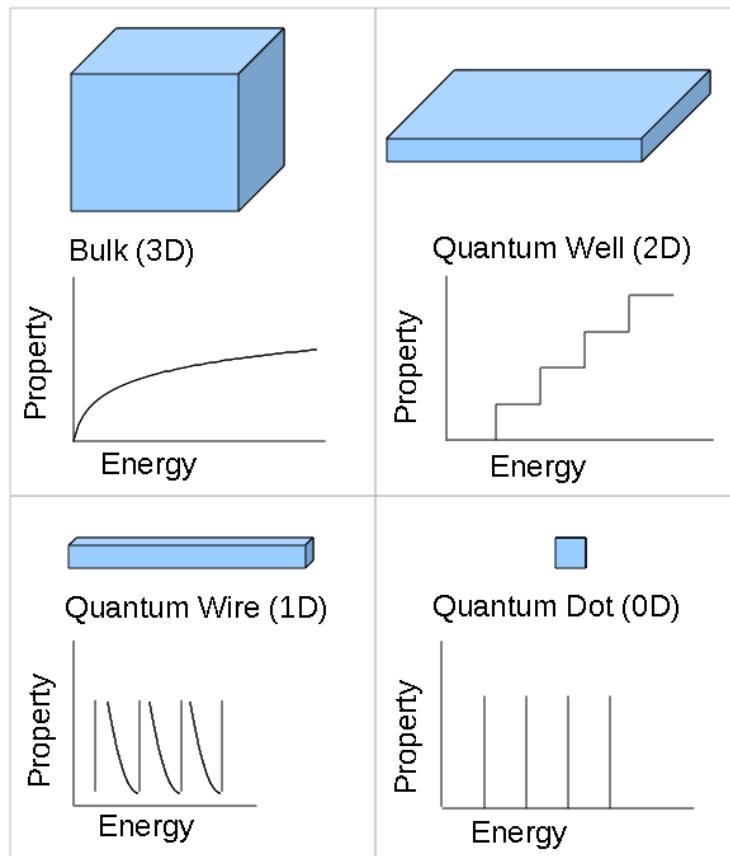
Self-assembly has been claimed as the new method to manufacture nanomaterial based devices [1-3]. It is widely known that this process can result in extremely small particles; however, the variation in size and shape of particles formed is still quite large [4-8]. Despite years of research, there seems to be no method to produce structures in a pre-defined manner using self-assembly. Self-assembly is a process that has been looked upon as a possible method for manufacturing for decades and there has not been even a single success story. Although self-assembly based techniques may be useful in making low-tech products and for bio-applications, this technique cannot be applied to semiconductor manufacturing. The objective of this chapter is to examine the experimental results reported to date and point out the fundamental limitations of self-assembly.

3.2 Nanostructured Materials

Any material with isolated structures of sizes between 1-100 nm is classified as a nanomaterial. A nanomaterial may have zero, one, two or three of its dimensions in this size, based on which, it is classified as a 0D, 1D, 2D, or 3D nano-structure. True quantum effects can be observed in a material in which the dimension approaches the de-Broglie wavelength of the electrons. In all cases, quantization of electron density takes place because of the size restriction and this gives nano-materials many interesting properties that cannot be observed in the bulk material.

0D particles include clusters of atoms in which the electrons are confined in all dimensions. 1D nano-structures include chains of atoms, like a nano-rod or a nano-wire or a nano-tube. 2D nano-structures include films of materials in the nano-dimension. 3D nanostructures are the most complicated nanostructures and are often comprised of other lower dimension nano-structures. Figure 3.1 shows the density of states as a function of energy in various materials.

Fig. 3.1: Quantization of Density of states



3.3 Properties of Nanomaterials

Properties of nano-materials differ vastly from their bulk properties and are a direct result of “quantum confinement”. These properties have been known to us for a few centuries, but their scientific explanation came about only in the last fifty years. For instance, Gold nano-particles have been used since the 17th century to color glass windowpanes in churches [9]. Carbon black has been used as an ingredient for manufacturing automotive tires since the 1990s. Carbon black is available in a variety of grades, one example being Super Abrasion Furnace, with particles of an average size of

20-25 nm [10]. Even though such applications exist, only nano-structures manufactured from lithography based techniques are being used in semiconductor products.

In semiconductor applications of nano-technology, each nano-structure plays a role in the working of the product. For instance, in the case of transistors based on nano-structured materials, each nano-structure acts as a transistor. If even one device does not function as expected, the circuit will malfunction. This concept is important, as currently manufactured ICs have several millions of transistors that work together. Each transistor should be located in a specific location and metal lines need to be connected between each device to enable circuit building. Another example is a photovoltaic module – which consist of several solar cells connected in series or parallel. In a series connection, the lowest current in the chain dominates and in a parallel connection, the lowest voltage in the connection dominates. This leads to significant losses, if the variation in individual cell efficiency is large [11].

Using the individual property of a nano-structured material is very different from building a technology to use its average property. IC manufacturing companies such as Intel and Toshiba are already making devices with feature sizes of 22-24 nm [12, 13]. These devices are still operating in a classical-regime and are not employing quantum confinement based properties for their operation. To achieve quantum confinement based properties, structures of still smaller sizes should be employed. For a silicon structure, the size below which quantum properties become observable is about 8 nm [14]. Figure 3.2 shows the variation of the optical band gap of silicon with variation in the diameter of silicon particles. Below 8 nm, the band gap changes significantly, while the band gap is

close to 1.1 eV as the diameter increases beyond 8 nm. General properties of nanomaterials vary as shown in Fig 3.3 [15]. It is important to understand that all properties of a material vary at low dimensions.

3.4 Manufacturing Nanomaterials

Lithography has been the standard technique for transferring patterns during IC manufacturing since its beginning. The minimum feature size, quantified as half-pitch has been steadily decreasing since the 1980s. Invention of better light sources and improved methods of exposure have driven this change. As of now, the half-pitch distance is 22 nm and the light source used has a wavelength of 193 nm, which is about six times the half pitch distance [16]. Further decrease in the light source wavelength to 13.5 nm using an extreme ultra violet (EUV) source, has the possibility to decrease the half-pitch to the range of a few nanometers. With lithography, patterns of half-pitch distance less than 10 nm have been created over a decade ago [17].

Fig. 3.2. Variation of Optical gap of Si with diameter. Simulated results from various authors [14]

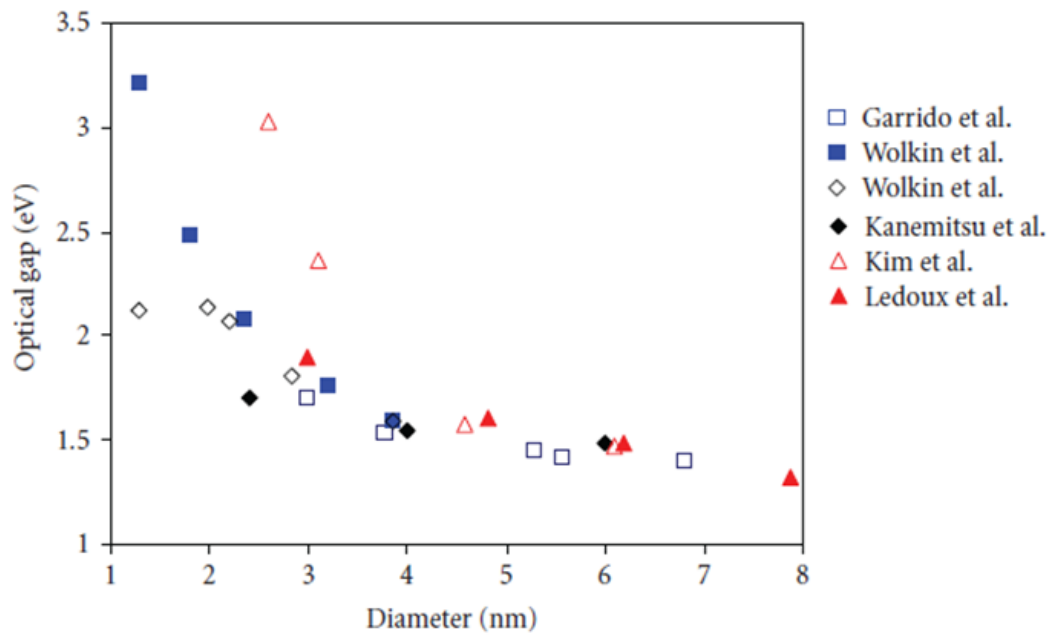
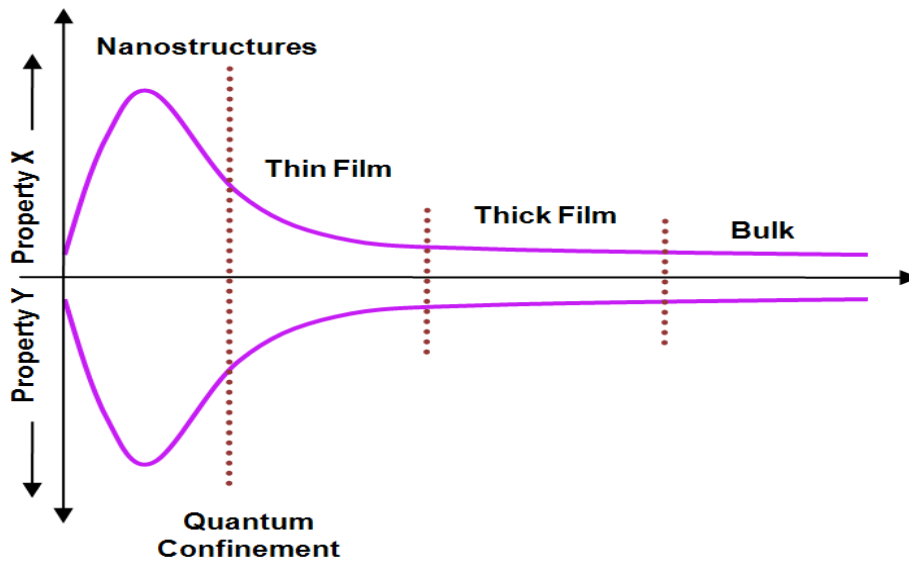


Fig. 3.3: Variation of property with size [15]



Apart from surface patterning abilities, manufacturing the nano-structured materials will require profiling abilities along the vertical axis. The Deep Reactive Ion Etching process is currently able to make vertical profiles with aspect ratios greater than 60 [18]. Thus, the traditional, semiconductor industry-based manufacturing technology can make nano-dimensional structures for research purposes. However, issues relating to non-homogeneity and process control will determine if these devices can be successfully manufactured on a large scale without defect related problems. Recently, a defect on one of Intel's chip was discovered and analysts predict that this defect is going to cost Intel about \$1 Billion [19]. Defects such as these will determine how successful a product will be.

The bottom up approach involves devices using an atom-by-atom, approach and is called self-assembly [20]. In our opinion, the meanings of "Self Assembly" have been taken wrongly. A true self-assembly process involves programmed cell death or apoptosis [21]. The so called "self-assembly" is actually selective chemistry. The atoms or molecules are forced by chemical, mechanical, or electrical means to assemble in a particular fashion. Researchers have often compared this method to what happens in the development of an animal or a plant.

A popular technique used in fabricating nano-materials using self-assembly is to create nano-structures in a solution and to remove the unwanted structures to get reasonable size and shape uniformity. Separation techniques include centrifuging, filtering and the use of electron microscopy to find the "correct" structure among other structures generated. However, due to economic considerations such techniques cannot

be scaled up for mass production as it leads to wastage and lost revenue. Moreover, most self-assembly based techniques result in only small quantities of material. On the other hand, actual production requires production of bulk quantities. In a previous publication we have shown that lower throughput with lower defect densities is a fundamental limit of self-assembly [22].

The best replication system can be thought as the one involving DNA replication. The error rate is about 1 per million nucleotides, this rate results in 120,000 mistakes when a cell divides; however, because of error correcting enzymes, most of such mistakes are caught and corrected [23]. This situation can be compared to a modern IC which has millions of transistors, each with multiple layers of materials. Such a high error rate means that most of the manufactured chips will have a defect that will render the chip useless and the overall yield will be insignificant, unless there is an error correction scheme after manufacturing. However, such schemes and concepts such as fault tolerant computing have not yet been proven to work.

3.4 Manufacturing Issues

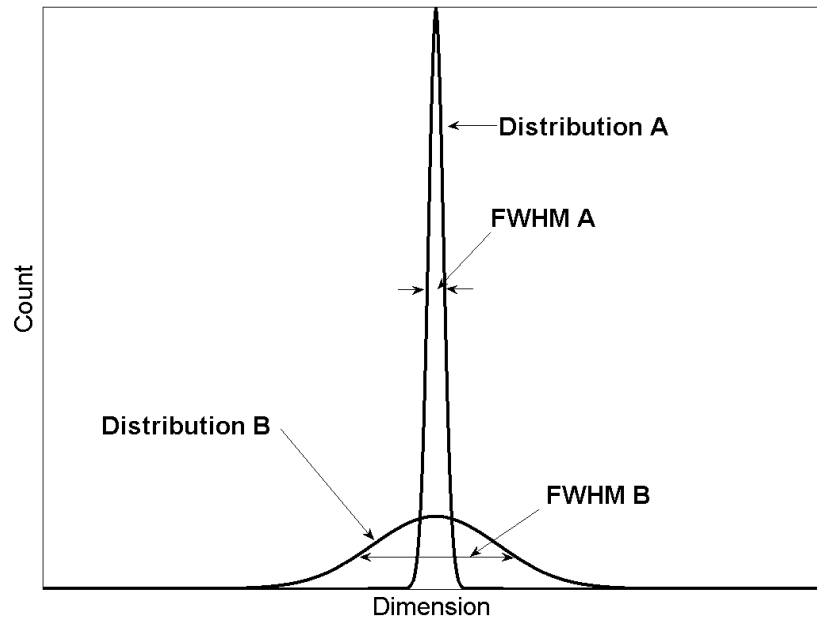
3.4.1 Variability

Nano-materials manufacturing will require very complicated process control to keep variability very low. Since the material dimension is only a few nanometers, the process window will be extremely small. In typical semiconductor manufacturing, the allowable three sigma process window is only 10%. Consider making a device of size 10 nm, the three sigma process window is +/- 1 nm, which means that 99.7% of the devices

must have a dimension between 9 and 11 nm. Such a narrow process window cannot be realized in a manufacturing process existing today. A new process must be invented which has process better than the current advance process control. Even after a picking favorable structures using electron microscopy, authors indicate a three sigma variation of 14% [24].

In Fig. 3.4, Distribution A shows the allowed variation in dimension sizes for exploiting the special properties that can be obtained with nano-material based devices; however, during manufacturing, due to a lack of absolute control on the dimension, the resulting distribution will resemble the Distribution B.

Fig. 3.4: Two statistical distributions of dimension sizes



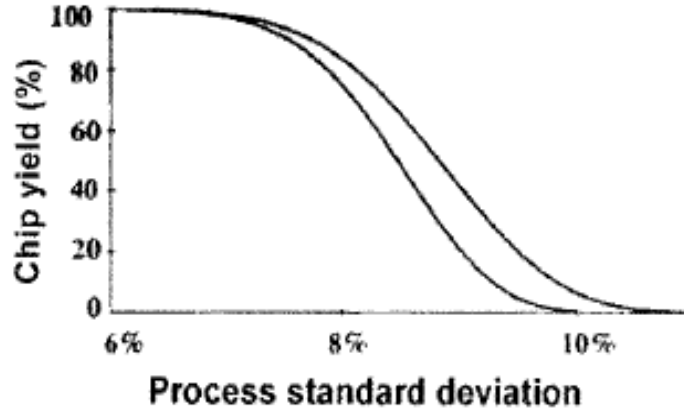
3.4.2 Yield

The yield of a particular process influences the final manufacturing cost of a product. Variability and yield are tied together. As shown in Fig 3.5, as process variability increases, the yield drops substantially. If the process standard variation in an IC manufacturing industry is greater than 10%, the yield is practically zero [25]. To make a commercial product involving mass manufacturing, a high-yield process is required.

3.4.3 Throughput

A processing technique should be able to process a sufficient number of devices to make the technology commercial. Otherwise, the fabrication process, even though scientifically sound, will not be commercially viable. For example, EUV lithography, which is still under development, suffers from throughput issues and is currently not used in production systems [26]. None of the self-assembly based processes for manufacturing electronic devices have been shown to have a high enough throughput. This is another fundamental barrier that should be addressed if ever self-assembly based technology becomes successful in the future.

Fig.3.5. Chip Yield vs. Process standard deviation [25].



As per the ITRS, future generations of ICs will have a defect density of $0.01/\text{cm}^2$, a throughput of at least 60 wafers per hour and the three-sigma variation in line widths will be less 10% [16]. Self-assembly, or any other technology, must be capable of exceeding these goals, to become technologically and commercially viable.

3.5 Conclusions

Even though it is widely known that one can make nano-particles using a simple wet chemistry based process, producing such particles in a controlled fashion has not been proven. Based on a wide literature search, we come to the conclusion that none of the self-assembly based technique is capable of producing reproducible nanostructures with the low variability required for manufacturing semiconductor devices. In addition, no control mechanism exists, as of today, to produce such nano-structures to make useful semiconductor products. Further, ideas such as fault tolerant computing have not yet been implemented outside research areas.

Lithography based top-down manufacturing techniques are currently capable of producing 22 nm structures and such products are already available in the market. Further innovations in lithography will drive the minimum feature size to even smaller dimensions.

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CHAPTER FOUR

MAKING SOLAR CELLS A REALITY IN EVERY HOME: OPPORTUNITIES AND CHALLENGES FOR PHOTOVOLTAIC DEVICE DESIGN

This chapter is based on the publication - R. Singh, G.F. Alapatt, and A. Lakhtakia, "Device Design Opportunities and Challenges for Making PV a Reality in Every Home", *IEEE J. of Electron Device Society*, vol. 1, no. 6, pp. 129-144, 2013

4.1 Introduction

Although the earliest patents on silicon solar cells, granted during the 1940s [1, 2], indicated that the devices had very low efficiencies ($< 1\%$), hopes of higher efficiencies continued to fuel research. In 1954, Chapin and co-workers reported 6%-efficient silicon solar cell [3]. Using the now obsolete International Electrochemical Commission (IEC) 60904-3: Ed 1 spectrum, Zhao and co-workers in 1999 [4] reported a silicon solar cell with 24.7% efficiency. Re-evaluating this same solar cell using the IEC 60904-3: Ed 2 spectrum, Green [5] in 2009 revised the efficiency to 25%.

The development of highly efficient silicon photovoltaic (PV) devices and related improvements in power electronics and module manufacturing led to predictions that PV electricity can be billed to consumers at the rate of \$0.10/kWh [6]. That prediction has been recently vindicated [7]. Moreover, the cumulative installed solar PV electricity generation capacity worldwide has topped the 100-Gigawatt (GW) mark [8]. In 2013, the

demand for new solar PV installations is expected to be 31 GW [9]. As shown in Fig. 4.1 [9], this PV demand is global, not being dominated in any particular region of the world. For sustained global economic growth in this century, PV electricity generation is highly attractive because solar energy is essentially unlimited and PV systems provide electricity without any undesirable impact on the environment [10]. The cumulative installed solar PV electricity generation capacity is expected to double from about 100 GW in 2012 to 200 GW in 2015, as shown in Fig. 4.2 [11]. The average selling price of PV panels has dropped to \$0.65 per peak watt (Wp) [12]. Dominated by the second most terrestrially abundant element—namely, silicon [13]—PV energy generation is firmly moving to the terawatt scale [14].

The magnitude of the current globally installed solar PV capacity, the continually lowering cost of installed PV systems, and the continually lowering cost of PV generated electricity are the three factors that have established that PV technology is no longer only purely a research area, but it is a very important means to generate green electricity for meeting the needs of rich and poor all over the world [15]. Since huge investments have already been made in the processing of silicon and the functioning of the associated supply chain, only a truly disruptive technology can replace the well-established silicon-based PV technology. Indeed, although over 200 companies started in 2008 with the goals of inventing and commercializing disruptive PV technologies, most of these companies have either gone bankrupt or do not exist anymore. That outcome was to be expected [16]. A complete list of deceased companies is given in Ref. 17. Thus it is very important to understand the nature of innovations that will continue to reduce the cost of

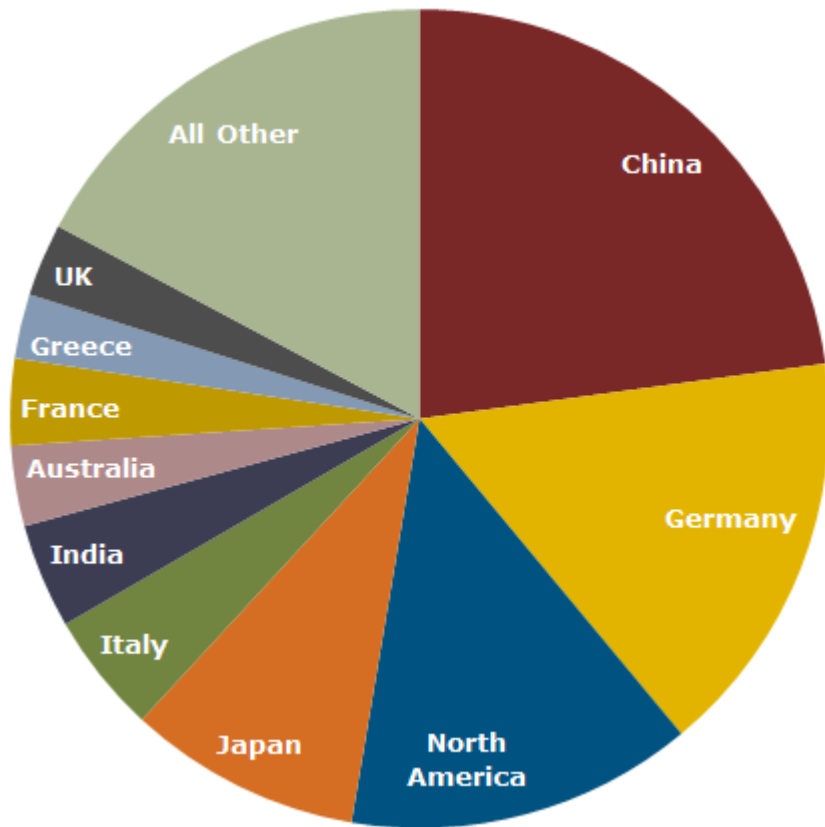


Fig. 4.1. Geographic breakdown of the PV electricity generation capacity expected to be added worldwide in 2013 [9].

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PV modules and other components of PV systems, similar to the cost-reduction history of silicon-based low-power electronics that has played and continues to play a vital role in enabling the information revolution.

For further cost reduction, design concepts for new manufacturable devices need to be developed beyond the current generation of bulk and thin-film solar cells. Several concepts—such as multiple exciton generation (MEG), carrier multiplication, hot-carrier

extraction, intermediate-band solar cells, nanostructured solar cells, etc.—have been proposed to replace the extant solar cells. The purpose of this review is to critically examine published theoretical and experimental results relating to the proposed concepts and suggest directions for further research on the design of PV devices.

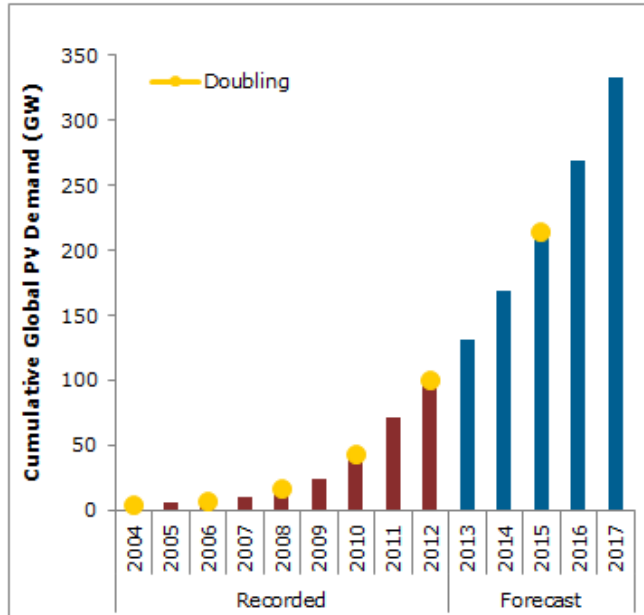


Fig. 4.2. Actual (2004-2012) and expected (2013-2017) growth in PV electricity generation capacity worldwide [11].

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4.2 Upper Efficiency Limit Of Photovoltaic Devices

On considering the sun as a black body of temperature $T = 6000$ K and assuming that a PV device (without any consideration of material related issues) is operating at a temperature of $T = 300$, the upper thermodynamic efficiency limit of the PV device is given by -

$$\eta = \left(1 - \frac{300}{6000}\right) \cdot 100 \% = 95 \% \quad \text{Equation (4.1)}$$

Any PV device (including concentration solar cells) operating at a temperature of 300 K will always have efficiency lower than 95 %. After the discovery of the silicon solar cell in 1954 [3], several attempts were made to predict the efficiency of a silicon solar cell as well as the optimum bandgap for obtaining the highest efficiency [18-21]. In 1961, Shockley and Queisser published a fundamental paper on the efficiency of a single junction solar cell [22] and predicted its upper limit. Popularly called the SQ limit, this is generally accepted as the theoretical upper limit because it is based on atomic processes described by the basic laws of physics.

The major factors accounted for in the calculation of the SQ limit are as follows: the bandgap of the semiconductor, the ratio of the temperature of the solar cell to the temperature of the sun, the probability that an incident photon with energy higher than the bandgap of the semiconductor will produce an electron-hole pair, a factor that involves the transmission of radiative recombination from the solar cell, and the angle subtended by the sun. Although practical solar cells cannot achieve the limit proposed by Shockley and Queisser, it is possible to achieve efficiency quite close to this limit by using a semiconductor that has a very small defect density. For single-crystal silicon solar cells, a maximum efficiency of 25% has already been achieved, whereas the SQ limit is approximately 30%. To date, no experimental results have indicated that the SQ limit can be breached.

The SQ limit of a single-junction solar cell can be extended to a multijunction solar cell wherein a large number of solar cells are arranged in such a way that the

topmost semiconductor has the highest bandgap and the bottommost cell has that lowest bandgap to absorb the entire solar spectrum. The SQ limit of such a multijunction solar cell is about 86.8 % [23].

4.3 Current Status Of Commercial PV Devices

Silicon solar cells dominate the PV market. As an example, of the 22-GW capacity added worldwide to PV electric generation in 2011, silicon solar cells accounted for 89%, while CdTe and CuInSe/CuInGaSe solar cells together accounted for the remaining 11% [24]. There is a direct relationship between the efficiency and the cost of a PV module, which translates into a direct relationship between the efficiency and the cost of an installed PV system. The efficiency of a PV module is lower than the efficiency of any individual small-area solar cell within the module, due to the series resistances of the interconnects and the variability in the efficiency of the individual solar cells [25].

The variability of any process has a Gaussian distribution and can therefore be characterized by the full-width-at-half-maximum (FWHM) of the distribution. Fig. 4.3 [25] is a schematic of the variation of the efficiency of a PV module with the FWHM of the overall processing variability that results in the variability of efficiency of individual solar cells. As the FWHM of a process parameter increases, the efficiency of the PV module drops. Current semiconductor manufacturing employs advanced process control (APC) [26]. The use of more APC equipment in the PV industry can reduce the FWHM of various processes and thereby increase the efficiency of the PV modules.

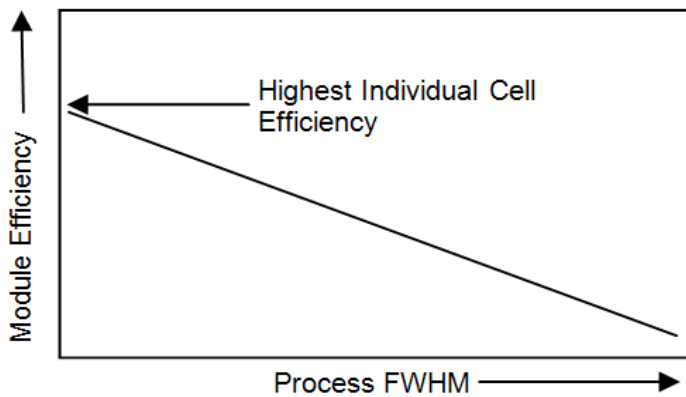


Fig. 4.3. Schematic of the relation between process FWHM and module efficiency [25].

Reprinted from G. F. Alapatt et al., “Fundamental issues in manufacturing photovoltaic modules beyond the current generation of materials,” *Adv. Optoelectron.*, vol. 2012, art. no. 782150, 2012..

Tables 4.1-4.3 present the efficiencies of different types of PV cells and modules that are commercially available, but data on “champion PV modules” were discarded from consideration. Both organic and DSSC modules are marginally commercially available only for a few small consumer applications but not for bulk power generation. Silicon solar cells are twice as efficient as organic solar cells and DSSCs. The low efficiencies of organic modules and DSSC modules are, in part, also due to the low efficiencies of the individual solar cells inside these modules. More importantly, these tables demonstrate that solar cells made with well-controlled processes make up modules with high efficiency. Whereas silicon modules of large area (more than 10,000 cm²) are available, the areas of organic and dye-sensitized solar-cell (DSSC) modules are very

small. Especially, DSSC modules do not exceed 17 cm^2 . It is difficult to make large-area modules with unreliable technology because of the loss of efficiency while interconnecting cells with diverse open-circuit voltages and short-circuit currents. The efficiency of an organic module is roughly half that of the individual cell, even when the module area is 300 cm^2 . If the area of a DSSC module or an organic module is significantly enhanced, the module efficiency is expected to drop significantly as well. This problem is not expected to afflict a-Si, CIGS and CdTe modules. Without any fundamental breakthrough in the material synthesis and performance of organic and DSSC solar cells, it is not possible that the PV modules based on these two types of solar cells will be ever used for bulk power generation.

Current PV technology can be classified into the following three categories: (a) power generation without concentration (Table 4.1), (b) power generation with concentration (Table 4.2), and (c) throw-away device technology (Table 4.3). Categories (a) and (b) represent mature technologies and cells with good long-term reliability. Category (c) represents cells of use mostly in products that have to be replaced every few years. These cells may be called throw-away cells. Reliability experiments indicate that the longest lifetime of organic PV (OPV) solar cells is only 3-4 years [33]. Although these experiments were not conducted consistently with industry standards [34], even so their results demonstrate the fundamental weakness of OPV technology. Other than for throw-away products and some niche applications, Organic PV cells and DSSCs are unsuitable for the large-scale PV generation of electricity.

TABLE 4.1: COMMERCIAL NON-CONCENTRATOR PV TECHNOLOGY:(ap) = APERTURE AREA ;

(da) = DESIGNATED ILLUMINATION AREA ; (ta) = TOTAL AREA.

Cell Type	Highest Cell Efficiency	Cell Area (cm ²)	Ref.	Highest Manufactured Module Efficiency	Module Area (cm ²)	Ref.
Si (mono crystalline)	25.0±0.5	4.00 (da)	27	21.5	16307 (ta)	28
Si (multi crystalline)	20.4±0.5	1.002 (ap)	27	15.3	16700 (ta)	29
CdTe Thin Film on Glass	18.3±0.5	1.066 (ap)	27	12.8	7200 (ta)	30
CIGS on Glass	19.6±0.6	0.996 (ap)	27	14.5	10713 (ta)	31
a-Si (tandem)	13.4±0.4	1.050 (ap)	27	10.4±0.5	905 (ap)	26

TABLE 4.2: COMMERCIAL CONCENTRATOR-BASED PV TECHNOLOGY; (ap) = APERTURE AREA; (da) = DESIGNATED ILLUMINATION AREA.

Cell Type	Highest Cell Efficiency	Cell Area (cm ²)	Ref.	Concentration Factor
GaInP/GaAs/GaInNAs	44.4	0.3124 (ap)	32	947
Si	27.6±1.0	1.00 (da)	27	92

TABLE 4.3: THROW-AWAY PV TECHNOLOGY. ALL AREAS ARE THOSE OF AN APERTURE.

Cell Type	Highest Cell Efficiency	Cell Area (cm ²)	Ref.	Highest Sub module Efficiency	Sub module Area (cm ²)	Ref.
Organic	10.7±0.3	1.021	27	6.8±0.2	294.5	27
DSSC	11.9±0.4	1.007	27	9.9±0.4	17.11	27

Benign solar intensity (about 0.75-1.0 kW/m²) does allow many types of PV systems to function reliably for over 25 years. Both III-V compound semiconductor solar cells and silicon solar cells are currently being used for concentration PV (CPV) application. Fundamentally, there is nothing wrong in assuming that CPV systems should provide electricity at lower cost compared to non-CPV systems. However, engineering problems that include thermal and optical challenges have not permitted the large-scale commercialization of CPV systems, lack of functional reliability—and therefore of economic bankability—being a major barrier [35]. Several companies are currently carrying out field trials of low-concentration MW-size PV systems, yet the cumulative installed solar CPV electricity generation capacity worldwide is only 130 MW as of March 2013 [36].

Due to many limitations on currently available materials, CPV systems have not provided a reliable and cost-effective solution for terrestrial applications. Silicon solar cells can be used at low concentration (~1-5 suns), and the cost of silicon CPV systems remains high. At high concentration (> 400 suns), III-V compound semiconductor solar cells are used. As these solar cells are used in space, the device-design concepts are already fairly advanced. Therefore, no major improvement in device design is expected that can cut down the cost of a III-V compound semiconductor CPV system for terrestrial applications.

Three proven device architectures are available for high-efficiency silicon PV modules: (a) passivated emitter with rear locally-diffused (PERL) architecture, (b) rear contact cell (RCC) architecture, and (c) heterojunction with intrinsic thin layer (HIT)

architecture. All three device architectures are shown in Fig. 4.4. A record efficiency of 25% was obtained for a PERL cell (Fig. 4.4a) by decreasing surface and bulk recombination as well as by improving contacts [5, 27]. In the RCC architecture (Fig. 4.4b), front contacts are moved to the rear of the cell, thereby increasing the area facing sunlight. Surface passivation and local contacts are employed to reduce recombination losses [37]. In laboratory testing, 24% efficiency has been achieved [37]. In an HIT cell (Fig. 4.4c), the surface of the crystalline silicon is properly passivated by coating it with amorphous silicon. This passivation along with better grid formation helps to increase efficiency of HIT cells up to about 25% [38]. A hybrid solar cell with amorphous silicon for passivation has also been fabricated in which silver is replaced by copper to reduce the cost (Fig. 4.4d); the efficiency of this cell is 22% [39].

Every record-setting single-junction silicon solar cell has an architecture that is either PERL or RCC or HIT. Only marginal improvements in efficiency can therefore be expected for single-junction solar cells.

4.4 Manufacturing Design Guidelines

For large-scale terrestrial applications, the following guidelines must be followed in the design of devices, systems, and processes: (a) The supply of raw materials must not be constrained. (b) The variability of every key process and process-induced defects must be kept as low as possible. (c) The unit production cost must be kept as low as possible. (d) There should be prospects for cost reduction in the future. (e) Manufacturing must follow green manufacturing principles to avoid environmental, health, and safety

problems. (f) The PV systems must have long-term reliability. Adherence to these guidelines would make the business enterprise economically bankable. Decision-makers at all levels—and, especially, device designers—must keep these guidelines in view, when considering any new material or device architecture.

4.4.1 Unconstrained Supply of Materials

To long-term researchers, the current interest in PV devices and other clean technologies appears pretty much at the same intensity as in the mid-1970s and early 1980s. During that period, several materials were proposed as candidates for solar cells. In 1980, one of us [40] co-authored a paper on the economic requirements for new materials for solar cells and predicted—based on the abundance of raw materials—that silicon was the best candidate. It is worth mentioning here that currently there is oversupply of polysilicon and underutilization of polysilicon manufacturing plants [41]. In the future, bulk silicon PV module manufacturers might migrate a higher proportion of their production to monocrystalline and n-type wafers in search of higher conversion efficiencies and thinner wafers ($\leq 140 \mu\text{m}$ thin) [42]. Increased demand for highly pure polysilicon by semiconductor and PV industries is likely to increase the price of that material. However, as explained in Ref. 43, such price increases are short lived. The abundant occurrence of silicon on earth will stabilize the price of polysilicon.

Over the last 33 years this prediction has been correct, and it is expected to remain true in the future [10, 13]. Indeed, the supply chain of indium, gallium, and tellurium for manufacturing CIGS and CdTe solar cells is not robust [43-45]. Knowing the limitations

of CIGS and CdTe solar cells, thin-film solar cells based on copper, zinc, tin and sulfur (CZTS) are being explored [46]. The CZTS solar cells are at an early stage of development and have the potential to replace CIGS and CdTe solar cells.

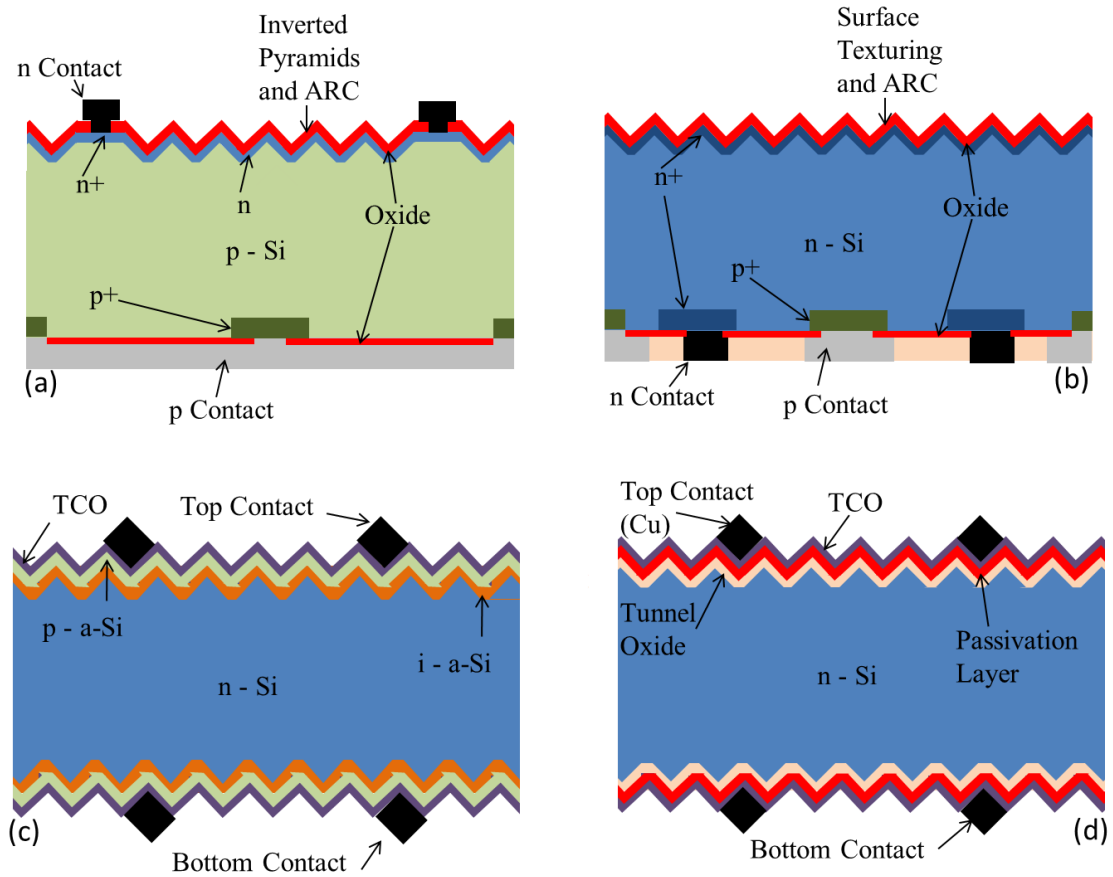


Fig. 4.4. Architectures of four highly efficient silicon solar cells: (a) passivated emitter with rear locally diffused (PERL) cell, (b) real contact cell (RCC), (c) heterojunction with intrinsic thin layer (HIT) cell, and (d) a hybrid solar cell with copper electrodes.

4.4.2 Low Variability of Key Processes

The cost of ownership [13] of a device is the ratio of (i) the sum of fixed costs, temporally variable costs, and the cost due to yield loss to (ii) the product of the throughput, the composite yield, and the utilization factor. As the cost of ownership decreases when the yield improves, key processes must have as little variability as possible. Furthermore, every process must induce as few defects as possible. In the present context, the power output of each solar cell in a PV module and the power output of each PV module in a PV system must lie within very narrow bands of acceptability. This is because in a series/parallel connection of multiple solar cells to get the desired voltage/current, the component with the minimum voltage/current will dictate the power output of the PV module. Likewise, performance variations of PV modules in a system will dictate the power output of the system.

Fig. 4.5a is a schematic of a PV module with $m \times n$ solar cells connected in series and parallel, and Fig. 4.5b is a plot of the power lost with variation in solar-cell performance [25]. The loss in output power increases from 10% to 65% as the variability in the performance of the components increases from 10% to 80%. Therefore, any manufacturing variability that affects the performances of solar cells will result in lower yields of modules, and is one of the main technical reasons for the failures of several thin-film solar-cell companies [25].

Fig. 4.6 schematically depicts the relationship between defect density and process complexity. As a process becomes more complex, the variability of its output decreases. Usually, more complex processes such as lithography result in microstructures with both low variability and low defect density. Simple processing techniques—such as non-

vacuum roll-to-roll processing and spin coating—yield microstructures with both high variability and high defect density. Bottom-up techniques, claimed to be very simple processing techniques, lead to poor industrial scenarios [47]. Although simple processing techniques might look inexpensive at first glance, metrics such as defect density, yield, and throughput decide the ultimate cost of ownership.

(a)

V_{11}	V_{12}	V_{13}	\vdots	$V_{1\ n-1}$	$V_{1\ n}$
J_{11}	J_{12}	J_{13}	\vdots	$J_{1\ n-1}$	$J_{1\ n}$
V_{21}	V_{22}	V_{23}	\vdots	$V_{2\ n-1}$	$V_{2\ n}$
J_{21}	J_{22}	J_{23}	\vdots	$J_{2\ n-1}$	$J_{2\ n}$
V_{31}	V_{32}	V_{33}	\vdots	$V_{3\ n-1}$	$V_{3\ n}$
J_{31}	J_{32}	J_{33}	\vdots	$J_{3\ n-1}$	$J_{3\ n}$
\vdots	\vdots	\vdots	\vdots	\vdots	\vdots
$V_{m-1\ 1}$	$V_{m-1\ 2}$	$V_{m-1\ 3}$	\vdots	$V_{m-1\ n-1}$	$V_{m-1\ n}$
$J_{m-1\ 1}$	$J_{m-1\ 2}$	$J_{m-1\ 3}$	\vdots	$J_{m-1\ n-1}$	$J_{m-1\ n}$
$V_{m\ 1}$	$V_{m\ 2}$	$V_{m\ 3}$	\vdots	$V_{m\ n-1}$	$V_{m\ n}$
$J_{m\ 1}$	$J_{m\ 2}$	$J_{m\ 3}$	\vdots	$J_{m\ n-1}$	$J_{m\ n}$

(b)

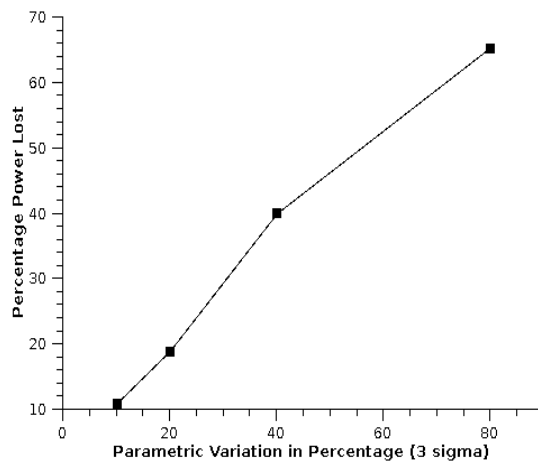


Fig. 4.5. (a) Panel with $m \times n$ cells. (b) Power lost as function of process variation [25]
Reprinted from G. F. Alapatt et al., “Fundamental issues in manufacturing photovoltaic modules beyond the current generation of materials,” *Adv. Optoelectron.*, vol. 2012, art. no. 782150, 2012..

4.4.3 Low Production Cost

For reducing the production cost of PV modules, it is necessary to use larger substrates rather than smaller ones—which is also the experience derived from integrated circuitry (IC) and display industries [43]. Other than the efficiency of PV modules, the energy consumed in the manufacturing processes, the cost of raw materials, the cost of automation, throughput, and yield are important factors in the overall production cost. Of course, factors such as labor cost and the cost of water and electricity also affect the cost of PV modules, along with waste disposal costs, environmental remediation costs and the costs of complying with legislated mandates. The appropriate production capacity of a manufacturing unit must be determined after considering all of these factors.

4.4.4 Prospects for Further Cost Reduction

Other than increasing the efficiency of PV modules, any chosen manufacturing process should be capable of further cost reduction. Scenario planning is likely to be an effective tool for future planning [48]. Alignment with the IC and display industries on the sizes of wafers and substrates appears highly desirable for the PV electricity generation industry. Real or virtual vertical integration of the supply chain and

distribution networks over time will further drive down the cost of PV modules, as will also co-location with manufacturing units for glass [6, 10, 15].

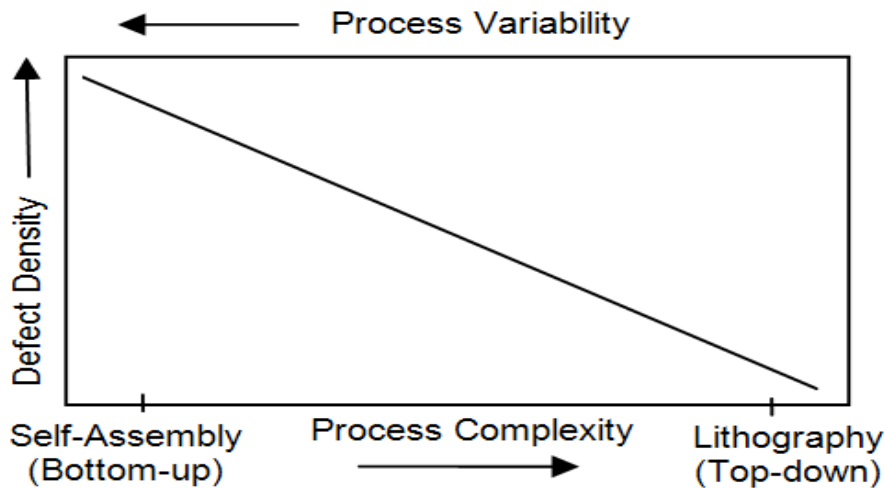


Fig. 4.6. Relationship of process variability to process complexity and defect density.

4.4.5 Environmental Safety and Health Issues

The techniques used for PV manufacturing are quite similar to manufacturing techniques for the \$350-billion semiconductor industry. Similar to the semiconductor industry, some potentially hazardous materials are utilized in the life cycle of photovoltaic systems, none of which present a risk different or greater than the risks found routinely in modern society [49]. As part of green manufacturing, recycling and conservation efforts are continuously considered and adopted by the manufacturers of solar panels [50].

The only material that poses additional concern in the current generation of PV devices is cadmium in CdTe solar cells [43]. In addition to the concern about the health

of the workers, public health may be compromised by chronic exposure to cadmium compounds released into the environment as by-products of different manufacturing steps. The same issues will arise from the uncontrolled disposal of spent photovoltaic modules containing CdTe solar cells. All of these issues may be accentuated if the hazardous elements and compounds are released as nanomaterials. Scenario planning appears necessary both for green manufacturing and risk management [51].

4.4.6 Reliability

The cost of electricity generated from a solar panel is calculated after assuming a certain lifetime performance for the PV modules. For solar panels, a long lifetime is particularly required since the lifetime directly influences the cost per watt of power output. In addition, solar panels can be used as long as they are functioning satisfactorily and are not subject to the same technology trends as other consumer electronic products are. Therefore, long-term reliability is a key issue.

Over the last 60 years, the reliability of semiconductor products has continually improved [52]. The same is true for PV solar cells. Solar cells of any type that cannot operate reliably for 25-30 years will not contribute to large-scale adoption of PV electricity generation technology. Silicon solar modules are now marketed with a guarantee that the output power will stay within 15% of the originally rated value during their 25-year lifetime [53].

As an evidence of the high inherent reliability of silicon-based electronics, silicon solar panels installed 20 years ago are still performing with minimal degradation (8.3%

decrease in nominal power output) [54]. In contrast, CdTe modules manufactured by First Solar experienced premature power loss associated with degradation at high temperatures [55]. The manufacturer posted a fourth-quarter loss as a major write-down, to account for costs associated with replacing defective solar panels [55]. Due to the weak nature of the bonds in organic materials, serious material degradation happens over just a few years, which renders organic solar cells and DSSCs economically unviable [31] except in niche applications.

4.5 Current Research Approaches

Both bulk and thin-film semiconductors are currently being explored to function as absorber layers in solar cells. The theoretically highest possible efficiency of a single-junction PV solar cell is the Shockley–Queisser (SQ) limit [22]. The derivation of the SQ limit is based on the assumption that only radiative recombination takes place in the semiconductor. Several approaches have been proposed to boost the efficiency of the single-junction solar cell beyond the SQ limit. Most of these approaches rely on either capturing the generated electron-hole pair (EHP) before it thermalizes, or on generating more than one EHP per incident photon, or on altering the solar spectrum available for energy conversion. Key approaches are listed in Tables 4.4 and 4.5.

4.5.1 Two-terminal Multi-junction Solar Cells

The upper bound on the efficiency of a single-junction solar cell has been known from the early days of PV development for terrestrial applications [71, 72]. In a multi-

junction cell, materials with different bandgaps are optically and electrically connected in series, each material absorbing a certain band of the solar spectrum. The thermodynamic limit on the efficiency of a solar module consisting of an infinite number of solar cells connected in series and operating at room temperature (300 K) is 86.8% [72].

Highly efficient current-matched multi-junction solar cells are often fabricated of III-V compound semiconductors [73]. Two-terminal multi-junction III-V compound semiconductor solar cells are the building blocks of PV modules for space applications. Commercial amorphous-silicon tandem solar cells [27] are also multi-junction devices. However, these thin film amorphous silicon solar cells have a much lower efficiency (~12%) [27] in comparison to the III-V multi-junction solar cells (~38%). III-V multi-junction CPV cells have achieved about 44% efficiency [32].

In multi-junction solar cells, current matching is a design imperative, because a departure leads to significant reduction in overall efficiency. Therefore, the thickness and the bandgap of each junction material are carefully selected. In addition, since the solar cells are electrically connected in series, tunnel junctions are created between each junction to allow the flow of charge carriers. Moreover, for some III-V multi-junction solar cells, the selected materials must be lattice matched to deliver optimal performance. Such matching constraints tend to complicate the processing of materials, and the resulting enhancement makes these solar cells economically uncompetitive for large-scale terrestrial applications.

TABLE 4.4: KEY APPROACHES FOR HIGH-EFFICIENCY SOLAR CELLS; (ap) = APERTURE AREA.

Approach	Year Proposed	Semiconductor	Cell Efficiency	Cell Area (cm ²)	Ref.
Multi-junction	1958 [56]	InGaP/GaAs/InGaAs	37.8 (April 2013)	1 (ap)	57
Intermediate- band	1955 [58]	InAs/GaAsSb	8 (June 2012)	Not Published	59
Multi-exciton generation	1993 [60.61]	PbSe	4.5 (Dec 2011)	Not Published	62
Down- conversion	2002 [63]	Eu, Y, etc.	17.2 (May 2012)	4	64
Plasmonics- based	1982 [65]	Ag, Au, etc.	6.6 (Jan 2012)	0.13	66

TABLE 4.5: KEY APPROACHES FOR HIGH-EFFICIENCY SOLAR CELLS, WITH NO EXPERIMENTAL ESTIMATE OF EFFICIENCY REPORTED

Approach	Year Proposed	Reference
Up-conversion	2002	63
Hot-carrier	1982	67
Time-asymmetry	2012	68
Strain-engineered artificial atom	2012	69
Magneto-electric Power Generation	2011	70

4.5.2 Down-conversion Solar Cells

In down conversion, an incoming photon with energy higher than twice the bandgap is converted into two or more photons for subsequent absorption [74]. A layer of material with down-conversion capability is deposited on the front face of the solar cell to alter the spectrum available to the solar cell. Till date, there has been no improvement in the efficiency of any solar cell above the SQ limit [22]. Most down-conversion layers act as anti-reflective coatings (ARCs) and offer minor improvements in the efficiency.

4.5.3 Up-conversion Solar Cells

In up conversion, several photons of energy lower than the bandgap of the absorber layer in the semiconductor are converted to a photon of energy higher than that bandgap [74]. The up-converting material is deposited on the back of the solar cell. Low-energy photons that have passed through the solar cell are absorbed by this material, and

the up-converted photon is sent back into the cell for absorption. To date, no improvement in the efficiency above the SQ limit has been reported [75].

4.5.4 MEG-Based Solar Cells

MEG is a process whereby high-energy photons create multiple charge carriers [76], and is quite similar to impact ionization [61]. One may be able to obtain several electrons and holes at the cost of a single photon, thus making good use of the high-energy photons in the solar spectrum. Some researchers argue that MEG can be observed in bulk semiconductors [77] while others argue that one can observe MEG only in nanostructures [78].

The chief evidence for the efficacy of MEG to break the SQ limit for single-junction solar cells has been provided by Semonin et al. [62]; this group fabricated and tested PbSe quantum-dot solar cells. However, the presented evidence is flawed. The open-circuit voltages reported in Ref. 62 for gaps of 0.72 eV and 0.98 eV are 0.18 V and 0.34 V, respectively, while the respective short-circuit current densities are reported as 38.67 mA/cm² and 33.34 mA/cm². According to the theory of the SQ limit, the AM1.5 G values of the open-circuit voltage should be 0.34 V and 0.59 V, respectively, and the corresponding values of the short-circuit current density should be 58.50 mA/cm² and 48.59 mA/cm².

Although the authors of Ref. 55 did not mention explicitly that they have surpassed the SQ limit, they did state: “Our findings are a first step toward breaking the single junction Shockley-Queisser limit of present-day first and second generation solar

cells, thus moving photovoltaic cells toward the third-generation regime.” The MEG has been claimed as a method to possibly break the SQ limit without showing any evidence to back up that statement. Thus, contrary to that claim in Ref. 55, current evidence does not indicate that the SQ limit has been exceeded.

Several reasons can be ascribed for the anomalous results reported in Ref. 62. First, the very low values of the open-circuit voltage clearly indicate the poor quality of the junction barrier. The fabricated solar cells must have high defect densities. Second, the solar cells had small areas, thereby facilitating peripheral collection of light—which leads to a falsely high value of the efficiency. Third, the reference cell and the test solar cells were not fabricated from the same material. Other sources of error include the consequences of chopped light beams, the uncertainty of the calibration source, and wrong assumptions regarding the spectral width of the monochromatic beam [79]. It would have been prudent to let the US National Renewable Energy Laboratory certify the efficiency [80].

Whereas the concept of generation of multiple charge carriers is physically well established [81], no experiment has shown that these charge carriers can be extracted for current generation. Indeed, it follows from experimental data presented in Fig. 2 of Ref. 81 that the charge carriers generated through MEG decay so quickly that it is impossible to extract those carriers to sustain a photo-generated electric current.

4.5.5 Intermediate-Band Solar Cells

In 1960 Wolf [21] discussed the role of intermediate-energy gap states in controlling the efficiency of solar cells. In an intermediate-band solar cell, an intermediate level within the bandgap is created and conditions are made such that this new intermediate level does not act as a recombination center [82]. With such a level within the bandgap, electrons are able to be excited from the valence band to the conduction band in a two-step process. First, the electron jumps from the valence band to the intermediate level, and then it further gets excited into the conduction band. In the normal excitation process, in contrast, the electron jumps from the valence band directly into the conduction band. The highest efficiency obtained is about 8%, which is far below than SQ limit [59, 83].

4.5.6 Hot-Carrier Solar Cells

The goal in a hot-carrier solar cell is to extract an EHP before it can thermalize. Thus, photo-generated hot electrons/holes can be transported across the bandgap to the conduction/valence band without losing excess energy. If such a scheme can be implemented, it will allow for better utilization of high-energy photons in the solar spectrum. Under AM1.5 illumination at 300 K, the maximum efficiency has been predicted to be 66% for ideal hot-carrier devices [84].

The practical realization of actual hot-carrier solar cells has never been successful. Thermalization in the absorber layer leading to insufficient collection of hot carriers at electrical contacts [84, 85], emission from the absorber layer, and radiation into the environment poses fundamental changes and seriously reduce the efficiency [86].

4.5.7 Nanopillar Solar Cells

Instead of planar layers of semiconductors, one could use an array of upright semiconductor nanopillars [87]. Each nanopillar would be an autonomous solar cell, the p-i-n structure being either longitudinal (i.e., along the length of the nanopillar) [88] or radial (i.e., in the transverse plane) [89]. The fabrication of nanopillar arrays is accomplished by a variety of processes including templating, etching, and ion-beam milling.

However, the maximum efficiency experimentally realized is under 7% with arrays of gallium-arsenide nanopillars [89] and under 14% with arrays of indium-phosphide nanopillars [88]. These efficiencies are considerably lower than those of the commercially sold single-junction silicon solar cells (25% efficiency), gallium-arsenide solar cells (29% efficiency), and indium-phosphide solar cells (22% efficiency) [27].

4.5.8 Thermophotovoltaic Cells

Thermophotovoltaic (TPV) systems convert heat into electricity by thermally radiating photons which are source of optical energy for a low energy gap PV device [90]. A TPV system is a remarkable example of how a PV system can be integrated with existing energy-generation systems. In comparison to the solar spectrum, the radiant light from a thermal source is concentrated mostly in the infrared and visible regimes. Hence, a semiconductor with a small bandgap must be used for enhanced conversion efficiency. Appropriate semiconductors include Ge, GaSb, InGaAs, and InAsSbP. The economics of

TPV systems will ultimately decide the feasibility of large-scale implementation. TPV systems have been built along with large furnaces and have also been integrated on to 1 cm² chips [91]. The achieved efficiency of such systems is generally low at present, with champion devices possessing efficiencies slightly above 10%. The use of expensive and less abundant materials in the fabrication of TPV device is a fundamental roadblock in commercialization.

4.5.9 Parametric Oscillators

Several theories have been put forth to use optical energy to produce electrical energy without using the photovoltaic effect. One of them is the parametric mechanism proposed in 1986 [92], whereby photons are used to periodically vary an energy defining parameter of a system, the parameter itself being oscillatory. Although theoretical descriptions exist, experimental verification has never occurred—although parametric oscillators are common in electronic circuits. The major bottleneck in developing a photoparametric energy converter is the absence of materials that are optimized for this process.

4.6 Light- Management Designs

Light management in a solar cell requires maximal entry of light into the solar cell followed by efficient absorption in the absorber layer(s). As light management paves the

way toward the use of thinner semiconductors, module costs reduce due to higher efficiency of material utilization. .

One way of enhancing the entry of light into the solar cell is the reduction of mismatch between the optical impedance of the semiconductor and the intrinsic impedance of vacuum (i.e., air). Accomplished by an ARC on the front face of the solar cell [93,94], this is a cost-effective way to increase the efficiency because coating techniques are highly developed in the optics industry [95]. Multilayered ARCs are being designed and tested towards broadband, polarization-insensitive, and omnidirectional reduction of reflection [96-98].

A recent experimental result [99] confirmed theoretical predictions [100-101] that a biomimetic coating can reduce reflection over a broad spectral regime and over a large range of incidence angles. The efficiency was found to have multiplied by a factor of 1.05 when an array of nanonipples made of acrylic resin was manually glued to the top of a crystalline-silicon PV module [99]. Such nanonipple arrays are said to replicate superhydrophobic cilia present on the eyelets of dipterans such as moths, house flies, and butterflies [102] and have long been known to reduce reflectance [103]. For acceptance of biomimetic coatings by the PV-module industry, long-term reliability and economics require serious investigation.

Another way to trap incident light and reduce the reflection is to texture the front face of the semiconductor at transverse length scales greatly larger than optical wavelengths in the solar spectrum [104]. Etching with an acid, KOH, or plasma are the most common ways to texture the front face into a random array of pyramids. U-shaped

and V-shaped grooves are also popular textures [105-107]. Bioinspired textures are being theoretically considered as well [108]. However, the downside of surface texturing is a larger surface area; thus, surface states and defects will increase the surface recombination rate unless special passivation is done.

The metallic back reflector of a solar cell can also be textured at transverse length scales greatly larger than a thousand nanometers, but planar backing appears to perform better [109]. In contrast, periodic texturing of the metallic back reflector was indicated in the early 1980s to help trap light better, if the period were a few hundred nanometers [110]. In other words, the use of a metallic diffraction grating as the back reflector may result in higher efficiency, thereby promising highly efficient thin-film silicon solar cells [111].

The realization that the periodically corrugated metal/semiconductor interface could guide surface-plasmon-polariton (SPP) waves [112] has led to much recent research. The reason is the existence of an electric field of large magnitude within a ~200-nm-thick region close to the interface inside the semiconductor when an SPP wave is excited, the high electric field being favorable to more EHP generation. If the semiconductor is periodically nonhomogeneous in the direction normal to the interface, multiple SPP waves can be excited in some wavelength range within the solar spectrum, leading to even better conditions for the generation of more EHPs [113]. Thereby, very thin films of solar-grade semiconductors will be needed, leading to reduction of manufacturing costs.

Plasmonics has had another impact on research on light management in a solar cell. Provided certain conditions are met, the polarizability tensor of a metallic nanoparticle embedded in a dielectric material (or even a semiconductor such as silicon) can have components of very large magnitude. Accordingly, very high electric fields can exist in the vicinity of a nanoparticle [114], leading to enhanced EHP generation. This phenomenon is being explored to enhance the absorptance of light in the 700-1100-nm wavelength regime in silicon thin films with embedded metal nanoparticles [115,116]. When the metal nanoparticles are positioned on an air/semiconductor interface, the enhancement of the electric field is much more in the semiconductor than in air [117]. This enhancement can lead to better trapping of light in a solar cell [118], so long as the surface density of the metal nanoparticles is not so high as to significantly block incoming light.

All of the current research focus seems to be on the enhancement of the electric field in the absorber layer(s) and on the enhancement of the short-circuit current density, but not on the open-circuit voltage. Although there is some evidence that plasmonics can improve the short-circuit current density, not a single carefully designed experiment with statistical analysis of the results has been reported as yet. Nevertheless, plasmonic strategies can be incorporated in solar cells, regardless of the semiconductor being used for PV electricity generation.

There is a recent proposal to deploy a time-asymmetric magneto-optical structure over a solar cell [68]. Functioning as a one-way shutter, the structure will stream light

towards the solar cell but not allow light traveling in the opposite direction to escape. Both practical realization and cost effectiveness are questionable.

The use of ARCs and planar metallic back reflectors, as well as front-surface texturing at multi-wavelength length scales, have been effective and commercially deployed strategies for improving the efficiency of silicon solar cells. The most efficient PERL cell uses double ARC, inverted pyramid surface texturing and a planar aluminum reflector [5]. The incorporation of plasmonics is hoped to provide a further boost to the efficiency. The discussed light-management strategies could be useful for a wide variety of PV solar cells.

4.7 Manufacturable, Ultra-High Efficiency, Low-Cost Solar Cells

Any new solar PV electricity generation system avoiding the existing state-of-the-art silicon solar cell is undesirable, since the silicon solar cell has already been successfully commercialized and monopolizes the PV electricity generation market. The huge investment made in silicon technology for five decades and the low cost of polycrystalline silicon are two major factors that will not allow the large-scale commercialization of competing devices based on other materials. In addition, if a competing device's efficiency does not exceed 25%, it will not have an adequate opportunity for commercialization. Indeed, history offers a lesson: Even though ICs based on indium phosphide or gallium arsenide have better switching speeds than silicon ICs, the latter command more than 90% of the \$1.5 trillion electronics market.

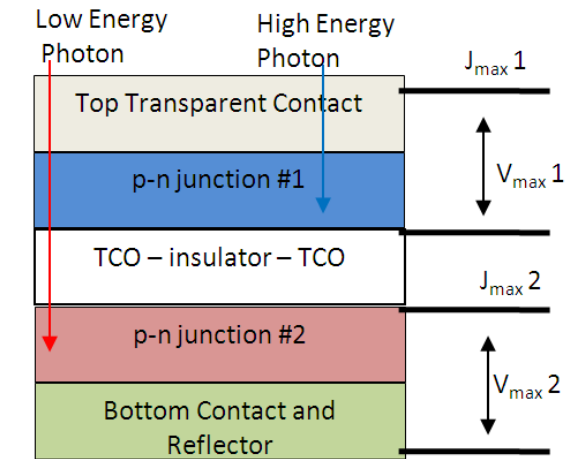
From a consideration of the current research approaches presented in Section V, it is evident that several will fail to deliver cost-effective and highly efficient PV solar cells. Multi-terminal-multi-junction solar cells offer the unique advantage that the current-matching requirement is unnecessary, as discussed in Section V (A). Junctions in such a solar cell are not electrically connected within the solar cell; instead, the solar cell has multiple terminals. In the simplest case of a solar cell of this type with two junctions, there are four terminals. As each junction electrically operates independently of all others, junctions with different electrical properties can be used in a single solar cell. This is a great advantage since we can build up a complete multi-junction solar cell on top of an existing optimized single-junction solar cell. This concept has not been commercialized, although it was proposed as early as 2005 [119-123].

We present here a strategy for a commercially promising multi-junction-multi-terminal PV solar cell that is built on the robust foundations of currently established silicon solar-cell technology. At its simplest, this novel electricity-generating device can be made by integrating a large-bandgap cell on top of an existing silicon solar cell. Commercial thin film deposition techniques can be used to integrate multi-junction multi-terminal solar cell. The design of the large-bandgap cell must satisfy the manufacturability guidelines discussed in Section IV, thereby enabling the technology to be ready for large-scale adoption without any manufacturing barriers. The cost of adding another cell on top of a silicon cell as well as interconnection cost will be far less than the cost reduction offered by the higher efficiency of proposed solar cell

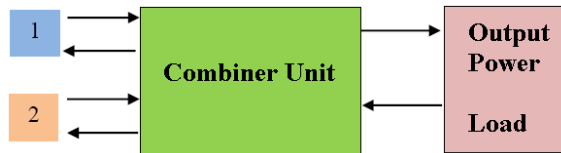
The schematic of this two-junction-four-terminal solar cell is shown in Fig. 4.7. It is worth mentioning here that we are not proposing a mechanically stacked 4 terminal cells with Si as the bottom cell. A transparent conducting oxide (TCO) is used for the electrodes and an optically transparent insulating layer is deposited between the upper and lower cells to keep them electrically separate. As mentioned earlier in this section, the multi-terminal nature of this device removes the current-matching requirement in the multi-junction architecture by using an external circuit such as a highly efficient dc-dc converter. In addition, the transparent insulating layer removes the need for lattice matching between the bulk and thin-film materials, thereby simplifying the manufacturing of the solar cell. It is worth mentioning here that the use of multi-junction-multi-terminal PV solar cells for local dc-power generation coupled with the delivery and the utilization of dc power will provide a solar PV electricity generation system with the highest energy efficiency [124].

Figure 4.8 shows the variation in the simulated efficiency of a two-junction-four-terminal solar cell with respect to the bandgap in the material of the upper cell, when the bottom cell is assumed to be made of silicon. This variation was calculated based on the standard solar-cell equations. Assuming the SQ limit, the maximum efficiency of 44% is obtained when the upper material's bandgap is about 1.8 eV. Based on material availability and the possible conversion efficiency of such a multi-terminal-multi-junction cell using silicon as the base material (for the lower cell), we have identified copper (I) oxide, Cu_2O as a candidate. This stable oxide of copper is a p-type semiconductor with a bandgap between 1.7 and 2.6 eV, depending on the conditions

prevalent during its fabrication [125-127], and is an inexpensive material. Several research groups have already identified it as a PV material [128, 129]. However, the maximum AM1.5 G efficiency of Cu₂O cell is about 2 %. [130]. Preliminary experimental results have shown that high-quality Cu₂O films can be grown using photo-assisted chemical vapor deposition [130]. As shown in Fig. 4.9 [130], the dark current density-voltage (J-V) characteristics of Cu₂O diode is much better than the data reported in the literature and indicates lower defects density in Cu₂O deposited by photo-assisted CVD technique.



(a)



(b)

Fig. 4.7. (a) Schematic of the proposed two-junction, four-terminal solar cell. (b) External electric circuitry to combine the electricity generated separately by the two junctions.

Cu_2O solar cells have been investigated in the past as standalone PV devices. Due to low efficiency, researchers became discouraged and progress has been very slow. In our proposed architecture, an ultra-thin film of Cu_2O with ultra-low defect density is supposed to provide highly efficient $\text{Cu}_2\text{O}/\text{Si}$ solar cells. The defect density in a thin film of an electronic material in general, and of Cu_2O in particular, depends on the method of deposition of the thin film and the purity of the precursor material. The monolayer rapid

photo-thermal-assisted chemical vapor deposition technique [133] using ultrapure precursors (at least five nines purity) is capable of providing ultra-high-performance semiconductor devices. In Fig. 4.9 we have used only 99% pure precursors and the results are better than the published results. Further understanding of the defect chemistry of Cu_2O and the use of a 99.999% pure precursor in the monolayer rapid photo-thermal-assisted chemical vapor deposition technique can potentially yield highly efficient $\text{Cu}_2\text{O}/\text{Si}$ solar cells.

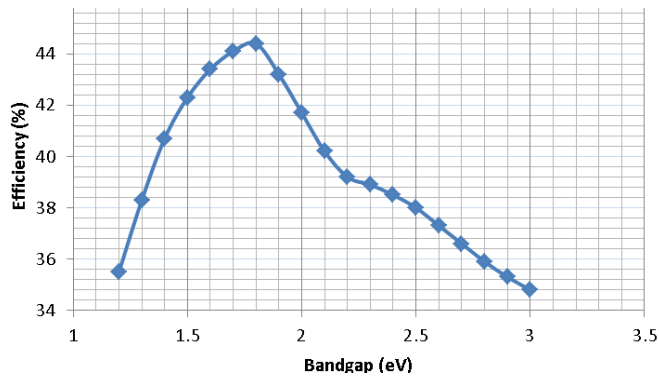


Fig. 4.8. Variation of the efficiency of a two-junction-four-terminal solar cell with the optical band gap of the material in the upper cell, when the lower cell is assumed to be a silicon solar cell.

Other existing materials in consonance with the manufacturability guidelines of Section IV can be identified, and perhaps entirely new ones could be synthesized. Light-management strategies can be adapted to further boost efficiency—for instance, by texturing the front surface of the upper cell at the multi-wavelength scale and periodically texturing the metallic back reflector at the bottom of the lower cell at the sub wavelength scale.

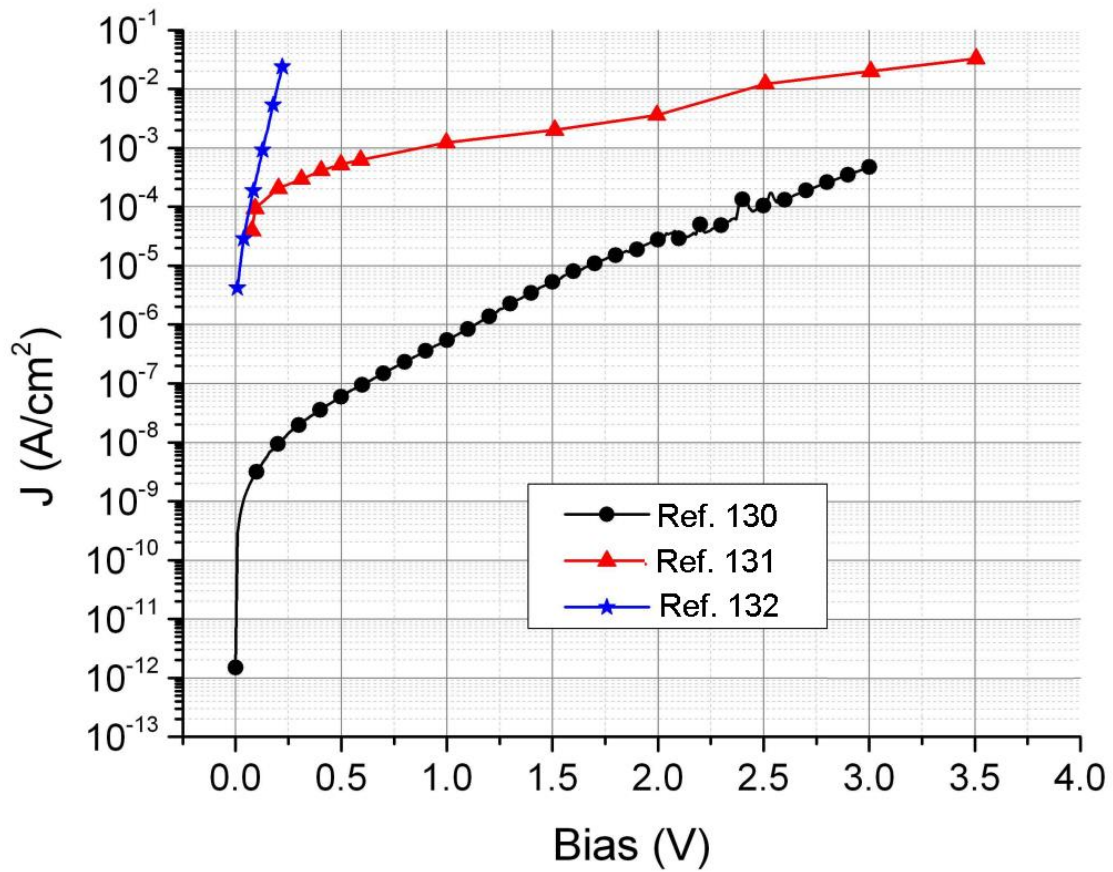


Fig. 4.9 Comparison of dark J–V characteristics of Cu₂O/n-Si diodes reported in the literature and present work [130]

Reprinted from N. Gupta et.al., "Deposition and characterization of nanostructured Cu₂O thin-film for potential photovoltaic applications," J. Mater. Res, vol. 28, pp. 1740-1746, 2013.

After successful commercialization of the two-junction-four-terminal solar cell, the number of junctions (and terminals) could be increased. The proposed strategy is

reminiscent of the development of silicon CMOS-based ICs from single-core microprocessors to dual-core and now multi-core microprocessors.

4.8 Discussion

To cover all terrestrial applications, PV modules employing bulk silicon as well as PV modules employing thin films are needed. For instance, building-integrated photovoltaics (BIPV) requires thin-film PV modules for semi-transparency. However, their lower efficiency makes them unattractive for rooftop electricity generation because the available area is limited. Therefore, in order to cater to customers of rooftop applications, First Solar, a manufacturer of CdTe thin-film PV modules, acquired TerraSun, a manufacturer of bulk-silicon PV modules [134].

Using the data presented in Table 4.1, we have analyzed the relative difference in the efficiency of an individual solar cell and the efficiency of a PV module comprising solar cells of the same type. As shown in Fig. 4.10, monocrystalline-silicon solar cells exhibit the smallest relative difference. Multicrystalline-silicon solar cells are also attractive, going by the chosen metric. Better understanding of electron-hole recombination at surfaces and interfaces in both bulk-silicon and thin-film solar cells will reduce the relative difference in efficiency. In addition, more use of advanced process-control equipment in the processing of thin-film solar cells can reduce the parametric variation of efficiency of solar cells in thin-film PV modules. The multi-junction-multi-terminal architecture presented in Section VII will be the ideal choice for manufacturing the next generation of solar cells.

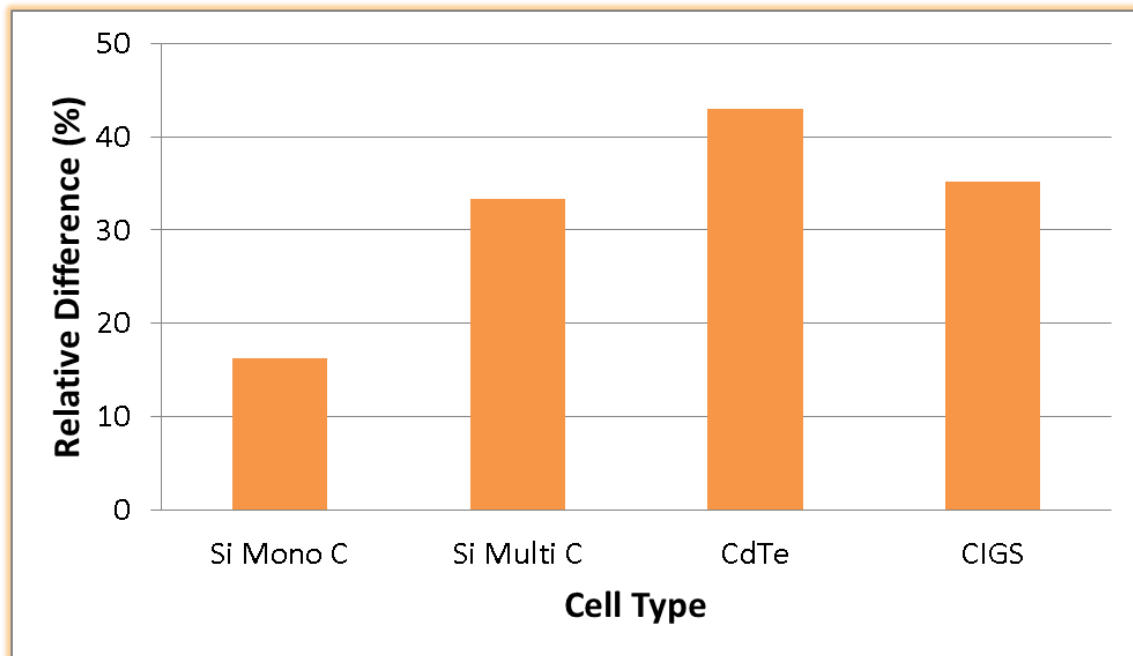


Fig. 4.10.. Relative difference between the efficiency of a small-area solar cell and the efficiency of a PV module comprising a multitude of solar cells of the specific type.

Several of the fabrication techniques mentioned in Section V involve self-assembly. Due to fundamental problem of process variability, self-assembly is not suitable for large-scale manufacturing of semiconductor products [15, 25, 47]. Even after many years of research, there is still no commercial future for PV solar cells fabricated by self-assembly.

As schematized in Fig. 4.11 [135], the properties of nanomaterials differ vastly from their bulk counterparts, due to the large ratio of volume to surface area and the phenomenon of quantum confinement [136, 137]. Although several properties of nanomaterials have been known for a few centuries, scientific explanations began to emerge only during the last fifty years.

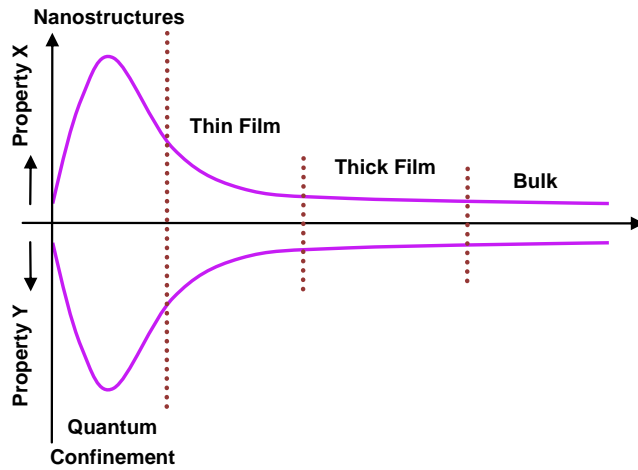


Fig. 4.11. Schematic of the size dependences of properties of any material.

Reprinted from R. Singh et al. "Semiconductor Manufacturing in the Nano World of the 21st Century", Proc. 25th International Conference on Microelectronics (MIEL 2006), Vol. 1, pp. 3-9, 2006.

The use of a specific property of a nanomaterial is very different from building an entire technology to exploit that property. Clever design concepts are necessary to exploit quantum confinement in nanostructured solar cells [138]. One enticing possibility is to use the dependence of the bandgap on the size of nanograins in nanostructured silicon. As shown in Fig. 4.12 [139], the direct bandgap of nanostructured silicon increases with the reduction of nanograin diameter below about 8 nm. If a new process can be invented that meets all the manufacturability guidelines discussed in Section IV, the device designer will have the freedom to design many types of ultrahigh-efficiency silicon solar cells that exploit the effects of quantum confinement. As shown in Fig. 4.13, starting with bulk

silicon as the substrate, hetero-face solar cells [140] with very low front-surface recombination can be designed. It should be similarly possible to design single-junction and multi-junction-multi-terminal solar cells of nanostructured silicon.

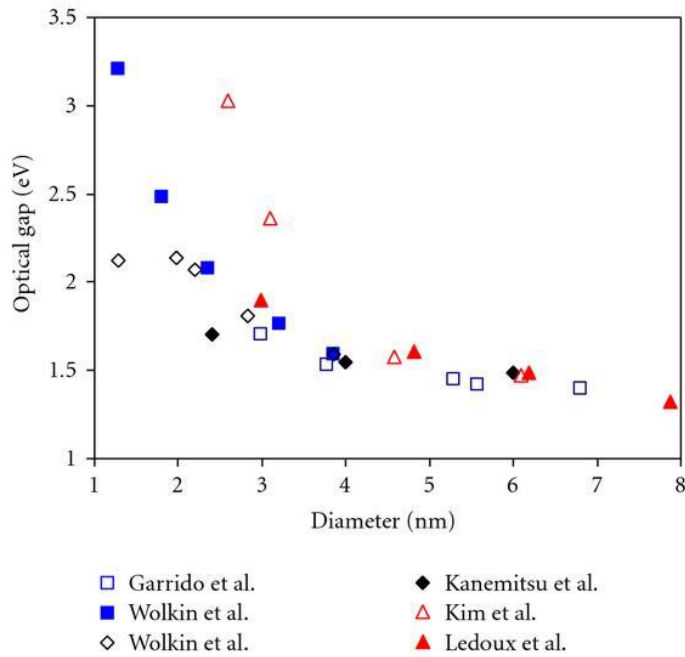


Fig. 4.12. Experimental results on the variation of optical bandgap of nanostructured silicon with diameter of silicon nanograins [139].

V. A. Belyakov et al., “Silicon nanocrystals: fundamental theory and implications for stimulated emission,” *Adv. Opt. Technol.*, vol. 2008, art. no. 279502, 2008.

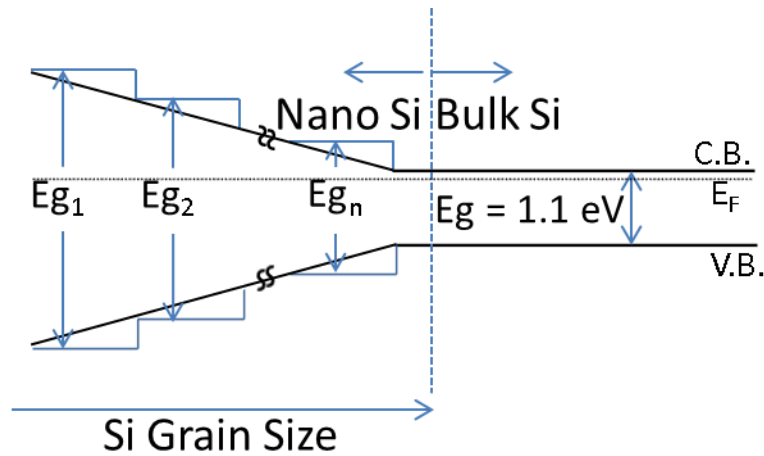


Fig. 4.13. Thermal equilibrium energy band diagram of hetero-face silicon cell utilizing quantum-confinement effects.

Since 2011, silicon ICs with identical features of 22 nm have been in production [141], with the gate length around 25 nm in a CMOS device. Very soon, 14-nm silicon ICs will be manufactured [142]; already, 5-nm silicon ICs can be fabricated for research and development [143]. Therefore, a nanostructured-silicon multi-junction PV solar cell can be made with adequate process control. This can be expected to become possible sooner rather than later, because not only the PV solar-cell industry but also the IC industry will benefit from the improvements in process control. Better process control that will work at dimensions of the order of 2 nm has the potential to create several useful and inexpensive devices based on actual nanotechnology, with silicon still the material of choice because of its abundance and low cost. The commercialization of solar cells based

on the use of nanostructured silicon has the potential of providing ultralow-cost and ultrahigh-efficiency solar PV dc electricity generation systems.

4.9 Concluding Remarks

In conclusion, many new materials and device designs for photovoltaic electricity generation are being proposed and researched in academic laboratories and by start-up companies. However, only those approaches will be commercially successful which will use very well-controlled and well-understood manufacturing processes as well as materials that are easily available and can be easily processed.

Researchers should be able to develop proof-of-concept devices with measurable electrical properties. Once a proof-of-concept PV device with efficiency considerably in excess of 25% has been fabricated and tested in a certifying laboratory, investors and decision makers can judge its merits and sponsor research on manufacturing it. This will lead to a tremendous growth in the generation of electricity from solar energy. Local dc-power generation by solar PV systems coupled with the delivery and the use of dc power will making energy available for rich and poor alike

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CHAPTER FIVE

A FIRST STEP TOWARDS IMPROVING SILICON PV PERFORMANCE USING MULTI JUNCTION MULTI TERMINAL TECHNOLOGY

5.1 Introduction

The global Photovoltaics (PV) cumulative capacity has grown to 102 GW in 2012 and in the Business-as-Usual scenario, the cumulative capacity is expected to touch 288 GW in 2017. With a policy driven approach, the cumulative capacity is expected to be as large as 422 GW in the same time frame [1]. These two numbers are based on previous trends in the market and the study assumes the absence of any major innovation. If critical innovations happen that can increase the economic value of PV generated power, the capacity increase will be significantly accelerated. Such innovations include a radical change in the power storage technology, the creation of dc grids, improvements in PV efficiency, and the deployment of PV in underdeveloped countries enabling their economic development. The focus of this chapter is to highlight progress towards a manufacturable technique that can be used to improve the efficiency of PV cell using a Multi-Junction Multi-Terminal approach

5.2 Silicon PV Technology

Silicon is the single most important element in the PV industry and is the starting material for over 90% of the panels made today. In 2009, the thin-film PV market share increased to 15% due to a shortage of polysilicon. However, after the shortage was solved, the thin-film PV market has declined to less than 10% and is predicted to collapse

to about 7% by 2017 [2]. Additionally, Si based technology has several advantages in comparison to Cadmium Telluride and Copper Indium Gallium Selenide based modules. These include material abundance of Si, non-toxicity and the existing Si based Integrated Circuit industry. The Si cell itself has been improved significantly since it was first developed in the 1950s. There are two major subdivision in the Si PV industry – single crystalline and multi crystalline PV. This classification is simply based on the crystal structure of the starting Si wafer. The single crystalline module technology is presently used to make the most efficient commercial terrestrial technology in the market today, the SunPower X Series Panels with 21.5% efficiency [3].

With improvements in production technology and increase in volume, the prices of Si PV panels have dropped steadily in the past. This historic pricing and volume trend is shown in Fig. 5.1 [4]. On an average, the price has decreased by 22% whenever the production volume has doubled. This trend is likely to continue and the price/watt can decrease faster than that predicted by the experience curve if improvements in the PV technology are made.

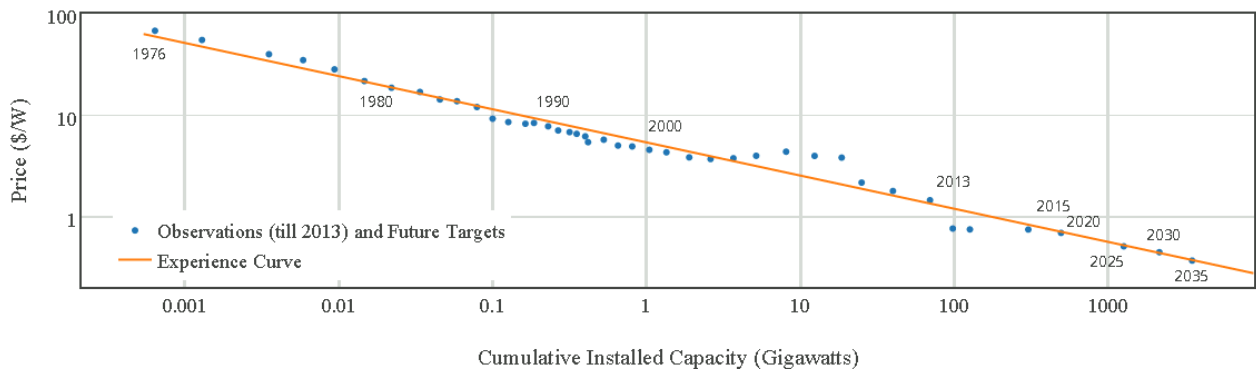


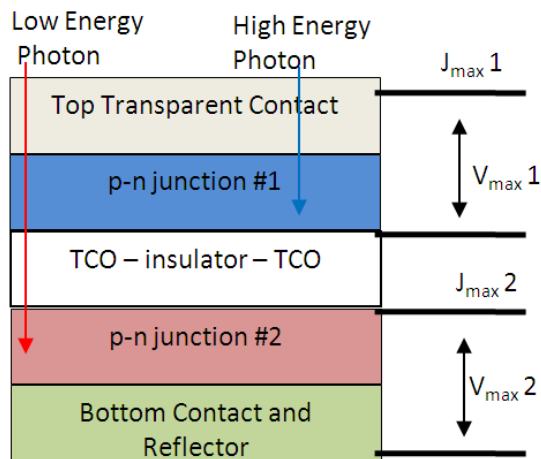
Fig. 5.1. Volume and Price trends of the Si PV cell [4].

The efficiency of the silicon PV panel has increased very slowly to 21.5% in the last few years. In addition, years of research have not been able to increase the efficiency of the Si PV cell even in a lab setting beyond 25% suggesting that the Si module efficiency may not increase significantly in the future [5]. Since Si based PV cell is the market champion, the plateauing of the Si PV cell's efficiency will set a limit on the maximum efficiency possible in the commercial PV industry. The task then is to look for potential solutions to increase the efficiency of a basic PV cell by creating a new architecture involving Si and another earth abundant material. Careful examination of all existing methods to increase the efficiency of PV cells suggests that no technique has yet reach a mature state to be implemented in a commercial fashion for terrestrial modules [6] The only proven technology to achieve efficiency beyond 25% is the multi-junction approach, however, the materials and manufacturing techniques used to produce these multi-junction cells are expensive and as of today, multi-junction cells are used mostly for space applications. It is possible to use the multi-junction approach in terrestrial PV cells if the current matching constraint can be avoided. This is best done using the Multi-Junction Multi-Terminal (MJMT) architecture [6]. This architecture removes the current matching constraint and one can use any material in the stack provided the material has the right band-gap and can be deposited with good electronic quality. This opens the possibility of using earth abundant materials alongside with Si in the PV cell. The development of another earth abundant material other than Si has the potential to revolutionize the PV industry by improving the efficiency of PV technology, while keeping the costs low.

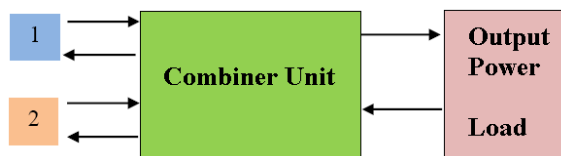
5.3 Multi Junction Multi Terminal Technology

The MJMT cell was proposed as early as 2005; however, this concept has not been commercialized till date [7-11]. The concept of the MJMT involves building a cell with multiple junctions and extracting carriers from each junction through separate terminals. The simplest case of an MJMT cell has two junctions and four terminals and such an arrangement is shown in Fig. 5.2. In this figure, part (a) depicts the various layers and connections of the MJMT cell; while part (b) is a Combiner Unit that should be used to combine the power from both the cells for use in external circuits. It is worth mentioning that the concept behind the MJMT cell is not mechanical stacking, but, deposition of layers above one another to achieve the desired cell structure. In this fashion, one can take the standard Si PV module and deposit a few extra layers of thin film over it to boost efficiency. The cost of depositing the thin films should not be issue since the module cost of an installed PV system is only 38%. The other 52% of the cost can be attributed to supply chain, installation, inverters, profits etc. [12].

The bottom p-n junction of the MJMT cell in Fig.5.2(a) involves a traditional Si PV cell and the top p-n junction is to be created using a material of band gap significantly larger than 1.1 eV to absorb high energy photons with better efficiency than silicon. The optimum bandgap of the top absorber layer is 1.9 eV and the theoretical efficiency possible in this case is 44%. [6]



(a)



(b)

Fig. 5.2. (a) Schematic of the proposed two-junction, four-terminal solar cell. (b) External electric circuitry to combine the electricity generated separately by the two junctions.

This arrangement permits the use of any material in the cell stack without the current matching consideration. In addition, it is possible to grow layers without lattice matching since an isolating layer of insulator material is grown over each junction.

PV technology of the future will only be based on abundant materials since PV has to remain low cost to be economically competitive. One of the recent examples in the PV industry is the replacement of silver with copper because of relative abundance of

copper in comparison to silver [13]. In the PV industry, there is a constant drive to increase module efficiency while simultaneously driving manufacturing costs down. Although it is possible to make cells with high efficiency using expensive and rare materials like gallium and indium, the probability that these cells will replace silicon based PV is low. This leads to the conclusion that earth abundant materials must be utilized to promote the growth of PV. Of particular interest is the copper – zinc – tin sulfide – (CZTS) material system, using which, a conversion efficiency of 11.1% [14] and recently 12.6% [15]. This material system employs earth abundant non-toxic materials and is a remarkable achievement; however, since Si based cells are now 25% efficient and has already become accepted as the best material for PV, it will be difficult to displace it. Instead, if an earth abundant material can be used to boost the performance of the standard Si cell, there will be far reaching changes in the overall PV industry.

Copper (I) Oxide (Cu_2O) was found to be a good candidate as an earth abundant material for creating the MJMT cell using Si as the base material. Cu_2O , an earth abundant, direct band gap semiconductor with p-type conductivity. The band gap of the Cu_2O thin films ranges from 1.7 eV to 2.6 eV depending on the growth conditions [16-18]. Assuming that the band gap of Cu_2O is 2.0 eV, theoretical calculations have shown Cu_2O cells by themselves can achieve about 22% conversion efficiency [19]

As early as 1975, the photovoltaic effect was demonstrated in a Cu_2O based diode [20]. The Cu_2O has several properties that make it an excellent choice for PV applications. These include a high absorption coefficient (in the range of 10^5 cm^{-1}) for

above-band gap wavelengths, good majority-carrier mobility ($\approx 90 \text{ cm}^2/\text{V.s}$) and minority carrier diffusion length of the order of $3.5 \mu\text{m}$ [21].

Cu_2O has been grown using several techniques such as Thermal oxidation, electrochemical oxidation, sputtering, pulsed laser deposition and chemical vapor deposition. Although, thin films and bulk Cu_2O has been grown, the quality of the resulting material varies with the deposition technique, the purity of the precursor and the chemicals involved. In this research, Photo assisted Chemical Vapor Deposition (CVD) was used to deposit the material.

The complete top junction cell will require an N type material – such as ZnO to form a heterojunction with Cu_2O . In this research, the focus has been to investigate the properties of only Cu_2O and ensure that high quality Cu_2O can be grown using a CVD process. An N type Si wafer was used as a substrate in this research only to investigate the Si- Cu_2O heterojunction. Obviously, it is impossible to use this combination of materials for the top junction. Further research is already in progress in our group trying to deposit an optimized thin film of ZnO on the Cu_2O layer to investigate a practical device.

5.4 Deposition and Characterization of Copper Oxide

5.4.1 Photo assisted CVD System

To investigate the properties of the Cu_2O thin films, a custom built Photo assisted CVD system was utilized to deposit thin films of Cu_2O on to a Si substrate. This step is necessary before building the full PV cell since defects in the Cu_2O layer will affect the

performance of the cell. The Photo assisted CVD processing is a proven technique to achieve best quality thin films [22]. The quantum effects associated with the photons of wavelength below 800 nm results in the following: [23]

1. Reduction of bulk and surface diffusion coefficients at a fixed temperature
2. Reduction in processing time
3. Reduction in defects and improvements in uniformity of microstructure leading to increased performance of devices. Also results in improved yield and reliability.

The processing system is a single walled cylindrical SS chamber with necessary ports and feedthroughs. A schematic of the processing chamber is shown in Fig. 5.3. A compressed air cooled UV lamp is employed as a UV source. The silicon wafer is heated using a low thermal mass Borolectric® resistance heater controlled using a variac. This allows for rapid heating and cooling cycles. The precursor was transported from their SS ovens in to the chamber using heated SS tubing. The temperature of the precursor oven and the tubes were controlled using a K type thermocouple interfaced with a controller module built using LabVIEW®. A Mass Flow Controller (MFC) was used to regulate the flow rates of the gases used during various stages of the deposition process and solenoid valves were used to connect and disconnect the system from the gas lines. The MFC and gas valves were also interfaced with LabVIEW® so that the complete deposition process could be computer controlled. A rotary pump was connected to the SS chamber to provide a clean low-pressure environment inside the chamber and to remove the reaction byproducts.

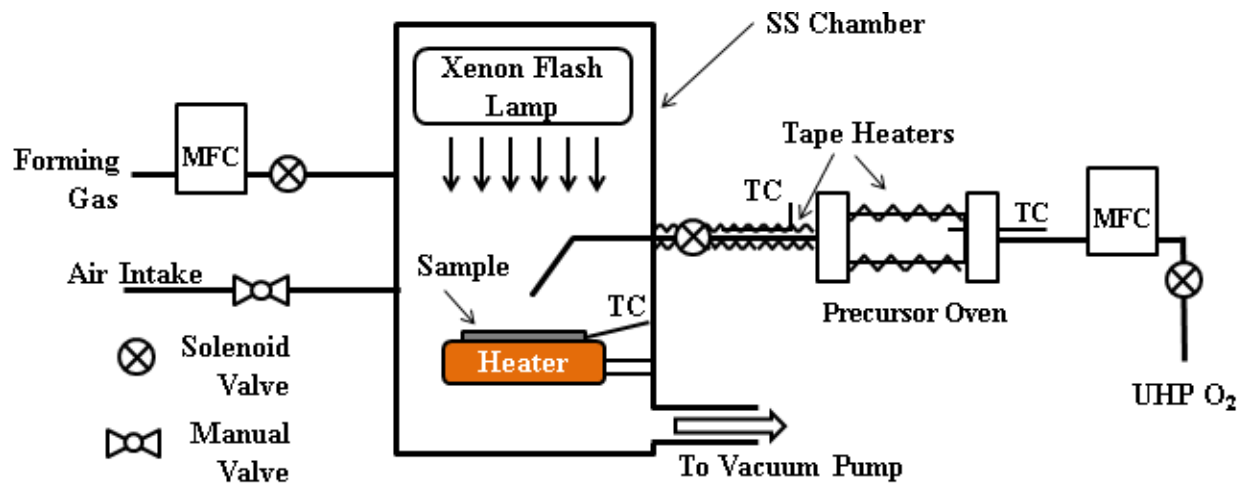


Fig. 5.3 Schematic of the MOCVD system utilized to deposit Cu₂O

5.4.2 Deposition of Copper Oxide

Deposition of Cu₂O was achieved using a custom built Photo assisted MOCVD system. The precursor, Bis(2,2,6,6 tetramethyl 3,5-heptanedionato) copper(II) [Cu(TMHD)₂], 99% was obtained from STREAM Chemicals and was used without further modification. Since N₂ has been identified as an N type dopant for Cu₂O, it was decided not to use N₂ during the deposition stage [24]. O₂ was used both as the carrier gas and as the oxidizing agent.

Prior to deposition, the <100> Si wafer was etched in HF, cleaned in RO water, and blow-dried using N₂. After this *ex-situ* cleaning, the wafer was loaded in to the chamber and an *in-situ* cleaning was performed while heating the sample at 750 °C and simultaneously letting in Forming gas (20% H₂ and 80% N₂) at 20 sccm under the UV radiation for five minutes. The chamber pressure was cleaning was maintained at 3 e-1 torr during cleaning.

Immediately following the *in-situ* cleaning, the deposition step was performed. This involved exposing the heated wafer to the gas phase of the precursor in an oxygen rich environment under UV radiation for ten minutes. Every aspect of the cleaning and deposition process was computer controlled. The precursor oven and delivery tubes were heated early enough so that during the deposition, both of them were maintained at 150 °C. Oxygen flow rate was set at 100 sccm and the temperature of the substrate during deposition was set at 450 °C. The chamber pressure during deposition was 8 e-1 torr. After the deposition process was completed, the sample was allowed to cool down to room temperature, after which the chamber was brought to atmospheric pressure. Further processing was carried out in a filament evaporator to deposit contacts. Aluminum was used as the back contact to the N type silicon and gold was chosen as the top contact to Cu₂O. After the Al was deposited through a shadow mask, the sample was annealed for 30 minutes in a thermal furnace. Subsequently, Au was deposited on top. This makes a complete diode structure ready for electrical measurements. The finished structure is shown in Fig. 5.4. The area of each diode was defined to 0.00785 cm². Care was taken to deposit contacts immediately after removal from processing chamber. In the case that electrical measurements were not required, the contact evaporation step was omitted.

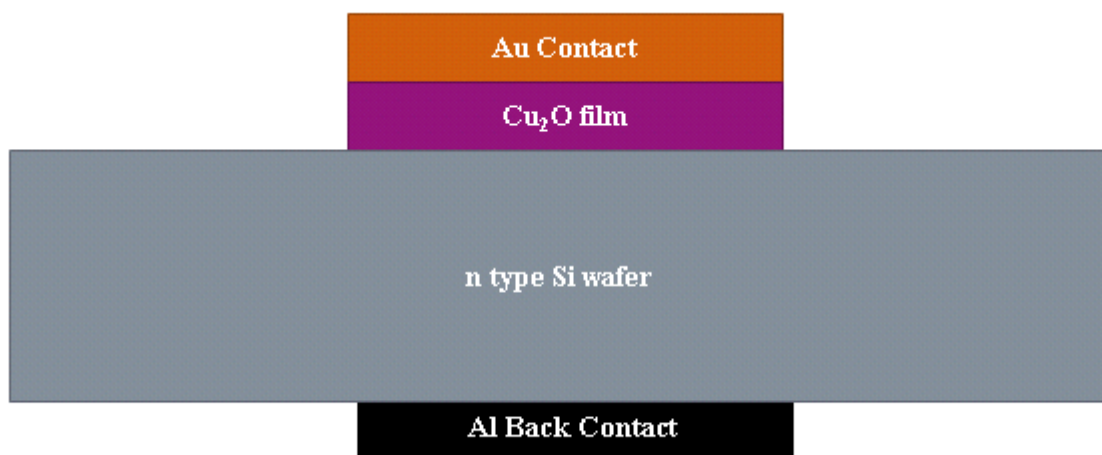


Fig. 5.4 – Complete device structure showing materials (not to scale)

5.4.3 Characterization

X-ray diffraction (XRD) measurements were performed on the deposited films with Si as the substrate materials using an angle dispersive diffractometer (Rigaku Ultima IV) with monochromatic Cu-K alpha ($\lambda = 1.540 \text{ \AA}$) radiation at 40 kV. XRD data were collected at a rate of $1.2^\circ 2\Theta$ per minute in $0.2^\circ 2\Theta$ steps. The DekTak III profilometer with software package version 1.2 was used to measure the thickness of the deposited films. A sharp glass spatula was used to remove material selectively after the deposition and the removed material was blown off using pressurized nitrogen. Several scans were performed on the sample and average thickness of the deposited film was measured.

To prepare cross-section TEM samples, Argon ion milling procedure was utilized with incidence angle of 3 degrees at 3 keV. A JEOL-2010F field emission TEM was used to study the microstructure. A variable angle spectroscopic ellipsometer (Sopra GES5)

was also used to measure film thickness. Electrical measurements were performed using the Keithley SCS 4200 and a probe station.

5.5 Results and Discussions

The XRD analysis reveal a peak at a 2θ of 42° corresponds to a (200) crystal orientation and the peak at 36.5 corresponds to a (111) crystal orientation. In Fig. 5.5, the data obtained from the XRD experiment is plotted. There is no indication of any unwanted CuO growth in this film. These results suggest that MOCVD can be used to grow crystalline Cu_2O films.

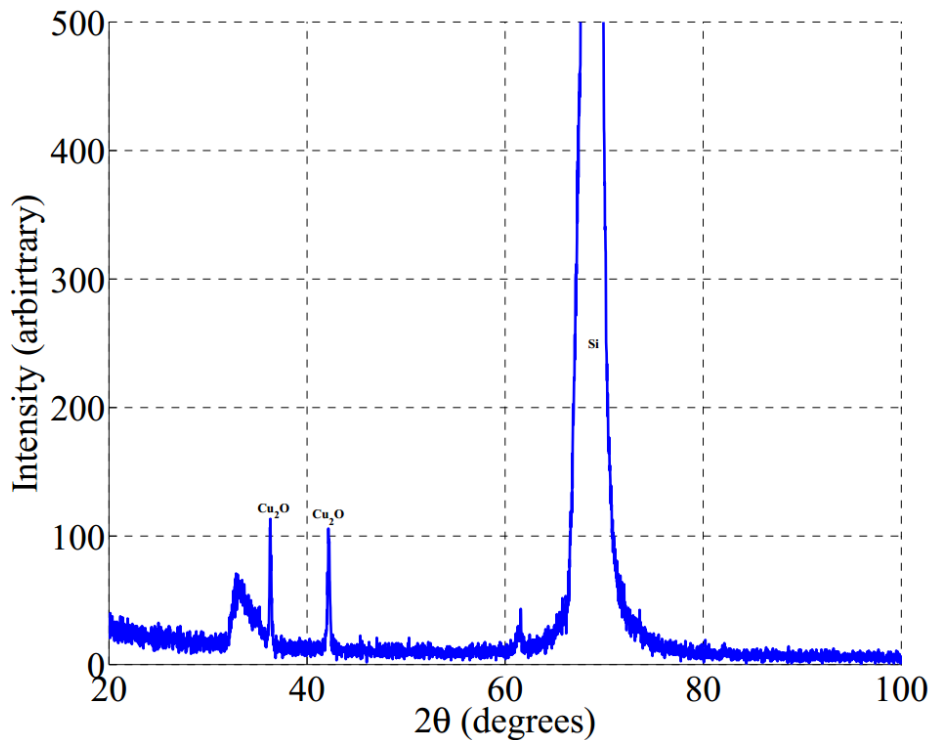


Fig. 5.5. XRD Result showing peaks of Cu_2O and Si

To further investigate the morphology of the film, TEM was utilized. The results from this analysis revealed two types of Cu_2O grains in the sample - On-zone grains and Off-zone grains. On-zone grains are always adjacent to the off-zone grains. Fig. 5.6 shows the resultant image and the average sizes of the two grains are summarized in Table 5.1.

Table 5.1: Width and Height of Grains

	Width (nm)	Height (nm)
Off-zone Grains	500-600	100-160
On-zone Grains	200-300	300-350

The Cu_2O film grows on the Si substrate via Volmer-Weber growth mode, in which adatom-adatom interactions are stronger than those of the adatom with the surface, this leads to the formation of three-dimensional adatom clusters (islands). The selected-area diffraction pattern also showed a nanocrystalline nature of the Cu_2O film.

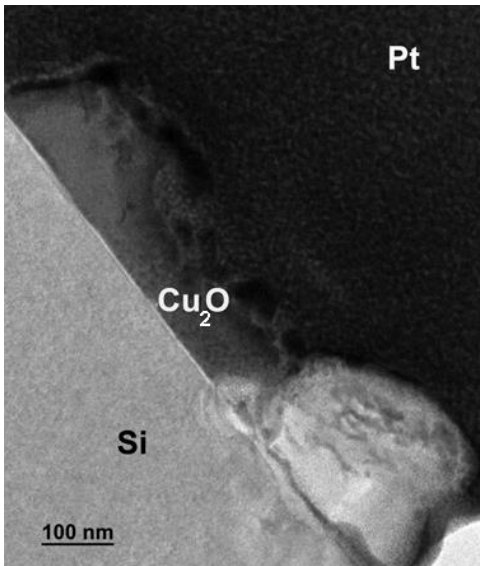


Fig. 5.6. TEM result showing morphology of Cu_2O layer

Results from both ellipsometry and surface profilometry indicate that the average thickness of the film grown was about 90 nm. The difference in thickness between these measurements the TEM is mostly due to the small size of the sample.

Electrical I-V measurements show diode like rectifying behavior at the junction formed between N type Si and Cu_2O , indicating that a PN heterojunction has been formed. The $I_{\text{on}}/I_{\text{off}}$ ratio of a diode shows how well the diode rectifies, an indicator of the quality of the materials and junction involved. Fig. 5.7 shows the I-V measurement result for 4 samples processed under identical conditions. In this case, the measured $I_{\text{on}}/I_{\text{off}}$ ratio is about 17,000 at ± 3 V, which is the highest reported value for such devices. The best reported ratio till date is only about 800 [25]. This suggests that MOCVD technique under the particular processing conditions used in this research is capable of forming high quality P type Cu_2O films with low defect density.

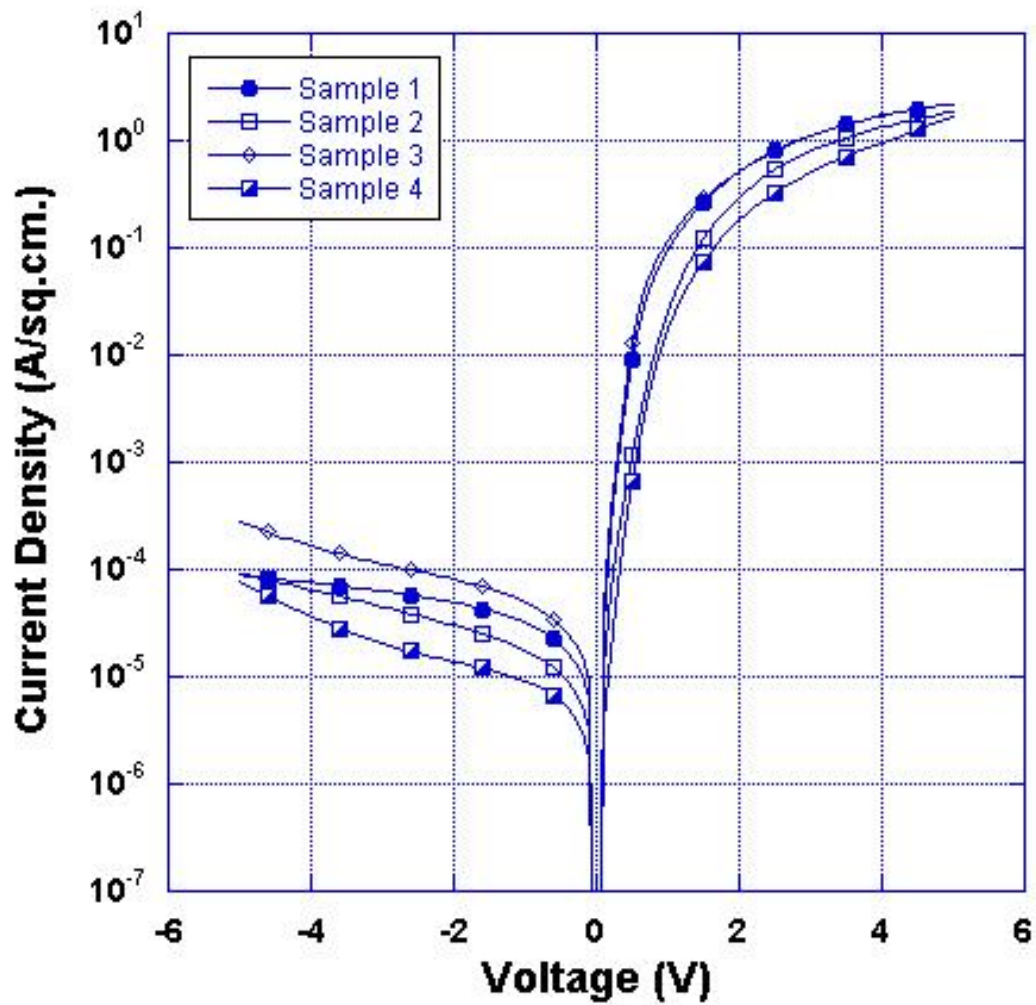


Fig. 5.7. J-V curve of 4 samples

Further I-V measurements were performed at six different temperatures, 300K, 325K, 350K, 375K, 400K and 425K. The results were analyzed to find possible conduction mechanisms. In the forward bias, the power law yields the best fit in the voltage range from 0.6 V to 5 V. The correlation coefficient, R , is almost unity for this fit at all temperatures. This can be seen in Fig. 5.8, a log I vs. log V plot in the relevant

voltage range. The power law can be approximated by the relationship $I = m_1 V^{m_2}$. Table 5.2 shows the value of the relevant parameters. The value of m_2 is close to 2 and is decreasing with increasing temperature. This temperature dependence of the m_2 indicates that the current conduction mechanism during the forward bias is dominated by the Space Charge Limited Current (SCLC). In addition, it was observed that SCLC is not present in the in the voltage range < 0.6 V. This is also consistent with the SCLC model since this conduction mechanism does not start until the injected excess free electron concentration becomes significant in comparison to the thermally generated carrier concentration [25].

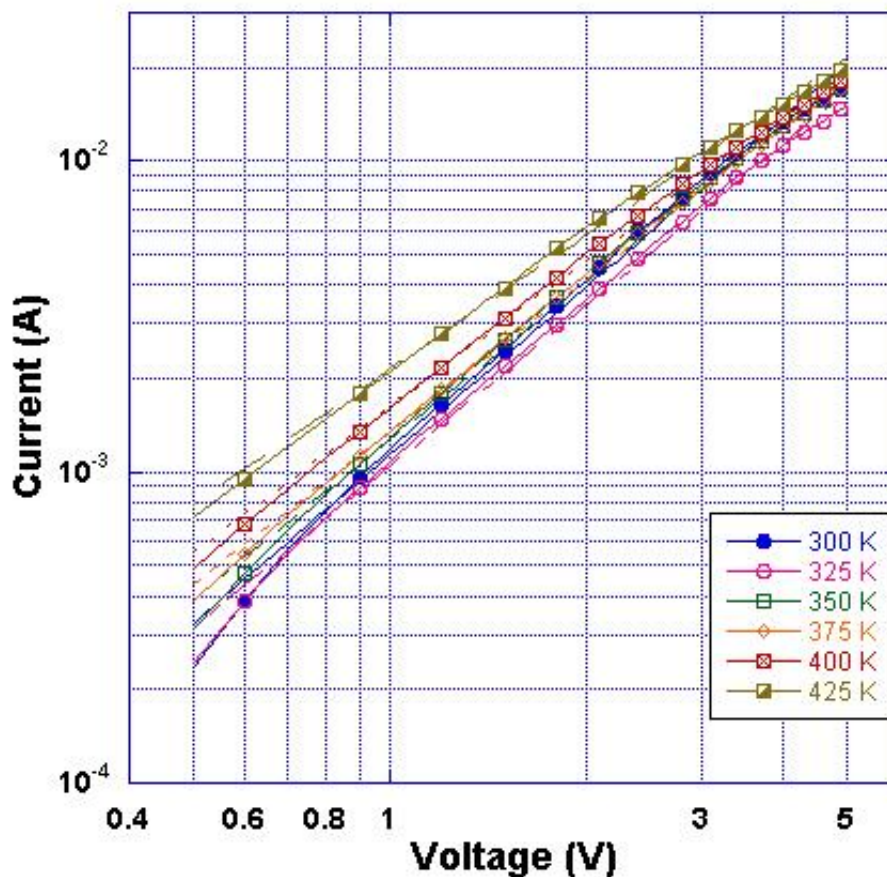


Fig. 5.8. Forward I-V characteristics plotted on a log I vs. log V graph.

Table 5.2: Fitting parameters to the power law fit.

Temperature (K)	m1	m2
300	0.0011359	1.7982
325	0.0010402	1.723
350	0.0012654	1.694
375	0.0013439	1.6308
400	0.0016215	1.5591
425	0.0021333	1.4342

In the reverse bias, the dominant mechanism has been found to be Thermionic emission across a barrier [26]. The reverse current can be modeled as

$$I = J_s \exp \left[\frac{\beta \sqrt{V}}{kT} \right] \quad \text{Equation (5.1)}$$

Where,

$$J_s = A^{**} T^2 \exp \left(\frac{-q\Phi}{kT} \right) \quad \text{Equation (5.2)}$$

In these equations, V is the reverse bias voltage applied, Φ is the barrier height, A^{**} is the Richardson constant, and β is a material parameter. The equation can be simplified as

$$J = m_1 \exp(m_2 \sqrt{V}). \quad \text{Equation (5.3)}$$

Where $m_1 = J_s$ and $m_2 = \beta/kT$.

Fig. 5.9 shows the $\log I$ vs. \sqrt{V} and linearity of this graph indicates a good fit to the Thermionic emission model. To further verify this model, $\log(I/T^2)$ vs. $1/T$ was plotted at about 4 V at various temperatures. Fig. 5.10 is the resulting plot and the linear nature of this plot verifies the presence of thermionic emission. Using the parameters, the value of the barrier height can be extracted. The extracted values are reported in Table 5.3. The barrier height obtained from the model extraction is also reported in Table 5.3.

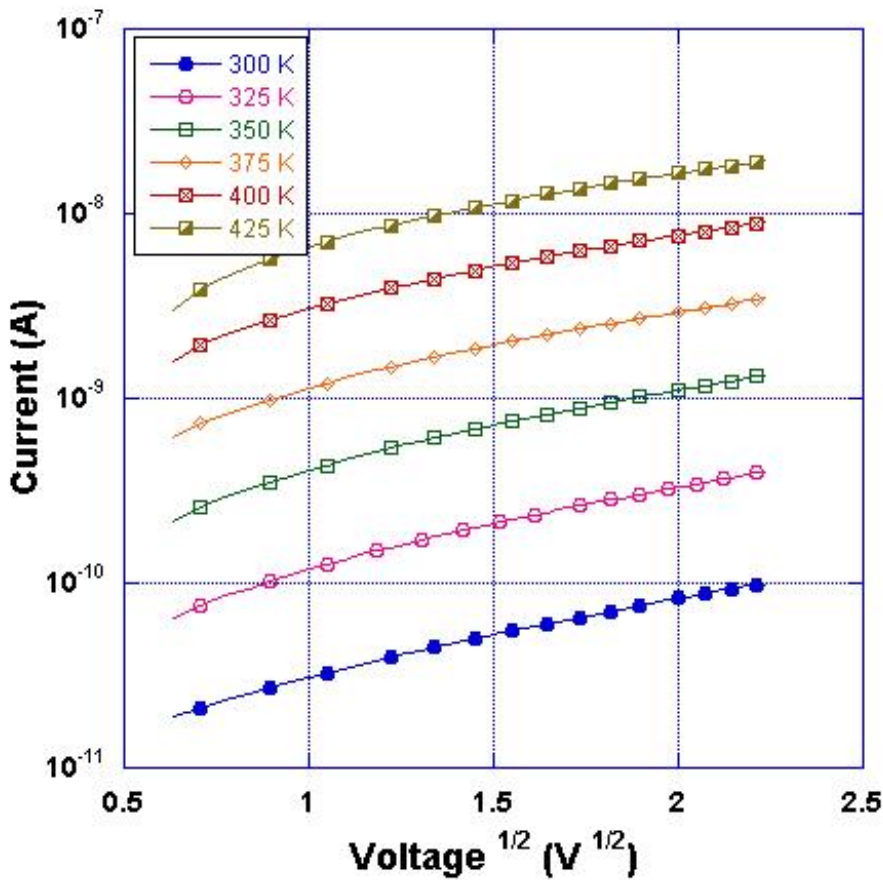


Fig. 5.9. Reverse characteristics plotted $\log I$ vs. \sqrt{V}

Table 5.3. Extracted parameters in reverse bias

Temperature (K)	m1	m2	Φ (eV)
300	1.00E-06	1.01	0.776
325	4.06E-06	1.089	0.806
350	1.63E-05	1.074	0.831
375	5.46E-05	1.027	0.856
400	1.68E-04	1.01	0.875
425	3.85E-04	1.047	0.905

5.6 Conclusions

Thin films of Cu_2O have been deposited on N type Si substrates. The resulting Cu_2O -N type Si heterojunction exhibits rectifying characteristics suggesting the formation of a PN heterojunction. The I_{on}/I_{off} ratio at $\pm 3\text{V}$ is about 17,000 and is the highest reported value for this junction. XRD and TEM analysis reveals the presence of crystalline structures of Cu_2O and crystal size as large as 600 nm. These results suggest that high quality Cu_2O has been grown, and the possibility of using this growth recipe for depositing Cu_2O layers for PV applications. The next step is to fabricate a PN heterojunction using Cu_2O and ZnO and to optimize this junction for best PV performance. Once this has been perfected, a complete device as shown in Fig. 5.2(a) needs to be fabricated to check for full device efficiency.

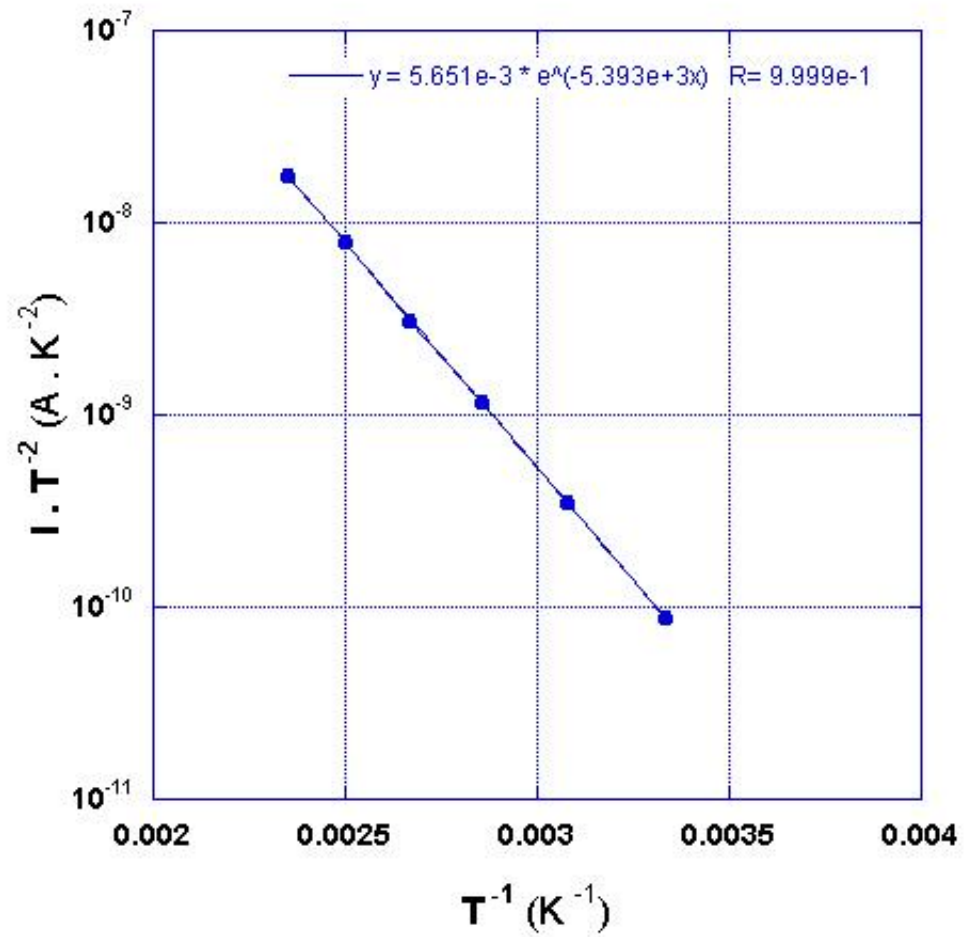


Fig. 5.10. Plot of $\log(I/T^2)$ vs. $1/T$

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CHAPTER SIX

CONCLUSIONS

Examination of the results published in open literature suggests the absence of a technique that can be used to increase the PV efficiency in a cost effective fashion. A whole section of concepts popularly called “Third Generation PV” have not resulted in any practical improvements of PV efficiency. The only concept that has shown a meaningful result is the Multi-junction cell, which was proposed as early as the 1960s. In addition, many proposed concepts involve the use of nano-materials, which have been impossible till date to manufacture with good uniformity and homogeneity. Self-assembly routes of building nano-material based semiconductor products is still in infancy although these concepts have been widely explored.

The growth of the PV industry can be accelerated if the price/watt can be improved, and Multi-Junction Multi-Terminal (MJMT) cells using an earth abundant material seems to be the logical way to move forward. Using the MJMT cell, conversion efficiency as high as 44% is theoretically possible if the right material combination is employed. To meet this goal, several earth abundant materials are being investigated.

Of particular interest is Cu_2O , an earth abundant stable oxide of Cu. To study the properties of Cu_2O , thin films of this material were deposited using a photo assisted Chemical Vapor Deposition process. Several methods such as XRD, Ellipsometry, I-V measurements, and TEM were used to study these deposited films. Results from these techniques suggest that high quality crystalline Cu_2O films were successfully deposited.

This Cu_2O can form an absorber layer in the top junction of the MJMT stack. A suitable N type semiconductor capable of forming a good PN junction with the Cu_2O needs to be developed to make further progress on improving the efficiency of commercial PV devices. Such improvements will decrease the net price/watt of PV deployments and has the chance to provide clean energy to billions of people worldwide and accelerate economic development.