



Processing and Optimisation of high-efficiency III-V Solar Cells

Internship Report

by

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Abstract

III-V semiconductors have several optical as well as electronic advantages over silicon which enable their application in a wide range of optoelectronic and photovoltaic devices.

During my stay I have worked on high efficiency III-V solar cells. The project was focused on Epitaxial Lift Off and processing methods of ultra high efficiency solar cells to reach 50% efficiency mark.

However, making the production of the III-V semiconductor technology on a large scale will still take a lot of years, primarily due to the high cost of the materials. So, the focus of my project at ISE was to produce ultra high efficiency solar cells at ultra low costs.

Acknowledgements

I feel a sense of sincere gratitude towards Dr. Frank Dimroth for giving me this great opportunity to work on my internship project at the prestigious Fraunhofer Institute for Solar Energy Systems in Freiburg. His encouragement and support to young and aspiring scientists is exceptionally kind.

I need to give a special mention to my supervisor, Dr. Felix Predan, for guiding me through the project and helping me take the smallest but first step towards realising my dream of contributing to the field of renewable energy.

I received a tremendous amount of technical and scientific aid from Dr. Eduard Oliva and Jana Wulf and would like to convey my deepest gratitude to them for the time and effort they spent on assisting me.

I cannot forget to mention here that Prof. S. Indu, who is also the academic supervisor of my internship, played pivotal roles in nurturing my interest to join the field. I thank them for their insightful lectures.

I sincerely appreciate and cherish the help and advice that I received from all the colleagues in the laboratory – Dr. Jens Ohlmann, Dr. Esther Lopez, Dr. Oliver Höhn, Dr. Henning Helmers, Dr. Birte Godejohann, Dr. Alexander Franke – each of whom supported me in their own unique way.

And most importantly, I would like to sincerely thank Mr. Mahinder Nath, Mr. Sunil Khanna, Mr. Rajesh Malhotra, Mr. Rakesh Sethi, Mr. Rasik Bahadur and Ms. Sonia Prashar for believing in me and supporting me financially. I own a lot to them for making my dream of working at a prestigious institute like Fraunhofer a reality.

Introduction

During the entire course of civilisation, humans have strived to build and innovate by modifying the resources accessible to them in order to improve the quality of daily life. This inherent desire to make the most of what is available is, perhaps, a strong motivation behind several ground-breaking scientific discoveries.

A resource that forms the backbone of every sphere of life is energy and the quest for the perfect mechanism to convert energy into usable electrical power has been ongoing for centuries. However, the need to tap into our diverse pool of sources of renewable energy is a much newer realisation.

Solar energy is one of nature's best gifts to humankind, being the starting point of the entire food chain. It was in the 1800's when the scientific community began to notice that this form of energy can indeed also be converted to an electrical signal by the use of some specific materials to harness it. In 1954, Bell Labs announced the invention of the first modern silicon solar cell amid great scientific euphoria, and The New York Times declared that solar cells were the answer to the perfect device that can be used to tap the "limitless energy of the sun". Soon, the search for materials that convert solar energy to electricity more efficiently than silicon began. However, silicon solar cells maintained their reigning position for several years due to the abundance of their raw materials and the compatibility with the electronics industry. It was only in the early 1970's that a true competitor arrived.

The first gallium arsenide (GaAs) heterostructure solar cells were developed in 1970 by the group of Zhores Alferov in the former-USSR. By the early 1980's, the efficiencies of the best GaAs solar cells had surpassed that of conventional crystalline silicon solar cells. In the 1990's, GaAs became the most commonly used material for photovoltaic arrays in satellite applications. Until the late 90's, the use of III-V photovoltaic devices was confined only to space applications (due to light weight, greater efficiency, higher electron mobility and higher temperature stability) since their price is much higher than the conventional silicon solar panels. However, the demonstration of high efficiency multijunction solar cells has generated great interest in III-V solar cells for high concentration terrestrial applications. The quest to constantly improve the performance of solar cells by using novel materials or methods to

overcome the Shockley Queisser limit is still underway. Nevertheless, the journey from 6% to around 46% efficiency has been an exciting one.

1. The Fraunhofer Society and Fraunhofer ISE

The Fraunhofer Society was established in 1949 and it is Europe's largest application-oriented research organization with 69 institutes, each focusing on different fields of applied science. It employs more than 25000 scientists and staff members and has an annual research budget of about € 2.3 billion. The society is named after Joseph von Fraunhofer (1787-1826), renowned German physicist, known for his work in the field of optics.

The Fraunhofer Institute for Solar Energy Systems ISE is one of the 69 institutes of the Fraunhofer Society. It was established in 1981 in Freiburg im Breisgau and it is the largest solar research institute in Europe, with around 1200 staff members and an operational budget of about € 72.9 million. Through its research activities, the institute aims to promote sustainable, economic, safe and socially just energy supply systems for the whole world. The experiments for this report were carried out in the group "III-V Epitaxy and Materials Development" which belongs to the department "III-V Photovoltaics and Concentrator

2.III-V semiconductors

Technology".

The III-V semiconductors are a family of materials developed from cations from group 13 and anions from group 15. These materials generally form a homologous series of compounds possessing the zincblende crystal structure. The exceptions are the nitride-based materials that are of the wurtzite crystal structure. The binary semiconductors, such as GaAs, InAs, InP, GaN, AlSb, etc., cover a broad range of electronic structures useful in technology. Many of the binary compounds also possess a very low electron effective mass that makes them ideal materials for the development of high-speed devices. They also have, in general, excellent thermal conductivity enabling the rapid dissipation of heat within a semiconductor device.

2.1.III-V semiconductors in photovoltaics

A key technological advantage of III-V materials is that many of them possess a direct bandgap, unlike silicon, that allows for the efficient absorption and emission of light. As a result, these materials have formed the basis of almost all of the thin film semiconductor devices that interact with light. Solid-state lasers, light-emitting diodes, and multi-junction or

cascade solar cells are several of the broad classes of devices that rely on III-V materials. Solar cells operate on the principle of photovoltaic effect. Sunlight incident on the semiconductor material creates electron-hole pairs that are collected in an external circuit. Two important parameters that give an indication of the efficiency of a solar cell are its short circuit current density (J_{SC}) and the open circuit voltage (V_{OC}). The maximum short circuit current density and open circuit voltage obtainable from any semiconductor material are both functions of the bandgap energy of the material. As the bandgap decreases, the maximum possible short circuit current density increases, as more photons in the solar spectrum are now capable of creating electron hole pairs in the material. However, the maximum obtainable open circuit voltage decreases with decreasing bandgap energy of the semiconductor. Thus there exists optimum bandgap energy for the semiconductor material in the range 1.4 to 1.6 eV to maximize the single-junction solar cell efficiency. GaAs has the optimal bandgap energy for solar cell applications, which enables a theoretical maximum possible efficiency of $\sim 25\%$.

2.2. Epitaxy and lattice matching

In order to design a semiconductor device with more than one type of material, a crystalline layer of one material has to be grown on a crystalline substrate. The process of depositing crystalline layers on a crystalline substrate is referred to as *epitaxy*. Epitaxial growth of one material on another can exert mechanical strain on the resulting structure if the crystalline lattices of the two materials are not compatible. Such a strain can physically alter the properties of the materials and to avoid this, it is important to grow layers of materials with similar lattice constants on top of each other. The process of selecting such materials is called *lattice matching*.

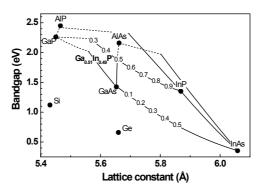


Figure 2.1: Bandgaps of various III-V semiconductors, silicon and germanium as functions of their lattice constants. An example of GaInP is shown with III-V ratio that results in lattice-matching with GaAs.

2.3. Solar cell structure

The typical III-V semiconductor solar cell structures at Fraunhofer ISE are grown on 10 cm wide and 450 µm thick circular GaAs (gallium arsenide) wafers. On the substrate are the functional layers of the solar cell, consisting of a III-V semiconductor base layer (often p-doped) which is a few microns thick, followed by a much thinner emitter layer of the same semiconductor (often n-doped), then a window layer which is a high bandgap semiconductor that is transparent to the wavelengths of light that will be absorbed by the solar cell and finally a GaAs cap layer that has the same polarity of doping as the emitter layer. In order to create electrical contacts, metals are deposited via techniques such as evaporation or electroplating on the front and back surfaces of the solar cell.

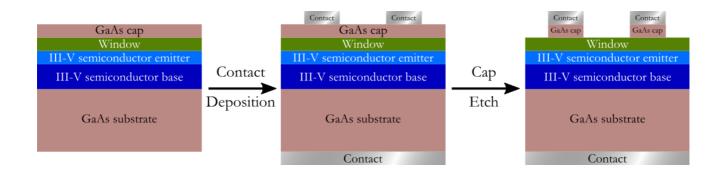


Figure 2.2: Schematic representation of a typical III-V semiconductor based solar cell structure grown on a GaAs substrate.

The base and the emitter of the solar cell can be any III-V semiconductor like GaAs, GaInP, AlGaAs, GaInAs etc. depending on the desired wavelength of light that the solar cell is designed to absorb. The role of the window layer is to reduce front surface recombination by passivating the surface and it is a material with bandgap greater than that of the base/emitter. Common choices for the window layer are AlInP (aluminium indium phosphide), GaInP (gallium indium phosphide) or AlGaAs (aluminium gallium arsenide). The cap layer is highly doped GaAs that prevents recombination and propagation of defects during the process of contact deposition and this layer is etched away once the metal contacts have been deposited on the surface of the device. For commercial solar cells, a final layer of anti-reflection coating (ARC) is deposited on the device to minimise optical losses due to reflection that reduce the quantum efficiency of the device. In this work, all samples studied were without the additional ARC layer.

2.4. Multijunction solar cells

Due to their relatively high cost compared to silicon solar cells, the most common application of III-V solar cells has been in multijunction concentrator cells which can exhibit very high efficiencies and thereby compensate for the cost. The aim of multijunction solar cells is to overcome the Shockley-Queisser limit that arises largely due to the fact that materials with high bandgaps fail to absorb photons of energy lower than their bandgap and materials with low bandgaps absorb high energy photons only to lose the excess energy to thermal relaxation of the excited carriers. Both these physical processes lead to loss of incident energy.

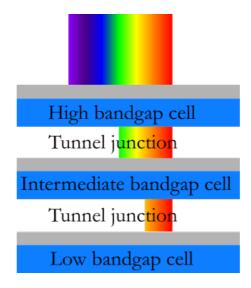


Figure 2.3: Schematic representation of multijunction solar cells with the highest bandgap material used in the top cell.

Multijunction solar cells work on the principle of multiple solar cells with different bandgaps grown on top of each other in order of increasing bandgap such that the top-most layer effectively absorbs the highest energy photons while passing the remaining photons to the subsequent layers below it. Such cells are a combination of two or more solar cell structures described in section 1.2.3 connected by highly doped tunnel junctions through which carriers can easily be collected. These cells are normally operated under concentrated sunlight rather than one sun illumination and often used in aerospace applications. The maximum theoretical efficiency of a stack with infinite number of solar cells under concentrated sunlight is 86% and an experimental efficiency of 46% has already been demonstrated for a four-junction cell.

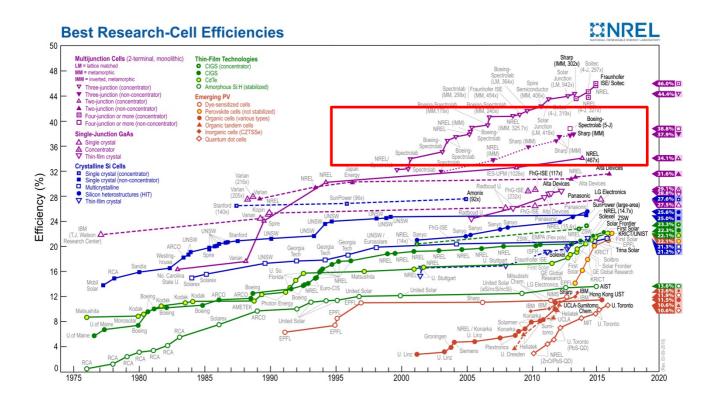


Figure 1.4: Graphical depiction of best research cell efficiencies reported for various different solar cell materials and fabrication techniques. The red box highlights the increase in efficiency for multijunction solar cell technology with time.

In this project, single junction solar cells of materials with a various range of bandgaps are studied with the goal of improving and optimising them for eventual application as the different cells in the stack of a high efficiency multijunction solar cell.

3. Background

3.1 Standard technology

Metalorganic Vapour Phase Epitaxy (MOVPE) grown III-V solar cells generally undergo several processing steps before they are fit for measurements and characterisation, which determine the performance and the quality of the cells. A standard fabrication process of the III-V solar cells includes wafer preparation, photolithography for mesa definition, individual cell isolation by mesa etching, photolithography for contact definition, front and back contact deposition by metal evaporation in a vacuum chamber, thermal annealing of contacts, cap etching, and often, deposition of an anti-reflection coating (ARC). Standard III-V solar cells at Fraunhofer ISE have some cells for EQE, TLM and Hall measurements along with a large number of concentrator cells made for measurements under concentrated sunlight of the order of several hundred suns.



Figure 3.1: Flowchart depicting the steps involved in standard technology processes.

3.2 Aim of this project

The main objective of this project is to understand the technology, fabricate devices using the technology and understand the results obtained from them.

4. Materials and Methods

This chapter describes the experimental methods and techniques that were employed to prepare and characterise the samples on which the results of the next chapter are based.

4.1. Sample Preparation

For this work, solar cell wafers made of GaInP, GaAs, GaInAs were used. These wafers are grown in-house by Metalorganic Vapour Phase Epitaxy (MOVPE) by the colleagues of the Epitaxy team of the III-V department at Fraunhofer ISE.

4.1.1.Metalorganic vapour phase epitaxy (MOVPE)

Metalorganic vapour phase epitaxy (MOVPE) is an epitaxial technique where the atoms constituting the material are transported to the growth surface by means of organometallic and/or hydride precursors. Another name frequently used for this technique is MOCVD (metalorganic chemical vapour deposition). It has become the preferred choice for the large-scale fabrication of a wide range of III-V semiconductor devices because of its versatility, repeatability and high growth rates.

MO sources Sample wafer reaction chamber HEATING (IR, RF)

H₂

AsH₃ PH₃

Gas mixing net

Figure 4.1: Schematic representation of a MOVPE reactor system configuration.

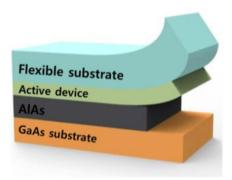
The MOVPE technology for the growth of III-V semiconductors involves metal atoms, with alkyl radicals attached, as precursors for the epitaxy. For the column V elements, however, hydrides are mostly used (AsH3 and PH3). The working principle of this epitaxy method is that the metalorganic and hydride precursor molecules are stable at room temperature, while they decompose at high temperatures, releasing the metal atoms that will take part in the epitaxy. The precursor and carrier gases (usually pure hydrogen) are flown into the reaction chamber in a proportion that must be calibrated before to obtain the precise stoichiometry, structural properties, doping levels, etc which are desired for each material. Then, they reach

the heated substrate where they decompose and contribute with their metal atoms to the growth of the semiconductor layers.

The wafers used for this work were grown by colleagues from the Epitaxy team of the III-V department at Fraunhofer ISE.

4.1.2 ELO

In the ELO method, the thin film is separated from the substrate by selectively etching a sacrificial layer between the active region and the substrate. This allows the transfer of the thin film to a foreign carrier and makes detached bulk substrate reusable. Manufacturing costs are significantly reduced by reusing the GaAs substrate.



A viable ELO process for manufacturing should satisfy three essential conditions:

- The surface of the reused substrate needs to be residue-free, and have low surface roughness (the root-mean-square (RMS) roughness of an epi-ready GaAs wafer is about 0.3 nm);
- The properties of subsequent layers grown on reused substrates should be identical to that of the first released film;
- The throughput of the ELO process should be high to drive down overall cost.

4.2. Sample Characterisation

4.2.1.SunsVoc

The majority of the results and conclusions presented in this report are based on SunsVoc measurements of the samples. These were performed using a Sinton WCT-120 SunsVoc machine. The working principle of the method is to measure under open circuit (no current) to obtain the open circuit voltage of a cell as a function of light intensity. In the experimental setup, a slow decaying flash lamp is used as the illumination source and a silicon reference cell is used to detect the intensity of illumination which corresponds to the V_{oc} obtained from the test cell. The software extrapolates an equivalent current density (J) from 0 to 1 sun, and together with the corresponding V_{oc} , a "pseudo J-V curve" is plotted and the "pseudo fill factor" (pFF) is calculated.



Figure 4.2: SunsVoc set-up with a decaying flash lamp and a sample measurement stage from Sinton Instruments

4.2.2.Quantum Efficiency (QE)

Another extremely important parameter to study and evaluate the performance of any solar cell is its quantum efficiency. The quantum efficiency (QE) is the ratio of the number of carriers collected by a solar cell to the number of photons of a given energy incident on the solar cell. If the measurement does not take into account the loss of efficiency due to optical phenomena, the output curve is called the external quantum efficiency (EQE). If the effect of optical losses due to reflection is compensated then the output curve is called the internal

quantum efficiency (IQE), which is always higher than the EQE. The quantum efficiency may be given either as a function of wavelength or of energy. If all photons of a certain wavelength are absorbed and the resulting minority carriers are collected, then the quantum efficiency at that particular wavelength is unity. The quantum efficiency for photons with energy below the band gap is zero.

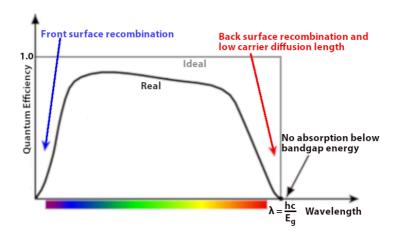


Figure 4.3: Depiction of an ideal and a real quantum efficiency curve for a solar cell. QE of a real solar cell is reduced for shorter wavelengths (higher energy) due to front surface recombination and for longer wavelength (lower energy) due to back surface recombination and low diffusion lengths. QE sharply drops to zero close to the bandgap wavelength.

4.2.3.Light J-V measurements

To obtain the current density (mA/cm²) versus voltage (V) characteristics of a solar cell, we apply a bias voltage ranging from 0 to its open-circuit voltage under steady-state 1 sun illumination and measure the corresponding current density. From these results, a J-V curve can be plotted, whereby values of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF) can be obtained. An ideal J-V curve would be a square/rectangle; however, a real solar cell has resistive effects. The tilt of the curve around the open circuit point is a measure of the series resistance and that about the short circuit point is a measure of the parallel/shunt resistance. The fill factor is the ratio of the maximum extractable power to the product of the short circuit current and open circuit voltage of the cell, also known as the measure of the "squareness" of the J-V curve.

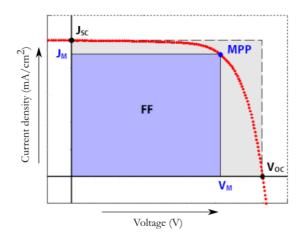


Figure 4.4: Graphical representation of current density (mA/cm^2) as a function of voltage (V) for a solar cell under illumination. J_{sc} is the current under short circuit conditions; V_{oc} is the voltage under open circuit conditions. The largest rectangle that fits into the real J-V curve is the Fill Factor of the given solar cell.

5. My work

• Epitaxial Lift Off (ELO)

Worked on the state of the art ELO process. Performed ELO of the new samples in HF bath under different conditions and parameters. Designed a new approach, that could make the whole process a lot more effective and faster.

(ELO holds the key to low cost high efficiency solar cells, and with the current progress, it is expected to be fully optimised for commercial scale in a few years)

• Measurements using Scanning Acoustic Microscope and Suns Voc

Measured and evaluated the newly processed samples using SAM specially customised for Fraunhofer ISE to get the information about the defect and the material quality of the layers.

• 'New Record' Project

Worked with the team on developing a new process for reaching new world record efficiency of solar cell. Part of the technology team and developed a state of the art method to do faster processing of the samples that will speed up the entire process.

6. FUTURE AND LIMITATIONS OF THE STUDY

Solar energy is growing exponentially around the world. In order to make it the primary source of energy generation, efficiency of the solar cell needs to be increased a lot from the current mark of around 20. III-V materials promises the best efficiency, having achieved around 46% (Fraunhofer ISE) for multi junction and 30% (Alta Devices) for single junction.

With the project I worked on at ISE, we expect to go beyond the 50% mark in a few years.

But till now III-V materials have been limited to just space solar cells market, essentially due to their extreme high costs. But with the research work now primarily focused on making them cheaper for terrestrial application, this could prove out to be revolutionary for the PV industry in the future. Tandem cells are the hot topic of PV research these days, in which Fraunhofer is the leader. Tandem cells could change the whole scenario of the Utility scale projects by bringing down the LCOE significantly.

Higher-efficiency materials can act as a turnaround for the struggling solar project economics, as higher efficiencies generates significant more power with fewer panels. And fewer panels essentially means less land, labor, and equipment requirement.

Applications in which area is a constraint, such as drones, automotives, electronics, rooftop, buildings(BIPV) etc. cheap III-V materials will change these industries completely, hopefully bringing complete autonomy to them.

The challenges that this industry faces are many, but the incredible potential make these hurdles exciting to cross.