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HIGH EFFICIENCY INTEGRATED III-V-NITRIDE SOLAR CELLS ON SILICON-BASED SUBSTRATES

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List of Publications

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Abstract

Solar energy has a huge potential to reduce the world's reliance on fossil fuels. However, due to the excess current wasted by the Ge sub-cell, the energy conversion efficiency of a typical lattice-matched triple junction (InGaP/Ga(In)As/Ge) photovoltaic (PV) cell can only reach 41% under concentrated suns. The addition of a 1-eV sub-cell between the Ga(In)As and Ge sub-cell has been predicted to achieve an energy conversion efficiency of 50% under concentrated suns. Thus, in this work, high efficiency PV cells were grown on a silicon substrate to increase the conversion efficiency and reduce the PV production cost.

We demonstrated a 1-eV GaNAsSb PV cell on a Si-Ge/Si substrate using molecular beam epitaxy (MBE). The cell exhibited the lowest ever reported $E_g/q-V_{OC}$ value of 0.50 eV. This indicates that the 1-eV GaNAsSb layer has a high crystalline quality with a long carrier lifetime. The growth conditions of the GaNAsSb layer were optimised by varying the As/Ga ratio, growth temperature, annealing temperature and annealing duration. The As/Ga ratio was found to affect the concentration of arsenic anti-site defects and nitrogen-related defects. On the other hand, the growth temperature was found to affect nitrogen phase separation or segregation. We found that annealing at 700°C for 5 mins can improve the performance of the PV cell by removing non-radiative defects. However, annealing at a temperature exceeding the optimal temperature of 700°C for more than 5 mins severely deteriorates the PV cell performance.

Previous modelling works assumed an ideal quantum efficiency for all the sub-cells. However, the experimental quantum efficiency of 1-eV GaNAsSb was well below the ideal condition. Modelling work was carried out to optimise the bandgap energies of the top two sub-cells using the published experimental quantum efficiency of InGaP, GaAs, 1-eV GaNAsSb and Ge. The bandgap energies of the bottom two sub-cells were fixed at 1.03 eV and

0.66 eV, which represented the GaNAsSb and Ge sub-cell, respectively. The model showed that the optimised bandgap energy of the first and second sub-cells were 2.00 eV and 1.56 eV, respectively. These bandgap energies are higher compared to the bandgap energies of the top two sub-cells in typical triple junction cells, which are 1.86 eV (InGaP) and 1.42 eV (Ga(In)As), respectively. An increase in the bandgap energy levels in the top two sub-cells allows more light to be transmitted to the third sub-cell. With the optimised bandgap of 2.00/1.56/1.03/0.66 eV in a quadruple junction cell, the energy conversion efficiency at the one-sun condition can be increased to 38.8%. The energy conversion efficiency can be boosted to 49% under the 500 suns condition. Under this configuration, a one-sun short circuit current density of 11.8 mA/cm², an open circuit voltage of 3.65 V and a fill factor of 90% can be achieved in a photovoltaic cell.

We also grew and fabricated 1.56 eV PV cells using Al_{0.11}GaAs on a Si-Ge/Si substrate. The material quality of the AlGaAs layer was optimised by varying the V/III ratio, growth temperature and base thickness to obtain maximum performance in the PV cell. The substrate temperature was found to affect the group III site vacancies while the V/III ratio was found to affect the V_{As}, Ga_{As} and As_{Ga}. Both parameters were also found to affect the incorporation of oxygen-related complexes. The AlGaAs PV cell grown on a Si-Ge/Si substrate seems to favour a lower substrate temperature of 630°C rather than a higher substrate temperature of 680°C on a GaAs substrate. The AlGaAs PV cell grown on a GaAs substrate has the best material quality at a substrate temperature of 680°C and a V/III ratio of 15. This growth process is important in showing the potential of the 1.56 eV AlGaAs PV cell on a Si-Ge/Si substrate and future integration with a 1-eV GaNAsSb PV cell as well as the 2.0 eV sub-cell (AlGaInP) and Ge sub-cell. The four materials are closely lattice-matched with GaAs and can be grown directly on the Si-Ge/Si substrate.

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Chapter 1 Introduction

According to the International Energy Outlook 2016, the demand for energy is increasing [1]. The demand for liquid fuel is projected to increase from about 90 million barrels per day in 2012 to about 100 million barrels per day in 2020. The rate is projected to reach over 121 million barrels per day in 2040. Natural gas consumption is projected to increase by about 70% in 2040. Furthermore, coal, the second largest energy source, has a current average increase of 0.6% per year. This huge amount of energy usage is to meet demands from increases in population and in the adoption of technology. The enormous consumption of fossil fuels is mainly used to produce electricity, heat and transportation. More energy is needed as the population and the demand for technology increases. This will result in scarcer fossil fuel and increased prices. The fluctuation of fuel prices not only depends on the availability of fuel in the region, but also on the political stability of the region and global demand. Additionally, the burning of fossil fuels for energy generation causes the production of greenhouse gases like CO₂ as well as toxic gases like SO₂ and NO_x. All these factors have increasingly made fossil fuels less desirable. There are other types of “cleaner” energy sources like nuclear energy. However, the by-products of nuclear energy remain harmful after many decades, and it requires specially designed underground storage facilities to shield people from harmful radiation. Thus, the next best alternative is renewable energy.

With the increasing awareness of global warming, more countries are looking towards renewable energy like photovoltaic (PV) panels, hydroelectric dams and wind turbines. Renewable energy has the added benefit of stable pricing as the investment costs are covered upfront and the daily operation and maintenance costs are predictable [2]. Additionally, renewable energy sources like sunlight and wind are free and abundant and

no special methods are required to extract or refine them. They can be harvested immediately to produce electricity, and no harmful waste is produced.

Solar energy is abundant and endless during the day. It can be stored in batteries for use at night to ensure a stable supply of electricity. The amount of sunlight falling on earth daily is more than enough to meet the world's yearly energy demands. The average flux arriving on the earth's surface is about 175 W/m^2 [3]. This number takes into account the dark side of the earth as well as absorption and scattering from the earth's atmosphere and clouds. Therefore, the total amount of sunlight falling on earth during one day is about $7.7 \times 10^{21} \text{ J}$. Comparing this to the predicted total energy consumption of $6.6 \times 10^{20} \text{ J}$ for the year 2020 [4], solar energy has great potential to provide the energy we require. However, due to the inefficiency of the panels, current solar systems are unable to extract a huge amount of power from sunlight.

1.1. Photovoltaic Cells

Photovoltaic (PV) cells are devices that convert light energy to electrical energy. Any photon energy larger than the bandgap of the material is absorbed while the rest of the energy is transmitted through the material. The absorbed photons will generate an electron-hole pair, where the electron is excited to a higher state of energy level. The excited electron will be swept off by an electric field in the depletion region of the pn-junction where it will go to the load and then recombine with a hole back in the PV cell. However, if the electron-hole pair is generated away from the depletion region, there is no electric field to sweep the electrons away. This will create a region with a higher concentration of electrons, and through random motion, the electrons will diffuse throughout the cell. Materials like silicon, a mixture of III-V elements, cadmium, tellurium or organic compounds have been researched widely.

The most popular PV panels in use are made of silicon. This is due to the low cost of silicon as compared to III-V materials and their relatively high efficiency when compared to thin film and organic PV panels, as shown in Figure 1.1 [5]. The highest efficiency PV panels as of 2017 are III-V multi-junction PV cells with an efficiency of 46%.

Figure 1.1. Best PV cell efficiencies sorted according to type. The best are III-V multi-junction cells followed by silicon, thin-film and emerging PV cells.

1.2. Progress of PV Cells

Current state-of-the-art PV cells use elements from the group III and V and have a record efficiency of 46% under multiple suns as of 2017. They use four sub-cells to collect and convert concentrated sunlight to electricity [6]. Multi-junction III-V PV cells have the potential to reach more than 50% efficiency as they use more than one sub-cell to absorb a portion of the spectrum of light, whereas the highest possible theoretical efficiency for a single junction PV cell is about 30% as described by the detailed balance limit [7] [8]. The addition of multiple sub-cells allows each layer to

absorb a specific region of the solar spectrum. This reduces loss caused by thermalization when the photon energy is larger than the bandgap (E_g) of the material. Thermalization is the result of the relaxation of electrons to the edge of the conduction band with the release of phonons due to the absorption of excess energy as shown in Figure 1.2. Additionally, this will cause an increase in cell temperature, which will further decrease the energy conversion efficiency of the cell.

Figure 1.2. Thermalization of electrons when the photon energy is larger than the bandgap of the material.

Another loss is due to the photon energy being smaller than the E_g . This will result in no generation of an electron-hole pair, as the electrons do not have enough energy to overcome the bandgap. Current advancements have been to push the efficiency limits further by introducing new materials, adding junctions and introducing different fabrication methods to improve the material quality.

The current state-of-the-art quadruple junction PV cell relies on a lift-off and wafer bonding process to circumvent the difference in the lattice constant between GaAs and InP [9]. This method allows different materials of different lattice constants to be stacked on top of one another without having to worry about dislocation densities forming. However, this process is tedious, as it requires polishing to reduce the surface roughness and cleaning before wafer bonding can be initiated. Another drawback of

this quadruple junction is that it uses InP substrates, which are costlier than GaAs or Si substrates.

1.3. Lattice-matched III-V PV Cell

Lattice-matched III-V PV cells provide a simple way to stack multiple sub-cells together without having to do complex lift-off and wafer bonding techniques or growing thick graded buffer. It allows materials of different bandgaps on one PV cell to be connected directly. Since the individual sub-cells are connected in a series, the voltage of the multi-junction PV cell is equivalent to the combined voltage of each sub-cell. However, the overall current of the multi-junction PV cell is limited by the lowest producing sub-cell. A latticed-matched PV cell is preferred, as it has fewer defects and dislocations compared to the lattice-mismatched PV cell. These defects and threading dislocations act as Shockley-Reid Hall (SRH) recombination centres and decrease minority carrier lifetimes: all of which reduce the performance of the PV cell [9].

Current typical triple junction lattice-matched PV cells are made of InGaP (1.87eV)/Ga(In)As (1.42eV)/Ge (0.66 eV). The lattice constants versus the bandgap of the different materials are shown in Figure 1.3. GaAs is only slightly mismatched with Ge, and thus it requires only a small amount of In to enable it to be lattice-matched to Ge. GaInP can be latticed matched to GaAs by adjusting the composition of Ga and In. This triple junction configuration has an energy conversion efficiency of ~41% at 484 suns and ~31% at 1 sun [10] [11]. However, the Ge sub-cell produces around twice the current of the other two top sub-cells [12] [13]. Due to the current matching condition of the multi-junction PV cell, half of the current produced by the Ge sub-cell is wasted. Furthermore, photon energy in the range of 0.7 eV to 1.4 eV causes thermalization of the carriers and the excess energy is dissipated as heat, which

further reduces the PV cell efficiency. These problems can be overcome with the insertion of a 1 eV sub-cell between Ga(In)As and the Ge sub-cell [14] [15]. Many researchers have reported this configuration (InGaP/Ga(In)As/1-eV/Ge) to be able to reach efficiencies above 50% under concentrated suns [16] [17] [18]. The increase in efficiency is due to proper current matching and the increase in voltage from the 1-eV sub-cell.

Figure 1.3. Lattice constants versus the bandgaps of different materials [20].

A lattice-matched quadruple junction with a 1-eV sub-cell consisting of GaInP/GaInAs/GaInNAs/Ge has been demonstrated using metal-organic vapour phase epitaxy (MOVPE). However, the efficiency is <25% under AM0. The low efficiency is due to the GaInNAs sub-cell current limiting the whole quadruple junction PV cell. The 1-eV GaInNAs sub-cell has an internal quantum efficiency of less than 50%, which could be due to the use of MOVPE. The use of MOVPE has

been reported to have problems of carbon impurity and hydrogen incorporation due to the usage of metal-organic sources [21] [22]. However, MBE only uses pure elemental sources in an ultra-high vacuum environment. Therefore, it will not have the above issues and could produce higher quality dilute-nitride layers [22].

1.4. 1-eV Sub Cell Materials

The best 1-eV sub-cell is lattice matched with GaAs. This method does not require any complicated lift-off and bonding techniques or a thick graded buffer. A small amount of nitrogen can be added to GaAs to decrease the bandgap. At the same time, it also will decrease the lattice constant [19] due to the small nitrogen atoms replacing the big arsenic atoms. The large decrease in the bandgap with the addition of small amounts of nitrogen can be explained using the band anti-crossing (BAC) model, which will be discussed later.

In order to shift the lattice constant back to that of GaAs, indium and/or antimony can be added. Both indium and antimony decrease the bandgap of GaAs, but increase the lattice constant as shown in Figure 1.3 [20] [21]. Indium containing dilute nitrides have been widely researched for use in infrared lasers, photodetectors and 1-eV PV cells. However, the addition of indium has been shown to lower nitrogen incorporation as well as increase the formation of nitrogen-related defects in InGaAsN [22] [23]. The addition of Sb to GaInNAs for PV cell devices has been researched and shown to degrade the open circuit voltage (V_{oc}) and the fill factor [24]. The same material was reported to have a lower PL intensity than GaInNAs [25]. Indium containing dilute nitride was also reported to increase nitrogen-related defects [23].

The addition of antimony has been reported to enhance nitrogen incorporation and increase photoluminescence (PL) intensity in GaNAsSb [21]. In contrast, lower

nitrogen-related defects were reported for GaNAsSb as compared to InGaAsN [26]. The absence of indium and the presence of antimony seems to aid in the efficient incorporation of substitutional nitrogen atoms, which decrease the formation of nitrogen-related defects [22] [23]. Antimony acts like a surfactant and increases the nitrogen incorporation with an increase in antimony [21]. The growth of a quaternary alloy like GaNAsSb and InGaAs is easier when compared with a quinary alloy like InGaAsSb. This shows that GaNAsSb seems to be the better material for the 1-eV sub-cell, since not only is it lattice-matched with GaAs, it has lower nitrogen-related defects and better material quality than indium containing materials. The lattice constant (L) of $\text{GaN}_x\text{As}_{(1-x-y)}\text{Sb}_y$ can be calculated using Vegard's Law

$$L(x, y) = xL(\text{GaN}) + yL(\text{GaSb}) + (1 - x - y)L(\text{GaAs}) \quad (1)$$

where $L(\text{GaN})$, $L(\text{GaSb})$ and $L(\text{GaAs})$ are the lattice constants of GaN, GaSb and GaAs, respectively.

1.5. Band Anti Crossing Model

Figure 1.4. Schematic diagram of the band anti-crossing model of GaNAs as shown by the two conduction bands E_- and E_+ .

Shan *et al.* first proposed the BAC model to describe the observed strong interaction between the conduction band of the GaInAs and the narrow resonant band formed by the N states [27]. This was shown to result in a splitting of the conduction band and thus a reduction in the bandgap of GaInNAs. It was discovered previously that the addition of small amounts of nitrogen to GaAs greatly reduces the bandgap [28]. This shows that the virtual-crystal approximation (VCA) model could not be used to study the large perturbation of the crystal lattice caused by the highly electronegative nitrogen atom.

The splitting of the conduction band is due to N-induced perturbation, which is increased with N concentration. The two conduction bands are denoted as E_- and E_+ , as shown in Figure 1.4 for GaNAs. The BAC model assumes there is no interaction between nitrogen and the valence band [29]. The equation of E_- and E_+ is

$$E_{\pm} = \frac{1}{2} [E_N + E_M \pm \sqrt{(E_N - E_M)^2 + 4V^2y}] \quad (2)$$

where , for the calculation of the bandgap of $\text{GaN}_y\text{AsSb}_x$, Dang *et al.* showed that the equations of E_M and E_N are

$$E_M(\text{GaAs}_{1-x}\text{Sb}_x) = (1-x)E_g(\text{GaAs}) + xE_g(\text{GaSb}) - 1.43x(1-x) \quad (3)$$

$$E_N(\text{GaAs}_{1-x}\text{Sb}_x) = 1.65(1-x) + 1.44x - 0.38x(1-x) \quad (4)$$

where the bandgap of GaAs ($E_g(\text{GaAs})$) is 1.42 eV and the bandgap of GaSb ($E_g(\text{GaSb})$) is 0.724 eV [29] [27]. The E_N is the position of the nitrogen-induced energy level with respect to the valence band maximum, while E_M is the bandgap of $\text{GaAs}_{1-x}\text{Sb}_x$. The value of V is the strength of interaction between E_M and E_N , and it is assumed to be 2.7 eV.

1.6. III-V PV cell on Si Substrate

The substrate used in the manufacturing of the PV cell plays a significant role in the final cost of the PV cell [27]. A typical multi-junction PV cell uses GaAs substrates, which cost more compared to Si substrates. Commercially available Si wafers are larger in diameter than GaAs wafers. Manufacturing a PV cell using a large wafer can reduce the cost of the PV cell since a higher number of cells can fit in one wafer and be processed together. This enables the production of more PV cells in the same timeframe as using a smaller wafer. Another advantage of using a GaAs-based PV cell on Si under concentrated suns allows the V_{OC} to be dominated by the diffusion current ($n=1$) and not by the recombination current ($n=2$) caused by the dislocations [28]. The goal is to combine the high efficiency of the multi-junction PV cell and the low cost of the silicon substrate.

1.7. Thesis Motivations and Objectives

A typical lattice-matched triple junction PV cell consisting of InGaP (1.87eV)/Ga(In)As (1.42eV)/Ge (0.66 eV) has an efficiency of ~41% under 484 suns. The efficiency can be further increased to 50% by inserting a 1-eV sub-cell between the Ga(In)As and Ge sub-cells: thus forming a quadruple junction PV cell. The 1-eV sub-cell will allow proper current matching between all the sub-cells, and at the same time, increase the overall voltage output of the PV cell. The high efficiency of the III-V quadruple junction PV cell can be combined with the low cost of silicon by growing the quadruple junction PV cell on a silicon substrate. This will not only reduce the production cost of the PV cell, but will allow the easy integration of it with other Si-based electronics.

The main objective of this thesis is to optimise and investigate the performance of a 1-eV GaNAsSb PV cell on a Si substrate by varying the As/Ga ratio, growth

temperature, annealing temperature and duration. This material is not widely researched, especially for PV cells. This material will be ideal for the 1-eV sub-cell to be placed in a typical triple junction PV cell forming a quadruple junction PV cell (InGaP/Ga(In)As/GaNAsSb/Ge). As discussed above, it has lower nitrogen related defects as compared to indium containing dilute nitrides and will have good crystalline quality. The growth of the 1-eV GaNAsSb PV cell on a Si substrate will be novel as well in showing the feasibility of a dilute-nitride based PV cell on a Si substrate. The performance of the 1-eV GaNAsSb PV cell will be investigated to understand the underlying effects of growth parameters on the material. The performance of the 1-eV GaNAsSb PV cell will also be compared with other published dilute nitrides.

In addition, modelling of a quadruple junction PV cell using experimental results from the optimised 1-eV GaNAsSb PV cell will be done to discover the highest efficiency possible. Modelling works of a quadruple junction PV cell published by other authors assume an ideal quantum efficiency (QE) for all sub-cells. However, due to the non-ideal QE of the 1-eV GaNAsSb PV cell, the bandgap configuration of the quadruple junction PV cell will be different. Therefore, this modelling work will have an optimum quadruple junction bandgap configuration so as to have the highest energy conversion efficiency using the experimental quantum efficiency of GaInP, GaAs, GaNAsSb and Ge. Using the bandgap modelling results, the second sub-cell will be optimised on a Si substrate.

1.8. Major Contributions

This thesis presents the material quality and the performance of a 1-eV GaNAsSb PV cell on a Si-Ge/Si substrate by focusing on three parameters: (i) annealing temperature and time, (ii) the As/Ga beam equivalent pressure (BEP) ratio and (iii) the substrate temperature. The material quality of the 1-eV GaNAsSb PV cell

grown on the Si-Ge/Si substrate was compared with other 1-eV dilute-nitride cells using the $E_g/q-V_{OC}$ value. The results showed that our 1-eV GaNAsSb PV cell on Si is comparable to other dilute-nitride cells grown on GaAs. The 1-eV GaNAsSb PV cell grown on a Si-Ge/Si substrate has the lowest reported $E_g/q-V_{OC}$ value.

Based on the results of the GaNAsSb PV cell with different annealing temperatures and times, the best annealing parameters are 700°C for 5 mins. The annealing parameter of 650°C for 10 mins produces good PV cell performance as well. At an annealing temperature of 700°C and a long annealing time of 10 mins, the PV cell junction deteriorated. The increase in annealing time from 1 min to 5 mins improved the PV cell performance, which can be attributed to the reduction in arsenic antisite defects and nitrogen-related defects.

The growth of the GaNAsSb PV cell on a Si-Ge/Si substrate with an As/Ga BEP ratio of 10 yielded a PV cell with the highest energy conversion efficiency. The increase in the As/Ga BEP ratio was found to increase the arsenic-antisite defects, which decrease the performance and material quality of the GaNAsSb PV cell. However, with a drastic increase in the As/Ga BEP ratio to 20, the nitrogen content decreased due to the increase in competition between arsenic and nitrogen and antimony for the group V site. The reduction in nitrogen content resulted in a decrease in nitrogen-related defects, which improved the performance and material quality of the GaNAsSb PV cells.

The substrate temperature of 420°C for the GaNAsSb PV cell showed the highest energy conversion efficiency. The increase in the substrate temperature of the GaNAsSb PV cell was found to increase the nitrogen phase separation and segregation, which decreased the PV cell performance. The increase in the substrate temperature from 420°C to 530°C decreased the antimony incorporation. The change

in the antimony content affected the degree of relaxation only for the sample grown with a substrate temperature of 530°C. It was found to have ~0.5% relaxation for GaNAsSb with respect to GaAs, which might have further reduced the performance of the PV cell.

The non-ideal QE of the 1-eV GaNAsSb PV cell cannot be directly integrated into a typical triple junction PV cell (1.9/1.4/0.7 eV) to form a quadruple junction PV cell. Bandgap optimisation of the top two sub-cells is required to allow more light to be transmitted to the 1-eV sub-cell and to increase the current output of the 1-eV sub-cell. The modelling results shows that, with a first and second sub-cell bandgap of 2.00 eV and 1.56 eV, a maximum efficiency of 38.8% under one sun can be achieved. This efficiency can be boosted to 49% under 500 suns.

With the second sub-cell bandgap obtained from the modelling results, the 1.56 eV AlGaAs PV cell was optimised by varying: (i) the substrate temperature and (ii) the V/III ratio. The AlGaAs PV cell grown on a GaAs substrate with a substrate temperature of 680°C and a V/III ratio of 15 has the best material quality. An increase in the substrate temperature showed an improvement in material quality, which could be due to the decrease in group III site vacancies and oxygen-related complexes. The reduction in these defects reduces the recombination rate and thus increases the performance of the PV cell. An increase in the V/III ratio has the same effect as the increase in substrate temperature, but with a further increase in V/III ratio from the optimal ratio, the performance of the AlGaAs PV cell decreased. This was due to an increase in arsenic-antisite defects.

1.9. Thesis Organization

This thesis is organised into eight chapters:

- Chapter 1 gives the introduction, motivation, objectives and contributions of the thesis.
- Chapter 2 consists of the experimental methods used in this thesis. This includes the molecular beam epitaxy (MBE) system used for the growth of the PV cells and the different characterisation tools used in understanding the performance and quality of the PV cell material.
- Chapter 3 reports on the effects of annealing temperature and duration on the GaNAsSb PV cell grown on a Si-Ge/Si substrate. The focus is to obtain maximum GaNAsSb PV cell performance on a Si-Ge/Si substrate with an optimal annealing temperature and time. The aims of this chapter are to (i) understand the effects of annealing temperature on GaNAsSb PV cells on the Si-Ge/Si substrate, (ii) understand the effects of annealing time on GaNAsSb PV cells on the Si-Ge/Si substrate and (iii) find out the optimal annealing temperature and time for GaNAsSb PV cells on the Si-Ge/Si substrate with maximum performance.
- Chapter 4 reports on the effects of the As/Ga BEP ratio on the GaNAsSb PV cell grown on a Si-Ge/Si substrate. The focus is to achieve maximum GaNAsSb PV cell performance with an optimum As/Ga BEP ratio. The aims of this chapter are to (i) understand the effects of the As/Ga BEP ratio on the performance of GaNAsSb PV cells on the Si-Ge/Si substrate and (ii) discover the optimal As/Ga BEP ratio for the GaNAsSb PV cell on the Si-Ge/Si substrate with maximum performance.

- Chapter 5 reports on the effects of the substrate temperature of a GaNAsSb PV cell on a Si-Ge/Si substrate. The focus is to achieve maximum performance for the GaNAsSb PV cell with an optimum substrate temperature. The aims of this chapter are to (i) study the effects of substrate temperature on a GaNAsSb PV cell on the Si-Ge/Si substrate and (ii) determine the optimal substrate temperature for the GaNAsSb PV cell on a Si-Ge/Si substrate with maximum performance.
- Chapter 6 reports on the modelling of a quadruple junction PV cell using the experimental performance of the 1-eV GaNAsSb PV cell. The QE of the 1-eV GaNAsSb as well as other reported dilute-nitride PV cells are not ideal. The aims of this chapter are to (i) optimise the top two sub-cell bandgaps by fixing the bottom two sub-cell bandgaps at 1.03 and 0.67 eV to obtain maximum efficiency, (ii) show that a non-ideal QE of the 1-eV sub-cell can be used in a quadruple junction PV cell to achieve high efficiency and (iii) understand why bandgap optimisation is required.
- Chapter 7 reports on the effects of the substrate temperature and V/III ratio on an $\text{Al}_{0.11}\text{GaAs}$ PV cell on a Si-Ge/Si substrate. The aims of this chapter are to (i) understand the effects and determine the optimal substrate temperature for the $\text{Al}_{0.11}\text{GaAs}$ PV cell on the Si-Ge/Si substrate and (ii) understand the effects and determine the optimal V/III ratio for the $\text{Al}_{0.11}\text{GaAs}$ PV cell on the Si-Ge/Si substrate.
- Chapter 8 provides a summary of the thesis and some recommendations for future work.

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Chapter 2 Experimental Methods

2.1. Overview

This chapter provides an overview of the experimental procedure of the growth and characterisation of the GaNAsSb PV cell on a 2 cm x 2 cm Si substrate. The 6° offcut to the in-plane $\langle 110 \rangle$ Si substrate has a graded $\text{Ge}_{1-x}\text{Si}_x$ buffer all the way to 100% Ge. Chemical mechanical polishing (CMP) was done when the graded buffer was at $\text{Ge}_{50}\text{Si}_{50}$, followed by the continuation of the graded buffer to 100% Ge in an ultra-high vacuum chemical vapour deposition (UHVCVD) system [1]. A final 100 nm cap layer of n+ GaAs was grown using metal organic chemical vapour deposition (MOCVD). This whole process was done by Professor Fitzgerald's team at Massachusetts Institute of Technology. The subsequent steps were done at Nanyang Technological University. All the samples were grown on the above Si-Ge/Si substrate using molecular beam epitaxy (MBE) unless otherwise stated. The structure of the GaNAsSb PV cell is as shown in Figure 2.1.

Figure 2.1. A schematic diagram of the MBE grown 1-eV GaNAsSb PV cell (green) on a UHVCVD grown Si/Ge graded buffer (blue) on Si substrate. Each cell dimension is 2 mm X 2 mm.

In order to increase the carrier lifetime of the GaNAsSb layer, an *in situ* annealing process was used. X-ray diffraction was done to compare the degree of relaxation and lattice-matching of the GaNAsSb layer with GaAs. Post-growth fabrication using photolithography, metallisation and mesa-isolation were performed to add the front and back contact and to isolate the individual PV cells on each sample. All the devices were characterised using a solar simulator to measure the illuminated current-voltage (I - V) where the short circuit current density (J_{SC}), open circuit voltage (V_{OC}) and fill factor can be derived. The best PV cell devices were further characterised for quantum efficiency (QE) followed by measurement to obtain the capacitance-voltage (C - V) curves.

The above characterisation were performed to obtain the performance of the devices for each growth parameter. From these measurement, the quality, bandgap and type of defects affecting the GaNAsSb layer can be deduced. The subsequent subsections will explain in detail the growth, fabrication and characterisation processes involved. All processes were executed by the author except where noted.

2.2. Molecular Beam Epitaxy

The ultra-high vacuum environment allows the growth of high quality epitaxial films. The chamber pressure can go as low as 10^{-10} Torr before growth which means that contamination is minimised.

Molecular beam epitaxy (MBE) uses highly-purified solid sources that are heated to a high temperature where the evaporated atoms will be weakly adsorbed on the substrate surfaces by physical absorption. The atoms will travel on the surface where they will be fixed to a specific site by chemical adsorption. This will result in the formation of growth centres as more atoms move, chemically interact and attach together. A monolayer growth is formed when all the growth centres are

interconnected together and the whole surface is uniformly covered. This process is repeated for thin film growth [2].

The high purity source and low vacuum level of the chamber produces high crystalline quality materials. With MOCVD, problems like carbon-doping and hydrogen related complexes arise [3]. In contrast, MBE allows a lower growth temperature, which avoids phase separation and cluster effects. It can even accurately control the ratio of group III to group V elements [4]. Molecular beam epitaxy also allows for the fast switching of sources, which is ideal for thin and alternating layers [5].

The nitrogen (N_2) required for the GaNAsSb layer is from a RF plasma nitrogen source with a DC bias of 20 V applied across the deflection plates at the source opening. In order to break the strong bonds of N_2 , RF plasma is employed to separate the N_2 into individual atoms. The downside of this process is that it produces monatomic, diatomic ions and radicals that degrade the optical properties of the layer and damage the substrate [6] [7]. The deflection plates at the source opening is used to deflect these high energy charged species of nitrogen. It was reported that, with the use of deflection plates, there was a reduction in non-radiative recombination, which is a result of ion damage-induced point defects [8] [9].

The schematic diagram of the MBE chamber is shown in Figure 2.2. It consists of three chambers: load-lock, transfer and growth. The cryopanel and cryoshroud are to be filled with liquid nitrogen before the start of growth, and together with the ion pump (under the growth chamber), the chamber pressure can go as low as 10^{-10} Torr. The growth chamber has five solid sources (Ga, In, Al, Si and Be) that are contained in pyrolytic boron nitride crucibles. The temperature of these sources is controlled and monitored by heating elements wrapped around the crucibles and a thermocouple that

is in contact with the crucible. The Ga source has an additional heating element at the crucible opening where the temperature is always 50°C higher than the inside. This is to prevent the Ga from condensing at the opening. The As and Sb flux are controlled using a valved cracker source, where the desired flux can be adjusted by adjusting the opening of the needle valve. The As source has a cracker to dissociate the arsenic into As_2 which is used for all the growth. All the sources except the nitrogen source have shutters in front of the opening that are computer controlled to ensure accurate exposure.

Figure 2.2. Schematic diagram of a Riber solid source molecular beam epitaxy used in the growth of all photovoltaic cells. The diagram is not drawn to scale.

The nitrogen content is controlled using a RF plasma nitrogen source connected to a gate valve with deflection plates at the opening. The amount of nitrogen can be controlled by adjusting the plasma power and the nitrogen flow rate using a mass flow controller. Before the nitrogen plasma is struck, the pressure in the nitrogen source chamber is increased to at least 1×10^{-3} Torr by increasing the nitrogen gas flow to around 0.8 sccm. The power is set to about 300 W and the plasma is strike. The impedance matching network is tuned manually by adjusting two control knobs until

the reflection of the RF power is less than 2 W. The plasma is struck when light can be seen from a window opening at the end of the source. Once the plasma is struck, the gas flow is gradually reduced to 0.25 sccm and the power is slowly adjusted to the desired value while minimising the reflection of the RF power. The nitrogen chamber needs at least 30 mins to be stabilised due to the decrease in gas flow. Additionally, the reflection of the RF power has to be constantly maintained below 2 W.

A day before growth, pieces of 2 cm x 2 cm Si-Ge/Si substrates were each secured onto molybdenum substrates holders and placed in a load-lock chamber. This was to minimise contamination and water from getting into subsequent chambers, especially the MBE growth chamber. The mechanical and turbo pump connected to the growth chamber were switched on as well to ensure as low as possible vacuum, but the gate valve to the growth chamber was not left open. Furthermore, the turbo pump connected to the nitrogen source was switched on.

On the day of growth, the substrates were outgassed on a heating block in the transfer chamber at 380°C for at least 45 mins to remove any moisture and contaminants on the substrate. Liquid N₂ was filled into the cryopanel and cryoshroud to reduce the pressure of the growth chamber. All the required elemental sources were outgassed at 20°C above the operating temperature for about 10 mins except for the nitrogen, antimony and arsenic sources. The desired flux was checked and set by adjusting the temperature of the sources. Once calibration of the flux was completed, the outgassed substrate was transferred into the MBE chamber where it underwent oxide-desorption with an As₂ over pressure of at least 1x10⁻⁶ Torr. The GaAs oxide-desorption temperature was reported to be at 580°C [10]. Reflection high-energy electron diffraction (RHEED) was used to observe a change in pattern from hazy to a 2x4 streaky pattern as the substrate temperature increased. This signified that the

GaAs surface had oxide-desorbed and the thermocouple temperature was calibrated to the GaAs oxide-desorption temperature of 580°C. To ensure complete oxide-desorption, the substrate temperature was raised 20°C above where oxide-desorption starts and was held for about 10 mins. During the substrate ramp up, the growth chamber main vacuum pump was switched from the ion pump to the mechanical and turbo pump. This was to prevent the ion pump from shutting off during the dilute-nitride growth, as pressure can reach to about 2×10^{-5} Torr when the nitrogen valve is open. The PV cell was grown after oxide-desorption.

During growth, the substrate was rotated to ensure uniform deposition throughout the substrate. The computer-controlled growth recipe determined the opening/closing of the source shutter, whereas the nitrogen source was controlled by the gate valve in front of the nitrogen source. This was to ensure accurate exposure when certain sources were required for that layer. The growth rate was set to 1 $\mu\text{m/hr}$ by calibrating the Ga flux. The Ga flux was constant for all the samples and for all the layers except for the AlGaAs layers. The AlGaAs layers were also grown at 1 $\mu\text{m/hr}$. The sample after growth was transferred out of the growth chamber into the transfer chamber, and a newly outgassed sample was transferred into the growth chamber where the next sample was grown again. A maximum of four samples can be grown in one day.

After all the growth ended, the samples were removed through the load-lock chamber and placed in a dry box awaiting further characterisation and fabrication, which will be explained in detail later.

2.3. 1-eV GaNAsSb Composition Calibration using X-Ray Diffraction

The two important criteria for GaNAsSb are that the bandgap needs to be 1-eV and lattice-matched to GaAs. Using the BAC model and Vegard's law discussed in

Chapter 1, a N composition of 2.5% and a Sb composition of 6.5% was calculated to have a GaNAsSb material of bandgap 1-eV and to be lattice-matched to GaAs.

The composition of the GaNAsSb was calibrated on GaAs substrates where different N and Sb compositions were introduced. The growth structure consisted of 50nm of GaAs buffer, 50 nm of GaAsSb and 200 nm of GaNAsSb. The nitrogen flow rate was fixed at 0.25 sccm and 0.30 sccm, while for each flow rate, the nitrogen plasma power was changed from 200 W, 300 W to 400 W. The Sb reservoir and cracker were set at 540°C and 900°C, respectively. For each nitrogen flow rate, the Sb valve opening was set at 150, 200 and 250. Therefore, there will be six samples with different N and Sb compositions.

X-ray diffraction (XRD) is a fast and non-destructive tool to determine the nitrogen and antimony composition of the GaNAsSb material. The x-ray diffraction of a crystal structure can be defined by Bragg's Law,

$$\lambda = 2d_{h,k,l} \sin\theta \quad (1)$$

where θ is the angle of the incident x-ray with respect to the plane, λ is the wavelength of the x-ray and $d_{h,k,l}$ is the spacing between (hkl) planes. The d spacing is defined by

$$d_{h,k,l} = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (2)$$

where a is the lattice constant of the crystal and h , k and l are the Miller indices numbers.

The XRD spectra of the calibration samples were obtained by performing a (004) rocking curve scan using a hybrid monochromator coupled to the x-ray source. The XRD spectra was fitted with simulated curves using the X'pert Epitaxy software based on the dynamic diffraction theory of Halliwell *et al.*, as shown in Figure 2.3 [10].

Figure 2.3. Measured (blue) XRD (004) rocking curve of a calibration sample. The simulated (Red) XRD curve shows a N composition of 2.5% and Sb composition of 9.3%.

The measured XRD curve was first fitted using GaAsSb by varying the Sb composition until the measured and simulated peaks were aligned. Since during the growth of GaAsSb and GaNAsSb in the same sample, the Sb flux was unchanged, the Sb content in the two layers will be the same. Therefore, using the same Sb content from the GaAsSb layer, the measured GaNAsSb peak was fitted by varying the N composition. With the above method, the N and Sb compositions can be determined for all the samples. The nitrogen flow rate and plasma power that gives the N composition of 2.5% and antimony valve opening that gives the Sb composition of 6.5% will be used in the growth of the 1-eV GaNAsSb PV cell.

2.4. Post-Growth Fabrication

The first step of fabrication involves the blanket deposition of an n-type ohmic metal contact on the back of the sample. The metal deposition was done using a HHV FL400 ebeam evaporator. The back n-type ohmic metal contact consisted of Ti(5 nm)/Ge(25 nm)/Au(100 nm)/Ni(20 nm)/Au(100 nm). The back metal contact was

annealed at 400°C for 5s in a rapid thermal annealing (RTA) reactor. This step is required in making the back metal contact ohmic.

The next step is the metallisation of the top metal contacts. First, an image reversal photolithography was used to pattern the fingers and busbar for the PV cell as shown in Figure 2.4. Image reversal photolithography involves the spin coating of the photoresist, AZ 5214, at 4000 rpm for 30s. The sample with the photoresist was pre-baked at 105°C on a hot plate for 1 min and 45 secs. The samples were exposed to the pattern for about 2 secs using a Karl Suss Mask Aligner MJB4 with a UV wavelength source of 405nm. The exposed samples were baked in an oven at 110°C for 7 mins and 30 secs. After baking, the samples were flood exposed using the same mask aligner for about 11 secs. Finally, the samples were developed in a 1:2 AZ developer to water solution for about 45 secs or until the patterned part of the sample was clean. The samples with the patterned photoresist were blanket deposited with Ti(50 nm)/Au(200 nm) and the excess metal was lifted off by dipping the sample in acetone. The final top metal contact looked exactly as shown in Figure 2.4.

Figure 2.4. Mask of busbar and fingers for patterning of top contact. The values shown are the dimensions of the busbar and finger spacing.

The final step involved the mesa isolation of each PV cell device. The first step was the photolithography of the mesa isolation area where the steps involved were the same as described above except the photoresist AZ 1518 was used and no oven baking and flood exposure were required. The mask used is shown in Figure 2.5. However, alignment was required to ensure that the 2 mm x 2 mm square fully covered the cell. This was done by positioning the “plus” alignment marks on the mask centrally in the “square” alignment marks on the wafer throughout the whole sample. The patterned photoresist after developing looked exactly as shown in Figure 2.5. Therefore, only a 2 mm x 2 mm PV cell area with top metal contacts was protected by the photoresist. The PV cell devices were isolated by dipping the sample in a solution of $\text{H}_2\text{O}_2:\text{NH}_4\text{OH}:\text{H}_2\text{O}$ (4:10:1000). The unprotected sides were etched away at a rate of about 170 nm/min. A surface profiler was used to confirm that about 1.3 μm was etched away before removal of the protective photoresist by acetone. The samples were then ready for characterisation using a solar simulator.

Figure 2.5. Mask used in the photolithography for the mesa isolation of the PV cell devices.

2.5. Solar Simulator and Quantum Efficiency Characterisation

The PV cells underwent characterisation using a solar simulator to obtain the performance for each growth condition. The solar simulator simulated an AM1.5 global solar condition and was certified as Japanese Industrial Standards (JIS) Class A. It was calibrated based on its spectral coincidence with the AM1.5 global solar radiation over the range of 400 nm to 1100 nm as shown in Figure 2.6. The intensity of the solar simulator was calibrated to 1 sun (100 mW/cm^2) using a Si photodetector. The PV cell devices were probed on the front contact while the back contact rested on a copper base plate which was connected to another probe. The short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor and efficiency can be derived from the I-V curve through which the PV cells from different samples can be compared.

Figure 2.6. Comparison of the spectral irradiance of AM 1.5G and the light output from the solar simulator.

The PV cell devices were further characterised to obtain the QE curves. This was performed using a quartz tungsten halogen lamp coupled to a monochromator. The diameter of the output light source was larger than the PV cell; therefore, the light

source was channelled into a 20x objective lens. Using the spectral response of the Si and Ge photodetector, which was calibrated by the vendor, the light output responsivity through the objective lens was calibrated for the wavelength ranges of 400-1100nm and 1100-1800nm, respectively. The responsivity of the two detectors were joined at 1100 nm using the BenWin+ program and is shown in Figure 2.7.

To ensure maximum light fell on the PV cell, a specific wavelength (530 nm) of light source was used. The PV cell was connected to the source measurement unit with the voltage set to 0 V. By adjusting the X and Y position of the cell and the height between the cell and the objective lens, the current on the source measurement unit was maximised. This showed that maximum light was entering the cell. Measurement began once the cell was connected to the QE measurement equipment.

Figure 2.7. Responsivity of the Si and Ge detector joined at 1100 nm used in the quantum efficiency calculation of the PV cells.

The bandgap is derived by plotting $[h\nu \cdot \ln(1-EQE)]^2$ vs photon energy [11] [12]. Using the plot, the linear region of the lower photon energy region is extrapolated until it intersects the x-axis. The intersection point shows the bandgap of the material. The bandgap-voltage offset ($E_g/q-V_{OC}$) value was used in the comparison of the PV

cell from each sample. This is due to the change in the bandgap of each sample as the growth condition changed, which resulted in an inaccurate way of using the V_{OC} as a means of determining material quality. The bandgap, carrier lifetime and $E_g/q-V_{OC}$ are related by Equation (1),

$$\frac{E_g}{q} - V_{OC} \approx \frac{2k_B T}{q} \ln \left[\frac{q W N_c^{1/2} N_v^{1/2}}{J_{sc} \sqrt{\tau_p \tau_n}} \right] \quad (1)$$

where W is the total depletion width, N_c and N_v is the effective conduction and valence band density of states, τ_p and τ_n are the electron and holes minority lifetimes, respectively, and E_g is the bandgap of the material [13].

2.6. Capacitance-Voltage Characterisation

The depletion length of the PV cell can be derived from the C-V measurement. The samples were measured using a Keithley two-probe system which is based on Equation (2),

$$C_{DUT} = \frac{I_{DUT}}{2\pi f V_{AC}} \quad (2)$$

where f is the test frequency (1 MHz), V_{AC} is the measured AC voltage (30 mV) and I_{DUT} and C_{DUT} are the current and capacitance for the device under test (DUT), respectively. A schematic diagram of the test setup is shown in Figure 2.8. Using the capacitance when the DC bias voltage is at 0 V, the depletion length is calculated using Equation (3),

$$d = \frac{A\epsilon}{C} \quad (3)$$

where A is the area of the sample, d is the depletion length, C is the capacitance from the measured results and ϵ is the permittivity of the material (GaAs $\epsilon = 12.9$).

Figure 2.8. Schematic diagram of the C-V test setup.

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Chapter 3 Effects of Annealing Temperature and Time on GaNAsSb Photovoltaic Cell

3.1. Introduction

Kondow *et al.* reported that the *in situ* annealing of GaInNAs greatly improves the crystallinity of the material and blue shifts the bandgap [1]. The annealing aids in the removal of non-radiative centres, thus increasing the carrier lifetime. However, Makino *et al.* showed that a long annealing time decreases the photoluminescence (PL) intensity, especially at higher annealing temperatures [2]. Zhao *et al.* have also shown that the effects of annealing have greatly improved the PL and full width at half maximum (FWHM) for GaInNAsSb material for 1.55 μm laser application [3]. They reported a two-step annealing process that involves rapid thermal annealing and *in situ* annealing. The two-step annealing process increases the PL intensity more than a single step anneal process.

The annealing of a strained GaAsSb_{0.1}N_{0.08}/InP molecular quantum well has also been shown to have maximum PL intensity at an annealing temperature of 650°C [4]. Bharatan *et al.* have shown that, for the 1-eV GaN_{0.026}AsSb_{0.068} PV cell on a GaAs substrate, annealing *in situ* prevents N and As diffusion to the surface and improves Ga-N bonding, which contributes to the highest PL intensity as compared to *ex situ* annealing [5]. However, no work has been done to show the effects of annealing temperature and time on the performance of a 1-eV GaNAsSb PV cell.

In this chapter, we will discuss the effects of *in situ* annealing temperature and time on the performance of a GaNAsSb PV cell grown on a Si-Ge/Si substrate. The annealing temperatures are 650°C and 700°C. For each annealing temperature, three annealing times of 1 min, 5 mins and 10 mins are performed. During annealing, the

samples are under As overpressure. The As/Ga beam equivalent pressure ratio is fixed at 13 while the growth temperature of the GaNAsSb layer is fixed at 460°C. The nitrogen plasma power was set to 200 W with a nitrogen flow rate of 0.25 sccm and the antimony flux was fixed at $\sim 1.2 \times 10^{-7}$ Torr for all samples. These were calibrated to have a nitrogen and antimony composition of $\sim 2.5\%$ and $\sim 6.5\%$, respectively. The growth, fabrication and characterisation processes of the GaNAsSb PV cells were discussed in Sections 2.2, 2.4 and 2.5, respectively.

3.2. Results and Discussion

The light I-V curves of the GaNAsSb PV cells annealed at different temperatures and times are shown in Figure 3.1. A trend plot of the V_{OC} , J_{SC} and fill factor at a different annealing temperatures and times are shown in Figure 3.2 (a), (b) and (c), respectively. The J_{SC} shown here were measured without any anti-reflective coating (ARC). The increase in annealing time from 1 min to 5 mins for the annealing temperature of 700°C increased the V_{OC} from 0.45 V to 0.53 V and the fill factor from 52.9% to 56.5%. However, the J_{SC} for both samples remained at 15 mA/cm². A further increase in the annealing time to 10 mins greatly deteriorated the performance of the GaNAsSb PV cell, as seen by the drastic decrease in the V_{OC} , J_{SC} and fill factor. The GaNAsSb layer annealed at 650°C showed an increase in the V_{OC} from 0.36 V to 0.46 V, an increase in the J_{SC} from 14.1 mA/cm² to 14.8 mA/cm² and an increase in the fill factor from 45.6 % to 50.2 % with an increase in annealing time. The efficiency of the 1-eV GaNAsSb PV cells annealed at 650°C for 1min, 5min and 10 mins are 2.3%, 1.2% and 3.4%, respectively, while those that were annealed at 700°C for 1min, 5min and 10 mins are 3.7%, 4.5% and 0.5%, respectively. The best annealing condition was at 700°C for 5 mins. The best annealing time for the annealing temperature of 650°C was 10 mins.

Figure 3.1. Light I-V curve of the GaNAsSb PV cells annealed at different temperature and time.

Figure 3.2. Trend plots of the (a) V_{oc} , (b) J_{sc} and (c) fill factor values of the GaNAsSb PV cells annealed at different temperatures and times extracted from the I-V curves.

The quantum efficiencies (QE) of the GaNAsSb PV cell annealed at 650°C and 700°C at different times are shown in Figure 3.4 and Figure 3.5, respectively. The bandgaps extracted from the band edge of the QE curves of the annealed GaNAsSb PV cell are shown in Table 3.1. The QE for the GaNAsSb PV cell annealed at 700°C for 10 mins is not shown in Figure

3.5, as the performance was too poor and the bandgap cannot be extracted. The QE of the GaNAsSb PV cell matches that of the J_{SC} . It can be seen that, at the longer wavelength range; the QE is low for all samples. This could be due to the short diffusion length within the base. Figure 3.3 shows the band diagram of the 1-eV GaNAsSb PV cell. The photo-generated electron carrier that are formed in the p+ AlGaAs and p+ GaNAsSb layers will be swept by the internal electric field towards the n- GaNAsSb. In the n- GaNAsSb the electron will be a majority carrier. However, electrons generated in the top p+ GaAs layer were blocked by AlGaAs layer. Since most of shorter wavelength photons were absorbed in area close to the surface, carrier blocking of AlGaAs layer resulted in a low quantum efficiency at shorter wavelength region.

Figure 3.3 Band diagram of 1-eV GaNAsSb.

Figure 3.4. Plot of the quantum efficiency curves of the GaNAsSb material annealed at 650°C for 1 min, 5 mins and 10 mins.

Figure 3.5. Plot of the quantum efficiency curves of the GaNAsSb material annealed at 700°C for 1 min, 5 mins and 10 mins.

Bandgap (eV)			
Temperature	Time		
	1 min	5 mins	10 mins
650°C	1.08	1.07	1.10
700°C	1.08	1.09	-

Table 3.1. Bandgaps extracted from the band edge of the quantum efficiency curves of the annealed GaNAsSb PV cells at 650°C and 700°C for 1 min, 5 mins and 10 mins.

The $E_g/q-V_{OC}$ value is a better way of comparing PV cells with different bandgaps, which is an accurate way of representing material quality. A lower $E_g/q-V_{OC}$ values indicates a better material quality (longer carrier lifetime) with an ideal value of ~ 0.4 eV. The $E_g/q-V_{OC}$ value is defined by Equation (1)

$$\frac{E_g}{q} - V_{OC} \approx \frac{2k_B T}{q} \ln \left[\frac{q W N_c^{1/2} N_v^{1/2}}{J_{sc} \sqrt{\tau_p \tau_n}} \right] \quad (1)$$

where N_c and N_v are the effective conduction and valence band density of states, W is the total depletion width, E_g is the bandgap of the material and τ_p and τ_n are the electron and holes minority lifetimes [6].

The plot of the $E_g/q-V_{OC}$ values of GaNAsSb PV cells annealed at different temperatures and durations is shown in Figure 3.5. The $E_g/q-V_{OC}$ value of the GaNAsSb PV cell annealed at 700°C for 10 mins is not shown, as the bandgap cannot be obtained from the QE. The poor performance of the GaNAsSb PV cell annealed at 700°C for 10 mins is due to the high series resistance and low shunt resistance as shown by the almost linear $I-V$ curve in Figure 3.1. This device is deemed to have deteriorated possibly due to thermal damage [7]. Another reason for the deterioration of the PV cell at the annealing temperature of 700°C for 10 mins could be due to the diffusion of Ge within the Si-Ge graded buffer [8] [9] [10]. The Ge was reported to diffuse into Si. This process is assisted by the interstitial Si atom where it replaces a Ge atom from a lattice site and it requires lower energy than Ge diffusing directly in. The increase in Ge diffusion was found to increase with temperature and the Ge deposition amount. This process could have altered the composition of the Si-Ge graded buffer used in the substrate, which could have increased the dislocation density greatly. Dislocation within the layers acts as a recombination centre that decreases the carrier lifetime [10]. The lowest $E_g/q-V_{OC}$ value of 0.56 eV is obtained using an annealing temperature of 700°C for 5 mins. Annealing at 700°C for less than 5 mins could have greatly prevented further diffusion of Ge within the Si-Ge graded buffer, while at the same time improving the GaNAsSb material quality. The $E_g/q-V_{OC}$ values of all the samples are far from ideal, which could mean that the carrier lifetime is poor for all the samples. This can also be seen from the low QE curves in the long wavelength range, since the diffusion length is proportional to the carrier lifetime.

This could be due to the non-optimised growth conditions for the GaNAsSb material, which have increased nitrogen-related defects and arsenic antisite defects. The GaNAsSb layer will be further optimised in the later chapters.

Figure 3.6. Plot of the $E_g/q-V_{OC}$ values of GaNAsSb PV cells at annealing times of 1 min, 5 mins and 10 mins and annealing temperatures of 650°C and 700°C.

The plot of depletion width versus different annealing times for the annealing temperatures of 650°C and 700°C is shown in Figure 3.6. The depletion width of GaNAsSb PV cells annealed at 700°C for 10 mins is not shown, as the data obtained is erroneous.

The depletion width is affected by the effective doping concentration (n_{eff}) and is expressed as

$$n_{eff} = n_d + n_{uid} \quad (2)$$

where n_d is the intentional doping and n_{uid} is the unintentional doping. It can be seen that, with an increase in annealing time, the depletion width widens. This could be due to the reduction in defects like arsenic antisite defects and nitrogen related defects [11] [12]. Arsenic antisite defects have been reported to be donor type defects [13]. The decrease in arsenic antisite defects would have decreased the n_{uid} of the n-type base. Therefore, the n_{eff} of the n-type base will decrease, which leads to an increase in

depletion width. However, nitrogen related defects have been reported to be acceptor type defects [14]. The decrease in nitrogen related defects would have resulted in an increase in the n_{uid} , which would have decreased the depletion width. The increase in depletion width with an increase in annealing time as shown in Figure 3.6 could mean that there are more arsenic antisite defects than nitrogen related defects. This could be due to the low growth temperature required for the nitrogen incorporation. However, the growth of high quality GaAs is best at a high growth temperature [16] [17] [18], as low temperature grown GaAs has been shown to have a high concentration of arsenic antisite defects [17].

The reduction in defects due to annealing can also be seen in Figure 3.5 where there is a decrease in the $E_g/q-V_{OC}$ value as the annealing time increases. The presence of arsenic antisite defects have been reported to increase non-radiative recombination in dilute-nitride materials [15] [16]. While the presence of nitrogen in dilute-nitride materials have been known widely to reduce material quality due to nitrogen related defects [14] [17] [18] [19], the increase in annealing time could have allowed more of the above defects to be removed. Nevertheless a longer annealing time at a high annealing temperature could have deteriorated the PV junction.

Figure 3.7. The depletion width calculated from the capacitance-voltage measurement results of the GaNAsSb PV cells with different annealing temperatures and times.

3.3. Conclusion

The GaNAsSb PV cell annealed with a temperature of 700°C for 5 mins showed the highest energy conversion efficiency with a V_{OC} of 0.53 V and a J_{SC} of 15.3 mA/cm². It has the lowest $E_g/q-V_{OC}$ of 0.56 eV among the other samples, which implies that annealing at 700°C for 5 mins gives the best material quality. The increase in annealing time improves the GaNAsSb PV cell performance. However, the high annealing temperature of 700°C and the long annealing time of 10 mins results in the deterioration of the PV junction. The improvement in the PV performance can be attributed to the reduction in arsenic antisite defects and nitrogen related defects as the annealing time increases.

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Chapter 4 Effects of the As/Ga Ratio on 1-eV GaNAsSb Photovoltaic Cell

4.1. Introduction

The arsenic/gallium (As/Ga) ratio is important in the growth of dilute-nitride, as it has been reported that a low arsenic flux is favoured for the growth of InGaAsN for long wavelength laser applications [1]. The low arsenic flux condition is desired due to the low growth temperature required to minimise the formation of antisite defects, arsenic interstitials and gallium vacancies [2] [3] [4]. Both of these growth parameters increase the photoluminescence (PL) intensity. However, for the growth of GaAsN, it was reported that a high arsenic flux together with a high growth temperature increases the PL intensity, which shows an improvement in the electronic quality of the material [5]. The effects of different arsenic flux on a 1-eV GaNAsSb PV cell have not been reported before.

In this chapter, we will discuss the effects of As/Ga beam equivalent pressure (BEP) ratios on 1-eV GaNAsSb PV cells on Si-Ge/Si substrates. The As flux was increased from 4.2×10^{-6} to 5.5×10^{-6} , 6.7×10^{-6} , 7.9×10^{-6} and 8.3×10^{-6} Torr, which gave As/Ga BEP ratios of 10, 13, 16, 18 and 20, respectively. The growth temperature of the GaNAsSb layer was fixed at 460°C for all the samples while the *in situ* annealing temperature and time were fixed at 700°C for 5 mins. The nitrogen plasma was set at 300 W with a nitrogen flow rate of 0.25 sccm. The Sb BEP flux used was $\sim 1.6 \times 10^{-7}$ Torr. The nitrogen plasma and antimony BEP flux were calibrated to have a nitrogen and antimony composition of $\sim 2.5\%$ and $\sim 6.5\%$, respectively. The growth, fabrication and characterisation processes of the GaNAsSb PV cells were discussed in Sections 2.2, 2.4 and 2.5, respectively.

4.2. Results and Discussion

The 1-eV GaNAsSb PV cells grown with different As/Ga BEP ratios were characterised using the solar simulator and the light I - V curves as shown in Figure 4.1. A trend plot of the V_{OC} , J_{SC} and fill factor at different As/Ga BEP ratios is shown in Figure 4.2. With an increase in the As/Ga BEP ratio from 10 to 18, the V_{OC} of the PV cell decreased from 0.53 V to 0.43 V. However, when the As/Ga BEP ratio was increased to a maximum of 20, the V_{OC} increased to 0.59 V. The J_{SC} was about 17 mA/cm² for the As/Ga BEP ratios of 10 and 13. As the As/Ga BEP ratio increased to 18, the J_{SC} decreased to 13.7 mA/cm². However, with a further increase of the As/Ga BEP ratio to 20, the J_{SC} increased to 14.9 mA/cm². The J_{SC} values shown in this study were measured from devices without an anti-reflective coating (ARC). Therefore, with an ARC, the J_{SC} could be 20% higher [6]. The efficiencies of the PV cells were 6.1%, 6.0%, 3.8%, 2.8% and 5.7% for the As/Ga BEP ratios of 10, 13, 16, 18 and 20, respectively. The effects of the As/Ga BEP ratios will be discussed in detail later along with other results.

Figure 4.1. Light I - V curves of 1-eV GaNAsSb PV cells grown on Si-Ge/Si substrates at different As/Ga BEP ratios.

Figure 4.2. Trend plot of the (a) V_{oc} , (b) J_{sc} and (c) fill factor values extracted from the I-V curves of the I-eV GaNAsSb PV cells grown at different As/Ga BEP ratios.

The external quantum efficiencies (QE) of the GaNAsSb PV cells along with the bandgaps of the GaNAsSb PV cells are shown in Figure 4.3. It can be seen in Table 4.2 that the bandgap of the GaNAsSb PV cell increased with the increase in As/Ga BEP ratio. The increase in the bandgap could be due to the decrease in the incorporation of antimony and nitrogen. The decrease in incorporation occurred because of the increase in competition between the antimony, nitrogen and arsenic atoms for the group V atomic site as the arsenic flux increased. The increase in arsenic flux at higher As/Ga BEP ratios prevented the incorporation of nitrogen and antimony atoms, which caused the bandgap of the GaNAsSb PV cell to increase [7] [8] [9]. The difference in QE in the short wavelength range was due to the emitter diffusion length, which depended on the material quality of the GaNAsSb emitter layer as the As/Ga BEP ratio changed. Additionally, the variation in surface roughness affected the reflectivity of the sample: thus reducing the QE in the short wavelength range.

Figure 4.3. Plot of (a) quantum efficiencies and (b) bandgaps extracted from the quantum efficiency of GaNAsSb PV cells on a Si-Ge/Si substrate grown at different As/Ga BEP ratios.

As/Ga BEP ratio	10	13	16	18	20
Bandgap (eV)	1.03	1.05	1.08	1.08	1.10

Table 4.2. The bandgaps extracted from the band edge of the quantum efficiency curves of GaNAsSb PV cells on a Si-Ge/Si substrate grown at different As/Ga BEP ratios.

It can be seen in Table 4.2 that the bandgaps of the GaNAsSb PV cells increased with increased in As/Ga BEP ratio. Therefore, the value of V_{OC} is not a precise way of representing material quality. A better representation of material quality is by the $E_g/q-V_{OC}$ value as shown in Equation (1),

$$\frac{E_g}{q} - V_{OC} \approx \frac{2k_B T}{q} \ln \left[\frac{q W N_c^{1/2} N_v^{1/2}}{J_{sc} \sqrt{\tau_p \tau_n}} \right] \quad (1)$$

where N_c and N_v are the effective conduction and valence band density of states, W is the total depletion width, E_g is the bandgap of the material and τ_n and τ_p are the holes and electrons minority lifetimes [10]. The material quality/carrier lifetime can be compared using the $E_g/q-V_{OC}$ value of PV cells with different bandgaps. The smaller value of $E_g/q-V_{OC}$ indicates a longer carrier lifetime in the material with an ideal $E_g/q-$

V_{OC} value of ~ 0.4 eV for a high-quality material. The $E_g/q-V_{OC}$ value of the samples are shown in Figure 4.4.

Figure 4.4. Plot of $E_g/q-V_{OC}$ values of 1-eV GaNAsSb PV cell grown at different As/Ga BEP ratios

Figure 4.5. A comparison of this study's $E_g/q-V_{OC}$ value (red empty circle) with other published results for the dilute-nitride PV cell. All results were tested under the AM1.5 spectrum except for Ref. [10] which was tested under the AM0 spectrum.

The GaNAsSb PV cell grown with the As/Ga BEP ratio of 10 had the lowest $E_g/q-V_{OC}$ value of 0.50 eV. A further decrease in the As/Ga BEP ratio may not yield better $E_g/q-V_{OC}$ value as it was reported that with a low V/III ratio, the photoluminescence decreases [1]. The increase of the As/Ga BEP ratio to 18 showed an increase in the $E_g/q-V_{OC}$ value of 0.66 eV. The increase of the $E_g/q-V_{OC}$ value showed that the material quality of the GaNAsSb layer deteriorated as the As/Ga BEP ratio increased. This could be due to the formation of arsenic antisites (As_{Ga}) defects

in the material as the As/Ga BEP ratio increased during the GaNAsSb growth [11]. The increase in As_{Ga} defects has been reported to act as a non-radiative recombination site in dilute-nitride materials [12] [13].

However, with a further increase in the As/Ga BEP ratio to 20, the $E_g/q-V_{OC}$ value decreased. It should be noted that the GaNAsSb PV cell grown using the As/Ga BEP ratio of 20 had the largest bandgap of 1.10 eV compared to other samples. This could mean that this sample compared to the other four samples had the smallest nitrogen content [10] [14]. The decrease in nitrogen content could be due to the interaction between the arsenic, nitrogen and antimony atoms. As the amount of arsenic increases, the competition for the group V sites is harder for the nitrogen and antimony atoms. The presence of antimony is reported to enhance the incorporation efficiency of nitrogen in dilute-nitride materials [8] [7] [15]. The degradation of the dilute-nitride material quality due to the increase of nitrogen concentration is widely reported [14] [16] [17] [18]. Therefore, it is possible that the decrease in nitrogen concentration in the material resulted in a decrease in nitrogen-related defects. This can be seen in Figure 4.2 (a), (b) and (c). In addition, when the As/Ga BEP ratio increased from 18 to 20, the V_{OC} , J_{SC} , fill factor and QE increased. The increase in the GaNAsSb PV cell performance could be due to the decrease in nitrogen-related defects, which increased the carrier lifetime of the GaNAsSb material. The GaNAsSb PV cell seemed to favour the lower As/Ga BEP ratio of 10 to 13 rather than a higher As/Ga BEP ratio. The performance of the GaInNAs PV cell was also reported to increase at a lower V/III ratio [19] [20]. This could mean that the growth of a good dilute-nitride material may require a low V/III ratio.

The improvement of the GaNAsSb PV cell performance for an As/Ga BEP ratio between 18 to 20 does not imply a decrease in As_{Ga} defects. However, it indicates that

the decrease in nitrogen-related defects was more substantial than the increase in As_{Ga} defects.

The $E_g/q-V_{OC}$ values are plotted in Figure 4.5 against their respective bandgap energies for all the GaNAsSb PV cells done in this study along with other published results. The $E_g/q-V_{OC}$ values of the GaNAsSb PV cell reported here are lower compared to our previously published results of an identical structure [21]. The $E_g/q-V_{OC}$ value of 0.50 for the GaNAsSb material grown using the As/Ga BEP ratio of 10 is as good as the lowest reported 1-eV p-i-n GaInNAs junction PV cell on a GaAs substrate with an $E_g/q-V_{OC}$ value of 0.49. The GaNAsSb PV cell grown on the Si substrate demonstrated a similar material quality to other published dilute-nitrides grown on a GaAs substrate, but with the additional benefit of simple integration with other Si-based devices. The $E_g/q-V_{OC}$ values shown in Figure 4.5 (a) are smaller compared with other published dilute-nitride based PV cells [10] [20] [22] [23], including those that we previously published with a similar structure [21]. The improvement in the performance of the GaNAsSb PV cell could be due to the difference in the N and Sb composition used in this study, which creates a GaNAsSb that is closely lattice-matched with GaAs. The N and Sb compositions used in the previous study were 1.8% and 8.5%, respectively, which have a lattice strain of ~0.5% in the GaNAsSb material. However, the lattice strain in this study is 0.03%, 0.11%, 0.27%, 0.12% and 0.12% for the As/Ga BEP ratios of 10, 13, 16, 18 and 20, respectively. The decrease in residual strain could have reduced the dislocation density in the material. The performance of the PV cell could have been reduced by the dislocation, which is a non-radiative recombination site [24].

The GaNAsSb PV cell was also measured using an 850 nm long pass filter under the solar simulator at 1 sun AM1.5. This was to mimic the solar conditions of a triple

junction PV cell (InGaP/GaAs/GaNAsSb) above the 1-eV sub-cell. The GaNAsSb PV cell grown using an As/Ga BEP ratio of 10 had the highest J_{SC} of 7.8 mA/cm² without an ARC. This value is higher compared to our previously reported GaNAsSb PV cell on GaAs with a J_{SC} of 6.9 mA/cm² [21].

The junction depletion width derived from the C - V measurement of GaNAsSb PV cells grown with different As/Ga BEP ratios is shown in Figure 4.6. The junction depletion width is affected by the effective carrier concentration (n_{eff}). The higher the n_{eff} , the smaller the junction depletion width in the base region of the GaNAsSb layer and vice versa. The change in n_{eff} can be seen in Figure 4.6 for the different As/Ga BEP ratios. The n_{eff} was higher for the sample grown using the As/Ga BEP ratio of 20 compared to the As/Ga BEP ratio of 10, which had the lowest n_{eff} . The n_{eff} can be expressed as a function of intentional (n_d) and unintentional (n_{uid}) doping concentration,

$$n_{eff} = n_d + n_{uid} \quad (3)$$

The n-type doping concentration was unchanged during growth at 2×10^{16} cm⁻³ for all samples. However, there was an increase in n_{uid} as the As/Ga BEP ratio increased. This is because of the change in the n_{uid} of the GaNAsSb layer as the As/Ga BEP ratio changed. The increase in n_{uid} could be due to the increase in As_{Ga} defects, which is a donor type defect [25]. This will result in an increase in the n-type n_{eff} or a decrease in the depletion width with an increase in the As/Ga BEP ratio [26].

Figure 4.6. Plot of the junction depletion width versus the As/Ga BEP ratio used in the growth of GaNAsSb PV cells. The depletion width results were derived from CV measurement data.

The decrease in nitrogen related defects might be another reason for the increase in n_{uid} as the As/Ga BEP ratio increased. The decrease in nitrogen composition as the As/Ga BEP ratio increased can be seen in Figure 4.3 (b). The decrease in nitrogen content decreased the nitrogen related defects in the GaNAsSb layer, which were reported to be acceptor type defects [14]. The nitrogen related defects would have counteracted the n_d in the GaNAsSb material. Thus, the higher As/Ga BEP ratio used in the growth of the GaNAsSb layer resulted in lower nitrogen related defects, which increased the n-type n_{eff} or narrowed the depletion width in the PV cell.

The antimony and nitrogen content for all the GaNAsSb PV cells were estimated using XRD and the BAC model and are shown in Figure 4.7 (a) while the arsenic content was calculated using the nitrogen and antimony content and is shown in Figure 4.7 (b) [27]. It can be seen that the nitrogen content decreased with the increase in the As/Ga BEP ratio, which supports our hypothesis. The decrease in nitrogen and antimony content between the As/Ga BEP ratios of 10 to 18 indicated an increase in the arsenic content in the GaNAsSb layer. This justified the increase in the $E_g/q-V_{OC}$ value due to the increase in As_{Ga} defects.

Figure 4.7. (a) Graph of the nitrogen (triangle), antimony (circle) and (b) arsenic (circle) content of the GaNAsSb layers grown using different As/Ga BEP ratios.

The increase in arsenic incorporation that results in an increase in As_{Ga} defects is further proven by comparing the plot of depletion width (Figure 4.6) with the plot of arsenic content (Figure 4.7 (b)) of GaNAsSb layers grown using a different As/Ga BEP ratio. The effect of arsenic on the n_{uid} in the GaNAsSb layer is the strongest, as it is the highest content compared to the antimony or nitrogen content. This effect can be seen for the As/Ga BEP ratio of 16 and 18 where the arsenic content decreased and the depletion width increased. These changes show that the GaNAsSb material might be sensitive to As_{Ga} defects, which might be due to the low temperature growth required for GaNAsSb. This forms a dilemma as a high growth temperature is required

for GaAs growth with low As_{Ga} defects while a low growth temperature is required for nitrogen incorporation [28] [29] [30].

4.3. Conclusion

The GaNAsSb PV cell grown in this study using an As/Ga BEP ratio of 10 had the highest energy conversion efficiency with a J_{SC} of 17 mA/cm² and a V_{OC} of 0.53 V. It is comparable with other dilute-nitride PV cells with an $E_{\text{g}}/q-V_{\text{OC}}$ of 0.50 eV. This shows that the GaNAsSb material grown on a Si substrate has excellent material quality compared to the results published by other groups. The increase of As_{Ga} defects was identified to decrease the carrier lifetime as the As/Ga BEP ratio increased from 10 to 18. However, a further increase of the As/Ga BEP ratio to 20 resulted in a decrease in nitrogen incorporation. This is due to a reduction in nitrogen related defects, which improves the quality of the GaNAsSb material.

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Chapter 5 Effects of Substrate Temperature on the 1-eV GaNAsSb Photovoltaic Cell

5.1. Introduction

The growth temperature of the GaNAsSb material is important in controlling the number of defects in the material. As discussed in the previous chapter, GaAs growth requires a high growth temperature to minimise arsenic antisite (As_{Ga}) defects while a low temperature growth is preferred for nitrogen incorporation [1] [2] [3]. For the growth of GaInNAs and GaAsN material, it was reported that the photoluminescence (PL) peak intensity and electron mobility was higher when grown at the substrate temperature of 520°C rather than 480°C even after annealing [4] [5]. However, it was reported that the XRD FWHM and intensity peaks improved when the substrate temperature was lowered to 360°C [4]. For GaInNAs PV cells grown at a substrate temperature of 440°C, Aho et al. reported the maximum output power for nitrogen concentrations of 1%, 2% and 3% [6]. Another study done on GaNAsSb material showed a decrease in the PL intensity as the substrate temperature increased from 475°C to 575°C [7].

In this chapter, we will discuss the effects of substrate temperature on the performance of GaNAsSb PV cells grown on a Si-Ge/Si substrate. The substrate temperature increased from 420°C, 460°C, 500°C to 530°C. The annealing temperature and duration was fixed at 700°C for 5 mins, while the As/Ga beam equivalent pressure ratio was fixed at 13. The nitrogen plasma was set at 300 W with a nitrogen flow rate of 0.25 sccm. The Sb BEP flux used was $\sim 1.6 \times 10^{-7}$ Torr. These were calibrated to have a nitrogen and antimony composition of $\sim 2.5\%$ and $\sim 6.5\%$, respectively. The growth, fabrication and characterisation processes of the GaNAsSb PV cells were discussed in Sections 2.2, 2.4 and 2.5, respectively.

5.2. Results and Discussion

The GaNAsSb PV cells grown at different substrate temperatures were measured under the one sun condition, and the light I - V curves are shown in Figure 5.1. The V_{OC} and J_{SC} values versus the different substrate temperatures used are shown in Figure 5.2. With an increase in the substrate temperature from 420°C to 530°C, the J_{SC} decreased from 18 to 13 mA/cm². In contrast, the change in V_{OC} was small from 0.53 V to 0.54 V as the substrate temperature increased from 420°C to 530°C. The change in the fill factor was insignificant when the substrate temperature increased from 420°C to 460°C and from 500°C to 530°C. However, there was a decrease of 7% in the fill factor when the substrate temperature increased from 460°C to 500°C. The efficiency of the 1-eV GaNAsSb PV cell grown with growth temperature of 420°C, 476°C, 500°C and 530°C are 6.4%, 6.0%, 5.1% and 4.1%, respectively. The J_{SC} values stated in this study were measured without any anti-reflective coating (ARC). Therefore, with ARC, the J_{SC} could be about 20% higher [8].

Figure 5.1. Light I - V curves of GaNAsSb PV cells grown at different substrate temperatures.

Figure 5.2. Trend plot of the (a) V_{oc} and (b) J_{sc} extracted from I-V curves of I-eV GaNAsSb PV cells at different substrate temperatures.

The quantum efficiency curves and the bandgap of the GaNAsSb PV cells grown at different substrate temperatures are shown in Figure 5.3 and Table 5.3, respectively. A red shift of the cut-off wavelength can be seen as the substrate temperature decreased.

Figure 5.3. Graph of the quantum efficiency (QE) curves of GaNAsSb PV cells grown at different substrate temperatures.

Growth Temperature (°C)	420	460	500	530
Bandgap (eV)	1.05	1.06	1.08	1.10

Table 5.3. Bandgap extracted from the band edge of the quantum efficiency for I-eV GaNAsSb PV cell grown at different substrate temperatures.

The use of V_{OC} values to compare PV cells is not a precise way of determining material quality, as the V_{OC} value is dependent on the bandgap energy and material quality. This can be seen in Equation (1)

$$\frac{E_g}{q} - V_{OC} \approx \frac{2k_B T}{q} \ln \left[\frac{q W N_c^{1/2} N_v^{1/2}}{J_{sc} \sqrt{\tau_p \tau_n}} \right] \quad (1)$$

where E_g is the bandgap of the material, τ_p and τ_n are the electron and hole minority lifetimes, W is the total depletion width and N_c and N_v are the effective conduction and valence band density of states [19].

Figure 5.4. Plot of $E_g/q - V_{OC}$ values versus substrate temperatures used for the growth of the GaNAsSb layers.

The $E_g/q - V_{OC}$ value as shown in Equation (1) is a better way of indicating the material quality of the PV cell. A smaller $E_g/q - V_{OC}$ value indicates a longer carrier lifetime, where an ideal $E_g/q - V_{OC}$ value is ~ 0.4 eV [6] [20]. The plot of $E_g/q - V_{OC}$ value with respect to the substrate temperature is shown in Figure 5.4. The material quality or the carrier lifetime of the GaNAsSb layers degraded with increasing substrate temperature as shown by the increase in the $E_g/q - V_{OC}$ value.

The decrease in the bandgap of the GaNAsSb PV cell could be due to the variation in the incorporation rate of nitrogen and antimony as the substrate temperature decreased [9] [10] [11]. The QE curves of the GaNAsSb PV cells decreased with an increase in substrate temperature, which could be due to the

deterioration of the GaNAsSb layer. This could be due to the increase in the phase separation and segregation of the nitrogen atoms within the GaNAsSb layer due to the solid-solubility of nitrogen [12] [13]. Kovash *et al.* showed the phase diagram of GaAsN over a range of substrate temperature and growth rates using a RHEED pattern [14]. The RHEED construction pattern at high temperature changed from 2 x 4 to 3 x 3, and this was reported to indicate the formation of a nitrogen-rich surface [15]. The increase in nitrogen clusters increases nitrogen-related defects: thus reducing the performance of the PV cell [12] [16] [17] [18]. The increase in the substrate temperature and nitrogen incorporation of GaAsN decreases the electron mobility due to the acceptor-like scattering centres, which are due to nitrogen defects [17] [16].

A previous study of GaInNAs reported the presence of nitrogen segregation at high substrate temperature [21]. The rough surface at a high substrate temperature was proposed to be due to nitrogen segregation, which enhances the lateral segregation of indium atoms. However, for GaNAsSb, nitrogen segregation still occurred, and without indium atoms, the surface after growth was smooth but the PV cell performance deteriorated. Additionally, it was reported that the decrease in PL intensity for GaAsN was due to the presence of nitrogen clusters. The PL intensity is dependent on the carrier lifetime, where a decreased carrier lifetime decreases the PL intensity. An increase in the nitrogen content in the GaAsN layers increases the nitrogen-related defects, which act as electron-scattering centres that reduce the free-carrier concentration and mobility [17]. Material degradation caused by carrier scattering from the nitrogen clusters is suggested to be more significant than ionised impurity. All these factors resulted in a decrease in QE and an increase in the E_g/qV_{OC} value as the substrate temperature increased.

The increase in substrate temperature reduced the antimony incorporation rate into the GaNAsSb material. It was reported that antimony atoms have a higher desorption rate at a higher substrate temperature [7] [11]. This can be seen by the increase in bandgap energy as the growth temperature increases, as shown in Table 5.3. The SIMS analysis also showed a decrease in antimony composition from 6.4% to 1.9% as the substrate temperature increased from 420°C to 530°C as shown in Figure 5.5. The SIMS analysis showed the nitrogen concentration was fixed at 2.2% even when the substrate temperature increased from 420°C to 530°C. This was also observed in a similar study done on GaNAsSb at different substrate temperatures [7].

Figure 5.5. SIMS analysis of the GaNAsSb layers for Ga, As, N and Sb compositions grown at substrate temperatures of 420°C (a) and 530°C (b). A, B and C correspond to the layers of GaAs, AlGaAs and GaNAsSb, respectively.

The (115) reciprocal space maps (RSMs) of the GaNAsSb PV cells grown using different substrate temperatures are shown in Figure 5.6. The circle and square indicate the GaAs and GaNAsSb layer peaks, respectively. The GaNAsSb layer for the substrate temperature of 420°C to 500°C is fully strained with respect to the GaAs. However, for the substrate temperature of 530°C, the degree of relaxation of the GaNAsSb layer is about 0.5%. Additionally, phase separation can be seen from the RSM scans for 1-eV GaNAsSb PV cells grown at 500°C and 530°C, due to the broadening of the GaNAsSb peak. This could be due to the nitrogen separation at high

growth temperature. These factors could have further decreased the performance of the PV cell.

Figure 5.6. (115) RSM scans of GaNAsSb PV cells grown at substrate temperatures of 420°C (I), 460°C (II), 500°C (III) and 530°C (IV). The square represents the GaNAsSb layer peak while the circle represents the GaAs layer peak.

5.3. Conclusion

The highest energy conversion efficiency GaNAsSb PV cell was grown at the substrate temperature of 420°C with the V_{OC} of 0.53 V and the J_{SC} of 18 mA/cm². The increase in the bandgap of the GaNAsSb PV cell was due to the decrease in antimony incorporation from 6.4% to 1.9% as the substrate temperature increased from 420°C to 530°C. The change in antimony content for the substrate temperature between 420°C to 500°C did not influence the lattice relaxation between the GaNAsSb and GaAs layers. However, for the substrate temperature of 530°C, there was ~0.5% relaxation, which deteriorated the performance of the GaNAsSb PV cell. Additionally, the increase in nitrogen phase separation and segregation as the substrate temperature increased decreased the performance of the GaNAsSb PV cell.

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Chapter 6 Bandgap Optimization of Quadruple Junction Photovoltaic Cell Efficiency

6.1. Introduction

Kurtz *et al.* reported on modelling calculations done for a triple junction PV cell with a bottom bandgap of 1.00 eV to 1.05 eV. The maximum efficiency can be increased to about 38%. This is higher than the typical triple junction PV cell (GaInP, Ga(In)As, Ge) by about 7% [1]. Moreover, with the addition of a Ge sub-cell to the above simulated triple junction configuration (1.9/1.4/1.0 eV), the efficiency can be further increased to over 40% under the AM0 (1 sun) spectrum and to over 50% under the AM1.5D (500 suns) spectrum.

The increase in efficiency for a quadruple junction PV cell is due to the 1-eV sub-cell absorbing a part of the Ge sub-cell's spectrum as shown in Figure 6.1. This will result in an increase in voltage output and thus efficiency, while at the same time allowing current matching conditions for all the sub-cells. However, the above discussion assumes that each sub-cell has close to a 100% quantum efficiency (QE). The QE of different 1-eV dilute-nitride based PV cells that are lattice-matched to GaAs are shown in Figure 6.2 [2] [3] [4] [5]. The poor material quality of the dilute-nitride results in a non-ideal QE. Therefore, to obtain maximum cell efficiency for a PV cell using realistic 1-eV sub-cell performance, optimisation of the top two sub-cell bandgaps is required to compensate for the low QE of the 1-eV sub-cell.

Figure 6.1. The plot of the approximate current produced by each sub-cell if the AM1.5G spectrum was divided into 3 sections and 4 sections representing a triple junction (1.9/1.4/0.7 eV) PV cell and a quadruple junction (1.9/1.4/1.0/0.7 eV) one, respectively.

Figure 6.2. Plot of quantum efficiencies of different published 1 eV dilute-nitride based PV cells that are lattice-matched to GaAs PV cells.

In this study, we report on the modelling results of a quadruple junction PV cell using previously reported experimental 1-eV GaNAsSb PV cell results [6]. The 1-eV sub-cell was placed in a typical triple junction PV cell (InGaP/Ga(In)As/Ge) between the Ga(In)As and Ge sub-cells: thus forming a quadruple junction PV cell.

6.2. Theoretical Modelling

The principle of the detailed balance limit was used in the modelling of the quadruple junction PV cell efficiency along with the following assumptions:

- Radiative loss is the only loss mechanism in the sub-cell.

- Photons with energy levels higher than the bandgap of the sub-cell will be absorbed by the sub-cell.
- Photons with energy levels lower than the bandgap of the sub-cell will be transmitted through the sub-cell.
- The photon energy that is higher than each of the top two sub-cell bandgaps will be fully absorbed by each of the sub-cells. None of it will be transmitted down to the bottom two sub-cells.
- Unabsorbed photon energy larger than the third sub-cell bandgap will be transmitted to the fourth sub-cell. The optimum base thickness for the third sub-cell is $<1\mu\text{m}$. Therefore, a considerable number of photons between 1.0 eV to 1.4 eV will not be absorbed.
- The respective QE levels of the top two sub-cells remain the same while the absorption edge is adjusted to meet the bandgaps of the top two sub-cells.
- The one sun open circuit voltage (V_{OC}) of each sub-cell is defined by Equation (1)

$$V_{OC} = E_g - 0.4 \quad (1)$$

- The current density-voltage (J-V) of a sub-cell is defined by the ideal-diode equation, as shown in Equation (2)

$$J(V) = J_L - J_o \left(e^{\frac{qV}{kT}} - 1 \right) \quad (2)$$

where

$$J_o = 0.1 \frac{2q\pi}{h^3 c^2} \left[kT \sqrt{E_g q} - 2(kT)^2 (E_g q) + 2(kT)^3 \right] e^{\frac{-E_g q}{kT}} \quad (3)$$

where J_L is the light-generated current, J_o is the dark saturation current, q is the elementary charge, V is the voltage, T is the cell temperature, k is the Boltzmann

constant, E_g is the bandgap of the material, c is the speed of light and h is the plank's constant. A diode ideality factor of 1 is assumed in Equation (2) [7].

The AM1.5 global solar spectrum from the ASTM G-173-03 reference standard was used in the calculation of the light-generated current (J_L). The photon flux ($F(\lambda)$) (no. of photons/m²/s) is defined by Equation (4)

$$F(\lambda) = \frac{P(\lambda)}{hc/\lambda} \quad (4)$$

where λ is the wavelength of the photon, c is the speed of light, h is the plank's constant and $P(\lambda)$ is the power (W/m²/nm) of the incident photon obtained from the AM1.5 global solar spectrum. J_L can be calculated for a specific bandgap (E_g) material by integrating Equation (4) over a range of wavelengths,

$$J_L = \frac{q}{hc} \int_{\lambda_o}^{\lambda_{Eg}} P(\lambda) \lambda \, d\lambda \quad (5)$$

where λ_{Eg} is the wavelength converted from the bandgap of the material and λ_o is the wavelength at the band edge.

The sub-cells in a multi-junction PV cell are connected in series and therefore have the same current density (J). Thus the power density in an n-junction PV cell is defined by Equation (6)

$$P_n(J) = 0.9 \times J \sum_i V_{oc} \quad (6)$$

The efficiency of the multi-junction PV cell can be calculated using Equation (7)

$$\eta = \frac{P_n}{P_{in}} \quad (7)$$

where P_{in} is the power density of the incident light on the solar cell. The 0.9 in Equation (6) represents the fill factor. This value was used as many published multi-junction PV cells have a fill factor close to 90% [8] [1] [9] [10].

This modelling study will use our previously reported 1-eV GaNAsSb PV cells grown on Si-Ge/Si substrate external QEs as shown in Figure 6.3 to calculate the appropriate top two sub-cell bandgaps for maximum efficiency [6]. The QE of the best GaNAsSb PV cell has been adjusted 30% to account for the lack of anti-reflective coating.

Figure 6.3. Plot of the experimental quantum efficiency curves of GaNAsSb PV cell grown on a Si-Ge/Si substrate (adjusted to compensate for anti-reflective coating).

The low QE is because of the presence of nitrogen-related defects and the low substrate temperature of the GaNAsSb layer, which increases the arsenic antisite defects [11] [12]. The low QE will have a low J_{SC} , which will result in the 1-eV sub-cell current limiting the whole quadruple junction PV cell. A solution to this would be to decrease the J_{SC} of the top two sub-cells while at the same time increasing the J_{SC} of the 1-eV sub-cell to ensure proper current matching. This can be done by increasing the bandgap of the top two sub-cells, thus allowing more light to be transmitted to the 1-eV sub-cell. This study will calculate the bandgap of the top two sub-cells to give maximum energy conversion efficiency.

In order to have a realistic QE, previously published results of GaAs, GaInP and Ge were extracted and are shown in Figure 6.4. These were used in the calculation of the intensity of light that will be absorbed by the respective sub-cells as shown in Figure 6.5. These intensities were used to calculate the bandgap required of the top two sub-cells to have maximum efficiency for a quadruple junction PV cell.

Figure 6.4. The published quantum efficiencies of GaInP, GaAs, GaNAsSb and Ge sub-cells [9] [13] [14].

Figure 6.5. The spectrum of light that will be absorbed by the GaInP, GaAs, GaNAsSb and Ge sub-cells, which are calculated from the quantum efficiencies from published results.

6.3. Results and Discussion

The calculated efficiencies of the quadruple junction PV cells using different first and second sub-cell bandgaps is shown in Figure 6.6. The bottom two sub-cell bandgaps were set at 1.03 eV and 0.66 eV, respectively. The calculation of the J_{SC} and V_{OC} was done using Equations (1) and (2). The efficiencies of the quadruple junction with the respective first and second junction bandgaps were calculated using Equations (6) and (7). With the first sub-cell bandgap of 2.00 eV and the second sub-cell bandgap of 1.56 eV, the highest efficiency of 38.8% was obtained.

Figure 6.6. Plot of efficiency versus different first and second sub-cell bandgap for a quadruple junction PV cell. The bottom two sub-cells were fixed at 1.03 eV and 0.66 eV, respectively.

The increase in the second sub-cell bandgap while the first sub-cell bandgap was fixed led to a reduction in efficiency. This was due to the reduced solar spectrum available for the second sub-cell to absorb. Therefore, the J_{SC} of the second sub-cell decreased and it current limited the quadruple junction PV cell: thus decreasing the efficiency. In contrast, a decrease in the bandgap of the second sub-cell resulted in a reduced solar spectrum for the 1-eV sub-cell to absorb. The 1-eV sub-cell thus current limited the quadruple junction PV cell. When the J_{SC} values of each of the sub-cells were almost identical, the quadruple junction PV cell had the highest efficiency.

The calculated first and second sub-cell bandgaps shown above are larger than the typical monolithically grown triple junction PV cell. This increase in the bandgaps of the first and second sub-cells allows more light for the 1-eV sub-cell to absorb, thereby increasing the J_{SC} of the 1-eV sub-cell and at the same time decreasing the J_{SC} of the top two sub-cells. Table 6.4 shows the calculated efficiency of the quadruple junction before and after optimisation. The optimisation is necessary due to the low QE of the 1-eV sub-cell. A quadruple junction before optimisation (1.87/1.42/1.03/0.66 eV) consisting of the low QE 1-eV sub-cell in a typical triple junction configuration is predicted to have an efficiency of 26.4%. This efficiency is lower than the calculated two and triple junction PV cells without the 1-eV sub-cell. The low efficiency of the non-optimised quadruple junction PV cell is due to the current limiting the 1-eV sub-cells, which have a current density of 8.6 mA/cm². The optimised quadruple junction PV cell will have a bandgap configuration of 2.00/1.56/1.03/0.66 eV with an increase in efficiency of up to 38.8%. The quadruple junction PV cell is predicted to have a V_{OC} of 3.65 V, a J_{SC} of 11.8 mA/cm² and a fill factor of 90%. The efficiency is higher than other multi-junction PV cells lattice matched to GaAs [15].

PV cell	J_{SC} (1 sun) (mA/cm²)	V_{OC} (V)	FF	$Efficiency$
Two junction [1.87/1.42],	13.6	2.49	90%	30.5 %
Three junction [1.87/1.42/0.66],	13.6	2.75	90%	33.7%
Non-optimized quadruple junction [1.87/1.42/1.03*/0.66 eV], with 1- eV GaNAsSb sub cell	8.6	3.41	90%	26.4%
Optimized quadruple junction [2.00/1.56/1.03*/0.66 eV], with 1- eV GaNAsSb sub cell	11.8	3.65	90%	38.8%

Table 6.4. Calculated quadruple junction efficiency before and after being optimized. The symbol * indicates the 1-eV GaNAsSb PV sub-cell.

The quadruple junction PV cell with a bandgap configuration of 2.00/1.56/1.42/0.66 eV was further calculated under different solar concentrations as shown in Figure 6.7. Each sub-cell J_{SC} is assumed to linearly increase with the number of suns. The V_{OC} is calculated using Equation (8),

$$V_{OC} = \frac{kT}{q} \ln \left(\frac{xJ_L}{J_0} - 1 \right) \quad (8)$$

where J_0 and J_L are calculated using Equations (3) and (5) and x is the number of suns. The efficiency for a particular solar concentration can be calculated using Equations (6) and (7) where P_{in} increases linearly with the number of suns. The efficiency of the optimised quadruple PV cell can be boosted to 49% at 500 suns, which is higher than other reported multi-junction PV cells under concentrated suns and with a PV cell temperature of 298K.

Figure 6.7. Calculated efficiency of the optimised quadruple junction PV cell under different solar concentrations.

6.4. Conclusion

An energy conversion efficiency of 38.8% can be attained using the 1 eV GaNAsSb sub-cell in a quadruple junction PV cell with an optimised bandgap configuration. The quadruple junction PV cell consists of a first junction bandgap of 2.00 eV, a second junction bandgap of 1.56 eV, a third junction bandgap of 1.03 eV and a fourth junction bandgap of 0.66 eV. This quadruple junction PV cell bandgap configuration is higher than the previously reported quadruple junction PV cell bandgap configuration because of the low QE of the 1 eV GaNAsSb sub-cell. The increase in the bandgap of the top two sub-cells allows more light to be transmitted to the 1 eV sub-cell to increase the J_{SC} . The optimised quadruple junction PV cell has a V_{OC} of 3.42 V, a J_{SC} of 11.8 mA/cm² and a fill factor of 90%. The efficiency can be boosted to 49% under 500 suns.

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Chapter 7 Optimisation of 1.56 eV AlGaAs PV Cell

3.4. Introduction

In the previous chapter, we showed that in order to have a maximum efficiency of 38.8% for a quadruple junction PV cell using the 1-eV GaNAsSb sub-cell, the first and second junction bandgaps must be 2.00 eV and 1.56 eV, respectively. In order to achieve a bandgap of 1.56 eV for the second sub-cell, Al_{0.11}GaAs was chosen as it is also lattice-matched to GaAs. This composition of Al_{0.11}GaAs for PV cell application has not been widely researched on. Most researched MBE grown AlGaAs PV cell have an aluminium composition of >15% [1] [2]. Therefore, in this chapter, we will discuss the effects of substrate temperature and V/III ratio on Al_{0.11}GaAs PV cells grown on GaAs and Si-Ge/Si substrates.

The increase in substrate temperature have been reported to increase the efficiency of the 1.7-eV AlGaAs PV cell with an optimum substrate temperature of 660°C [1]. At the optimal substrate temperature of 660°C, the AlGaAs PV cell was reported to have smaller bulk recombination rates which might have suggested a decrease in the density of energy states in the mid-gap. It was reported for Al_{0.20}GaAs, the increase in the substrate temperature decreases the group III site vacancies or their complexes [3]. A decrease in these defects increases the photoluminescence (PL) intensity of the AlGaAs material.

A V/III ratio of 18 was shown to have the highest PL intensity for Al_{0.20}GaAs material compared to a V/III ratio of 29, which showed a diminished PL intensity [4]. Yamanaka *et al.* reported that a decrease in the V/III ratio leads to a decrease in arsenic antisite defects, which improves the PL intensity of the AlGaAs material [3]. This may indicate that AlGaAs with a <20% aluminium content requires a low V/III ratio to achieve good quality material.

In this chapter, we will discuss the 1.56-eV $\text{Al}_{0.11}\text{GaAs}$ PV cell performance grown with different substrate temperatures and V/III ratios. The substrate temperature was varied from 580 °C to 680 °C and the V/III ratio was varied from 10 to 15 to 18. The V/III ratio was varied by increasing the As flux from 4.4×10^{-6} to 6.6×10^{-6} to 8.0×10^{-6} Torr. The AlGaAs PV cells were grown on both GaAs and Si-Ge/Si substrates. The structure of the AlGaAs PV cell along with the doping concentration and thickness of the respective layers are shown in Figure 7.1. The growth, fabrication and characterisation processes of the GaNAsSb PV cells were discussed in Sections 2.2, 2.4 and 2.5, respectively.

Figure 7.1. Schematic diagram of the AlGaAs PV cell structure grown on (right) a GaAs substrate and (left) a Si-Ge/Si substrate.

3.5. Results and Discussion

The light I - V curves of the AlGaAs PV cells grown on GaAs and Si-Ge/Si substrates with different substrate temperatures and V/III ratios are shown in Figure 7.2 and Figure 7.3, respectively. The AlGaAs PV cells grown with different V/III ratios were all grown with a substrate temperature of 680°C. In contrast, the AlGaAs PV cells grown with different substrate temperatures were all grown with a V/III ratio of 10. The AlGaAs PV cells were characterised without an anti-reflective coating (ARC). The efficiency of the AlGaAs PV cell grown on GaAs substrate with growth temperature of 680°C, 630°C and 580°C are 7.3%, 5.3% and 4.8%, respectively, while those that were grown with V/III ratio of 10, 15 and 18 are 7.3%, 7.4% and 7.3%, respectively. The efficiency of the AlGaAs PV cell grown on Si-Ge/Si substrate with growth temperature of 680°C, 630°C and 580°C are 0.4%, 3.6% and 4.2%, respectively, while those that were grown with V/III ratio of 10, 15 and 18 are 0.4%, 3.4% and 3.1%, respectively.

Figure 7.2. Light I - V curves of AlGaAs PV cell grown using a V/III ratio of 10 and different substrate temperatures on (a) a GaAs substrate and (b) a Si substrate.

Figure 7.3. Light I-V curves of AlGaAs PV cell grown using a substrate temperature of 680°C and different V/III ratios on (a) a GaAs substrate and (b) a Si substrate.

The increase of substrate temperature from 580°C to 680°C showed an increase in V_{OC} from 0.73 V to 0.96 V for AlGaAs PV cell grown on GaAs substrate. However, the increase in substrate temperature did not have a significant effect on the J_{SC} . The rise in substrate temperature was reported to reduce the group III site vacancies or their complexes [3]. This type of defect is inherent for aluminium containing GaAs and was not observed in MBE grown pure GaAs. The formation of group III site vacancies is favoured at low substrate temperatures due to the lower mobility of Al compared to Ga. The best AlGaAs PV cell on GaAs substrate performance is with a substrate temperature of 680°C, which is close to the reported optimal substrate temperature of 660°C for a 1.7-eV AlGaAs PV cell on GaAs [1]. This suggests that AlGaAs on a GaAs substrate with the aluminium content of <20% has an optimal substrate temperature between 660°C and 680°C.

The increase of substrate temperature from 580°C to 630°C for the AlGaAs PV cell grown on the Si-Ge/Si substrate only showed a slight increase in the J_{SC} and V_{OC} from 10.0 mA/cm² to 10.3 mA/cm² and from 0.67 V to 0.68 V, respectively. However,

with a further increase in substrate temperature to 680°C, the V_{OC} and J_{SC} decreased to 0.17 V and 9.9 mA/cm², respectively.

The increase of V/III ratio from 10 to 15 showed an increase in V_{OC} from 0.96 V to 0.99 V for AlGaAs PV cell grown on GaAs substrate as shown in Figure 7.3(a). With a high V/III ratio of 18, there was no effect on the V_{OC} . The increase in the V/III ratio from 10 to 15 showed no change in the J_{SC} of 10.0 mA/cm² for both samples. However at high V/III ratio of 18, the J_{SC} decreases to 9.6 mA/cm².

The increase of the V/III ratio from 15 to 18 for the AlGaAs PV cell grown on the Si-Ge/Si substrate decreased the V_{OC} and J_{SC} slightly from 0.73 to 0.72 V and 9.4 to 9.2 mA/cm², respectively. However, at the V/III ratio of 10, the AlGaAs PV cell had the poorest performance, as shown by the low V_{OC} of 0.17 V. This result suggests that the material quality of the AlGaAs layer is very poor. The low AlGaAs material quality may be due to the presence of the dislocation density that is inherent within the Si-Ge/Si substrate [5] [6]. Additionally, the growth conditions for the AlGaAs PV cells on the Si-Ge/Si substrate was not ideal, which further decreased the material quality of the AlGaAs layer. The V_{OC} and J_{SC} of the AlGaAs PV cells grown on the Si-Ge/Si substrate had a similar trend to those grown on the GaAs substrate for a V/III ratio between 15 and 18. Nevertheless, because of the presence of dislocations within the Si-Ge/Si substrate, the performance was lower for the AlGaAs PV cells grown on Si-Ge/Si substrates than for those grown on GaAs substrates.

The QE curves of the AlGaAs PV cells grown on GaAs and Si-Ge/Si substrates with different substrate temperatures and V/III ratios are shown in Figure 7.4 and Figure 7.5, respectively. The bandgaps of the AlGaAs PV cells grown on GaAs and Si-Ge/Si substrates are 1.52 and 1.50 eV, respectively.

The increase of substrate temperature from 580°C to 680°C was seen to affect the short wavelength range (<650 nm) of the QE curve. The increase of the QE curve in the short wavelength range suggest a decrease in the front surface recombination. The front surface recombination is high, as can be seen by the low QE in the low wavelength range for all the samples which could have resulted in the low J_{SC} . The increase in V/III ratio was seen to affect the QE in the long wavelength range (>600 nm), with maximum QE attain at V/III ratio of 15 for both substrates.

Figure 7.4. The quantum efficiency curves of AlGaAs PV cells grown on (a) a GaAs substrate and (b) a Si substrate at a V/III ratio of 10 and different substrate temperatures.

Figure 7.5. The quantum efficiency curves of AlGaAs PV cells grown on (a) a GaAs substrate and (b) a Si substrate at the substrate temperature of 680°C and different V/III ratios.

The target J_{SC} of the AlGaAs PV cell was $\sim 30 \text{ mA/cm}^2$. However, as a result of the thin base layer, a maximum J_{SC} of only 11.74 mA/cm^2 and 10.2 mA/cm^2 was achieved for the AlGaAs PV cells grown on the GaAs and Si-Ge/Si substrates,

respectively. The absorption of incident light for AlGaAs material can be estimated using the GaAs absorption coefficient spectrum by shifting the absorption edge to coincide with the bandgap of AlGaAs. The amount of aluminium is low and is assumed to not affect much on the absorption spectrum of GaAs. The bandgap of $\text{Al}_{0.11}\text{GaAs}$ is modelled at 1.56 eV (795 nm), however the bandgap of GaAs is 1.42 eV (870 nm). Therefore, the whole absorption spectrum of GaAs is shifted backwards by 75 nm ($870 - 795 = 75$). This will give us the estimated absorption spectrum of $\text{Al}_{0.11}\text{GaAs}$. The calculation for the amount of absorbed light (A) for a specific thickness (x) of material is defined by Equation (1),

$$A = 1 - e^{-\alpha x} \quad (1)$$

where α is the absorption coefficient of the material. With a maximum cell thickness of 1.5 μm (emitter + base), only 50% of the light is absorbed in the 700 nm wavelength. In order to have 95% absorption in the 700 nm wavelength, a 6 μm thick cell is required.

A better way of comparing different samples is by using the $E_g/q-V_{OC}$ value as discussed in the previous chapters. The ideal $E_g/q-V_{OC}$ value is 0.4 eV with a smaller $E_g/q-V_{OC}$ value indicating a higher material quality. The plot of $E_g/q-V_{OC}$ values with respect to the V/III ratio and the substrate temperature used in the growth of AlGaAs PV cells on GaAs and Si-Ge/Si substrates is shown in Figure 7.6. The $E_g/q-V_{OC}$ values for the AlGaAs PV cell grown with a V/III ratio of 10 and a substrate temperature of 680°C on the Si-Ge/Si substrate are not shown, as the bandgap of the PV cell cannot be determined. Nevertheless, the $E_g/q-V_{OC}$ value can be assumed to be very high.

Figure 7.6. Line graph of $E_g/q-V_{OC}$ values of AlGaAs PV cells grown on GaAs (black line) and Si (red line) substrates at different (a) V/III ratios and (b) growth temperatures.

The increase in the substrate temperature for the AlGaAs PV cells grown on the GaAs substrate decreased the $E_g/q-V_{OC}$ value, as shown in Figure 7.6 (b). The improvement in material quality could be due to the reduction of group III site vacancies or their complexes [3]. It was also reported that, with a reduction in these defects, the PL intensities of the AlGaAs material increases. Another possible defect that is widely reported to be present in the AlGaAs material is oxygen-related mid-gap defects [7] [8] [9]. An increase in the aluminium content in AlGaAs was shown to have an increase in oxygen incorporation in both the MBE and OMVPE system [7] [8]. This result suggests that oxygen has a higher affinity to aluminium than it has to gallium. Akimoto *et al.* reported an increase in PL intensity with an increase in the substrate temperature for $\text{Al}_{0.3}\text{GaAs}$ [7]. The high substrate temperature allows the aluminium-oxygen complex to evaporate from the surface during growth. The decrease in aluminium-oxygen complex, which is a non-radiative centre, increases the PL intensity of the AlGaAs material [7] [10]. The $E_g/q-V_{OC}$ value of the AlGaAs PV cell grown using a substrate temperature of 680 $^{\circ}\text{C}$ can be reduced further by increasing the V/III ratio to 15, as shown in Figure 7.6 (a). This shows that the AlGaAs

PV cell grown on the GaAs substrate with a V/III ratio of 15 and a substrate temperature of 680°C has the best material quality compared to the other samples.

The decrease in the $E_g/q-V_{OC}$ value with an increase in the V/III ratio from 10 to 15 could be due to the decrease in V_{As} and/or Ga_{As} [11]. This could be due to the increase in perfect AlGaAs stoichiometry with an increase in the V/III ratio. The presence of V_{As} has been reported to be a non-radiative recombination centre, which might have reduced the AlGaAs material quality at the low V/III ratio of 10 [12]. Moreover, the increase in the V/III ratio could have decreased the incorporation of oxygen in the group V site due to the increase in competition between arsenic and oxygen [8]. The reduction of the above defects improved the AlGaAs material quality, as shown by the decrease in the $E_g/q-V_{OC}$ value. However, a further increase in the V/III ratio to 18 could have resulted in an increase in As_{Ga} defects [13] due to the increase in arsenic flux, which deviated from the perfect AlGaAs stoichiometry. As_{Ga} defects have been reported to be a non-radiative recombination centre, which increases the $E_g/q-V_{OC}$ value at the V/III ratio of 18 [5].

The $E_g/q-V_{OC}$ value of the AlGaAs PV cell grown on a Si-Ge/Si substrate is higher than that grown on the GaAs substrate. The dislocations present in the Si-Ge/Si substrates could have decreased the material quality of the AlGaAs PV cell. However, the optimum substrate temperature for the AlGaAs PV cell on the Si-Ge/Si substrate seemed to be at 630°C instead of 680°C for the AlGaAs PV cell grown on the GaAs substrate. This can be seen in Figure 7.6 (b). The lowest $E_g/q-V_{OC}$ value of 0.82 eV was attained when the substrate temperature was 630°C. The difference in the optimal growth temperature for AlGaAs on GaAs (680°C) and Si-Ge/Si (650°C) substrate could be due to the diffusion of Ge within the Si-Ge/Si substrate resulting from the long exposure (<1hr for growth of AlGaAs PV cell) to the high temperature (680°C)

growth [6]. This can also be seen in Chapter 3 where the 1-eV GaNAsSb on Si-Ge/Si substrate annealed at 700°C for 10 mins showed the worst performance. The high temperature of 680°C and the long growth process (<1hr) of the AlGaAs PV cell might have caused diffusion of Ge atoms within the Si-Ge graded buffer. Another highly possible cause is the difference in thermal expansion of Si and GaAs which are 2.6×10^{-6} and 5.7×10^{-6} °C, respectively. The two times difference in thermal expansion and the diffusion of Ge atoms could have increased the dislocation density greatly thus resulting in a reduced in PV cell performance. Additionally, the high growth temperature of 680°C coupled with the low V/III ratio of 10 might have resulted in an arsenic deficiency that deteriorated the AlGaAs layer [15]. Thus, a lower optimum temperature is required to obtain a good quality AlGaAs layer.

The $E_g/q-V_{OC}$ value of the AlGaAs PV cell on the Si-Ge/Si substrate grown at 630°C was high, as the V/III ratio is not optimised for that temperature. It can be seen in Figure 7.6 (a) that the increase of the V/III ratio from 10 to 15 for the AlGaAs PV cell on the Si-Ge/Si substrate grown using a substrate temperature of 680°C greatly improved the AlGaAs material quality. This showed that an increase in the V/III ratio for the AlGaAs PV cell grown on the Si-Ge/Si substrate using the substrate temperature of 630°C may improve the performance further. An optimum V/III ratio is required to reduce oxygen-related defects and arsenic antisite defects, as discussed above.

3.6. Conclusion

In this study, the AlGaAs PV cell grown on the GaAs substrate with a substrate temperature of 680°C and a V/III ratio of 15 had the lowest $E_g/q-V_{OC}$ value. This indicated that the AlGaAs material quality was good compared to other growth parameters. However, due to the presence of dislocations within the Si-Ge/Si

substrate, the performance of the AlGaAs PV cell grown on the GaAs substrate was better than that of the cell grown on the Si-Ge/Si substrate. The substrate temperature of 630°C seems to be optimal for the AlGaAs PV cell on the Si-Ge/Si substrate. An increase in substrate temperature was discovered to decrease the group III site vacancies and oxygen-related complexes, which improved the material quality of the AlGaAs PV cell and thus increased the performance of the cell. An increase in the V/III ratio from 10 to 15 decreased the V_{As} and/or Ga_{As} as well as oxygen-related complexes, which improved the AlGaAs material quality. A further increase of V/III ratio to 18 increased the As_{Ga} defects, which decreased the performance of the AlGaAs PV cell.

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Chapter 8 Summary and Future Works

8.1. Summary

In this project, we achieved the growth optimisation of a 1-eV GaNAsSb PV cell on a Si-Ge/Si substrate. Based on the experimental quantum efficiency (QE) of the 1-eV GaNAsSb PV cell, the top two sub-cell bandgaps of a quadruple junction PV cell were modelled to obtain maximum energy conversion efficiency. Finally, using the modelled bandgap of the second sub-cell, an AlGaAs (1.56 eV) PV cell was optimised on the Si-Ge/Si substrate.

The 1-eV GaNAsSb PV cell grown using the As/Ga BEP ratio of 10 has the highest energy conversion efficiency with a V_{OC} of 0.53 V and a J_{SC} of 17 mA/cm². It has an $E_g/q-V_{OC}$ value of 0.50 eV, which is comparable to other dilute-nitride PV cells grown on GaAs substrates. This shows that the GaNAsSb PV cell grown on the Si-Ge/Si substrate has good material quality. It was found that the increase of the As/Ga BEP ratio from 10 to 18 decreased the carrier lifetime due to the increase of arsenic antisite defects. With a further increase in the As/Ga BEP ratio to 20, there was a decrease in nitrogen incorporation. This led to a decrease in nitrogen related defects, which improved the GaNAsSb material quality.

The 1-eV GaNAsSb PV cells grown with a substrate temperature of 420°C have the highest energy conversion efficiency with a V_{OC} of 0.53 V and a J_{SC} of 18 mA/cm². From the SIMS analysis, it was found that, with an increase in substrate temperature from 420°C to 530°C, there was a decrease in antimony incorporation from 6.4% to 1.9%. The decrease in the antimony content did not affect the lattice relaxation for the substrate temperatures between 420°C and 500°C. However, there was an estimated 0.5% relaxation for the substrate temperature of 530°C, which could have further reduced the performance of the GaNAsSb PV cell. The increase in the substrate

temperature could have increased the nitrogen segregation and phase separation, which decreased the performance of the GaNAsSb PV cell.

The 1-eV GaNAsSb PV cell annealed with a temperature of 700°C for 5 mins had the highest energy conversion efficiency with a V_{OC} of 0.53 V and a J_{SC} of 15 mA/cm². It had the lowest $E_g/q-V_{OC}$ value of 0.56 eV compared to other samples, which implies that annealing at 700°C for 5 mins gives it the best material quality. It was seen that, with an increase in annealing time, the performance of the GaNAsSb PV cell increased. However, at the annealing conditions of 700°C for 10 mins, the GaNAsSb PV cell junction deteriorated. The improvement of the PV cell performance can be attributed to the reduction in arsenic antisite defects and nitrogen related defects as the annealing time increased.

The modelling of a quadruple junction PV cell was performed using the experimental quantum efficiency of GaInP, GaAs, GaNAsSb and Ge. The quadruple junction using the 1 eV GaNAsSb sub-cell can achieve an energy conversion efficiency of 38.8% with an optimised bandgap. The quadruple junction PV cell bandgap configuration is 2.00/1.56/1.03/0.66 eV. The last two bandgaps belong to the GaNAsSb sub-cell and Ge sub-cell, respectively. The increase in the top two junction bandgaps compared with the typical triple junction PV cell is to allow more light to be transmitted to the low QE 1-eV GaNAsSb sub-cell. The optimised quadruple junction PV cell is predicted to have a V_{OC} of 3.42 V, a J_{SC} of 11.8 mA/cm² and a fill factor of 90%. The efficiency can be boosted to 49% under 500 suns.

The optimal substrate temperature and V/III ratio of the AlGaAs PV cell on the GaAs substrate were found to be 680°C and 15, respectively. These growth parameters have the best AlGaAs material quality. The AlGaAs PV cell grown on the Si-Ge/Si substrate seems to favour a growth temperature of 630°C. The increase in the substrate

temperature was found to decrease the group III site vacancies and oxygen-related complexes, which are reported to be non-radiative recombination sites. This resulted in an increase in the performance of the PV cell. The increase in the V/III ratio was found to decrease the V_{As} and/or Ga_{As} and oxygen-related complexes, which improved the performance of the PV cell. However, with a further increase in the V/III ratio, the performance of the AlGaAs PV cell decreased. This could be due to an increase in As_{Ga} defects.

8.2. Future Works

8.2.1. 2.0 eV Sub Cell Optimisation

The first junction material of a typical triple junction PV cell is GaInP. This material is lattice-matched to GaAs, but the bandgap is only 1.87 eV. The first junction of our optimised quadruple junction PV cell needs to have a bandgap of 2.00 eV. Therefore, $Al_{0.09}Ga_{0.43}In_{0.48}P$ could be a suitable candidate for the first sub-cell. Further optimisation of the growth parameters like the V/III ratio, growth temperature, annealing temperature and annealing duration are required for the growth of a AlGaInP PV cell on a Si-Ge/Si substrate using MBE.

Faucher *et al.* reported that introducing a graded region between the AlGaInP layer and both the window layer and the back surface field layer improves the carrier collection [1]. This method increases the QE across all wavelengths and thus increases the J_{SC} of the AlGaInP PV cell. The optimum growth temperature, annealing temperature and duration were also reported to be important in improving the performance of the AlGaInP PV cell [1]. In addition, optimising the base thickness is crucial in maximising the absorption

potential of the AlGaInP PV cell while at the same time preventing carrier recombination [2].

With the optimised parameters for the AlGaInP sub-cell, integration can be done together with AlGaAs, GaNAsSb and Ge on the Si substrate: thus forming a quadruple junction PV cell. The optimisation of AlGaInP was not performed in this thesis due to the lack of a phosphorus source in the MBE chamber. This also means that fabrication of the quadruple junction in our MBE chamber is not possible.

8.2.2. Integration of all the Sub Cells on Si substrate

The integration of all the sub-cells should be done in a step-by-step process. First, a dual junction PV cell consisting of AlGaAs/GaNAsSb on Si and GaAs substrates should be tested. This requires the use of a tunnel junction to connect the two sub-cells together.

The use of a tunnel junction in a multi-junction PV cell is important in minimizing energy loss by lowering the series resistance of the cell. An AlGaAs/GaAs tunnel junction was simulated by Wheeldon *et al.* to require a lower doping concentration than a GaAs/GaAs tunnelling junction to reach a resistance of $<10^{-4} \Omega\text{cm}^2$ [7]. A high doping concentration ($>1 \times 10^{19} \text{ cm}^{-3}$) of the tunnel junction is required to ensure that the conduction band of the n side is aligned with the valence band of the p side. This will allow the electrons to tunnel through with little resistance. However, the high doping concentration of ($>1 \times 10^{19} \text{ cm}^{-3}$) and a high growth temperature can result in the formation of micro-precipitates, which degrade the PV cell performance [4] [5] [6]. The increase in the size of the micro-precipitates with an increase in growth temperature was shown by Kang *et al.* to reduce the electron mobility [4]. Thus,

the optimisation of the growth conditions for each doping level is required to ascertain the highest doping concentration with the minimum micro-precipitates for the tunnel junction.

The type of dopant used for the n and p type tunnel junctions will affect the performance of the PV cell. Kang *et al.* reported that Te doped n-GaAs has a lower tunnelling resistance than Si doped n-GaAs [8]. Gotoh *et al.* reported the use of carbon doped p-GaAs has a higher tunnel peak current density as opposed to beryllium doped p-GaAs [9]. Our MBE system only has beryllium and silicon as dopants, which might not be the ideal dopants for a tunnel junction. One of the ways to overcome this, is the addition of the two sources into the MBE chamber. However, this solution requires the venting of the chamber and the acquiring of additional components like a shutter controller, PID temperature controller, ultra-pure source, effusion cell, etc. Another possible way is to grow the tunnel junction using MOCVD. However, this solution requires a proper transfer process between the MBE chamber and MOCVD chamber to minimise contamination to the sample. A possible way to transfer the wafer is to deposit an amorphous layer of As on the surface which can be easily be removed by heating the wafer in the chamber.

The integration of an AlGaInP sub-cell on AlGaAs/GaNAsSb can be achieved after the successful integration of AlGaAs/GaNAsSb where maximum efficiency is obtained. This triple junction can be grown on Si and GaAs substrates to compare the performance and to identify potential problems for refinement.

The final integration requires AlGaInP/AlGaAs/GaNAsSb to be on a Ge sub-cell. Since our MBE chamber does not have a Ge source, the Ge sub-cell

could be grown first in an MOCVD chamber before transferring it to an MBE chamber for the growth of the top three sub-cells. In-diffusion of group V atoms to form an n-type emitter in Ge was reported to be unsuccessful due to the low sticking coefficient of the group V atoms [8]. Therefore, a Ge source is required in the MBE chamber for the growth of the Ge sub-cell. Growth of the quadruple junction can be done on Si and GaAs substrates to compare the performance not only between the different substrates, but also to compare it with the reported theoretical efficiency value. This will allow the identification of problems for rectification.

The final quadruple junction PV cell can be characterised under solar concentration to determine the maximum experimental efficiency. Additionally, it can be tested under real world conditions by setting up reflectors and a cooling system to concentrate the sunlight onto the PV cell. With this setup, the real-world efficiency of the quadruple junction PV cell can be obtained.

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