Low temperature silicon-based epitaxy for solar cells applications

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**NANYANG
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Low Temperature Silicon-Based Epitaxy For Solar Cells Applications

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Abstract

Epitaxial silicon (Si)-based solar cell technology is an attractive alternative for large-scale and high-throughput manufacturing of cost-effective solar cells through reduced Si consumption. However, due to the optical losses related to reduced Si thickness, it is critical to improve the short-circuit current density (J_{sc}) of the solar cell. Thus, it becomes imperative to explore a robust scheme to achieve high J_{sc} for the epitaxial Si solar cells to realize its full potential. The aim of this work is to design, fabricate and characterize epitaxial emitter (epi-emitter) Si solar cells that yield higher J_{sc} . Three schemes are investigated and compared to determine the most effective scheme to improve the J_{sc} of the solar cells. Firstly, low temperature Si epitaxy technique is employed to form epi-emitter Si solar cells using bulk crystalline Si substrates, with POCl_3 diffused solar cells as the control cell. Next, to lower the contact resistance, the effects of back germanium (Ge) epilayer on an active epitaxial cell performance have been studied; using both highly doped and optimally doped Si substrates. Finally, the effects of architectural and peripheral modifications on the performance of epi-emitter Si solar cells are evaluated.

An alternative approach has been demonstrated to grow phosphorus-doped epitaxial Si emitter by ASM 2000 at low temperature ($T < 700^\circ\text{C}$). A PCE_{pseudo} of $(10.2 \pm 0.2)\%$ and J_{sc} of 28.8 mA/cm^2 has been achieved for the solar cell with epi-emitter grown at 700°C , in the absence of surface texturization, antireflective coating, and back surface field enhancement, without considering front contact shading. Secondary ion mass spectroscopy revealed that lower temperature Si

epitaxy yields a more abrupt p - n junction; suggesting potential applications for radial p - n junction wire array solar cells. Mechanical twinning observed in the epi-emitter improves the optical absorbance of the cells. Based on the results, a higher PCE can be achieved by increasing the J_{sc} through optimization of the contact.

In order to lower the contact resistance with back aluminum (Al) contact, the epi-emitter Si solar cells have been fabricated using a back Ge epilayer on highly boron (B)-doped Si substrates. The fabrication of these cells involved a two-step epitaxy process to grow the back Ge epilayer, followed by the front side epi-emitter. Control samples are fabricated under identical conditions for comparison. It is found that J_{sc} of the epi-emitter cell with back Ge epilayer and back B-doped Ge epilayer is $\sim 12.4\%$ and $\sim 16.6\%$ higher than that of the control cell, respectively.

The performance of epi-emitter Si solar cells with back Ge epilayer grown on optimally doped Si substrates is compared to the cells with conventional BSF scheme. A maximum PCE of 10.2% and J_{sc} of 27.2 mA/cm^2 have been achieved for the epi-emitter cell with back Ge epilayer. When compared to the control cell, a remarkable relative J_{sc} improvement of $\sim 24.3\%$ is seen. Moreover, the cells with back Ge epilayer exhibit a significant improvement in EQE response around the infrared region due to enhanced charge separation by the Si/Ge heterojunction, when compared to the cells with BSF epilayer. It is also found that the cell with back Ge epilayer and the cell with BSF epilayer have comparable PCE s.

The effect of architectural and peripheral modifications of epi-emitter Si solar cells has been studied. Firstly, the synergistic approach of direct FIB etching and FGA step on the defective epi-emitter layer forms Si nanocone array with Si nanocrystals. An absolute J_{sc} improvement of 0.3 mA/cm² is observed with a very small textured surface of ~0.1% and the presence of Si nanocrystals. This suggests the potential of using FIB etch and FGA step to improve the light trapping capability for epitaxial Si solar cells. In addition, such direct patterning technique is ideal for very thin cells that are incompatible with lithography. Secondly, we have demonstrated that the reduced broadband reflectance and the *PL* property of embedded Si nanocrystals in the Si₃N₄ layer of the bilayer ARC can improve the *PCE* of epi-emitter Si solar cells. It is found that the Si nanocrystals could downshift high-energy ultraviolet photons to lower-energy photons to enhance the overall *PCE*. A relative J_{sc} enhancement of 12.5% is observed for the epi-emitter cell with bilayer ARC and back Ge epilayer as compared to the control cell with back Ge epilayer. However, front surface recombination, due to poor passivation between the interface of epi-emitter and the Si nanocrystals, may have caused the *PCE* degradation for the cell with bilayer ARC and back Ge epilayer. To minimize losses due to front surface recombination and enhance the *PCE* of epi-emitter Si solar cells in future studies related to architectural and peripheral modifications, we recommend using remote hydrogen plasma passivation to passivate the surface of the Si nanocrystals.

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1. Introduction

1.1 Motivation

Over the past decades, the decreasing availability of fossil fuel sources and the awareness of the detrimental climatic effects due to greenhouse gas emissions [1] have led to the growth of interest in renewable energy sources. Moreover, an additional driving force is the increasing global sensitivity towards energy security and oil price instability. Amongst the various renewable energy sources, the direct conversion of solar energy to electricity by photovoltaic (PV) cells is highly regarded as a more promising candidate for future power production. Solar energy is almost inexhaustible, non-polluting and available on all continents. The Earth receives $\sim 1.2 \times 10^5$ terawatts of solar power, while the world's total annual power consumption is ~ 13 terawatts. This implies that harvesting a small fraction of the solar energy that reaches Earth can meet the current total energy demand of the planet. [2]

Figure 1.1: Evolution of World Annual PV Market from 2000 to 2012 (MW).

Currently, solar energy collection contributes only a minute portion ($\sim 0.03\%$) of the world's electrical energy consumption. [3] Since 2000 the average annual growth rate of the PV market is tremendous as shown in Figure 1.1. [4] Although the PV market slowed down from 2011, there is still enormous potential in global energy utilization based on PV modules.

Figure 1.2: Average annual factory-gate price for solar modules between 2005 and 2012 (Source: Solarbuzz).

Commercial solar cell modules can be grouped into two main categories: (i) crystalline silicon (Si) and (ii) thin-film. Crystalline Si solar cells (e.g. single crystalline Si and polycrystalline Si) are known as the first generation PV technology that accounts for ~85% of the PV market and have high power conversion efficiency (*PCE*) of between 14% and 24%. These modules are made from high quality Si and have proven to be long-lived, low-maintenance, and stable in harsh climate. From Figure 1.2, the price of these modules is ~US\$0.85/W_p (W_p is defined as the power under peak solar intensity), which is ~1.28 times higher than electricity from fossil fuels. [5] In contrast, the thin-film PV technology, which is known as the second-generation solar cells, accounts for ~15% of the PV market. [6] Thin-film solar cell modules are innovative and a promising candidate because they involve depositing low-cost materials (e.g. amorphous Si (a-Si),

micromorph Si, Cadmium-Telluride (CdTe), Copper-Indium-Diselenide (CuInSe₂), and Copper-Indium-Gallium-Diselenide (CIGS)) onto cheaper glass or metallic substrates. For this reason, the price of thin-film solar cell modules is lower than US\$0.85/W_p. [7] Nevertheless, thin-film modules have lower *PCE* of between 9% and 13% as compared to the first generation PV technology. The emerging third generation PV technology comprise of dye-sensitized solar cells and organic solar cells. These cells have great potential for cost reduction and large area production, [8] but they have a long materials and development route ahead when compared to its predecessors in terms of *PCE* and modular lifetime. More importantly, the key for the development of any PV technology is the cost reduction related to the economies of scale. This has been evident in the case of the first two-generation PV technology as the increase of the cumulative production rate reduces the price of the solar cell modules. Thus, it is imperative that future PV technologies have to feature very low material consumption to offer competitive prices and to make a significant contribution to the world's energy requirements. Additionally, another major consideration comes from the materials availability, which demands that environmentally friendly (non-toxic) and abundant elements should be employed for the fabrication of practical energy devices. [9] It is evident that more effort is required to develop a new class of solar cells that are cost-effective and yet highly efficient. In this light, a hybrid solar cell that offers the synergistic advantages of crystalline and thin-film Si technologies is considered to be the more promising candidate for future solar cell production (see Figure 1.3).

Figure 1.3: Efficiency Positioning of PV Module Manufacturers. (Source: Yole Développement)

It has been reported that epitaxial Si solar cells offer the advantages in terms of performance, stability, and low material consumption that lead to potentially low cost manufacturability. [10-12] In recent years, epitaxial emitter (epi-emitter) formation by epitaxial reactor is an attractive option amongst the thin-film technologies due to its viability towards large-scale manufacturability. [13, 14] Recently, it has been reported that Crystal Solar has modified the epitaxial reactor to produce up to 500 wafers per hour and it costs less than USD\$5 million. This would imply to more than 50% reduction of wafer cost from US\$0.30/W_p to US\$0.13/W_p. [15] In this work, epi-emitter formation is prepared using the ASM Epsilon 2000 epitaxial reactor (ASM 2000) and it is preferred over the lengthy POCl₃ diffusion because:

- (i) It is fast (*e.g.* growth rate is >1 μm/min above 1100°C);

- (ii) *In-situ* dopant incorporation during the epitaxial growth implies that no extra chemical etching of the phosphorus glass silicate is needed after emitter formation;
- (iii) An ultrathin (*e.g.* ~50 nm) and abrupt *p-n* junction can be formed readily;
- (iv) It allows precise control of emitter thickness and dopant profile for enhancement of the blue response of the solar cells.

Epitaxial Si solar cells have been demonstrated using ASM 2000 at high temperature process of ~1130-1170°C and using trichlorosilane as the gas precursor. [16, 17] However, the outdiffusion of phosphorus (P) in Si at temperature over 1000°C has been evident in a previous study. [18] Thus, there is a strong motivation to accomplish Si epitaxial growth at a lower temperature for better dopant profile control through lower dopant interdiffusion and better thermal budget control. This is favorable for the formation of an abrupt and conformal *p-n* junction on advanced solar cell architectures such as nano/micro-wire array [19]. Meyerson has reported using ultra high vacuum CVD and silane gas precursor to grow low temperature Si epitaxy. [20] A more controlled epitaxial growth at lower temperature may promote a better interfacial quality between the emitter and substrate, which is necessary to prevent performance degradation due to material-induced shunt. [21]

1.2 Objectives

In this thesis, low temperature Si epitaxy schemes are investigated. The epi-emitter Si solar cells are fabricated by growing *n*-type Si epi-emitter and using back Ge epilayer on monocrystalline Czochralski (CZ) *p*-type Si substrate. The scope of the research work comprises of the design, fabrication and characterization of these solar cells. The objectives of this project are listed as follows:

- (i) Investigate the feasibility of forming an abrupt *p*-*n* junction by growing *n*-type Si epi-emitter onto CZ *p*-Si substrate at a low thermal budget using ASM 2000 and dichlorosilane (DCS) as the gas precursor. The electrical performance of epi-emitter solar cells fabricated using different epitaxial growth temperature and the reference solar cell using POCl₃ diffusion will be studied. We will specifically focus on the effect of dopant profile on the photovoltaic performance of the cells, including short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), power conversion efficiency (PCE), and internal quantum efficiency (IQE). We will further analyze their electrical performance based on the results of material and optical characterizations.
- (ii) Investigate the back Ge epilayer scheme with epi-emitter Si solar cells fabricated using highly doped *p*-type (p^+) Si substrate (Figure 4.2). Study the electrical performance of epi-emitter solar cells fabricated using undoped back Ge epilayer and B-doped Ge epilayer and the reference solar cell. We will specifically focus on the effect of the Si/Ge heterojunction on the photovoltaic performance of the cells, including short-circuit current density (J_{sc}), open-

circuit voltage (V_{oc}), fill factor (FF), power conversion efficiency (PCE), and external quantum efficiency (EQE). We will further discuss the mechanism using the capacitance-voltage ($C-V$) measurements.

(iii) Investigate the comparative advantage(s) of the back Ge epilayer scheme versus the conventional back-surface field effect with epi-emitter Si solar cells fabricated using optimally doped p -Si substrate. The electrical performance of the epi-emitter solar cells fabricated using undoped back Ge epilayer and B-doped Si epilayer and the reference solar cell will be studied. We will specifically focus on the effect of the Si/Ge heterojunction on the photovoltaic performance of the cells, including short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), power conversion efficiency (PCE), and external quantum efficiency (EQE).

(iv) To compare the comparative advantage(s) of the back Ge epilayer scheme versus surface texturization by exploring the feasibility of using focused ion beam (FIB) etching to form Si nanocone array on thin defective epi-emitter layer to reduce the effects of material-induced shunting and improve light absorption. The forming gas anneal step used to improve the metallization contact at the end of the solar cell fabrication process can be simultaneously utilized to form Si nanocrystals surrounding the Si nanocone array which can help in downshifting of light for better PCE . This alleviates the need to use the lengthy wet bench processes to perform surface texturization, hence ensuring

cost-effectiveness of the fabrication process for commercial application. The cells with and without Si nanocone array with nanocrystals will be fabricated and characterized.

- (v) To compare the comparative advantage(s) of the back Ge epilayer scheme by investigating the use of bilayer ARC with embedded Si nanocrystals on unpassivated planar epi-emitter layer to improve light absorption and to downshift the solar spectrum for higher *PCE*. The cells with and without the improved bilayer ARC with embedded Si nanocrystals will be fabricated and characterized.

1.3 Organization of the thesis

This thesis comprises of a total of seven chapters. Chapter 1 provides an introductory overview related to the potential capabilities of thin-film Si solar cells. It also covers the motivation, objectives and major contributions of this project. Chapter 2 presents the fundamental physics and operation of a solar cell. It also gives a detailed review of the key findings in the earlier work on epitaxial Si solar cells. Chapter 3 explains the motivation behind using low temperature Si epitaxy to grow the epi-emitter. It includes the experimental results and also provides the correlation between the optical and structural properties of the solar cells to its electrical performance. Chapter 4 presents an alternative back germanium (Ge) epilayer to improve the efficiency of epi-emitter Si solar cells grown on highly doped p^+ Si substrates, and the effect of doping the Ge epilayer. Chapter 5 studies

Chapter 1 Introduction

the comparative advantage of back Ge epilayer scheme with the conventional back-surface field effect with epi-emitter Si solar cells grown on optimally doped p -type Si substrates. Chapter 6 describes the architectural and peripheral modifications to the epi-emitter Si solar cells that can be incorporated to improve optical absorption and their corresponding efficiencies. Chapter 7 summarizes the experimental findings, recommends future plan for this project and mentions the major contribution of this work.

2. Literature review

This chapter reviews the research work reported in literature on crystalline and thin-film Si solar cells. The chapter begins by elaborating the fundamentals of solar cells and introducing the process flow of industrial solar cells. The advantages of thin-film Si solar cells over conventional solar cells will be briefly discussed. Following this, the motivation behind epitaxial Si solar cells will be highlighted and various epitaxial Si solar cells that have been realized in literature will be presented.

2.1 Fundamentals of solar cells

A solar cell is basically a semiconductor diode that has a p - n junction as shown in Figure 2.1. The semiconductor material absorbs light (i.e. photons) and converts them into electron-hole pairs. For photogeneration to occur, the energy of the incoming photons must be equal or greater than that of the energy bandgap of the semiconductor.

Figure 2.1: Cross-sectional schematic of a typical solar cell.

The maximum limit for the photogenerated current density J_{ph} is therefore given by the flux of the incoming photons with energy greater than the energy bandgap. Hence, J_{ph} decreases as the energy bandgap widens. In addition, the semiconductor material must be thick enough to absorb all the useful incoming photons. This criterion is hard to be achieved in semiconductor with indirect bandgap, such as crystalline Si, due to their poor absorption coefficients. Thus, crystalline Si can only be used when the thickness is sufficiently high (i.e. 125 μm Si to absorb 90% the above-bandgap photons [22]).

The second step of the energy conversion step involves the separation and transportation of the electron-hole pairs via the diffusion mechanism due to the internal electric field of the p - n junction. Figure 2.2 shows the equivalent circuit of a non-illuminated p - n diode. The current in the equivalent circuit can be described by the Shockley solar cell equation: [23]

$$I = I_L - I_0 \left(e^{\frac{qV}{K_B T}} - 1 \right) \quad (2.1)$$

Where I_L is the photo-generated current, I_0 is the diode saturation current and K_B is the Boltzmann constant.

It should be noted that once these photogenerated carriers are separated, they are in a metastable state and will recombine due to the exponential decay of the minority carrier lifetime when the time equals to the minority carrier lifetime. Hence,

recombination mechanism will degrade the performance of the solar cell and should be minimized.

Figure 2.2: Equivalent circuit of solar cell.

Figure 2.3 shows the typical illuminated I - V characteristics of a solar cell, with three characteristic parameters:

- (i) The short circuit current I_{sc} , which is the current flowing through the cell when the voltage across the cell is zero;
- (ii) The open circuit voltage V_{oc} , which is the maximum voltage available from the cell when the net current in the circuit is zero;
- (iii) The fill factor, which denotes the ratio of P_{max} to the product of I_{sc} and V_{oc} , where P_{max} is the maximum power, generated by the solar cell, and the corresponding current and voltage at this point is I_{mp} and V_{mp} .

Figure 2.3: Illuminated I - V characteristic and solar power generated of a solar cell.

From Figure 2.3, the short circuit current I_{sc} is the current flowing through the cell when the cell is short-circuited (*i.e.* when $V = 0V$), whereas the open circuit voltage V_{oc} refers to the maximum voltage available from the cell when the net current density in the external circuit is zero. P_{max} represents the maximum power generated by the solar cell, and the corresponding current and voltage at this point are labeled as I_{mp} and V_{mp} . The fill factor FF denotes the ratio of P_{max} to the product of I_{sc} and V_{oc} [23]:

$$FF = \frac{I_{mp} \times V_{mp}}{I_{sc} \times V_{oc}} \quad (2.2)$$

The power conversion efficiency (PCE) of the solar cell is determined by the maximum output electrical power generated by the cell divided by the input power from the sunlight and can be expressed as:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{sc} \times V_{oc} \times FF}{P_{in}} \quad (2.3)$$

2.2 Industrial Silicon Solar Cells

It is evident from Figure 2.4 that material cost (~40%) is still the largest contributor to the overall cost of crystalline Si solar cells.

Figure 2.4: Cost breakdown for solar modules. [5]

Figure 2.5: Industrial process from quartz to single-crystal Si cells. The energy input for electric-arc furnace, Siemens process, and Czochralski growth is ~50, ~200 and ~100 kWh/kg, respectively.

Figure 2.5 provides further insights into the high cost of crystalline Si solar cells by looking at the industrial process to convert quartz to monocrystalline Si wafers. All the major processes in Figure 2.5 involve high-energy input and the process steps are:

- (i) Melting and reducing of silicon dioxide to get metallurgical solar grade Si (MGS);
- (ii) Conversion of MGS to a volatile Si compound by distillation;
- (iii) Chemical vapor deposition of trichlorosilane to form polycrystalline rod (Siemens process);
- (iv) Zone refining for the Czochralski growth of Si ingot;
- (v) Sawing of ingot.

Instead of going through the high-energy inputs and to bypass the long and costly fabrication processing of the solar cells, trichlorosilane gas precursor can be employed to deposit high quality active layers directly on low-cost substrates. This observation brings out an important concept: the energy payback time, which is defined as the time for a solar cell to produce the same amount of energy that was spent for fabricating it. Assuming that there is no *PCE* degradation, the energy payback time for monocrystalline Si solar cell to produce the same amount of energy used for its fabrication is ~2.5 years.

2.3 Thin-Film Silicon Solar Cells

In order to substantially reduce the cost and energy input of crystalline Si solar cells, the material usage of high purity Si in conventional solar cell architecture should be minimized. As most of the optical absorption for crystalline Si takes place in the upper 125 μm [22], the remaining Si material is basically used for mechanical support. One approach to reduce the Si consumption is to use thinner Si wafers. However, there are concerns over the process yield when fabricating

cells with Si wafers of less than 200 μm thickness. An alternative approach to reduce solar cell costs consists of growing a thin active crystalline Si layer onto a cheaper MGS wafer. The latter approach, also known as crystalline thin-film Si solar cells, is one of the most promising midterm alternatives for manufacturing cost effective industrial solar cells. As mentioned earlier, almost half the cost of Si solar cell module is ascribed to the material cost of Si. It should be highlighted that more than half of the Si ingot is lost as Si sawdust during the wafer sawing process. [24] The employment of thin-film Si solar cells is a viable route to realize a more cost-effective way to fabricate solar cells. Schmich *et al.* has reported a cost reduction of up to 5% cheaper per peak watt when using thin-film Si solar cells over cells with POCl_3 diffusion. [25] This is because only a thin epitaxial Si ($\sim 40 \mu\text{m}$) is used as the active layer grown on low-cost supporting carrier substrates. More importantly, thin-film Si solar technology offers the potential to increase the power conversion efficiency (*PCE*) of the cells since the reduction of Si thickness will reduce the bulk recombination of photogenerated carriers. [26] With proper passivation and optical confinement techniques, we can expect a higher *PCE* of thin-film solar cells with optimal Si thickness between 50 μm to 100 μm as compared to the bulk cells. The improvement in *PCE* can be attributed to the reduction of saturation current density (J_o). The relationship between the V_{oc} and J_o is shown in the equation below:

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{J_{ph}}{J_o} + 1 \right) \quad (2.4)$$

Where k_B is the Boltzmann constant, T is the temperature, q is the electron charge, J_o is the sum of the emitter saturation current density and base saturation current density and J_{ph} is the light generated photocurrent density. Herewith, the base saturation current density (J_{ob}) summarizes all the saturation current densities contributed by the base material and the backside of the solar cell. J_{ob} can be expressed as:

$$J_{ob} = \frac{qn_i^2 D_p}{N_A L_n} \frac{S_b L_n / D_n + \tanh(W_b / L_n)}{1 + (S_b L_n / D_n) \tanh(W_b / L_n)} \quad (2.5)$$

Where n_i is the intrinsic carrier concentration of Si, N_A is the base doping, D_p is the hole diffusion coefficient in base, D_n is the electron diffusion coefficient in emitter, L_n is the diffusion length of electron in the base, S_b is the back surface recombination velocity, W_b is the thickness of the base, W_n is the thickness of the emitter.

Both equations describe the direct relationship of the thickness of the base W_b and the V_{oc} ; the thinner the cell thickness (W_b), the lower the V_{oc} . This is attributed to the increasing dominance of the surface recombination velocity (SRV) of the minority charge carriers, with respect to the bulk volume recombination velocity. SRV is a parameter used to quantify the recombination at the surface. With the assumption that the bulk lifetime is infinite, Sproul has derived an expression to calculate the maximum effective surface recombination velocity ($S_{eff,max}$) as follows:

$$S_{eff,max} = \frac{W_b}{2\tau_{eff}} \quad (2.6)$$

, where W_b is the thickness of the base and τ_{eff} is the effective minority carrier lifetime. [27]

In reality, there is minimum effective lifetime because electrons and holes must diffuse relatively slow towards the surfaces in order to recombine. Hence, the minimum effective lifetime can be calculated using the below equation:

$$\tau_{eff(S=\infty)} = \frac{W_b^2}{12D_p} \quad (2.7)$$

, where W_b is the thickness of the base and D_p is the hole diffusion coefficient in base.

Combining Equation 2.6 and Equation 2.7, we will get:

$$S_{eff,max} = \frac{6D_p}{W_b} \quad (2.8)$$

, where W_b is the thickness of the base and D_p is the hole diffusion coefficient in base.

For a 50 μm thick p -Si substrate with resistivity of 0.60 ohm.cm, and a diffusion coefficient for holes $D_p = 10.14 \text{ cm}^2 \text{ s}^{-1}$, the maximum effective surface recombination velocity that can be expected for an unpassivated surface is $S_{eff} = \sim 1.22 \times 10^4 \text{ cm}^{-1} \text{ s}^{-1}$. Therefore, it is vital the surface of the thin-film cells must be well passivated to ensure the back surface recombination velocity is low. Aside

from this, advanced light management techniques are required to increase the optical path length of light within the thin cell.

2.4 Epitaxial Silicon Solar Cells

The concept of epitaxial Si solar cells has been proposed by Dalal *et al.* in 1975 [28]. They suggested that these cells could perform better under concentrated light as compared to conventional diffused cells. Since then, research on epitaxial Si solar cells has gained in importance, owing to the shortage of poly-Si feedstock. Epitaxial Si solar cells represent a synergistic technology that combines the advantages of thin film technologies and bulk Si solar cells. It is thus seen as an attractive option to transit gradually from wafer-based solar cells to thin-film monolithic modules. The potential cost reduction of this concept, although not as substantial as other thin-film technologies, is nevertheless significant. The epitaxial Si solar cells has shown a high level of maturity, with industrial solar cell modules reaching efficiencies of about 13%. To further improve the performance, it is suggested and proven that optical confinement is necessary to increase the path length of light within the epitaxial layers. [17]

Table 2.1 shows the record *PCE* of epitaxial Si solar cells that have been achieved with this concept. The epitaxial layers have always been deposited on monocrystalline Si by chemical vapor deposition (CVD) technique at high temperatures of above 1000°C, unless otherwise mentioned. It is important to note that subsequent process steps (i.e. front surface texturing and application of Bragg

reflectors) may differ for each cell. From Table 2.1, we can notice that record *PCEs* of epitaxial Si solar cells above 17% have been achieved by several research groups since the mid-1990s. However, this was only feasible with the use of complicated fabrication methods that are difficult to be implemented in the solar cell industry. Thus, in the subsequent years, the focus has shifted to fulfilling the requirements for industrial production (e.g. rapid and simple process steps), while maintaining the performance of the thin-film solar cells.

Table 2.1: Record *PCEs* of epitaxial Si solar cells in chronological order. [29]

Institution	W_{Epi} [μm]	η [%]	V_{OC} [mV]	FF [%]	J_{SC} [mA/cm^2]	Comments
IPE Stuttgart (1994) ^a	50	17.3	655	81.1	32.5	Locally-diffused emitter, inverted pyramide texture
UNSW (1996) ^b	32	16.4	645	78.5	32.3	Liquid Phase Epitaxy (LPE), textured
UNSW (1996) ^b	17	17.6	661	81.4	32.8	n-p-n-p-n-p ⁺ structure, inverted pyramid texture
FhG ISE (1998) ^a	37	17.6	661	82.2	32.5	Locally-diffused emitter, inverted pyramid texture
IPE Stuttgart (2002) ^a	45	16.6	645	78.2	32.8	Lift-off technique, random pyramid texture
ZAE Bayern (2003) ^a	26	15.4	623	75.5	32.7	Lift-off technique, random pyramid texture
FhG ISE (2004)	35	15.2	649	79.7	29.4	Blue sens. emitter, rand. pyr. text., cell area 143 cm ²
ISFH (2007) ^a	24	14.5	588	74.2	33.3	Lift-off technique, auto-diffused emitter, textured
FhG ISE (2008) ^a	17	15.2	651	80.6	28.9	Standard epi-emitter, no texture
IMEC (2009)	25	16.9	627	78	34.6	2-step epi-emitter, porous Si reflec., rand. pyr. text.
IMEC (2010)	20	14.8	639	77	29.9	2-step epi-emitter, porous Si reflec., no texture
IMEC (2010)	20	16.1	621	78	33.2	2-step epi-emitter, porous Si reflec., plasma texture

^a Independently confirmed by Fraunhofer ISE CalLab.

^b Independently confirmed by Sandia National Laboratories.

Schmich *et al.* demonstrated an epitaxial Si solar cell with *PCE* of 15.2%, comprising of a standard epi-emitter, 17 μm epitaxial absorber and no surface texturization. [25] In another work, van Nieuwenhuysen *et al.* reported a more sophisticated cell architecture with *PCE* of 16.9% that comprises of a two-step epi-emitter, a porous Si reflector and random pyramid texture. [17] More recently, Rosenits *et al.* have shown promising epitaxial Si solar cells with *PCE* of 16.3% using high throughput batch-processing CVD. [29]

Figure 2.6: ASM Epsilon 2000 equipment used in Nanyang Nanofabrication Centre and the schematic drawing of major components in the equipment. [30]

In this work, the ASM Epsilon 2000 epitaxial reactor is used to grow single-sided epitaxy on Si substrate, as shown in Figure 2.6. The reactor consists of four parts, namely the nitrogen purged load-locks, wafer-handling section, quartz process chamber and gas exhaust cleaning section. A robotic arm transfers the wafers from the load-lock to the process chamber. Inside the process chamber, halogen tungsten lamps are employed on the topside and bottom side to perform rapid thermal

adjustments between the temperature range of 550-1200°C. The process pressure can be altered between 15 Torr to atmospheric pressure. Precursor gases used are as follow: Dichlorosilane (SiCl_2H_2) and germane (GeH_4) as the Si and Ge sources. The dopant gas precursors are diborane (B_2H_6) and phosphine (PH_3) as B and P sources diluted in H_2 to 1% concentration. Hydrogen (H_2) and nitrogen (N_2) are used as carrier and purge gases in the reactor. Hydrogen chloride (HCl) gas is used for removing the sidewall depositions within the quartz chamber. In-line purifiers are installed in both HCl and H_2 gas lines to reduce O_2 contamination during the epitaxial growth.

It is worthwhile to note that the concentration of gas flowing over the wafer surface (surface concentration) decreases with increasing temperature since surface reactions increases exponentially with temperature in Arrhenius behavior. When temperature is high enough, the surface concentration is close to zero because the gas molecules near the surface will react immediately. Thus at elevated temperature, the growth rate is limited by not by the surface reactions, but by the gases diffusing through the surface (i.e. boundary layer). This is known as the mass transport limited regime. On the other hand, at lower temperature, the epitaxial growth rate is dominated by the slower surface reactions. This is known as the reaction-rate limited regime. Figure 2.7 illustrates the plot of epitaxial growth rate versus inverse temperature with the two growth regimes. To meet industry demand, a synergistic technique could be adopted for epitaxial based solar cells by rapidly growing the thicker epitaxial base layer at mass transport limited regime and by

controlling the dopant profile of thin epi-emitter layer at the reaction rate limited regime.

Figure 2.7: Plot of growth rate versus inverse temperature of the mass transport limited and reaction rate limited growth regimes.

This technology, which is adopted from the integrated circuit (IC) industry, provides freedom in designing the dopant profiles of the epitaxial layers. It should be pointed out that a significant cost reduction of epitaxial Si solar cell can be realized with high throughput CVD reactor [15, 29] for future commercialization in the PV industry.

3. Low Temperature Epitaxial Emitter Silicon Solar Cells

This chapter describes the technique used to fabricate low temperature epi-emitter Si solar cells prepared by ASM Epsilon 2000 epitaxial reactor (ASM 2000). This chapter firstly presents the motivation behind using dichlorosilane as the gas precursor for Si epitaxy. Following that, the fabrication steps of the epi-emitter solar cells will be described. Finally, the electrical, materials and optical properties of the fabricated solar cells will be presented.

3.1 Introduction and motivation

Figure 3.1: Key fabrication process of commercial monocrystalline Si solar cell (Source: Yole Développement).

Figure 3.1 shows the fabrication process of the commercial monocrystalline Si solar cell. It typically starts with a *p*-type Si (100) wafer with resistivity of $\sim 1 \Omega\cdot\text{cm}$. The wafer is first etched in alkaline solution (e.g. NaOH or KOH) to remove the saw damage and also form micro-scale pyramids with (111) facets on the wafer surface. The textured surface minimizes the light reflection and increases the optical path length of light within the wafer. The emitter layer is formed by diffusing phosphorus (P) from the deposited phosphorus silicate glass (PSG) into the front side of the boron-doped substrate at high temperature. An additional step is necessary to remove the PSG layer after the phosphorus diffusion. The antireflective coating, commonly silicon nitride (Si_3N_4), is deposited on the front side of the wafer for surface passivation and to further reduce the light reflection. The front contact is screen-printed with a silver (Ag) paste and the back contact is also screen-printed using aluminum (Al) paste. The solar cell is then fired to form Ohmic contacts. From Figure 3.1, we can see that emitter formation is an important step in the fabrication of the solar cell. As aforementioned, the conventional emitter formation involves phosphorus diffusion from gaseous or solid dopant sources, in a batch-type resistive furnace. After diffusion, the residues of the dopant gas or dopant paste needs to be removed by wet chemical etching in hydrofluoric (HF) acid. This current technique for emitter formation has several disadvantages, as diffusion is the most time-consuming step in solar cell manufacturing and wet etching chemicals are needed. In this light, an alternative emitter formation via Si epitaxy was introduced. Emitter epitaxy would be able to avoid the disadvantages related to conventional emitter formation:

- (i) It can have very high throughput due to high deposition rates. [31]
- (ii) No dopant deposition is needed since emitter formation involves *in-situ* doping.
- (iii) No wet chemical etching step is required since no phosphorus silicate glass is formed.
- (iv) Doping concentration and dopant profile can be controlled for process optimization.
- (v) No edge isolation is needed.

Epitaxial Si solar cells have been fabricated using ASM 2000 at high temperature of above 1000°C and trichlorosilane as the gas precursor. [16, 17] Since phosphorus (P) outdiffusion in Si at such high temperature is significant as shown in a previous study, [18] we propose to accomplish Si epitaxial growth at a lower temperature using DCS gas precursor for better dopant profile control through lower dopant interdiffusion. This is favorable for the formation of an abrupt and conformal *p-n* junction on advanced solar cell architectures such as nano/micro-wire arrays [19] which are fabricated to enhance light harvesting for higher *PCE*. Additionally, a more controlled epitaxial growth at a lower temperature may promote a better interfacial quality between the emitter and substrate, [32] which is necessary to prevent performance degradation due to material-induced shunt. [21] In this chapter, the epi-emitter was grown directly onto the Si substrate in order to

investigate the quality of the emitter-substrate interface after the low temperature epitaxial growth.

3.2 Fabrication of the Epitaxial Emitter Silicon Solar Cells

All $1\text{ cm} \times 1\text{ cm}$ cells used in this work are diced from $650\text{ }\mu\text{m}$ p-type Czochralski (CZ) Si substrates with a resistivity in the range of $4\text{-}10\text{ }\Omega\cdot\text{cm}$. Si wafers are first cleaned with standard RCA clean to ensure a pristine growth interface prior to the epitaxial growth. Inside the ASM 2000 reactor, the substrates are heated in-situ in ultra pure H_2 at 1100°C to reduce the native surface. Dichlorosilane (DCS) and phosphine (PH_3) dopant gas precursors are used for the in-situ n-type doped epitaxial growth. Low temperature epitaxy formation is performed at 700°C and 900°C respectively, and the emitter thickness is fixed at $\sim 600\text{ nm}$. Spike anneal at 1000°C was employed to ensure complete dopant activation. POCl_3 diffused (900°C) cell is also fabricated for comparison purpose. The emitter layer is passivated with 10 nm thermal SiO_2 via rapid thermal oxidation. Front side contact with $\sim 10\%$ optical shading are defined by photolithography and a bimetallic layer, consisting of titanium (Ti) and aluminum (Al), is evaporated consecutively. Blanket Al is also evaporated on the wafer backside as contact. The cells are then subjected to forming gas anneal (FGA) at 400°C for 30 min . In order to avoid ambiguity introduced by process variations, surface texturization, antireflective coating, and back-surface field (BSF) are excluded in the fabrication of the cells to allow investigation of the junction quality. Similar solar cell architectures have been studied by M. J. Keevers [33] and Reber *et al.* [13]. Figure 3.2 summarizes the process flow of the solar cell with an epi-emitter fabricated in this project.

Figure 3.2: Fabrication process flow of a solar cell with *n*-type Si epi-emitter.

3.3 Materials Characterization of Epitaxial Emitter Silicon Solar Cells

Figure 3.3: AFM images of (a) DCS 900°C cell and (b) POCl₃ 900°C cell, illustrating the surface morphology of the respective cells.

Atomic force microscopy (AFM) scans were performed to compare the surface topology of the epi-emitter grown using DCS 900°C and the POCl₃ diffused emitter. It has been reported that both growth temperature and hydrogen (H₂) dilution can affect the surface roughness of the epitaxial layer. [34] Since the growth temperature for both processes is fixed at 900°C, the factor that determines the surface roughness of the Si epitaxy must be attributed to the H₂ dilution. As the flow of gas precursors in the smaller reactor chamber for epitaxial growth is expected to be less laminar than that in the larger furnace tube for POCl₃ diffusion, there should be more fluctuations in H₂ content within the gas precursors for the furnace tube. As illustrated in Figure 3.3, the surface topology of DCS 900°C epi-emitter (RMS value = 1.5 nm) is rougher as compared to the POCl₃ diffused emitter (RMS value = 1.0 nm). This observation can be explained by the following equations:

During the epitaxial Si growth using DCS gas precursor, the hydrogen chloride (HCl) by-product formed in the reversible process may cause etching of the epitaxial Si, thus leading to a rougher surface topology.

Figure 3.4: SIMS depth profiles of P dopant in the emitter layer of the epi-emitter Si solar cells and the reference POCl₃ diffused solar cells.

Dynamic secondary ion mass spectroscopy (SIMS) is employed to elucidate the P dopant distribution within the epi-emitters and the reference POCl₃ diffused emitter. Figure 3.4 shows the SIMS depth profiles of the epi-emitters and the POCl₃ diffused emitters. As expected, the reference diffused emitter has a Gaussian profile that tails gently into the substrate, while both epi-emitters have step-like

profiles. It is clear that a lower growth temperature at 700°C gives a more abrupt p - n interface since the diffusivity of the phosphorus dopant within Si has Arrhenius temperature dependence. A decrease in P concentration toward the emitter surface is observed for all cells. This observation can be explained by the P outdiffusion across the n-type emitter during the cooling step after the dopant activation at 1000°C. P outdiffusion can be avoided by flowing PH_3/H_2 mixture during cooling as previously reported in [25]. Moreover, a low contact resistance between the emitter layer and the front metallization is critical to produce a solar cell with high fill factor (FF). Thus, the lower surface dopant concentration will result in poor contact issue that can lead to poor FF of the cells. [35]

3.4 PC1D Simulation of Epitaxial Emitter Silicon Solar Cell

PC1D simulation [36] was carried out to evaluate the cell efficiency of the epitaxial DCS 700°C cell shown in Figure 3.4 by assuming that the metallization scheme is ideal. The cell parameters used for the PC1D simulation are shown in Table 3.1.

Table 3.1: Cell parameters used for PC1D simulation.

Parameter	Value
Cell thickness	650.6 μm
Emitter dopant concentration, N_D (measured by SIMS)	3.5×10^{19} atoms/ cm^3
Surface	Flat
Optical coating	10 nm SiO_2
Bulk lifetime	600 μs
Front surface recombination ($N_D > 1 \times 10^{18} \text{ cm}^{-3}$)	$S \approx 10^{-16} \times N_D$ [37]
Back surface recombination	250 cm.s^{-1}

Due to energy band gap narrowing, the front surface recombination velocity increases linearly with surface dopant concentration (N_D), for dopant concentration higher than $1 \times 10^{18} \text{ cm}^{-3}$. [37] The results of the PC1D simulation are as follow: $J_{sc} = 28.3 \text{ mA/cm}^2$; $V_{oc} = 498 \text{ mV}$; $PCE = 6.5 \%$. The lower cell efficiency is attributed to the absence of surface texturization, antireflective coating or back surface field as mentioned earlier. Figure 3.5 illustrates the simulated J - V curve of the DCS 700°C cell.

Figure 3.5: Current density-voltage (J - V) characteristics of $1 \text{ cm} \times 1 \text{ cm}$ epi-emitter Si solar cell fabricated at DCS 700°C under AM 1.5G solar irradiance, using PC1D simulation.

3.5 Electrical Characterization of Epitaxial Emitter Silicon Solar Cells

The photovoltaic current density-voltage (J - V) characteristics of the cells were measured with a Keithley 2400 Source-Meter unit under 100 mW/cm^2 illumination (AM 1.5G) from a solar simulator (Class AAA). The intensity of the light source

was calibrated by a Si reference cell, which is traceable both to the National Renewable Energy Laboratory (NREL), and to the International System of Units (SI).

Table 3.2: Solar cell parameters measured using solar simulator for $1 \times 1 \text{ cm}^2$ samples.

Process	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (%)	FF_{pseudo} (%)	PCE_{pseudo} (%)	R_{shunt} (Ω)	R_{series} (Ω)
DCS 700°C	28.8	459	50.1	6.6	77.5	10.2	115	5.8
DCS 900°C	24.5	452	38.6	4.3	78.0	8.7	112	10.3
POCl ₃ 900°C	27.2	499	55.3	7.5	73.7	10.0	196	4.9

Table 3.2 presents the illuminated parameters measured using solar simulator for the $1 \text{ cm} \times 1 \text{ cm}$ solar cells under one sun and AM 1.5G conditions at 25°C. From Table 3, we observe that all cells have low V_{oc} values, which can be associated to the usage of moderately low resistivity Si substrate of $\sim 4\text{-}10 \text{ }\Omega\cdot\text{cm}$ and the high shunt resistance (R_{shunt}). It is well known from literature that V_{oc} will increase with increasing doping level until a certain limit. [38] Beyond this limit, both the V_{oc} and FF will decrease. Thus, an optimal base doping level with resistivity $< 1 \text{ }\Omega\cdot\text{cm}$ is often used in the industry. The POCl₃ diffused solar cell has better V_{oc} value than both solar cells with epi-emitter layer. In general, an abrupt p-n junction like the profiles obtained in the epi-emitters in Figure 3.4 will contribute to a higher V_{oc} value because the space charge region is narrower, thus leading to a reduction in dark current. From the lower calculated R_{shunt} values of the epi-emitter cells as compared to diffused emitter cell, it is possible that the defective epi-emitter induces additional recombination losses. The poor FF for all cells can be

explained by the calculated high series resistance (R_{series}) due to the high line resistivity of the thin front metallization (i.e. 800 nm) and also due to a very low surface doping concentration ($\sim 4\text{-}5 \times 10^{18}$ atoms/cm³). Experimental PCE of the epi-emitter cell grown at 700°C is 6.6% is comparable to the simulated PCE (6.5%) of the same cell by PC1D (Table 3.1). Since the J_{sc} of the all cells are reasonably comparable, from the V_{oc} and FF , we can expect that the diffused emitter cell will have the highest PCE (7.5%). By comparison, the PCE of epi-emitter cell grown at 700°C is $\sim 50\%$ higher than that grown at 900°C. This can be explained by the calculated R_{series} of the latter cell being almost twice the R_{series} of the epi-emitter cell grown at 700°C.

Pseudo J-V analyses are performed on the cells to predict the PCE_{pseudo} , which is independent of R_{series} . J_{sc} - V_{oc} curves are measured at a range of sun intensity from 1 to $\sim 10^{-3}$ sun controlled by using neutral density filters. *Pseudo J-V* result is obtained by subtracting the $J-V$ curve with J_{sc} at 1 sun. PCE_{pseudo} represents the solar cell efficiency when R_{series} is not included. The PCE_{pseudo} obtained are 10.2% (epi-emitter cell grown at 700°C), 8.7% (epi-emitter cell grown at 900°C), and 10.0% (diffused emitter cell). The result suggests that there is still potential for the cell with an epi-emitter grown at 700°C, despite its corresponding lower PCE . The J_{sc} of the cell with an epi-emitter grown at 700°C is $\sim 17\%$ higher than that of the cell with an epi-emitter grown at 900°C. To explain this observation, the internal quantum efficiency (IQE) of the cells is measured.

Figure 3.6: Internal quantum efficiencies of the epi-emitters and the diffused emitters.

The shape of the spectral response measurement, also known as quantum efficiency (QE), can be used to understand the photocurrent generation, recombination, and diffusion mechanisms of the solar cell. [39] The external quantum efficiency (EQE) is measured with a characterization system consisting of a Xenon lamp, a chopper controller, a monochromator, and a lock-in amplifier. The reflectance spectra of different samples were obtained using an integrating sphere by a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer system. Both results are then used to determine the internal quantum efficiencies (IQE) as illustrated in Figure 3.6. An initial observation of the spectra shows that the spectral response of the cells corroborates very well with their respective short-circuit current density as presented in Table 3.2. To further understand the performance of each cell, we have to study their spectral response at different regions for the entire light spectrum. From the spectra, considerable front surface

recombination is present in all cells since blue light is absorbed very near to the cell surface. This implies that 10 nm of thermal oxide is insufficient to provide complete surface passivation; therefore thicker oxide will be employed in future work. Moreover, it is evident that the diffused emitter cell has a better blue response than the epi-emitter cell. At ~400 nm, the spectral response for the diffused emitter is about 50%, for the cell with an epi-emitter grown at 700°C is around 25% and for the cell with an epi-emitter grown at 900°C is close to 0%. In principle, if the starting Si surface is used for all cells is the same, a better blue response could be expected for the cells with an epi-emitter due to the possible presence of a dead layer for the case of the diffused emitter. However, in this study, the defective epi-emitters (i.e. deduced from the calculated R_{shunt} values), coupled with the lack of proper surface passivation, may have attributed to the trends observed in the blue response. In addition, these defects in the epi-emitter appear to be more significant at higher growth temperature. Transition to the green light region (~500 nm – 600 nm) shows a better QE for the cell with an epi-emitter grown at 700°C than the POCl_3 diffused cell and cell with an epi-emitter grown at 900°C. This result shows that the diffusion length for the photogenerated carriers within the bulk of the cell with an epi-emitter grown at 700°C is the highest, followed by the POCl_3 diffused emitter cell and the cell with an epi-emitter grown at 900°C. A detailed explanation will be furnished in the next section on cross-sectional TEM analysis. Lastly, in the red light region to the near-infrared region (~600 nm – 900 nm), cells with an epi-emitter layer have better spectral response than the POCl_3 diffused emitter cell. The improved IQE for the cells with an epi-

emitter layer could be attributed to an increased carrier collection probability in the bulk of these solar cells that are relatively far from the emitter region.

3.6 Optical Characterization of Epitaxial Emitter Silicon Solar Cells

Figure 3.7: Cross-sectional TEM image of the cell with an epi-emitter grown at 900°C, with an inset showing the EELS line scan for oxygen content at the interface between the emitter and the substrate.

Cross-sectional transmission electron microscopy (TEM) analysis of the solar cell in Figure 3.7 reveals a uniform interface between the epitaxial *n*-Si emitter and the Ti metal layer. However, it shows a poor interface between the *n*-Si epi-emitter and *p*-Si bulk substrate with the presence of stacking faults. These defects may contribute to material-induced shunts due to strongly recombinative crystal defects,

[21] which will lead to the *IQE* degradation in the cell with an epi-emitter grown at 900°C. In fact, the presence of stacking faults in epitaxial Si has been reported by Finch *et al.* [40]

Scanning transmission electron microscopy (STEM) equipped with an electron energy loss spectroscopy (EELS) system is used to detect the presence of oxygen at the emitter-substrate (*n-p*) interface. EELS analysis is performed using a line scan across the *n-p* interface, with a nominal probe size of 0.24 nm, at 100 kV and $< 2 \times 10^{-9}$ torr. An organic film (MEH-PPV) is used to quantify the oxygen signal. After scanning the spectrum of the *n-p* interface in the oxygen K-edge range, an adjacent area without the sample was scanned under the same conditions. An integration of the edge over a 30 eV is performed after removing the pre-edge background. From the molecular formula of MEH-PPV ($C_{17}H_{24}O_2$), its density (~ 1.4 g/cm³), the film thickness and the scan area, the number of oxygen atoms in the blank scan. This will give a conversion of the integrated area to oxygen atoms, which can be used to determine the number of oxygen atoms at the *n-p* interface. On the other hand, it has been reported that the concentration of the recombination center formed under illumination as electron collection increases linearly with the substitutional boron and quadratically with the interstitial oxygen concentration. It has been proposed that the recombination center is a defect complex B_sO_{2i} generated by the capture of a mobile interstitial oxygen dimer O_{2i} by an immobile substitutional boron B_s . [41] The inset of Figure 3.7 shows a EELS scan, which

indicates negligible oxygen traces at the emitter-substrate interface, which implies longer minority carrier lifetimes that is critical for solar cell performance.

Figure 3.8: Cross-sectional HRTEM images of (a) the cell with an epi-emitter grown at 700°C, (b) the cell with an epi-emitter grown at 900°C.

Cross-sectional high resolution transmission electron microscopy (HRTEM) analyses of the samples in Figure 3.8 reveal mechanical twinning at the interface between the epitaxial n-Si emitter and p-Si bulk substrate and it also shows that the twinning is more severe in the cell with an epi-emitter grown at 900°C. These twins may contribute to material-induced shunts due to strongly recombinative crystal defects, [21] thus corresponding to the low calculated R_{shunt} values.

Figure 3.9 (a) Selected region of the cross-sectional TEM for selected-area diffraction (SAD) of: (b) p -Si (100) substrate and (c) n -Si epi-emitter/ p -Si substrate interface.

The existence of twins can be discerned using the selected-area diffraction (SAD) technique, which is sensitive to the differences in orientation between a *twin* (*i.e.* epi-emitter) and *matrix* (*i.e.* substrate). If the twinned domains lay side by side with the untwinned *matrix* regions and the incident beam straddles both regions then a simple superposition of two diffraction patterns will occur, one from the matrix and one from the twin. Figure 3.9 (a) illustrates the area selected at the n - p interface to perform the SAD technique, whereas Figure 3.9 (b) depicts the SAD pattern of the (100) p -Si substrate. From Figure 3.9(c), we can observe the SAD pattern (110) n -Si epi-emitter with overlapping matrix and twin domains. Some of these extra spots can arise from multiple diffraction effects. [42] However, the full pattern in Figure 3.9 (c) can be understood by considering the tripling of the periodicity, which occurs in this direction when the twin and matrix structures are overlapped.

Figure 3.10: Absorbance measurements of blanket p-Si substrate, the cell with an epi-emitter grown at 700°C and the cell with an epi-emitter grown at 900°C using UV-Vis spectroscopy.

Absorbance of the material is a logarithmic ratio of the radiation falling upon the material, to the radiation transmitted through the material. [5] By Beer's Law,

$$A = 2 - \log_{10} \%T \quad (3.3)$$

where A is the absorbance of the material and $\%T$ is the transmittance of the same material.

The absorbance spectra of different samples, as shown in Figure 3.10, were characterized using an integrating sphere by a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer system. With reference to Equation 3.3 and Figure 3.10, by substituting the absorbance (A) values when the wavelength of the light source is 300 nm, it is calculated that ~14.1% reduction in light transmittance is achieved once the n -Si epi-emitter is grown at DCS 900°C on p -Si substrate. This could imply that the presence of the mechanical twinning (*i.e.* evident in Figure 3.8) increases the optical path length of light due to changes in the crystallographic orientations, indirectly leading to an enhancement in optical absorption. It has been reported that high absorptance may be obtained by exposing the (111) equivalent crystallographic places in the inverted pyramids. [43] These surface modifications can reduce reflection as well as increase the absorptance by trapping weakly

absorbed light within the cell. This suggests that the mechanical twins of (111) crystallographic orientation at the p - n interface may have led to the enhancement in optical absorption. The band-band absorption coefficient of Si at 300 K drops from 3.5 cm^{-1} at the bandgap of Si (1,103 nm) to 10^{-3} cm^{-1} at 1,250 nm. [44] From Figure 3.10, the higher absorbance values for the Si substrate with epi-emitters grown can be correlated to the defects with the epilayer, which can lead to formation of intermediate states within the bandgap.

Figure 3.11: PL mapping of (a) the cell with an epi-emitter grown at 700°C, (b) the cell with an epi-emitter grown at 900°C.

Photoluminescence (PL) mapping was employed to detect the defects in the samples as illustrated in Figure 3.11. Fewer defects in the Si will result in more radiative recombination, and more emitted photons, and vice versa. The samples are the rectangular objects within the circle (Figure 3.11). We can see that the cell with an epi-emitter grown at 700°C emits higher PL intensity as compared to the cell with an epi-emitter grown at 900°C, thus indicating that there are lesser material defects in the cell with an epi-emitter grown at 700°C. The region surrounding the sample (*i.e.* sample stage) is different for Figure 3.11 (a) and that of Figure 3.11 (b) because the voltage range for each PL mapping figure is

individually calibrated. In addition, the peak wavelength where the *PL* is detected is ~ 947 nm as shown in Figure 3.12. This may suggest the presence of oxidized porous Si along the mechanical stacking faults as shown in Figure 3.8. [45]

Figure 3.12: *PL* spectrum of the cell with an epi-emitter grown at 700°C.

3.7 Conclusion

In summary, we have demonstrated that Si epitaxial growth results in a more abrupt *p-n* junction than the POCl_3 diffused emitter. It is shown that the lower growth temperature of 700°C produces a more defined *p-n* junction with lesser defect, as compared to the epi-emitter grown at 900°C. In addition, it was found that low temperature epitaxial growth induces mechanical twins within the Si epi-emitter, evident from the selected area diffraction patterns. This mechanical twinning alters the orientation of the crystal planes and increases the optical path length of light within the epi-emitter, thus improving optical absorption by reducing light transmission by at least $\sim 14.1\%$. On the other hand, *PL* mapping suggests that lower temperature growth induces lesser material-induced shunts at

the p - n junction, which is supported by R_{shunt} measurements. A relatively good PCE of $(6.6 \pm 0.3)\%$ was achieved for the solar cell with epi-emitter grown at 700°C , despite the presence of stacking faults due to oxygen contamination. The PCE will be up to 7.3% if the front contact shading is neglected. A PCE_{pseudo} of $(10.2 \pm 0.2)\%$ obtained for this solar cell suggests that low temperature Si epitaxy has the potential to be used for radial p - n junction growth on wire array solar cells and can be synergistically integrated to high temperature Si epitaxy to realize better performance in epitaxial thin film Si solar cells.

4. Low Temperature Back Germanium Epitaxy on Epitaxial Emitter Silicon Solar Cells (highly doped substrate)

This chapter demonstrates an alternative approach to improve the *PCE* of epitaxial emitter Si solar cell, fabricated with highly doped p^+ Si substrate. By incorporating a back germanium (Ge) epilayer, the resulting silicon/germanium (Si/Ge) valence band offset facilitates hole transport under solar irradiance. The back aluminum/germanium (Al/Ge) contact formed an Schottky barrier height (Φ_B) for electrons due to strong Fermi level pinning of Ge near the charge neutrality level (Φ_0), which is close to the valence band edge of Ge. [46] A high reflection barrier for electrons is thus formed to reduce the recombination of minority carriers at the backside of the solar cell. Moreover, the close alignment of the Fermi level of Al to the valence band edge of Ge will promote hole collection at the back contact, thus enhancing J_{sc} of the solar cell. The design and fabrication of the back Ge epilayer solar cell will be presented first. The electrical and material properties of such cells will then be compared with a control solar cell without the back Ge epilayer.

4.1 Introduction and motivation

In Chapter 3, we have demonstrated that an abrupt p - n junction can be achieved using low temperature Si epitaxy, yielding a solar cell with higher PCE_{pseudo} than that of a $POCl_3$ diffused solar cell. [47] Further *PCE* improvement can be achieved by integrating a high Ge content Si_xGe_{1-x} to the bottom of a thin-film solar cell. Improvement comes from increased absorption of optical light in the infrared

region. [48, 49] More recently, Sun et al. reported their simulation results of a ~ 100 μm crystalline tandem solar cell that can achieve a *PCE* of 19% under AM1.5G solar irradiance, without surface passivation and light trapping techniques. Their proposed architecture has a hetero-diode sandwiched between a thin front Si *p-n* junction and thick back Ge *p-n* junction as shown in Figure 4.1. [50]

Figure 4.1: Illustration of (a) the Si-Ge tandem solar cell (b) the energy band diagram and carrier flow under solar irradiance. [50]

The underlying reason of employing Ge as the bottom junction material is due to the following attributes of Ge:

- (i) Ge has a wider absorption depth because of its nearly direct band gap of 0.66 eV ;
- (ii) Ge has ~ 4 times better electron and hole mobility as compared to Si; [51]
- (iii) Ge can be a good etch stop candidate during Si emitter texturization as it is resistant to etchants such as tetramethylammonium hydroxide (TMAH) and potassium hydroxide (KOH); [52]
- (iv) Ge has exhibited good properties as the bottom junction material in tandem solar cell. [53]

However, the above approach did not include the challenges related to large-scale manufacturing and the *PCE* degradation caused by the defective Si/Ge hetero-interface, with the latter being more critical. Due to the large mismatch in lattice parameters between Si and Ge during chemical vapor deposition, defects will either develop as threading dislocations or will be localized at the Si/Ge heterojunction. These defects can act as either (a) an electronic trap where an electron or a hole can be trapped at this level for certain duration, or as (b) a carrier-recombination center, where one charge carrier annihilates with an oppositely charged carrier. Hence, defects can strongly affect the minority carrier transport in the solar cell. Threading dislocations will lower *PCE* by creating more recombination centers that shorten minority carrier lifetimes, inside and outside of the depletion region of the *p-n* junction, resulting in smaller J_{sc} and larger dark current. On the other hand, both the localized defects that act as carrier-recombination centers and the large valence band bending may improve hole tunneling across the Si/Ge heterojunction. This can potentially increase the tunneling current and lead to a positive impact on the J_{sc} . It is thus vital to devise a fabrication technique to confine the defects at the Si/Ge heterointerface without the defects to propagate into the active region of Si or Ge epilayers.

To address the concern, we report an alternative architecture using back Ge epilayer grown on a highly doped *p+* Si substrate with a front side *n*-Si epi-emitter as shown in Figure 4.2(a). The use of the *p+* Si substrate is to ensure that there is minimal contribution of photo-excited minority carriers (*i.e.* electrons) by the bulk

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p^+ substrate to front side n -Si epi-emitter. Thus, any PCE change can be attributed to the effect of Ge epilayer on the hole collection at the backside.

Figure 4.2: (a) Schematic of the epi-emitter Si solar cell with back Ge epilayer; (b) Simulated PC1D energy band diagram of back Ge epilayer on p^+ Si substrate illustrating the hole transport into the Ge epilayer.

This geometry of Si/Ge heterojunction offers several benefits in the application of Si solar cells:

Firstly, when Ge is epitaxially grown on Si at lower temperature to prevent excessive intermixing, the energy band alignment of Si/Ge heterojunction leads to a valence band offset that results in the thinning of the potential barrier at the valence band edge as illustrated in Figure 4.2(b). The PC1D simulation result in Figure 4.2(b) also indicates the valence-band-edge rising, which can facilitate hole transport to enhance interfacial electrical conductivity for higher PCE of the solar cell. [54] Secondly, recombination centers in defective Ge epilayer can favor the alignment of the Fermi level of metal closer to the Ge valence band, thus

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promoting hole collection into the back contact and improving J_{sc} . [55] Thirdly, the Schottky barrier height (Φ_B) (Figure 4.3) due to Fermi level pinning close to the Ge valence band edge forms a reflection barrier for electrons to reduce minority carrier recombination at the backside of the cell. [56, 57]

Figure 4.3: The interface states of metal/semiconductor contact pin the Fermi level of the metal close to the charge neutrality level (Φ_0), forming an Schottky barrier (Φ_B). [57]

Last but not the least, it would be expedient that the Ge epilayer is grown on the highly doped p^+ Si substrate (i.e. metallurgical grade Si or back surface field) to realize possible modular implementation of this platform into the current manufacturing process flow of epitaxial thin-film Si solar cells. Epi-emitter Si solar cells with doped and undoped back Ge epilayer, together with the control sample, have been fabricated. As a result, an absolute PCE improvement of 1.8% has been achieved for the solar cell with back B-doped Ge epilayer when compared to the control sample.

4.2 Device fabrication process

Figure 4.4 shows the entire fabrication process flow of the epi-emitter Si solar cells with back Ge epilayer. A two-step epitaxial growth process was employed to fabricate the epi-emitter Si solar cell with back Ge epilayer.

Figure 4.4: Fabrication process flow of epi-emitter Si solar cell with back Ge epilayer.

The starting wafer used to fabricate the solar cells was double-polished, monocrystalline, *p*-type Czochralski (CZ) Si substrate with a thickness of 650 μm and a low resistivity of $\sim 0.015 \Omega\cdot\text{cm}$. The wafers underwent standard RCA cleaning to ensure a pristine Si interface prior to the epitaxial growth using ASM

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Epsilon 2000 CVD reactor system. Inside the reactor, the substrates were heated *in-situ* in ultra pure H_2 at $1100^\circ C$ to remove the native surface oxides. From a previous study, [58] an open-circuit voltage (V_{oc}) degradation of the solar cell was observed when the back Ge epilayer was grown after epitaxial growth of the *n*-Si emitter. To rectify this issue, the growth sequence of Si and Ge epilayers was reversed. ~ 600 nm Ge epilayer was first grown using germane gas precursor at $825^\circ C$ on the wafer backside with a three-step growth approach. [59] ~ 500 nm of phosphorus-doped Si emitter was subsequently grown using dichlorosilane and phosphine gas precursors on the front side at $900^\circ C$, [47] in order to achieve an abrupt *p-n* junction for better V_{oc} . [28] The emitter layer was then deposited with 75 nm of plasma-enhanced chemical vapor deposition (PECVD) silicon nitride (Si_3N_4) as an antireflective coating. Solar cells of $1\text{ cm} \times 1\text{ cm}$ were defined by photolithography. The front side (50 nm Ti/ 50 nm Pd/ 1000 nm Ag; $\sim 13\%$ optical shading) and backside (Al) metallization were subsequently evaporated before subjecting them to forming gas anneal ($N_2:H_2 = 90:10$) at $400^\circ C$ for 30 min. A reference cell is fabricated without back Ge epilayer for comparison purpose. To avoid ambiguity introduced by process variations, surface texturization and the absorber base are excluded in the cell fabrication to aid analysis of the Si/Ge interface.

4.3 Materials and Optical Characterization

Figure 4.5: Cross-sectional TEM image of undoped Ge epilayer grown on the backside of the p^+ Si solar cell at (a) lower magnification and (b) high magnification.

Cross-sectional TEM analysis is employed to investigate the interfacial quality of the undoped Ge epilayer grown on a p^+ Si substrate as shown in Figure 4.5. It can be observed in Figure 4.5(a) that most of the misfit dislocations are confined near the Si/Ge interface. This can be attributed to the three-step Ge epitaxial growth process [59] that employs a low-temperature Ge buffer layer to avoid three-dimensional nucleation of Ge. None of these misfit dislocations thread downwards to form threading dislocations at the surface of the Ge epilayer. Instead, the misfit dislocations join and annihilate in the region between the low-temperature Ge buffer layer and the high-temperature Ge epilayer, thus promoting Ge epilayer growth with no observable threading dislocation. A higher TEM magnification, in

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Figure 4.5(b), reveals severe faceting at the Si/Ge interface due to the 4.2% mismatch in lattice constants between crystalline Si and crystalline Ge. [51]

Figure 4.6: Cross-sectional TEM image of B-doped Ge epilayer grown on the backside of the p^+ Si solar cell at (a) lower magnification and (b) high magnification.

In-situ B-doping was employed, during the Ge epitaxial growth, to reduce the contact resistance between the Al metal and the Ge epilayer for a better performance epi-emitter Si solar cell. Figure 4.6(a) displays the TEM image of B-doped Ge epilayer grown on p^+ Si substrate. It appears that co-doping B during Ge epitaxial growth exacerbates the defects within the epilayer. In stark contrast to Figure 4.5(a), more misfit dislocations that start at the Si/Ge interface and propagate towards the surface of the p -Ge epilayer are present. In addition, more severe faceting is evident at a higher TEM magnification. These structural defects, which are analogous to the defects observed in Figure 3.8, may result in material-induced shunting via recombination of the photo-excited minority carriers.

Thus, we predict that the epi-emitter Si solar cell with B-doped Ge epilayer will have a poorer electrical performance as compared the solar cell with undoped Ge epilayer. Furthermore, due to the severely defective TEM image in Figure 4.6(b), selected-area diffraction (SAD) analysis was performed to check the crystallinity within the p -Ge epilayer, away from the defective interface. SAD patterns in Figure 4.7(a) and Figure 4.7(b) indicate that both the p^+ Si substrate and the p -Ge epilayer are monocrystalline in nature. The three-step Ge epitaxial growth process [59] promoted Ge epilayer with no observable threading dislocation, by limiting the misfit dislocations in the region between the low-temperature Ge buffer layer and the high-temperature Ge epilayer.

Figure 4.7: Selected region of the cross-sectional TEM for selected-area diffraction (SAD) analysis of: (a) p^+ Si (100) and (b) p -Ge epilayer.

Figure 4.8: HRXRD profiles of bulk Ge and Ge epilayers.

Figure 4.8. The XRD peaks of the samples can be readily indexed to a cubic phase of Si (JCPDS No. 27-1402). Strong Ge (400) peaks from both Ge epilayer samples reaffirmed that they are single crystalline in nature. The asymmetrical shoulder of the both the Ge peak signals, at higher incidence angle, indicate that Si/Ge intermixing at the interface during the emitter epitaxial growth. This results in an intermediate $\text{Si}_{1-x}\text{Ge}_x$ layer.

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The perpendicular lattice constant ($a^\perp$) of the Ge epilayer in the growth direction can be calculated from the XRD diffraction peak using Bragg's Law:

$$a^\perp = \frac{2\lambda}{\sin\left(\frac{\omega_{Ge}}{2}\right)} \quad (4.1)$$

where λ is the incident wavelength of the radiation (Cu $K_{\alpha 1}$ line, $\lambda=1.5406\text{\AA}$) and ω_{Ge} is the HRXRD of Si(004). The in-plane lattice constant ($a^\parallel$) can be defined as:

$$a^\parallel = \left(\frac{1+\nu}{2\nu}\right) \left[a_{Ge} - a^\perp \left(\frac{1-\nu}{1+\nu}\right) \right] \quad (4.2)$$

where ν is the elastic modulus of Ge, $\nu=0.271$, and the unstrained Ge lattice constant, $a_{Ge}=5.6576\text{\AA}$.

The residual strain (ε) of Ge epilayer can be calculated by the following equation:

$$\varepsilon = \frac{a_{Ge}^\parallel - a_{Ge}}{a_{Ge}} \quad (4.3)$$

With reference to the peak position of the bulk Ge substrate, the in-plane tensile strain for undoped Ge epilayer and B-doped Ge epilayer are calculated to be 0.21% and 0.26%, respectively. The tensile strain in the Ge epilayers is mainly due to the differences in thermal expansion coefficients between Si (2.6 ppm/ $^\circ\text{C}$) and Ge (5.8 ppm/ $^\circ\text{C}$), which increase during the cooling process after the epitaxial growth. [60]

Figure 4.9: Normalized Raman spectra of bulk Ge and Ge epilayers.

Raman spectroscopy measurements were performed with an excitation wavelength of 488 nm and the results were evaluated to quantify the strain with the Ge epilayers as illustrated in Figure 4.9. When compared to bulk Ge substrate, the peak shape of the Ge epilayers resembles excellent quality. It is noteworthy to point out that the peak positions of the Ge epilayers shifted left; clearly indicating that tensile strain is introduced in Ge epilayers due to the mismatch in thermal expansion coefficients with the p^+ Si substrate. The average in-plane strain (ϵ_{xx}) calculation [61] is as follows:

$$\epsilon_{xx} = \frac{\omega_{\text{expt}} - \omega_{\text{ref}}}{b} \quad (4.4)$$

where b is the phonon-strain coefficient in Ge (-408 cm^{-1}) and ω is phonon frequency of the Ge. The tensile strain within the undoped Ge epilayer and B-doped Ge epilayer are calculated to be 0.19% and 0.57%, respectively. Although the calculated strain values differ from that obtained from the HRXRD analysis due to the resolution limits of the two characterization techniques, it is evident that B-doped Ge epilayer experienced a higher tensile strain than undoped Ge epilayer. Yu *et al.* have reported that tensile strain can improve the out-of-plane hole mobility in Ge as illustrated in Figure 4.10. [62] Based on the tensile strain values calculated from Raman analyses, the out-of-plane hole mobility in the undoped Ge epilayer and B-doped Ge epilayer from Figure 4.10 are $702 \text{ cm}^2/\text{V.s}$ and $787 \text{ cm}^2/\text{V.s}$, respectively. Doping the Ge epilayer can increase the out-of-plane hole mobility by $\sim 12\%$, thus enhancing hole collection and *PCE* of the epi-emitter Si solar cells as compared to the cells with undoped Ge epilayer.

Figure 4.10: The hole mobility as a function of biaxial strain for hole mobility obtained with (open symbols) and without (filled symbols) the constant relaxation-time approximation. [62]

Furthermore, there is an *ab initio* study indicating that strain can result in significant shifts of the energy bands at the Si/Ge interface, [63] implying that back Ge epilayer can behave like a back-surface field (*BSF*). [64]

4.4 Electrical Characterization

The photovoltaic measurements were performed using Newport 94023A Class AAA solar simulator with an air mass (AM) 1.5G filter. The light intensity was calibrated to 100 mW/cm^2 using a Newport reference Si solar cell 91150, During our J - V measurement process, the outskirt region of our device is shielded by a stainless steel mask with an opening area of 0.95 cm^2 as shown in Figure 4.11. This is to ensure that there is no contribution of photocurrent from light absorption in the outskirt region of the active device with an area of 0.95 cm^2 .

Figure 4.11: Photo of the stainless steel mask used to cover the outskirt region of the solar cell during photovoltaic current density-voltage (J - V) measurement.

Figure 4.12: Illuminated current density-voltage (J - V) characteristics of 1 cm $\times$ 1 cm epi-emitter Si solar cells without and with back Ge epilayer under AM 1.5G solar irradiance.

Table 4.1: Summary of photovoltaic parameters of 1 cm $\times$ 1 cm epi-emitter Si solar cells without and with back Ge epilayer under AM 1.5G solar irradiance.

Sample	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (%)
Control	14.5	518	45.7	3.4
600 nm undoped back Ge epilayer	16.3	551	54.0	4.8
600 nm B-doped back Ge epilayer	16.9	556	55.6	5.2

Figure 4.12 shows the current density-voltage (J - V) characteristics of the epi-emitter solar cells without and with back Ge epilayer under simulated AM 1.5G irradiation. The photovoltaic parameters of J_{sc} , open circuit voltage (V_{oc}), fill factor (FF) and PCE are presented in Table 4.1. It is observed that a low PCE of 3.4% with poor FF of 45.7% has been recorded for the epi-emitter Si solar cell (*i.e.* control sample) fabricated using very low resistivity Si substrate. As mentioned

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earlier in Chapter 3, this result is expected because when base doping exceeds an optimal level of $\sim 1 \text{ } \Omega\cdot\text{cm}$, both the V_{oc} and FF will decrease. It is thus worth noting that the n -Si epi-emitter contributes most of the photocurrent, whereas the contribution via light absorption in the p^+ Si substrate is minimal due to the short minority carrier lifetime. On the other hand, a relative PCE improvement of $\sim 41\%$ and $\sim 53\%$ is observed for the epi-emitter Si solar cells with undoped back Ge epilayer and boron-doped (B-doped) back Ge epilayer respectively, when compared to the control sample. Both solar cells with back Ge epilayers have higher V_{oc} and FF . It is believed that the low solid solubility in Ge leads to B segregation at the p^+ Si/ p^+ Ge interface, resulting in enhanced back surface field that reduces the base component of recombination current, thereby accounting for the higher PCE of 5.2% for the solar cell with B-doped Ge back epilayer. This behavior is analogous to the well-known BSF effect. [64] Additionally, the Al/Ge Schottky barrier, [57] due to Fermi level pinning of Al close to valence band edge, forms a reflection barrier for electrons to reduce minority carrier recombination at the backside of the cell.

Figure 4.13 illustrates the dark J - V characteristics of the solar cells and corroborates well with the reduction in recombination current when back Ge epilayers are incorporated into the epi-emitter Si solar cells.

Figure 4.13: J - V characteristics of $1\text{ cm} \times 1\text{ cm}$ epi-emitter Si solar cells without and with back Ge epilayer under dark conditions.

Figure 4.14: External quantum efficiencies of $1\text{ cm} \times 1\text{ cm}$ epi-emitter Si solar cells with and without back Ge epilayer.

From Table 4.1, the J_{sc} of the epi-emitter cell with back Ge epilayer and back B-doped Ge epilayer is $\sim 12.4\%$ and $\sim 16.6\%$ higher than that of the control cell,

respectively. As mentioned earlier, the out-of-plane hole mobility increases $\sim 12\%$ by doping the Ge epilayer with B, thus resulting in a higher J_{sc} for the epi-emitter cell with back B-doped Ge epilayer. To understand this observation, the external quantum efficiency (EQE) of the epi-emitter cells is measured. Figure 4.14 exhibits the external quantum efficiency (EQE) response of the epi-emitter Si solar cells. The EQE response of the solar cells is consistent with their respective measured J_{sc} value, as presented in Table 4.1. Poor blue EQE response indicates that considerable front surface recombination is present in the cells due to insufficient surface passivation by the 75 nm Si_3N_4 , correlating well to the low V_{oc} values. It is shown that in line with higher J_{sc} values, the introduction of back Ge epilayer has enhanced the overall spectral response of the epi-emitter Si solar cell with the highest EQE of 69% at ~ 500 nm for the cell with B-doped Ge epilayer. It is also evident that the high dopant concentration in the p^+ Si substrate reduces the minority carrier lifetime with diminishing EQE response from 600 to 1100 nm. Electron mobility in Si is well known to be higher than hole mobility. [51] Thus, more electrons can drift from the p^+ Si substrate to n -Si epitaxial layer, whereas most of the holes from the n -Si region will recombine within the p^+ Si substrate before reaching the p - n junction for charge separation. We postulate that the incorporation of back Ge epilayer introduces a valence band offset that facilitates hole transport and supplies holes to recombine with electrons in the external circuit to produce higher J_{sc} . Furthermore, it was reported that deformed p -Ge shows a higher hole concentration, suggesting the introduction of dislocation-related acceptors. [65] To elucidate this hypothesis, a 100 μm by 100 μm metal-oxide-

semiconductor (MOS) capacitors with and without the undoped Ge epilayer were fabricated.

Figure 4.15: Capacitance-Voltage ($C-V$) characteristics of Metal-Oxide-Semiconductor (MOS) capacitor with undoped Ge epilayer grown on p -Si substrate and its corresponding control sample.

The Capacitance Voltage ($C-V$) characteristics of the MOS capacitors were measured using the Cascade/Suss Microtec PM8PS probe station, together with Keithley 4200-SCS semiconductor characterization system. Figure 4.15 shows the high-frequency (1 MHz) capacitance versus gate voltage ($C-V$) characteristics of MOS capacitors with and without the undoped Ge epilayer. The higher capacitance value obtained and the positive flat-band shift show that holes are effectively accumulated when the undoped Ge epilayer is added to the MOS capacitor. This observation suggests that it is easier to accumulate holes at the Ge epilayer region due to the valence band offset at the Si/Ge heterojunction, thereby facilitating hole

collection at the back contact for J_{sc} improvement of the epi-emitter Si solar cells as seen in Table 4.1.

4.5 Conclusion

In summary, it has been demonstrated that a thin back Ge epilayer can be utilized on highly doped p^+ Si substrate to improve the solar cell efficiency. PC1D simulation of the energy band diagram of the cell with back Ge epilayer suggests a thinned potential barrier due to the valence band bending that facilitate hole transport across the Si/Ge heterointerface. A relative PCE improvement of at least $\sim 41\%$ is observed with the incorporation of back Ge epilayer, with an absolute PCE improvement of $\sim 1.8\%$ when B-doped back Ge epilayer is grown on the epi-emitter Si solar cell. Both Raman and XRD analyses validated that the in-plane tensile strain within the Ge epilayer increased with B co-doping. The in-plane tensile-strained Ge epilayer is likely to contribute to higher out-of-plane hole mobility. TEM images reveal misfit dislocations along the Si/Ge heterointerface and more severe faceting with B-doped Ge epilayer. Such strain and defects present at the Si/Ge interface can modify the energy bands and form intermediate energy states, leading to the Si/Ge heterojunction-assisted hole transport that improves J_{sc} and consequently enhances PCE . The positive flat-band shift in $C-V$ characteristics of MOS capacitors with undoped Ge epilayer verifies that holes are effectively accumulated at the Si/Ge interface. Therefore, the back Ge epilayer is an attractive platform that can be adopted modularly on an existing BSF layer for better performance epi-emitter Si solar cells.

5. Low Temperature Back Germanium Epitaxy on Epitaxial Emitter Silicon Solar Cells (optimally doped substrate)

This chapter focuses on the fabrication and characterization of back Ge epilayer on epi-emitter Si solar cells using optimally doped p -type (p -Si) substrate. To evaluate the viability of future implementation of the back Ge epilayer scheme, the electrical, material and optical properties of these cells will be compared to a control epi-emitter Si solar cell with back B-doped Si epilayer (i.e. *BSF* epilayer).

5.1 Introduction and motivation

Figure 5.1: Schematic of the epi-emitter Si solar cell with back Ge epilayer; (b) Simulated PC1D energy band diagram of back Ge epilayer on p -Si substrate illustrating the hole transport into the Ge epilayer.

Figure 5.1(a) depicts the architecture of the epi-emitter Si solar cells with back Ge epilayer that is fabricated using optimally doped p -Si substrate. As discussed in Chapter 4, the energy band alignment of the Si/Ge heterojunction leads to a valence band offset that promotes hole tunneling due to the thinned potential

barrier at the valence band edge (Figure 5.1(b)). Moreover, the defective Si/Ge interface can introduce intermediate energy states that also enhance hole transport across the Si/Ge heterojunction. Aside from this, the Schottky barrier height due to Fermi level pinning of Al close to the Ge valence band edge forms a reflection barrier for electrons to reduce minority carrier recombination and hence the dark saturation currents at the backside of the cell. The in-plane tensile strain within the back Ge epilayer shifts the Ge energy band upwards to form a favorable band alignment with *p*-Si and promotes effective hole collection into the back contact to increase J_{sc} . It was observed in Chapter 4 that the tensile strain within Ge epilayer increases the out-of-plane hole mobility and it increases even more when the Ge epilayer is B-doped. However, it is necessary to mention that any photogenerated electrons from the Si/Ge heterojunction must be collected by the *n*-Si epi-emitter before they can contribute to J_{sc} .

From an economical prospective it is critical in thin-film Si solar cells to reduce the thickness of the active region of the solar cell. Aside from employing optical confinement to avoid possible J_{sc} degradation, it is also viable to incorporate a lower bandgap material in the base region of the cell to expand the spectrum response and boost optical absorption. Wang *et al* has reported a Si-SiGe-Si heterostructure cell with a *PCE* of 4.5% under AM 1.5G illumination. [49] However, this *PCE* is lower than that of the epi-emitter Si solar cell with back B-doped Ge epilayer (*PCE* = 5.2%) as presented in Chapter 4. The difference in *PCE* is possibly due to the presence of two heterointerfaces arising from the Si-SiGe-Si heterostructure. Thus, the back Ge epilayer scheme can potentially offer the

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combined advantages of *BSF* effect and enhanced light harvesting, and lead to a new generation of high *PCE* thin-film Si-based solar cells. In this chapter, we will provide a quantitative insight to the incorporation of back Ge epilayer on the epi-emitter Si solar cell by comparing it to an equivalent cell with a *BSF* epilayer and a reference cell.

5.2 Device fabrication process

Figure 5.2: Fabrication process flow of epi-emitter Si solar cell with back Ge epilayer or back B-doped Si epilayer.

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The entire fabrication process of epi-emitter Si solar cells with back Ge epilayer or back B-doped Si epilayer is shown in Figure 5.2. The starting wafer used to fabricate the solar cells was monocrystalline *p*-type Czochralski (CZ) Si substrate with a thickness of 575 μm and optimal resistivity of $\sim 0.60\text{-}0.80\ \Omega\cdot\text{cm}$. [38] The wafers underwent standard RCA cleaning to ensure a pristine Si interface prior to the epitaxial growth using ASM Epsilon 2000 CVD reactor system. Inside the reactor, the substrates were heated *in-situ* in ultra pure H_2 at 1100°C to remove the native surface oxides. $\sim 600\ \text{nm}$ Ge epilayer was first grown using germane gas precursor at 825°C on the wafer backside by a three-step growth approach. [59] $\sim 500\ \text{nm}$ of P-doped Si emitter was subsequently grown using dichlorosilane and phosphine gas precursors on the front side at 900°C , [47] in order to achieve an abrupt *p-n* junction for better V_{oc} . [28] Another cell with $\sim 600\ \text{nm}$ back B-doped Si epilayer is grown using dichlorosilane and diborane gas precursors to fabricate the *BSF* solar cell. $75\ \text{nm}$ of plasma-enhanced chemical vapor deposition (PECVD) silicon nitride (Si_3N_4) was then deposited as an antireflective coating on the epi-emitter. Front side contact with an optical shading of $\sim 13\%$ were defined by photolithography. Front side (50 nm Ti/ 50 nm Pd/ 1000 nm Ag) and backside (Al) metallization were subsequently evaporated before subjecting them to forming gas anneal ($\text{N}_2:\text{H}_2 = 90:10$) at 400°C for 30 min. In addition, a reference cell without back Ge epilayer is fabricated for comparison purpose. Surface texturization and surface passivation are excluded in the cell fabrication to avoid ambiguity introduced by process variations and aid analysis of the Si/Ge interface.

5.3 Materials and Optical Characterization

Figure 5.3: Raman spectra of *p*-Si substrate, Ge epilayer and B-doped Si epilayer.

Raman spectroscopy is used to calculate the strain of the Ge epilayer and B-doped Si epilayer. It can be seen in Figure 5.3 that there is a red shift of peak position between the Ge epilayer (299.02 cm^{-1}) and that of the Ge bulk reference (301.93 cm^{-1}). This peak shift to the left depicts the tensile strain within the Ge epilayer, which is aforementioned in Chapter 4. Based on Equation 4.4 and Figure 4.10, the in-plane tensile strain can be calculated to be 0.71% with a corresponding out-of-plane hole mobility of $805 \text{ cm}^2/\text{V.s}$. Moreover, the lattice mismatch at the defective Si/Ge heterointerface results in inhomogeneous strain within the Ge epilayer, evident from the broadening of Ge-Ge Raman peak in Figure 5.3. This result correlates well to the TEM images of the defective Si/Ge heterointerface in Figure 4.5. On the other hand, no strain is introduced within the Si epilayer during

epitaxial growth since both peak positions of B-doped Si epilayer and Si bulk reference coincide at 520.18 cm^{-1} . In addition, the Raman spectra also depict that a monocrystalline Ge epilayer and Si epilayer were grown using the ASM Epsilon 2000 CVD reactor system.

Figure 5.4: UV-Vis absorbance spectra of *p*-Si substrate, Ge epilayer and P-doped Si epi-emitter on *p*-Si with back Ge epilayer.

The absorbance spectra of different samples, as shown in Figure 5.4, were characterized using an integrating sphere by a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer system. We can observe in Figure 5.4 that there is an improvement in the infrared absorption between the wavelengths of 1000 nm to 1600 nm when the back Ge epilayer is grown on the *p*-Si substrate. Moreover, when the *n*-Si epitaxial layer is added to the cell as the emitter, a clear reduction of ~10% in light transmittance can be clearly seen. This absorption enhancement is because of the extended optical path length of light due to changes in the

crystallographic orientations by the mechanical twins, as reported in a recent paper by Lai *et al.* [66] This improvement in optical absorption may translate to an increased probability of generating minority charge carriers.

5.4 Electrical Characterization

Figure 5.5 shows the photovoltaic current density-voltage (J - V) characteristics of the epi-emitter solar cells, without and with back Ge epilayer, that were measured with a Keithley 2400 Source-Meter unit under 100 mW/cm² illumination using Newport 94023A Class AAA solar simulator with AM 1.5G filter. The light intensity was calibrated to 100 mW/cm² using a Newport reference Si solar cell 91150, which is traceable both to the National Renewable Energy Laboratory (NREL), and to the International System of Units (SI). During the J - V measurement process, the outskirt region of the devices is shielded by a stainless steel mask with an opening area of 0.95 cm² as shown previously in Figure 4.11.

Figure 5.5: Illuminated current density-voltage (J - V) characteristics and *pseudo* J - V analyses of $1\text{ cm} \times 1\text{ cm}$ various epi-emitter Si solar cells under AM 1.5G solar irradiance.

Table 5.1: Summary of photovoltaic parameters of various $1\text{ cm} \times 1\text{ cm}$ epi-emitter Si solar cells under AM 1.5G solar irradiance.

Process	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (%)	FF_{pseudo} (%)	PCE_{pseudo} (%)
Control	21.8±0.1	520±2	61.7±0.1	7.0±0.2	76.7	8.7
600 nm undoped back Ge epilayer	27.1±0.2	556±3	67.6±0.2	10.2±0.4	75.2	11.3
600 nm B-doped back Si epilayer	27.0±0.2	550±3	68.0±0.2	10.1±0.4	75.5	11.2

Five cells were investigated for each type of epi-emitter solar cells and the statistical distributions of the J_{sc} , V_{oc} , FF and PCE are shown in Table 5.1. It is noteworthy to point out that there is a relative PCE improvement of 42.8% with reference to the equivalent cell reported in Table 3.2. The higher PCE of the cell here is attributed to the usage of optimally doped Si substrate of ~ 0.60 - $0.80\ \Omega\cdot\text{cm}$ and Si_3N_4 antireflective coating, thus resulting in a higher V_{oc} and J_{sc} . [38] With

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reference to the control cell in Table 5.1, a remarkable absolute *PCE* improvement of ~3.1% was achieved by the epi-emitter Si solar cells with either back Ge epilayer or back B-doped Si epilayer. Compared to the control cell, the *PCE* of the cell with back Ge epilayer increases substantially from 7.0% to 10.2%, as a result of improvements in the J_{sc} from 21.8 to 27.1 mA/cm², V_{oc} from 520 mV to 556 mV and *FF* from 61.7% to 67.6%. The cell with back Ge epilayer has a slightly higher *PCE* of 10.2% than that of the cell with B-doped Si epilayer (10.1%). The higher V_{oc} and J_{sc} can be attributed to the valence band offset at the Si/Ge heterointerface of the Ge epilayer scheme that is as effective, if not better, as the *BSF* effect of the B-doped Si epilayer to improve hole transport and reduce photogenerated carriers recombination at the backside of the cell. This implies that the space charge region may be narrower at the Si/Ge heterojunction, hence contributing to a better V_{oc} . The moderately high fill factor (*FF*) can be explained by the high series resistance (R_{series}) due to the thinner front Ti/Pd/Ag metallization as indicated by the decreased slope ($dJ/dV|_{V=V_{oc}}$) as seen in Figure 5.5.

Pseudo J-V analyses are performed on the best cells to predict the PCE_{pseudo} , which is independent of R_{series} . The PCE_{pseudo} calculated are 11.3% (epi-emitter cell with back Ge epilayer), 11.2% (epi-emitter cell with back B-doped Si epilayer), and 8.7% (control cell). The *Pseudo J-V* result suggests the potential of the back Ge epilayer scheme, which is as good as the *BSF* scheme, if not better. The J_{sc} of the epi-emitter cell with back Ge epilayer is ~24.3% higher than that of the control cell. To explain this observation, the external quantum efficiency (*EQE*) of the cells is measured.

Figure 5.6: External quantum efficiencies (EQE) of various $1\text{ cm} \times 1\text{ cm}$ epitaxial emitter Si solar cells.

Figure 5.6 illustrates the EQE of the different cells. The result from the spectral response of the cells agrees well with their respective J_{sc} values as presented in Table 5.1. We have to evaluate the spectral response of each cell at different regions for the entire light spectrum to understand the electrical performance further. From the spectra, considerable front surface recombination is present in all cells since blue light is absorbed very near to the cell surface. This implies that 75 nm Si_3N_4 is insufficient to provide complete surface passivation. In addition, it is evident that the cell with back B-doped Si epilayer has a better blue response than the other two cells. At $\sim 400\text{ nm}$, the spectral response for the cell with back B-doped Si epilayer is about 50%, while for the cell with back Ge epilayer and control cell are around 20%. In principle, if the surface passivation used for all cells is the same, they should have similar spectral responses. However, it is possible that during the backside B-doped epitaxial growth process, mobile

interstitial oxygen dimer O_{2i} is captured by the substitutional boron B_s , which hence reduces the formation of the defect complex B_sO_{2i} (*i.e.* recombination center). [41] This would imply a longer minority carrier lifetime and therefore accounting for the trends observed in the blue response. This trend continues when we transit to the green light region ($\sim 450\text{ nm} - 600\text{ nm}$) where the cell with B-doped Si epilayer shows a better *EQE* for the cell than the other two cells. This result shows that the diffusion length for the photogenerated carriers within the bulk of the cell with B-doped Si epilayer is the highest, followed by the cell with Ge epilayer and the control cell. Finally, in the red light region to the near-infrared region ($\sim 600\text{ nm} - 1400\text{ nm}$), the cell with back B-doped Si epilayer may contain higher concentration of defect complex B_sO_{2i} (*i.e.* within the back Si epilayer) that act as recombination centers, hence reducing the diffusion length of minority carriers and resulting in a poorer spectral response. On the other hand, the better infrared *EQE* response for the cell with Ge epilayer could be attributed to the enhanced optical absorption within the bulk Si (Figure 5.4). It has been reported that the tensile strain within the Ge epilayer can decrease the energy gap difference the direct and indirect energy band gap of Ge, [67] thereby thus increasing the probability of photogeneration of minority carriers by the lower energy photons. Furthermore, we postulate that backside Al metallization alloys with Ge epilayer to form Al_xGe_{1-x} during the forming gas anneal step, leading to a very thin Ge epilayer near the Si/Ge heterointerface.

Figure 5.7: Phase diagram of aluminum/germanium system. [68]

During the forming gas anneal step at 400°C, considering the temperature variation between the load and source of the furnace to be $\pm 20^\circ\text{C}$, it is highly possible to form eutectic $\text{Al}_{0.284}\text{Ge}_{0.716}$ back contact at $420 \pm 20^\circ\text{C}$ as illustrated in Figure 5.7. Therefore, the built-in electric field at the Si/Ge heterojunction fully depletes the Ge epilayer, assisting photogenerated holes to be swept more rapidly across the Si/Ge interface to the $\text{Al}_x\text{Ge}_{1-x}$. This results in a better *EQE* result for the cell with back Ge epilayer, therefore accounting the high J_{sc} values reported in Table 5.1.

Figure 5.8: J - V characteristics of various $1\text{ cm} \times 1\text{ cm}$ epi-emitter Si solar cells under dark conditions.

Figure 5.8 illustrates the dark J - V characteristics of the solar cells. The ideality factor can be determined from the slope of these dark J - V curves. The fundamental cell equation for dark J - V is:

$$J = J_o \left(\exp\left(\frac{qV}{nkT}\right) - 1 \right) \quad (5.1)$$

, where J is the current density through the diode, V is the voltage across the diode, J_o is the dark saturation current, n is the ideality factor and T is the temperature measured in Kelvin, q is the Columbic charge and k is Boltzmann constant. When V is greater than $0.050 - 0.100\text{ mV}$, Equation 5.1 can be expressed as:

$$J = J_o \exp\left(\frac{qV}{nkT}\right) \quad (5.2)$$

By taking the natural logarithm of both sides of the equation:

$$\ln(J) = \ln(J_o) + \left(\frac{q}{nkT}\right)V \quad (5.3)$$

In practice, the ideality factor, n , of a solar cell can deviate from 1, indicating that there are recombination mechanisms or the recombination is fluctuating in magnitude. [69] Therefore, the ideality factor can be used for examining the recombination mechanism in a solar cell. Table 5.2 shows the ideality factor n and J_o values of the cells that were estimated experimentally from the slopes of plots of $\ln(J)$ against V and the extrapolation to 0 V of the straight-line regions of the $\ln(J)$ - V characteristics, where there were no series resistance and shunt conductance. [70]

Table 5.2: Ideality factor n and J_o values of various 1 cm $\times$ 1 cm epi-emitter Si solar cells determined experimentally from their respective dark $\ln(J)$ - V curves when $V > 0.4$ V – 0.6 V.

Parameters	J_o (A/cm ²)	n
Control	3.72E-5	2.72
600 nm undoped back Ge epilayer	2.97E-7	1.96
600 nm B-doped back Si epilayer	1.88E-7	1.90

From Table 5.2, it is evident that the incorporation of either back Ge epilayer or back B-doped Si epilayer reduces the recombination and suppresses the dark saturation current density by 2 orders of magnitude, correlating well with the higher V_{oc} obtained with these cells as compared to the control cell.

5.7 Conclusion

In conclusion, we have demonstrated an alternative technique to *BSF* effect by using back Ge epilayer to improve the *PCE* of epi-emitter Si solar cells. PC1D simulation of the energy band diagram of the cell with back Ge epilayer suggests a thinner potential barrier due to the more valence band bending that facilitate hole transport across the Si/Ge heterointerface. Raman analysis indicates in-plane tensile strain of 0.71% within the Ge epilayer and verifies the monocrystallinity of the Ge and Si epilayers. As compared to the control cell, the cell with back Ge epilayer offers higher J_{sc} and *PCE* of 27.1 mA/cm² and 10.2%, respectively. This improvement in electrical performance can be attributed to the presence of in-plane tensile strain, improved optical absorption and reduced dark saturation current. With reference to the cell with B-doped Si epilayer, both cells have comparable *PCE* and *PCE_{pseudo}*. We also found that the cell with back Ge epilayer have better *EQE* in the infrared spectrum. This can be attributed to both a better optical absorbance and an enhanced out-of-plane hole mobility at the tensile-strained Si/Ge heterojunction, hence resulting in comparable *PCE* with the cell with *BSF* effect. Moreover, the back Ge epilayer scheme only involves germane gas precursor as opposed to the back *BSF* epilayer scheme that requires both the dichlorosilane and borane gas precursors. Furthermore, a more cost-effective germanium tetrachloride (GeCl₄) gas precursor to grow the Ge epilayer should be considered over the costly germane gas precursor. Therefore, this suggests the

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commercial viability for employing the back Ge epilayer scheme for future integration with the production of epitaxial Si solar cells.

6. Architectural and Peripheral Modifications of Epitaxial Silicon Emitter Solar Cells

6.1 Introduction and motivation

In Chapters 3, 4 and 5, we have demonstrated that Si-based epitaxy improves the electrical performance of planar epi-emitter Si solar cells. However, it is necessary to reduce the thickness for material cost savings and a more efficient minority carrier transport, as mentioned in Chapter 2. An effective light management technique is hence required for a thinner active layer. To address this concern, we present two different light trapping approaches. First, we investigate the feasibility of using focused ion beam (FIB) to synergistically etch nanocone array on defective Si epi-emitter to alleviate material-induced shunting and to form spectral downshifters to increase optical absorption for epi-emitter Si solar cells. [71] This two-step technique will be discussed and the electrical performances of the cells are evaluated. Next, we employ solar spectral downshifters by depositing a bilayer antireflective coating (ARC) by PECVD. The embedded nanocrystals within the high refractive index (RI) Si_3N_4 layer is able to downshift high-energy ultraviolet photons to lower energy photons, which can improve the photovoltaic performance. The electrical characteristic of epi-emitter Si solar cells with the bilayer ARC is compared to the conventional silicon nitride.

6.2 Device fabrication process

In Chapter 3, it is discussed that epi-emitter grown at 900°C has more severe twinning that could have contributed to material-induced shunting, thus resulting in poorer cell performance. In the Si nanocone array study, DCS 900°C epi-emitter cell from Chapter 3 was selected for surface texturization using FIB etching to alleviate the issue related to strongly recombination crystal defects. [21] The device fabrication process is presented in Section 3.2. The Ga^+ ion source is used, with ion energy of 30keV and a dose of $8.40\text{nC}/\mu\text{m}^2$. The Si nanocone array is formed on the defective Si epilayer by FIB bombardment at high oblique incident angle by raster scanning with the Ga^+ ion beam. At high incident angle of 70° , the sputtering yield is larger for planar surfaces, yet is lower than that of the Ga droplet, shadowing effects due to the fixed droplets, results in the formation of the Si nanocone array. Due to the required FIB raster scanning; only a small area of Si nanocone array ($100\ \mu\text{m} \times 1\ \text{mm}$) was etched on $1\ \text{cm} \times 1\ \text{cm}$ DCS 900°C epi-emitter Si solar cells (see Figure 6.1). In addition, to avoid ambiguity due to process variations, electrical measurement was performed on the cell after cell fabrication, and on the same cell after the Si nanocone array formation and FGA step.

Figure 6.1: Schematic of the epi-emitter Si solar cell with ordered Si nanocone array formed by FIB etching.

Figure 6.2: Schematic of the epi-emitter Si solar cell with bilayer ARC layer.

Figure 6.2 illustrates the architecture of the epi-emitter Si solar cell with bilayer ARC layer. The entire fabrication process of epi-emitter Si solar cells without and with back Ge epilayer is similar to the fabrication sequence described in Chapter 5.

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The bilayer ARC was deposited via PECVD by controlling the flow rates of different precursor gases, chamber pressure, RF power, temperature, and deposition time. Silane (SiH_4) and ammonia (NH_3) were used to perform *in-situ* deposition of 59 nm high RI Si_3N_4 (*i.e.* 2.28) with embedded Si nanocrystals on a cold substrate in the process chamber. [72] 82 nm low RI SiO_2 layer (*i.e.* 1.48) was subsequently deposited using SiH_4 , N_2 , and N_2O gas precursors. The process parameters of the bilayer ARC layer are tabulated in Table 6.1. It should be highlighted that the deposition of the bilayer ARC layer is cost-effective because it was performed in a single process within the PECVD chamber. Control epi-emitter solar cells with conventional Si_3N_4 layer were fabricated for comparison.

Table 6.1: Detailed process parameters used to deposit the bilayer ARC.

Process	High RI Si_3N_4 layer	Low RI SiO_2 layer
SiH_4 flow rate (SCCM)	100	100
N_2 flow rate (SCCM)	700	600
N_2O flow rate (SCCM)	0	30
RF power (W)	40	60
Pressure (mTorr)	200	800
Temperature ($^{\circ}\text{C}$)	50	300

6.3 Effect of silicon nanocone array with silicon nanocrystals using focused ion beam etching

It is expected that commercial solar cells in production will be thinner than 100 μm thick by 2023. [73] The main driver for such trend is lower material costs and yield improvement due to reduced thin-film deposition time. Epitaxial thin-film Si solar cells offer a viable pathway to achieve the performance of conventional Si solar cells with low-cost manufacturability. [13, 74, 75] However, it is crucial that the electrical performance of the solar cells is not compromised by the reduced thickness. Typically, a thinner wafer will result in poorer optical absorption of the solar spectrum. Surface texturization can be performed to enhance light absorption and reduce reflection. Si nanostructures such as Si nanocone arrays are introduced as these nanostructures serve as active absorbers as well. Moreover, a theoretical study reveals that using Si nanocone arrays could result in broadband light harvesting. [76, 77]

In order to fabricate ordered Si nanocone arrays, both top-down planar lithography and deep reactive ion etching are required. It is typically difficult to obtain the desired critical dimension (CD) of the Si nanocone array by optical lithography, as it is limited to a fraction of the wavelength. [78] Aside from the limitation posed by conventional lithographic technique, more advanced nanoimprint lithography [79] and the self-powered parallel electron lithography (SPEL) [80] could also be used to form Si nanocone arrays. However, both techniques likewise require tedious masking and etching processes. Apart from this, it is known that focused ion beam (FIB) etching will amorphize and damage the Si during the etching process. [81]

Annealing the FIB-etched Si may induce crystallization of nanocrystals at the interface between the amorphous Si and crystalline Si. The presence of these Si nanocrystals can aid in light scattering and increase the optical path length of light within Si. In this work, we investigate the feasibility of the synergistic two-step process to etch Si nanocone array directly on the defective epi-emitter and anneal to form Si nanocrystals.

Figure 6.3: Tilted cross-sectional FESEM image of the Si nanocone array. The scale bar = 2 μm .

LEO 1550 Gemini field emission scanning electron microscopy (FESEM) was used to characterize the morphology of the Si nanocone array formed on top of the epi-emitter. The Si nanocone array has a dimension of 500 nm (height) $\times$ 600 nm (diameter) as depicted in Figure 6.3.

Figure 6.4: Illuminated current density-voltage (J - V) characteristics of $1\text{ cm} \times 1\text{ cm}$ epi-emitter Si solar cells without and with Si nanocone array under AM 1.5G solar irradiance.

Table 6.2: Summary of photovoltaic parameters of various $1\text{ cm} \times 1\text{ cm}$ epi-emitter Si solar cells without and with Si nanocone array under AM 1.5G solar irradiance.

Process	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (%)
Control	21.8	474	54.9	5.7
Si nanocone array with nanocrystals	22.1	477	55.7	5.9

Figure 6.4 shows the J - V characteristics of the epi-emitter Si solar cells without and with the Si nanocone array under 100 mW/cm^2 illumination (AM 1.5G). The photovoltaic parameters of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and PCE are summarized in Table 6.2. It should be highlighted that the measured PCE does not account for the loss due to the $\sim 10\%$ optical shading of the front side metallization. It is seen that the V_{oc} is moderately low which can be explained by the use of moderately low resistivity Si substrates

of $\sim 4\text{-}10\ \Omega\cdot\text{cm}$ as compared to the optimal base resistivity of $\sim 1\ \Omega\cdot\text{cm}$. [82] The poor FF can be associated with the high line resistivity of the thin front metallization ($\sim 700\ \text{nm}$). With reference to the control cell, the solar cell with Si nanocone array achieved a relative PCE improvement of $\sim 3\%$ from 5.7% to 5.9% . This enhancement can be attributed to the passivation of the Si surface arising from the amorphization during FIB etching and the FGA step. Consequently, the calculated shunt resistance (R_{shunt}) increased from $467\ \Omega\cdot\text{cm}^2$ to $1134\ \Omega\cdot\text{cm}^2$, resulting in an absolute increase in V_{oc} of $3\ \text{mV}$. In addition, the Si nanocone array has increased the J_{sc} by $0.3\ \text{mA}/\text{cm}^2$. Both improvements in V_{oc} and J_{sc} for the cell with Si nanocone array resulted in an absolute increase in FF by 0.8% as shown in Figure 6.4 and Table 6.2.

Figure 6.5: EQE spectra of the epi-emitter Si solar cells, without and with Si nanocone array, measured with bias light.

From Figure 6.5, the J_{sc} increment can be explained by the EQE enhancement at longer wavelengths from $850\ \text{nm}$ to $1100\ \text{nm}$, due to better light trapping

capability. However, Lu *et. al.* reported that although the regimented Si conical-frustum array solar cells with 600 nm lattice contact contributes the lowest reflectance, it showed increasing transmittance for the wavelength near the bandgap region of 800 nm – 1100 nm. [83] Thus, we postulate that the *EQE* improvement, as observed in Figure 6.5, could be explained by the downshifting effect of Si nanocrystals formed around the Si nanocones during FGA step.

To verify the postulation, we performed Raman spectroscopy to detect the presence of Si nanocrystals on the Si nanocone array.

Figure 6.6: Raman spectra of FGA Si nanocone array (red), bulk crystalline Si and bulk amorphous Si (green), and convoluted signal from both bulk crystalline Si and bulk amorphous Si (blue).

Raman spectroscopy measurements were performed with an excitation wavelength of 488 nm and the spectra are plotted as shown in Figure 6.6. The spectra in green represent both the Raman peaks for bulk crystalline Si (520 cm⁻¹) and bulk

amorphous Si (480 cm^{-1}). With reference to the convoluted peak (blue) from bulk crystalline Si and bulk amorphous Si, it is evident that the spectrum of the FGA Si nanocone array cannot be satisfactorily fitted using only the two peaks from the bulk samples. Therefore, nanocrystalline Si must be present amidst the FGA Si nanocone array. To validate this result, we performed HRTEM analysis on the FGA Si nanocone array.

Figure 6.7: Cross-sectional HRTEM image of (a) the Si nanocone, and (b) the tip of the Si nanocone.

Cross-sectional HRTEM analysis is employed to investigate the presence of Si nanocrystals on the FGA Si nanocone. From Figure 6.7(a), it can be observed that amorphous Si is present due to the FIB-induced surface amorphization. At a higher magnification, Figure 6.7(b) reveals the Si nanocrystals at the interface between the amorphous Si shell and crystalline Si nanocone, corroborating well with the Raman result. Both the FIB-induced defects and the defective Si epilayer increase the surface energy on the Si nanocone surface. These high surface energy sites serve as

the location for heterogeneous nucleation of the Si nanocrystals at the interface. Such observation is similar to a study reported by Mehta *et al.* [84] In addition, the defective interface can act as sinks for phosphorus (P) in-diffusion. A higher P concentration in the Si nanocrystals can improve radiative recombination and increase the *PL* intensity. [85] Furthermore, highly P-doped Si nanocrystals can acts as a front surface field (FSF) to repel photogenerated electrons and reduce front surface recombination. The interface between the highly P-doped region (*i.e.* Si nanocrystals) and lowly P-doped region (*i.e.* Si nanocone) behaves like a *p-n* junction and an electric field forms at the interface which introduces a barrier for photogenerated electrons to flow towards the front side. The minority carrier concentration is thus maintained at higher levels in the Si nanocones and hence the FSF has a net effect of passivating the front surface.

6.4 Effect of spectral downshifters using silicon nitride with embedded silicon nanocrystals

In the previous section, we have demonstrated using Si nanocone array surface texturization and FGA step to improve light trapping for the epitaxial thin-film Si solar cells. However, although surface texturization can improve the *PCE* of a cell, it can also exacerbate surface recombination, which has a detrimental effect on the electrical performance. In addition, surface texturization may be incompatible with some thin-film deposition techniques for very thin cells. In such instances, a good antireflective coating (ARC) with passivating properties can be employed to enhance light absorption. Silicon nitride (Si_3N_4) is commercially used as an ARC due to its respectable performance, affordability and excellent passivating property. [86] Furthermore, the refractive index (RI) of Si_3N_4 (n_1) can be related to the RI of air (n_0) and RI of Si (n_2) by this equation:

$$n_1^2 = n_0 n_2 \quad (6.1)$$

This means that the single layer ARC of Si_3N_4 can reduce the reflection to zero at one particular wavelength. Hence, the conventional Si_3N_4 can maximize optical absorption in the 450 nm – 750 nm wavelength range, which corresponds to the highest energy region of the solar spectrum. To extend the optical absorption to a broadband spectrum, a material of higher RI (*e.g.* TiO_2) can be sandwiched between a lower RI material (*e.g.* MgF_2) and the Si epi-emitter layer of the solar cell. However, high RI material, such as TiO_2 , incurs a higher material cost. [86, 87] Aside from this, such multilayer ARC may involve a separate surface passivation step of the emitter layer that increases process cost and complexity.

Thus, it is meaningful to explore a cost-effective ARC layer that provides good antireflective property over a broadband solar spectral range. Zhang *et al.* demonstrated that Si_3N_4 embedded with Si nanocrystals could result in a high RI material. Embedded Si nanocrystals can downshift an incident higher energy photon into a lower energy photon, which can be utilized by Si solar cells. Downshifting, otherwise known as *PL*, [88] can be employed to overcome poor blue response of solar cells due to lack of proper front surface passivation. [89] As energy is lost due to non-radiative relaxation, the quantum efficiency of the downshifting process is lower than unity. [90] Interestingly, by downshifting the solar spectrum to the red region, a *PCE* enhancement of $\sim 10\%$ is expected when the internal reflection ensures the absorption of all the re-emitted light into the Si substrate. [91] More importantly, downshifting thin-films can also be used to circumvent absorption of higher energy photons in a heterojunction cell. [92] Therefore, in this work, we investigate the viability of employing an improved bilayer ARC to enhance broadband optical light absorption and downshift high energy photons to lower energy photons that can be utilized to improve the *PCE* of epi-emitter Si solar cells with and without back Ge epilayer.

Figure 6.8: Reflectance spectra of blanket *p*-Si substrate, conventional Si₃N₄ and bilayer ARC.

Reflectance analysis was performed on the bilayer ARC and the conventional Si₃N₄ were deposited on polished blanket Si substrate, using the aforementioned PECVD process. Figure 6.8 shows the reflectance spectra of different samples that were characterized using an integrating sphere by a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer system. It is clearly evident that the bilayer ARC can suppress reflection over a broadband wavelength of 400 nm – 1100 nm as compared to the conventional single Si₃N₄ coating, with the lowest reflectance of 0.05% at 730 nm.

Svreck *et al.* were able to incorporate Si nanocrystals successfully into spin-on-glass (SOG) on top of crystalline Si solar cells as a downshifter, leading to an experimental enhancement of 0.4% (using Si nanocrystals of 7 nm diameter with a broad emission centered around 700 nm). [93] More importantly, W. D. A. M. de

Boer *et al.* demonstrated that the red spectral shift caused by the *PL* of Si nanocrystals does not involve phonons. [94] To validate whether the embedded Si nanocrystals in the Si_3N_4 matrix can emit photons of visible and near- infrared light, [95] we subject the sample with bilayer ARC to an excitation source of 325 nm.

Figure 6.9: *PL* spectrum of bilayer ARC with embedded Si nanocrystals excited by a 325 nm excitation source (Courtesy of Dr. Wong Jen It).

Figure 6.9 depicts the photoluminescence (*PL*) spectrum of the bilayer ARC with embedded Si nanocrystals deposited on Si substrate under the excitation of a 325 nm excitation light source. As seen in Figure 6.9, the *PL* spectrum ranges from ~500 nm to ~1100 nm with a peak emission at 775 nm. This process is vital as the embedded Si nanocrystals can circumvent thermalization processes by downshifting ultraviolet photons to visible and near-infrared photons that can be used by Si solar cells more effectively, [95] hence improving the *PCE*. Moreover, with reference to the Si nanocrystals study conducted by Ray *et al.*, the size of the

Si nanocrystals can be estimated to be 3 nm from the excitonic *PL* peak of 775 nm.

[96]

Figure 6.10: Illuminated current density-voltage (*J-V*) characteristics of 1 cm × 1 cm epi-emitter Si solar cells without and with conventional or bilayer ARC and / or back Ge epilayer under AM 1.5G solar irradiance.

Table 6.3: Summary of photovoltaic parameters of various 1 cm × 1 cm epi-emitter Si solar cells without and with conventional or bilayer ARC and / or back Ge epilayer under AM 1.5G solar irradiance.

Process	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (%)
Conventional Si ₃ N ₄ ARC	21.8	520	61.7	7.0
Conventional Si ₃ N ₄ ARC with back Ge epilayer	27.1	556	67.6	10.2
Bilayer ARC	22.8	520	66.2	7.5
Bilayer ARC with back Ge epilayer	30.5	537	56.1	9.2

Figure 6.10 shows the *J-V* characteristics of 1 cm × 1 cm epi-emitter Si solar cells without and the bilayer ARC and / or back Ge epilayer under 100 mW/cm²

illumination (AM 1.5G). The photovoltaic parameters of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and PCE are summarized in Table 6.3. With the V_{oc} remaining constant, the FF and PCE of the control sample improved from 61.7% to 66.2% and 7.0% to 7.5%, respectively. This improvement can be attributed to the increment in J_{sc} , mainly due to the reduced reflectance of the bilayer ARC. The contribution by the embedded Si nanocrystals in the bilayer ARC to the improved J_{sc} is minimal because the intensity of 325 nm wavelength in the AM 1.5G illumination is many folds weaker than the laser excitation source used in the PL measurement. It is worthy to point out that the contributions by embedded Si nanocrystals will be significant when concentrated light illumination (*e.g.* 100 $\times$ suns) is employed. In stark contrast, the FF and PCE of the control sample with back Ge epilayer and bilayer ARC drops substantially from 67.6% to 56.1% and 10.2% to 9.2%, respectively. The performance degradation in FF could be attributed to higher front side recombination due to presence of Si nanocrystals at the ARC-emitter interface. This increased front side recombination resulted in a drop in V_{oc} by 19 mV and also the material-induced shunting, as evident in the decreased slope ($dJ/dV|_{V=0}$) in Figure 6.10. It is vital to point out that the bilayer ARC requires a passivation layer (*i.e.* doped amorphous Si) at the interface between the high RI Si_3N_4 and the Si epi-emitter to improve the V_{oc} . Nevertheless, it can be seen that the incorporation of the bilayer ARC has led to an increase in J_{sc} , from 21.8 mA/cm² to 22.8 mA/cm² for the control sample and from 27.1 mA/cm² to 30.5 mA/cm² for the sample with back Ge epilayer, respectively.

Figure 6.11: External quantum efficiencies (EQE) of $1\text{ cm} \times 1\text{ cm}$ epi-emitter Si solar cells without and with the bilayer ARC and / or back Ge epilayer, measured with bias light.

Figure 6.11 shows the EQE spectra of $1\text{ cm} \times 1\text{ cm}$ epi-emitter Si solar cells without or with the bilayer ARC. The change in the J_{sc} is accounted by the shift of the spectra from blue to red region of the solar spectrum. As seen in Figure 6.8, the reflectance of the bilayer ARC is further reduced because of the light trapping capability of the Si nanocrystals. As a result, the EQE (Figure 6.11) is enhanced for the cell with bilayer ARC and back Ge epilayer, reaching a maximum value of 82.7% at 715 nm. Aside from this, the low EQE value of the cell in the shorter wavelength region is observed for the samples with the bilayer ARC, indicating a high front surface recombination rate, possibly due to the poorly passivated interfaces between the embedded Si nanocrystals and the Si_3N_4 matrix. This result is consistent with the lower V_{oc} observed in Table 6.3. In contrast, longer

wavelength photons are being absorbed in the samples with the bilayer ARC, owing to the downshifting of the high-energy photons into the lower energy photons by the embedded Si nanocrystals.

6.5 Conclusion

In summary, we have demonstrated a synergistic two-step process to etch nanocone array on defective epi-emitter using FIB and form Si nanocrystals from the FIB-induced surface damage using FGA, evident from the Raman spectra and HRTEM images. Moreover, an absolute *PCE* enhancement of 0.2% is observed even with a small textured area ($\sim 0.1\%$), suggesting the potential of large-area surface texturization of defective Si epi-emitter using FIB etch and FGA step to significantly improve solar cell performance. *EQE* response from 850 nm to 1100 nm, measured under bias light, indicates downshifting of high-energy photons to lower energy photons by the Si nanocrystals. Such technique will be favorable for very thin cells that are incompatible with lithographic means due to the mechanical integrity of the substrate. However, this synergistic technique could only be possible when there are technological advancements in FIB etching equipment for large-area surface texturization. Furthermore, in order to minimize front surface recombination due to the embedded Si nanocrystals within the amorphous Si matrix, we propose to perform remote hydrogen passivation over FGA in future study. [97, 98]

We have also investigated a bilayer ARC, consisting of a upper layer of low RI SiO_2 layer and a lower layer of high RI Si_3N_4 with embedded Si nanocrystals, on the electrical performance of epi-emitter Si solar cells. *PL* analysis confirms the *PL* property of the embedded Si nanocrystals within the bilayer ARC. The estimated size of the Si nanocrystals is ~ 3 nm based on the *PL* emission of 775 nm when

excited by a laser source with 325 nm wavelength. These Si nanocrystals are able to downshift ultraviolet photons to lower-energy photons that can be utilized by the Si solar cells to significantly improve the *PCE*, only under concentrated light illumination. Due to the broadband reduction in reflectance, a 0.5% absolute *PCE* enhancement is observed for the epi-emitter cell with bilayer ARC, as compared to the control cell, mainly due to the J_{sc} increment. On the contrary, front surface recombination due to poor passivation of the Si nanocrystals may have caused the performance degradation for the cells with bilayer ARC, evident from their poor *EQE* responses in the UV region. It is thus critical to consider hydrogen plasma passivation to passivate the Si nanocrystals to render such bilayer ARC suitable for practical photovoltaic applications.

In conclusion, it is evident that the enhancements in electrical performance for the epi-emitter Si solar cells by architectural and peripheral modifications, without additional surface passivation, are not as significant as the back Ge epilayer scheme aforementioned in Chapter 4 and Chapter 5. Nonetheless, it ascertains the importance of the back Ge epilayer scheme for future thin-film solar cells applications.

7. Conclusion, future work and major contribution

7.1 Conclusion

In this project, low temperature Si-based epitaxy was employed to fabricate epi-emitter Si solar cells. This technique is fast, cost-effective and scalable to industrial standards. Different types of epi-emitter Si solar cells have been fabricated by lithographic methods and characterized in this study. At the same time, architectural and peripheral modifications were performed on these cells for comparative analyses with the low temperature epitaxy scheme.

In Chapter 3, an effective P dopant profile control in the epi-emitter layer has been demonstrated employing low temperature Si epitaxy. The cells were fabricated using ASM 2000 with dichlorosilane and phosphine gas precursors. It has been demonstrated that low temperature Si epitaxy produces a more abrupt *p-n* junction than emitter profile obtained through the conventional POCl_3 diffusion and also requires lesser process steps. *PL* result indicates that a lower growth temperature at 700°C yields a more defined *p-n* junction with lesser defect, as compared to the epi-emitter grown at 900°C. In addition, low temperature Si epitaxy induces mechanical twinning within the Si epi-emitter at the emitter-substrate interface, evident from the selected area diffraction patterns. Twinning modifies the crystallographic orientation and increases the optical path length of light within the epitaxy film, thus improving optical absorption. The cell with epi-emitter grown at 700°C exhibits a relatively good *PCE* of $(6.6 \pm 0.3)\%$. It is found that the performance is limited by the presence of stacking faults due to oxygen

contamination. The potential of low temperature Si epitaxy to be employed for radial p - n junction growth on wire array is demonstrated by the PCE_{pseudo} of $(10.2 \pm 0.2)\%$ of this cell.

In Chapter 4, we employed using a thin back Ge epilayer to improve the performance of epi-emitter Si solar cells grown on highly B-doped Si substrate. The fabrication of these cells involved a two-step epitaxy process to grow the back Ge epilayer, followed by the front side epi-emitter. PC1D simulation of the energy band diagram of the cell with back Ge epilayer suggests a thinned potential barrier due to the valence band bending that facilitate hole transport across the Si/Ge heterointerface. It is found that the J_{sc} of the epi-emitter cell with back Ge epilayer and back B-doped Ge epilayer is $\sim 12.4\%$ and $\sim 16.6\%$ higher than that of the control cell, respectively. The incorporation of back Ge epilayer led to a relative PCE improvement of at least $\sim 41\%$. The cell with B-doped back Ge epilayer was found to have an absolute PCE improvement of $\sim 1.8\%$ when compared to the reference cell. The PCE improvement is attributed to a higher out-of-plane hole mobility within the tensile-strained Ge epilayer, as confirmed by both Raman spectroscopy and XRD analyses. TEM images reveal misfit dislocations along the Si/Ge heterointerface and more severe faceting with B-doped Ge epilayer. This implies that the strain-induced energy band shifts and defects can result in a Si/Ge heterojunction-assisted hole transport that improves J_{sc} . Furthermore, the positive flat-band shift in C - V characteristics of MOS capacitors with undoped Ge epilayer validates that holes are effectively accumulated within the Ge epilayer. It should

be highlighted that V_{oc} remained unchanged despite the presence of structural defects in the Ge epilayer.

In Chapter 5, we have demonstrated the comparative analysis between the back Ge epilayer scheme and the conventional *BSF* scheme to improve the *PCE* of epi-emitter Si solar cells. PC1D simulation of the energy band diagram of the cell with back Ge epilayer suggests a thinner potential barrier due to the more valence band bending that facilitate hole transport across the Si/Ge heterointerface. The cell with back Ge epilayer displayed higher J_{sc} and *PCE* of 27.1 mA/cm² and 10.2%, respectively, when compared to the control cell. We attributed the enhancement in electrical performance to the tensile-strained Ge epilayer, broadband optical absorption and the reduced dark saturation current. The cell with back Ge epilayer and the cell with *BSF* epilayer are also found to have comparable *PCE* and PCE_{pseudo} . Moreover, the cell with back Ge epilayer revealed a better *EQE* response in the infrared spectrum, which can be due to better optical absorbance and an enhanced out-of-plane hole mobility at the tensile-strained Si/Ge heterojunction, thus resulting in comparable *PCE* with that of the cell with *BSF* epilayer. The potential of material cost savings can be realized when the germane gas precursor is replaced by germanium tetrachloride gas precursor.

In Chapter 6, we presented two studies on the architectural and peripheral modifications of epi-emitter Si solar cells. Firstly, we have shown that direct patterning of the epi-emitter layer with nanocone array can be achieved with FIB

etching. Due to the FIB-induced surface damage, a subsequent FGA anneal on the Si nanocone array resulted in the formation of Si nanocrystals, as confirmed by HRTEM images and Raman spectroscopy. Moreover, a moderate absolute *PCE* enhancement of 0.2% is observed even with a small textured area ($\sim 0.1\%$), suggesting the potential of using FIB etch and FGA step to improve the light trapping capability for epitaxial thin-film Si solar cells. In addition, such direct patterning technique will be ideal for very thin cells that are not suitable with lithography. Secondly, we have demonstrated the *PL* property of embedded Si nanocrystals in the bilayer ARC. It was found that the presence of $\sim 3\text{nm}$ Si nanocrystals could downshift high-energy ultraviolet photons to lower-energy photons, which can be better utilized by Si solar cells to significantly improve *PCE*, only under concentrated light illumination. A 0.5% absolute *PCE* enhancement is observed for the epi-emitter cell with bilayer ARC due to the reduced broadband reflectance. On the contrary, front surface recombination due to poor passivation of the Si nanocrystals may have caused the performance degradation for the cell with bilayer ARC and back Ge epilayer. To improve the electrical performance of epi-emitter Si solar cells in future study, we propose to use remote hydrogen plasma passivation to passivate the Si nanocrystals and minimize losses due to front surface recombination. It is also apparent that the enhancements in electrical performance for the epi-emitter Si solar cells by architectural and peripheral modifications, without additional surface passivation, are not as significant as the low temperature Si epitaxy or the back Ge epilayer scheme. Nonetheless, this

observation establishes the value of the low temperature Si-based epitaxy for future thin-film solar cells applications.

To conclude, it should be stated that the studies on epi-emitter Si solar cells with back Ge epilayer is at its infancy. The emphasis is placed on understanding the dopant profile on the epi-emitter, the nature of the Si/Ge heterojunction and the effects of nanocone and nanocrystals on the optical absorption and *PCE* of these cells. Thick Si substrates have been used in these studies to expediently demonstrate the various concepts, rather than as the final platform where such devices will be fabricated. In order to circumvent the use of expensive thick Si substrates, we envision that ultimately these concepts will be easily and practically adopted on epitaxial thin-film Si solar cells using metallurgical grade Si substrate or Si epifoil. The strong motivation behind research on solar cells using low temperature Si-based epitaxy is because of its cost-effectiveness, industrial scalability, and simplicity of process integration that they offer, thus suggesting its potential for thin-film solar cells applications in the near future.

7.2 Recommendation for future research

There are several aspects of the current research work that can be further explored.

7.2.1 Hydrogenated amorphous silicon surface passivation of n-type silicon epi-emitter solar cells

The surface defects on the unpassivated epi-emitter tend to shorten the minority carrier lifetime due to high recombination velocity. Thus, a-Si:H passivation can alleviate the detrimental effects of band-gap narrowing and dopant-dependent mobility degradation in a highly doped homojunction emitter. It not only saturate the dangling bonds at the c-Si surface, but it can also establish front reflection barriers for minority carriers at the a-Si:H/c-Si heterointerface. A thin and highly doped a-Si:H contact is needed to facilitate tunneling of the majority carriers across the blocking barriers. [56] This could be done by employing PECVD system to deposit hydrogenated amorphous Si and passivate the surface dangling bonds. [99]

7.2.2 Effect of thickness of back germanium epilayer on the performance of epitaxial emitter silicon solar cell

Screen-printed Al-BSF is commonly employed due to its simplicity and cost-effectiveness. It is found that a thicker BSF layer and a higher p^+ doping level typically reduces back surface recombination and delivers better passivation property, thus resulting in a higher V_{oc} . [100] Hence, we would like to investigate the effect of varying the back Ge epilayer on the electrical performance of epi-emitter Si solar cell.

7.2.3 *p*-type silicon epitaxial emitter silicon solar cell with back germanium epilayer

It is well known that *n*-Si has a higher tolerance to common transition metal impurities, such as those present in Si produced from quartz. This tolerance could potentially result in higher minority carrier diffusion lengths as compared to *p*-Si substrates. [101] Moreover, boron-oxide defects that leads to light-induced degradation are also absent in *n*-Si. Additionally, a defect-free Ge epilayer can prevent formation of intermediate energy states along the potential barrier of the valence band edge at the Si/Ge heterointerface (Figure 7.1), thus reducing minority carrier recombination at the backside. Therefore, we would like to investigate the electrical performance of *p*-type epi-emitter Si solar cell with back Ge epilayer.

Figure 7.1: Simulated PC1D simulated energy band diagram of the proposed *p*-Si epi-emitter solar cell on *n*-Si substrate with back Ge epilayer.

7.2.4 Epifoil silicon solar cells with back germanium epilayer

Layer transfer process (*LTP*) offers an alternative, cost-effective route to fabricate high-efficiency monocrystalline thin-film epitaxial Si solar cells. [102] A

sacrificial porous Si layer is formed beneath the surface of the wafer via electrochemical etching. The Si active layer of $\sim 50\text{ }\mu\text{m}$ is epitaxially grown on top of the porous Si layer. The resulting epifoil is bonded to a glass carrier before detaching it from the parent substrate. A key advantage to this *LTP* technique is material cost-reduction because it allows the parent substrate to be reused for subsequent fabrication of more epifoils. It is thus worthwhile to explore modularly integrating the back germanium epilayer scheme into the Si epifoil. The eutectic temperature of conductive Al/Ge is much lower than that of Al-Si, thus lowering thermal budget of process to form the back contact. In addition, Ge can be a good etch stop candidate during Si emitter texturization, as it is resistant to etchants such as tetramethylammonium hydroxide and potassium hydroxide. [52] The large thermal coefficient of expansion (CTE) difference between Al and Ge will aid in the detachment of the epifoil from the parent substrate, thus suggesting that back Ge epilayer can be an attractive platform that can be adopted for better performing thin-film epitaxial Si solar cells. The fabrication steps are schematically illustrated in Figure 7.2.

Figure 7.2: The fabrication steps of the *LTP* technique together with the back Ge epilayer scheme.

7.3 Major contribution of the thesis

Epi-emitter Si solar cells with emitter thickness of 600 nm have been successfully fabricated by low temperature Si-based epitaxy. The process is simple, economical and scalable for large-scale manufacturing. Various kinds of epi-emitter Si solar cells have been successfully fabricated and characterized. Their electrical performance is compared to the electrical results obtained via the architectural and peripheral modifications performed on these cells.

An alternative approach of fabricating epi-emitter Si solar cells based on low temperature Si epitaxy has been demonstrated. The cells are fabricated by using ASM 2000, along with dichlorosilane and phosphine gas precursors. Low temperature Si epitaxy with *in-situ* P-doping offers a more abrupt dopant profile of the emitter than that obtained by the conventional POCl_3 diffusion and also requires lesser process steps. The epi-emitter Si solar cell grown at 700°C achieved a maximum PCE_{pseudo} of 10.2% and J_{sc} of 28.8 mA/cm², which are higher than that of 10.0% and 27.2 mA/cm² attained by the 900°C POCl_3 diffused cells. We have shown that low temperature Si epitaxy induces mechanical twinning within the epi-emitter, which improves optical absorption. In addition, *PL* result reveals that lower growth temperature during Si epitaxy yields fewer defects. It was found that the oxide windows for epitaxial growth lead to performance degradation due to the presence of stacking faults.

We have subsequently fabricated the epi-emitter Si solar cells, grown on highly B-doped Si substrate, with a back Ge epilayer to improve optical absorption. The fabrication of these cells involved a two-step epitaxy process to grow the back Ge epilayer, followed by the front side epi-emitter. Control samples are fabricated under identical conditions for comparison. It is found that the J_{sc} of the epi-emitter cell with back Ge epilayer and back B-doped Ge epilayer is $\sim 12.4\%$ and $\sim 16.6\%$ higher than that of the control cell, respectively. An absolute PCE improvement of $\sim 1.8\%$ was achieved with the cell with B-doped back Ge epilayer when compared to the control cell. The PCE improvement is attributed to a better carrier mobility within the tensile-strained Ge epilayer, as confirmed by both Raman spectroscopy and XRD analyses. Moreover, the $C-V$ characteristics of MOS capacitors with undoped Ge epilayer attests that holes are effectively accumulated at the Si/Ge interface. This implies that the strain-induced energy band shifts can result in a Si/Ge heterojunction-assisted hole collection that improves J_{sc} .

We further fabricated epi-emitter Si solar cells with back Ge epilayer grown on optimally doped Si substrates and compare its performance with the cells that employ the conventional BSF scheme. PC1D simulation of the energy band diagram of the cell with back Ge epilayer suggests a thinner potential barrier due to the more valence band bending that facilitate hole transport across the Si/Ge heterointerface. Raman analysis indicates in-plane tensile strain of 0.71% within the Ge epilayer and verifies the monocrystallinity of the Ge and Si epilayers. A maximum PCE of 10.2% and J_{sc} of 27.2 mA/cm^2 have been achieved for the epi-

emitter cell with back Ge epilayer of 600 nm. The *PCE* improvement can be attributed to the tensile-strained Ge epilayer, broadband optical absorption and the reduced dark saturation current. Moreover, cells with back Ge epilayer exhibit a significant improvement in *EQE* response around the infrared region, when compared to the cells with *BSF* epilayer. This result indicates better optical absorbance and an enhanced out-of-plane hole mobility at the tensile-strained Si/Ge heterojunction. The cell with back Ge epilayer is also found to have comparable *PCE* and PCE_{pseudo} with the cell with the *BSF* epilayer, thus demonstrating the potential of material cost savings since the back Ge epilayer scheme only need one gas precursor, whereas the *BSF* epilayer scheme that requires two gas precursors. A more cost-effective germanium tetrachloride ($GeCl_4$) gas precursor should be considered for commercial viability of employing the back Ge epilayer scheme for future integration with the production of epitaxial Si solar cells.

To evaluate the competitive advantage of the back Ge epilayer scheme, we conducted two studies on the architectural and peripheral modifications of epi-emitter Si solar cells. In the first study, we have shown the direct patterning of the defective epi-emitter layer with nanocone array using FIB etching. Formation of Si nanocrystals from the FIB-induced surface damage on the Si nanocone array is the result of subsequent FGA anneal, as confirmed by Raman spectroscopy. Moreover, a moderate absolute *PCE* enhancement of 0.2% was observed which can be attributed to the minute textured surface of $\sim 0.1\%$ and the presence of Si

nanocrystals. This implies the prospect of using FIB etch and FGA step to improve the light trapping capability of epitaxial thin-film Si solar cells. Furthermore, such direct patterning technique will be ideal for very thin cells that are incompatible with lithography due to the mechanical integrity of the substrate. In the second study, we have demonstrated the *PL* property of a bilayer ARC, consisting of an upper layer of low RI SiO₂ layer and a lower layer of high RI Si₃N₄ with embedded Si nanocrystals. It was found that the presence of ~3 nm Si nanocrystals could downshift high-energy ultraviolet photons to lower-energy photons, which can be better utilized by Si solar cells to significantly improve *PCE*, only under concentrated light illumination. Due to the reduced broadband reflectance, a 0.5% absolute *PCE* enhancement is observed for the epi-emitter cell with bilayer ARC as compared to the control cell. On the contrary, front surface recombination due to poor passivation of the Si nanocrystals may have caused the performance degradation for the cells with bilayer ARC, evident from their poor *EQE* responses in the UV region. To minimize losses due to front surface recombination and enhance the *PCE* of epi-emitter Si solar cells in future studies related to architectural and peripheral modifications, we recommend using remote hydrogen plasma passivation to passivate the Si nanocrystals. It is also clear that the enhancements in electrical performance for the epi-emitter Si solar cells by architectural and peripheral modifications, without additional surface passivation, are not as significant as the low temperature Si epitaxy or the back Ge epilayer scheme. Nonetheless, such observation suggests a potential route to realizing cost-

Chapter 7 Conclusion, future work and major contribution

effective and efficient solar cells fabricated with low temperature Si-based epitaxy for future thin-film solar cells applications.

Author's publications

Author's publications

Journal Publications as 1st author

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