

Liquid phase epitaxial growth of silicon thin film for solar cell application

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LIQUID PHASE EPITAXIAL GROWTH OF SILICON THIN FILM FOR SOLAR CELL APPLICATION

by

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A thesis submitted to the University of New South Wales in fulfillment of the requirements for the degree of Master of Engineering

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TO MY PARENTS

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ABSTRACT

Thin film crystalline silicon offers the promise of high performance solar cells at low cost. The objective of this thesis is to achieve high efficiency thin film silicon solar cells by Liquid Phase Epitaxy (LPE). In this work, the morphologies of LPE layers were investigated under various growth conditions. Ga and Al were used as p-type dopants and Sb was used as an n-type dopant. The segregation coefficients of Ga in Sn and Indium solutions, Al in Sn solution and Sb in Sn solution were measured. Hall effect analysis showed that carrier mobilities in the LPE layers grown in H₂/Ar mixture are similar to values found in Ga-doped bulk silicon material, which indicates that the LPE silicon thin films are suitable for high efficiency solar cells. The effects of quality, thickness and doping concentration of the thin film on solar cell performance were modelled by using the PC-1D computer program to determine the optimum cell design. Modelling the effect of a heavily doped substrate on solar cell operation showed that such a substrate would only act as a seed and support for the epitaxial layer and not contribute to the solar cell performance. Therefore diffused junction solar cells were fabricated on LPE layers grown on heavily doped substrates. Open circuit voltage and conversion efficiency up to 649 mV and 15.6% under AM1.5G illumination at 25°C were achieved. The effects on cell performance of using various dopants and solvents were determined. Cells fabricated using Al as the p-type dopant always had poorer performance than those made using Ga. Similarly, films grown from In solution produced better cells than those grown from Sn solutions. Drift field solar cells incorporating a diffusion

were fabricated by LPE, because such a field may increase the effective diffusion length. LPE grown p-n junction cells and polycrystalline thin film solar cells were also made. Open circuit voltages up to 606 mV and 592 mV respectively were demonstrated.

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Chapter 1

Introduction

1.1 Photovoltaics

The photovoltaic effect, the capability of some materials to convert light into electrical power, was discovered by Becquerel in 1839. In the 1950's Chapin, Fuller and Pearson at Bell Telephone Laboratories, fabricated the first diffusedjunction silicon solar cell which had a conversion efficiency of about 6%. During the 1960's silicon solar cell technology matured as photovoltaics proved to be an ideal power supply for satellites. Most of the research effort was concentrated on improving the conversion efficiency and reliability of the solar cells without considering the cost. Although the cost per peak-Watt did decrease from \$350 in 1956 to \$100 in 1970 due to improved processing and technology [1], this price still prohibited large-scale terrestrial applications. By 1972, a conversion efficiency over 15% was achieved in a silicon space cell (AM0) [2]. With the "Energy Crisis" in 1973, increased attention was paid to the potential of solar cells to meet large-scale terrestrial power needs. Solar cells have advantages of providing an inexhaustible source of energy, of being modular and suitable for decentralised use and of being environmental benign but the disadvantage of high initial cost. Since 1973, Si solar cell manufacturing techniques have improved dramatically and cost per-Watt decreased from \$15 in 1977 [3] to \$6.5 in 1985 [4]. During this time, much effort

was devoted to developing thin film solar cells based on other materials such as cadmium sulfide, copper indium and amorphous silicon. Although not as efficient as silicon based solar cells, they held promise as candidates for economical mass production. If photovoltaics are to make a significant contribution to future energy needs, still greater initial cost reduction is needed. A price of \$0.5 to \$1 per peak-Watt is regarded as a target for the photovoltaic industry [5, 6].

The cost of photovoltaic power is determined by initial manufacturing cost, operation lifetime and conversion efficiency. Operating lifetime determines the return on investment. Conversion efficiency determines the balance of system component of the overall cost because for a given power requirement, a low efficiency system will require more area. Thus, more contact grids, AR coatings packaging, land and other area related expenses are required, raising the total cost of the complete system.

1.2 Silicon Solar Cells

The basic structure of a solar cell is a p-n junction. A typical junction is formed by diffusing a dopant into a 300-500 microns thick Si wafer. When light is incident on a cell, some of incident light is absorbed in the thin emitter (n-type Si) and base (p-type Si). Light-generated minority carriers diffuse to the junction due to a concentration gradient. Upon reaching the depletion region, the minority carriers are swept across the p-n junction by the built-in electric field. In this way, minority carriers become majority carriers and can be collected by an ohmic contact and

grids to do useful work in an external circuit. The light generated current is determined by the amount of light absorbed and the percentage of generated minority carriers being collected. The quantum efficiency will be less than 100% due to incomplete light absorption and collection efficiency. Losses in collection efficiency are due to recombination of minority carriers in the bulk, surface and contact regions. To minimise bulk recombination, the material should have a high minority carrier lifetime. Surface recombination can be reduced by passivating the surface of photovoltaically active layers. Voltage is determined by the doping of each layer, the quality of the junction, and the effect the bulk and surface recombination have on the reverse-saturation current of the junction.

Many semiconductors have been used as photovoltaic materials [8, 9]. The most extensively used material is silicon. Although the 1.1 eV bandgap of Si is somewhat below the optimum of 1.4 eV [10, 11], a theoretical conversion efficiency of about 29% is predicted [12].

Silicon is an elemental semiconductor which can be substitutionally doped either por n-type over a wide range of concentrations with a high doping efficiency. This feature simplifies device fabrication and permits fabrication of a homo-junction solar cell. Long operating lifetime of silicon solar cells is also a major advantage of silicon over many other semiconductor materials. A lifetime in excess of twenty years without severe degradation of the conversion efficiency is indicated [12]. Other obvious features of silicon as a solar cell material are : (1) silicon's abundance; (2) its highly developed technology base; (3) the ability to passivate interfaces with a thermal oxide thereby reducing surface recombination losses; (4) proven techniques to passivate grain boundaries in polycrystalline material and (5) the low toxicity of silicon and most compounds used in processing. Finally, the ease with which ohmic contact can be made to both p- and n-type silicon is noteworthy.

Because silicon is an indirect bandgap semiconductor, it has a relatively low absorption coefficient in comparison with other semiconductors. While devices made in other materials, such as GaAs, can generate virtually all of their maximum current within a thickness of 1 micron, a silicon solar cell requires several hundred microns before approaching its maximum current. Thus, on the basis of light absorption alone, a silicon solar cell of comparable efficiency will require much more active material than solar cells made of other highly absorbing semiconductors. This is a distinct disadvantage for silicon since it seems to prohibit high efficiency silicon solar cells from being achieved in thin film configuration. From the collection point of view, because a significant number of minority carriers are generated relatively far from the junction, the active layers must be of high quality to ensure a high minority lifetime for good collection efficiency. Production of most silicon solar cells are based on fabrication of the photovoltaic device in a wafer of silicon. The price of the wafer constitutes the largest part of the final solar cell cost.

1.3 Thin Film Silicon Solar Cells

Thin film approaches to solar cell design and production have generated much interest [8,13]. Similarly to conventional cells, development of high efficiency thin film solar cells also requires material with a diffusion length exceeding the cell

thickness. Therefore a thin film cell can tolerate material of poorer quality and can use less active material, giving lower costs. For a typical thin film solar cell, one or two layers of silicon are deposited on a substrate. These layers form the emitter and base of the solar cell. The substrate provides mechanical support for the thin silicon layers perhaps also acting as a rear ohmic contact. Since the substrate is not a photovoltaically active part of the device, it need not be a semiconductor but instead can be a much cheaper material such as metal, glass or graphite. Thus, the amount of expensive silicon wafer is reduced and sawing and polishing operations are eliminated. Since only very thin layers of semiconductor are used, the deposition time is short and could be done in a continuous mode with high throughput. The commercial advantages of continuous processing over the batch processing that is used in conventional silicon solar cell technology are well known [48,49]. Due to the weak absorption coefficient (particularly in the infrared part of the solar spectrum), a thin film solar cell would sacrifice current relative to a much thicker conventional silicon solar cell. Theoretically, increasing the thickness will increase the current. However, in a practical solar cell, it nearly impossible to collect minority carriers generated far from the p-n junction, since collection probability decreases exponentially with increasing distance of the point of generation away from the junction depletion region [12]. The characteristic decay length is just the minority carrier diffusion length. On average, minority carriers generated more than a diffusion length from the junction will not be collected and a diffusion length over 500 microns which is achievable in high efficiency silicon solar cells is not typical even in the best commercial silicon solar cell material [14]. Therefore, a current density of about 42mA/cm² may be regarded as a practical upper limit. To compare

the performance of conventional silicon solar cells, a solar cell with a thickness of 10 microns will generate 68% of this, one with a thickness of 20 microns will achieve 81%, and 50 microns thick solar cell will produce 89% of this practical limit. However, incorporating light confinement features [50] in thin film solar cells can significantly improve current generation above these figures.

Since thin film silicon solar cells do not require material with long minority carrier diffusion length [70], as long as the diffusion length is more than the thickness, a high collection efficiency is possible. Therefore in the interest of lowering cost, the semiconductor quality of the silicon may be reduced since a high minority carrier lifetime is not critical to maximising efficiency in the thin film configuration. An interesting consequence of this is the possibility of achieving improved open circuit voltage by increasing the doping level of the absorber [15,16]. In conventional silicon solar cells, a trade off is evident between the high voltage obtained in a heavily doped junction and high short circuit current made possible by a lightly doped absorber. The theoretical optimisation of a thin film silicon solar cell reveals a trend toward higher doping for improved open circuit voltage. The expected concomitant reduction in short circuit current is not seen, although the reduced minority carrier diffusion length is reduced due to the heavy doping. For polycrystalline silicon thin films, a much smaller grain size may be tolerated due to the higher collection efficiency [17].

For space application, there has been a trend towards thinning silicon solar cells to reduce the power to weight ratio, minimise heating due to weakly absorbed infrared light and improve radiation tolerance [18,19]. Such solar cells are usually made by

thinning silicon wafer chemically or mechanically to a thickness of between 50 to 100 microns. Obviously, this method does not save on high quality silicon, because much silicon is wasted in the thinning process. However, it is interesting to note that silicon cells as thin as 50 microns have been reported efficiencies over 14% (AM1) [20].

1.4 Thin Film Technique

Many physical and chemical crystal growth methods are available for thin film deposition of silicon. These technique can be broadly classified in the following categories: (1) growth from melt, i.e. pure molten silicon; (2) vapour phase growth; (3) recrystallization; (4) solution growth.

The Honeywell Dip Coating Process [21,22,24], also referred to as silicon on ceramic (SOC), involves dipping a ceramic or graphite substrate into molten silicon. Providing the molten silicon wets the substrate, the substrate is coated with a layer of silicon upon withdrawal from the melt. The high temperature of the process excludes inexpensive substrate materials such as glass, quartz, plastic and most metals. Reported efficiencies for solar cells made by this and similar processes are around 10% [23]. Surface tension effects during the wetting of the substrate, however, often make it difficult to deposit very thin silicon films. A minimum thickness of 100 microns is typical for the SOC process. In general, dip coating processes have many similarities to various sheets forming schemes and thus share many of the same disadvantages.

Vacuum evaporation of silicon on silica, silicon, aluminium, steel and glass substrates [25,26,27, 28] has resulted in films of insufficient quality for solar cells, primarily due to the small grain size (~ 1 micron) and contamination. Silicon films on sapphire, spinel and silica [29,30,31] generally yielded poor quality material due to dislocations formed in the film and along the substrate/film interface by the lattice mismatch.

Chemical Vapour Deposition (CVD), a process of thermal or plasma enhanced decomposition of a gaseous compound of silicon such as silane and trichlorosilane, has been used by many investigators to deposit polycrystalline silicon on steel [32], aluminium [27], graphite [32], glass [33] and upgraded Metallurgical grade (MG) silicon [32,34]. Apart from CVD, other vapour phase deposition techniques such as sputtering [29] or e-beam evaporation (or ion assistéd) [36] have been used to prepare polycrystalline silicon thin films for solar cell applications on various low cost substrates such as bare or metal coated (Mo or Ti) glass and ceramic substrates. However, unsuitably small grain size (less than 5 μ m) is a common problem acting to limit the performance of solar cells due to the recombination of light-generated carriers at grain boundaries. To improve the conversion efficiency of polycrystalline thin film silicon solar cells, the grain size in the films must be substantially increased (i.e. to greater than the film thickness) or the effects of grain boundaries minimised.

Various recrystallization techniques have also been developed to produce good quality silicon thin films on insulators for IC applications since the 1960's [35].

Various recrystallization techniques have also been developed to produce good quality silicon thin films on insulators for IC applications since the 1960's [35]. These recrystallization techniques, especially zone melt recrystallization (ZMR), are commonly adopted to enlarge the grain size within silicon thin films for solar cell applications. ZMR is the recrystallization of a film by heating and moving a narrow molten zone across the film. This approach was first used in the 1960's although it did not received wide interest until the early 1980's. A range of energy sources have been used for ZMR of silicon (and other semiconductor) thin films [37]. including laser beams, incoherent-light sources, strip heaters, electron beams, radiofrequency (RF) heaters and others. In all these versions of ZMR, more or less oriented Si films were prepared with corresponding grain sizes up to several millimetres wide and several centimetres long. An inconvenient but necessary complication for these approaches is the use of a dielectric capping layer such as silicon dioxide or silicon nitride to prevent the molten silicon from balling up during ZMR if a substrate with poor wettability with silicon is used. A common approach has been to produce a silicon buffer layer with good crystallinity on the dissimilar substrate and then subsequently fabricate the thin film solar cells by successive deposition of p- and n^+ -type layers in conjunction with appropriate hydrogen passivation of the grain boundaries [35]. Efficiencies in the vicinity of 15% have been demonstrated by this approach [35].

The precipitation of solid material from liquid solution is a classical method for growth crystal. Growth from molten metal solution has been found to provide an ideal means for preparing single-crystal semiconductors of high quality. Solution

growth also has many advantages over other crystal growth methods, including low growth temperature, low contamination level, and simple equipment. Liquid phase epitaxy (LPE) has been widely used for preparing III-V compound materials for semiconductor device application [38-41,45]. Recently, increased interest has been shown in the use of LPE for the growth of silicon films [41,42].

1.5 Liquid Phase Epitaxial Growth of Silicon

Liquid phase epitaxy (LPE) has become an important method of crystal growth, primarily because of its importance to the fabrication of semiconductor devices. Unlike normal solution growth, a seed, which may not be of the same composition as that of the depositing epitaxial layer, is always present. The grown layer is epitaxial in that it takes up the same crystal habit as the substrate seed. Basically, LPE differs only in degree from solution growth. The most important difference is that the solution is usually more dilute, leading to slower growth rate, to fewer spontaneous crystallites, and to more stoichiometric layers. The epitaxial layers are often very pure, because the dilute solution and favourable segregation coefficients keep unwanted impurities in solution. The growth process has a tendency to anneal out dislocations in the substrate [47]. Other features of LPE contributing to high crystal quality are the increased mobility of adatoms in the liquid phase. So LPE will, in general, produce devices that are superior in performance to these grown by other methods [46]. The usual method of LPE is a transient mode of growth whereby the melt is cooled (typically 10°C to 200°C over a period of one hour) to precipitate the thin film from a metallic solution. The films can be very thin with

thickness of the order of microns rather than millimetres. LPE also permits the growth of multi-layer devices with a wide range of layer thickness and doping profiles.

Early investigations indicated that tin and lead are electrically inactive in silicon [51], i.e these metals do not either act as donors or acceptors and they do not introduce deep recombination levels in silicon. A reasonably long minority carrier lifetime can be anticipated due to the absence of deep level recombination centers. D'Asaro [51] also reported that bulk carrier mobilities in silicon grown from tin and lead were comparable to those observed in silicon grown by more conventional methods. There was also lower carbon contamination in LPE silicon than in melt grown silicon. More recent work by Possin [52], and especially Baliga [53,54] has proved the electrical inactivity of tin in silicon. Scott [55] indicated that, although indium is electrically active in silicon, its solid solubility is sufficiently low (about 10^{16} atoms per cm³) so as to yield good semiconductor quality silicon.

Extensive work on silicon LPE from a variety of metallic solvents has been carried out at the Max Plank Institute since 1981 by Bauser [56,57], Linnebach and Bauser [58], Appel [59], and Lu and Bauser [61]. These researchers demonstrated the feasibility of growing silicon structures comprised of very thin planar layers with a wide range of doping levels. D'Asaro [51], Linnebach [58] and Kass [62] have also reported LPE silicon layers which had a very low density of defects, compared with silicon growth by other methods. Ciszek [43] grew silicon epitaxial layers from Cu/Si solution. Because of the low solid solubility of Cu in Si (at 900°C, 10¹⁷ cm⁻³), Ciszek showed that incorporation of this impurity had minimal effect on solar cell

performance. LPE silicon may be more perfect than melt grown, since low growth temperature results in fewer defects being "frozen-in" during cooling. These investigations confirmed that silicon LPE can be adequately described by well-known models of crystal growth theory.

For LPE applications in photovoltaics, the consequences of growth from metallic solution needs to be considered. LPE growth of GaAs and related III-V compounds has produced some of the highest efficiency solar cells obtained [63]. LPE also appears to remain the preferred method of fabrication when these solar cells are mass produced [63,64]. With proper selection of the metallic solvent, solution growth is also a suitable technique for the growth of silicon solar cells. The application of metallic solution growth for the fabrication of silicon solar cells has been successful. Solar cells have been fabricated by growing p^+ LPE emitter layers from aluminium [65] and gallium [66] solutions on n-type silicon substrates. Efficiencies for unoptimized devices without anti-reflection coatings were in excess of 10%. Similarly, Possin [52] grew an n-type collector from a tin/antimony melt on a high resistivity substrate but did not report any solar cell data. Mauk and Barnett [67] grew both the absorber and collector layers from metallic solutions using a very low resistivity silicon substrate. Under AM1.5G conditions, V_{oc} between 570 and 590 mV and J_{sc} as high as 21 mA/cm² (no AR coatings) were reported. Because heavily doped substrates are photovoltaically inactive due to an extremely short minority carrier diffusion length (<1 micron), the effective thickness of the solar cell was that of the epitaxial layers, which in this case was only 20 microns. Application of an AR coating could lead to a solar cell with a conversion efficiency exceeding 13%. This result was for a device without light

conversion efficiency exceeding 13%. This result was for a device without light trapping. Ciszek, et al. [43] fabricated solar cells with efficiencies of more than 15% (AM1) on layers grown from Cu/Si solution. Blakers et al. [44] produced LPE silicon thin film solar cells grown from In solution with V_{oc} up to 663 mV. Werner et al [71] achieved a record 14.7% efficient thin film silicon solar cell with a thin film thickness of 16.8 μ m and ratio of effective diffusion length to thickness up to 14. The performance of LPE grown silicon solar cells indicates that LPE growth is a viable process, competitive with CVD or melt growth.

It seems that LPE can be scaled-up to produce large-area devices. Recently, a centrifugal system for LPE was reported [72]. Silicon epitaxial layers on 100 mm diameter silicon substrates were grown with thickness uniformity $\pm 4.9\%$ over the central 90 mm diameter region. The thin films showed high quality which may be suitable for solar cell applications.

1.6 LPE Growth as a Low Cost Fabrication Process For Silicon Solar Cells

LPE growth is a potentially inexpensive fabrication process for silicon solar cells. Thin film silicon solar cells will considerably reduce material costs. The low process temperatures will also reduce energy costs, simplify process control and place less constraints on process equipment. The work reviewed above describes solution growth of silicon thin films on single crystal silicon substrates. From a cost

point of view, this is a serious drawback because it forgoes one of the major advantages of a thin film approach, namely, the possibility of substituting a very low cost substrate in place of the semiconductor wafer. To this end, a MG polycrystalline silicon wafer can be used as the substrate. In this case, the LPE thin film will be polycrystalline, replicating the grain structure of the substrate seed. When CVD or other processes are used to grow silicon solar cells, grain boundaries can result in significant recombination loss due partly to the precipitation of impurities at the grain boundaries. In contrast, the LPE growth process can ameliorate this effect because impurities will tend to segregate to the liquid metallic phase rather than precipitate at grain boundaries. By analogy with LPE grown GaAs [68], it is possible that grain boundaries in LPE grown silicon will be much less electrically active than those in silicon grown by other methods. The formation of the junction by solution growth of the emitter also avoids the diffusion of impurities along grain boundaries which may create shunts. Contamination of the deposited layer by substrate impurities may be avoided through the use of a metallurgical barrier between the low purity substrate and the high quality deposited layers [69].

1.7 Objective

The objective of this work is to investigate the growth of LPE silicon in a purged forming gas system and the potential for applying these layers in thin film silicon solar cells. The whole thesis is composed of five chapters. Chapter 2 describes the principles, mechanisms and methods of LPE. Chapter 3 investigates the growth principles, mechanisms and methods of LPE. Chapter 3 investigates the growth kinetics, doping behaviour and electronic properties. Chapter 4 presents the results of thin film silicon solar cells fabricated on the LPE layers. Chapter 5 summarises results and makes recommendation for future work.

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Chapter 2

Liquid Phase Epitaxy

2.1 Introduction

In this chapter, the principles of liquid phase epitaxy (LPE), the experimental system and technique are briefly described. The experimental processes are also demonstrated.

2.2 Epitaxy

The concept of "epitaxy" was first presented by Royer [1] in 1928. The term epitaxy can be defined as the deposition of a crystalline layer on a crystalline substrate in such a way that the crystalline structure of the substrate is continued into the layer. Epitaxy can be classified either as homoepitaxy when the epitaxial layer and substrate are of the same material or elas as heteroepitaxy when the epitaxial layer is of a different material from the substrate. Liquid phase epitaxy is a technique to grow the epitaxial layers from solution at elevated temperature.

From the definition of epitaxy given above, it follows that the two conditions below must be satisfied: (1) the crystal structures of layer and substrate should be of the same crystallographic space group; (2) that the unit cell dimensions or lattice
parameter of the layer and substrate should be closely matched, though how closely, is not theoretically specified. As a general rule, however, it is found that if the lattice mismatch, ε defined as,

$$\varepsilon = (a_l - a_s)/a_{av} \tag{2.1}$$

where a_1 is the lattice parameter of the layer, a_s is the lattice parameter of the substrate, and

$$a_{av} = (a_l + a_s)/2$$
 (2.2)

has a value less than 10^{-3} , then epitaxial growth will occur albeit with some distortion of the unit cell of the epitaxial layer in order to maintain exact lattice plane continuity across the substrate and epi-layer interface. For $\varepsilon > 10^{-3}$, there is an increasing tendency towards the generation of misfit dislocations either at the interface or else as threading dislocations, and an increasing difficulty in nucleating the epitaxial layer growth.

2.3 Phase Relationship

The basis of liquid phase epitaxy is the control of the liquid/solid phase equilibrium. The temperature-composition equilibrium phase diagram of Fig.2.1 illustrates the phase relationship for a binary or pseudo-binary system which is typical of that required for solution growth. T_A is the melting temperature of the metal solvent A



Fig. 2.1 Generalised temperature -composition equilibrium phase diagram for the system A-B.

and T_B is the melting temperature of the desired solute substance B. Component A may be a single element or an alloy, B may be a single element or a compound. The liquidus line defines the temperatures and compositions at which to the solid solute and solute components in the liquid are in equilibrium.

A solution of composition X at temperature T_x is represented by position 1 in the completely liquid region of the diagram above the liquidus line. Solid-liquid equilibrium can be attained by movement to the liquidus line. This can be accomplished either by a change in composition of the solution to correspond Y, or by a reduction in the temperature of the solution to T_c which is represented by position 2 on the liquidus line, or by the use of a combination of both processes. In any case, after the liquidus line is reached, further cooling under equilibrium conditions will cause material of composition B to precipitate. It is assumed here that no supercooling of the saturated solution occurs as the temperature is lowered. Since the average composition of the entire solid-liquid system must retain constant during the process, the solution becomes richer in A as B precipitates from it. Thus, the amount of solid B which is formed at a given temperature is in direct proportion to the distance from pure A to the liquidus line at that temperature. The composition of the remaining liquid solution follows the liquidus line towards T_A as indicated by the arrows. It is important to note here that it is the component with the higher melting point which precipitates from the solution under these conditions.

Depending on the amount and form of the solute which is dissolved in the solvent and which is in contact with the solution at a specific temperature, a solution can be considered to be in one of the following states: Depending on the amount and form of the solute which is dissolved in the solvent and which is in contact with the solution at a specific temperature, a solution can be considered to be in one of the following states:

1. understaturated - not enough solute is in solution(e.g. position 1 in Fig.2.1) and solute can't exist undissolved when in contact with the solution.

2. saturated - exactly enough solute is in solution, which is the case for any position on the liquidus line.

3. supersaturated - more than enough solute , which is in solution (e.g. position 3 in Fig.2.1) in which case the solution will adjust towards equilibrium (i.e. by moving to position 4 at constant temperature) given rise to solute precipitation and therefore, crystal growth.

4. saturated plus excess - excess solute is in contact with a saturated solution which is, for example, the state of a solid-liquid system after crystal growth has occurred, or as a charge of solid solute plus solvent metal is being heated but remains below the saturation temperature.

2.4 LPE Apparatus

The LPE growth systems used in our experiments are horizontal sliding boat systems.

2.4.1 Sliding Boat Apparatus for LPE



Fig. 2.2 Graphite slider boat apparatus.

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Fig. 2.3 Schematic diagram of LPE growth system.

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Fig. 2.2 shows the sliding boat made of a high purity graphite block. The wells are designed to contain the solutions. Temperature is monitored by a thermocouple embedded in the block. There are two wafer recesses in the slider, one is for the source wafer and another is for the substrate. The slider can be moved along the direction depicted so that the recesses can be relocated under the wells. The entire apparatus is placed in a furnace being purged with a hydrogen and argon mixture. To operate the boat, the furnace containing it is brought up to desired temperature, and then a push rod is used to position the wafer under the melt.

2.4.2 LPE Growth System

The LPE growth system, depicted in Fig. 2.3, is a new setup in which the LPE layer grows in a purified hydrogen and argon mixture. Gas purification is performed by a point-of-use purifier/filter. The design enables purifications of the process gas to be maintained and avoids unnecessary dead volume. We used a Zr-based getter purifier with a specified outlet impurity of 1 ppb each for oxygen, moisture and hydrocarbons [2]. This type of purifier [3] is cheaper and more versatile than the palladium diffusion cells commonly used for pure hydrogen.

The high purity part of the gas supply was made up from ultra-high vacuum type welded metal to metal seals in order to avoid leakage and outgassing from "o"-rings [4]. The flow rate was $5 \sim 8$ std l/min through a 13 cm diameter silica tube which contained the high purity graphite slider boat described above. The exhaust side of the silica tube was sealed by "o" rings. In order to avoid hydrocarbon related contamination problems, an oil free diaphragm pump was used to repeatedly

related contamination problems, an oil free diaphragm pump was used to repeatedly rough pump the system after insertion of the wafer and prior to growth. The furnace was profiled to obtain a 20 cm zone in the centre with temperature variation within $\pm 0.5^{\circ}$ C.

2.5 Growth Process

LPE growth can be divided into several controlled processes as shown in Fig. 2.4. Process I involves the heating the metal to the saturation temperature at which the solvent is in the liquid state. Process II is the saturation process during which the molten solvent contacts the source wafer and comes to equilibrium with it for solvent saturation. Process III occurs without contact to either the source or the substrate and can be either a supersaturation in which case a few degrees of supercooling prior to contact with the substrate for growth, or else a melt-back, in which case the temperature is raised a few degrees after contacting the substrate to etch a small amount of the substrate before growth. Process IV involves controlled ramping down of the temperature through a specified temperature interval at a specified cooling rate. Silicon LPE layer deposition starts when the cooling starts and terminates as the substrate and the solution are separated by a sliding action. A 20%H₂/Ar mixture can flow in the system before process III has taken place to protect the substrate from oxide formation. After solution contacts the substrate, a 4%H₂/Ar mixture can be used until the growth process is completed.

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Fig. 2.4 Schematic LPE growth process.

2.6 Segregation

In crystallization from a melt, there are various impurities contained in the melt, including both intentional and unintentional impurities. These impurities are incorporated into the crystal during crystal growth. The impurity concentration of the solid phase, in general, differs from that of the liquid phase due to a segregation phenomenon. In the limit of vanishingly slow growth, the ratio of the solubility of impurity A in the solid phase $[C_A]_S$ to that in the liquid phase $[C_A]_L$ remains constant over a certain concentration range [5-7]. This ratio is referred to as the equilibrium segregation or distribution coefficient K₀,

$$K_0 = [C_A]_S / [C_A]_L$$
 (2.3)

The segregation coefficient defined above actually represents the ratio of the difference in thermodynamic potential due to the interaction and entropy of mixing of impurity with the host material in the solid and liquid phase [7]. If the impurity solubility in the liquid phase is higher than that in the solid phase, i.e., $K_0 < 1$, the impurities tend to accumulate in the melt rather than being incorporated into the solid lattice.

The equilibrium segregation coefficient can be obtained by calculation from the binary phase diagram under the assumption that the solidification rate can be approximated as zero, that is, an equilibrium phase transition occurs. In the case of higher solidification rate, however, impurity atoms with $K_0 < 1$ are rejected by the

higher solidification rate, however, impurity atoms with $K_0 < 1$ are rejected by the advancing solid at a greater rate than they can diffuse into the bulk of the melt. The rejected impurity atoms begin to accumulate in the melt layer near the growth interface and diffuse towards the bulk of the melt. An impurity concentration gradient thus develops ahead of the advancing crystal. An effective segregation coefficient K_{eff} can be defined at any moment if stirring and convection currents in the liquid keep [C₁] virtually uniform [7]:

$$K_{eff} = K_0 / [K_0 + (1 - K_0) exp(-G_s d/D)]$$
 (2.4)

where G_s is the solidification rate, D is the diffusion coefficient and d the diffusion boundary layer thickness

Each impurity atom incorporated in the layer was assumed to be singly ionised thus giving 1:1 correspondence between carrier concentration and impurity concentration.

Having now described the growth system, the following chapter describes growth experiments.

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Chapter 3

LPE Growth of Silicon Thin Film

3.1 Introduction

In this chapter, LPE growth of silicon thin films in a purified H_2/Ar mixed ambient is discussed. The crystal quality of the silicon epi-layers was evaluated by optical microscopy. The mobilities and doping properties of Ga, Al and Sb were determined by Hall effect measurements and spreading resistance analysis.

3.2 Melts and Samples Preparation

The metals Sn and In were used as growth solvents; Ga, Al and Sb were added to the growth solutions to get p-type and n-type epitaxial layers respectively. All metals were of purity above 5N and were weighed with a precision of 10^{-4} gram. Prior to the experiments, the metals were immersed in dilute HCl (10%) for about 10 minutes and then rinsed in DI water, subsequently rinsed in alcohol and finally dried with N₂ gas.

Single crystal silicon wafers with orientations of (111) and (100) were used to demonstrate liquid phase epitaxial growth. The silicon wafers were sliced from CZ ingots. They were polished on one side and had a thickness of $250 \sim 300 \ \mu$ m. For

thin film solar cell fabrication, wafers with resistivities as low as 0.001 Ω cm were used as the substrates for growth of LPE layers. High resistivity wafers (up to 100 Ω cm) were used as substrates to grow LPE layers for characterisation purposes such as Hall effect and lifetime measurements.

The source and substrate wafer were cleaned with RCA standard solutions [18]. The RCA1 solution, typically 5:1:1 to 7:2:1 parts by volume $H_2O:H_2O_2:NH_4OH$ was designed to remove organic contaminants. The RCA2 solution with proportion 5:1:1 to 8:2:1 by volume $H_2O:H_2O_2:HCl$ was used to remove alkali and transition metals from the wafer surface. After the two cleaning steps described above, the wafers were dipped in dilute HF solution (10%) to remove oxide from their surfaces before being loaded into the boat.

3.3 Morphologies of LPE Thin Film

Most applications of LPE layers require very smooth surfaces for subsequent device processing. For this reason, considerable effort has been made to examine the factors influencing surface morphology. Previous LPE growth of silicon thin films was conducted either in pure hydrogen ambient or else under vacuum. Although high quality thin films were grown in pure hydrogen ambient, this introduces both cost and safety issues. Films grown in vacuum systems often had poor quality [2] and an in-situ melt-back process was needed prior to epilayer growth to remove the native oxide from the silicon substrate surface. This step is a possible source of additional surface roughness, solvent inclusions and the introduction of impurities from the substrate. In a practical epitaxial growth system, the stability of an oxide free silicon surface depends on the vapour pressures of residual water-vapour and oxygen in the growth chamber. The crucial role of the residual oxygen and moisture concentration on the quality of epitaxial growth has long been recognised and has been quantified in the case of a silicon surface heated under vacuum [3,4]. The reducing effect of hydrogen [4] on the morphology of epitaxial silicon layers has recently been demonstrated [5].

The experimental system used was described in Chapter 2. Depending on the process, Ar or a mixture of H_2 and Ar was selected to enter the growth system. The Zr-based getter purifier used in the system has a specified outlet impurity of 1 ppb each for oxygen, moisture and hydrocarbons [6]. When epitaxial silicon was deposited on (100) oriented substrates from supersaturated Sn/Al solution in a $4\%H_2$ /Ar ambient over a range of saturation temperatures from 990°C to 880°C, only silicon-islands were obtained [5]. When a $20\%H_2$ /Ar mixture was used, a continuous film was achieved. After the saturated solution contacted the substrate, however, a $4\%H_2$ /Ar gas mixture can be used until the growth process was completed without lowering the film quality..

The growth started at 950°C or 923°C with a cooling rate $0.1 \sim 0.68$ °C/min. Segregation coefficients are often temperature dependent, so doping gradients within the layer could result if large growth temperature intervals were used. In the experiments, the growth was limited to a temperature interval of about 100°C with

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slow cooling rate. The silicon layers had the desired thickness (20 μ m) for thin film solar cell applications.

Step features always appeared on the epi-layers grown on (111) oriented substrates. The wafer's misorientation from (111) which was less than 0.5°C, causes the steps on the surface. The height of the steps, however, depends on the cooling rate and thickness of the epi-layer. Fast cooling rates or thicker epi-layers result in a high terrace morphology as shown in Fig. 3.1 while slow cooling rates or thinner epilayers produce a rather smooth surface(not shown). A similar result from a pure hydrogen system was reported in ref.[7].

For epi-layer on (100) oriented substrates, there are some shallow pits appearing on the surface as shown in Fig.3.2. The depth of these pits is less than 100 Å and they can only be observed with a Nomarski Differential Interference Contrast (NDIC) microscope. These shallow pits are believed to be generated by an inhibition to nucleation caused by contaminants such as oxygen or carbon particles on the substrate surface. The poor morphology in Fig.3.3 apparently originates from carbon particle contamination, since there was carbon powder found at the surface. The right-hand side of Fig.3.4 shows an epi-layer which formed under the graphite block. It is obvious that it has a higher density of pits and melt inclusions than the left-hand side of the epi-layer which cause the poorer morphology of the layer. The graphite block covering the silicon surface could slow down or block the gas flowing across the surface. This increases the opportunity for oxide formation on

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Fig. 3.2 Pits in a LPE layer grown on a (100) oriented substrate. $(50\times)$



Fig. 3.3 LPE layer contaminated by carbon particles.(50×)



Fig. 3.4 LPE layer grown below graphite block (with heavy pinhole density part at right-hand side).

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Fig. 3.5 Cross lines appearing on (100) epitaxial layer.(NDIC 50×)





Fig. 3.7 Surface profile of the sample shown in Fig. 3.6.



Fig. 3.9 Surface profile of the sample shown in Fig. 3.8.

the silicon surface. The other possible reason is that graphite particles easily fall on the surface. The size and density of the shallow pits on the epi-layer depended on the size and density of contaminants on the substrates. As the film grows thicker, some shallow pits disappear and so the density of shallow pits decreases on the epilayer surface. In Fig.3.5, the cross lines which appeared on (100) oriented epitaxial layers were always parallel to the (011) or (0 $\overline{11}$) orientation, which indicates that those cross lines originate from the (100) substrate.

The epitaxial growth of silicon layers on polycrystalline substrates was also briefly investigated. Fig. 3.6 shows an epitaxial layer grown from tin solution at 950°C with 10° C melt-back on unpolished polycrystalline substrate. Five morphologically distinct regions are very apparent. Each of these regions corresponds to the grain of the substrate upon which the epitaxial layer was seeded. Surface profiling (Dektak) showed that the average surface roughness of an epitaxial layer was about a few microns. The roughest regions were along the grain boundaries as shown in Fig. 3.7. Fig. 3.8 shows a thin film deposited on a polished polycrystalline silicon wafers. In this case, the surface was much smoother, having a thickness variation less than 20% of the epi-layer thickness as shown in Fig. 3.9.

3.4 Doping Studies

During the LPE growth of thin film silicon, Ga and Al were used as p-type dopants and Sb as an n-type dopant. Although silicon LPE was systematically investigated by Baliga [7], very little research on the segregation coefficient of different impurities in Sn and In solution has been reported. In this section, the segregation coefficients of Ga, Al and Sb in Sn solution and Ga in In solution at deposition temperature between 950°C and 880°C were measured.

The segregation coefficient of an impurity was defined in Chapter 2.

The doping type and concentration were determined by spreading resistance analyses and Hall effect measurements.

3.4.1 Background Doping

Fig. 3.10 and Fig. 3.11 show the doping profiles of silicon epi-layers grown from 5N and 6N purity Sn solution with background carrier concentration of about 5×10^{16} cm⁻³ for 5N and 10^{16} cm⁻³ for 6N. Although the source wafers were p-type (100 Ω cm), n-type doped layers were obtained. This is probably due to residual n-type impurities existing in Sn (ESPI product). When a small amount of Ga was added to the Sn solution, the epi-layer became p-type. A similar result was obtained for silicon grown from In solution.

3.4.2 Melt-back and Supersaturation Effect

Fig. 3.12 shows the doping profiles for epi-layers grown from Sn solution doped with Ga with: (1) melt-back; and (2) supersaturation prior to growth. A graded junction was obtained with melt-back while an abrupt change in doping profile





between the substrate and epitaxial layer resulted from supersaturation. The doping concentration within the film changed gradually, because the segregation coefficient is temperature dependent and a wide growth temperature range was used.

3.4.3 Segregation Coefficient

In the experiments preferred to determine the segregation coefficient, the cooling rate was slow enough $(0.09 \sim 0.68 \text{ }^\circ\text{C/min})$ to keep the solid and liquid in thermal equilibrium. The doping concentration in the epitaxial layers was profiled by spreading resistivity measurements in Solecon Labs. These measurements showed that, for a small growth temperature range, the doping profiles were approximately constant in the epitaxial layers from interface to the surface. The concentration of a dopant in the epitaxial layer as a function of the amount of the same dopant in the growth solution was plotted (not shown). Within experimental error, a linear relationship fits well in all cases. From table 3.1, for a given growth temperature range, larger cooling rates caused larger effective segregation coefficients because the faster growth rate depleted dopant close to the interface in the liquid. This is in agreement with equation (2.4). For a given cooling rate, the segregation coefficient decreases as the average growth temperature reduced. Ga when used in a high purity solution often has a larger segregation coefficient than it does in a low purity solution due possibly to a compensating impurity present in the low purity metal. Al often has a larger segregation coefficient in Sn solution than Ga does. Ga in In solution has a larger segregation coefficient than Ga in Sn solution. It seems that Sb

is unsuitable as an n-type dopant for the emitter of a solar cell due to a low solubility.

Segregation coefficient	Dopant	Doping type	Solvent	Solvent purity	Growth temperature	Cooling rate(°C/min)
4.15×10 ⁻⁴	Ga	Р	Sn	5N	950°C	0.68
1.12×10 ⁻⁴	Ga	Р	Sn	5N	950°C	0.09
2.02×10 ⁻⁴	Ga	P	Sn	5N	923°C	0.68
2.54×10 ⁻⁴	Ga	Р	Sn	6N	950°C	0.68
6.76×10 ⁻⁴	Ga	Р	In	6N	950°C	0.68
8.20×10 ⁻⁴	Al	Р	Sn	6N	950°C	0.09
2.22×10 ⁻³	Sb	N	Sn	5N	906°C	0.68

table 3.1 segregation coefficient

3.4.4 Carrier Mobility

At room temperature, for a p-type film, the theoretical concentration dependence obtained from the neutrality condition is

$$p - n - N_{A}^{*} = 0$$
 (3.2)

The experimental concentration data can be obtained from the measured Hall coefficient $R_{\rm H}$,

$$p = r_{\rm H}/qR_{\rm H} \tag{3.3}$$

where q is the elementary charge and r_{H} is the Hall scattering factor which depends on the various scattering mechanisms and is in general a function of temperature and magnetic field [9]. Because of difficulties involved in determining $r_{\rm H}$, Hall data are often analysed by assuming $r_{\rm H}=1$ at all temperatures. The activation energy of the majority carrier levels, the concentration of the majority carriers in each level and the concentration of compensating levels are adjusted to give the theoretical concentration dependence that best fits the experimental p data. Table 3.2 displays the experimental data from the samples. The mobility as a function of the carrier concentration is also plotted in Fig.3.13. The filled diamonds correspond to $\mu_{\rm H}(p)$ data from our Ga doped LPE layers grown from Sn solution. These data are consistent with those reported by Arch [10] for films grown from In solution, but are lower than the Hall mobilities in B-doped bulk silicon material over the entire carrier concentration range. Data in table 3.2 also show that the hole mobility in Aldoped silicon decreases faster with increasing doping concentration than does the hole mobility in Ga-doped silicon.

Sample I.D	Solvent	thickness (µm)	doping ratio film/sub.	doping conc. Hall (cm ⁻³)	type	mobility (cm²/Vs)
R604(1)	6N Sn/Al	13.5	100	2.3×10 ¹⁷	р	169
2006(2)	5N Sn/Ga	6.5	26	5.6×10 ¹⁷	р	163
1707(3)	6N Sn/Al	4.4	140	5.2×10 ¹⁷	р	151
0507(4)	5N Sn/Ga	7.8	370	1.5×10^{18}	р	86
1207(5)	6N Sn/Ga	4.4	150	1.6×10^{18}	р	97
1307(6)	6N Sn/Ga	4.2	50	6.5×10 ¹⁷	р	137

Table 3.2 Hall Measurements



Fig. 3.13 Mobility vs carrier concentration. The filled circles are μ_{Hp} vs p_H data for p-type LPE Si grown from In/Ga solutions, and \blacksquare are the μ_{Hn} vs n_H for n-type LPE Si grown from In/As solutions. The + and \diamond represent, respectively, data of μ_{Hp} vs p_H for p-type Si and μ_{Hn} vs n_H for n-type Si from ref. [11]. The \times and O represent data of μ_{Hp} vs p_H for B-doped Si and μ_{Hn} vs n_H for As-doped Si, respectively, from ref. [12]. The ∇ depicts μ_{Hp} vs p_H data for B-doped cz Si from ref. [13] Also - - -is a theoretical μ_{Hp} curve for p-type Si [14],--- is an analytical fit to μ_{Hp} for B-doped Si [16], and — —is an analytical fit to μ_p for B-doped Si [17].

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Chapter 4

Thin Film Silicon Solar Cells

4.1 Introduction

In this Chapter, results of the modelling of thin film solar cells using the computer program PC-1D [1] are reported. Thin film solar cells were fabricated on the LPE layers grown on heavily doped substrates. Such substrates act only as a seed and support for the epitaxial layers. The p-n junction was formed by phosphorous diffusion or else by LPE growth directly on oppositely doped thin film which had been previously deposited. Diffused junction cells achieved open circuit voltage (V_{oc}) and conversion efficiency up to 649 mV and 15.6% on a 4.12 cm² area. For LPE grown p-n junction and polycrystalline thin film solar cells, Voc as high as 606 mV and 592 mV were respectively achieved.

4.2 PC-1D Modelling Thin Film Solar Cells

The PC-1D program was used to model thin film solar cells and predict their performance. The thin film solar cell parameters used for this modelling are listed in table 4.1.

	type	doping concn.(cm ⁻³)	thickness (µm)	surface recom. velocity	reflection (%)
Emitter (diffuse)	n	2×10 ¹⁹	1	10 ³ cm/s	30
LPE layer (grown)	р	5×10 ¹⁶	20	10^{-15} A/cm^2	-
Substrate	р	2×10 ¹⁹	150	10 ⁴ cm/s	90

Table 4.1 modelling parameters: cell area 1 cm², under AM1.5G

Initially the effect of the thin film quality on solar cell performance was tested. The open circuit voltage and short circuit current were modelled as functions of the ratio of the minority carrier diffusion length to the base thickness. The epitaxial layer thickness was fixed here at 20 μ m. The previous ratio represents the thin film quality. If the silicon epi-layer is heavily doped, the diffusion length is inherently limited by an internal PC-1D formula which determines the upper bound of the minority carrier diffusion length. Otherwise, the diffusion length is manually set to simulate the bulk recombination level. Fig. 4.1 shows that when the ratio is greater than 3.5, V_{oc} and J_{sc} only increase slightly with increasing the ratio, but if the ratio is less than 2, V_{oc} and J_{sc} decrease drastically. Therefore, in the thin film case, very large ratio doesn't improve thin film solar cell performance significantly. In the case of poor thin film quality, surface recombination has less effect on V_{oc} and J_{sc} .

The variation of open circuit voltage V_{oc} and short circuit current J_{sc} with base doping concentration is shown in Fig. 4.2. Theoretically, impurities can introduce energy levels within the silicon bandgap which allow carrier generation via impurity levels. When the doping concentration exceeds 10^{18} cm⁻³, the optical absorption coefficient increases significantly at long wavelengths [2]. On the other hand, the impurities can act as recombination centres which may reduce the minority carrier





thin film doping concentration (/cm**3)

Fig.4.2(a) Variation of Voc and Jsc with thin film doping concn.


diffusion length. So finding a suitable doping concentration in the thin film configuration is necessary. From the modelling result, J_{sc} always decreases as the doping level increases, and V_{oc} reaches a maximum value at a doping concentration of ~10¹⁸ cm⁻³. From the $V_{oc}*J_{sc}$ curve in Fig.4.2(b), the maximum output range can be obtained. So for ideal cell performance, the optimum thin film doping concentration range is $5 \times 10^{15} \sim 10^{17}$ cm⁻³.

To find the ideal thin film thickness(assuming same quality material here), the dependence of V_{oc} and J_{sc} on base thickness was also modelled. As shown in Fig. 4.3, when the thickness is less than 10 μ m, both V_{oc} and J_{sc} increase markedly with increasing thickness. As the epitaxial layer becomes thicker (>30 μ m), V_{oc} and J_{sc} increase only slightly with increasing thickness. Experimental epitaxial layer thickness is subject to many factors and is difficult to control precisely. For thin film solar cell application, a thin layer (20~30 μ m) with a longer diffusion length (a few times the thickness) is required.

Finally, as shown in Fig.4.4, the influence of the heavily doped substrate on the thin film solar cell performance was modelled. The resistivity of the substrate was fixed at 0.005 Ω cm which is the same as that used in the experiments. A series of substrate thicknesses was chosen from $0 \sim 150 \mu$ m. From 150 μ m to 3 μ m, the solar cell performance was only weakly affected. From the modeling result, the substrate always had an negative effect on the cell performance which indicates that the heavily doped substrate doesn't improve the cell operation and only acts as a seed and support for the thin film, also provides the low interface recombination



Fig.4.3 Variation of Voc and Jsc with thin film thickness



Fig.4.4(a) Variation of Voc and Jsc with the thickness of the heavily doped substrate.



thickness(micron)

Fig.4.4(b) Variation of output power with heavily doped substrate thickness

velocity. If the substrate is thinned from 150 μ m to 3 μ m, a 1.1% (absolute) improvement of the conversion efficiency is expected.

4.3 LPE Thin Film Silicon Solar Cells

4.3.1 Preparation of Thin Films by LPE

LPE thin films were grown from Sn and In solution on (100) and (111) oriented single crystalline or multicrystalline silicon substrates. Ga and Al were used as p-type dopants and Sb as an n-type dopant. The growth temperature range and cooling rate were 950 °C ~ 800 °C and $0.2 \sim 0.8$ °C/min, respectively. For p-n junctions grown by LPE, a p-type epitaxial layer was grown first and subsequently overgrown by an n-type layer.

4.3.2 Solar Cell Fabrication

The thin film Passivation Emitter Solar Cell (PESC) processing sequence [3] is as follows:

- (1) Thin film wafer cleaning.
- (2) Oxidation for SiO_2 layer.
- (3) Photolithography: open 2×2 cm² or 3×3 cm² emitter diffusion window.
- (4) Diffusion: n-type Phosphorus diffusion to form p-n junction.

- (5) Passivation: passivate thin film surface by oxidation.
- (6) Photolithography: open finger grid pattern 1×1 cm² or 2×2 cm² on front surface.
- (7) Metal contact for front and back surfaces and lift-off.
- (8) Sintering.
- (9) AR coatings.
- (10) Edge isolation.
- (11) Solar cell characterization.

4.3.3 Thin Film Solar Cell Results

Table 4.1 shows the performance characterization of solar cells fabricated on the LPE layers.

From these results, a confirmed V_{oc} of 649 mV and efficiency of 15.6% were obtained. Fig.4.5 shows the doping profile of the best cell determined by spreading resistance measurement. The thickness of the n-type emitter created by diffusion is about 0.25 µm. A doping gradient exists in the thin film with doping concentration varying from 1.4×10^{17} cm⁻³ to 6×10^{16} cm⁻³ within a thickness of 18 µm. Fig. 4.6 shows the dark I-V characteristic of the best cell. Two linear regions indicating ideality factors n of about 1.24 and 2.43 can be seen. The data can be fitted by the least square method to the two exponential model [4]:

$$I = I_{01}[exp(qV/n_1kT) - 1] + I_{02}[exp(qV/n_2kT) - 1] + V/R_{sh}$$
(4.1)





Fig. 4.6 Dark I-V characteristic of the best cell.

where the first two terms represent the contributions of the diffusion and recombination currents, respectively, and R_{sh} is the shunt resistance. The reverse saturation currents, I_{10} and I_{20} , are 1.63×10^{-10} A/cm² and 5.29×10^{-7} A/cm², respectively. These values are comparable with those of good quality conventional silicon solar cells [5].

To determine the effect on cell performance of using either Ga or else Al as dopant, Ga doped and Al doped LPE films were grown on the same substrate in one experiment, keeping the same doping concentration in the two films. From the results, Ga-doped LPE silicon films grown from Sn solution produced a solar cell having higher V_{oc} and J_{sc} than a similar cell made from Al-doped LPE silicon.

For testing the effect of solvent on cell operation, films grown from In/Ga solution yielded solar cells having better V_{oc} and J_{sc} than did those grown from Sn/Ga solution, when the doping concentrations were comparable. Table 4.2 lists the solid solubility of In, Ga and Al in silicon at 900°C ~ 1000°C and the mobility and diffusion length measured at room temperature on samples grown at the above-mentioned temperatures. LPE layers grown from pure In/Si solution are p-type doped and have a concentration of about 10¹⁶ cm⁻³ and a mobility of 285 cm²/V-s. when grown at 950 °C. For Sn/Ga grown LPE layers, although Sn doesn't introduce either shallow or deep impurity levels, the solubility of Sn in silicon is as high as 10²⁰ cm⁻³. Such a large proportion of impurity could reduce the mobility, although high lifetime in the bulk has been observed [6]. For Sn/Al solution

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growth, only data of layers grown at 750°C are given, because the solubility of Al reaches 10^{19} cm⁻³, and the mobility and diffusion length are reduced dramatically.

Sample	substrate(p-type)				V _{oc}	J _{sc}	FF	Eff	
#	resistivity(Ωcm)		solvent	impurity	(mV)	(mA/cm ²)		(%)	Comment
									*
010294	(100)	.00101	In	Ga	649	29.9	0.802	15.6	confirmed
									*
180194	(100)	.00101	In	Ga	643	29.4	0.786	14.9	confirmed
	1								drift
060893	(100)	.005023	In	-	642.1	30.2	0.7888	15.31	field
			_						drift
100993	(100)	.00101	In	-	634.9	31.7	0.7626	15.34	field
									Al
0703L	(100)	.00101	Sn	AI	591.1	29.3	0.7288	12.64	doped
				~	<i></i>				Ga
0703R	(100)	.00101	Sn	Ga	602.5	32.4	0.7688	15.02	doped
				-					on (100)
110893	(100)	.005023	Sn	Ga	632.3	30.5	0.7851	15.14	substrate
									on (111)
010793	(111)	.004009	Sn	Ga	614.6	29.7	0.7712	13.96	substrate
									grown
300693	(111)	.004009	Sn	Ga/Sb	606.1	30.2	<u>,</u> 0.7059	12.9	p-n
									grown
250693	(111)	.004009	Sn	Ga/Sb	575.4	24.2	0.6566	9.13	p-n
									poly-
040893	-	~1	Sn	Ga	592.0	2.20	0.2319	0.302	crystal
									poly-
020893	-	~1	Sn	Ga	590.8	1.68	0.2390	0.207	crystal

Table 4.1 Silicon LPE thin film solar cells (4 cm² under AM1.5G 100 mw/cm², 25° C).

* measured at Sandia National Labs. others measured in the PV Centre UNSW.

Table 4.2 Reported semiconductor properties of solution-grown Si

	Growth	Solvent	ρ	τ	μ	L	
solvent	Temp.(°C)	Incorp.(cm ⁻³)	(Ω-cm)	(μs)	$(cm^2/V-s)$	(µm)	Ref.
Al	750	1019			20	~3	7
Ga	900	~ 10 ¹⁹	0.013		28	1	8
Ga	600	~ 10 ¹⁸	0.42		70	~1	7
In	950	1016	2.17		285	~1	9
In	1000	5×10 ¹⁶	1.28		275		9
In	1150 -	5×10 ¹⁷	0.36		243		9
Sn	900	1020	0.02-0.7	0.3-1.0		15-30	10
Sn	950	1019	25-100	5-10			11
Sn	1000	1020		100			6

Drift field solar cells were also investigated by a one-step LPE grown p-n junction. In fact, a drift field always exists in LPE grown layers because of the variation of the segregation coefficient with reducing temperature. This is most apparent when a large growth temperature interval is applied, as shown in Fig. 4.7. This p-n junction was grown in pure In solution between 1000°C to 900°C. The doping profile of the film deposited in this way varies from p-type $(4 \times 10^{15} \text{ cm}^{-3})$ through to n-type $(3.5 \times 10^{15} \text{ cm}^{-3})$. The source of the n-type dopant is not yet identified. The surface was doped n-type to $2 \times 10^{19} \text{ cm}^{-3}$ by diffusion. Two drift field solar cells were fabricated on #100993 and #60893 with different base thickness.

The electric field was built into the thin film of the cell because of a concentration gradient of the acceptor impurities. The electric field causes the energy band edges to be sloped and the field at any point is given by:

$$E = (kT/q)(dlnN_A/dx)$$
(4.2)

where N_A is the ionised impurity concentration. Under the drift field, the effective minority carrier diffusion length is given by [12] :

$$L_{\rm eff} = L_{\rm n}(E/E_{\rm c} + 1) \tag{4.3}$$

where $E_c = kT/qL_n$. Thus, the drift field incorporated in the base layer assists in minority carrier diffusion toward the junction, and hence leads to an enhancement of J_{sc} . On the other hand, a drift field reduces V_{oc} by the voltage drop across the layer in which it acts [13]. Thus one requires a doping gradient without simultaneous reduction of the lifetime. From this, drift fields are useful for materials with short diffusion length such as low cost silicon or polycrystalline material and may have application to radiation tolerant cells.

Cells fabricated on LPE layers grown on (111) oriented substrates often have lower V_{oc} and J_{sc} than their counterparts on (100) oriented substrates. The lattice packing density on (111) substrates is higher than that on (100), so a high density lattice mismatch may be introduced on (111) p-type epitaxial layers during the LPE growth process. Also a terrace pattern always exists on (111) epitaxial layers caused by a misorientation of the substrate which was discussed earlier in 3.1. This may also introduce defects /recombination centres in the bulk and surface which could reduce cell performance. A larger effective saturation current density was obtained [14] for (111) p-type epitaxial cells than for cells grown on (100) substrate.

P-n junction solar cells were made by depositing two layers by LPE on (111) substrates as an alternative to growing one layer and forming a diffused junction. From the profiles of the p-n junction in Fig. 4.8, the low segregation coefficient of Sb in Sn solution results in an n-type concentration of 2×10^{17} cm⁻³.



Thin film silicon solar cells were made on polished multicrystalline substrates. The layer deposited on a polished polycrystalline substrate had the morphology shown in Fig. 3.8. Because most grain sizes were larger than 100 μ m, the cell performance may not be affected greatly by this factor [15]. V_{oc} up to 592 mV was been achieved. The very low J_{sc} and FF are attributed to bad ohmic contact, especially at grain boundaries.

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Chapter 5

Conclusions and Future Work

5.1 Introduction

This chapter summarises the results achieved in this thesis and makes recommendation for future work.

5.2 Summary of Results and Conclusions

The purpose of thin film solar cell research is to demonstrate low cost, high performance devices for large scale photovoltaics application. Liquid phase epitaxy was chosen as a method for investigation due to its advantages over other methods, such as relatively low growth temperature and high crystal quality.

LPE layers of silicon were grown on (111) and (100) silicon substrates from Sn(5N)/Ga, Sn(6N)/Ga, Sn(6N)/Al and In(6N)/Ga solutions. The morphologies of (111) epitaxial layers always exhibited a terrace pattern due to misorientation of the substrate. The height of the step depended on the cooling rate and the thickness of the epitaxial layer. Slower cooling rate or thinner layers produced lower terrace morphology. For (100) oriented epitaxial layers, shallow pits appearing on the surface may be caused by substrate surface contamination, such as oxygen or

carbon particles. Smooth, continuous polycrystalline films were also deposited on polished polycrystalline silicon wafers.

The segregation coefficients of p-type dopants such as Ga, Al and n-type dopant Sb in Sn and In solutions were determined. Within the same growth temperature interval, faster cooling rates cause larger apparent segregation coefficients. The segregation coefficient also decreases with reducing temperature. Ga in a high purity solution often has a larger segregation coefficient than it does in a lower purity solution. Al has a larger segregation coefficient than Ga in Sn solution. Ga in In solution has a larger segregation coefficient than Ga in Sn solution. From the result, the low segregation coefficient of Sb in Sn shows that it is unsuitable as an n-type dopant for emitter of a solar cell by LPE.

Either abrupt or gradual doping concentrations could be realised by using supersaturation or melt-back. The mobilities of samples grown in a 20% H_2/Ar ambient indicate that the quality can match that of films grown in a pure hydrogen ambient system.

The PC-1D program was used to determine the optimum design of a thin film solar cell. In the thin film case, in contrast to bulk devices, pursuing very high quality thin film doesn't significantly improve solar cell performance. The effect of the thin film doping concentration on V_{oc} and J_{sc} was modelled. The optimised doping range was selected for device fabrication. The effect of the heavily doped substrate on the thin film solar cell operation was also studied. From the modelling result, such a low resistivity substrate always has a negative effect on the solar cell, which

such a low resistivity substrate always has a negative effect on the solar cell, which shows that the substrate acts only as a seed and support for the epitaxial layer. Improved efficiency is expected, if the substrate is thinned.

Thin film silicon solar cells were fabricated on the LPE layers. V_{oc} and conversion efficiency up to 649 mV and 15.6% were achieved. Ga is better than Al as a p-type dopant for solar cells. In/Ga solution grown cells often have higher V_{oc} than those from Sn/Ga solution. Thin film solar cells made on (100) oriented epitaxial layers were superior to cells on (111) thin films. Drift field thin film solar cells were grown by LPE, which could increase effective diffusion length. LPE grown p-n junction (2 epitaxial layers) solar cell and polycrystalline thin film solar cells with V_{oc} of 606 mV and 592 mV were presented.

5.3 Future Work

High efficiency single film solar cells were made during the thesis. Solar cells having grown p-n junction haven't achieved comparable results compared to a diffused junction. This is due to low segregation coefficient of the n-type dopant Sb in Sn or In solution. Therefore another n-type dopant with high K_s is required if grown p-n junction solar cells are to achieve high efficiency.

Incorporating light trapping or optical confinement [1] in a thin film solar cell can significantly enhance current generation, which can compensate the disadvantage of the thin active layer in the absorption of light.

For high efficiency thin film solar cells, the impurity photovoltaic (IPV) effect can also be considered [2]. Improvements of cell current, subgap and energy conversion efficiency are quantified.

To enhance red absorption, Si/Ge alloys can be incorporated into thin film devices [3], but Si/Ge thin film solar cells haven't yet been reported.

Drift fields can easily be formed by LPE. Their depth and doping concentration gradient need to be further investigated for optimum solar cell design. Due to its effect of diffusion length enhancement, a drift field can be applied in materials with short diffusion length such as low cost silicon or polycrystalline material.

In the interest of lowering cost, high efficiency polycrystalline thin film solar cells produced by LPE need to be studied further.

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