Rapid Melt Growth of Crystalline Germanium for Solar Energy Harvesting Applications

Submitted by

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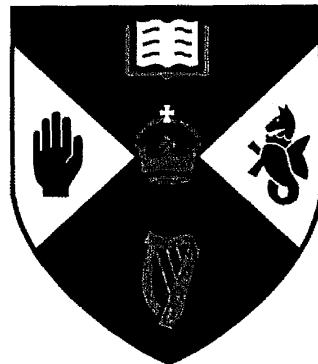
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Abstract

Recent development of energy conversion devices namely photovoltaic (PV) cells or solar cells and thermophotovoltaic (TPV) cells require the use of bulk germanium as substrate material for efficient device performance. Germanium is employed in solid-state terrestrial or space energy conversion devices due to its excellent electrical properties. With a bandgap of 0.66 eV, energy from infrared region of solar or thermal spectrum can be absorbed and converted into electrical energy. At present, multi-junction solar cells with bulk germanium substrates show the highest performance but have complex and expensive manufacture processes. The major contributor to the high cost is the germanium substrate, which is an expensive and scarce material. One of the possibilities to reduce cost is by using thin film instead of thick bulk germanium. To date, development of thin film germanium for energy conversion devices has not been established. By providing germanium on insulator structures a good quality thin film germanium can be attained and thus, offer a low cost route. The rapid melt growth (RMG) technique has been proposed, where it potentially produces thin film germanium with quality similar to that of bulk material. In the existing RMG technology germanium thickness has been limited to 100 nm. For photovoltaic applications thicker germanium films are required to increase energy absorption for efficient performance. For these reasons, alternative RMG routes to producing thin films for energy conversion devices have been investigated. The feasibility and efficacy of the RMG technique has been evaluated for different germanium deposition methods namely physical vapour deposition

(PVD) and chemical vapour deposition (CVD). In this study, a novel RMG technology has been established in order to produce high quality thick germanium films (above 100 nm). Experiments have been conducted with various anneal temperature, germanium patterns, substrate and crucible materials to achieve optimum crystalline quality. Micro-Raman spectroscopy has shown that the technology has the capability to produce thick germanium films that are free from major defects such as cracks and delamination, with crystalline quality similar to that of bulk material. This thesis highlights the use of PVD germanium compared to CVD germanium in minimising silicon diffusion through the crystal growth process, which has resulted in longer length of crystal germanium. The mechanism of germanium lateral crystallisation has been investigated in this thesis by depositing germanium onto non-silicon substrates. A prototype germanium photovoltaic has been fabricated to demonstrate the potential of the RMG technique in production of future solar cells.

Contents

Chapter 1
Introduction

1.1 Energy conversion devices

Over past decades there has been a rapid development of energy conversion devices such as solar cells or photovoltaic (PV) cells that convert solar energy into electrical energy. Thermophotovoltaic (TPV) cell is another conversion device that has similar approach except it converts thermal energy (i.e thermal radiation) into electrical energy. The rapid growth of these energy conversion devices is due to environmental issues such as depleting fossils, greenhouse gases and fluctuating fuel and oil prices which have forced researchers to find an alternative renewable energy. Solar energy is free and easily available is one source of renewable energy. Thus, it is valuable source to be selected as an alternative energy to resolve our dependency on fossil fuel or gases. One type of solar cell that has been commercially used is the solar panel which can be found on rooftop of houses or buildings and is widely used in countries such as United States, Germany and Austria [1]. The performance of existing solar cell devices that generally uses silicon cannot be denied but the main issue of concern is the trade-off between cost and performance. To have good energy conversion performance, high prices will be charged and the manufacturing process can be complex. To date, different materials and techniques have been used to improve the energy conversion performance and reducing the manufacturing cost.

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For example the highest efficiency of up to 40 % [1], [2], [3], is for multi-junction solid-state solar cells along with a light concentrator system but these normally suffer with high manufacturing cost. On the other hand, cells with the lowest manufacturing cost use electrochemical or sol-gel techniques have the lowest energy conversion performance of 1% to 3% [4], [5]. A review of energy conversion devices namely photovoltaic cells and thermophotovoltaic cells will be discussed in sections 1.1.1 and 1.1.2, respectively.

1.1.1 Photovoltaic cells

Extensive research on development of solid-state solar cells has been conducted to achieve high conversion efficiency, through the use of single and multi-junction structures. To date, the most efficient of semiconductor solar cells to be reported consists of triple junctions with a concentrator system for terrestrial application and has 41.6 % efficiency [6]. This compares to stand alone solar cells with energy conversion of 7.8 % for the case of a bulk germanium device [7]. In the multi-junction system, one can achieve highest efficiency solar cells by combining the bandgaps of lattice matched semiconductor materials [8], [9]. Researchers have been used III-V and II-VI semiconductor materials for this approach. For example in the construction of III-V triple junctions, material with the highest bandgap such as gallium indium phosphide (GaInP), E_g = 1.9 eV is placed on the top cell and gallium indium arsenide (GaInAs) with a lower bandgap, E_g =.1.4 eV is located in the middle cell. A wide bandgap such as germanium (Ge), E_g = ~0.7 eV is positioned on the

bottom cell as a substrate. The reasons for having different bandgaps in the multi junction structure is because solar energy in different regions of the spectrum can be absorbed thus leading to high device performance. Figure 1.6 illustrates the cross-section of a triple junction solar cell with different bandgaps materials. Nevertheless, it is important to consider that only few materials are available to use as substrate for constructing multi-junction solid-state solar cells. This is because substrate materials that have bandgaps that are lattice matched to III-V or II-IV semiconductor are rarely found [8]. The common substrates that are used in multi-junction solar cell are germanium, gallium arsenide and indium phosphide [2], [8]. Figure 1.5 shows the bandgap of compound semiconductors as functions of lattice parameters for III-V and II-VI semiconductor materials [9]. A proper material pair can be obtained by having a vertical line in figure 1.1, for example Indium Gallium Phosphide / Indium Gallium Arsenide / Germanium (InGaP / InGaAs / Ge) have minimal lattice mismatch.
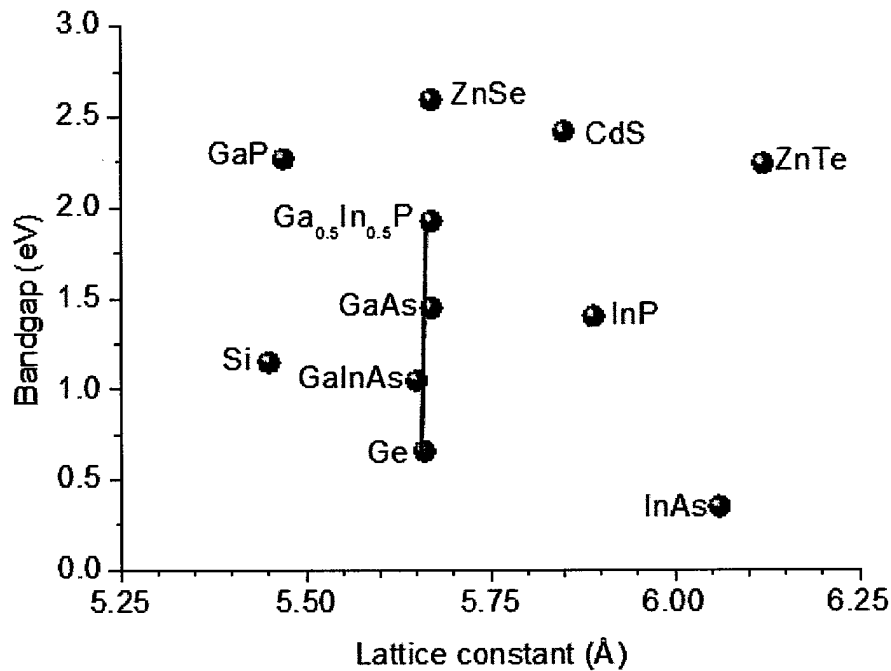
Figure 1.1: Bandgaps and lattice parameters of photovoltaic materials. Solid green lines shows the minimal lattice mismatched InGaP/InGaAs/Ge [9].

According to King *et al.*, [8] enhancement of energy conversion efficiency either in space or terrestrial application could be obtained by having germanium as substrate material in multi-junction solar cells. This is due to the wide photoabsoption spectrum, where it is claimed that the indirect band gap of germanium could perform as tunnel junction in the splitting spectrum (multi-junction) device. Bosi *et al.*, [10] have reported that the multi-junction performance via germanium substrate is more efficient than other substrate materials such as gallium indium arsenide (GaInAs). By using germanium as substrate the energy conversion efficiency of multi-junction solar cells can increase by 3 to 4 % with either III-V or II-VI cells. Figure 1.2 illustrates the cross-section of a triple junction III-V solar cell with bulk germanium

as a substrate material. To date, the highest energy conversion efficiency (40 %) for terrestrial application is from a triple junction solar cell with germanium substrate. This has surpassed the efficiency of mature silicon based solar cells (28 %). However, higher cost will be incurred for an overall system of triple junction solar cells in a flat panel for terrestrial application.
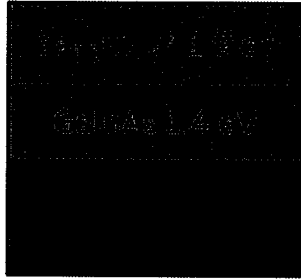
Figure 1.2: Illustration of cross-section triple-junction solar cells with different band gap for lattice matched structures [9].

A light concentrator has been suggested for adoption along with multi junction solar cells in order to reduce the overall expenditure. This can be achieved by having a concentrator with a large area to collect the light and then transmit this into the PV cells. With this technique, more energy can efficiently collected and the number of PV cells employed in the system can be reduced. According to Xie *et al.*, [11] the development of concentrator technology for terrestrial multi junction solar cells has been used with different approaches. A common concentrator can be made by Fresnel lenses using glass or plastic [12], [13], [14]. Figure 1.3 shows a demonstrator PV concentrator with dome shape and multi junction solar cells connected in series.
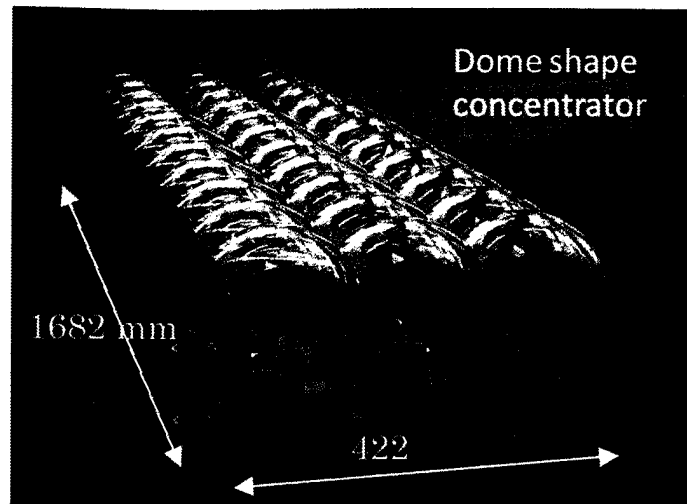
Figure 1.3: Prototype of dome shape Fresnel lenses concentrator tested with triple junction PV cells [13], [14].

In the existing solar flat panel applications, a large number of PV cells were used to achieve greater energy conversion. However, high overall expenditure will be acquired if multi junction structures are being manufactured into the solar panel. Therefore, concentrators have been adopted in order to reduce the overall expense.

To collect more energy, a sun tracking system can be included in parallel with the concentrator lenses. According to Mousazadeh *et al.*, [15] by using a sun tracking system, 10 − 100 % of the incident solar energy can be collected depending on the time and geographical conditions. Figure 1.4 depicts the Fresnel lenses concentrator with sun tracking system for terrestrial application. Despite the fact that the sun tracking system can boost the amount of collected energy; this approach has issue of high energy losses due to heating [16]. A cooling system is required to avoid the

energy losses. This additional requirement has effect on the overall expense and results in a high budget for maintaining the system.
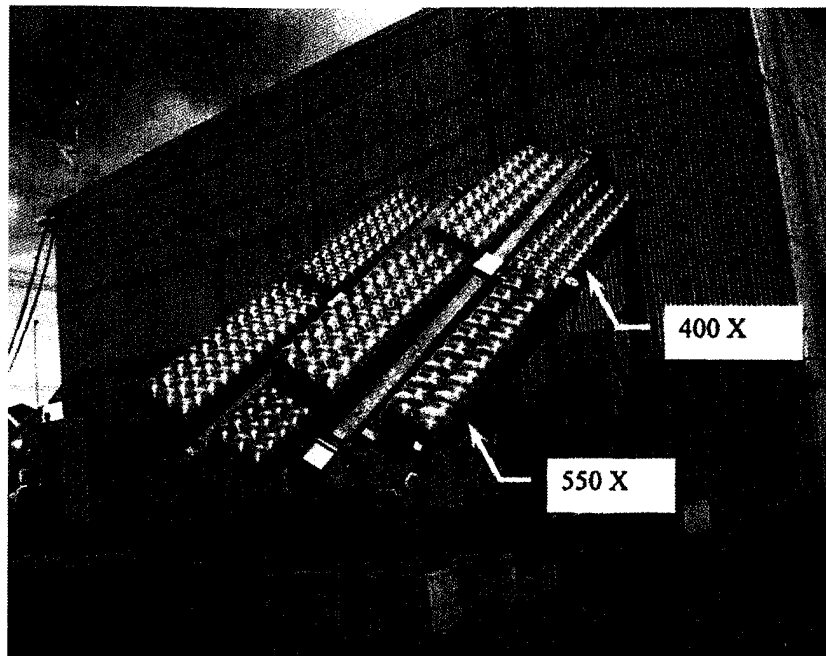
Figure 1.4: Two-axis of dome-shape with 500x and 400x modules Fresnel lenses concentrator with sun tracking system [12].

To date, another approach has been investigated namely the used of luminescent solar concentrators (LSC) [16]. In this case, a transparent concentrator such as glass or plastic is doped with luminescent species (dyes) covered with anti-reflective coating on top of the device and connected to the PV cell at the edge. The incoming photons are absorb and via luminescent corresponding photon emitted, the majority of which are confine within the panel and directed to PV cells for conversion to electricity energy [17]. The advantage of this approach is that it does not require sun tracking and cooling systems hence reduces the overall cost. Furthermore, it is

claimed [16] that the optical absorption properties of the luminescent solar concentrator can be made tunable by stacking several type of luminescent. According to Debije *et al.*, [17] and El-Bashir *et al.*, [16] this type of concentrator is suitable to be applied in windows for buildings with integrated PV systems. Trapped light on the window frame could provide generation of electricity [16], [17]. It is believed that by adopting luminescent solar concentrators along with multi junction solar cells, the overall cost could be reduced compared to a concentrator with sun tracking system. This clearly shows that by adopting a concentrator, smaller dimension of PV cells can be used compared to a large flat panel. As a result, better overall energy conversion performance can be attained.

Efforts have also attempted to resolve the expense issue by finding materials that have good photovoltaic properties in parallel with a low cost per unit power generation. According to Wadia *et al.*, [18] iron sulphide has been identified as the lowest cost material per unit power generation compared to 23 inorganic materials used for photovoltaic devices as shown in figure 1.5 [18]. With the properties it can offer, iron sulphide is a promising candidate for future solar cells. Iron sulphide, also known as pyrite, has good electrical properties and functions as a good solar absorber with a low band gap (E_g = 0.95 eV) giving peak absorption in the solar spectrum. Most of the solar cell development using pyrite has used electrochemical cells rather than solid-state structures. A solid-state solar cell has been produced using pyrite as shown in figure 1.6 but has low performance with only 1 % conversion efficiency [19]. Moreover, instability of the chemical structure of pyrite during the manufacturing processes make it difficult to construct and less viable to

produce. The best performance pyrite electrochemical solar cells have achieved only

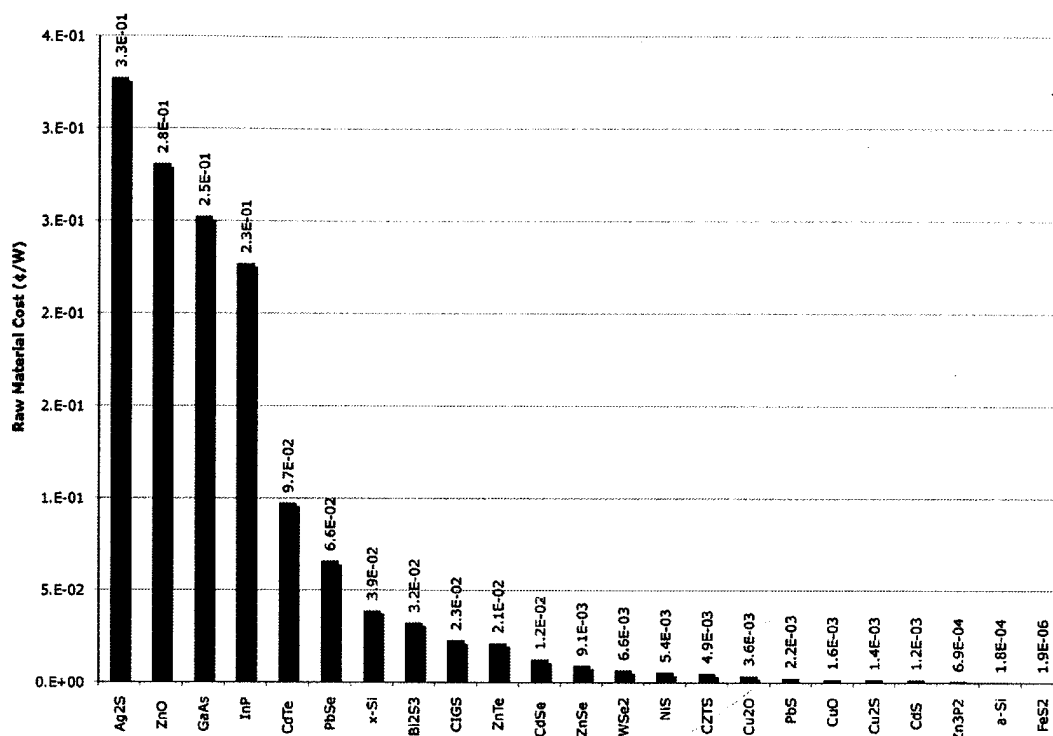2.8 % efficiency conversion [18].

Figure 1.5: Comparisons prices of 23 inorganic photovoltaic materials in cent / Watt

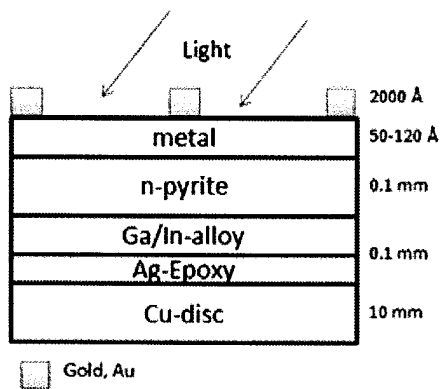(¢/W) as strong indicator for future deployment [18].

Figure 1.6: Cross section of semiconductor pyrite / metal diode [19].

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Copper sulphide is another material that has good electrical properties with a band gap (E_g = 1.3 eV) about 0.35 eV higher than pyrite. It performs as a good solar absorber and also is low cost compared to silicon [18], [20], [21]. Due to a lattice match between copper sulphide and cadmium sulphide, a solid-state solar cell can be constructed. However, poor stability of copper ions can lead to long-term performance degradation. Besides, the toxicity of cadmium sulphides [20] makes it undesirable for future solar cells. An improvement to this issue is to replace cadmium sulphide with titanium dioxide; this is particularly due to its superior chemical stability. Most metal sulphides (iron and copper) have instability of metal ion that can lead to low performance of the device.

Despite pyrite or iron sulphide being the cheapest photovoltaic material, the conversion performance is low compared to existing solar cells due to the instability in stoichiometry of pyrite during the development process. Low cost materials such as metal sulphides do not offer better performance, and issues of reproducibility make the structures less viable to produce. On the other hand, germanium has good properties with a low band gap (E_g = 0.66 eV) [15] compared to metal sulphides (iron and copper) and silicon (E_g = 1.1 eV). Energy can be absorbed from the infrared region of solar or thermal spectrum due to the low band gap and then converted into electrical energy. Figure 1.7 shows the absorption coefficient of germanium in the infrared region. Germanium has been used in the multi junction photovoltaic stack for space applications and revealed high energy conversion performance [1], [8].

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Chapter 6 deals with implementing the RMG technique for development of photodiode cell. This chapter gives an overview of to date approaches that had been taken by researchers for development of photodiode. Fabrication process of the photodiode is explained for better understanding. The results obtained from the fabricated device will be discussed.

Chapter 7 concludes this research work and provides suggestions for future work.

1.5 References

[1]   S. S. Sun, N. S. Sariciftci, *"Organic Photovoltaics Mechanism, Materials and Devices,"* Taylor & Francis, 2005.

[2]   R. R. King, D. C. Law, K. M. Edmondson, C. M. Fetzer, G. S. Kinsey, H. Yoon, R. A. Sherif, and N. H. Karam, "40% efficient metamorphic GaInP / GaInAs / Ge multijunction solar cells," *Applied Physics Letters*, vol. 90, no. 18, p. 183516, 2007.

[3]   R. R. King, D. Bhusari, D. Larrabee, X. Liu, E. Rehder, K. Edmondson, H. Cotal, R. K. Jones, J. H. Ermer, C. M. Fetzer, D. C. Law, and N. H. Karam, "Solar cell generation over 40 % efficiency," *Prog. Photovolt: Res. Appl.*; April, vol. 20, pp. 801–815, 2012. DOI: 10.1002/pip.1255

[4]   A. Ennaoui, S. Fiechter, Ch. Pattenkofer, N. Alonso-Vante, K.Buker, M. Bronold, Ch. Hopfner and H. Tributsch, "Iron disulfide for solar energy conversion, " *Sol. Energy Mater. Sol. Cells*, vol. 29, pp. 289-370, 1993. DOI: 10.1016/0927-0248(93)90095-K

[5]   G. W. Crabtree and N. S. Lewis, "Solar energy conversion," *Physics Today*, March, vol. 60, pp. 37–42, 2007.

[6]   R. R. King, A. Boca, W. Hong, X. Liu, D. Bhusari, D. Larrabee, K. M. Edmondson, D. C. Law, C. M. Fetzer, S. Mesropian, and N. H. Karam, "Band-gap engineered architectures for high-efficiency multijunction concentrator solar cells," *24th European Photovoltaic Solar Energy Conference and Exhibition*, Hamburg, Germany, Sep., pp. 21–25, 2009.