Fabrication of Silicon Photovoltaic Micro-Particles for Low-Cost Solar Energy Generation

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FABRICATION OF SILICON PHOTOVOLTAIC MICRO-PARTICLES FOR LOW-COST
SOLAR ENERGY GENERATION

A Thesis
Presented to
The Faculty of Engineering and Computer Science
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ABSTRACT

The relatively high cost of the high quality semiconductor materials (typically silicon) and complex conventional techniques for the fabrication of solar cells result in the overall high cost of the commercially available solar cells. Although, research in the field of solar technologies has been going on for a long time, but, utilization of solar energy still remains limited to a very few applications, owing to the high manufacturing costs and lower efficiency. In this work we present a new solar technology based on silicon photovoltaic micro-particles and demonstrate a fabrication technique for such particles. The photovoltaic micro-particles can be manufactured from waste or low grade silicon, thus, keeping the material and manufacturing costs low. Different diffusion techniques have been explored in this work to implement this fabrication process and manufacture the most efficient silicon PV particles. Different sets of silicon PV particles of different sizes have been fabricated, tested, and compared. It has also been demonstrated, how these silicon photovoltaic particles can be used to generate hydrogen from electrolytic solutions. Some future applications have also been proposed, such as, micro-particles based photo-electrochemical hydrogen generation system, self-assembled micro-particle based thin solar cells, and solar spray-paint. Further research in the growth of this technology may give rise to a whole new revolutionary solar cell technology.
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Chapter 1 – Introduction

The growth in the world population, along with further industrialization and higher living standards, has resulted in a dramatic increase in the global energy demand in the past few decades. Since 1971, the global energy demand has increased by around 70% and is increasing at an annual rate of 2% [1]. About 80% of this demand is fulfilled by the use of fossil fuels, which, being non-renewable sources of energy, are expected to exhaust in the near future [1]. With this growth in the energy demand and rapid depletion of the non-renewable sources of energy on one hand, and carbon related environmental issues and global warming prospects on the other hand, a lot of emphasis has been placed on the deployment of the alternative environment-friendly and renewable sources of energy. Of all the energy utilized from renewable sources, about 87% comes from hydropower production, while, solar energy makes just a small fraction of this [1]. However, considering all the advances in the solar technology and on-going research and development, it is estimated that by the year 2100; solar energy (both thermal and photovoltaic) will supply around 70% of the world’s total energy demands [1].

The rate of energy emission by the sun is 3.8x10^23 kW out of which about 1.08x10^14 kW is received by the surface of the earth. Utilization of a mere 0.1% of this energy at an efficiency of 10% would be enough to generate 12000GW, i.e. four times the total generation of the world today [1]. Figure 1 shows the average insolation on the earth surface; i.e. the amount of solar radiation received on a given surface area in given
time. The black dots represent the land area that could be utilized, at an efficiency of 8%, to replace the world’s primary energy supply by photovoltaic electricity [2].

Figure 1 - Average insolation and the land area (black dots) required to replace primary energy sources by solar electricity. [2]

The use of solar energy by humans can be dated back to the 7th century B.C. when it was utilized with the aid of magnifying glass to create fire and burn ants [3] [4]. Solar thermal energy or indirect use of solar energy to generate electricity has been developed and used for a long time. In 1839, photovoltaic effect was observed by French physicist Edmond Becquerel, for the first time while working with electrolytic cells [3] [4]. Later on, the discovery of selenium as a photoconductive material by Willoughby Smith in 1873 gave rise to further interest in the development of systems capable of direct
conversion of light to electricity [3] [4]. This was followed by the development of systems called the photovoltaic or solar cell systems.

Although, the photovoltaic systems have been developed to generate electricity at relatively high efficiencies, but, the application of photovoltaic systems is very limited, mainly due to the high manufacturing costs. Due to the high costs of high efficiency solar cells, they are mostly used as a source of electricity for satellites or at remote places where other alternatives are costlier, or only if price is not a constraint. Other applications include the use of solar cells for small devices such as watches, calculators, etc. A lot of research is being performed on development of different photovoltaic materials and fabrication techniques in order to reduce the overall cost of solar cells that can produce electricity at a reasonably high efficiency. In this work we propose new solar technologies based on low-cost silicon photovoltaic micro-particles.

1.1 Photovoltaic Cells

1.1.1 Timeline of solar cells

The first ever solid photovoltaic material discovered was selenium. The first solar cells were made from selenium wafers by Charles Fritts in 1883 [3] [4]. Although, these selenium based solar cells were rejected due to the low efficiency (less than 1%) [5] and inability to generate considerable electricity, but, for the first time they demonstrated the generation of electricity from light by a solid device which had no moving parts or heating issues. Later, in 1904, Wilhelm Hallwachs’ discovery of photoelectric effect in the combination of copper and cuprous-oxide gave rise to further investigation of
different materials that can be used as photovoltaic cells. This was followed by the key discoveries of the existence of a barrier layer in photovoltaic devices (in 1914) and then a technique to grow single crystal silicon (by Jan Czochralski in 1918). The first ever silicon based solar cells were made in the year 1954 at the Bell Laboratories by Daryl Chapin, Calvin Fuller, and Gerald Pearson [3] [4]. This was the first ever solar cell achieving an efficiency of 4%, which later increased to 6%. This high efficiency lead to the commercialization of the photovoltaic technology in the following year, and the solar cells were successfully utilized to power devices such as dollar bill changers. Further research by the Hoffman Electronics resulted in the achievement of efficiencies of 8%, 9%, 10%, and 14%, in 1957, 1958, 1959, and 1960, respectively [3] [4] [5]. In 1958, for the first time, a photovoltaic array capable of generating less than 1 Watt was used to power the radios of a space satellite. Since then, photovoltaic cell arrays were considered a reliable source of energy for space satellites and all satellites consisted of onboard photovoltaic systems. The following years saw a rapid development of solar cells and photovoltaic technology [3] [4]. Emerging semiconductor technologies such as thin film technology were being employed for solar cells manufacture.

Silicon wafer based solar cells with efficiency of more than 20% were made at the University of New South Wales in Australia in the year 1985 [3]. The following year, a commercial thin film solar cell module, G-4000, was introduced by ARCO Solar. This followed the commercial use of solar cells for applications such as standalone photovoltaic systems.
The development and intensive research after the 1980s has resulted in achievement of much higher conversion efficiency in solar cells. Although not cost efficient, efficiencies of over 40% have been demonstrated in research labs to date [6]. Figure 1 shows one such solar cell that has the efficiency of 41.1%. This solar cell has been developed at the Fraunhofer Institute for Solar Energy Systems ISE and is a multi-junction solar cell made from GaInP/GaInAs/Ge (gallium indium phosphide, and gallium indium arsenide on a germanium substrate) [6].

![Solar Cell](image)

**Figure 2 – A multi-junction GaInP/GaInAs/Ge solar cell with an efficiency of 41.1% developed at the Fraunhofer Institute for Solar Energy Systems ISE [6]**

Even after all these advancements in the manufacturing of solar cells and achievement of high efficiencies, solar cells are still used for very limited applications. This is due to the fact that manufacturing of high efficiency solar cells is still too costly to be able to compete with conventional energy sources, and therefore, solar devices are typically used when cost is not a factor [6] [7]. The numerous high temperature and high vacuum fabrication processes involved in the manufacturing of solar cells and
requirement of very high purity materials are the main reasons for the relative high cost of existing solar cells.

![Progress of different solar cell technologies and their highest efficiencies](image)

**Figure 3** - Progress of different solar cell technologies and their highest efficiencies [8]

### 1.1.2 Three generations of solar cells

The first generation of solar cells consists of the high-cost high-efficiency wafer based solar cells. These solar cells are manufactured using high-purity silicon substrates, and use a single junction for photovoltaic conversion. The maximum theoretically achievable efficiency of these cells is 33%, due to the limits imposed by the nature of the material and various other reasons [9] [10]. In 2007 the market share held by these cells was around 89.6% [9] [10], but due to the expensive and laborious manufacturing process, the demand for these cells is on a decline. [9] [10] [11]
The second generation is marked with the introduction of low cost, but, low efficiency solar cells, developed in the 90s and early 2000s, and is associated with the thin-film solar cells [9] [10]. Technologies such as vapor deposition and electroplating were introduced for solar cell manufacture, and proved to be very advantageous as the resulting solar cells were much cheaper compared to the first generation solar cells. Nanosolar is an example of one such second generation solar cells which can be manufactured by simply printing the solar cells by a special machine, at a very fast rate [12]. The second generation solar cells are much cheaper in comparison to the first generation cells as they use minimal amount of materials and cheaper fabrication techniques [9] [11]. Materials such as cadmium telluride (CdTe), copper-indium-gallium-selenide, amorphous silicon (a-Si) and micromorphous silicon, have been extremely popular among the second generation materials and are commonly used for the fabrication of thin-film solar cells [9] [11].

The third generation of solar cells consists of low cost and high efficiency solar cells, which are still under the research phase, and does not actually exist yet. Some of the third generation technologies include multijunction solar cells [6], nanostructured and nanocrystalline solar cells [13], dye sensitized solar cells [14], polymer or organic solar cells [15], tandem or stacked cells [16], and cells that use excess thermal generation for enhanced voltages. The goal of third generation technologies is to achieve cell efficiencies of 30%-60% at lower costs, but, this goal is not predicted to be achieved before 2020 [9] [10] [11].
1.2 Working Principles of Semiconductor Photovoltaic Cells

A solar cell works on the principle of photovoltaic conversion of solar energy into electrical energy. The very basic constituent of a photovoltaic cell is the PN junction. The PN junction, when exposed to light, absorbs energy and converts it into electricity, making use of the photovoltaic conversion.

1.2.1 Semiconductors

A semiconductor in its purest form is known as intrinsic semiconductor, and ideally, does not contain any kind of impurities. This type of semiconductor is a very poor conductor (almost an insulator) as it has almost no or negligible amount of free electrons due to the strong covalent bonds that exists between its atoms [17-22]. As shown in Figure 4, in an intrinsic silicon lattice, there are four strong covalent bonds between each silicon atom and its surrounding silicon atoms.

![Intrinsic silicon lattice and Covalent bonds](image)

Figure 4 - Intrinsic silicon lattice and Covalent bonds [21]
On the other hand, extrinsic semiconductors contain small amount of impurity atoms. When the impurity atoms are introduced in an intrinsic semiconductor, they replace some of the silicon atoms in the lattice. If the added atoms have a different number of electrons capable of bonding to surrounding atoms in their outer electron layer, there will be extra unbound electrons or a lack of extra electrons to comply with the rest of the semiconductor lattice [17-22]. In the former case, a number of free electrons, i.e. free negative charges, will be available in the lattice; while, in the latter case electron deficiency leads to free positive charges in the lattice, commonly, referred to as holes [17-22]. The semiconductor which has a high population of free electrons is referred to as N-type doped semiconductor, while the semiconductor that has a high deficiency of electrons or high population of holes is called P-type doped semiconductor. Addition of a very small amount of dopant (impurity) can significantly improve the conductivity of the intrinsic semiconductor and form P or N semiconductors. The type of extrinsic semiconductor directly depends upon the kind of dopant added to the semiconductor. In case of silicon, penta-valent (elements from the 5th group in the periodic table) and trivalent (elements from the 3rd group in the periodic table) impurities are added to alter the electrical properties and obtain extrinsic semiconductor [17-22].
N-type doped semiconductor

Penta-valent impurities such as phosphorus (P) or arsenic (As) are added in silicon to make it N-type doped. A penta-valent atom contains five valence electrons. Four of these five electrons are utilized in bonding with silicon atoms, but the fifth electron remains free, as shown in Figure 5. As more penta-valent dopant atoms form bonds with silicon atoms, more free electrons are released, thus, increasing the overall conductivity of the semiconductor material. The resulting material has a high population of free electrons i.e. free negative charges, and therefore, it is called N-type doped semiconductor [17-22]. The number of free electrons directly depends upon the amount of penta-valent dopant atoms introduced in the material. An N-type doped semiconductor, no matter how highly doped, essentially contains a very small number of holes, i.e. free positive charges or empty electron spaces, which in this case are called the minority charge carriers, while, the free electrons are called majority charge carriers [17-22].
The penta-valent impurities used as dopant for silicon are arsenic (As), phosphorus (P), antimony (Sb), and bismuth (Bi). Figure 4 shows the bonding of four silicon atoms with one phosphorus atom [17-22].

**P-type doped semiconductor**

A trivalent dopant when introduced in the silicon lattice increases the number of holes, thus, forming a P-type doped silicon. The trivalent dopant atoms contain three valence electrons, i.e. one less than the number of valence electrons in silicon atom. These three valance electrons of the trivalent impurity atom form covalent bonds with three silicon atoms, but, the valence electron in the fourth silicon atom remains unbound, thus, resulting in electron deficiency [17-22]. Such electron deficiency is referred to as hole. As more covalent bonds are formed between trivalent impurity atoms and silicon atoms, the semiconductor material becomes more electron-deficient, thus, increasing the number of holes, i.e. free positive charges [17-22]. Due to the presence of high population of positive charges, this type of semiconductor is called P-type doped. In this case, holes are the majority charge carriers, whereas, the very small amount of free electrons essentially present in this type of semiconductor are referred to as minority charge carriers. Figure 6 shows the bonding of trivalent boron (B) atom and four silicon atoms and formation of a hole. The other trivalent impurities used as dopants for silicon are aluminum (Al), indium (In), and gallium (Ga) [17-22].
1.2.2 PN junction

A PN junction is obtained when an N-type doped region is formed on a P-type doped semiconductor surface, or vice versa. For simplicity and theoretical explanation, it is assumed that a PN junction is formed when a P-type doped semiconductor block and an N-type doped block are brought together and placed in perfect contact; however, in actual practice, the PN junction is fabricated in a different way, which will be discussed later. When P and N type doped blocks are brought together in contact, the majority charge carriers from the N-type region near the junction diffuse into the P-type doped region, and vice versa [23]. The diffused electrons combine with the holes in the P-type region, while the diffused holes from the P-type region combine with the electrons in the N-type region [23]. This is termed as recombination of electrons and holes to form electron-hole pairs. As a result of recombination of electrons and holes, a narrow region on either sides of the junction is left with no mobile charges, and therefore, this region is called depletion region [23]. Because of the attracted electrons, the part of the depletion region...
layer extending into the P-type region attains a net negative charge; whereas, the part of the depletion layer extending into the N-type region attains a net positive charge. Therefore, an electric field is setup over the depletion region which avoids further diffusion of electrons and holes across the junction; and as the junction stabilizes a PN-junction is said to be established [5] [23] [24].

Figure 7 - Diffusion of electrons and holes resulting in the formation of the depletion regions [23].

This explanation has been based on the assumption that a P-type semiconductor and an N-type semiconductor are brought together, joined, and kept in perfect contact with each other. In actual, formation of a PN junction is done in a completely different way. Usually, an already doped semiconductor substrate, say P-type, is doped with opposite type dopant, i.e. N-type, to diffuse impurity atoms on the surface of the substrate. As the substrate is doped, two regions are formed; one with electrons as the majority charge carriers and other with holes as the majority carriers; while, both P and N regions contain some electrons and holes, respectively, as minority charge carriers.
Different doping techniques, such as diffusion and ion implantation, are employed to form the PN junction.

### 1.2.3 The Photovoltaic effect

As explained in the Bohr’s theory of atoms, only well-defined energy levels can be occupied by the electrons in an isolated atom [24]. Bonded atoms consist of discrete energy bands with energy levels occupied by electrons, and separated by energy band gaps. Commonly, these energy bands are differentiated as valence band and conduction band, and the gap is called band gap or the forbidden band [24].

In case of semiconductors, the valence band is almost full of electrons, while the conduction band is almost completely empty. For semiconductors to conduct, energy equivalent to or larger than the band gap is required by the electrons to jump from valence band to conduction band, where they are free to move [24]. This energy can be applied externally, say, in the form of photons contained in light.

![Figure 8 - Formation of electron-hole pair by the action of photons [25]](image-url)
When photons strike the electrons in a semiconductor, electrons absorb the energy contained in the photon, and if this energy is higher than the band gap, electrons would jump to the conduction band, resulting in the formation of electron-hole pairs, wherever light is absorbed [5] [24]. When a PN-junction is exposed to light containing photons of energy higher than the forbidden band, the electrons in the valence band absorbs the energy of the photons and jump to conduction band, giving rise to holes, forming electron-hole pairs [5] [24]. These electrons, generated in the N-type doped region, may diffuse into the P-type region for recombination, but, are prevented by the electric field established over the depletion region. Therefore, if an external load is connected, the electrons in the N-type region will take the external path towards the holes in the P-type region, giving rise to a potential difference. This phenomenon, thus, involving the interaction of photons and electrons in a semiconductor to generate electricity, is known as the photovoltaic effect [5] [24].

![Figure 9 - A PN-junction solar cell connected to an external load and exposed to sunlight.](image)

As mentioned, the energy of the photons must be at least equivalent to, or higher than the band gap. The photon energy varies according to the wavelength of the light. The complete sunlight spectrum, from UV to IR, ranges from around 0.5 eV to around
2.9 eV in energy, where eV stands for electron-Volts. Materials such as crystalline silicon, which has a band gap of 1.1 eV, are used to make PN-junction diodes, as shown in Figure 9, to utilize the solar energy and generate electricity via the photovoltaic effect.

A solar cell’s conversion efficiency is defined as the ratio of the electrical output generated photovoltaically to the radiative power received by it. Semiconductors only absorb the portion of the light spectrum, that has energy higher than the band gap, and the remaining part is left unabsorbed or unused [5] [24]. This poses a natural limit to the efficiency of the semiconductor material. Other major factor that confines the natural or theoretical efficiency achievable by a semiconducting material is recombination. After photovoltaic excitation, the excited electrons and holes may recombine again, and this recombination, thus, attempts to restore the non-equilibrium carrier densities to their dark, equilibrium state, which reduces the overall efficiency of the material [5] [24]. A semiconductor material’s quality is expressed by the lifetime for minority carriers. Other important aspect for solar cells is the diffusion length, i.e. the distance that an excess carrier can travel by diffusion before recombination. Diffusion length must be larger than the cell thickness, for high efficiency output [5] [24].

1.4 Solar Cell Fabrication Techniques

Solar cells have been developing from several decades. The three generations of solar cells consists of cells from as simple as a PN-junction diode to extremely complex cell structures, resulting from the introduction of different fabrication techniques, basically, for the semiconductor industry. The common solar technologies will be briefly explained in this topic.
1.4.1 A basic solar cell structure

The simplest semiconductor solar cell is a PN-junction diode, which can be made by doping a P-type semiconductor substrate with N-type dopant or vice versa. But, a proper solar cell consists of a few more components [27]. As seen in the schematic diagram of a solar cell, a P-type silicon substrate is doped with N-type impurity atoms on the top surface. This N-type doped surface is then covered with an anti-reflection coating, for better solar absorption [27]. Anti-reflective coating is a very thin layer of material of lower refractive index than the solar cell material under it. Back and front metal contacts are provided for connection of external load. The top surface of the solar cell is covered with a glass [27].

![Figure 10 - Basic structure of a silicon solar cell [28]](image)

Even the manufacture of a basic solar cell, such as the one shown in Figure 10, involves many fabrication steps, from the manufacture of silicon substrate to the final
solar cell. Figure 11 shows the various steps involved in the fabrication of a multi-crystalline solar cell. This includes the raw material being processed and molded, then sliced into individual multi-crystalline wafers [26]. These substrates are then treated, followed by the formation of PN-junction [26]. Then, an anti-reflection coating is formed on the surface. Final step involves the formation of back and front electrodes [26].

**Figure 11 - Steps involved in the fabrication of solar cells [26]**

### 1.4.2 Crystalline silicon solar cells

Even after the many years of progress of solar cell technologies, the very initial wafer based silicon technology still remains prevalent. It is also known as the crystalline silicon solar technology. This can be further categorized as mono-crystalline and polycrystalline [29] [30]. Single crystal substrates are used to make mono-crystalline silicon solar cells. The efficiency of mono-crystalline solar cells is high (up to 24%), however, the cost is also high owing to the expensive material and the costly
manufacturing process [29]. The manufacture of mono-crystalline silicon solar cell involves the conversion of polycrystalline silicon to single crystal silicon in the form of ingots from which layers or wafers of single crystal silicon are sliced to make solar cells. Polycrystalline silicon (also called polysilicon or multi-crystalline silicon) solar cells can be made with much lower manufacturing costs and less expensive material, although, the module efficiency is also very low (14% to 16%) compared to mono-crystalline solar cells. It holds the largest market share (more than 55%) due to the low manufacturing costs [29] [30].

![Crystalline solar cell](image)

Figure 12 - Crystalline solar cell [16]

### 1.4.3 Thin film solar cells

Thin film technology is another prevailing process in the fabrication of silicon solar cells. Instead of growing ingots of crystalline silicon, and cutting wafers, deposition of thin layers of materials on a substrate is done to make the solar cell [30]. Amorphous silicon (a-Silicon) is used in this process and is deposited by chemical vapor deposition (CVD), electroplating, or other deposition techniques. Only a 1 micron layer of the PV material is required to make the thin film cells; therefore, a lot of material is saved and overall cost is reduced significantly [30]. The materials can be deposited over large areas
thus requiring less processing for bulk manufacture of solar cells. The low cost of thin film solar cells is a boon; however, the low efficiency of thin film solar cells, just 6% to 8%, is a major drawback in the commercialization of these cells [29] [30] [31] [32].

![Thin film solar cell](image)

Figure 13 - Thin film solar cell [33]

1.4.4 Latest trends in fabrication of solar cells

Presently, the solar cells being researched or manufactured are far more advanced than the basic cells, and involve many complex processes. The highest recorded solar cell efficiency to date is 41.1% [6]. A common trend involves fabrication of solar cells with textured surface, to increase the surface area [34], and therefore, enhance the absorption of light [35]. Multijunction solar cells have also been developed that make use of materials such as GaAs (gallium-arsenide), Ge (germanium), GaInP$_2$ (gallium-indium-phosphide), etc. in different layers to form multiple junctions [31]. Manufacture of the solar cell that has achieved efficiency of 41.1% under laboratory conditions, involved fabrication of multiple junctions of gallium indium phosphide and gallium indium arsenide on a germanium substrate [6]. One more recent solar cell technology, the dye-sensitized solar cells [14], involves the use of monolayer of light absorbing material such as ruthenium metal-organic dye for enhanced absorption of light. Many other solar cells
such as 3-D solar cells [36], nanoparticles based solar cells [37], transparent UV solar cells, and infrared solar cells, have been developed.

1.4.5 Relevant Issues

Though, the solar cells have been around for a very long time and seen many technological advances, the share held by solar cells in the present energy market remains very less. The main reason for this is the high cost of high efficiency solar cells. This high cost is mostly result of the expensive manufacturing processes and the costly high purity photovoltaic materials. The focus of most of the contemporary solar cell research in the world is on the development of low cost high efficiency solar cells. As a solution to the high cost of solar cells, many different low cost techniques are being explored, along with utilization of low cost materials instead of using expensive materials such as high-purity single crystal silicon or gallium-arsenide. Other method of reduction of cost of solar cells is by reducing the amount of solar cell material. One such attempt includes a micromachining technique in which the silicon wafers are cut into very thin slices (~50 µm thick) to reduce the amount of material used, but, this makes the processing a lot more complex [38]. Other efforts include the use of very cheap metallurgical grade silicon (MGS) which costs just about $50/kg, but, the major problem associated with this technique is the very short life-time of carriers (small diffusion length) due to high defect and impurity density. Several other approaches have been developed, but due to the associated limitations, none of them have proved to be cost-efficient.
1.5 Hypothesis

We hypothesize a fabrication process for the manufacture of silicon photovoltaic micro-particles. This process was implemented and silicon photo-voltaic micro-particles of different sizes were fabricated. Experiments were conducted with different sets of particles; and photo-electrolytic generation of hydrogen in electrolytic solutions containing these particles has been demonstrated. Some future applications such as micro-particles based thin solar cells, photo-electrochemical hydrogen generation system, and solar paint, are also proposed. Further development of this technology could lead to future discoveries towards reduction of solar cell fabrication costs.
Chapter 2 – Silicon Photovoltaic Micro-Particles: Justification and Fabrication

2.1 Introduction

A number of different solar technologies have been discussed in the previous chapter; however, none of them promises to be an outstanding technique to make low-cost photovoltaic conversion possible. The quest for low-cost solar technology is the motivation for the development of photovoltaic micro-particles. Photovoltaic micro-particles can be prepared from low-cost materials such as metallurgical grade silicon (MGS). Furthermore, the fabrication process, proposed in this chapter, make use of simple techniques such as thermal diffusion, for forming a PN junction on each of the particles. Some of the applications envisioned for the photovoltaic micro-particles include micro-particle based thin film solar cells, photo-electrochemical fuel generation, and solar spray-paint, which are discussed in detail in Chapter 5.

The theory underlying the development of photovoltaic micro-particles technology has been explained in this chapter. Later, a fabrication process for the manufacturing of silicon photovoltaic micro-particles has been proposed.

2.2 Photovoltaic Micro-particles

Photovoltaic micro-particles are semiconductor particles that contain a P-type doped region and an N-type doped region, on each one of them. Each micro-particle has a PN-junction which acts as an individual photovoltaic converter that utilizes solar energy
and converts it into electrical energy. The particle size may vary from submicron to a few
tens or hundreds of microns. These particles can be fabricated in bulk from low cost
semiconductor materials such as waste electronic grade silicon or metallurgical grade
silicon; or can be prepared from other materials such as gallium-arsenide (GaAs) or
silicon-carbide (SiC) for high efficiency results.

Carrier recombination is a factor that largely affects the efficiency of photovoltaic
cells. The optically generated electrons and holes always face the risk of being
recombined with each other before reaching the cell terminals, thus reducing the
conversion efficiency of the solar cell. The electric field over the depletion region drifts
electrons and holes in opposite directions with relatively high speeds, hindering the
recombination of electrons and holes. The size of the photovoltaic micro-particle
structures is very small, and therefore, the length of path travelled by the carriers, to the
surface of the particles, is also very short. This path is completely or mostly covered with
the electric field at the depletion region. This electric field acts as a hindrance for the
excited excess carriers to recombine, and so, prevents the probability of recombination of
electrons and holes, thus, considerably improving the conversion efficiency of the micro-
particles. This allows the use of low quality materials such as metallurgical grade silicon
(MGS) or waste electronic grade silicon (EGS). Metallurgical grade silicon, which is
around 30 times cheaper than the high-quality electronic grade silicon, is not used for
semiconducting purposes, and is only used for metal alloy or ceramics production. If
silicon photovoltaic micro-particles are manufactured from MGS or waste EGS, to make
solar cells, effective reduction in the overall cost can be achieved. Furthermore, the
amount of material required to make a thin film photovoltaic micro-particle based solar cell is much less, which further cuts down the overall cost. Besides, micro-particles can also be prepared from low-cost low-quality versions of different semiconductor materials, e.g. GaAs and SiC.

The rough surfaces present on the micro-particles add to their advantages. The photovoltaic micro-particles produced after fabrication naturally contains rough surfaces, which are very good absorbers of sunlight incident upon them. Therefore, no anti-reflection or surface texturing is required to improve the absorption of the surface, in order to obtain higher efficiency. If solar cells are made from photovoltaic particles, as proposed in Chapter 5, internal reflection between the layers of micro-particles would further enhance the absorption of light. Along with this, the proposed fabrication process involves few simple steps; unlike other solar technologies that make use of complex fabrication processes such as lithography and thin-film deposition. This reduces the manufacturing cost, and further cuts down the overall cost.

2.2.1 Summary of Merits of the Photovoltaic Micro-particles Technology

- In the micro-particles structures, due to the small size of the PN-junction particles, the short carrier path (submicron to a few microns) to the surface of the particles assures that all or most of the path is covered by the electric field of the PN junction. This significantly reduces the probability of carrier recombination and allows relative high efficiencies to be achieved even with low quality materials such as MGS.
• The use of micro-particles for various applications also reduces the amount of required structural materials, thus, reducing the overall cost.
• The fabrication process can be implemented with a variety of materials such as GaAs and SiC, for high efficiency results.
• The internal reflections in the structures comprising of millions of particles ensures better absorption of the incoming light.
• Light absorption is further enhanced by the rough surfaces naturally present on the micro-particles.
• The simple fabrication process requires a very few steps, and thus, eliminates the need for expensive processes such as lithography, thin-film deposition, surface texturing, etc. This helps in considerable reduction in the fabrication cost.
• Micro-particles based technologies can be further developed for many applications such as thin solar cells, or photo-electrochemical fuel generation.

2.3 Thermal Diffusion of Impurity Atoms on the Surface of Silicon

One of the most commonly used techniques for selective introduction of dopant atoms in a silicon substrate is by diffusing the impurity atoms on its surface. Diffusion is the process of migration of dopant atoms from higher concentration areas to lower concentration areas, i.e. a concentration gradient results in redistribution of the impurity atoms until there is no concentration gradient [39]. For preparation of crystalline solar cells, the primary dopant is usually added while growing the silicon boule, from which the base substrate is obtained [40][41][42]. This base substrate, usually, has an almost uniform doping concentration throughout the wafer. To form the required PN- junction, a
thin layer of silicon with the opposite doping type should be formed on the substrate by diffusing the dopant atoms inside the surface of the silicon substrate, as illustrated in Figure 14. This thin layer formed after doping, generally, ranges from a few nanometers to tens of microns.

The doping of silicon by thermal diffusion of impurity atoms is shown in Figure 14. Diffusion in solids is a very slow process, but, it depends upon the temperature at which diffusion takes place; higher the temperature, faster will be the rate of diffusion. Concentration gradient of impurity atoms has almost no effect initially, but as the temperature is increased, faster diffusion is achieved; thus, the name thermal diffusion. After the required diffusion depth and/or impurity concentration is obtained, the temperature is again lowered back to normal to stop further diffusion. This results is the formation of a thin doped layer on the surface of the silicon substrate, and thus, a PN-junction is formed which is required for the photovoltaic conversion to take place.
If the same process of diffusion is carried out and the silicon substrate is doped from all the sides. The resulting substrate will have a doped layer on all the surfaces, with no exposed PN-junctions. As this doped layer is extremely thin, the core of the silicon substrate remains undoped; i.e. a P-type silicon substrate diffused with N-type dopant on all the surfaces will have N-type doped surfaces and P-type core, refer to Figure 15. This substrate cannot be utilized as a photovoltaic PN-junction as the junction is not exposed, making it impossible to provide the required electrical connections. If the silicon substrate is broken down into smaller pieces, the P-type core will be exposed, and smaller pieces with PN-junction are obtained. A similar process can be utilized to fabricate silicon photovoltaic particles.

Figure 15 - Exposed PN-junctions after breaking a silicon substrate doped from all sides into pieces of smaller size.
2.4 Process Sequence to Fabricate Silicon PV Particles

The process for fabrication of silicon photovoltaic micro-particles involves just a few simple steps. Pre-doped silicon is first crushed into fine particles, which are then doped to form a doped layer on their surfaces, and finally the doped particles are crushed again to expose the covered PN junctions and obtain the photovoltaic micro-particles. The steps are explained as follows:

**Step 1 - Crushing of silicon into small particles**

Pre-doped silicon, e.g. P-type, is crushed into fine particles. The size is kept slightly larger than the required size of photovoltaic particles. For example, the initial particles are crushed to a size of 150-200µm if the required micro-particles size is approximately 50µm.

![Figure 16 - Step 1: Silicon crushed to particles](image)

**Step 2 - Diffusion**

The particles are then doped by diffusion of opposite type dopants. As the impurity atoms diffuse into the surfaces of the particles, a thin doped layer is formed on
the surfaces of the particles, which entirely covers the undoped core of the particles.

These particles contain the unexposed PN-junctions.

**Figure 17 - Step 2: Diffusion of dopant**

**Step 3 –** Further crushing to expose the PN-junctions and get the PV particles.

The particles are crushed again to a slightly smaller size than the initial particles. This further crushing exposes the buried PN-junctions and, thus, the silicon photovoltaic micro-particles are obtained.

**Figure 18 - Step 3: Doped particles crushed to smaller PV particles**
After observing the nature of the PN-junction formed when a silicon substrate is doped by diffusion of impurity atoms, a process has been developed for the fabrication of silicon PV particles. This process requires a few steps that include crushing of silicon into small particles, doping of these particles, and further crushing into smaller particles to obtain the photovoltaic micro-particles. The proposed process does not involve any complex fabrication techniques such as slicing of silicon into thin wafers as in crystalline solar cells, or deposition of thin layers as in the case of thin-film cells. The experimental implementation of this process has been explained in the following chapter.
Chapter 3 – Practical Implementation of the Process to Fabricate Silicon PV Micro-Particles

3.1 Introduction

A simple process flow to fabricate silicon photovoltaic micro-particles was proposed and explained in the previous chapter. This fabrication process can be implemented in several different ways. The most important part of this process is the doping of silicon particles. Two of the commonly used methods of diffusion of dopant atoms in silicon particles have been tried in this work. Initially, a solid planar dopant source was used, but, no promising results were obtained. Good PV particles were obtained when a spin-on-diffusant was used for doping silicon particles. In most of the cases, P type silicon wafers with low surface resistivity were used to prepare particles, and phosphorus dopants were used as the N-type impurities to form the PN-junctions. In a very few cases, particles were prepared from N type silicon wafers and doped with boron, a P-type dopant. The doping techniques are explained in detail in the following sections.

3.2 Preparation of particles

Although the ultimate goal of the envisioned technology is utilization of lower quality metallurgical grade silicon (MGS) powder as the initial material, but for the current development activities, higher quality electronic grade silicon (ESG) wafers were used to generate silicon powder. The very first step of the fabrication requires crushing of
silicon wafers to prepare particles to be doped. For this purpose a simple mortar and pestle set, made of marble, was used. Particles of different sizes were separated using wire meshes of different size selections. Silicon particles of different sizes, ranging between 2-2.5mm through 100µm, were prepared. Figure 20 shows images of particles of sizes approximately (a) 1mm and (b) 100-200µm.

Figure 20 - Particles of different sizes. (a) Particle size ~1mm (b) Particle size ~100 - 200microns
3.2.1 Buffered oxide etch (BOE) treatment of particles

Buffered oxide etch is a solution of ammonium fluoride (NH$_4$F) and hydrofluoric acid (HF). It is used to etch away silicon-dioxide from the surface of silicon. A thin layer of silicon-dioxide (SiO$_2$), on the surface of silicon, prevents diffusion of dopant atoms into its surface. Usually, silicon may contain a very thin layer of silicon-dioxide on its surface; therefore, silicon particles were treated with BOE before diffusion to get rid of any pre-deposited layer of silicon-dioxide. It is very important to clean the silicon particles with BOE, before doping them, so as to get a well doped surface on the particles. The particles were kept in a small amount of BOE solution for about 2 minutes. Water was added to dilute the solution, which was then filtered to take out the particles.

3.3 Doping of Particles by Different Diffusion Techniques

This is the most important step in the fabrication process, as proper diffusion technique assures better efficiency of the PV particles. The dopant sources used for photovoltaic micro-particle fabrication purposes in this work, are high concentration dopants, i.e. the resulting sheet resistivity is low. The first diffusion method used in this work utilizes a solid planar dopant source. It did not yield any efficient results due to various reasons which will be discussed later in this chapter. However, the second approach used to dope the particles, utilizes liquid spin-on-diffusant as a dopant source. Good silicon PV particles were produced using this technique and it proved to be a much easier method that can be applied to dope the silicon particles in bulk.
3.3.1 Doping of particles using solid planar dopant source

A planar dopant source is a solid disc, made of inert material, containing the dopant, e.g. glassy layers of potassium silicates and borates containing boron as dopant. This process requires the planar source to be placed very close to the wafer at elevated temperature in a furnace. Although, this process is relatively straightforward and simple for doping silicon wafers; but, in case of silicon particles, it is quite inefficient and did not yield any promising results. Therefore, not much emphasis is placed on this process, only the procedure is explained.

![Planar dopant source](image)

Figure 21 - Planar dopant source [43]

The setup for doping a silicon wafer using a planar dopant source is shown in Figure 22. The dopant sources are kept very close to the wafer, the distance between the wafer and the source should be around 0.060 inch to 0.100 inch [43]. Generally, a quartz boat with slots for wafers and dopant sources is used for this purpose. Then, the quartz boat, along with wafers and sources, are placed in the furnace, and the temperature is elevated to the required diffusion temperature, e.g. 1000°C. Usually, the maximum doping temperature limit is 1150°C [43]. In most cases, different ambient gases, such as
nitrogen, argon, oxygen, are also supplied inside the furnace to achieve the desired doping results. The diffusion time varies as per the requirements, and is between 30 minutes to a couple of hours, for the commonly used dopant sources.

The dopant source used for diffusion of silicon particles is *Techneglas PhosPlus TP-470*, a phosphorus dopant source [43]. The sheet resistivities that can be achieved with this dopant source at different doping times and temperatures are shown in Figure 20. The typical doping temperatures for TP-470 vary from 1000°C to 1150°C, which can be done for upto 3 hours. Generally, the diffusion time decreases as the doping temperature is increased [43].

Figure 22 - Diffusion using a planar dopant source [43]

![Diffusion using a planar dopant source](image)
The crushed and cleaned particles were doped at different temperatures from 1000°C to 1150°C, using the TP-470 dopant source. The maximum doping time was 2 hours at 1000°C and 30 minutes at 1150°C. Nitrogen gas was supplied into the furnace during diffusion, in some cases; while other diffusions were carried out in ambient gases. Silicon wafer was used as a base plate, on which particles were kept for doping. This wafer was kept at the base of a quartz boat, and the dopant source was kept on top of the quartz boat. The distance between the base plate and the dopant source was around 5 mm. Only one layer of particles was placed on the base plate, for proper exposure to the dopant source. The schematic is shown in Figure 24. The setup is then placed in the furnace for diffusion. After diffusion, the furnace is allowed to cool down and the setup is taken out of the furnace. The particles are then removed from the base wafer surface and cleaned with HF to remove the oxide layer formed during diffusion. This is followed by further crushing of the particles.
As the particles are placed on a silicon base plate, the particles’ surfaces which are opposed to the dopant source, and in contact with the base plate, remains unexposed, and so, are not doped properly. And as the particles need proper exposure to the dopant source, only one layer of particles can be doped at one time, as one more layer would avoid exposure of particles at the bottom to the source; therefore, the amount of particles that can be doped at any one time is very small. This is a major drawback of this diffusion technique, which is overcome by the use of spin-on-diffusant source which provides the advantage of fabricating PV particles in bulk.

3.3.2 Doping of particles using spin-on-diffusant (SOD)

Spin-on-diffusant is a mixture of silicon-dioxide (SiO$_2$) and the dopant (usually boron or phosphorus) in a liquid solution. It is also referred to as spin-on-dopant or spin-on-glass, and is a commonly used diffusion technique for the fabrication of silicon solar cells. The wafer is spin coated with the solution containing the dopant which results in the formation of a thin glass layer with a high concentration of dopants on the silicon substrate. The wafer is then kept in a furnace at high temperature for the dopants to
diffuse from the glass layer into the silicon wafer. SOD forms a very uniform and consistent doped layer on the silicon surface; and the method is pretty simple with good controllability. The spin-on-diffusant can be applied to the wafer surface in many different ways such as by spraying, painting, spin-coating, or screen printing [40] [42] [44].

A wide variety of spin-on-diffusants are available from different manufacturers which can be used for many different purposes. The one used for doping of silicon particles is *Filmtronics P512 phosphorus spin-on-diffusant*, which has a high dopant concentration and gives low resulting sheet resistivity after diffusion. The P512 solution contains about 10.5 % of phosphorus dopant compound and 5 % of silicon-dioxide in a solvent [44]. One of the major advantages of this solution is that it does not cause any surface damage upon diffusion; while, most of the other SODs does. The shelf life of this diffusant is around 3 months at room temperature, and longer if stored in refrigeration at temperature between 32°F and 40 °F. [44]

The process steps, as recommended by the supplier [44], are:

I. A pre-diffusion clean.

II. Application of dopant to silicon. Around 1 ml or less is needed for a 2 inch wafer.

III. Spinning at speed between 2000 and 6000 rpm to produce an oxide looking film. A polypropylene or delrin chuck should be used for spinning. The dopant should wet out uniformly on the surface.
IV. A pre-bake at 200 °C for 10-15 minutes to harden the film.

V. Diffusion at temperature between 900 °C and 1300 °C depending upon requirements. Nitrogen and oxygen can be supplied (usually 90% nitrogen and 10% oxygen) can be supplied for precise results.

VI. HF-clean after diffusion.

Figure 25 – Process for diffusion on a wafer with SOD

According to the data provided by the manufacturer, sheet resistivity as low as 2.1 Ω/square can be obtained when a P-type wafer, spin-coated at 5000 rpm, is diffused at 1100 °C for 2.5 hours or 1235 °C for 90 minutes [44]. Diffusion at 1100 °C for 30 minutes should give sheet resistivity of 3.1 ohm/square, and 2.8 ohm/square if diffusion is done at 1220 °C for 1 hour [44]. Although, highly recommended, it is not necessary to supply nitrogen and oxygen during diffusion. This low resultant sheet resistivity and ease of application makes P512 highly suitable for doping of silicon particles. The process for application of the SOD to the particles is somewhat different from the typical process
used to coat the wafers. The complete process for doping of silicon micro-particles, as followed in the laboratory, is explained in steps below.

**Step 1 – Application of SOD**

The spin-on-diffusant (N-Type) is applied to the P-type silicon particles, which are already BOE cleaned as explained in section 3.2. A few drops of the SOD solution are dropped on the particles, in a container. A 3 ml dropper was used for this purpose. Around 2-3 ml of solution is applied to the particles made from a complete 6 inch wafer. The particles are shaken and mixed several times, while applying the dopant, in such a way that all the particles get properly wet and coated with the SOD solution.

![Figure 26 - Application of SOD](image)

**Step 2 – Pre-diffusion bake**

After the SOD is applied, particles are kept on a hot plate at 200°C for pre-diffusion bake. A silicon wafer is used as a base plate for the particles. This is done for about 10-15 minutes. A pre-diffusion bake is required to remove excess solution and to harden the film on the particles [44].
Step 3 - Diffusion

After a pre-diffusion bake, the particles along with the base plate wafer are kept in the furnace for diffusion. A quartz boat is used for this purpose. The different temperatures for diffusion of particles ranged from 900°C to 1150°C, and the diffusion times were between 1 hour and 2 hour 30 minutes, this excludes the time required by the furnace to elevate to the required diffusion temperature. No gases were supplied to the furnace for diffusion. The best results were obtained with diffusion at 1100°C for 2 hours, although, very slightly different from the results obtained at 1000°C [44].

Step 4 - HF Clean

After diffusion, the furnace is allowed to cool down to the room temperature and the particles are taken out of the furnace. Drying of the SOD at high temperature results
in the formation of silicon-dioxide due to which the particles get firmly stuck to the base plate and to each other forming a pile. Figure 29 shows the pile of particles on the diffusion quartz boat after diffusion. As the particles are firmly attached to the base wafer, they need to be scratched off from that wafer, and comes out as a piece of chunk (Figure 29). This pile is then kept in HF solution which cleans up the silicon-dioxide formed during diffusion. Water is added to HF solution containing silicon particles, to make it dilute, and then filtered to take the particles. Then, the particles are rinsed thoroughly to assure that no HF is left after the cleanup. The particles are then dried on a hot plate at a temperature of around 100°C. Instead of scratching the base plate to remove the particles, the base wafer, along with the stuck particles, can be kept for HF clean. This will separate the particles from the base wafer, which can then be removed from the solution to be filtered to take out the particles. This assures clean separation of particles from the base wafer, although, sometimes the wafer may break into very small pieces making it difficult to separate them from the doped particles.

Figure 29 - Pile of particles formed after diffusion
Figure 30 – Steps for fabrication of silicon PV micro-particles using SOD.
3.4 Final Crushing

This is the final step to prepare the silicon PV particles. After HF clean, the particles are further crushed to smaller size to expose the PN junctions, and thus, to get the PV particles. A simple marble mortar and pestle set is used for this. The particles are separated while crushing; from the smaller already crushed particles. The particles should be crushed to a slightly smaller size. If bigger particles are crushed to a much smaller size, the resulting set may contain many particles without any doped surfaces; due to the fact that only the surfaces of the initial particles are doped and the undoped core of the particles may result in formation of many smaller particles which does not contain the PN junction. The crushed particles are the required silicon photovoltaic micro-particles, and are ready for further applications.

3.5 Selective Copper Deposition Test

Presence of small amounts of metallic compounds in HF-aqueous solutions used for silicon fabrication processes, result in deposition of metal on the silicon surface, e.g. a presence of a very small amount of copper-sulfate (CuSO₄) in HF solution (water:HF = 100:1) would result in deposition of a thin layer of copper on silicon kept in this solution. This has been verified in various laboratory tests [45] [46] [47]. This method is called *electrochemical deposition* of metals. It is usually known for contamination of metals on wafer surfaces during wet cleaning processes with solutions such as HF. The deposition of metals depends upon many factors such as pH value of the solution, type and concentration of the dopant, and oxygen content in the solution [47]. In lower pH solutions, reduction and deposition of metal ions on the surface takes place; while, in
higher pH solutions, metal ions are precipitated and included as metal oxide or hydroxide into the oxide layer. Figure 31 shows the reduction and oxidation reactions involved in the deposition of copper on silicon surfaces immersed in HF and copper-sulfate solution.

\[
\begin{align*}
Cu^{2+} + 2e^- & \rightarrow Cu(s) \quad E = +0.34V \\
Si(s) + 2H_2O & \rightarrow SiO_2(s) + 4H^+ + 4e^- \quad E = +0.91V \\
SiO_2(s) + 4H^+ + 6F^- & \rightarrow SiF_6^{2-} + 2H_2O \\
2Cu^{2+} + Si(s) + 6F^- & \rightarrow 2Cu(s) + SiF_6^{2-}
\end{align*}
\]

Figure 31 - Copper deposition on the surface of silicon when kept in a solution containing HF and copper-sulfate [59]

A very useful property of electrochemical copper deposition on silicon surface, found during various tests in the laboratory, is the selective nature of deposition on a PN junction diode. When copper is deposited on a P-type silicon substrate that has a partial N-type doped region, i.e. a PN-junction; copper selectively deposits on the P-type doped region. The rate of deposition of copper on the P-type surface of partially doped silicon is much higher than that on the N-type region. Therefore, the PN-junction silicon, when kept in CuSO$_4$ – HF solution, for electrochemical deposition, for a short time, would get a thin layer of copper on the P-side while very less, almost invisible, layer of copper on the N-side, with the PN-junction clearly exposed. This is opposite in case copper is electrochemically deposited on an N-type base silicon piece having P-type doped region;
i.e. in this case, N-type regions will have more copper compared to P-type doped regions. Several tests were carried out in the laboratory to verify this and to get the actual rate of deposition which would give an easily distinguishable deposition of copper on P and N sides. Figure 32 shows one such partially doped silicon piece in which P-type and N-type sides can be easily distinguished by the thickness of the deposited copper. The squares that have almost no copper on them are the N-type doped regions; while, the outer, dark reddish part, is the P-type regions.

![Figure 32- Selective copper deposition on PN-junction.](image)

This property has been utilized to verify the formation of PN junctions, on the silicon PV particles. A solution containing 200 ml water, 1 gram copper sulfate, and 0.5 to 1 ml hydrofluoric acid was prepared. PV particles were kept in this solution for a few minutes for selective deposition of copper. The solution was then filtered to take out the particles. The particles were then inspected under optical microscope as well as by static electron microscope (SEM) to see the PN junction boundaries clearly. Varied
concentrations of copper-sulfate and HF were used to prepare solutions for copper deposition, and it was observed that increase in amount of HF increases the rate of copper deposition. A microscopic image of a PV particle with partial copper is shown in Figure 33. Figure 34 shows two SEM images of micro-particles with copper partially deposited on their P-type surfaces. The particles in Figure 34 are approximately 100µm to 200µm in size.

Figure 33 – Microscopic image of surface of a PV particle with partially copper coated surface.
Figure 34 - SEM pictures silicon PV particles with partial copper deposition
3.6 Apparatus, Equipments, and Chemicals Used for Fabrication

- Furnace with working temperature upto 1200°C. The one used for diffusion with planar dopant source is a sophisticated furnace with easy controllability, and inlets for gas supply. The other one, used for diffusion with SOD, is a simple high-temperature oven with very limited functions.
- Marble mortar and pestle set for crushing wafers and particles.
- Wire mesh filters for separating particles of different sizes.
- Hot plate, a simple one, with highest working temperature upto 400°C, used for pre-diffusion bake, and drying particles after HF and BOE clean.
- 3 inch and 6 inch quartz boats, for diffusion. A quartz boat was used as a base for keeping particles for diffusion, and is used for diffusion with both SOD and planar source.
- Buffered oxide etch (BOE), for removing oxide from the particles. A BOE clean is required to remove silicon dioxide from particles for good doping results.
- Hydro fluoric acid (HF), for HF-treatment. It is necessarily used after SOD based diffusion, to remove the thick silicon-dioxide formed during diffusion.
- Copper sulfate (CuSO₄), for selective copper deposition test. Small amounts of copper sulfate are added to HF + water solution for selective deposition of copper on the particles.
- Technegas PhosPlus TP 470 planar phosphorus dopant source, for diffusion. In a very few cases, BoronPlus planar boron dopant source was also used.
- Filmtronics P512 phosphorus spin-on-diffusant, for diffusion.
Plastic beakers and containers were used for BOE and HF treatments. Glassware cannot be used for handling BOE and HF.

Filter papers for filtering particles out of the solutions.

Other basic laboratory apparatus such as glass beakers, containers, spatula, and tissue papers, etc.

3.7 Observations and Discussion

Results and observations from the two techniques implemented for the fabrication of silicon photovoltaic micro-particles are discussed in this section. All the results and observations related to performance of the PV particles are based on the selective copper deposition tests and photo-electrolysis tests, which is explained in the next chapter.

3.7.1 Preparation of particles

It is very necessary that particles be prepared properly. It has been observed that the particles which are not BOE cleaned prior to doping would not yield good results. Wafers were BOE cleaned each time before crushing to particles, and the particles are also BOE cleaned before diffusion. This ensures proper diffusion of particles and better performance.

3.7.2 Diffusion with planar dopant source

No good results were obtained from this doping method. Both P and N type particles were doped at different diffusion temperatures and ambient gases. The following table gives an account of the different sets of particles prepared with this diffusion technique.
<table>
<thead>
<tr>
<th>Particles Type</th>
<th>Dopant Type</th>
<th>Size</th>
<th>Diffusion Temperature</th>
<th>Diffusion Time</th>
<th>Gas Supplied</th>
</tr>
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<tr>
<td>P</td>
<td>N</td>
<td>1 - 2 mm</td>
<td>1000°C</td>
<td>1 hour</td>
<td>None</td>
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</tr>
<tr>
<td>N</td>
<td>P</td>
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</tr>
</tbody>
</table>

Table 1 – Results from PV particles fabricated using solid planar dopant source

As already mentioned, no good PV micro-particles were obtained from this doping technique, therefore, no remarks are made on the performance of the particles.

**3.7.3 Diffusion with Spin-on-diffusant**

Good results were obtained with this doping technique. Particles of different sizes were prepared and doped at different diffusion temperatures. All the particles were made from P-type silicon wafers and doped with N-type SOD. No ambient gases were supplied during thermal diffusion. The details are given in the following table. The comments on particle performance are based on copper deposition and photo-electrolysis tests. Rate of generation of hydrogen bubbles during photo-electrolysis tests of different sets of particles under similar conditions (sunlight, type of solution, etc.) was observed and the performance was compared. The ‘best’ is for the fastest rate of bubble formation, while, ‘good’ relates to comparatively slower rates.
<table>
<thead>
<tr>
<th>Particles Type</th>
<th>Wafer Sheet resistivity</th>
<th>Dopant Type</th>
<th>Size</th>
<th>Diffusion Temperature</th>
<th>Diffusion Time</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>~ 370 mΩ/sq</td>
<td>N</td>
<td>1 - 2 mm</td>
<td>1000°C</td>
<td>2 hours</td>
<td>Good</td>
</tr>
<tr>
<td>P</td>
<td>~ 370 mΩ/sq</td>
<td>N</td>
<td>~500 μm</td>
<td>1000°C</td>
<td>2 hours</td>
<td>Good</td>
</tr>
<tr>
<td>P</td>
<td>~ 370 mΩ/sq</td>
<td>N</td>
<td>~500 μm</td>
<td>1100°C</td>
<td>1 hour</td>
<td>Good</td>
</tr>
<tr>
<td>P</td>
<td>~ 268 mΩ/sq</td>
<td>N</td>
<td>~100 μm</td>
<td>1100°C</td>
<td>1.5 hours</td>
<td>Best</td>
</tr>
<tr>
<td>P</td>
<td>~ 4 Ω/sq</td>
<td>N</td>
<td>~500 μm</td>
<td>1050°C</td>
<td>1 hour</td>
<td>Good</td>
</tr>
<tr>
<td>P</td>
<td>~ 9 Ω/sq</td>
<td>N</td>
<td>~100 μm</td>
<td>900°C</td>
<td>2 hours</td>
<td>No results</td>
</tr>
<tr>
<td>P</td>
<td>~ 300 mΩ/sq</td>
<td>N</td>
<td>~500 μm</td>
<td>950°C</td>
<td>2 hours</td>
<td>No results</td>
</tr>
<tr>
<td>P</td>
<td>~ 700 mΩ/sq</td>
<td>N</td>
<td>~500 μm</td>
<td>1050°C</td>
<td>1.5 hours</td>
<td>Good</td>
</tr>
<tr>
<td>P</td>
<td>~ 8 Ω/sq</td>
<td>N</td>
<td>~100 μm</td>
<td>1050°C</td>
<td>1 hour</td>
<td>Good</td>
</tr>
</tbody>
</table>

Table 2 - Results from PV particles fabricated using Spin-on-diffusant

Particles prepared from low sheet resistivity wafers and doped at 1100°C produced the best results in the hydrogen generation tests. It was also observed that no diffusion occur at temperatures 950 °C or below. There was no difference in the performance of particles prepared at 1000 °C and 1050 °C; while, a very little difference in results from particles doped at 1000 °C and 1100 °C was observed. Size of the particles
also played an important role in the performance of the particles, which is explained in the later chapters.

3.7.4 Selective Copper Deposition Test

After selective electrochemical copper deposition test, different sets of particles prepared by diffusion with SOD and planar dopant sources were observed. No PN junctions were detected after electrochemical copper deposition on particles prepared from planar diffusant source, unlike the particles prepared using SOD source. Particles crushed to a very small size compared to initial size contained copper on most of the surface; and most of the particles were covered completely with copper. This is because of the fact that most of the inner core of the particles remains undoped; and too much crushing of bigger particles result in the formation of very small particles which may contain very little or no N-type doped region, and thus, no PN junction; and therefore, selective deposition results in formation of copper layer on most of the particle surfaces.

3.8 Conclusion

Different fabrication techniques were explored to implement the process explained in chapter 2, for the fabrication of silicon PV micro-particles. Particles were prepared by crushing silicon wafers using a mortar and pestle set made of marble. Two different diffusion techniques were employed to find the better and simpler way to dope silicon particles and make them photovoltaic. A planar dopant source was used in the first diffusion method, but, did not produce any good PV particles. The second technique for doping particles, in which spin-on-diffusant was used, proved to be a very efficient and simple method, as compared to the former doping technique. A comparison of results
obtained from different sets of particles, after various tests, reveals that the most efficient 
PV particles are obtained when diffusion is done using a spin-on-diffusant at temperature 
1100°C for around 2 hours. The particles were tested by selective copper deposition and 
photo-electrolysis tests, as explained in the following chapter.
Chapter 4 – Photo-electrolysis of Water Using PV Micro-particles

4.1 Introduction

Hydrogen has long been considered a very clean and efficient source of energy. Hydrogen is not freely available in the atmosphere, however, it is found in the form of compounds, and can be produced and used as a fuel. There are already numerous techniques to generate and utilize hydrogen, and many other techniques are being scavenged to efficiently generate hydrogen, which could be utilized using devices such as a fuel cell or internal combustion engine. One of the most commonly known techniques for the production of hydrogen is the electrolysis of water. Water can be decomposed into hydrogen and oxygen by passing an electric current to generate hydrogen gas to be used in the form of fuel. Generation of hydrogen by electrolysis of water has already been implemented for applications such as vehicles run by hydrogen, utilization by a fuel cell to generate electricity, and many others; which utilize other renewable sources to electrolyze water.

Electrolysis of water requires external energy (electricity) to be applied to split water (H$_2$O) into hydrogen (H$_2$) and oxygen (O$_2$). Utilization of solar energy for this purpose, such as in photo-electrolysis [48], has been explored for a long time, but, due to its cost inefficiency, it has found very few practical applications. It has been explained in this chapter, how silicon photovoltaic micro-particles can be used to generate hydrogen by photo-electrolysis of electrolytic aqueous solutions. Tests were carried out with PV
particles of different sizes and prepared under varied conditions, to demonstrate the utilization of these particles for photo-electrolysis and analyze the performance of particles prepared under different sets of conditions.

4.2 Electrolysis of Water

Electrolysis means decomposition of bonded elements and compounds with the passage of electric current. When an electric current is passed through water (containing electrolytes), decomposition of water molecules takes place through oxidation and reduction reactions, resulting in the formation of oxygen and hydrogen, which comes out in the form of gas [49] [50].

The apparatus in which electrolysis is carried out is called electrolytic cell. A basic electrolytic cell contains two electrodes, a cathode (negative) and an anode (positive). These electrodes are immersed in an electrolytic solution, usually water containing electrolytes. Electricity is supplied externally, e.g. through a battery connected to the two electrodes. When an electrical current is passed through water, it dissociates and forms H\(^+\) and OH\(^-\) ions [49] [50]. These ions move towards the electrodes of opposite charge, i.e. H\(^+\) ions move towards the cathode and OH\(^-\) ions move towards anode. On reaching the respective electrodes, the ions give rise to two separate reactions; reduction and oxidation [49] [50]. Gain of electrons by a molecule, atom or ion is referred to as reduction; and the ion accepting the electrons is said to have been reduced. Loss of electrons by a molecule, ion or atom is termed as oxidation; and the ion that loses its electron is said to have been oxidized [49] [50]. When two H\(^+\) ions accept electrons at the cathode, they reduce and pair up to form hydrogen gas (H\(_2\)). On the other hand, four OH\(^-\)
ions oxidize at the anode and combine to form oxygen gas \( (O_2) \), molecular water, and four electrons released from oxidation [49] [50]. These hydrogen and oxygen gases come out in the form of bubbles from cathode and anode, respectively. Schematic of an electrolytic cell is shown in the following figure. [49] [50]

![Electrolysis of water](image)

**Figure 35 - Electrolysis of water [51]**

In order for reduction and oxidation reactions to take place, sufficient voltage needs to be applied. The least voltages required for red-ox reactions are known as the half reaction standard potentials. The reduction and oxidation reaction that takes place at cathode and anode, along with the standard potentials [49] [50], are as follows:

**Anode (Oxidation):** \[ \text{H}_2\text{O} \rightarrow \text{O}_2(g) + 4 \text{H}^+ + 2e^- \quad E^\circ = -1.23 \text{ v} \]

**Cathode (Reduction):** \[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \quad E^\circ = 0.0 \text{ v} \]

**Overall reaction:** \[ 2\text{H}_2\text{O} \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \]
4.3 Photo-electrolysis Using Silicon PV Particles

A single junction silicon solar cell produces approximately 0.5 – 0.6 v of potential between its two terminals. Each individual silicon photovoltaic micro-particle is a single junction silicon solar cell; therefore, the voltage generated by each silicon particle is approximately 0.5 – 0.6 v. Generation of hydrogen by electrolysis of water requires decomposition of water and reduction reactions to take place, and the standard potential required for reduction reaction is higher than the 0.5 – 0.6 v generated by the PV particles. Electrolysis of water, which is an insulator in pure form, is not possible with the small voltage generated by the PV particles, and therefore, no hydrogen can be formed using the PV particles. This issue can be resolved by adding some suitable electrolytes to water. Electrolytes are compounds which contain free ions; which are released when these compounds are added to water, thus, improving the conductivity of water, and reducing the required potential for electrolysis. For example, sulfuric acid (H$_2$SO$_4$) when used as an electrolyte in water, releases H$^+$ and SO$_4^{2-}$ ions, and increases the conductivity of water. Aqueous solution of different electrolytes such as sulfuric acid (H$_2$SO$_4$), sodium iodide (NaI), etc. were used to test and demonstrate photo-electrolysis and generate hydrogen with the help of silicon photovoltaic micro-particles.
Each silicon PV particle acts as an individual micro solar cell, with N-type doped side as cathode and P-type side as anode. When these particles are suspended in aqueous solutions containing appropriate electrolytes, and exposed to sunlight; the 0.5 to 0.6 v generated by each of the micro-particle results in reduction reaction to take place at the particle cathodes, i.e. the N-type surfaces, and hydrogen bubbles are formed at that surface as shown in Figure 36. Figure 37 shows the schematic of hydrogen bubbles coming out of the electrolytic aqueous solution containing PV particles, when exposed to sunlight.
4.4 Experimental Verification and Observations

Many different electrolytes were used to prepare electrolytic solutions to test the generation of hydrogen from different sets of micro-particles. Sulfuric acid ($\text{H}_2\text{SO}_4$) and sodium iodide (NaI) were used as electrolytes in most of the solutions prepared for testing the particles. Few other solutions contained vanadium bromide (VBr), isopropyl alcohol (IPA), acetone, hydrofluoric acid (HF), or sodium chloride (NaCl) as electrolytes. Before the actual photo-electrolysis tests with silicon PV particles, electrolysis tests were carried out with sulfuric acid solutions and silicon electrodes. It was observed during the electrolysis tests that a layer of silicon dioxide is formed on the silicon anode. This is due to the fact that silicon itself oxidizes easily as the oxidation
reaction takes place and a silicon dioxide layer is formed as a result. This was one of the major reasons for selecting NaI as an electrolyte. It was expected that formation of iodine, as a result of oxidation, would prevent silicon from being oxidized and provide longer lifetime to the particles in NaI solution. But, this did not prove to be of any help and no increase in the lifetime of particles in solution was noticed. A few other attempts include addition of a few drops of HF in electrolytic solutions, and use of IPA as an electrolytic solution to get increased lifetime of particles; but, they also proved to be unsuccessful.

Electrolytic solutions were prepared with precisely measured quantities of electrolytes and water. In an Erlenmeyer flask, particles were added to the solution, and exposed to sunlight to observe the formation of bubbles of hydrogen. Particles prepared with the first diffusion method, i.e. using a planar dopant source, did not generate any hydrogen bubbles during the tests. Particles prepared with spin-on-diffusant method, produced hydrogen at considerable rate. Particles prepared at 950°C, 1000°C, 1050°C, and 1100°C were tested in different electrolytic solutions. No bubbles were formed from particles prepared at 950°C, although, the particles prepared at higher diffusion temperatures generated hydrogen at a significant rate. Tests with PV particles of different sizes revealed that performance of particles largely depends upon the size of the particles. The different sizes of particles ranged from around 2mm to as small as 100 µm.

It was noticed during the photo-electrolysis tests that the lifetime of the silicon photovoltaic micro-particles is very short in the solution. This is due to the fact that silicon itself oxidizes very easily in water. While the reduction reaction takes place at the N-type doped cathode surface, hydrogen is formed and comes out as bubbles; but, the
oxidation reaction at the anode results in the oxidation of the P-type anode silicon surface, instead of releasing oxygen. As the silicon-dioxide layer grows thicker, the P-type region gets insulated and the photo-electrolytic process slows down eventually, and stops after some time. This results in the short lifetime of photovoltaic particles in aqueous electrolytic solutions. A short BOE/HF treatment of the particles cleans up the oxide layer, and the particles can be reused. As this work is oriented towards the performance of PV particles and demonstration of photo-electrolysis, lifetime of PV particles in solutions is of very little concern.

4.4.1 Tests with particles of size ~1 mm

These were the biggest PV particles tested for hydrogen generation. The approximate size of these particles was between 1 mm and 1.5 mm. The particles were prepared by spin-on-diffusant method at diffusion temperature 1100°C for 2 hours. The particles were first tested in a dilute sulfuric acid solution, and later, in a solution containing sodium iodide and dilute sulfuric acid. The solution was clear and contained no suspended particles, as the particles settled down at the bottom after about 2 minutes of addition to the solution. Bubbles started to form as soon as the solution was exposed to sunlight. The bubbles were held at the bottom of the flask and were not released from the bunches of particles, to the surface; this can be seen in the image in Figure 38 and 39. Only a few bubbles were noticed at the top surface of the flask. The bubbles and bunches were seen forming very quickly for the first half to one hour of sunlight exposure, after which, almost no bubbles formed. After about 3-4 hours, it was noticed that, all the bubbles were released and the bubbling i.e. formation of hydrogen stopped completely.
The following images show the bubbles formed during hydrogen generation test of the 1 mm size particles.

Figure 38 - Bubbles generated by 1mm sized particles
4.4.2 Tests with particles of size ~500 – 700 µm

This set of PV particles contained particles of approximately 500 µm or larger and were prepared by spin-on-diffusant doping method. No noticeable difference in the results obtained from tests of particles prepared at temperatures 1000°C, 1050°C, and 1100°C was observed. Most of the solutions, in which the particles were tested, were prepared by adding a very small amount of sodium iodide (NaI) in a very dilute sulfuric acid aqueous solution. The particles were added to the solution and exposed to strong sunlight. Unlike the bigger particles, after addition of particles to the solution, the particles did not settle down readily, and were suspended in the liquid for some time; giving it a very slightly murky appearance which became clearer as the particles settled at the bottom. A very slow bubble formation was noticed when exposed to incandescent
light, which grew rapid as soon as exposed to sunlight. The particles formed small bunches, but unlike the bigger particles, the bubbles were not strongly attached to the particles, and were easily released. On formation of bubbles, the particles were easily lifted along with the bubbles, and, as they reached the surface of the liquid, the bubbles were released and the particles came back down to the bottom of the container. The following figure shows the images of the bubbles formed by the particles.
Figure 40 - Images of bubbles formed particles of size 500 µm
4.4.3 Tests with particles of size ~200 – 400 µm

The particles in this set were between 200 and 400 µm and were prepared using spin-on-diffusant, at diffusion temperatures 1000°C, 1050°C, and 1100°C. The doping times for different sets of particles varied from 30 minutes to 2 hours 30 minutes. No significant difference was noticed, in the performance of the particles doped for different doping times at 1100°C. Initial tests were carried out in a solution prepared by adding around 10ml of concentrated sulfuric acid into about 500 ml of water. Particles were then added to the solution in a flask and exposed to sunlight. The solution became very dark and murky initially, but later, it became a little clearer as the particles settled down. A slow bubbling was noticed when the solution containing the particles was exposed to incandescent light. The bubbling became very rapid when exposed to strong sunlight. In the first test, it was noticed that as the particles formed the hydrogen bubbles, they were easily lifted to the surface of the liquid, where the particles would leave the bubbles and turn back to the bottom of the flask. It was noted that the particles continued the generation of gas for as long as 3 hours.
The smaller size of the particles means more surface area exposed to sunlight and more surface area available for the red-ox reactions to take place, which is seen as the reason for better performance of smaller particles, as compared to the bigger ones. One more advantage of smaller size of particles, as observed, for such an application is the dark color of the solution, which assures that more sunlight is absorbed by the particles in the solution. Therefore, it can be concluded that the photo-electrolysis test largely depends upon the size of the particles; and smaller particles perform notably better than the bigger ones.
Figure 42 - Images of 200 µm particles generating bubbles.
4.4.4 Tests with particles of size ~100 µm

With particles of size approximately 100 µm, this set appears like very fine silicon powder. All the sets of particles of this size were prepared with spin-on-diffusant technique, at diffusion temperature of 1000°C or 1100°C, and diffusion times ranging from one hour to two-and-a-half hours. The best results were obtained from particles doped at 1100°C for 2 hours or more. A very slight difference in the performance of particles doped at lower temperatures was noticed. Due to the very small size of the particles, the hydrogen bubbles formed were also very small in size, but exceptionally rapid, compared to bigger particles.

Figure 43 - Image of solution, right after the addition of particles.

The first set of particles was tested in a solution prepared by adding 10 ml sulfuric acid and 2 g of sodium iodide in 500 ml water. The particles were tested in both incandescent light and sunlight. Addition of a very small amount of particles turned the
whole solution very dark, almost completely opaque; as seen in Figure 43. It took some
time for the particles to settle down, but, as soon as the solution becomes a little clearer, a
very rapid formation of bubbles is noticed. After about one hour of addition of particles,
the solution becomes much clearer, and very rapid bubbling is seen, even in incandescent
light.

The particles were seen generating bubbles upto as long as 3 hours, which slowed
down afterwards, ceased completely after about 4 hours. The generation of bubbles in a
solution containing ~100 µm particles is shown in the images in Figure 44. Due to the
very small size of the particles and dark color of the solution, the bubbles that are formed
cannot be seen so clearly, but, very tiny bubbles can be noticed attached to the particles in
the following images. Due to limitations of manual crushing, no other set of particles has
been prepared containing particles smaller than the 100 µm ones, and therefore, no
further tests were performed.
Figure 44 - Images of bubbles generated by 100 μm particles
4.5 Detection of Formation of Gas

Plenty of simple techniques are available to detect or collect the gas being generated during a chemical reaction. One such method for collection of gas is by displacement of water [52]. As seen in Figure 45; hydrogen gas generated by the chemical reaction of zinc and hydrochloric acid (HCl) comes out of the tube immersed in water, in the form of bubbles. An inverted tube, completely filled with water, is placed above the opening of the tube, and as the gas comes out, it gets collected inside the tube while water in the tube displaces and flows down into the container.

![Image: Water displacement method for collection of hydrogen](image)

Figure 45 - Water displacement method for collection of hydrogen [52]

Although this setup can be easily implemented, no attempt has been made to collect the hydrogen generated by PV particles, as we are not concerned with the collection of gas; we are rather interested in detecting that a gas i.e. hydrogen is actually being produced by the photo-electrolysis of water. Tests were performed in a dilute
sulfuric acid solution containing particles of size approximately 100 µm. The setup is shown in the image in Figure 46. As the gas is released by the particles, it displaces the air inside the flask. Hydrogen, being lighter than air, is lifted up and comes out of the tube due to the air pressure developed inside the flask. The other end of the tube is immersed in water to see the gas coming out in the form of big bubbles. Figure 47 shows an image of a bubble of gas generated in the flask, coming out of the tube, when the flask containing the particles in a sulfuric acid solution is exposed to strong sunlight.

Figure 46 - Setup for detection of gas
Formation of oxygen would require a much higher potential than the 0.5–0.6v generated by the PV particles; therefore, the gas coming out of the flask has to be hydrogen, and no verification test is required.

4.6 Measures Taken for the Test

Certain measures were taken to avoid any errors while the tests for the generation of hydrogen were carried out, which are as follows:

- De-ionized (DI) or distilled water was used in all the tests
- Normal water contains mixed gases, which can be seen in the form of bubbles formed on the sides of a container when water is kept for a while. To remove these mixed gases, water was heated (not boiled) at 70-80°C for 15-20 minutes and then allowed to cool down to room temperature. No vague bubbles were seen after this.
- All the containers, flask, etc. were cleaned thoroughly before use, to make sure no contaminants are present, which could lead to false results.
o All the solutions were first exposed to sunlight without any suspended particles to make sure no reaction is triggered in the solution itself due to sunlight. It was observed that the color of solution containing NaI changes due to sunlight exposure, but, this does not affect the tests of PV particles.

o Solutions were also tested with undoped (not PV) silicon particles, for the assurance that no reaction takes place between silicon and the solution, resulting in formation of bubbles.

o Electrolysis tests were performed with all the electrolytic solutions and silicon electrodes, before testing the PV particles.

o Electrolytes were selected on the basis of their standard electrode potentials.

o PV particles were cleaned with BOE every time before the tests.

o Fresh solutions were prepared before the tests and no solution was reused for any test.

4.7 Conclusion

Photo-electrolysis of water with the help of silicon photovoltaic micro-particles has been demonstrated. Different electrolytes were tested to get the suitable ones for generation of hydrogen by photo-electrolysis. After testing the different sets of particles in different solutions, it is concluded that smaller sized particles produce the best results. One of the major drawbacks of this system is that the particles generate hydrogen bubbles for just about 2-3 hours; after which due to the formation of oxide layer on the particles’ surfaces, bubbling slows down and finally stops. But, a short BOE or HF treatment makes the PV particles reusable.
Chapter 5 – Future Works

5.1 Introduction

The fabrication of silicon photovoltaic particles and different tests demonstrated in this work are just the first step in the growth of semiconductor photovoltaic particles technology. Future applications envisioned for photovoltaic particles include thin solar cells, solar spray-paint, and photo-electrochemical hydrogen generation system. Self-assembly techniques that involve use of gravitational force, electric field, or magnetic field, can be utilized to align the photovoltaic micro-particles, and make thin solar cells or solar spray-paint. Another application is the photo-electrochemical fuel generation system, which makes use of the micro-particles for photo-electrolysis to generate hydrogen for a fuel cell, as demonstrated in Chapter 4. Some enhancement or variations that can be implemented incorporate the use of high efficiency materials such as GaAs or SiC, or the reduction in the size of the particles up to the submicron level.

5.2 Alternative Semiconductor Materials

The main concern of this work is the development and demonstration of an optimum fabrication process to make photovoltaic micro-particles, therefore, only silicon has been taken into account. Materials such as gallium arsenide (GaAs) and silicon carbide (SiC) have long been considered as options for making very high efficiency single junction solar cells [53] [54]. Although, gallium arsenide is very expensive compared to silicon, it can be utilized to make highly efficient photovoltaic micro-
particles. The band gap of gallium arsenide is 1.43 eV while that of silicon carbide is 3.0 eV, which makes them remarkably suitable for manufacturing highly efficient photovoltaic micro-particles [53] [54].

5.3 Submicron Sized Particles

The particles of size as small as approximately 100µm have been fabricated and tested. Different tests performed on particles of different sizes from ~1mm to ~100µm reveals that the small size of particles is advantageous in several ways. Particles of size as small as a few hundreds of nanometers can be fabricated using sophisticated techniques. Smaller particles provide much better surface area which assures higher efficiency. It has already been verified that smaller particles perform much better when used for hydrogen gas formation by photo-electrolysis of water. Apart from that smaller sized particles are well suited for other proposed applications such as self-assembles particles based solar cells and spray-paint.

5.4 Micro-particles Based Photo-Electrochemical Fuel Generation System

The previously mentioned photo-electrolysis tests consisted of solutions prepared by simple electrolytes such as sulfuric acid and sodium iodide. Along with this, the shorter life of particles in electrolytic aqueous solutions, due to oxidation of silicon in water, poses limitations to the use of this technique. A system has been proposed which can be used to generate and collect hydrogen, not just for a couple of hours, but for a much longer time. This is a closed cycle fuel generation system that would generate hydrogen for fuel cell, which upon utilization of this hydrogen would restore the
electrolytic solution by a reverse reaction, and feed it back to be utilized by the PV particles.

For such a system the red-ox couple is selected in such a way that photo-electrolysis would result in the reduction reaction to take place, but not the oxidation reaction; which would result in the formation of hydrogen gas and an oxidant. The oxidant formed by the reduction reaction should be easily separable from the generated hydrogen in the form of either a gas or an insoluble liquid. The generated hydrogen and

![Figure 48 - A closed loop system based on hydrogen generation by the photo-electrolysis of a solution containing PV micro-particles.](image)

the oxidant formed by this chemical reaction would be then stored separately, and supplied to the fuel cell connected to them. As the fuel cell utilizes the generated hydrogen and the oxidant, they would be reduced back to their initial state by a reverse chemical reaction. This restored electrolytic solution would be supplied back to the
photo-electrolysis chamber for generation of hydrogen and the oxidant, thus, forming a closed cycle.

The short life of micro-particles in electrolytic solutions, just about 2 hours, serves as a major hindrance in the development of such a system. This problem can be solved if the electrolytes chosen are such that they oxidize on the P-type surface, more easily than silicon itself, thus, giving a prolonged life to the silicon photovoltaic particles. A possible key to this issue can be the use of organic molecules instead of simple electrolytes; which could serve both the purposes, i.e. provide protons for reduction, and avoid silicon micro-particles from getting oxidized.

One such organic red-ox couple is the hydroquinone / benzoquinone. Hydroquinone being inexpensive, is easily available, and does not add to the cost of the photo-electrochemical system to be developed. To prepare the derivatives, simple relevant chemistry is required; and the red-ox potentials of most of them are known, which adds up to the advantages of this organic red-ox couple. Many other similar options can be utilized and tested to come up with the most optimum way of making such a continuous, long-term, large scale system that could use the silicon PV particles to generate hydrogen to be used by a fuel cell.
Figure 49 - Reduction and oxidation of hydroquinone / benzoquinone red-ox couple on the particle surfaces.

5.5 Self-Assembly of Micro-Particles

Assuming each micro-particle to be an individual source, then, in order to extract substantial amount of energy from these sources, they need to be properly aligned; i.e. the positive (P-type) side of all the individual particles should be in one direction while the negative (N-type) side in opposite direction. This means that all the PN junctions will be arranged parallel and in the same direction, thus, said to be as aligned or assembled. Numerous self-alignment techniques can be exploited for the utilization of photovoltaic particles for applications such as self-assembled micro-particle based thin solar cells, and solar spray-paint.

5.5.1 Gravitational self-assembly

If the PN junction micro-particles are selectively coated with a conductive material of density significantly different than that of silicon; e.g. either of the P or N sides of the particles is covered with a metal layer, transparent conductive oxide or polymer layer, which causes a mass density imbalance in each individual particle. When these particles are allowed to fall freely on a base substrate, due to the difference in
densities of the two materials, i.e. silicon and the other coated material, the particles will automatically get aligned due to the effect of gravity, and will fall on the substrate with the P-sides of all the particles in one direction and N sides in opposite, as shown in the following figure.

One way of implementing gravitational self-assembly could be with the help of selective copper-deposition on PV particles. It has already been demonstrated that copper can be partially deposited on the PV particles. Copper has a density of 8900 kg/m$^3$, which is much more than silicon’s 2330 kg/m$^3$ density. Selective deposition of copper on the P-type particles with N-type doped regions results in the P-type sides being coated while the N-type sides remain almost uncoated. This creates the density difference required for the self-alignment of particles. Therefore, when particles, partially coated with copper, are made to fall freely, they land on the side covered with copper, due to the density difference, which results in the alignment of particles.

5.5.2 Self-assembly in electrostatic field

It is known that diodes or dipoles align themselves, when an electric field is applied externally, in the direction of that electric field [55]. If suspended in an inert
liquid or in some other medium, and a strong electrostatic field is applied externally, the photovoltaic micro-particles will align themselves in the direction of the applied field, and thus, will be self-assembled.

![Figure 51 - PV particles self-assembly in external electrostatic field](image)

### 5.5.3 Magnetic self-assembly

A thin layer of iron or nickel can be partially deposited on either P-type or N-type side of the particles; in a similar manner as selective copper deposition on PV particles. Then, on application of a magnetic field with the help of a permanent magnet or electric magnet, the PV particles will be self-assembled.

### 5.6 Self-Assembled Micro-Particles Solar Cells

The aforementioned self-assembly techniques can be utilized to make thin solar cells. Using different self-assembly techniques, layers of self-assembled photovoltaic micro-particles can be deposited between transparent conductive glass substrates to make a thin solar cell.
To employ gravitational self-assembly technique, first, the particles can be partially deposited with a metal, such as copper. Then, the particles should be made to fall freely on a substrate. A conductive glass substrate can be used, and covered with a thin layer of transparent and flexible adhesive, to hold the self-aligned particles in place. The freely falling PV micro-particles would align themselves due to the density difference of silicon and the deposited metal, and the glue would hold them in place without disturbing the alignment, as they fall on the surface of the substrate. Then, this layer can be covered with another conductive transparent glass substrate on top, to make a thin solar cell. Refer to Figure 52.

Figure 52 - Solar cell manufacturing by gravitational self-assembly of micro particles
Another self-assembly technique that can be implemented to make a thin photovoltaic micro-particle based solar cell is electrostatic self-alignment. For this, the particles can be suspended freely in an inert fluid. Then, a strong electric field can be applied using transparent electrodes. As the particles align in the direction of the applied electric field, the electrodes can be brought close together, and packed to make a solar cell. In this case also, an extremely thin layer of transparent glue should be used to hold the aligned particles together without misaligning them. This technique is shown in the Figure 53.

Figure 53 - Solar cell manufacturing by self-assembly of micro particles in electrostatic field
Magnetic self-assembly and several other self-alignment techniques can be explored and implemented to make thin and flexible solar cells, which can prove to be an efficient and a low cost alternative to the existing conventional solar cells.

5.7 Self-assembled Micro-particles Spray-Paint

Self-assembly of micro-particles can be utilized to make a paint-like spray that contains millions of such particles in an adhesive solution. When made to fall freely on a horizontal surface, due to self-assembly, e.g. gravitational self-assembly, the particles will get aligned as they fall. These self-assembled particles will then stick on the horizontal surface due to the adhesive in the paint. This method can be utilized to make on-the-spot solar cells that can be formed or embedded on the surfaces of different structures.

5.8 Conclusion

Different future applications, such as photo-electrochemical hydrogen generation system and thin micro-particle based solar cells, have been proposed. Different techniques are also proposed in this chapter, which can be researched or utilized in the future for the development of these applications. Implementation of these techniques still requires extensive research, but, once developed, this technology can prove to be a major alternative to the common solar technologies.
Chapter 6 – Conclusion

We proposed that silicon photovoltaic particles (or powder) can be manufactured by employing simple fabrication techniques. The three step fabrication process includes, crushing of silicon into small particles, doping of these particles, and further crushing to expose the PN-junctions on the particles. After the theoretical development of this fabrication process, it was practically implemented to fabricate silicon photovoltaic micro-particles. Different diffusion techniques were considered and implemented to get the optimum process for fabrication of silicon PV particles. Different tests were carried out to test the particles obtained after fabrication.

Two different diffusion techniques implemented were; first, by use of a solid planar dopant source, and second, by applying liquid spin-on-diffusant on the particles. Particles were first fabricated using the solid planar dopant source. After the fabrication of particles, many shortcomings were observed in this thermal diffusion method. One of the major disadvantages of this process was that very small amount of particles could be doped at one time, and the particles fabricated with this technique did not produce any good results upon testing. The second technique, i.e. spin-on-diffusant method, proved to be a simple one, and the particles fabricated by this technique produced good results upon selective copper deposition and photo-electrolysis tests. Particles of different sizes ranging from a few millimeters to about 100 microns were prepared with this technique.
The first test performed on the silicon PV particles was the selective copper deposition test. It was observed that copper can be deposited selectively on P-type side of the PN-junction silicon, and the P and N sides of the junction can be distinguished. Selective deposition of copper on silicon PV particles revealed the P-type surfaces and the N-type doped surfaces of the particles.

Photo-electrolysis of electrolytic aqueous solutions with the use of photovoltaic micro-particles has been demonstrated. Particles were tested in different aqueous solutions containing electrolytes such as concentrated sulfuric acid, and sodium iodide. The results reveal that particles doped at temperatures above 1000°C produce very good results. It was observed that the generation of bubbles greatly depended on the size of the particles. Smaller particles generated bubbles more rapidly compared to bigger ones.

After successful fabrication of silicon PV particles, some improvements and future applications were proposed. Some of the applications include fabrication of self-assembled micro-particle based thin solar cells, and micro-particle based photo-electrochemical system. Further work and thorough research in the improvement of PV micro-particles, might result in the development of a promising technology, capable of challenging other solar technologies.
Bibliography


[34] **Ruby, D. S., et al.** *RIE-Texturing of Multicrystalline Silicon Solar Cells.*


[44] **Spin-on-diffusants - Product informations.** s.l. : Filmtronics Inc.


[47] **X-ray Absorption spectroscopy on copper trace impurities on silicon wafers.**


