Chapter 1
Silicon Based Photovoltaic Materials

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Abstract

Solar energy is an idea renewable energy resource due to its abundance and inexhaustibility. Solar cells, which convert sunlight into electricity, are the most direct devices to use solar energy. Silicon is the most widely used material for solar cells due to its abundance in nature, stability, non-toxicity and well established refining and processing technologies. This chapter, which is divided into five sections, presents a brief review on the research progress of silicon as photovoltaic materials. After a short introduction in section 1, section 2 summarizes the history and current situation of the traditional wafer-based crystalline silicon solar cells. Section 3 draws attention to the development of thin-film silicon solar cells which have the significant advantage in cost reduction. The recently active and compelling nano-structured silicon technologies are reviewed in section 4. Finally, a conclusion and perspective is presented as section 5.

1.1 Introduction

Energy is the lifeblood of modern era. Fossil fuels (coal and oil) are the most important ingredients in producing energy for our lives. But unfortunately, we are facing a global energy crisis with natural reserves of fossil fuels being depleted fast due to over consumption. A possible solution of the global energy crisis is to exploit renewable instead of non-renewable sources of energy. Solar energy is an ideal renewable energy resource due to its abundance and inexhaustibility. By using values for the solar constant and Earth's albedo, it has been found that our Earth receives 1.56×10^{18} kW·h of solar energy per year, which is ~10 000 times

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larger than that of current worldwide energy consumption[1]. This means that the Earth receives more solar energy in an hour than the total energy it consumes in an entire year.

We've used the solar energy for drying clothes and food for thousands of years, but only recently have we been able to use it for generating power. Solar cells convert sunlight directly into electricity. When sunlight is absorbed by the semi-conducting materials of the solar cells, the electrons absorb the photons and become liberated from their atoms and flow through the material to produce electricity. This process of converting light (photons) to electricity (voltage) is called the photovoltaic (PV) effect (Figure 1.1).

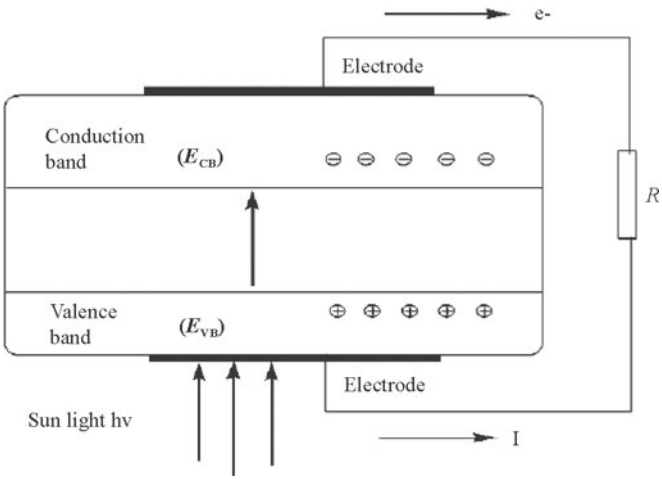

Figure 1.1 The photovoltaic process in a solar cell

Over 95% of all the solar cells produced so far are composed of Silicon. There are several reasons for this. First of all, silicon is a nontoxic element and can be available in sufficient quantity due to its abundance in earth's crust. Secondly, silicon is an ideal semiconductor with good stability and a well-balanced set of electronic, physical and chemical properties. Another reason why silicon cells have been so dominant is that the success of silicon in microelectronics can ensure the supply of high quality silicon wafers for the presently smaller photovoltaic industry.

Most silicon cells have been fabricated using thin wafers cut from large cylindrical ingots. The wafer-based crystalline silicon (c-Si) solar cells yield stable solar cells with good module efficiencies (over 16%) and can be fabricated conveniently by using processing technologies developed for microelectronics industries. However, the wafers have to be sufficiently thick (several hundred

microns) due to the poor optical absorption of crystalline silicon, resulting in the huge consumption of silicon materials. On the other hand, the sawing of ingots into wafers produces significant silicon wastes. To reduce the amount of silicon material required in creating a solar cell, thin-film technology has been developed. In spite of its low photo-conversion efficiency and light induce instability (Staebler–Wronski effect), thin film solar cells have become more and more popular due to the lower costs and other advantages including flexibility, lighter weights, and ease of integration. Recently, nano-structured silicon, with unique electrical and optical properties, has emerged as a new form of silicon for constructing new architecture of solar cells. If the technical challenges including proper surface passivation, shunting, and fabrication of high quality contacts can be solved, nano-structured silicon would be a promising candidate toward low-cost, high-efficiency solar cells.

This chapter intends to provide a concise overview of the development of silicon based photovoltaic materials. Excellent in-depth discussions about historical and ongoing perspective of silicon based photovoltaic materials can be found in the reviews and books list in the reference[2~10].

1.2 Wafer-based crystalline silicon

As the name implies, wafer-based silicon solar cells are fabricated from slices of silicon derived from ingots. Wafer-based crystalline silicon has dominated the photovoltaic materials since the birth of solar PV technology, due to its mature technology and stable photo-conversion efficiency. Despite the numerous attempts at making better solar cells by using new and exotic materials, the reality is that most solar cell manufacturers are currently only equipped to produce wafer-based solar cells. Consequently, a large body of research is being done all over the world aiming to manufacture silicon wafer-based solar cells at lower cost and to increase the conversion efficiencies without an exorbitant increase in production cost.

1.2.1 Mono-crystalline silicon

In mono-crystal silicon, the arrangement of atoms in the material is uniform, and the crystal lattice of the entire sample is continuous and unbroken with no grain boundaries. This uniformity is ideal for transferring electrons efficiently through the material.

The mono-crystalline silicon wafers are generally made from scrap material of microelectronic industry through Czochralski process, Float-zone process or Bridgman techniques[2].The scrap silicon materials are produced in the following way: First, a lower grade of silicon known as “metallurgical grade” is produced by

the reduction of quartzite by carbon. This metallurgical grade silicon is of about 98% purity and is produced in large quantities. The metallurgical grade silicon is then converted to trichlorosilane, which is then purified to 99.9999999% (nine "nines") purity by fractional distillation. The purified trichlorosilane are finally decomposed into silicon in a highly purified form. In this process, electrically heated silicon rods are exposed to a trichlorosilane/hydrogen mixture which reacts on the surface of the rods, depositing silicon onto them. These rods grow with a fine-grain polycrystalline silicon microstructure. After the rod diameter has increased to the required size, the process is stopped and the rods mechanically broken into smaller chunks, which maintain "nine-nines" purity. These chunks then become the starting point for the growth of ingots. In the Czochralski process for growing crystalline ingots, the purified silicon chunks are melted in a quartz crucible. A precisely oriented seed crystal, mounted on a rod, is dipped into the molten silicon. The seed crystal's rod is very slowly pulled upwards and rotated at the same time. By precisely controlling the temperature gradients, rate of pulling and speed of rotation, it is possible to extract a large, single-crystal, cylindrical ingot from the melt. Typically ingots are grown to about 10~15 cm in diameter and 1~2 m in length, weighing 50~100 kg (Figure 1.2(a)). The crystallographic orientation of the seed is transferred to the grown crystal. Generally, for photovoltaic use, the crystal is grown with a preferred orientation so that the wafers which are sliced from the crystal perpendicular to the growth axis have surfaces parallel to {100} crystallographic planes.

Prior to slicing these ingots into wafers, the ingots are generally grinded along the length of the ingot to remove the slight fluctuations in diameter that occur during crystal growth. The ingots are then "squared-off" by sawing off large sections parallel to the growth axis, giving "quasi-square" shape (Figure 1.2(b)). The large pieces of silicon sawn off in this approach are then generally recycled by re-melting as feedstock for the Czochralski growth. The "quasi-square" silicon ingot is then sliced into very thin wafers (Figure 1.2(c)). This is usually done with a diamond saw. This process produces considerable wastage of silicon known as "kerf" loss[2].

Fabrication of solar cells using silicon wafers starts by chemically cleaning and etching their surfaces, generally in a sodium hydroxide etchant, to remove saw damage from the wafers. Crystallographic texturing is then performed using a more dilute solution of sodium hydroxide. The composition and temperature of this solution determines the texturing quality, including the size of the pyramidal features resulting from the texturing and the percentage of wafer surface area successfully covered by such features.

The next major stage of processing is the diffusion of the cell junction. This is generally achieved by spraying or spinning a compound containing phosphorus onto the cell surface, followed by heating at high temperature to allow phosphorus dopant atoms to seep into the cell surface by thermal diffusion. Typically, the depth of diffusion is less than 1 μm. The same thermal diffusion process is widely used in microelectronics but processing for photovoltaics generally involves cruder equipment and techniques, since the aim is to produce cells at the lowest possible cost without unduly sacrificing cell performance.

The screen printing of metal contacts onto the front and rear surfaces is an another step of cell processing. Silver paste consisting of a suspension of fine particles of silver and glass frit in an organic medium together with appropriate binders is squeezed through a patterned screening mesh onto the cell surface. After application, the paste is dried at low temperature and then fired at a higher temperature to drive off the remaining organics and to allow the silver regions to coalesce. The glass frit is important in promoting adhesion to the silicon substrate. Often pastes are doped with phosphorus to help prevent the screened contact from penetrating the thin phosphorus skin that it is intended to contact. The paste for the top surface is printed in a characteristic finger pattern to minimize the resistive losses in the cell while allowing as much light as possible into it. Sometimes the rear contact is also patterned, not to allow light into the cell, but merely to reduce the amount of paste required and hence reduce the cost of this processing step.

A quarter wave antireflection coating can be applied to the cell at this stage. Generally, titanium dioxide is used as the antireflection coating material due to the simplicity of depositing and its almost ideal refractive index for this application. Some manufacturers deposit the antireflection coating before the metal paste-firing step and fire the paste through this coating.

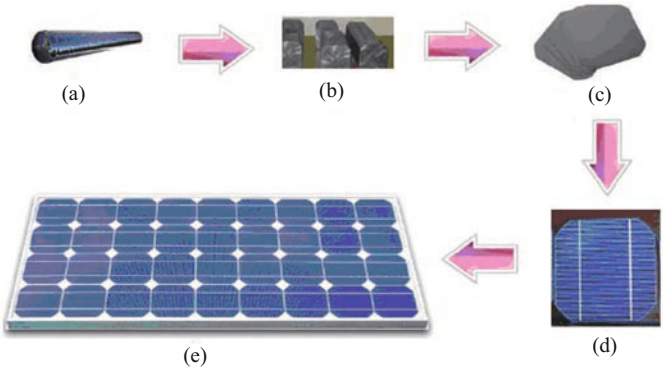

Figure 1.2 The process for fabricating mono-crystalline silicon photovoltaic modules

The as processed solar cells (Figure 1.2(d)) are then packaged and interconnected to form a solar panel (module) (Figure 1.2(e)). The solar panel is used as a component in a larger photovoltaic system to offer electricity for commercial and residential applications. The performance of solar panel is generally determined by that of the worst cell in the module, resulting in large power losses within mismatched modules. Even worse, low output cells can become reverse-biased under some modes of module operation and destroy the module by localized over-heating. Therefore, cells are usually graded based on their short-circuit currents or currents at a nominal operating voltage, e.g., 450 mV, before assembling into modules. Generally, cells are sorted into 5% performance bins. The sorting is important to reduce the amount of mismatch within the completed module.

Commercial single-crystal silicon solar cell with photo-conversion efficiency above 16% has been generally reached in photovoltaic industry. However, this efficiency is still much lower than the theoretical limiting efficiency of 29%[10], indicating there are enormous potential for further efficiency improvement in commercial devices. Part of this potential has been recently realized with the commercialization of solar cells with new structures or processing technology in some world leading company such as Sunpower, Sanyo, BP Solar, Suniva, Suntech Power, Trina Solar, Yingli Solar, JA Solar. In the laboratory in The University of New South Wales, the single crystalline silicon solar cells are approaching the theoretical limiting efficiency (Figure 1.3). If these new technologies can be commercialized in industry without inducing too much additional costs, energy payback period will be significantly shorted.

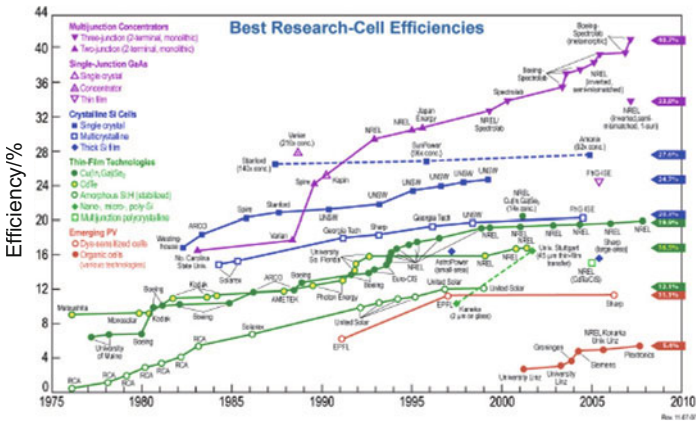

Figure 1.3 The best research-cell efficiencies all over the world
(Source:http://www.nrel.gov/pv/thin_film/docs/kaz_best_research_cells.ppt)

1.2.2 Multi-crystalline silicon

Multi-crystalline silicon, in contrast, consists of numerous smaller crystals or grains, which introduce boundaries. These boundaries impede the flow of electrons and encourage them to recombine with holes to reduce the power output of the solar cell. Therefore, solar cells based on multi-crystalline silicon are generally less efficient. However, multi-crystalline silicon is much less expensive to produce than single-crystalline silicon.

Multi-crystalline silicon is produced using silicon feedstock (Figure 1.4(a)) through casting technology[2] .This technique involves controllably solidifying molten silicon in a suitable container to give silicon ingots with large columnar grains generally growing from the bottom of the crucible upwards. Techniques may differ between different manufacturers in the choice of crucible material, the method of loading silicon into the crucible and the method for controlling the cooling of the melt. Typically, the feedstock made by purification of silicon or by alternative refining methods is charged in a silicon nitride coated quartz crucible and heated until all the silicon is melted. Heat is then extracted from the bottom of the crucible by moving the heat zone up and/or cooling the bottom of the crucible. Therefore, a temperature gradient is created in the melt and the solidification will start at the bottom. Crystals will grow upwards, and grain boundaries will grow parallel to the solidification direction (Figure 1.4(b)). To obtain a directional solidification the heat must be transported through the steadily growing layer of solid silicon. It is necessary to maintain a net heat flux over the solid-liquid interface, and the temperature at the lower part of the crucible must be decreased according to the increase in solid silicon thickness to maintain a steady growth rate. The growth rate is proportional to the temperature gradient difference between the solid and the liquid silicon.

The large ingots are sawn into smaller sections as shown in Figure 1.4(c), eventually to give wafers generally 10~15 cm along the sides (Figure 1.4(d)). These smaller sections can be sawn by the standard inner-diameter or continuous wire sawing processes.

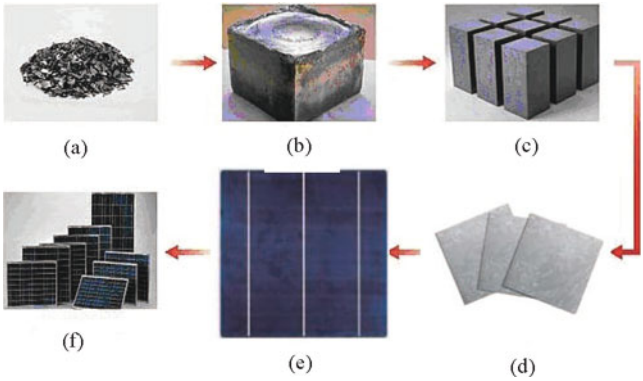

Figure 1.4 (a) Directional solidification of silicon within a mould. (b) sawing of large ingot into smaller sub-sections.

The processing of multi-crystalline silicon wafer is very similar to that of mono-crystalline silicon wafer. The main difference lies in the texturing of wafer surface. Texturing of mono-crystalline silicon is usually done by etching in alkaline solutions. However, these methods are inefficient for multi-crystalline silicon due to the presence of random crystallographic grain orientations and high selectivity of etching along specific directions. There are three different kinds of texturization techniques for multi-crystalline silicon solar cells: ① acid texturization[11,12], ② reactive ion etching[13], and ③ mechanical texturization[14,15] .Each of them has some advantages and drawbacks. The application of etches based on HF-HNO_3 induces irreproducible results due to random distribution of grains of different crystallographic orientation on the surface of multi-crytalline silicon and necessity of precise control of temperature as well as composition of etches. Reactive ion etching creates a needle-like surface, on which screen printing is difficult. Mechanical texturing may be effective, but has some limitations related to textured material. It cannot be applied specially for thin, wraped, and fragile materials.

The resulting multi-crystalline silicon cells are capable of producing cells of about 80% of the performance of a mono-crystalline cell fabricated on a Czochralski wafer. However, because of the higher packing density due to their square or rectangular geometry, this performance difference is largely masked at the module level with multi-crystalline module performance lying in the range demonstrated by modules made from mono-crystalline cells. Therefore, the market share of multi-crystalline silicon (mc-Si) has increased remarkably in recent years due to the reduction of production costs.

1.2.3 Sheet and ribbon silicon

As above mentioned, the silicon ingots have to be sawed into wafers before cell fabrication. This process creates large amounts of micron-sized silicon powder “kerf” which is currently discarded as waste. These “kerf” losses together with contaminated parts near the edges of the ingot that cannot be used for cell processing add up to more than 30% of the silicon starting material. With the rapid increase of silicon based photovoltaic market, the shortage of silicon feedstock will become the bottleneck in restricting the expansion of photovoltaic industry. Therefore, it is important to investigate an alternative way to slicing wafers out of a crystallized ingot while maintaining the well proven processing techniques developed for mc-Si solar cells. In principle, ribbon technology is the most promising one where liquid silicon is directly crystallized in the form of a silicon wafer without the need for sawing. However, the wafer produce from ribbon technology have to reach sufficient material quality and solar cell efficiency to reduce the electricity cost. It was only recently that some of the ribbon technologies, such as in the cases of the edge-defined film-fed growth (EFG) and the string ribbon (SR) technologies, reached maturity and manufactured on megawatt scale[2] .Other technologies such as the silicon film, dendritic web, ribbon growth on substrate (RGS) and rotational solidification techniques are under development at pilot demonstration phases[16].

The typical EFG process involves the pulling of a thin sheet of silicon ribbon from a strip of molten silicon formed by capillary action at the top of a graphite dye (Figure 1.5). The molted silicon is contained in a graphite crucible. Extensive temperature control by radiation shields, cold shoes, and after-heating realizes a maximum temperature gradient where plastic flow is possible, in order to allow for a maximum growth rate. Individual wafers are then cut from the sides of the silicon ribbon, normally by laser scribing wafers from each of the sides[17] .

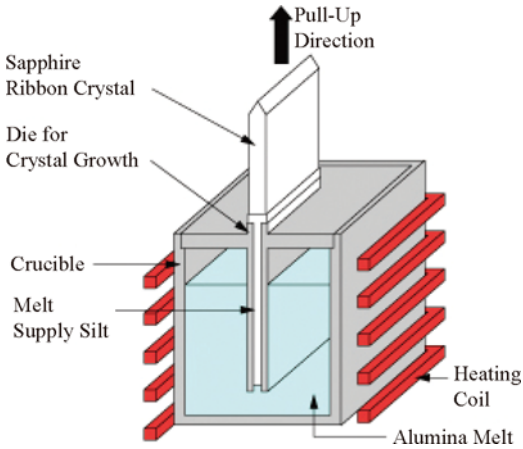

Figure 1.5 A schematic drawing of the EFG process
(Source:http://americas.kyocera.com/kicc/industrial/crystal.html)

The material produced is multi-crystalline with elongated grains and of a similar quality to the standard directionally solidified multi-crystalline material. The solid silicon ribbon is (super)saturated with carbon due to the contact with graphite-containing materials near the liquid–solid interface. Oxygen and transition metals are also presented, although mostly in concentrations not limiting material quality.

Before fabrication of ribbon silicon based solar cells using regular processing techniques adopted for wafers, additional steps of gettering and hydrogenation are implemented to improve the material quality. It was shown that defect structures presented in the as-grown ribbon material can be substantially reduced by gettering and hydrogenation. This is in contrast to the case for mono-crystalline material, where the main task of post-processing is to maintain the high as-grown material quality.

Somewhat related to the above ribbon approaches are other sheet approaches which produce silicon films on substrates from which they are subsequently detached. The most developed version of this technology is the via hole etching for separation of thin film (VEST) technology developed by Mitsubishi[2] .The VEST process is based on the silicon on insulator (SOI) technology. SOI structure is obtained using zone-melting recrystallization (ZMR) method. Large grain polycrystalline silicon thin films on the supporting substrate covered with the silicon dioxide layer can be obtained by ZMR. Via-holes are formed in the silicon film and the silicon dioxide layer is etched away by introducing the hydrofluoric

acid through the via-holes. Thus the silicon film is separated from the supporting substrate, which is reused to form the silicon dioxide layer and the silicon film. If this detached layer is too thin to be self-supporting, it could be transferred to structurally strong components such as the glass layer in a structural superstrate design.

As no kerf losses occur in ribbon and sheet technologies, and almost 100% of the silicon feedstock ends up in the wafer material, a dramatic decrease in wafer costs is available. Apart from the better silicon usage, energy costs are reduced as well, as time and energy-consuming ingot growth is eliminated. Therefore, a significantly reduced energy payback time (i.e., the time required for the photovoltaic solar module to 'pay back') for the PV module can be expected. However, the cells made from ribbon silicon are generally less efficient than mono-crystalline silicon. Promising efficiencies over 16% have been obtained from this approach for substrates that are only 60~70 μm in thickness, but are still self-supporting. On the other hand, the advantages of ribbon and sheet silicon based wafer technologies in consuming less silicon has been surpassed by the more economic thin film technology. Ribbon silicon solar cells have to improve their efficiency and stability in the future to maintain their cost-effectiveness.

1.3 Thin-film silicon

Thin-film silicon solar cells require a far lower amount of silicon material than the 'classical' wafer based crystalline silicon solar cells, indicating that they have, on a medium-term time scale, a more pronounced cost reduction potential. Furthermore, the energy payback time, which may be a decisive item in the long run, is at least a factor of two lower in the case of thin-film silicon solar cells than for wafer-based crystalline silicon solar cells. Therefore, thin film solar cell industry in recent years been rapidly developed.

There are two forms of thin-film silicon materials that can be used for constituting such a solar cell: hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (mc-Si:H).

1.3.1 Hydrogenated amorphous silicon (a-Si:H)

Amorphous solids, like common glass, are materials whose atoms are not arranged in any particular order. They don't form crystalline structures at all, and they contain large numbers of structural and bonding defects, such as dangling bonds (Figure 1.6). Dangling bonds provide places for electrons to recombine with holes, but they may be neutralized somewhat with hydrogen.

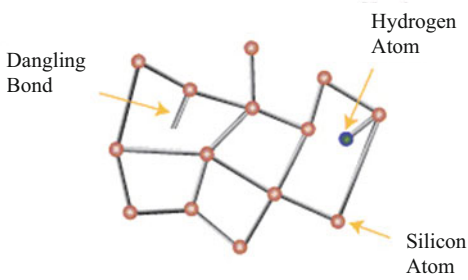

Figure 1.6 Structure model of amorphous silicon
(Source:http://www.eere.energy.gov/basics/renewable_energy/types_silicon.html)

Amorphous silicon (a-Si:H) layers were first deposited by Chittick[18] .He was experimenting with silane (SiH_4) plasmas and accidentally obtained a-Si:H layers in a remote part of his plasma reactor. Chittick's results were taken up by Spear and co-workers at Dundee University[19], who published the first systematic study on plasma-enhanced chemical vapour deposition (PECVD) with silane plus (optional) doping gases. Their results show that doping of a significant percentage of hydrogen atoms bonded into the amorphous silicon structure is essential to the improvement of the electronic properties of the plasma-deposited material[20]. As a consequence, the improved form of amorphous silicon has generally been known as hydrogenated amorphous silicon (or, more briefly, a-Si:H). In recent years, many researchers have used the term amorphous silicon to refer to the hydrogenated form, which acknowledges that the unhydrogenated forms of amorphous silicon are only infrequently studied today.

The bandgap of amorphous silicon depends on the species and concentration of doping atoms and can range from 1.4 to 1.8 eV, which is considerably larger than that for c-Si (1.1 eV). One may concluded that a-Si:H would absorb less photos than c-Si by comparing their bandgaps. However, the real situation is: the "selection rules" in "indirect bandgap" semiconductors that greatly reduce optical absorption in c-Si do not apply to a-Si. The structural disorder present in a-Si 'relaxes' the quantum mechanical selection rules. Amorphous silicon absorbs solar radiation 40 times more efficiently than singce-crystal silicon does, so a film only about 1 micrometer—or one-millionth of a meter—thick can absorb 90% of the usable light energy shining on it. This is one of the chief reasons that amorphous silicon could reduce the cost of photovoltaics since less silicon are needed.

After the first report of amorphous silicon solar cells in 1976 by Carlson and Wronski[21], extensive efforts have been devoted to a-Si:H based photovoltaic

technologies. For doped a-Si:H, it turns out that minority photocarriers (holes in n-type a-Si:H, electrons in p-type a-Si:H) do not move very far (around 0-1 μm, while over 200 μm in crystalline silicon), and so a p-n structure would only collect photocarriers from photons generated in an extremely thin layer of doped a-Si:H. Because of this reason p-i-n diodes are always used for a-Si:H solar cells. The fundamental photodiode inside an amorphous silicon–based solar cell has three layers deposited in either the p-i-n (Figure 1.7) or the n-i-p sequence. The three layers are a very thin (typically 20 nm) p-type layer, a much thicker (typically a few hundred nanometer) undoped intrinsic (i) layer, and a very thin n-type layer. In such a p-i-n cell the main part of light absorption and photogeneration of carriers will take place in the intrinsic (i) part of the solar cell.

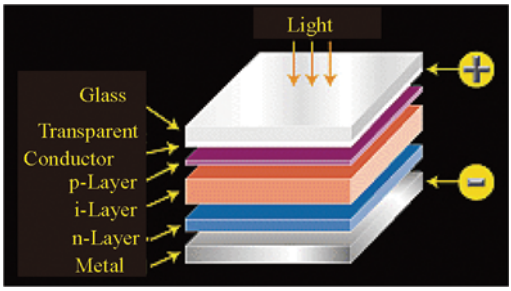

Figure 1.7 The typical amorphous silicon cell employs a p-i-n structure
(Sources:http://www.usc.edu/dept/architecture/mbs/tools/thermal/controls_activesolar.html)

In the following years after their introduction[22], p-i-n-type amorphous silicon solar cells made rapid progress in reaching higher efficiencies. By 1982, a-Si:H solar cells with (initial) efficiencies over 10% had been obtained[23]. However, a-Si:H solar cells suffer from a light-induced degradation effect (the so-called Staebler–Wronski effect)[24]. The electrical output of a-Si:H solar cells decreases over a period of time when first exposed to sunlight. Eventually, however, the electrical output stabilizes. This effect can result in up to a 20% loss in output before the material stabilizes.

Considering that amorphous silicon has a higher optical absorption coefficient for photons with energies greater than 2 eV, while lower optical absorption coefficient for photons with energies lower than 2 eV compared to microcrystalline silicon (Figure 1.8), recent researches have been focus on multi-junction thin-film silicon solar cells with aim to better exploit the solar spectrum. The multi-junction thin-film silicon solar cells consist in stacking two (tandem) or even three (triple) junction structures on top of each other, the different subcells being connected in

series. Taken a tandem solar cell made from a-Si:H (top) and mc-Si:H (bottom) for example, the a-Si:H solar cell can effectively use the high energy photons. The longer wavelength photons, which are not absorbed in the a-Si:H solar cell, get absorbed in mc-Si:H and thus achieving high efficiency.

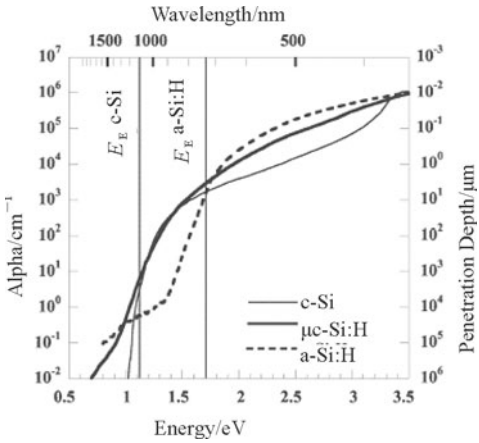

Figure 1.8 Curves for the optical absorption coefficient α and the penetration depth $d\lambda = 1/\alpha$ of monochromatic light with photon energy $h\nu$ and wavelength λ, for wafer-type crystalline silicon (c-Si) and typical device-quality a-Si:H and mc-Si:H layers on glass. [8]
(Reprinted with permission of John Wiley&Sons,Inc)

1.3.2 Hydrogenated microcrystalline silicon (c-Si:H)

Hydrogenated microcrystalline silicon (c-Si:H) is a mixed phase material, containing a crystalline silicon fraction and an amorphous silicon fraction. The crystallites are generally only a few nanometers to a few tens of nanometers in diameters, and are present in “bunches” or “conglomerates” in the layers. These conglomerates are much larger than the crystallites themselves, up to a micron or even larger. Because the crystallites are in the nanometer range, microcrystalline silicon is often referred to as “nano-crystalline silicon”. The two names are nowadays used interchangeably. Like amorphous silicon, microcrystalline Si contains a lot of hydrogen (several percents), which is incorporated in situ during deposition and ensures passivation of most defects in the layers. The term “microcrystalline Si” covers, in fact, a whole range of materials, ranging from amorphous silicon with a few percents of crystalline phase to a material with only a few percents of amorphous silicon. The properties of the materials at the two extremes are quite different. In practice, the best devices are obtained with material

close to the edge between microcrystalline and amorphous Si, so most recent papers refer to this type of material, which contains a large amorphous fraction. The development of thin-film polycrystalline silicon (polysilicon) for solar cells can be seen as the continuation of this trend towards higher crystallinity. Thin film polysilicon is a material with grain size in the range 1 μm to 1 mm. In contrast to microcrystalline silicon, this material does not contain any amorphous tissue, or only a very small amount (well below 1%). One could think that the border between microcrystalline and polycrystalline silicon is not very sharp. In practice, there is a very clear distinction between the two materials because polysilicon is very far from the amorphous-to-crystalline transition, and always involves much higher temperatures than those used for microcrystalline silicon. Thin-film polysilicon solar cells have active layers that are usually thinner than 5 μm, often about only 2 μm. The technology is more recent and less mature than amorphous and microcrystalline silicon, but progress in the last few years has been very fast.

Microcrystalline silicon (mc-Si:H) layers were first produced by Veprek and Marecek in 1968 in Prague by a low-temperature plasma-assisted deposition process[25]. The bandgap of microcrystalline Si depends on the fraction of amorphous silicon in the material. Layers with a substantial crystalline fraction have a bandgap close to that of mono-crystalline silicon (1.1 eV). The apparent higher absorption (Figure 1.8) for such microcrystalline layers compared to mono-crystalline silicon has been demonstrated to be caused by light scattering at the layer surfaces. The absorption below the bandgap is much higher than that for crystalline silicon, and is caused by defects within the bandgap.

The device structure of microcrystalline silicon solar cells is very similar to that of amorphous silicon solar cells. As with amorphous silicon, both superstrate (p-i-n) and substrate (n-i-p) configurations are possible. The optimal thickness of the i-layer is much larger than that for amorphous Si cells, from 1 to 2 μm. This is related with the weaker absorption by the microcrystalline silicon. The mc-Si:H solar cells generally do not suffer from a pronounced Staebler–Wronski effect. However, recent work shows that mc-Si:H, if deposited at deposition conditions very near to the microcrystalline/amorphous transition, may indeed show a considerable amount of light-induced degradation.[30]

1.4 Nano-structured silicon

Nano-structured silicon is expected to possess significantly different optical properties from their bulk-length counterparts because they are smaller than the wavelength of visible light. The low optical reflection from ordered arrays of nano-structured silicon could be exploited to improve the photon absorption efficiency

of solar cells. Moreover, solar cells made from nano-structured silicon may offer a mechanically flexible alternative to Si wafers for photovoltaics. In this section, we will focus on the recent progress in synthesis, characterization, and fabrication of nano-structured silicon based solar cells.

1.4.1 Silicon nanowire

As early as 1964, Wagner and Ellis firstly reported the growth of silicon whiskers.[31]Later Givargizov elucidated the growth mechanism of silicon whiskers in 1975[32]. Subsequently, there were extensive investigations carried out on the synthesis, physical properties, and device fabrication and application of Silicon nano-wires (SiNWs). It has been showed that the energy gap of SiNWs was found to increase with decreasing SiNW diameter from 1.1 eV for 7 nm to 3.5 eV for 1.3 nm in diameter, in agreement with previous theoretical predictions[33,34] . Many other structure parameters i.e. growth directions, cross section, may also affect band structure and thus physical properties of SiNWs, especially for ultra tiny SiNWs[35,36]. Kelzenberg [37] reported that the diffusion length in Si NWs can be as long as 2 μm, which corresponds to a minority carrier lifetime of ~15 ns. All these results show that silicon nano-wire may have great advantages over their bulk-length counterparts in future design of high efficiency solar cells.

In order to fabricate solar cells based on SiNWs, the basic issue is to realize controllable synthesis of large-scale high quality SiNWs. The well-known vapour-liquid-solid (VLS) reaction have been used to grown SiNWs for a long time[38]. In the VLS reaction, metal particles, for example gold particles on Si substrate, are generally used as the mediating solvent to direct the growth of SiNWs. Some other methods, such as oxygen-assisted-growth (OAG)[39,40], vapor-solid-solid (VSS)[41,42] and electroless etching methods[43~46], have also been developed to synthesize SiNWs in largescale. Usually SiNWs grown by using VLS or VSS techniques have been proved to be obviously advantageous compared with OAG and electroless etching techniques in terms of well-defined surface and well-controlled diameter. Moreover, the VLS and VSS techniques can prepare ordered vertically standing epitaxial nanowires on single crystal substrate with better control of growth direction as a device platform, avoiding pick-and-place approaches or nano-manipulations in the fabrication of nano-devices. Unfortunately, metals especially gold and copper using as catalyst to direct the growth of SiNWs by VLS or VSS techniques may induce deep levels in SiNWs, which would trap electrons and holes in Si, and then depress the optical and electronic properties of the nanowires. Indeed much effort has already been made to solve this problem by altering metal catalysts such as Al[47]. At present, most of the SiNWs used in solar cells are

synthesized with VLS and VSS methods.

To get uniform doping in SiNWs is also a key issue to fabricate high performance SiNWs-based soalr cells. At the present time, the doping methods of SiNWs mainly include thermal diffusion, ion implantation and in-situ doping during growth process by co-flowing doping gas with silane or tetrachlorosilane. These methods have some disadvantages such as inducing defects and doping fluctuation especially for high level doping. Precise doping of semiconductor nano-materials remains as a challenge to be solved.

SiNWs solar cells have many kinds of structures. Their heterojunctions may be aligned in axes or radius. But typical structure of SiNWs solar cells is core-shell p-type/instinct/n-type (p-i-n) or p-type/n-type(p-n) configuration, namely, radial junctions[47~49]. By orthogonalizing the direction of light absorption and carrier collection, radial junctions can enable efficient carrier collection in optically thick nano-wire arrays, even when minority carrier diffusion lengths are shorter than the optical absorption length. The schematic drawing of the radial p-n junction cell is shown in Figure 1.9. This design has the potential to enable energy-conversion efficiency approaching that of wafer-based crystalline Si solar cells but competitive with thin film technologies at costs. Tiam et al[47]. fabricated single SiNWs solar cell of this structure to drive ultralow power devices, yielding a maximum power output of 200 pW per single nanowire device and an energy efficiency of 3.4%. Atwater[48] created a new type of flexible solar cell using arrays of long, thin silicon wires embedded in a polymer substrate. The silicon-wire arrays absorb up to 96% of incident sunlight at a single wavelength and 85% of total collectible sunlight. In addition to its high performance in absorbing lights, this kind of solar cell only use a fraction of the expensive silicon materials required by conventional solar cells. It would be expected that more and more efforts will be devoted to the novel SiNWs based solar cells in future in spite that the experiment efficiency of solar cells based on SiNWs is still far less from the academic calculation (15%~18%)[50].

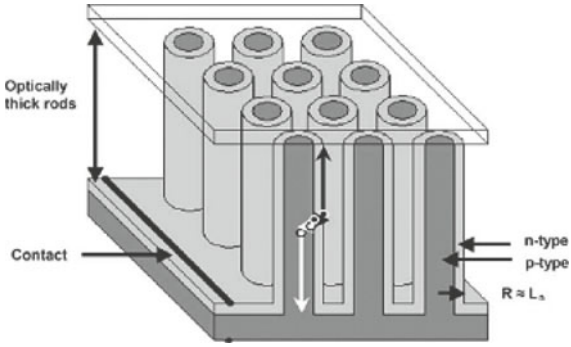

Figure 1.9 Schematics of a radial p-n junction nanorod solar cell [52]
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1.4.2 Silicon quantum dots

Given the spectrum of photons received from the Sun, there exists an optimum bandgap for a semiconductor absorber in a single-junction conventional photovoltaic device. As the bandgap increases, less energy is absorbed, but less of that absorbed energy is lost as heat due to rapid intra-band thermalization. The optimum bandgap for a single bandgap solar cell is between about 1.0 and 1.6 eV. The upper theoretical power conversion efficiency limit is 33.7% and is referred to as the Shockley–Queisser (SQ) limit [51]. Recently, Hanna and Nozik point out that photo-conversion efficiencies exceeding the SQ limit are possible for single junction devices by means of quantum dots.

When a normal photovoltaic material captures a photon of sunlight, it produces a negatively charged electron, which leaves behind a positively charged "hole" in the material. Under the solar cell's electrical field, the two charge carriers migrate to the terminals of the cell and produce a current. But quantum dots produce "excitons," consisting of electrons loosely bound to positive holes. Photons with energy equal to n times the bandgap can potentially produce n excitons at the bandgap, where n is an integer, in accordance with energy conservation. If the excitons can be effectively dissociated into electrons and holes and then migrate to the cell terminals without recombination, photo-conversion efficiencies higher than SQ limit would be expected. Hanna and Nozik's calculations show that a power conversion efficiency of 44% is possible under unconcentrated AM1.5G light for solar cells based on a single junction multiple exciton generation (MEG) absorber with a bandgap of 0.7 eV. Under full light concentration, this limit rises to 66% [52] .

To use the incipient free energy after MEG occurs, it is important to find materials with quantum yields for exciton generation greater than 100%. Currently, efficient MEG has been observed in silicon, making it possible to fabricate solar cells based on silicon quantum dots [53~55]. More recently, tandem solar cells formed by combination of silicon quantum dot and crystalline silicon wafers has been demonstrated [56]. This result is an encouraging step towards the realization of high efficiency solar cells based on silicon quantum dot materials.

1.5 Conclusion and perspective

Silicon wafer based solar cells is and will be the main focus of photovoltaic manufactures due to its stable efficiency and mature technologies in large scale production. However, the wafers will be more and more thinner in the future. Improved processing sequences, such as the buried contact and HIT approaches, now both in pilot production, will come to the fore as wafer thickness decreases and material quality increases. The trends in producing higher efficient solar cells with thinner wafer result in that fabrication technique, such as surface passivation of both front and rear surfaces, will become more and more important.

A laboratory scientist, however, may have more interest in the low-cost, thin-film silicon technology. It would be expected that the commercial product based on this technology should be mature in the near future, with energy conversion efficiency approaching that of its wafer counterpart. The present bottlenecks of thin-film silicon solar cell technology are the relatively high temperature and low deposition rates. The high temperature results in the difficulty in fabricating solar cells on organic substrates which is the fundamental requirement for flexible photovoltaic devices. The low deposition rates induce long deposition time and high energy consumption. If these problems can be tackled, thin-film solar cell will be the most promising technology toward low-cost, high-efficiency solar cells.

Nano-structured silicon materials, including silicon nanowires and quantum dots, show great potential for future solar cell devices. However,extensive efforts, such as improving the materials parameters (resistivity, size, purity, etc.) and optimizing device fabrication process, are required to improve their photovoltaic performances. Success in nano-structured silicon solar cells may lead to greatest leap in the efficiency improvement in silicon based solar cells.

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