Yong Zhou
Editor

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（清洁可再生能源材料）

With 130 figures

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Editor
Yong Zhou
Ecomaterials and Renewable Energy Research
Center (ERERC), Nanjing University
Nanjing, Jiangsu, China
Email:zhouyong1999@nju.edu.cn

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Preface

Since the beginning of the 20^{th} century, there have been great improvements in the daily life of human through the use of petroleum as a basic material. However, we now face the problem of petroleum supply and depletion. Meanwhile, global warming, the most threatening problem, stimulates the research towards alternative fuel sources using eco- and renewable energy typically such as solar energy. Material technology plays a particularly important role in the field of energy. Rapid depletion of fossil fuels and growing environmental concerns make energy one of the greatest challenges facing humankind in the 21st century. We need sustainable energy production and efficiently use natural energy to meet socio-economic and environmental targets. To cover various topics in such an interdisciplinary area, it is high time to provide timely review of a number of important developments in this field.

The science of energy-harvesting materials is experiencing phenomenal growth and attracting huge interest. *Eco- and Renewable Energy Materials* showcases the basic principle and the latest developments of the materials technologies, which are related to prevent global warming and secure energy resources from the viewpoint of materials science. Chapter 1 by Chenghui Li provides a concise overview of the development of silicon based photovoltaic materials. With the consideration of the uniqueness of perylenes, Chen Li and Klaus Müllen in Chapter 2 review the development of perylenes in organic photovoltaics. Jianguo Liu et al illustrate carbon corrosion in the electrocatalysts of polymer electrolyte membrane fuel cell in Chapter 3. Chapter 4 by Tingyue Gu and coworkers summarizes various recent advances in bio-fuel cell research using various biomass feed stocks. Yonggang Wang et al in Chapter 5 survey new progress in using nanostructured materials as cathodes and anodes to develop lithium-ion batteries with high energy density, high rate capability, and excellent cycling stability. In Chapter 6, Dechun Zou et al summarize the updated fabrication and development of flexible solar cells. Chapter 7 by Zhaosheng Li and coworkers introduce history and operating principles of the photoelectrochemical cell for hydrogen generation. In Chapter 8, Huanting Wang et al describe the application of metal-organic frameworks to CO_2 capture. They also review in Chapter 9 recent activities in the development of CO_2 selective separation membranes, focusing on the fabrication and separation performance of current polymeric membranes and their modification, inorganic membranes and mixed-matrix membranes.

In working on this book, I had great pleasure interacting with the authors, and are grateful to all of them for their friendly and competent co-operation. Thanks are due to the financial support from 973 Programs (No. 2011CB933300/2011CB933303) and Jiangsu Provincial Funds for Distinguished Young Scientists (No. BK2012015). I sincerely hope that this book will provide researchers in these fields with newest developments in this rapidly evolving field for advancing research. I also wish to stimulate the next generation of breakthroughs of the eco- and renewable energy, which will further enrich human life.

Yong Zhou
Nanjing,P.R.China
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Contents

Chapter 1
Silicon Based Photovoltaic Materials

Chenghui Li

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China

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 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).

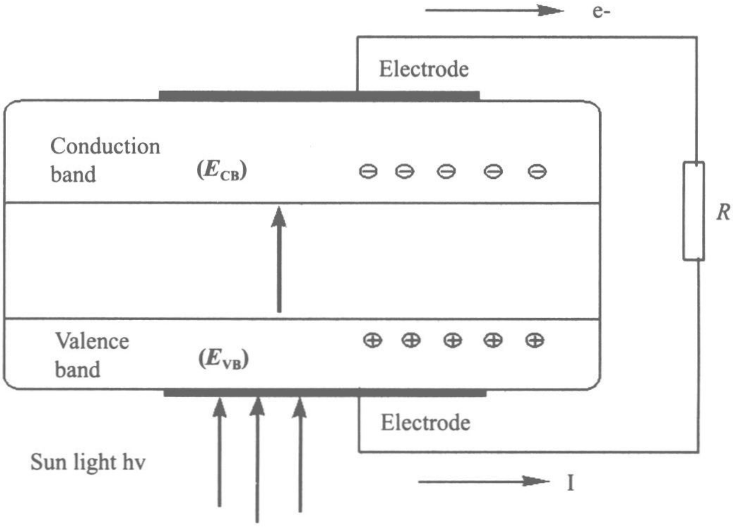

Figure 1.1 The photovoltaic process in a solar cell

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.

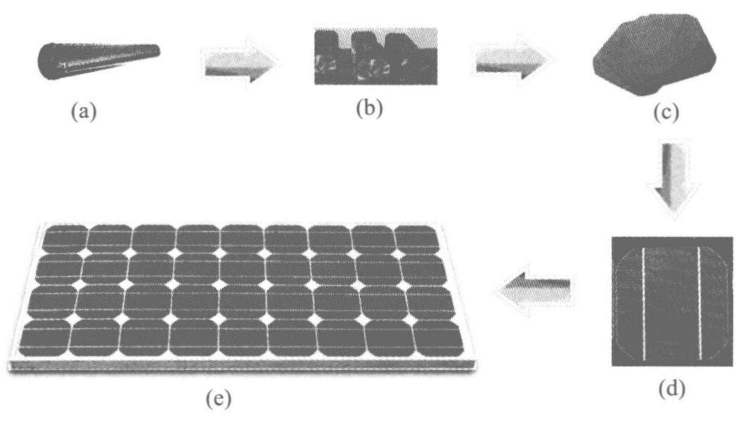

Figure 1.2 The process for fabricating mono-crystalline silicon photovoltaic modules

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.

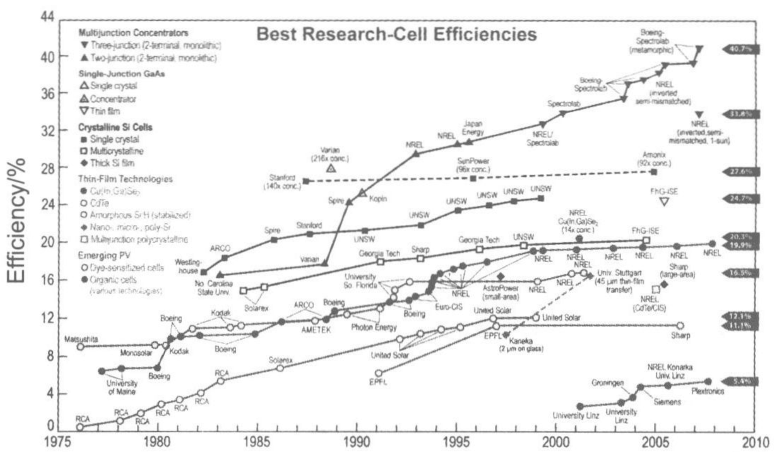

Figure 1.3 The best research-cell efficiencies all over the world

(Source:http://www.nrel.gov/pv/thin_film/docs/kaz_best_research_cells.ppt)