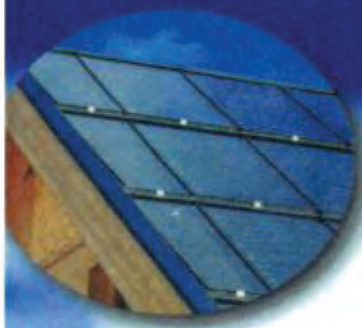


SOLAR ENERGY

THE STATE OF THE ART

ISES POSITION PAPERS



EDITED BY **JEFFREY GORDON**



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Published by James & James (Science Publishers) Ltd
35-37 William Road, London, NW1 3ER, UK

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A catalogue record for this book is available from the British Library.

ISBN 1 902916 23 9

Printed in the UK by The Cromwell Press

Cover photos courtesy of AEE (1 and 2), FLABEG Solar International (3), Sandia National Laboratories (4),

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Preface

Periodically, it is beneficial to pause and commit to the printed page a retrospective summary of the progress, status and leading challenges in a scientific discipline. This book is an initiative of the International Solar Energy Society (ISES) for the broad and rich interdisciplinary field of solar energy. The approach of the year 2000 in part provided the motivation and timing for this undertaking.

The book comprises 12 chapters each of which covers a major solar energy sub-discipline and is authored by a leading scientist in the particular field. These background papers are intended to survey the history of the particular technology and field, to review the state-of-the-art, to discuss the rudiments, to present major applications, and to identify the principal remaining challenges. The authors were asked to tailor their chapters to an audience of university students, fellow researchers, engineers in the field, and solar energy practitioners.

This book took form in early 1997 while Terry Hollands was spending his sabbatical with me. Terry, in his capacity then as editor-in-chief of Solar Energy, and David Mills in his capacity as president of ISES at the time, recommended that a book of this nature be published under the auspices of ISES during the year 2000. Terry and David asked if I would accept the challenge of editing the book, namely, of identifying the principal categories for the chapters, of securing the agreement of the foremost scientists in the respective areas to write the chapters, to oversee the assembly of the book including adherence to deadlines, and to coordinate matters among the authors, ISES and the publisher. With Terry's valuable input, the major categories were selected, a list of prospective authors was drafted, and the project was underway.

What motivated me was the prospect of emerging with an invaluable reference book for any serious student or scientist entering one of the tributaries of solar energy research or development - the type of book that would concentrate a wealth of accumulated wisdom and experience between

two covers, and would save considerable efforts in literature searches and attempts to gain a clear understanding of the basic concepts required to move forward in solar energy studies. With nearly twenty years having elapsed since the publication of a book of comparable scope and high scientific level, I concurred it would be an honor, as well as a gratifying experience, to be part of this endeavor.

If you, the reader, find the list of topics incomplete, it is not necessarily because we overlooked or belittled other disciplines. Rather it stems from human frailty. There were other chapters to which prominent scientists committed themselves. But, after more than one year into the project, they reneged and left us with insufficient time to find a replacement and still meet our deadline.

Those colleagues who did accept the chalice imparted the unique perspective of the intellectual leaders who have pioneered progress in each field, have gained extensive experience teaching it in university settings, and can succinctly condense that wisdom into one chapter. To them, I, and I trust all readers of this book, extend profound gratitude.

As editor, I also wish to express my appreciation to the reviewers of these chapters. Whereas with authors of this caliber an accept-or-reject review was uncalled for, I did feel that a constructively critical review by a colleague of comparable scientific standing would help each author to improve and sharpen his chapter. In order to preserve the promised anonymity of the reviewers, I am not at liberty to thank them by name here. Nonetheless, I wanted to explain that each chapter has undergone peer review at the highest level and was indeed revised in accordance with the referees' comments.

Recognition is also in order to ISES publication officers Chris Findlay and Burkhard Holder of ISES headquarters in Germany. It is thanks to their dedication to this project that a respectable publishing house was found, legal and financial arrangements were reached, and the book was published.

For all the years I've spent as a researcher and instructor in solar energy studies, I was excited and humbled at the amount I learned from reading these chapters and supervising their review. I can only hope that you, the reader, will share that intellectual exhilaration along with a renewed enthusiasm to tackle the challenges that remain in solar energy research in the years ahead.

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Selectively solar-absorbing coatings

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3.1 INTRODUCTION

An energy-efficient solar collector should absorb incident solar radiation, convert it to thermal energy, and deliver the thermal energy to a heat-transfer medium with minimum loss at each step. Figure 3.1 serves as a convenient introduction to the design of a flat-plate solar collector and outlines the most salient components. The collector comprises a thermally well-insulated arrangement whose upward-facing side is transparent so that solar radiation can penetrate to an absorbing surface, with carefully tailored properties, in contact with a heat-transfer medium such as water or air. Thermal losses are diminished by placing the absorber surface below a cover glass. Even smaller losses can be obtained by the use of transparent insulation in the air gap between the absorber and the cover glass. In principle, the energy efficiency of the collector can be boosted by surface coated glass: antireflection coatings as well as infrared-reflecting coatings are of interest. It should be stressed that Figure 3.1 refers to the commonly used fixed flat-plate collector. Most of the treatment below will be done with such collectors in mind, but some discussion of absorber surfaces designed for high-temperature applications primarily in evacuated tubular collectors is also included. Some solar collector constructions have solar reflecting and tracking facilities.

The requirements for energy efficiency can be introduced with reference to the 'natural' radiation in our surroundings. The pertinent radiative properties are shown in Figure 3.2. The solid curve reproduces a typical spectrum for *solar irradiance* at the ground. Specifically, the curve gives an air mass (AM) 1.5 spectrum according to the ISO standard 9845-1 (1992). It is seen that almost all of the solar radiation comes at a wavelength λ below $3\ \mu\text{m}$. The absorber surface of the solar collection device should absorb this energy. The surface then heats up and emits thermal radiation. The dashed curves

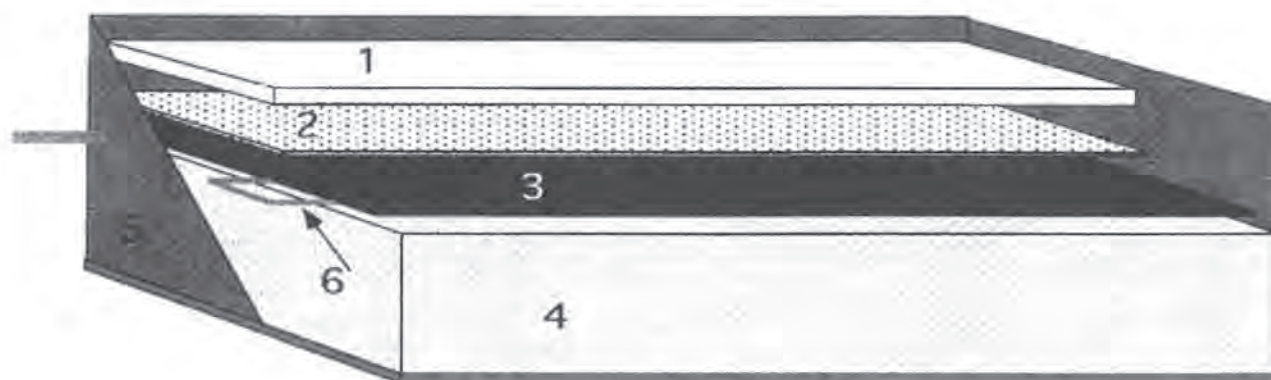


Figure 3.1 Principle design of a flat-plate solar collector. The numbers denote glazing (1), transparent insulation (2), absorber (3), insulation (4), collector box (5) and pipes (6). The different components are not to scale.

in Figure 3.2 indicate black-body spectra at three temperatures; the emitted energy is negligible at $\lambda < 3 \mu\text{m}$ for temperatures below 100°C . The losses associated with thermal emission should be avoided in order to gain energy efficiency. This can be accomplished in two different ways. The first one relies on a cover glass with a coating that reflects at $\lambda > 3 \mu\text{m}$ so that the radiation emitted from the absorber surface is brought back to this same

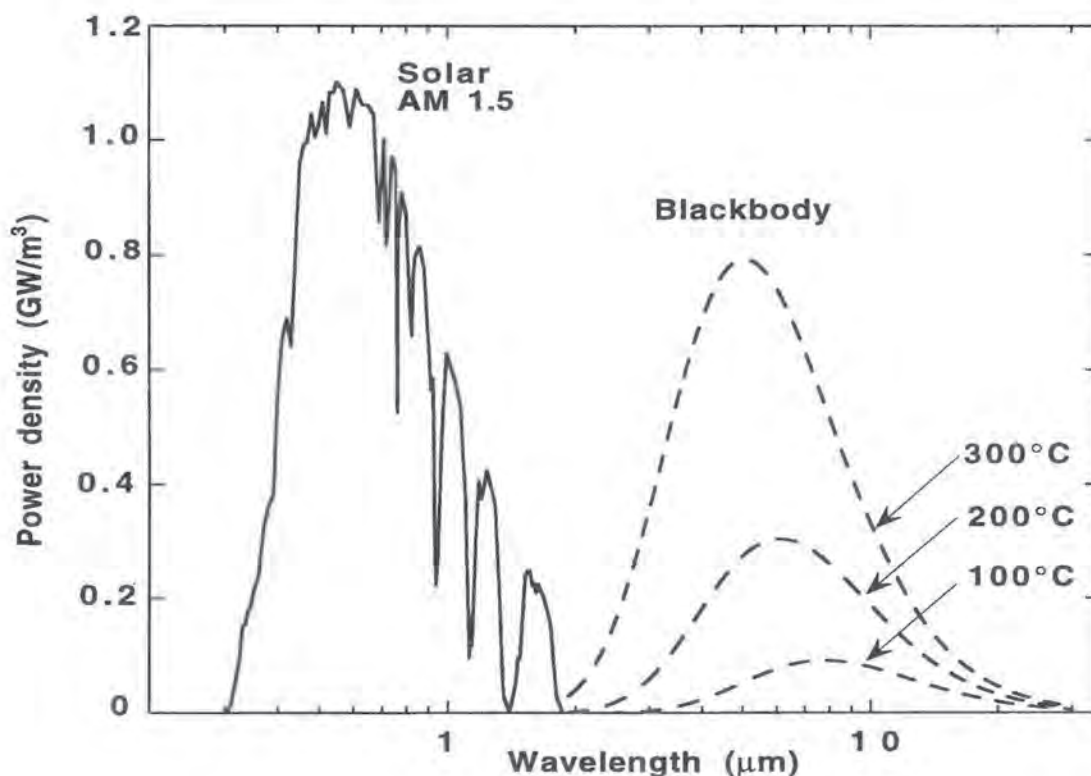


Figure 3.2 Spectra for characteristic solar irradiance and for black-body exitance pertaining to three temperatures.

surface. Another, and more commonly used, way to diminish the heat losses is to have an absorber surface whose thermal emittance is low. The second condition leads to the selectively solar-absorbing surfaces to be discussed in this chapter. They are characterized by low reflectance at $\lambda < \lambda_c$ and high reflectance at $\lambda > \lambda_c$ where $\lambda_c = 3 \mu\text{m}$ for temperatures below 100°C . At increased operating temperatures, λ_c should be displaced towards a lower value, and at 300°C it is adequate to put $\lambda_c = 2 \mu\text{m}$.

Qualitative performance criteria can be formulated by use of the normal solar absorptance A_{sol} and the normal or hemispherical thermal emittance (E_{therm}^n and E_{therm} respectively). These parameters are defined by

$$A_{\text{sol}} = \frac{\int d\lambda \phi_{\text{sol}}(\lambda)(1 - R(\lambda, 0))}{\int d\lambda \phi_{\text{sol}}(\lambda)} \quad (3.1)$$

$$E_{\text{therm}}^n(\tau) = \frac{\int d\lambda \phi_{\text{therm}}(\lambda, \tau)(1 - R(\lambda, 0))}{\int d\lambda \phi_{\text{therm}}(\lambda, \tau)} \quad (3.2a)$$

$$E_{\text{therm}}(\tau) = \frac{\int d\lambda \int_0^{\pi/2} d(\sin^2 \theta) \phi_{\text{therm}}(\lambda, \tau)(1 - R(\lambda, \theta))}{\int d\lambda \phi_{\text{therm}}(\lambda, \tau)} \quad (3.2b)$$

$$\phi_{\text{therm}}(\lambda, \tau) = c_1 \lambda^{-5} [\exp(c_2 / (\lambda \tau))] \quad (3.3)$$

where ϕ_{sol} is the solar irradiance (for example the AM1.5 spectrum), $R(\lambda, \theta)$ is the reflectance as a function of wavelength and incidence angle, τ is the absorber surface temperature, $c_1 = 3.7814 \times 10^{-16} \text{ W m}^{-2}$ and $c_2 = 1.4388 \times 10^{-2} \text{ m K}$. Clearly, the desired spectral selectivity implies that A_{sol} should be close to unity and that E_{therm} should be minimized. The normal thermal emittance is often used for characterization, although the hemispherical emittance is more adequate. Thermal emittance for other specific angles than normal can also be calculated with Equation 3.2a by replacing $R(\lambda, 0)$ with the reflectance $R(\lambda, \theta)$ for the actual angle of incidence.

Coatings and surface treatments with high A_{sol} and low E_{therm} were subject to intense research and development in many laboratories around the world during the 1970s and early 1980s. This work has been reviewed in considerable detail (Meinel and Meinel, 1976, Seraphin and Meinel, 1976, Seraphin, 1979, Lampert, 1979a, b, Agnihotri and Gupta, 1981, Niklasson and Granqvist, 1991). An annotated bibliography (Niklasson and Granqvist, 1983), covering the period 1955–1981, was published in 1983. It lists 565 scientific papers, including studies of almost 280 different coatings or surface treatments. Much laboratory research was done during this period and it resulted in a number of coatings for commercial production of solar absorbers. Rather than reviewing this vast, and somewhat stale, field once

again, here the focus is on certain key issues and on the developments during the 1990s. This chapter first considers design principles for obtaining spectral selectivity and data for several solar collector surfaces used in practice. Then follows a discussion of theoretical models for the optical properties and examples where modelling has been applied in the research on solar absorbers. A brief review is given of the work by the International Energy Agency (IEA) on accelerated degradation tests for solar absorbers.

3.2 SELECTIVELY SOLAR-ABSORBING SURFACES: DESIGN AND DATA

3.2.1 Principles

It is possible to exploit several different design principles and physical mechanisms in order to create a selectively solar-absorbing surface. Six of these principles are shown schematically in Figure 3.3. The most straightforward one is to use a material whose *intrinsic radiative properties* have the desired kind of spectral selectivity. Generally speaking, this approach has not been very fruitful, but work on ZrB_2 (Randich and Allred, 1981, Randich and Pettit, 1981) and on some other compounds indicates that intrinsically selective materials do exist. In practice, useful solar absorbers are based on two layers with different optical properties; they are referred to as tandem absorbers. A semiconducting or dielectric coating with high solar absorptance and high infrared transmittance on top of a non-selective highly

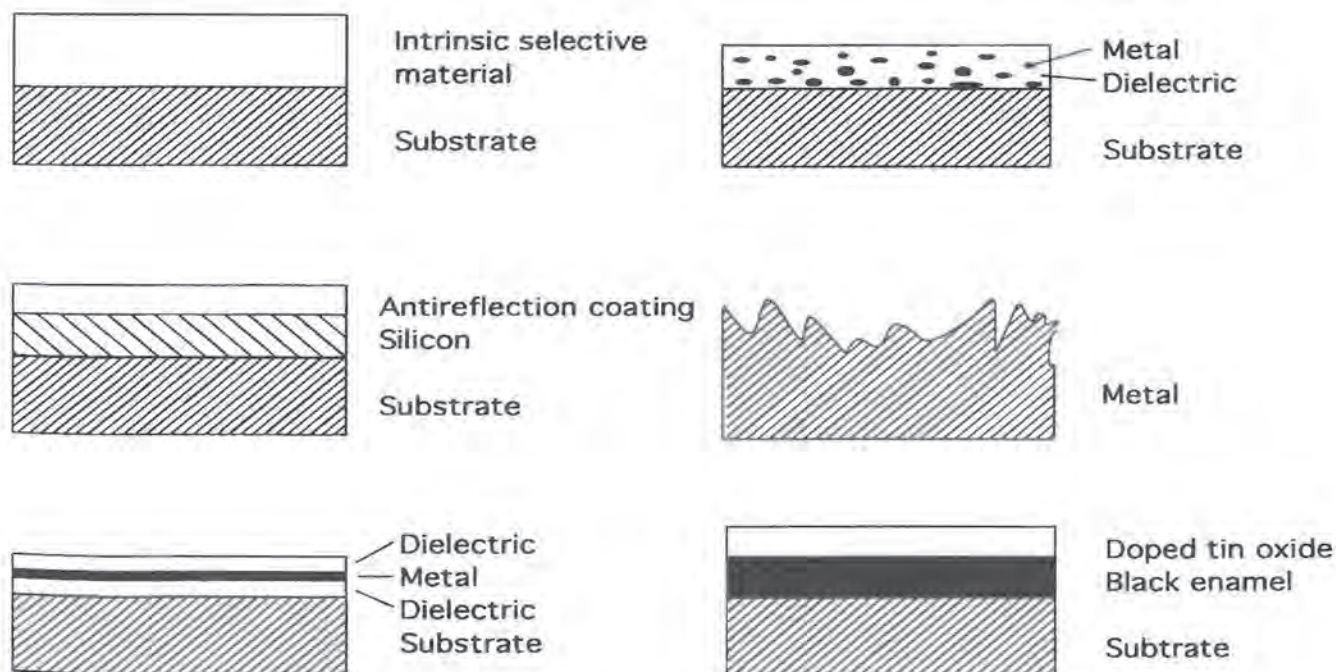


Figure 3.3 Cross-sectional schematic designs of six types of different coatings and surface treatments for selective absorption of solar energy.

reflecting material (i.e. a metal) constitutes one type of tandem absorber. Another alternative is to coat a non-selective highly absorbing material with a heat-mirror (having high solar transmittance and high infrared reflectance). The different choices of material combinations for tandem absorbers are described in detail below.

Semiconductor-metal tandems

These can give the desired spectral selectivity by absorbing short-wavelength radiation in a semiconductor whose bandgap is ~ 0.6 eV and having low thermal emittance as a result of the underlying metal. The useful semiconductors have undesirably large refractive indices, which tends to yield high reflection losses. Hence it is necessary to antireflect the surfaces in the range of solar radiation. Early work in this category (Seraphin, 1976, 1979, Janai *et al.*, 1979) was centred on Si based designs and coatings prepared by chemical vapour deposition.

Multilayer-metal tandems

These can be tailored so that the multilayer stack becomes an efficient selective absorber of solar radiation. It is comparatively easy to compute the optical performance, which facilitates design optimization. One interesting example is an $\text{Al}_2\text{O}_3/\text{Mo}/\text{Al}_2\text{O}_3$ triple layer, which was originally developed for the US space programme (Schmidt and Park, 1965). This type of surface has been produced by large-area sputtering technology for high temperature applications (Thornton and Lamb, 1982).

Metal-dielectric composite-metal tandems

These have a coating consisting of very fine metal particles in a dielectric host. This coating is also labelled 'cermet' from the abbreviation of ceramic-metal. The ensuing optical properties can be intermediate between those of the metal and of the dielectric. The metal-dielectric concept offers a high degree of flexibility, and the optimization of the solar selectivity can be made with regard to the choice of constituents, coating thickness, particle concentration, shape and orientation of the particles. The size of the particles is restricted so as to be much smaller than the wavelengths in the solar spectral range in order to absorb instead of scatter the solar light. It has been shown that particle sizes should be less than 0.1 to $0.2\ \mu\text{m}$ (Arancibia-Bulnes and Ruiz-Suarez, 1998). Effective medium theories, which will be treated in a later section, are of great value for modelling the optical performance. The composite coatings can be produced by a variety of techniques such as chemical conversion, electroplating, anodization, inorganic coloration of anodized aluminium, chemical vapour deposition, reactive evaporation or sputtering of the metal, and co-evaporation or co-sputtering of metal and dielectric. Several of these possibilities will be discussed below.

Thickness sensitive spectrally selective (TSSS) paints

These are also based on the same tandem principle and require a metallic substrate. The paint consists of a solar-absorbing inorganic pigment dispersed in a resin. The pigment forms large agglomerates and therefore causes both absorption and scattering. It is crucial that the resin has high infrared transmittance and that the paint thickness is as small as possible so that the thermal emittance is brought to a minimum.

Textured surfaces

These can produce a high solar absorptance by multiple reflections against metal dendrites that are $\sim 2 \mu\text{m}$ apart, while the long-wavelength emittance is fairly unaffected by this texture. Well known examples are dendritic tungsten prepared by chemical vapour deposition (Pettit *et al.*, 1978) and textured copper, nickel and stainless steel surfaces made by sputter etching (Harding and Lake, 1981). The nickel based 'Black Forest' absorber is a practical example of this type of surface (Wardell, 1997).

The final concept considered here involves a *selectively solar-transmitting coating on a blackbody-like absorber*. The absorber can be chosen from among materials with proven long-term durability (such as black enamel), and the coating can be a heavily doped oxide semiconductor (for example $\text{SnO}_2\text{:F}$). Coatings of this type have not come to any practical use so far.

The solar absorptance is often boosted by antireflection (AR) treatments, which can be applied to all types of surfaces described above. The refractive index of the AR coating should be lower than that of the underlying layer; numerically it should be the square root of the refractive index of the surface below. The AR coating is sufficiently thin so that it does not increase the thermal emittance significantly.

Commercial products are most frequently based on the cermet-metal type of solar selective absorber, as will be clear from the examples given in the next section. The absorptance is usually improved by an AR treatment and/or by an inhomogeneous distribution of metal particles through the cross-section of the coating. A continuous grading of particle content, with the highest concentration at the metal-cermet interface and no metal at the front surface of the coating, tends to suppress thin film interference for light in the solar wavelength range, thereby enhancing the solar absorptance.

3.2.2 Results for some practically useful surfaces

Much of the progress during recent years has been based on the implementation of vacuum techniques in production of fin type absorbers for low temperature applications. The chemical and electrochemical processes used for the commercialization were readily taken over from the metal finishing industry, since the absorber coatings were similar to those used for automotive components, building facades, and roofs. The requirements on solar absorbers used in high temperature applications, namely extremely low

thermal emittance and high temperature stability, were difficult to fulfil with conventional wet processes. Therefore large-scale sputter deposition was developed in the late 1970s, in parallel to a similar development in the glass coating industry. The vacuum techniques are nowadays mature, characterized by low costs and have the advantage of being less environmentally polluting than the wet processes. They play a large part in the production of low temperature fin type absorbers. The following section will present examples of commercial solar absorbers, grouped under the deposition technique.

Electroplating

The most widely used selectively solar-absorbing surface seems to be 'black chrome', which is a complex composite of metallic chrome and dielectric Cr_2O_3 . The metal concentration is graded, as described in the previous section. The selective solar absorption appears to be a result of the combination of the effect of the metal-dielectric composite and of the pronounced surface roughness that has been observed in these films (Smith *et al.*, 1985). Black chrome has a high void fraction and consists of rounded particles with sizes of about 100 nm (Sweet *et al.*, 1984). The chrome crystallites are smaller, though, with sizes of the order of 10 nm, and are probably embedded in the oxide phase (Lampert and Washburn, 1979). The inset in Figure 3.4(a) gives a schematic picture of the microstructure. The original work on black chrome for solar energy applications was carried out by McDonald (1975), who modified the procedure for making decorative electroplated layers. Several commercial coatings are presently produced by MTI Inc., Energie Solaire AS and Batec A/S. The MTI and Batec black chrome coatings are deposited on nickel plated copper, and the Energie Solaire coating is backed by stainless steel. Figure 3.4(a) shows that the spectral reflectance is low in the solar range and high in the thermal range, i.e., the spectral selectivity is large and approximately matches the ideal property indicated by the dotted lines in Figure 3.4(a). The MTI coating has $A_{\text{sol}} \approx 0.97$ and $E_{\text{therm}}^n(100^\circ\text{C}) = 0.09$ (Carlsson *et al.*, 1994).

Black nickel coatings have also been developed on the laboratory scale (Tabor, 1955, Peterson and Ramsey, 1975, Koltun *et al.*, 1994, Monteiro *et al.*, 1992, Wäckelgård, 1998). The coating was not stable at high humidity in combination with high temperature (Lin and Peterson, 1976). The electrochemical bath was subsequently changed so that it contained nickel and sodium chloride (Koltun *et al.*, 1994). The resulting coatings were found to be temperature stable but their humidity resistance appeared different in different tests (Koltun *et al.*, 1994, Wäckelgård, 1998). A black nickel coating on copper, called 'Black Forest', has recently been developed at Sandia National Laboratory (Wardell, 1997). The nickel-based crystallites are large enough to be light trapping. The coating has a protective layer which provides good corrosion resistance. It has been reported (Lampert, 1997) that Energy Laboratories in Jacksonville, Florida, will start production of this new coating.

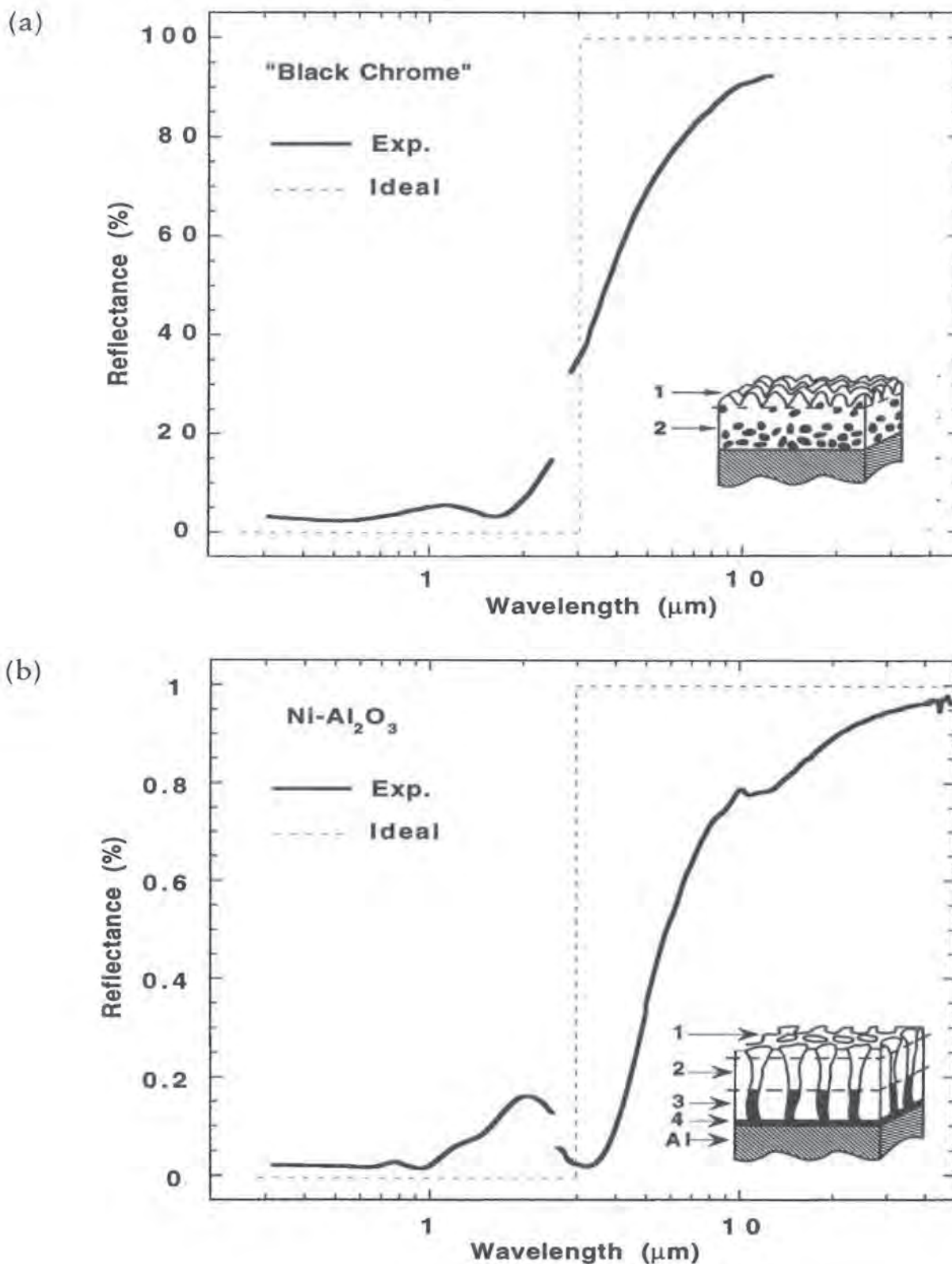


Figure 3.4 Spectral reflectance measured for a 'black chrome' coating on nickel-plated copper from MTI Solar Inc. (a) and for a nickel-pigmented anodic Al₂O₃ coating produced by Sunstrip (b). Dotted lines represent an ideal reflectance profile. The inset in part (a) indicates a microstructure with a graded cermet layer (2), having Cr particles

dispersed in a Cr_2O_3 matrix, and a rough surface layer (1) of Cr_2O_3 . The inset in part (b) indicates an aluminium oxide diffusion barrier (4), a $\text{Ni-Al}_2\text{O}_3$ composite with nickel in the pores of the alumina (3), and a plain porous aluminium oxide (2) whose pores increase towards the top surface (1).

Anodization and electroplating

Other commercially produced selectively solar-absorbing coatings comprise metallic Ni particles embedded in anodic Al_2O_3 . The initial work was by Andersson *et al.* (1980). These coatings are made in a two-step process with an initial anodization of aluminium sheet in dilute phosphoric acid. This treatment transforms the surface layer of the metal into porous Al_2O_3 with pore channels perpendicular to the surface which extend through the oxide layer. Subsequently metal is precipitated inside the pores by AC electrolysis in a bath containing nickel sulphate. Metal particles are formed as rods in the pore channels (Pontifex *et al.*, 1991) with a diameter of about 30–50 nm and a length of about 300 nm (Wäckelgård, 1996b). The pore volume fraction is about 30% (Pavlovic and Ignatiev, 1986). By using other metal sulphates in the second step, one can precipitate particles of other metals. A detailed study of the relation between deposition conditions and spectral selectivity is reported in Uchino *et al.* (1979). Coating thickness optimization is discussed by Wäckelgård *et al.* (1990). In essence, the coating comprises a nickel pigmented Al_2O_3 layer located under a porous Al_2O_3 layer. The porosity is highest at the outer surface. The bottom of the coating consists of a thin compact Al_2O_3 sheath serving as diffusion barrier. The main part of Figure 3.4(b) shows spectral reflectance for a commercial $\text{Ni-Al}_2\text{O}_3$ coating produced by Sunstrip in Sweden. Showa Aluminum Co. in Japan has also produced this type of coating. The Sunstrip coating has $A_{\text{sol}} \approx 0.96$ and $E_{\text{therm}}(100^\circ\text{C}) \approx 0.15$, while the Showa coating has $A_{\text{sol}} \approx 0.93$ and $E_{\text{therm}}^n(100^\circ\text{C}) \approx 0.13$ (Carlsson *et al.*, 1994).

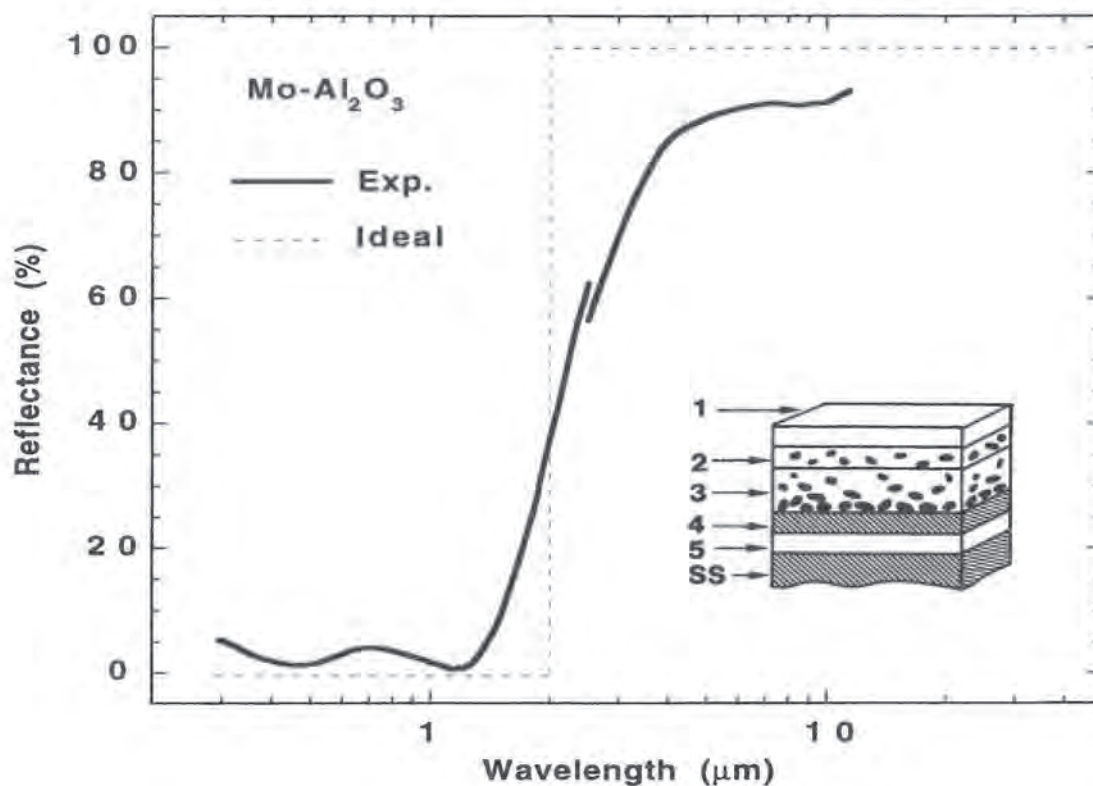
Chemical conversion

Among the coatings that have been commercially produced, one should note a chemically treated rough nickel surface, known under the trade name MAXORB (Mason and Brendel, 1982). The spectral selectivity of this absorber is very good with $A_{\text{sol}} \approx 0.97$ and $E_{\text{therm}}(100^\circ\text{C}) \approx 0.08$.

Evaporation

A selective solar absorber consisting of a cermet of TiN_xO_y on copper and AR coated with silicon dioxide is produced by activated reactive evaporation. The titanium oxynitride has a columnar structure, and the thickness of the optimized coating is in total 150 nm including the AR layer of 95 nm (Lazarov and Sizmann, 1993). The German company TiNOX GmbH has commercialized this absorber and uses roll coating in their manufacturing

(a)



(b)

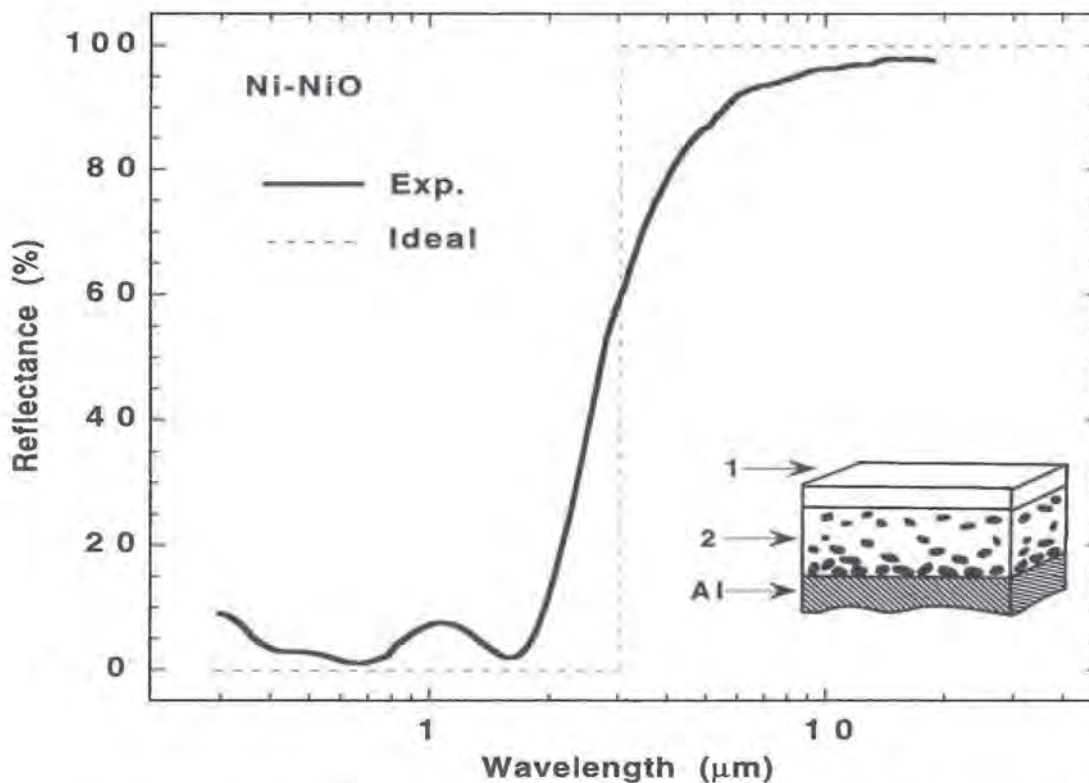


Figure 3.5 Spectral reflectance measured for sputter deposited coatings, specifically a Mo-Al₂O₃-based design from Lanxner and Elgat (1990) (a) and a Ni-NiO design from Wäckelgård and Hultmark (1998) (b). Dotted lines represent an ideal reflectance profile. The inset in part (a) shows a five-layer structure with a stainless steel (SS) substrate, Al₂O₃

(5), Mo (4), graded Mo-Al₂O₃ (3), graded Mo-SiO₂ (2), and a top layer of SiO₂ (1). The inset in part (b) shows an Al substrate, graded Ni-NiO (2) and an antireflecting layer (1).

process. The spectral selectivity is characterized by $A_{\text{sol}} = 0.95$ and a thermal emittance of 0.05 at 100°C. The absorber is thermally stable up to 400°C (Lazarov and Sizmann, 1993).

Sputtering

Lanxner and Elgat (1990) reported work on sputter deposited molybdenum-based composite coatings for use on large-scale tubular solar collectors designed to operate at $\tau > 300^\circ\text{C}$. The microstructure of the absorber, indicated in the inset of Figure 3.5(a), embodies two graded Mo-dielectric composite layers backed by an infrared reflecting molybdenum layer. An antireflecting SiO₂ layer at the top and a diffusion barrier of Al₂O₃ at the bottom complete the design. Figure 3.5(a) shows that the reflectance has a high degree of spectral selectivity, with the steepest reflectance change around $\lambda \approx 2 \mu\text{m}$. It should be remarked that the main reflectance step should occur at a shorter wavelength for a coating devised to operate at a high temperature than for one to be used at $\sim 100^\circ\text{C}$, which is easily inferred from Figure 3.2. The coating in Figure 3.5(a) is characterized by (Lanxner and Elgat, 1990) $A_{\text{sol}} = 0.97 \pm 0.01$, $E_{\text{therm}}(50^\circ\text{C}) \approx 0.10$ and $E_{\text{therm}}(350^\circ\text{C}) = 0.17 \pm 0.01$. This type of coating is used on tubular absorbers in solar thermal-electric power plants in California.

Large-scale sputtering of selectively solar-absorbing coatings has also been developed at the University of Sydney in Australia for use in all-glass concentric evacuated tubular solar collectors. A graded stainless steel carbide (SS-C) cermet on copper was developed already in the late 1970s. A cylindrical magnetron sputtering system was capable of depositing the coating on twenty glass tubes in each batch (Harding *et al.*, 1980). Sputtered SS-C absorbers have been produced by Shiroki in Japan since the 1980s. All-glass vacuum collector tubes with a solar selective graded Al-N coating on aluminium are mass produced in China (Suping *et al.*, 1992) for uses in hot water and steam applications (Zhang, 1998a). The optical performance of this absorber implies a $A_{\text{sol}} = 0.92$ and a thermal emittance of about 0.06 at 100°C (Suping *et al.*, 1992).

A new type of double-layer coating has recently been developed by Zhang (1998b) at the University of Sydney. A series of M-AlN (M for metal) cermets such as SS-AlN, NiCr-AlN, W-AlN and TZM-AlN (TZM is a molybdenum-based alloy) were sputtered on aluminium coated glass substrates. The M-AlN cermet consists of two multilayer stacks; each stack contains alternating AlN and M sub-layers of thickness less than 2 nm. The metal volume fraction was chosen to be higher in the base stack than in the top stack. An AR coating of AlN was deposited as the uppermost layer. A planar DC magnetron sputtering system was used with two sources, one

for depositing the metal sub-layers and one aluminium source for depositing the aluminium infrared reflector on the glass as well as the AlN ceramic sub-layers. The latter were deposited reactively in a gas mixture of argon and nitrogen. Collaboration between the University of Sydney, Peking University and Beijing TurboSun Co. in China has resulted in a commercial SS-AlN selective surface with the optical performance $0.94 < A_{\text{sol}} < 0.95$, $0.06 < E_{\text{therm}}^n(100^\circ\text{C}) < 0.07$ and $0.12 < E_{\text{therm}}^n(350^\circ\text{C}) < 0.14$ (Zhang *et al.*, 1998). A dual-target cylindrical DC magnetron sputter system with thirty-two glass tubes in each batch is used for the production.

Two new fin-type absorbers for flat plate collectors have been developed recently: a nickel–nickel oxide coated aluminium absorber produced by Sunstrip, Sweden, and a chrome oxide–chrome nitride coating on copper produced by Interpane, Germany. The Sunstrip absorber is deposited in a roll coater by DC magnetron sputtering. The production started in 1996. The coating unit is loaded with a 1000 m long coil of aluminium strip in each batch. The absorber layer is sputtered using three magnetrons. A metallic nickel barrier layer is deposited with the first target. The second magnetron produces a graded nickel–nickel oxide cermet by employing reactive sputtering in an oxygen-containing gas. The third target is used for making an antireflection layer. The coating is described in detail in Wäckelgård and Hultmark (1998). The cross-sectional composition of the nickel–nickel oxide absorber is seen in Figure 3.5(b).

The coating thickness is about 200 nm, including 50 nm for the AR film. The characteristics evaluated from the reflectance in Figure 3.5(b) give $A_{\text{sol}} = 0.96$ and $E_{\text{therm}}^n(100^\circ\text{C}) \approx 0.10$. The sample reported on in the figure does not have the nickel barrier layer, and the thermal emittance becomes slightly higher when such a layer is included.

The production of a sputter deposited graded chrome oxide–chrome nitride ($\text{CrN-Cr}_x\text{O}_y$) coating started in 1998 by Interpane. High solar absorptance is achieved with a high/low concentration of $\text{Cr}_x\text{O}_y / \text{CrN}$ in the base of the coating (Graf *et al.*, 1997). The CrN content is gradually increased towards the front surface, and the total thickness of the coating is about 100 nm. A DC magnetron sputter facility is used in a production line similar to the one employed for coating window glass. The optical characteristics of the coating are $A_{\text{sol}} > 0.93$ and $E_{\text{therm}}^n(100^\circ\text{C}) < 0.07$ when deposited on copper (Graf *et al.*, 1997).

Paints

Selectively solar-absorbing paints have also recently reached commercialization, and there are at least two such products on the market: the Solarect-ZTM paint developed at the National Institute of Chemistry in Ljubljana, Slovenia, and the SolkoteHI/SORB-IITM paint sold by SOLEC (Solar Energy Corporation), USA.

The Solarect-ZTM paint is prepared from an organically modified siloxane resin and an inorganic pigment of FeMnCuO_x -P320 (Orel, 1999) with a

pigment volume fraction of about 0.2. It is a TSSS paint, which implies that low thermal emittance is achieved by using thin layers, being only 2 to 3 μm thick (Gunde *et al.*, 1996). The optical performance is characterized by $0.90 < A_{\text{sol}} < 0.92$ and $0.20 < E_{\text{therm}}^n(100^\circ\text{C}) < 0.25$ for coatings deposited by a draw bar coater on highly reflecting aluminium foil (Orel, 1999). The siloxane resin used in TSSS paints has less infrared absorption than most other binders. It is shown in Figure 3.6 that the main absorption of the resin is due to vibrational modes of siloxane Si–O–Si bonds in the wavelength range 8–10 μm . The Solarect-ZTM paint is stable up to 300°C when deposited on aluminium (Orel, 1999). The reflectance curve in the figure stems from a Solarect-ZTM spray painted sample backed by rolled aluminium.

The Solkote product is also a TSSS paint and contains a binder consisting of 100% silicone polymer. It is high temperature stable and can be used up to 530°C. Depending on the substrate and coating thickness, a solar absorptance of 0.88 to 0.94 and a thermal emittance of 0.28 to 0.49 can be obtained. The absorber can be coated using simple spray guns, such as those used in automotive body repair facilities.

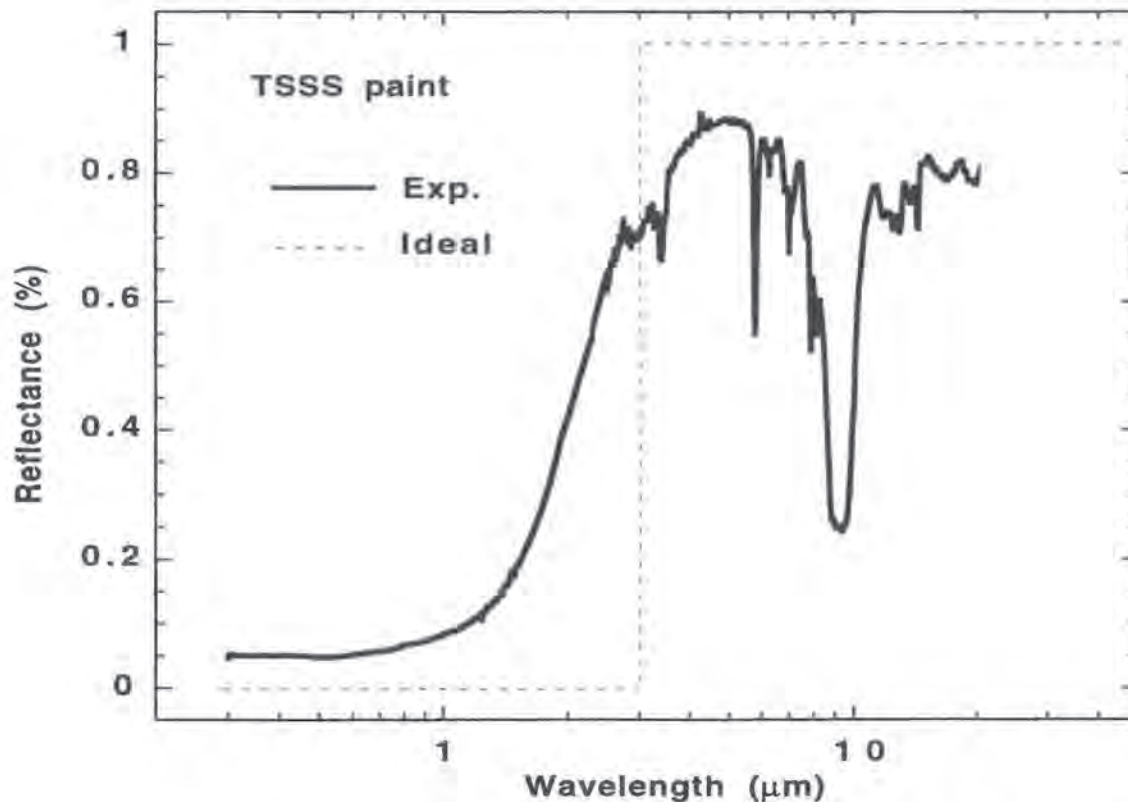


Figure 3.6 Spectral reflectance of a Solarect-ZTM thickness sensitive spectrally selective paint sprayed onto an aluminium substrate. Dotted lines represent an ideal reflectance profile.

3.3 MODELS FOR MICROSTRUCTURE AND OPTICAL PROPERTIES

The previous section pointed out that most commercially produced selectively solar-absorbing coatings consist of a mixture of metallic particles in a dielectric matrix and are backed by a metallic substrate. Commercial coatings are still largely produced by electrochemical methods, but physical vapour deposition techniques are employed for most of the new solar absorbers. Physical vapour deposition has been widely used in basic work to extract detailed information about the relation between microstructural parameters of the coatings and their optical properties and spectral selectivity. This section considers microstructural models based on characterization studies of the pertinent coatings. These models are then used to discuss theories for the optical properties of selectively solar-absorbing surfaces with a metal-dielectric composite configuration.

3.3.1 Microstructure

A distinction can be made between metal-dielectric composites with homogeneous and with graded composition. A homogeneous layer has the same structure throughout, while a graded layer displays a metal content that varies with the depth in the layer. In practice, it is advantageous to have a metal content that is high close to the substrate and continuously decreasing towards the front surface. Thin film optical interference is suppressed in this structure. However, grading with a too high metal content in the base layer will cause an increase in thermal emittance since the base of the graded coating will act as a poor infrared reflector (Buhrman, 1986).

A large amount of research has been carried out on metal-dielectric composites (Niklasson and Granqvist, 1983). A single composite layer on top of a metal substrate does not usually give sufficient solar absorptance and therefore more complicated designs have to be used. There are basically two ways to improve the optical properties of the coatings; they are shown schematically in Figure 3.7. First, one may use AR coatings on top of the composite layer. This 'Type I' design consists of, in order from the bottom up, a metal substrate, a metal-dielectric composite layer, an AR layer usually comprising a dielectric, and a rough surface layer that may or may not be present. The outermost rough surface layer can be regarded as a composite of dielectric and air. This Type I configuration is often used in selective solar absorbers produced by evaporation and sputtering. The absorbing layer usually consists of a transition metal dispersed in an oxide. In general, one can obtain $A_{\text{sol}} \approx 0.95$ and $E_{\text{therm}}^n(100^\circ\text{C})$ ranging from 0.05 to 0.10. Among the commercially used coatings, it has been shown by Andersson *et al.* (1980) that the structure of metal pigmented anodic aluminium oxide solar absorbers is well represented by the Type I configuration. The model describes the optical properties of the coatings as well as the degradation of the solar absorptance at high temperatures, as discussed below.

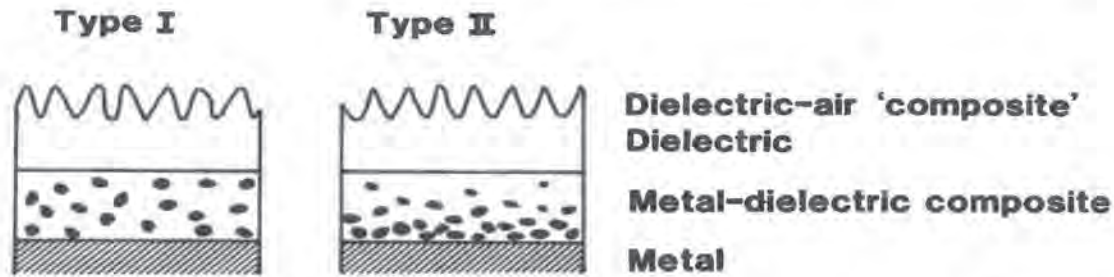


Figure 3.7 Microstructural models for selectively solar-absorbing coatings.

In the second configuration (denoted 'Type II' in Figure 3.7), the homogeneous metal–dielectric composite layer is replaced by a graded one, but otherwise the design is similar to that of Type I. As before, the upper dielectric–air layer may or may not be present. The Type II structure is in principle able to give a higher A_{sol} than the Type I structure, but in most cases the improvement is not very large.

Chemically and electrochemically deposited coatings display a very complex structure with graded or homogeneous composite layers, voids, oxide films, surface roughness, etc. This makes the modelling of their optical properties more difficult than for the sputtered and evaporated coatings. However, in many cases the Type II configuration in Figure 3.7 appears to be a suitable qualitative model for selective solar absorbers with a complex microstructure. Black chrome is known to have a very complicated structure (*cf.* Figure 3.4(a)), and grading models have been tried in order to describe its optical properties (Sweet *et al.*, 1984, Ritchie *et al.*, 1979/80). Sputtered cermetes can also be made graded, for example as in the Sunstrip nickel–nickel oxide absorber and the AlN cermet produced on all-glass evacuated tubes described in Section 3.2.

3.3.2 Effective medium theories for the optical properties

The microstructural models in Figure 3.7 form a suitable starting point for optical modelling by the use of an Effective Medium Theory (EMT). This section considers models for the metal–insulator composite layers. It is of prime importance to establish the connection between the properties of the composite and those of the constituents. This facilitates materials selection and optimization of practical coatings. The optical properties of composite materials can be described in the quasistatic approximation if the size of the inhomogeneities is much smaller than the wavelength of the electromagnetic radiation. The optical properties of the material are obtained from the effective dielectric permeability of the composite, which can be related to the dielectric permeabilities of the constituents in the EMTs (Landauer, 1978, Aspnes, 1982, Niklasson and Granqvist, 1986). These theories are also sensitively dependent upon the actual microgeometry of the composite material. Actually a rigorous expression for the effective dielectric permeability can

only be obtained if the detailed geometrical arrangement of the constituents is known. When limited structural information is available, as is always the case in practice, the various EMTs can give no more than approximate expressions.

The microstructure is first represented by Random Unit Cell (RUC) models, which are simple enough to permit a theoretical treatment and yet do not leave out the essential physics. Figure 3.8(a) and (b) show two cases which are regarded as typical: a separated-grain structure, with particles of 'A' embedded in a continuous host of 'B', and an aggregate structure in which 'A' and 'B' enter on an equal footing to form a space-filling random mixture. RUCs are now defined (Niklasson *et al.*, 1981, Niklasson and Granqvist, 1986, Smith, 1977, 1979) so as to account for the major features of the microstructures. The RUC is taken to be embedded in an effective medium, whose properties are as yet undefined. For the separated grain structure, the RUC is a core of 'A' surrounded by a concentric shell of 'B', as depicted in Figure 3.8(c). The ratio of the core volume to the total volume is equal to f_A . For the aggregate structure, the inherent structural equiva-

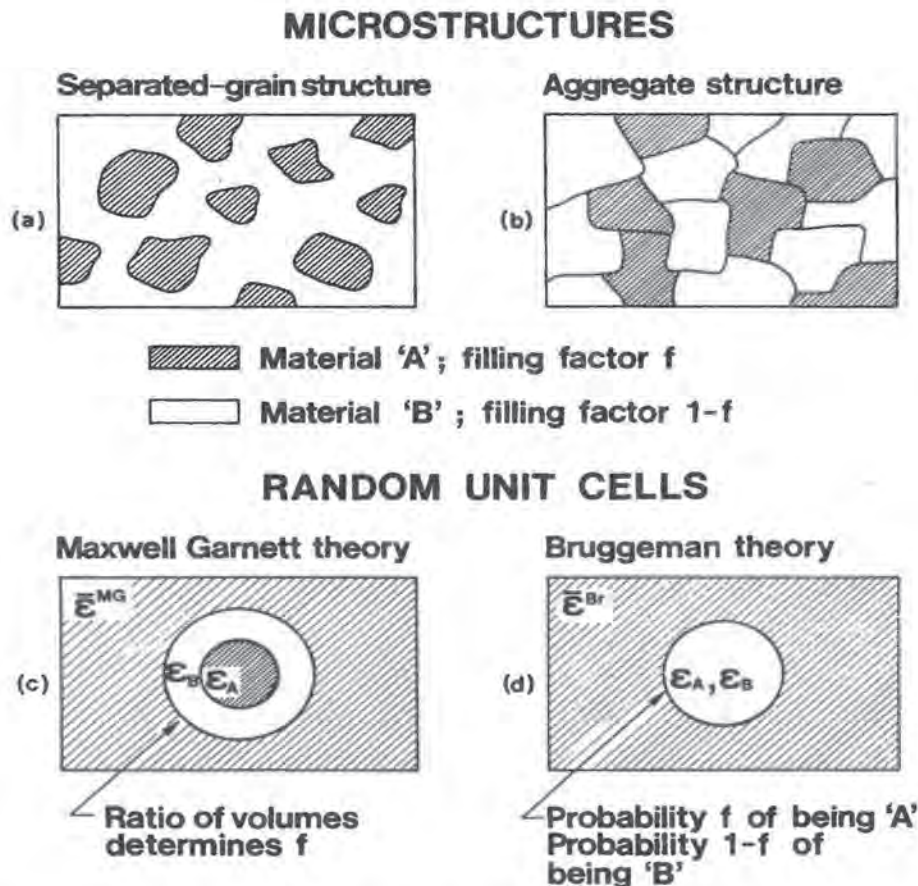


Figure 3.8 Parts (a) and (b) depict two microstructures of two-phase composite materials. Parts (c) and (d) show the corresponding RUCs used to derive the Maxwell Garnett and Bruggeman EMTs. The RUCs are embedded in the effective media (from Niklasson and Granqvist, 1984).

lence of the components is ensured by letting the RUC have a probability f_A of being 'A' and a probability f_B of being 'B', as shown in Figure 3.8(d). The RUC is spherical or non-spherical depending on the shape of a 'typical' particle.

The basic definition of an effective medium is that the RUC, when embedded in the effective medium, should not be detectable in an experiment using electromagnetic radiation confined to a specific wavelength range. In other words, the extinction of the RUC should be the same as if it were replaced with a material characterized by $\bar{\epsilon}$, the effective dielectric permeability. EMTs are first derived for RUCs with a spherical geometry; these results are then extended to the case of spheroids. The scattering of the RUC can be written from Lorenz-Mie theory (Kerker, 1969, Hulst, 1981, Bohren and Huffman, 1983) as an expansion in (kb) where b is the RUC radius and k the wave vector of the interacting electromagnetic wave.

The Maxwell Garnett (MG) theory (Garnett, 1904, 1906) corresponds to the RUC in Figure 3.8(c). By taking the first term in the series expansion appropriate to a coated sphere (Kerker, 1969, Bohren and Huffman, 1983) and applying the condition of zero scattering for the RUC in the effective medium, one obtains a well known expression for small spheres, namely

$$\overline{\epsilon}^{\text{MG}} = \epsilon_B \frac{\epsilon_A + 2\epsilon_B + 2f_A(\epsilon_A - \epsilon_B)}{\epsilon_A + 2\epsilon_B - f_A(\epsilon_A - \epsilon_B)} \quad (3.4)$$

with

$$f_A = \frac{a^3}{b^3} \quad (3.5)$$

Here a signifies the radius of the sphere of material 'A' and b the radius of material 'B'. Equation 3.4 is the constitutive formula for the Maxwell Garnett EMT. By making the replacements $A \leftrightarrow B$, one obtains analogous relations for the inverted structure. This derivation does not require that f_A is small. However, it is clear that for a sufficiently large filling factor one reaches a point where the detailed particle-particle interactions must be considered explicitly. Obviously, such structural multipole features can not be encompassed by the MG approach, but supplementary information is demanded. To shed some light on this issue, it could be noted that the Maxwell Garnett theory is in acceptable agreement (Perrins *et al.*, 1979) with exact theories (McKenzie *et al.*, 1978, Doyle, 1978, McPhedran and McKenzie, 1978) for cubic arrangements of identical spheres as long as $f_A < 0.4$. For aperiodic arrangements – such as those normally occurring in experimental samples – the structural multipoles are expected (Lamb *et al.*, 1980) to set in at lower filling factors since close approaches among the spheres are permitted.

The MG theory can be extended to the case of spheroidal RUCs. This is not trivial, as discussed in Niklasson and Granqvist (1984, 1986), but

depends on the shape of the shell in the RUC. The shape of the spheroid is described by a set of three effective depolarization factors, L_i , with values between zero and unity. Their sum is equal to one and the subscript $i = x, y, z$ denotes the directions of the principal axes. Two of the principal axes are equal for a spheroid, and hence $L_x = L_y = (1 - L_z)/2$. When the shell in the RUC has the same depolarization factors as the inner particle, a simple result is obtained for the case of aligned spheroids with their major axes pointing in the same direction, namely

$$\overline{\varepsilon}^{\text{MG}} = \varepsilon_B + \frac{f_A \varepsilon_B (\varepsilon_A - \varepsilon_B)}{\varepsilon_B + L f_B (\varepsilon_A - \varepsilon_B)} \quad (3.6)$$

Light incident along the major axes (the z -direction) was considered in this case, and hence the depolarization factor pertaining to the x - and y -directions should be used in the formula. The situation becomes much more complicated for randomly oriented ellipsoids and one has to devise a scheme for averaging over the three principal axes.

The Bruggeman theory (1935) is derived from the RUC in Figure 3.8(d). One can use the series expansion for a sphere (Kerker, 1969, Hulst, 1981, Bohren and Huffman, 1983) and obtain in the small sphere limit

$$f_A \frac{\varepsilon_A - \overline{\varepsilon}^{\text{Br}}}{\varepsilon_A + 2\overline{\varepsilon}^{\text{Br}}} + (1 - f_A) \frac{\varepsilon_B - \overline{\varepsilon}^{\text{Br}}}{\varepsilon_B + 2\overline{\varepsilon}^{\text{Br}}} = 0 \quad (3.7)$$

Here f_A is the probability that the RUC has $\overline{\varepsilon} = \varepsilon_A$ and f_B is the probability that it has $\overline{\varepsilon} = \varepsilon_B$. Equation 3.7 is the constitutive formula for the Bruggeman theory. For high f_A s, the structural multipole effects are expected to enter as for the MG theory, but no detailed study has yet appeared. Note that Equation 3.7 is symmetrical with respect to exchange of the components of the material.

The generalization to the case of randomly oriented spheroids is straightforward. It is obtained by first modifying Equation 3.7 to include the L_i s describing the geometry of the spheroids and then averaging over the three principal directions. The result becomes

$$\sum_i \left\{ f_A \frac{\varepsilon_A - \overline{\varepsilon}^{\text{Br}}}{\varepsilon_A + L_i(\varepsilon_A - \overline{\varepsilon}^{\text{Br}})} + (1 - f_A) \frac{\varepsilon_B - \overline{\varepsilon}^{\text{Br}}}{\varepsilon_B + L_i(\varepsilon_B - \overline{\varepsilon}^{\text{Br}})} \right\} = 0 \quad (3.8)$$

The limits of validity of the simple EMTs can be assessed by computing the contribution of the higher order terms of the Lorenz-Mie expansion to the effective dielectric permeability (Niklasson and Granqvist, 1984, 1986). These large-size limits depend on the filling factor, the wavelength and the dielectric permeabilities of the constituent materials, and no general rules can be given. However, for the case of metal-insulator composites it appears that the diameter of the metal particles should be less than $\sim \lambda/20$ in order that the EMTs remain accurate (Niklasson and Granqvist, 1984, 1986).

Effective medium theory is often used to represent the effects of surface roughness on the optical properties. The surface roughness is then modelled as a graded composition profile of the coating material and air. The profile of the dielectric permeability is derived from the composition profile by using EMTs (Stephen and Cody, 1977). This approach works well when the period of surface roughness is much less than λ , although the volume fraction to be used in the EMT and the modelled thickness of the grading do not always correspond to the physical values (Rönnow *et al.*, 1995). The limit of validity of EMTs depends also on the height of the surface roughness (McPhedran *et al.*, 1982). The period and height of the surface roughness in electrochemically deposited coatings can be far outside the limits of validity of EMT. One example is the black chrome coatings studied by Smith *et al.* (1985), for which the optical properties were modelled by diffraction theory instead of by EMT.

3.3.3 Computational procedures for multilayered coatings

The EMTs treated in Section 3.3.2 can be used to derive the dielectric permeabilities of the inhomogeneous layers indicated in Figure 3.7. This kind of theory will be used to describe the surface as well, keeping in mind the problems associated with EMTs in the case mentioned above. The next step in the analysis entails calculations of the reflectance of multilayered thin films from the optical properties of the individual layers. Graded layers can also be treated as multilayers, i.e., the grading profile can be approximated by a large number of superimposed homogeneous layers. The optical properties of a multilayer thin film can be calculated by standard methods (see, for example, Born and Wolf (1980)). The basic steps are as follows:

- (a) First the wavelength dependent dielectric permeability $\varepsilon(\lambda)$ of the various layers needs to be known. For composite layers, EMT can be used for this purpose, provided that the dielectric permeabilities of the components and the composition are known. The most widely used EMTs are those of Maxwell Garnett (1904, 1906) and Bruggeman (1935). The permeabilities of the constituents of the AR coating and the metal substrate may be obtained from independent measurements or from extensive tables that are readily available (Weaver *et al.*, 1981, Palik, 1985).
- (b) This information, together with the thickness d of the individual layers, can now be used to obtain the optical response of the multilayer stack. The most convenient way is probably the method of characteristic matrices (Born and Wolf, 1980). The characteristic matrix $\mathbf{m}$ of a single layer is written as

$$\mathbf{m} = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} \quad (3.9)$$

where (Born and Wolf, 1980)

$$m_{11} = m_{22} = \cos [2\pi n(\lambda) d \cos \theta / \lambda] \quad (3.10)$$

The complex refractive index $n(\lambda)$ is the square root of the dielectric permeability. The other components of the matrix are given by (Born and Wolf, 1980)

$$m_{12} = -i \sin [2\pi n(\lambda) d \cos \theta / \lambda] / P \quad (3.11)$$

and

$$m_{21} = -iP \sin [2\pi n(\lambda) d \cos \theta / \lambda] \quad (3.12)$$

Here $P = \sqrt{\epsilon/\mu} \cos \theta$ for s-polarized light and $P = \sqrt{\mu/\epsilon} \cos \theta$ for p-polarized light, where μ is the magnetic permeability (which often can be set to unity). With knowledge of the characteristic matrices of the various layers in the stack, it is now fairly simple to obtain the resulting optical response. It can be shown (Born and Wolf, 1980) that the characteristic matrix $\mathbf{M}$ of the multilayer stack is simply the product of the matrices of the constituent layers.

- (c) The final part of the analysis considers a stack with layers numbered from 1 at the surface to N at the substrate. Since opaque metallic substrates are of interest, only the reflection from the system is non-zero. The reflection coefficient r of the multilayer film is then obtained from (Born and Wolf, 1980)

$$r = \frac{(M_{11} + M_{12}P_{N+1})P_0 - (M_{21} + M_{22}P_{N+1})}{(M_{11} + M_{12}P_{N+1})P_0 + (M_{21} + M_{22}P_{N+1})} \quad (3.13)$$

Here P_0 and P_{N+1} denote the values of the quantity P defined above for the medium of incidence and the substrate, respectively. Finally, the reflectance is given by $R = |r|^2$.

3.4 THE USE OF MODELLING

Modelling can be used for different purposes, such as optimization of solar selectivity, or for understanding basic physical and optical properties of complex thin film structures. The subsections below present some examples of different applications of modelling used in the research on solar absorbers.

3.4.1 Theoretical optimization of selectively solar-absorbing surfaces

The modelling of selectively solar-absorbing surfaces has mainly been used in the design of physical vapour deposited coatings, since layer thickness

and mixture of constituents in a composite can be controlled on a nano-scale level. In the optimization of the $\text{CrN-Cr}_x\text{O}_y$ coating produced by Interpane, the relation between structural parameters and process variables was determined and used in the modelling (Graf *et al.*, 1997). Also Zhang (1998a) used modelling for the design of the sputtered SS-AlN double layer cermets. However, it is difficult to reach the same optical performance for the real samples as for the optimized, modelled samples, and the models then serve as theoretical limits for what can be obtained in the ideal case.

3.4.2 Microstructure evaluation from modelling

Filling factors and particle shape can be determined indirectly by fitting calculated reflectance of EMT modelled coatings to experimental reflectance data. However, the correlation between fitted and directly measured values is seldom good. Reasons for this discrepancy can be that features in the real structure, such as size and distribution of particles, are difficult to determine in direct microscopic observations, especially for nano-size crystalline or amorphous structures. Clustering of small metallic particles, and irregular shape of particles, provide other examples when Maxwell Garnett and Bruggeman EMTs are not strictly applicable but still used in modelling. The exact chemical composition can also be hard to define since the coatings always contain impurities. Thus the chemicals of the baths can be incorporated in films produced by wet processes, while the deposition system can contribute water vapour due to outgassing for the case of vacuum techniques. Contamination often shows up as hydroxide in reactively sputtered oxide films (Wäckelgård and Hultmark, 1998). For well defined two-component materials, with gold pigmented anodized aluminium oxide being a typical example, one can obtain good agreement between fitted and experimental structural parameters, such as film thickness and volume fraction of metal (Foss *et al.*, 1994).

When simple mathematical models such as the Maxwell Garnett EMT are used, it is often found that the theoretical metal content lies below the experimental value (Smith *et al.*, 1998). Both the Maxwell Garnett and the Bruggeman EMT treat the particles as isolated from each other, thereby neglecting the polarization effect from the surrounding particles. Smith *et al.* (1998) have made a theoretical investigation and compared the Maxwell Garnett EMT with models which explicitly treat particle interaction. They found that the filling factors appropriate for the MG theory were too low and interpret this as an effect of screening of the applied field by the induced polarization due to the surrounding particles. This effect implies that the particles appear to be smaller than they actually are.

3.4.3 Evaluation of solar absorbers by the use of models

Solar absorbers have to withstand climatic effects during their service lifetime in the solar collector. Studies of absorber degradation have accompanied

the development of absorbers closely, since stability of absorber materials is as crucial as their optical performance.

One major effect on solar absorber coatings of the cermet type is oxidation of the metallic component taking place at elevated temperatures. The following two examples show clearly how modelling with EMT can be used to determine the oxidation progress in the coating. The first example considers aged Ni-Al₂O₃ coatings and investigates the structural modifications which lead to the observed changes in the optical spectra. After heat treatments in air at elevated temperatures, the optical properties of the Showa and Sunstrip nickel pigmented alumina coatings change in the same way. The main effect is a gradual increase in the reflectance at $\lambda > 1 \mu\text{m}$ as the heat treatment progresses, as clearly seen in Figure 3.9 which depicts data (Carlsson *et al.*, 1994) for the Showa coating. Qualitatively similar results were obtained for Sunstrip (Carlsson *et al.*, 1994). This effect leads to a gradual lowering of A_{sol} . One can see also a slight shift to shorter wavelengths of the peak at about $1 \mu\text{m}$. In the infrared, one can notice that the reflectance increases (Carlsson *et al.*, 1994), which suggests that oxidation of the nickel particles is the main degradation mechanism.

The oxidation of the nickel in the coating can be described through two limiting models (Niklasson, 1990). One possibility is that the oxidation of nickel in layer 3 (referring to the inset in Figure 3.4(b)) takes place uniformly

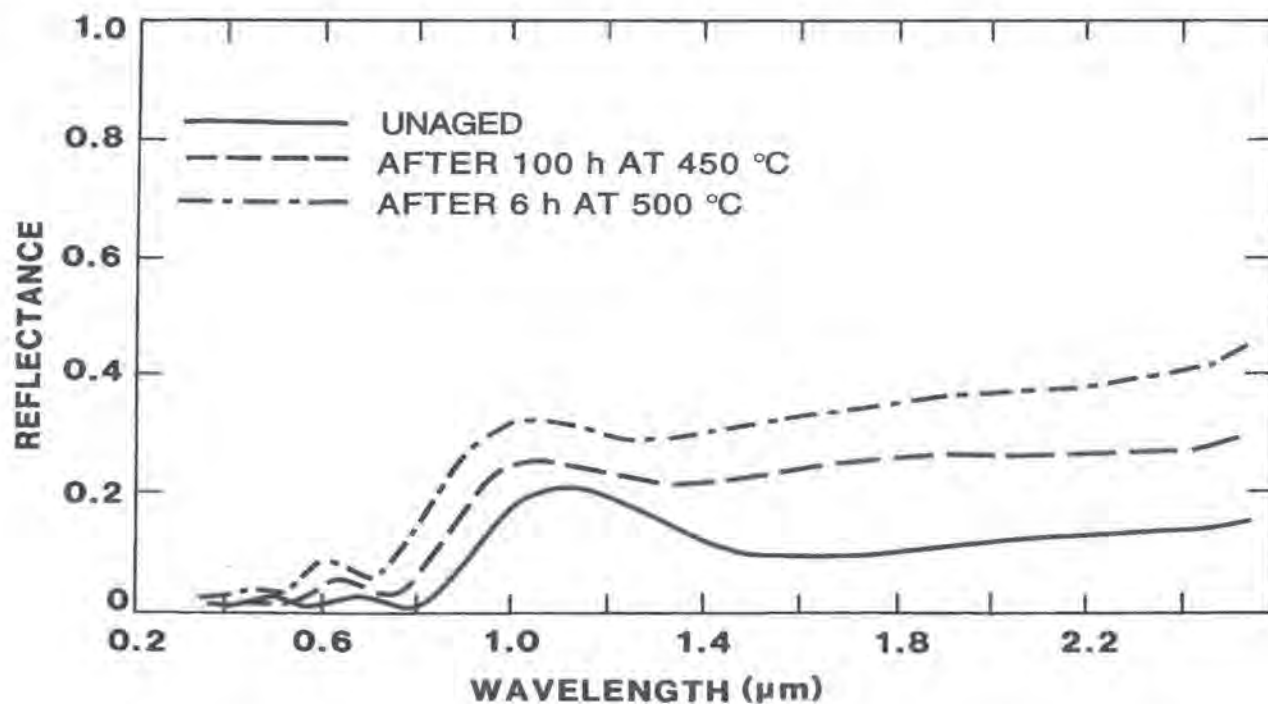


Figure 3.9 Experimental spectral reflectance for nickel pigmented anodic aluminium oxide coatings produced by Showa. The continuous curve shows results for an unaged coating, while dashed and dash-dotted curves refer to aged coatings as indicated (from Carlsson *et al.*, 1994).

throughout the layer. In this case the filling factor decreases as degradation proceeds, but the thickness of layer 3 remains constant. Model calculations for this case are shown in Figure 3.10(a) with parameters pertinent to the Showa coating. The EMT of Bruggeman is used for obtaining the effective optical constants of the cermet layers. The calculations reproduce the qualitative features of the experiments, except that the shift of the peak at $\sim 1 \mu\text{m}$ appears to be larger in the experimental data. Furthermore, the experiments show very flat reflectance curves at $\lambda > 1.5 \mu\text{m}$, while the calculated reflectance goes up somewhat with increasing wavelength. However, these discrepancies are only minor, and one can be confident that the degradation mechanism is a rather uniform oxidation of the nickel particles throughout the composite layer.

Secondly, an oxidation front may proceed into the coating, causing layer 3 to gradually decrease and layer 2 to increase as degradation continues. This possibility is explored in Figure 3.10(b), which presents calculations pertinent to the Showa coating with $f = 0.23$ and various values of the thickness of layer 3. The nickel content is given by the relative value Q , which is defined by

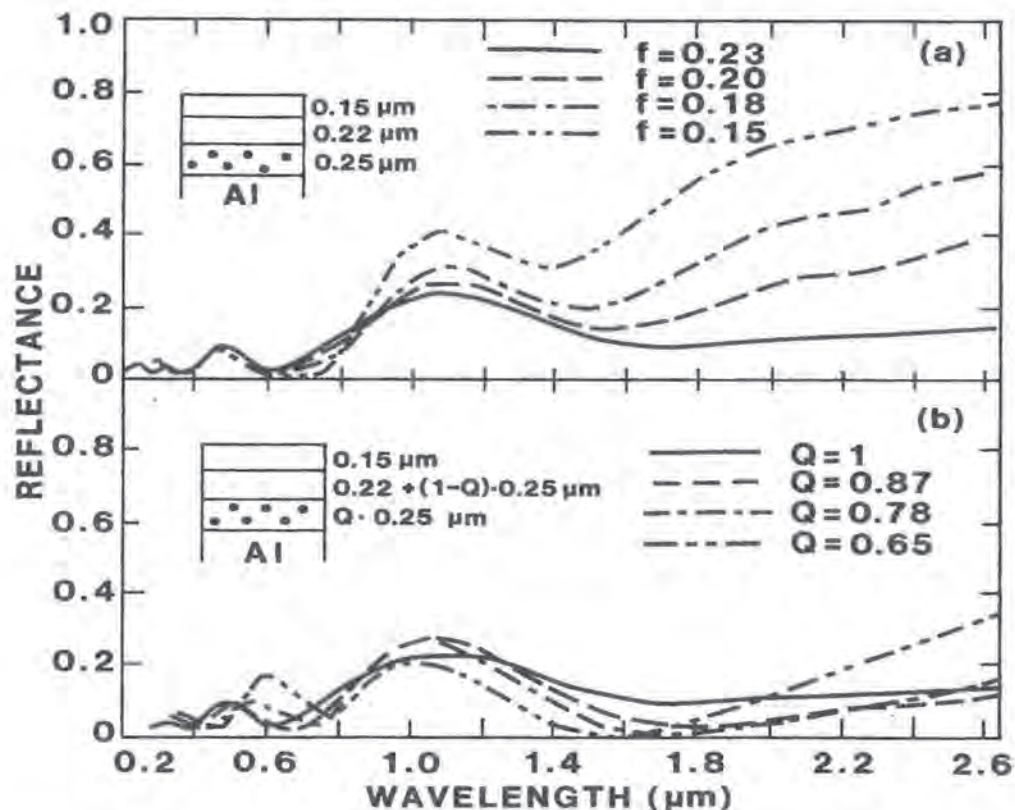


Figure 3.10 Calculated spectral reflectance for nickel pigmented aluminium oxide coatings. Parameters pertinent to the Showa coating were used. The insets indicate the layers 1 to 3 of Figure 3.4(b). Parts (a) and (b) refer to uniform oxidation of Ni particles and to a progressing oxidation front, respectively, with f denoting Ni filling factor and Q denoting normalized Ni content (from Niklasson, 1990).

$$Q = W/W_0 \quad (3.14)$$

where W is the actual nickel metal content and W_0 denotes the initial nickel metal content. In Figure 3.10(b), Q is the ratio of the composite layer thickness after and before degradation. The values of Q were chosen so that they should be the same as in the calculations in Figure 3.10(a), where Q is simply given by the ratio of the actual filling factor to its initial value. It is seen in Figure 3.10(b) that only slight changes in the reflectance spectra occur as Q decreases, and in fact A_{sol} actually increases somewhat. This is clearly in contradiction to the experimental results, and therefore the oxidation front model cannot explain the experimental spectra of heat treated samples. Calculations for the Sunstrip coating yielded the same qualitative features.

The high temperature stable, sputter deposited Mo-Al₂O₃ graded cermet, described in Section 3.2, has been exposed to temperatures between 400 and 850°C in a low-pressure atmosphere (Gatt *et al.*, 1992). The reflectance was modelled using a multilayer stack for the grading, and the Bruggeman EMT was used to model each sub-layer. The same models as above for front- and uniform oxidation were exploited, and in this case the front oxidation model provided the best fit of the change in experimental spectral reflectance with time of exposure (Gatt *et al.*, 1992).

3.4.4 Modelling used to elucidate some physical phenomena

The interaction between electromagnetic fields and materials such as cermets and multilayer coatings is not always easy to predict without performing the type of modelling described in Sections 3.3.2 and 3.3.3. This point is elaborated next in two examples for which simulations have been used to understand the results of optical measurements: angular dependent solar absorptance, and angular dependent thermal emittance.

Modelling has been used to interpret the observed difference in angular dependent solar absorptance between a sputtered Ni-NiO graded cermet and an electrodeposited Ni-Al₂O₃ cermet. The two coatings are commercial and were manufactured by Sunstrip on the same rolled aluminium sheet. As seen in Figure 3.11, the solar absorptance of the Ni-Al₂O₃ sample remains high at larger angles of incidence than for the Ni-NiO sample. Both are selectively solar-absorbing cermets but of different microstructure, as described in Section 3.2.2. The aim of the study was to investigate which of the structural parameters had the dominating influence on the angular absorptance (Tesfamichael *et al.*, 1999). Bruggeman EMT was used to represent the effective optical constants. In the model of a sputter deposited 0.2 µm thick coating, the grading was approximated with eight homogeneous sub-layers with a linear increase in volume fraction of metal with coating depth. The front surface layer had no metal and the base layer had a filling factor of 0.6. The Ni-Al₂O₃ cermet was modelled with a pure

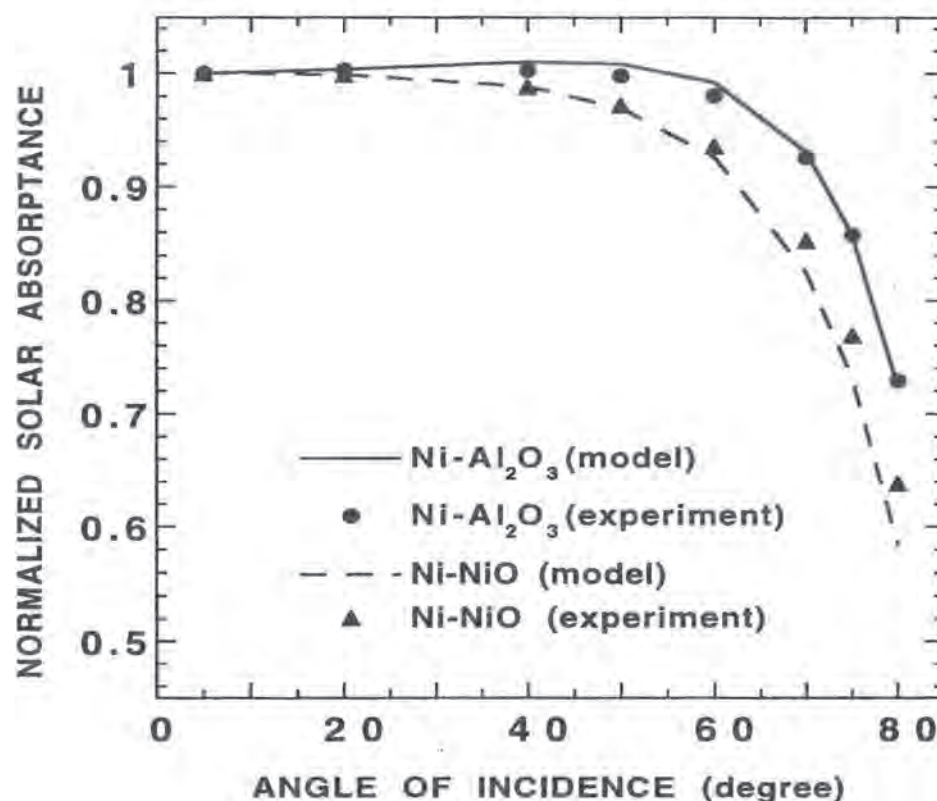


Figure 3.11 Angular dependent solar absorptance, normalized to the value at 5° angle of incidence, for electrochemically deposited Ni-Al₂O₃ and sputter-deposited Ni-NiO. Symbols (curves) denote experimental (calculated) data (from Tesfamichael and Wäckelgård, 1999).

amorphous layer of 0.2 μm thickness on top of a nickel pigmented 0.3 μm thick alumina base layer with cylindrical nickel rods having their long axes perpendicular to the surface plane. The volume fractions of air in the alumina top layer and of nickel in the base layer were set to 0.3. Figure 3.11 presents the calculated angular solar absorptance of the two coatings. The difference in these data at high angles of incidence depends mainly on the layer structure. It was found that the thickness of the pure alumina top layer is crucial for maintaining high solar absorptance in a wide angular interval. This could be deduced from simulations in which the thickness of the alumina top layer and the nickel filled base layer were varied. The calculations were also performed for spherical particles, and it was found that the angular solar absorptance was almost the same as for cylindrical particles. Thus, surprisingly, the shape of the metal inclusions has a very small effect on the angular absorptance. One might have expected that Ni-Al₂O₃, with nickel rods perpendicular to the surface, which is highly anisotropic would give rise to polarization effects in the absorptance for non-normal angles of incidence.

Angular dependent thermal emittance has been studied for electrochemically deposited Ni-Al₂O₃ (Wäckelgård, 1996b). Thermal emittance of pure

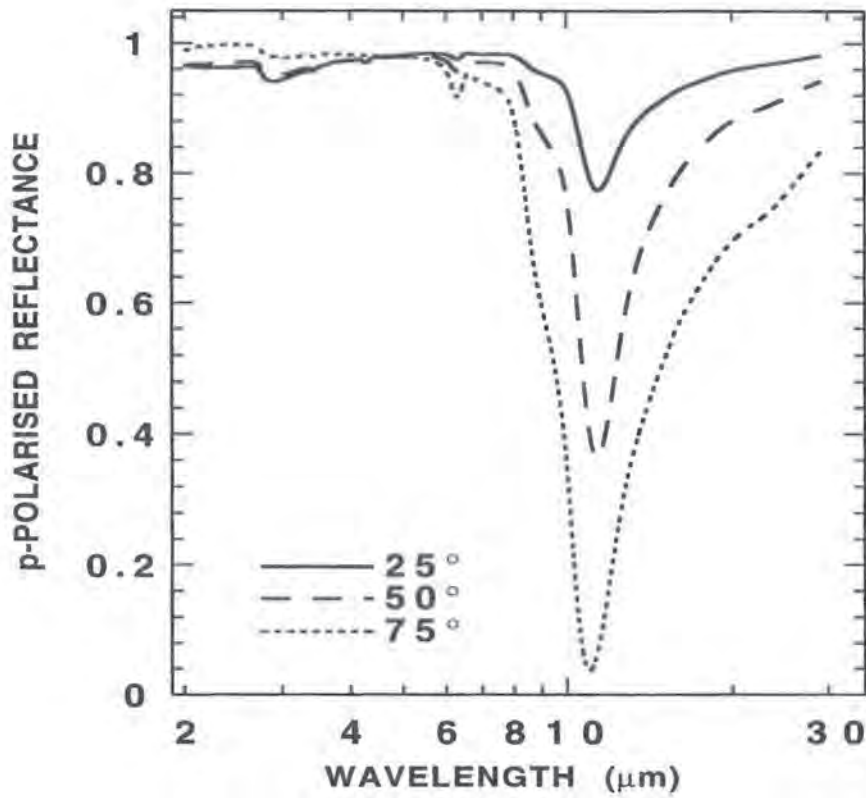
alumina increases with thickness and is larger for oblique than for normal angle of emission (Eriksson *et al.* 1981). This is due to the longitudinal optical (LO) phonon mode of alumina which is active around $11\text{ }\mu\text{m}$. The LO phonon mode is broad for the anodic oxide because of its amorphous structure. Figure 3.12(a) presents the experimental p-polarized infrared reflectance around the LO phonon vibrational mode for a $0.5\text{ }\mu\text{m}$ thick pure anodic aluminium oxide layer on a highly reflecting, smooth aluminium substrate. The LO mode absorption is manifested as a reflectance dip (Berreman 1963) around $11\text{ }\mu\text{m}$ for non-normal angles of incidence. Figure 3.13 shows the angular dependent emittance of this alumina obtained by integrating over the measured wavelength range according to Equation 3.2a for each angle of incidence. The angular dependent emittance values presented in Figure 3.13 are multiplied by $\cos\theta$, being the surface projection factor. By integration over the measured angular range as in Equation 3.2b, one obtains $E_{\text{therm}}(100^\circ\text{C}) = 0.09$. When the alumina is pigmented the reflectance increases in the LO mode wavelength range, as seen in Figure 3.12(b). The angular dependent emittance is higher at near-normal angles but has lower values than for the pure alumina at higher angles (Figure 3.13). Integration over measured angles gives $E_{\text{therm}}(100^\circ\text{C}) = 0.10$. This alumina coating is pigmented in a $0.3\text{ }\mu\text{m}$ thick base layer of the $0.5\text{ }\mu\text{m}$ thick oxide. Samples with different thicknesses of the pigmented base layer were prepared, and one can observe in Figure 3.14(a) that the reflectance increases in the LO mode wavelength range when the thickness of the pigmented layer increases.

Maxwell Garnett EMT was used to model the effective optical constants of a two-layer Ni- Al_2O_3 cermet. The reflectance was calculated for different thicknesses of the pigmented base layer with the restriction that the total oxide thickness was kept at $0.5\text{ }\mu\text{m}$. It is clear from Figure 3.14(b) that the theoretical reflectance follows the same behaviour as the experimental one in Figure 3.14(a). For pigmentation to the front surface (i.e., no pure top oxide), the LO mode absorption is completely quenched. The quenching originates from the high electric field at the long side surface of the nickel rods induced by the incident p-polarized electromagnetic wave. The conclusion from this investigation of the thermal emittance of Ni- Al_2O_3 is that the pure alumina top layer should be thin in order to reduce the contribution from the LO mode to the thermal hemispherical emittance. This has also been proposed by Wäckelgård *et al.* (1990).

3.5 DEGRADATION AND DURABILITY

Durability and degradation are extremely important for the technical application of selectively solar-absorbing coatings. Degradation studies, and the determination of service lifetime of solar absorbers from accelerated ageing tests, has been of interest for a long time. The most rigorous report on the subject is entitled *Accelerated Life Testing of Solar Energy Materials*, published by the Working Group of the International Energy Agency Task

(a)



(b)

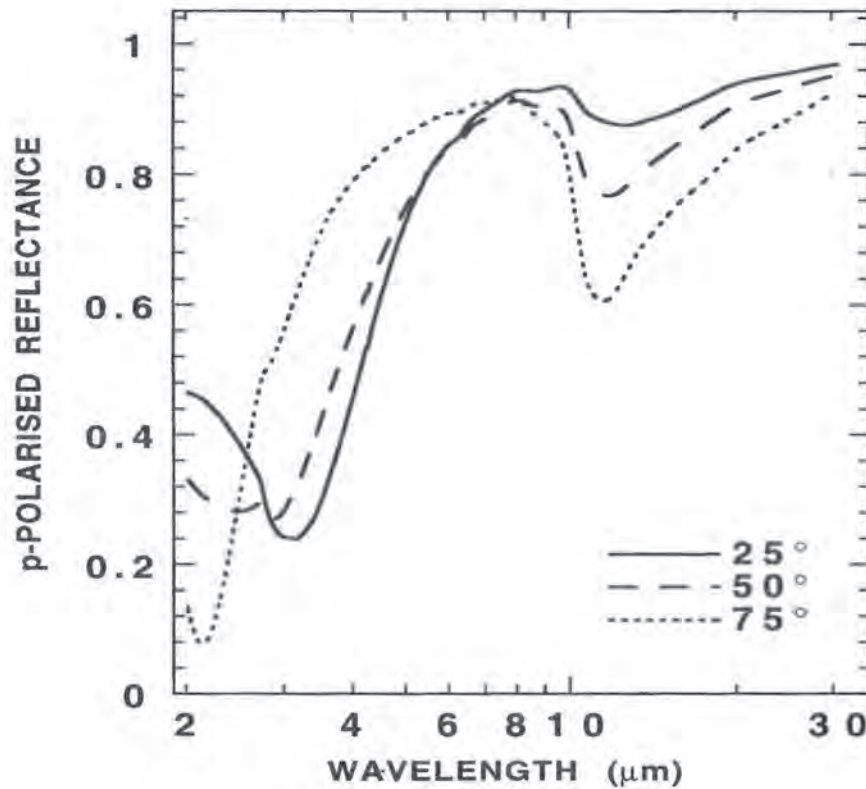


Figure 3.12 Spectral infrared reflectance of anodized aluminium without (a) and with (b) nickel pigmentation, as reproduced from Wäckelgård (1996a) and (1996b) respectively. The data pertain to p-polarized light with the shown incidence angles.

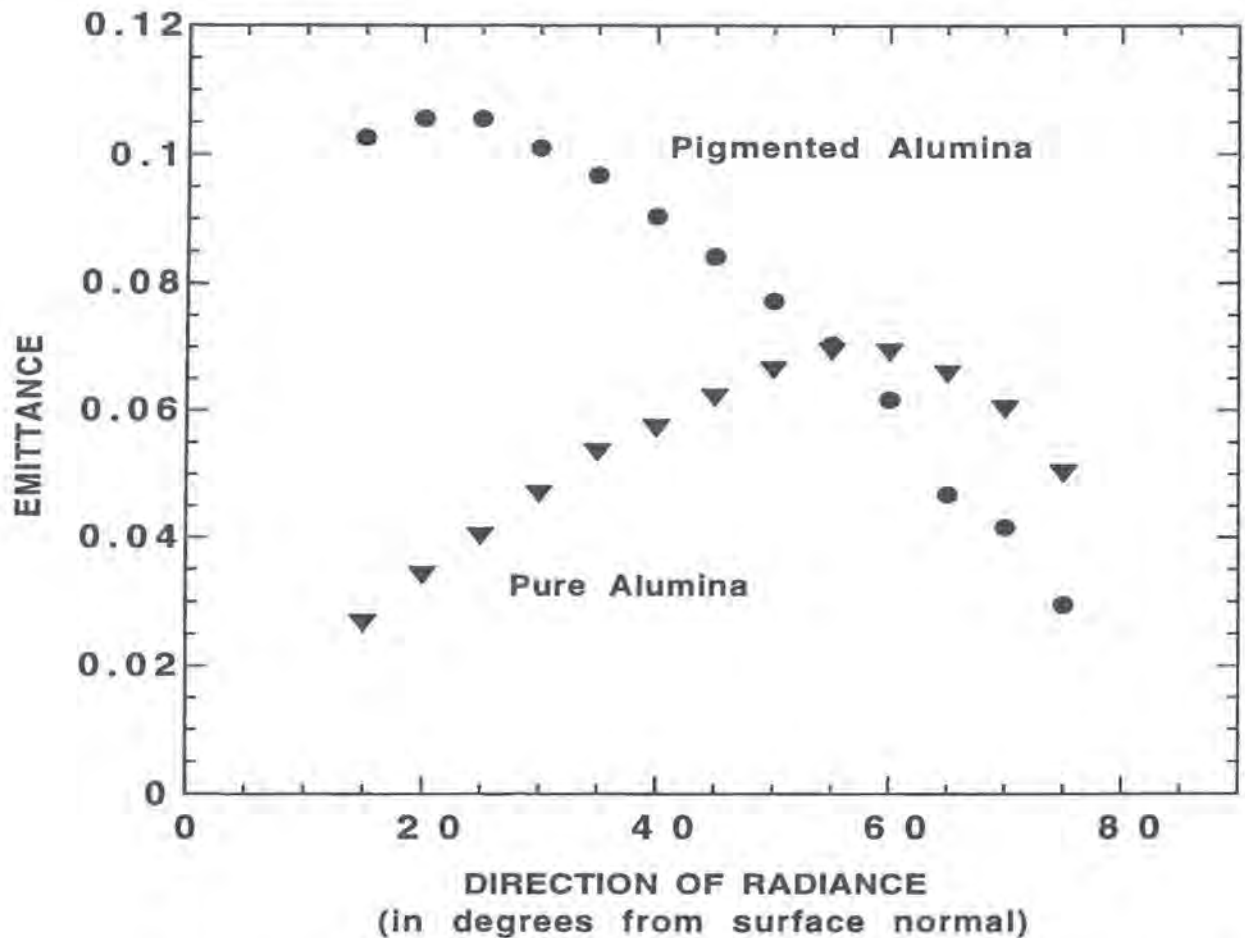


Figure 3.13 Angular dependent thermal emittance at 100°C of anodized aluminium without and with nickel pigmentation. The data are multiplied by $\cos \theta$, the surface projection factor.

X 'Solar Materials Research and Development' (Carlsson *et al.*, 1994). The Working Group has also compiled a qualification test procedure that has been adopted by ISO. This procedure has recently been prepared as a draft internal standard, designated ISO/DIN 12952 (Carlsson *et al.*, 2000). This work by the IEA Task X Working Group is briefly reviewed here.

3.5.1 Qualification test

The qualification test is based on a quantitative measure of degradation in solar absorptance and thermal emittance. The so-called performance criterion function PC combines the allowed change in solar absorption ΔA_{sol} and thermal emittance ΔE_{therm} (Carlsson *et al.*, 1994) by

$$PC = -\Delta A_{\text{sol}} + 0.25\Delta E_{\text{therm}} \leq 0.05 \quad (3.15)$$

If the PC value exceeds 0.05, the absorber has failed in the qualification test. The PC function has been formulated from simulations of solar hot

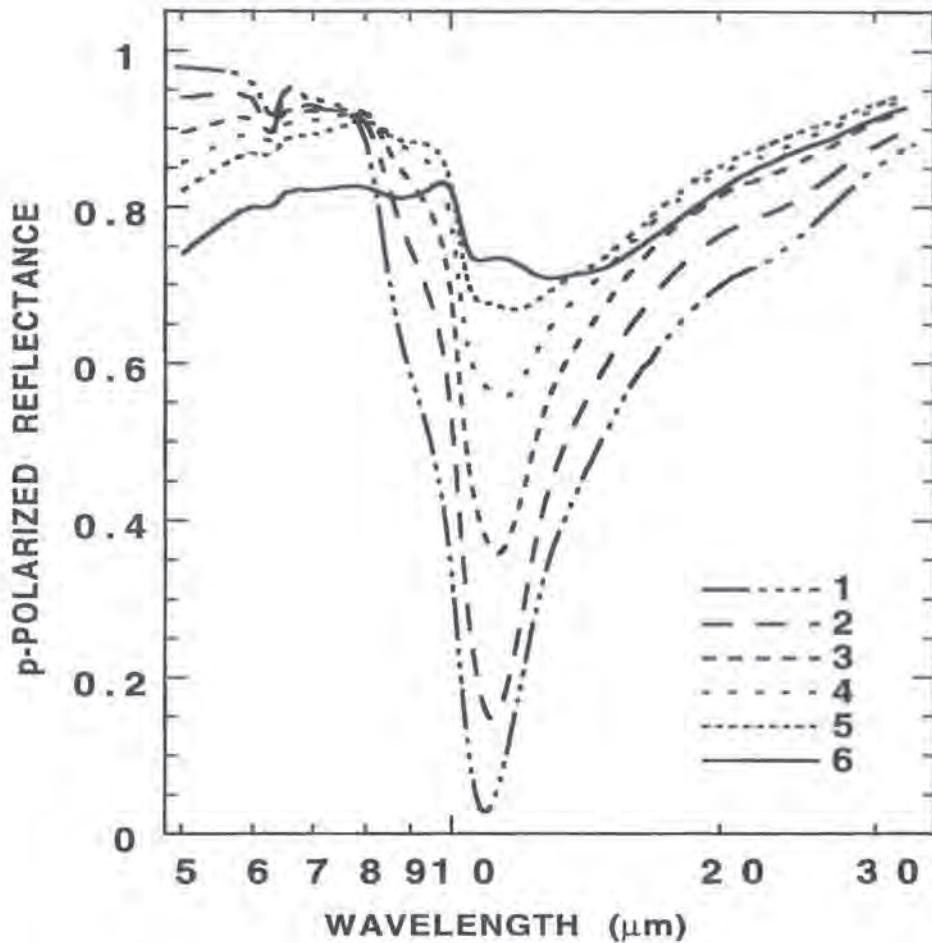


Figure 3.14a

Figure 3.14 Experimental (a) and calculated (b) spectral infrared reflectance for $0.5\ \mu\text{m}$ thick alumina based layers on Al. The data refer to p-polarized light with 75° incidence angle. The results in part (a) were obtained as a series of samples with 1 being pure alumina and 2 to 6 signifying increasing amounts of Ni pigmentation. Part (b) shows computed data with x denoting the fraction of non-pigmented alumina.

water systems, for which the requirements are that degradation in optical performance of the absorber should not reduce the annual solar heat contribution to the system by more than 5%. The calculations have been made for single-glazed flat plate collectors, and the relation is approximately valid if the solar heat fraction is low in the system.

The IEA Working Group found in their case studies (Carlsson *et al.*, 1994) that the most important environmental factors for absorber surface durability are temperature, humidity and sulphur dioxide in high-humidity air. The internal collector microclimate was studied by logging several climatic variables related to these three environmental stresses in long-term test collectors in domestic hot water systems under operation and stagnation conditions. The Working Group proposed the following three situations for which the environmental load on the absorber causes degradation:

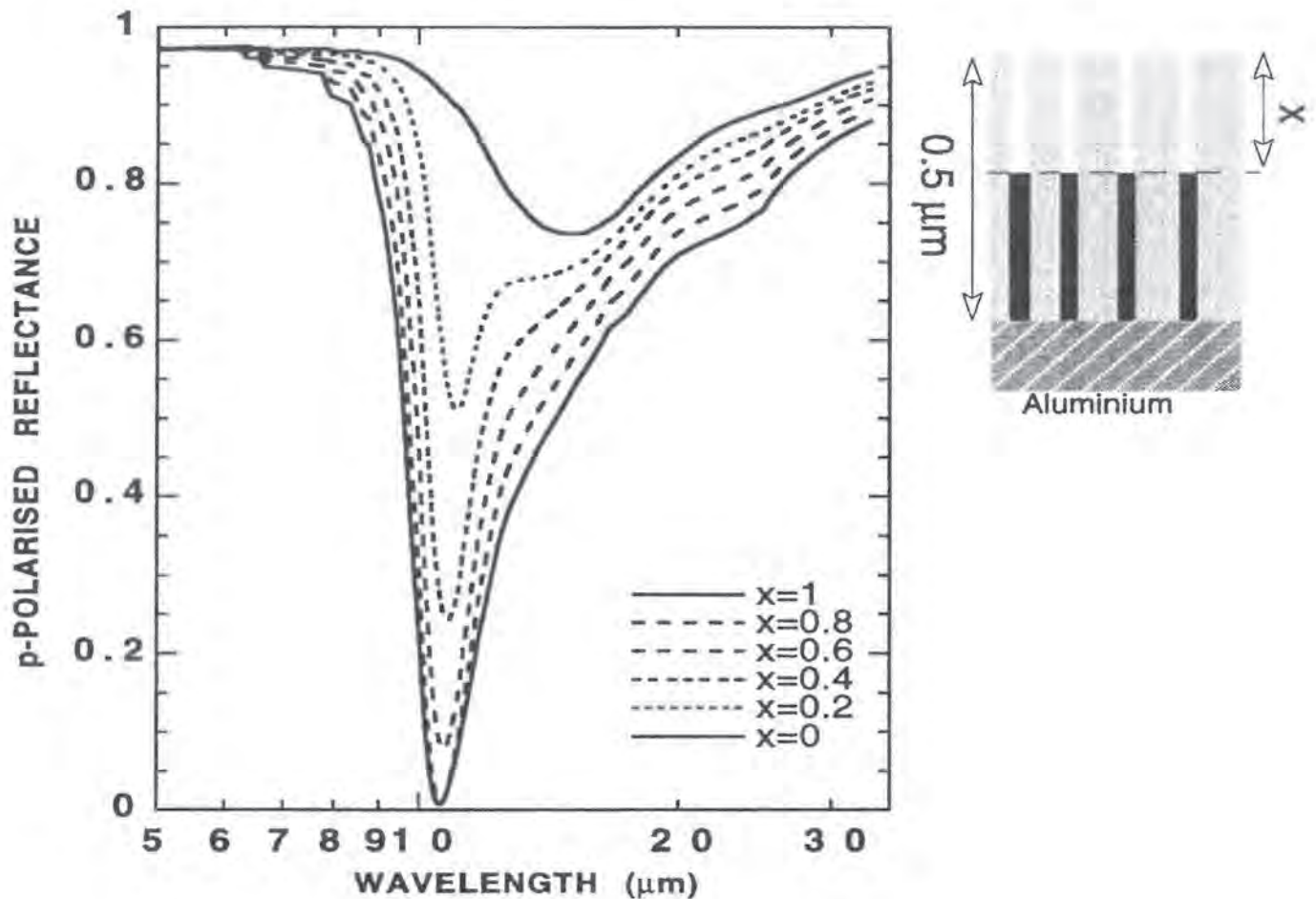


Figure 3.14(b)

- Under operation and stagnation when the temperature is relatively high and the humidity is low. These contributions may cause oxidation of the metal in the absorber coating and/or the substrate.
- Under starting up and non-operation, when the relative air humidity is high and the temperature is low. Air pollutants such as SO_2 can cause corrosion.
- Under severe humidity, as in the case of a non rain-tight collector or when the dew-point is reached. Condensation can lead to hydration or hydrolysis.

The qualification procedure is based on the assumption that the long-term degradation can be converted to short-term accelerated degradation at elevated stress by time transformation functions.

3.5.2 Lifetime evaluations

The qualification test procedure is a lifetime evaluation for solar collector coatings based on accelerated ageing tests. The purpose of such tests is to

obtain the same degradation of the sample as after a lifetime under operating conditions, but in a much shorter period. The assumption is made that the degradation proceeds by the same mechanisms both under service conditions and during high loads in the laboratory tests. The Task X Working Group elaborated time transformation functions to be used to convert service lifetime requirements into equivalent failure times in accelerated short-term tests. A scheme of short-time tests, which causes the three degradation modes mentioned above, has to be applied. The tests are particularly well suited for electroplated and sputtered surfaces, since these were used in the case study of the IEA Task X Working Group (Carlsson *et al.*, 1994). The following test measurements are proposed to be performed in climate chambers:

- (a) high-temperature stability at 200°C, 250°C and 300°C;
- (b) condensation resistance at 95% relative humidity (RH) with the absorber surface kept at 5°C lower temperature than in the surrounding climate chamber. The temperature should be set to 30°C, 40°C and 60°C;
- (c) corrosion resistance in circulating air with 95% RH, a temperature of 20°C, and with a concentration of sulphur dioxide of 1 ppm.

Measurements of solar absorptance and thermal emittance should be performed, and coating adherence should be checked. The details of the test procedure are given in Carlsson *et al.* (2000) together with recommendations of adequate test equipment.

High-temperature degradation tests should be carried out by exposing the sample to higher temperatures than those usually encountered during normal operation of a solar collector. The case studies in the IEA report show that the degradation of the solar absorptance of nickel pigmented aluminium oxide and black chrome coatings is thermally activated. In this case, the following time transformation function is used to convert the design service life of 25 years into a shortest acceptable failure time y_R for a constant test temperature τ_R :

$$y_R = 25 \exp\left[-\frac{E_\tau}{R_G} (\tau_{\text{eff}}^{-1} - \tau_R^{-1})\right] \quad (3.16)$$

The effective mean temperature τ_{eff} of the absorber surface is evaluated from a yearly-based frequency function for the service temperature of the absorber surface. The activation energy E_τ has to be determined from the tests. R_G is the ideal gas law constant, equal to 8.314 J/K mole. A full description with all details is given in Carlsson *et al.* (1994).

A failure time for condensation can be treated in an analogous way since hydration and hydrolysis are chemical reactions that can also be described by an Arrhenius behaviour so that they can be characterized by an activation energy. The same type of equation is used, but in this case the effective

mean temperature $\tau_{H,eff}$ is based on the yearly-based frequency function for the service temperature of the absorber surface under the condition that $RH \geq 99\%$. One should note that the activation energy $E_{H,\tau}$ is not the same as for high temperature oxidation and has to be determined from the condensation tests. The relation for y_R can be written

$$y_R = 25t_H \exp \left[-\frac{E_{H,\tau}}{R_G} (\tau_{H,eff}^{-1} - \tau_R^{-1}) \right] \quad (3.17)$$

where t_H is the yearly time fraction with a relative humidity in the collector that is equal to or higher than 99%.

High humidity air with SO_2 pollutants can be described as an accelerated electrochemical corrosion that can attack both the metal substrate and particles in the coating. The test method relates the absorber corrosion to the corrosion rate of zinc as a quantitative measure of degradation. The time transformation function was assumed to be the same as for the corrosion of zinc:

$$y_{R,\alpha} = (25 \cdot 0.1) / \rho_{Zn} \quad (3.18)$$

and

$$y_{R,\beta} = (25 \cdot 0.3) / \rho_{Zn} \quad (3.19)$$

where ρ_{Zn} is the corrosion rate of zinc in the accelerated test in units of g/m^2 year. The corrosion is considered to be dependent on the type of collector. A rain-tight and well-ventilated collector box (type α) will have a less humid micro climate than a non rain-tight collector with uncontrolled ventilation (type β); the two equations above represent these cases.

As pointed out by the IEA Task X Working Group, the actual observed in-service degradation in the optical performance of electrodeposited $Ni-Al_2O_3$ solar absorbers shows a very good agreement with predicted results from the accelerated tests made in the case study (Carlsson *et al.*, 2000). This serves to validate their qualification procedure.

3.6 CONCLUSION AND REMARKS

This chapter introduced spectrally selective absorber surfaces for efficient photo-thermal conversion of solar energy. The key feature is a high solar absorptance combined with a low thermal emittance. The exposition is not complete but serves to update earlier reviews, particularly as regards in-practice useful coatings.

Several different design principles for achieving spectrally selective absorption were presented. In many cases, a metal-dielectric composite layer is responsible for the high solar absorptance, whereas the reflectance of an

underlying metal substrate gives the low thermal emittance. The solar absorptance is often augmented by the use of antireflecting layers, porosity, surface roughness, etc. At least the majority of the in-practice useful selectively solar-absorbing surfaces of today have a metal-dielectric layer as their most crucial component. Many of the coatings – including black chrome and nickel pigmented anodic aluminium oxide – are prepared by electrochemical technology, but the more recent coatings, developed during the 1990s, are prepared by ‘dry’ methods such as DC magnetron sputtering or evaporation. We report on two new sputtered fin type absorbers, the Sunstrip Ni–NiO graded cermet on aluminium and the Interpane CrN–Cr_xO_y coating on copper. Apart from these, several cermet coatings for all-glass evacuated tubular collectors have come into production in China and Japan; the coatings were originally developed at The University of Sydney in Australia. Electrochemically produced coatings can be made with relatively inexpensive equipment, but they require processing of large quantities of hazardous chemicals. Physical vapour deposition utilizes more capital-intensive equipment but does not normally lead to hazardous exhausts.

The different microstructures of relevance for selectively solar-absorbing surfaces were introduced, and the pertinent Effective Medium Theories – needed for computing optical properties – were covered superficially. Multi-layer configurations, surface roughness and graded metal–dielectric compositions were discussed.

The applicability of modelling was exemplified. Modelling of the optical design for selectively solar-absorbing coatings has been employed for developing a new sputtered double layer SS–AlN cermet. Also the CrN–Cr_xO_y coating was optimized through modelling.

From computations based on Effective Medium Theory it was shown that the degradation of Ni–Al₂O₃ progressed via oxidation of the nickel, so that the density of metallic nickel decreased uniformly across the metal pigmented layer. An alternative model, with an oxidation front that moves gradually toward the substrate during degradation, could not explain the data. The high temperature degradation of sputtered Mo–Al₂O₃ showed the opposite behaviour, namely that the oxidation proceeds according to the front model.

Examples illustrated the use of models to understand optical properties of composites. The angular dependent solar absorptance of electrochemically deposited Ni–Al₂O₃ remains high at higher angles of incidence than for sputtered Ni–NiO coatings. The modelling with Effective Medium Theory revealed that the solar absorptance for high angles of incidence depends on thin film optical interference. More precisely: the solar absorptance is increased at high angles of incidence for a certain thickness of the pure alumina top layer in the double-layer Ni–Al₂O₃ coating. This effect cannot be achieved in a graded index type of solar absorber such as the Ni–NiO coating.

An important part of this report dealt with degradation and durability of solar-absorbing surfaces. The work done by the IEA Task X Working Group on accelerated lifetime testing of solar absorbers was reviewed. The

Working Group has compiled a qualification test procedure that was presented briefly.

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Photovoltaic physics and devices

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6.1 INTRODUCTION

Photovoltaics, 20th century technology poised to reach full maturity in the 21st, provides a simple, reliable and elegant way of converting sunlight directly into electricity. When entering a typical photovoltaic solar cell (Figure 6.1), the photons constituting sunlight release electrons that can then flow through an electrical load connected between the positive and negative terminals of the solar cell.

Although solar cells are very simple to use, the physics and technology underlying this use are closely linked with the development of quantum mechanics and microelectronics, arguably two of the most sophisticated and

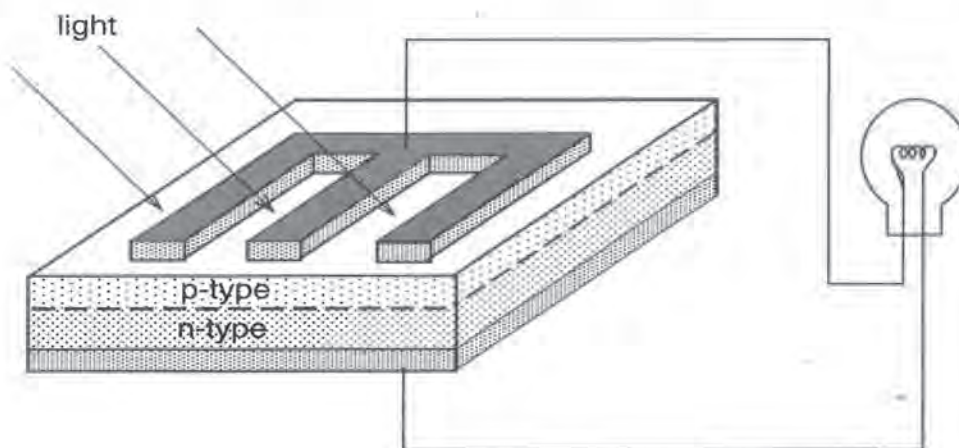


Figure 6.1 Typical solar cell consisting of a thin sheet of semiconductor material into which a rectifying p-n junction has been formed by introducing two different types of dopant impurities with positive-type (p-type) and negative-type (n-type) properties. Photons in the incident sunlight are converted to electrons flowing through the external load.

significant scientific and technological developments of the 20th century. The simplicity in use leads to modular, easily deployed systems ideal for remote area power supply but now surfacing in an increasing variety of urban applications. The latter range from lining the roofs of private homes, the facades of buildings and even the bodies of automobiles, to being deployed in dedicated fields of photovoltaic panels that silently and effortlessly generate larger quantities of power for urban electricity distribution grids.

The first part of this chapter explores the physics and operating principles underlying this very direct energy conversion process, in a way intended to be accessible to a non-specialist while perhaps stimulating a new insight or two for the specialist. Of particular interest are the processes that determine the energy conversion efficiency (ratio of electrical power output to the total power in the incident sunlight) and strategies that may remove the present performance limits, in the future. The second half of the chapter demonstrates the status and range of different approaches to photovoltaic device design by discussing the different solar cell technologies of current commercial interest and the directions in which these are evolving.

6.2 THE PHOTOVOLTAIC PROCESS

6.2.1 Background and essentials

Photovoltaic devices were first demonstrated experimentally in the 19th century (Green, 1990, Perrin, 1999), well before the associated physics were sufficiently advanced to be able to describe how the devices were operating. Important 20th century milestones in physics relevant to photovoltaics were the study of black-body radiation that first suggested the quantization of energy, the revival of a corpuscular theory of light, the development of wave mechanics (Jammer, 1989), the development of the electronic theory of semiconductors, and the development of semiconductor p-n junction theory.

One essential component for solar photovoltaics is sunlight. The wavelength distribution of energy from the sun approximates that from a 'black body' heated to a temperature of 6000 K, the temperature at the Sun's surface (a black body is merely a perfect absorber of light and, by a fundamental reciprocal relationship, also a perfect light emitter).

In attempting to understand the way such hot bodies were known to emit light of different wavelengths, Max Planck is usually credited with proposing the quantization of energy exchange in internal atomic transitions (Planck, 1900, but see also Kuhn, 1978 and Jammer, 1989). Einstein took a further bold step forward in postulating the quantization of energy exchange in interactions between light and atomic matter in his Nobel prize winning work on the photoelectric effect (Einstein, 1905). In such interactions, light can be considered to be made up from particles each having a specific energy equal to hf where h is Planck's constant and f is the

frequency of the light related to its wavelength, λ , and velocity c , by $f = c/\lambda$. Some time later, these particles were given their present name of photons (Lewis, 1926). The wave-particle duality of light stimulated the suggestion of similarly dual properties of matter (de Broglie, 1923), which led very quickly to the development of wave mechanics (Schrödinger, 1926). Wave mechanics were soon applied to the understanding of crystalline semiconductors (Wilson, 1931).

In a general description of the photovoltaic effect (i.e., creating a voltage output directly from light), semiconductor material is not an essential requirement as discussed in Section 6.8.1. However, as outlined below, semiconductors have properties that make them ideally suited for photovoltaics and are involved in all modern photovoltaic devices.

6.2.2 Semiconductors, Fermi-levels and light absorption

Wilson (1931) showed that the well-known discrete energy levels available to electrons in atoms broaden into bands of allowed energy when these atoms are brought close as in a crystalline solid.

The difference between a metal, semiconductor and insulator according to this band theory is shown in Figure 6.2. In a metal, states available to electrons in an allowed band of states are occupied up to a certain energy, known as the Fermi level, E_F , while all states above are unoccupied. This sharp demarcation is valid strictly only at low temperatures. At a higher temperature, T , the transition between occupied and unoccupied states is centred at the Fermi level but is smeared out over an energy range of the order kT , known as the thermal energy, where k is Boltzmann's constant. At 300 K, the thermal energy equals 25.852 meV [an electron volt (eV) is a small unit of energy equal to 1.6×10^{-19} joules]. Mathematically the

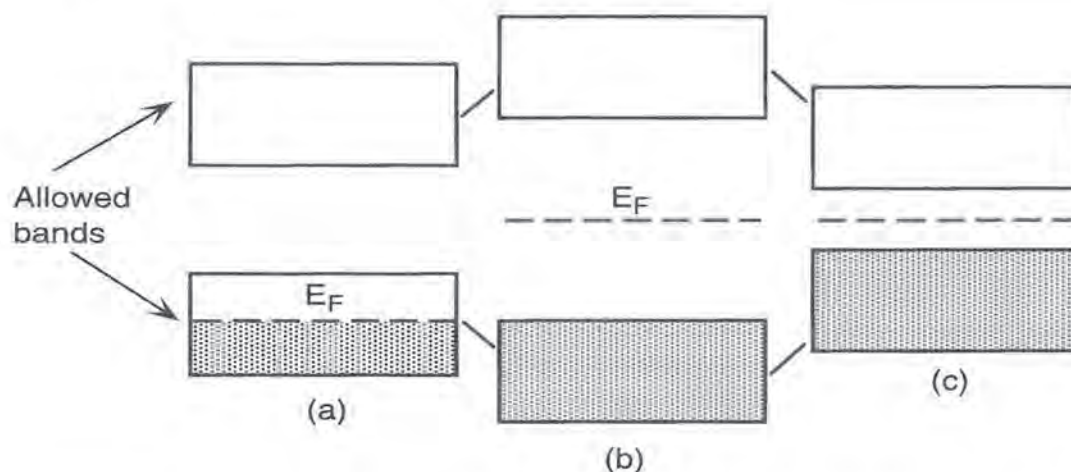


Figure 6.2 Diagrams showing the way in which allowed states are occupied by electrons in: (a) a metal; (b) an insulator; (c) a semiconductor.

smearing of electrons about E_F is described by the Fermi–Dirac distribution function, which gives the occupation probability of allowed states at energy E :

$$f_E = 1/(1 + \exp[(E - E_F)/kT]) \quad (6.1)$$

Metals are good electrical conductors since there are many vacant states into which electrons can be excited as they progressively gain energy from an applied electric field. A semiconductor, like an insulator, has the property that, at low temperature, one band (known as the valence band) is completely full of electrons, while the next highest in energy (the conduction band) is empty. These full and empty bands are separated by an energy known as the bandgap energy, E_G . It follows that the Fermi level must lie somewhere in the forbidden gap between these two bands, actually very close to the centre of this gap in pure material, as shown below. At low temperatures, semiconductors are poor conductors because electrons in the full valence band cannot contribute to current flow since there are no vacant states into which electrons can be excited as they gain energy from an applied field.

In a semiconductor, as opposed to an insulator, E_G is sufficiently small (less than a few electron volts) so that an appreciable number of electrons are thermally excited across the bandgap as temperature increases. Electrons excited into the conduction band are mobile since there are plenty of vacant states in this band into which they can move. The much larger number of electrons left remaining in the valence band also become mobile since there are now the vacant states in this band, necessary for movement, left behind by the electrons excited to the conduction band. Just as it is more natural to think of bubbles as a physical entity moving through a liquid rather than thinking of the motion of liquid into the void constituting a bubble, it is easier to think in terms of the motion of these vacancies, known as ‘holes’, in the valence band. Holes behave as particles with the opposite electrical charge to electrons. Often, when talking of semiconductors, the term ‘electrons’ is used to refer only to those electrons in the conduction band, whereas ‘holes’ refer to the quasi-particles corresponding to the vacancies in the valence band.

The number, n , of electrons excited to the conduction band in pure semiconductors and holes, p , thereby created in the valence band can be calculated using the Fermi–Dirac distribution function. Largely resulting from the fact that the Fermi-level lies several kT from the energies of both the conduction band E_C and valence band E_V , the result takes a simple form (e.g., Green, 2002):

$$n = N_C \exp[(E_F - E_C)/kT] \quad (6.2)$$

$$p = N_V \exp[(E_V - E_F)/kT] \quad (6.3)$$

where N_C and N_V are the effective densities of states associated with the respective bands (equal to about 10^{19} cm^{-3} for typical semiconductors such as silicon near room temperature). The exponentials in Equations 6.2 and 6.3 have large, negative arguments, meaning that n and p are quite small, much smaller than N_C and N_V , about 10^{10} cm^{-3} in silicon at room temperature. The total number of atoms in silicon is about $5 \times 10^{22} \text{ cm}^{-3}$, with each atom contributing 14 electrons, giving $7 \times 10^{23} \text{ cm}^{-3}$ as the total number of electrons in the material. This highlights the very small fraction of the total number of electrons that gives semiconductors their interesting properties!

Since, in pure semiconductors, $n = p = n_i$ where n_i is known as the intrinsic carrier concentration, Equations 6.2 and 6.3 can be equated to give:

$$E_F = \frac{E_C + E_V}{2} + \frac{1}{2}kT \ln\left(\frac{N_V}{N_C}\right) \quad (6.4)$$

Multiplying the same two equations together gives another important result:

$$np = n_i^2 = N_C N_V \exp(-E_G/kT) \quad (6.5)$$

where $E_G = (E_C - E_V)$ is the bandgap, previously introduced.

Energetic photons in sunlight can be absorbed in a semiconductor, giving up their energy by exciting an electron from the valence band to the conduction band, creating an 'electron-hole pair' (the energy of a photon equals 1.24 eV divided by its vacuum wavelength in microns, the peak photon density in sunlight occurs around 0.6 microns, the wavelength to which the eye is most sensitive, corresponding to an energy of about 2 eV). A semiconductor therefore has two properties that make it well suited for photovoltaics: (i) an excited state into which electrons can be excited from a ground state, the latter acting as a source of electrons, by the absorption of sunlight photons, and (ii) a conduction path for carriers to and from the point of excitation in both the ground and excited states. These two properties are essential for the photovoltaic effect.

Since both electron and hole concentrations increase under illumination, Equation 6.2 and 6.3 can no longer be valid in this case. New parameters, electron and hole quasi-Fermi energies, E_{Fn} and E_{Fp} , are introduced (Figure 6.3), related to the new electron and hole concentrations by:

$$n = N_C \exp[(E_{Fn} - E_C)/kT] \quad (6.6)$$

$$p = N_V \exp[(E_V - E_{Fp})/kT] \quad (6.7)$$

Note that, multiplying together and using Equation (6.5):

$$np = n_i^2 \exp[(E_{Fn} - E_{Fp})/kT] \quad (6.8)$$

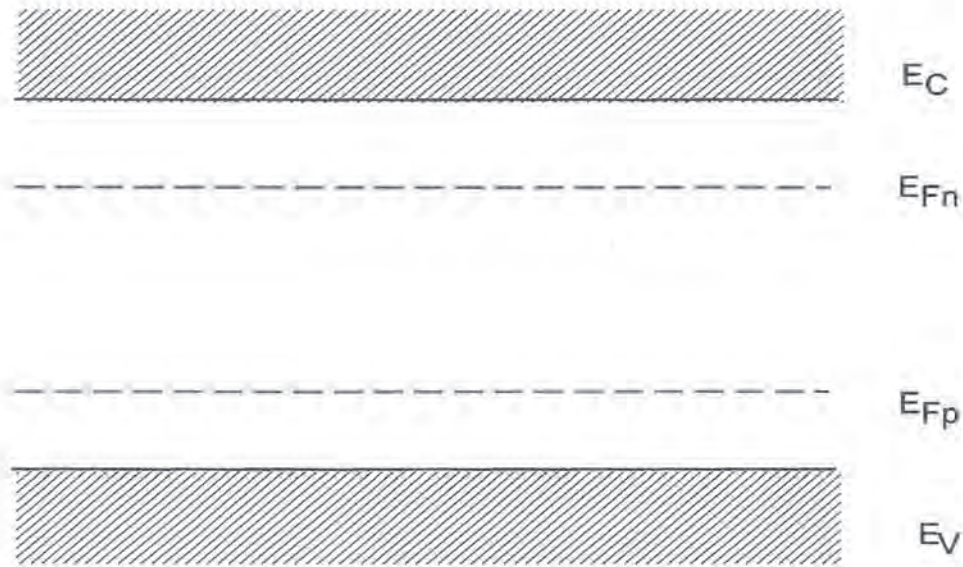


Figure 6.3 In semiconductor material under illumination, the Fermi level splits into electron and hole quasi-Fermi levels, E_{Fn} and E_{Fp} .

Instead of there being one Fermi-level as in the equilibrium case, there are separate quasi-Fermi levels for electrons and holes (Figure 6.3). The electron-hole product depends on the energy separation between these quasi-Fermi levels (quasi-Fermi levels are equivalent to the electrochemical potentials of irreversible thermodynamics).

The quasi-Fermi levels are more useful than merely for describing the non-equilibrium concentration of electrons and holes. From irreversible thermodynamics, the current density, J_n , due to the flow of electrons in the conduction band and J_p , due to the similar flow of holes in the valence band, are proportional to the gradients of these levels. Specifically,

$$J_n = \mu_n n \nabla E_{Fn} \quad (6.9)$$

$$J_p = \mu_p p \nabla E_{Fp} \quad (6.10)$$

where μ_n and μ_p are proportionality constants known as the mobility of the respective carrier and ∇ is the gradient operator (reduces to a differential when symmetry allows the problem to be formulated as one dimensional).

6.2.3 Doped semiconductors

Semiconductors have another set of properties that are an additional bonus for use in photovoltaics. Their electronic properties can be controlled by adding small quantities of specific impurities, known as dopants. These dopants modify the relative concentration of electrons and holes in a semiconductor as shown in Figure 6.4 for the case of, technologically, the most important semiconductor, silicon, from Group IV of the periodic table.

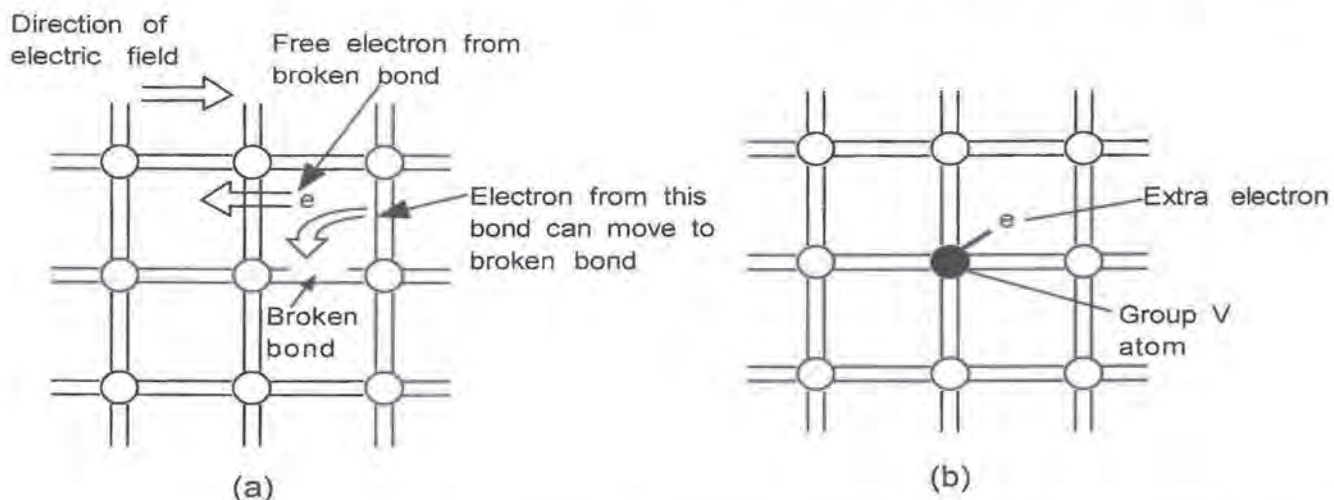
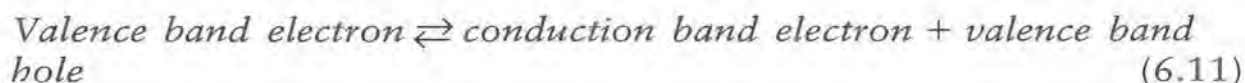


Figure 6.4 (a) Schematic representation of a silicon crystal lattice showing covalent bonds joining silicon atoms together, with one bond shown broken; (b) portion of the silicon lattice where a Group V atom has replaced a silicon atom.

Figure 6.4(a) schematically represents the chemical bonding arrangement in a crystal of pure silicon, where each silicon atom is bonded to each of four neighbours by a covalent bond, each bond involving two electrons shared between the silicon atom and an immediate neighbour. Electrons in such bonds correspond to valence band electrons in the energy diagram of Figure 6.3. Excitation of an electron to the conduction band corresponds to the breaking of a covalent bond, creating an unbonded electron (conduction band electron) and one broken bond (vacancy or valence band hole). Both the unbonded electron and the broken bond can propagate through the crystal, the latter when an electron in a nearby unbroken bond jumps from this bond to the broken one. Excitation by light increases the number of broken bonds, although no permanent damage results! (This bond breakage can be detected as a slight decrease in the mechanical strength of silicon, although intense laser light is required for any measurable effect; the extra broken bonds disappear when the light is switched off!)

If small quantities (typically parts per million) of phosphorus (or other Group V element) are added to silicon, the Group V atom can substitute at atomic sites for silicon as shown in Figure 6.4(b). Four of the Group V element's five valence electrons become strongly bonded into covalent bonds with the four neighbouring silicon atoms. The surplus fifth electron is in a completely different situation. It becomes weakly bonded to the single unneutralized positive charge centred at the phosphorus atom. Due to the weakness of this bond, this electron is easily torn away from its original host and becomes free to move through the crystal, indistinguishable from an electron freed from a much stronger covalent bond, i.e. it easily becomes a fully-fledged conduction band electron.

Adding a Group V impurity is therefore a way of introducing conduction band electrons into silicon (such impurities are known as ‘donor’ impurities on this account). What happens to the valence band holes? One might, at first sight, think that the release of electrons from covalent bonds would continue as before and the concentration of holes would remain unchanged from undoped material. However, this overlooks the dynamics of the bond breaking and reconstruction process whereby:



While the rate of this process to the right is unchanged by moderate quantities of dopants, the possible rates to the left are greatly enhanced by the increased concentration of conduction band electrons, n (per unit volume). To balance that to the right, it follows that the concentration of valence band holes, p , must reduce. In fact, since the rate of the process to the left depends on the product of the electron and hole concentrations, np , it follows that, in the case of thermal equilibrium (no illumination):

$$np = \text{constant} = n_i^2 \quad (6.12)$$

even in the doped material. Increasing n by adding donor dopants has the important ancillary effect of suppressing p !

Doping the silicon by Group III impurities similarly increases the concentration of valence band holes by introducing unsatisfied covalent bonds into the lattice. These dopants are known as acceptors, since the broken bonds are able to accept electrons from nearby unbroken bonds (corresponding to hole motion in the valence band).

By introducing appropriate dopants, it is possible to control the concentrations of electrons and holes in different regions of a semiconductor device, a feature of key importance in microelectronics. The concentration of electrons and holes in thermal equilibrium (no illumination) in uniformly doped material can be calculated by noting, on a macroscopic scale, there must be electrostatic neutrality. Electrons and acceptor dopants contribute negative charges while holes and donors give positive. Hence, for material doped with a concentration N_D of donors:

$$n = p + N_D \quad (6.13)$$

Combining with Equation 6.12 allows a quadratic equation to be set up, which is easily solved. However, due to the relative magnitudes, the approximate solution $n \approx N_D$ and $p \approx n_i^2/N_D$ is sufficiently accurate for most purposes.

This ability to control the electronic properties of semiconductors by introducing dopants was discovered by accident in the 1940s as a direct result of its importance for photovoltaics (Riordan and Hoddeson, 1997).

In 1940, Russel Ohl at Bell Laboratories in Homdel near New York was experimenting with silicon samples when he noticed unexpectedly large photovoltages (about 0.5 V) across some specimens when illuminated by a flashlight. Further investigation showed that the silicon in these samples exhibited two types of properties called 'positive' (p-type) and 'negative' (n-type). The large photovoltages arose in material where there was found to be a junction (a p-n junction) between the two types, serendipitously formed in the samples. It was soon shown that the n-type regions were regions with phosphorus incorporated, while the p-type had excess boron. This was due to the relatively impure starting material and the particular way these impurities segregated when the sample solidified from the molten state during preparation. The definitive theory of the p-n junction formed between differently doped regions was given by Shockley (Shockley, 1949) and led to the first practical transistors.

6.3 p-n JUNCTION THEORY

6.3.1 Characteristics in the dark

Equation 6.12 can also be established directly from the earlier Equations 6.2 and 6.3, both of which remain valid in doped material. The Fermi-level will have to change from its value near midgap in undoped (intrinsic) material (Equation 6.4) to give the correct values for n and p . It moves closer to the conduction band in material doped with donors and closer to the valence band in acceptor doped material (Figure 6.5).

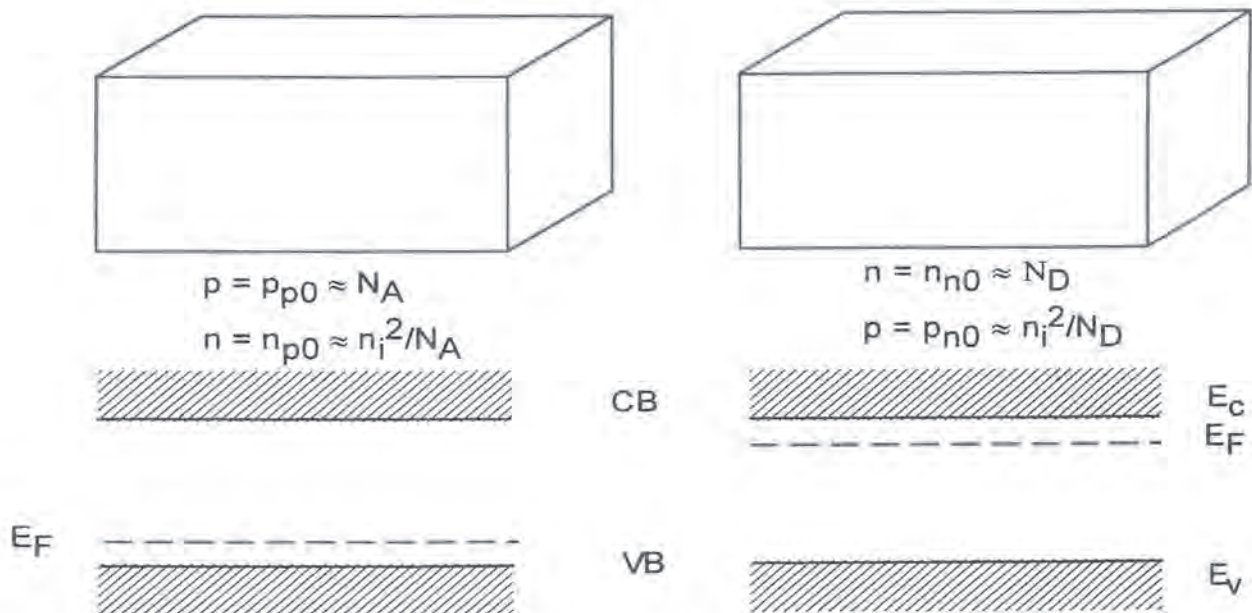


Figure 6.5 Energy of the Fermi level as a function of the concentration of donors and acceptors.

If two separate pieces of p-type material and n-type material are joined together, the overriding consideration in determining the resulting properties is that the Fermi-level throughout the combined system must remain constant in thermal equilibrium (Figure 6.6). Away from the junction in the 'bulk' regions, the material retains the electron and hole concentrations of the original p-type or n-type material. Right at the junction, there is a transition region formed where holes spill over from the p-type side as do electrons from the n-type side, due to the concentration difference at the junction. As these carriers spill over, they leave behind unneutralized positive and negative charges at the sites of correspondingly exposed acceptor and donor atoms, respectively. This creates an electric field at the junction which builds up in a direction and to a value at each point in space to balance exactly the diffusive flow of holes and electrons. The field has its maximum value right at the junction and drops to zero at the edge of the transition region (also known as the 'depletion' region).

A potential corresponding to the work function difference between the p-type and n-type regions is built up by this field. This 'built in' potential, V_{bi} , is readily calculated as:

$$V_{bi} = \frac{kT}{q} \ln(N_A N_D / n_i^2) \quad (6.14)$$

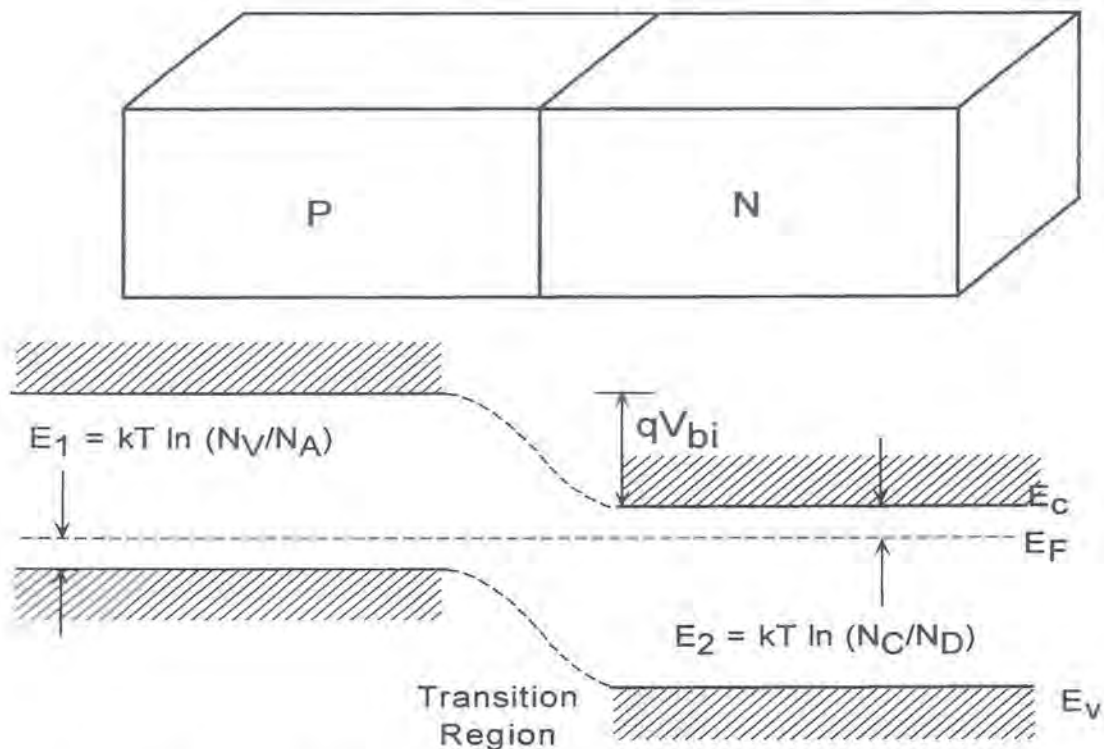


Figure 6.6 A p-n junction formed by bringing the isolated p-type and n-type regions together. Also shown is the corresponding energy-band diagram at thermal equilibrium.

where kT/q is a normalizing parameter, related to the thermal energy, that has the dimensions of voltage and is known as the 'thermal voltage' (equal to 25.852 mV at 300 K).

An external voltage applied to the p-n junction modifies this built-in potential. A positive voltage to the p-type side subtracts from it, restarting the diffusive flow of electrons and holes across the junction. The concentrations of those carriers that are in the minority near the junction increase, exponentially, as a positive voltage increases. The current flow through the diode ideally is determined by the rate these can diffuse away from the junction into bulk regions. With the opposite voltage polarity, the barrier height at the junction increases, and minority carrier concentrations near the junction are suppressed. Current flows again ideally are limited by the rate at which minority carriers can be generated in the bulk and diffuse to the junction.

When voltage is applied or the p-n junction is illuminated, there is no longer a constant Fermi level throughout the device. In n-type material, n is large and p is small. Accordingly, one consequence of Equations 6.9 and 6.10 is that, for moderate current levels, there will be little change in the electron quasi-Fermi level, E_{Fn} , across the n-type region but there could be a large change in E_{Fp} . The reverse is true for p-type material. As indicated in Figure 6.7, it follows that, near the junction, the energy separation $E_{Fn} - E_{Fp}$ approximately equals qV , where V is the voltage applied across the junction. From Equation 6.8, it then follows that the minority carrier concentrations near the junction increase exponentially with the normalized voltage qV/kT . As previously noted, current flows depend on the rate at which carriers can flow from the junction into the bulk region. This rate is proportional to their concentration near the junction and hence also depends exponentially on voltage.

The current-voltage relationship of an ideal p-n junction diode in the dark is therefore given by:

$$I = I_0 [\exp (qV/nkT) - 1] \quad (6.15)$$

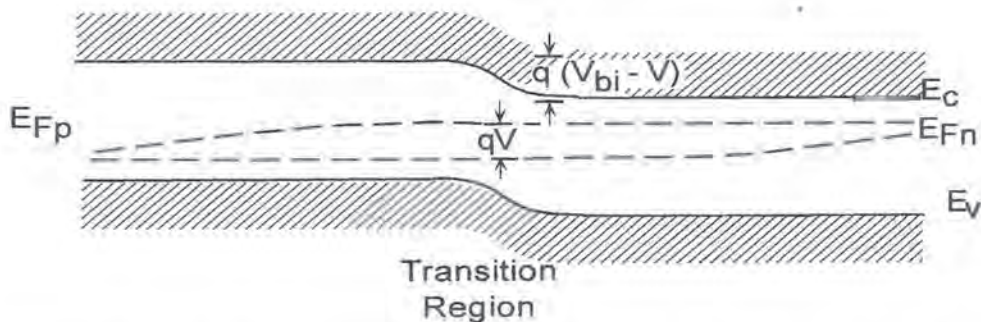


Figure 6.7 A p-n junction energy-band diagram for a non-equilibrium situation, such as when a positive voltage is applied to the junction.

with n , here the ‘ideality factor’, equal to 1. I_0 is the dark saturation current of the diode. For an ideal diode, this current equals the number of carriers generated in the bulk region in the dark that find their way to the junction:

$$I_0 = \left(\frac{qAD_n n_i^2}{N_A L_n} F_p + \frac{qAD_p n_i^2}{N_D L_p} F_N \right) \quad (6.16)$$

where q is the electronic charge, A is the diode area, D_n and D_p are the diffusivities of electrons and holes, L_n and L_p are their diffusion lengths (the typical distance they can diffuse before recombining) and F_p and F_N are factors that depend on the dimensions of the diode and the way electrical contact is made to it. For example, F_N is given by (Green, 2002):

$$F_N = \frac{S_p \cosh(W_N/L_p) + (D_p/L_p) \sinh(W_N/L_p)}{(D_p/L_p) \cosh(W_N/L_p) + S_p \sinh(W_N/L_p)} \quad (6.17)$$

where W_N is the width of the bulk n-type region and S_p is the effective surface recombination velocity at the contact to this region. For high performance cells, F_p and F_N should be as small as possible, achieved by having W_N and W_p small compared with L_p and L_n , respectively and S_n and S_p small compared with D_n/L_n and D_p/L_p respectively.

In actual diodes as opposed to ideal, additional processes increase the current flow. The junction transition region, despite its narrow width, can be a very effective site for recombination and generation of electron-hole pairs. Within this region, a large range of combinations of electron and hole concentration are present, ensuring perfect conditions for efficient recombination/generation somewhere in it. This is important particularly for recombination/generation via defects, which introduce allowed energy levels for electrons into the normally forbidden gap. Such junction recombination gives rise to an additional component of current, with a different, higher value of I_0 than from Equation 6.16 and an ideality factor close to 2.

6.3.2 p-n junction solar cell

Under illumination, photons provide an additional mechanism for electron-hole pair generation, augmenting that from thermal generation (including by background radiation). Under reverse bias, the normal dark thermal generation current is supplemented by the optically generated current. In fact, the entire current-voltage curve for the diode is shifted downwards by this optically generated current as shown in Figure 6.8. Note that this gives a region in the third quadrant where the voltage across the cell and the current have the opposite relation to that of a diode in the dark. This means that power is generated by the diode when operating in this quadrant.

Since the active power generation quadrant is the one of prime interest for solar cell operation, the current-voltage curves are normally shown

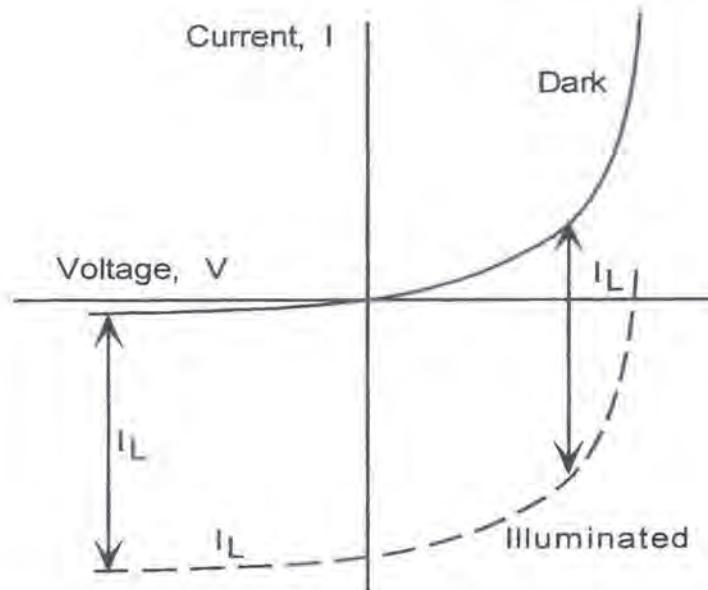


Figure 6.8 The light-generated current is superimposed upon the normal rectifying current-voltage characteristics of the diode. This results in a region in the fourth quadrant where electrical power can be extracted from the device.

reflected about the voltage axis as shown in Figure 6.9(a). Plotted this way, the current-voltage relationships are given by:

$$I = I_L - I_{on}[\exp(q(V + IR_S)/nkT) - 1] - (V + IR_S)/R_{SH} \quad (6.18)$$

where R_S and R_{SH} are parasitic series and shunt resistances associated with the diode. The series resistances are quite predictable and arise from resistance to current flows within the semiconductor material, through the metal conductors connecting the cells to the outside world, or across the metal-semiconductor contact itself. Shunt resistances are less predictable and generally arise from imperfections in the cell junction.

The electrical equivalent circuit of the cell is shown in Figure 6.9(b). The parameters I_{on} , n , R_S and R_{SH} usually are regarded as fitting parameters that generally can be assigned values allowing the characteristics of an individual cell to be matched quite closely. Sometimes an ideal diode component I_{o1} with $n = 1$, is added as indicated in Figure 6.9(b), allowing a more physically based fit to the device characteristics (of course, different values of I_{on} and n will be required to give a good fit if this component is included).

Looking more closely at the characteristics of Figure 6.9(a), the power output is zero when the cell is short-circuited (short-circuiting is not harmful for individual cells since the current is limited to the light generated current I_L). The power output initially increases as the voltage across the cell increases, but again drops to zero at the open-circuit voltage (V_{oc}) point.

The maximum power output occurs close to the 'knee' of the curve in Figure 6.9(a) but, as can be seen, this power must always be smaller than

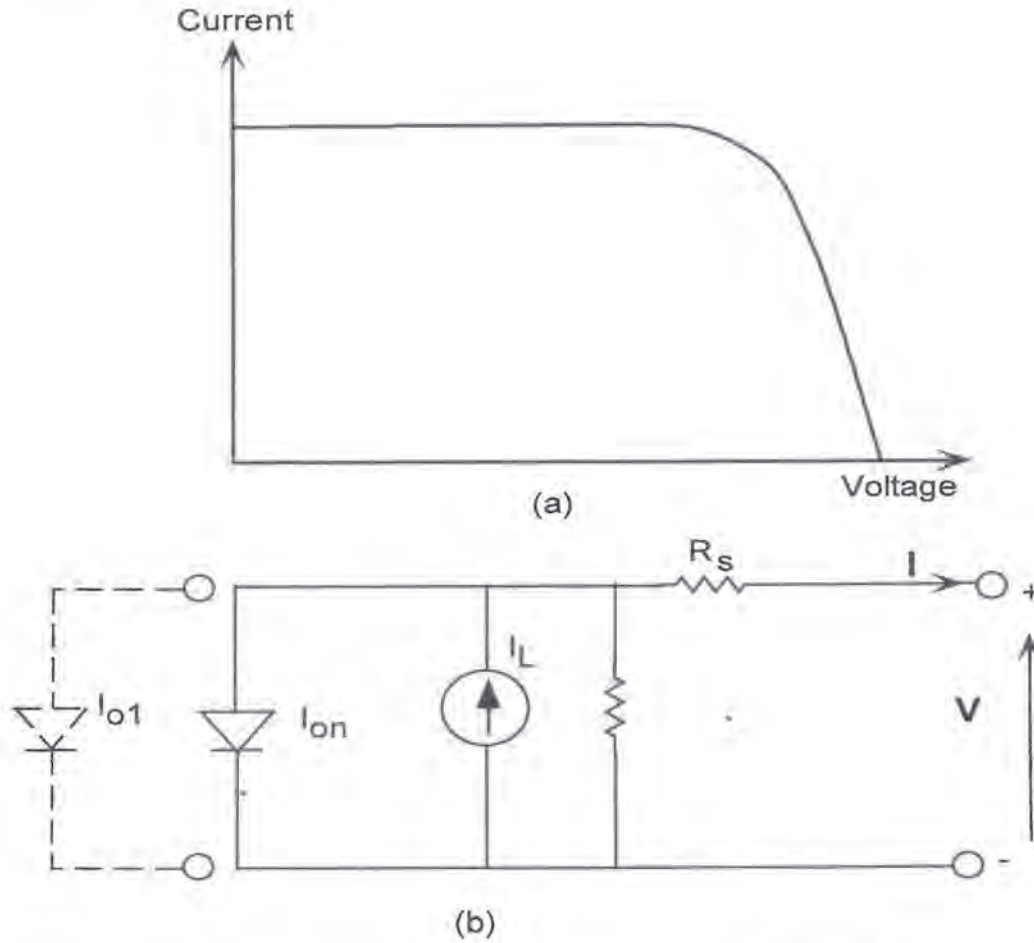


Figure 6.9 (a) Output characteristics of a solar cell as normally plotted; (b) electrical equivalent circuit in terms of diode with ideality factor, n , and saturation current density, I_{on} , the current generator, I_L , modelling photogeneration, and the parasitic shunt and series resistance, R_{SH} and R_s . Sometimes, an additional diode is added with unity ideality factor (shown dashed).

the product $V_{oc}I_{sc}$. The maximum power, P_m , is often expressed in terms of the latter product by introducing a fill factor, FF , parameter:

$$P_m = V_{oc}I_{sc}FF \quad (6.19)$$

where FF is always smaller than unity. In the absence of series and shunt resistance, FF is a function of V_{oc} and n only and is given to acceptable accuracy for all practical situations by (Green, 1982):

$$FF_o \approx \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1} \quad (6.20)$$

where $v_{oc} = V_{oc}/(nkT/q)$ is the normalized value of the cell open-circuit voltage. When series resistance is important, the fill factor is reduced to a value (Green, 1982):

$$FF_s \approx FF_o(1 - 1.1r_s) + r_s^2/5.4 \quad (6.21)$$

provided $r_s < 0.4$ where $r_s = R_s/(V_{oc}/I_{sc})$ is the normalized value of the cell series resistance. If shunt resistance is important, the fill factor is reduced further to:

$$FF \approx FF_s \left[1 - \frac{(v_{oc} + 0.7)}{v_{oc}} \cdot \frac{FF_s}{r_{sh}} \right] \quad (6.22)$$

provided $[r_s + (1/r_{sh})] < 0.4$, where $r_{sh} = R_{sh}/(V_{oc}/I_{sc})$.

Figure 6.10 compares the output characteristics of cells with different combinations of cell parameters. In Figure 6.10(a) an increased I_L is modelled, such as caused by increased sunlight intensity. It is assumed the temperature of the cell remains unchanged and that series and shunt resistances are negligible. As well as increasing I_{sc} , (not surprisingly since I_L is usually equal to I_{sc}), increasing I_L also marginally increases V_{oc} , and hence FF since, from Equation 6.18:

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{I_L}{I_{on}} + 1 \right) \quad (6.23)$$

It appears from Equation 6.23 that increased ideality factor n and temperature T will also increase V_{oc} due to the linear dependence in the nkT/q prefactor, but this simple argument overlooks the much stronger dependence of I_{on} on these parameters!

Figure 6.10(b) shows the effect of increased solar cell operating temperature. I_{sc} is increased slightly since semiconductors become stronger light absorbers at high temperature (due to a bandgap reduction with temperature). However, the open-circuit voltage is reduced more significantly due to the strong temperature dependence of I_o . FF is also reduced slightly.

Two cells with the same I_{sc} and V_{oc} but different values of n are compared in Figure 6.10(c). A high n is associated with 'softer' output characteristics and reduced FF .

The effect of series resistance, R_s , is most apparent near the open-circuit voltage as shown in Figure 6.10(d). R_s can become sufficiently large (above V_{oc}/I_{sc}) to decrease I_{sc} below I_L . In this case, the cell output characteristics become nearly linear with a fill factor close to 25%. Such linear characteristics are surprisingly commonly observed during cell development programmes and can be observed in any cell either by increasing the light intensity (such as by using focused sunlight) or, due to the shunting effects described below, by decreasing the light intensity.

Shunt resistance affects the cell characteristics near short-circuit as shown in Figure 6.10(e). Shunt resistance can become sufficiently low (below V_{oc}/I_{sc}) to decrease V_{oc} , which again causes the output characteristics to become linear.

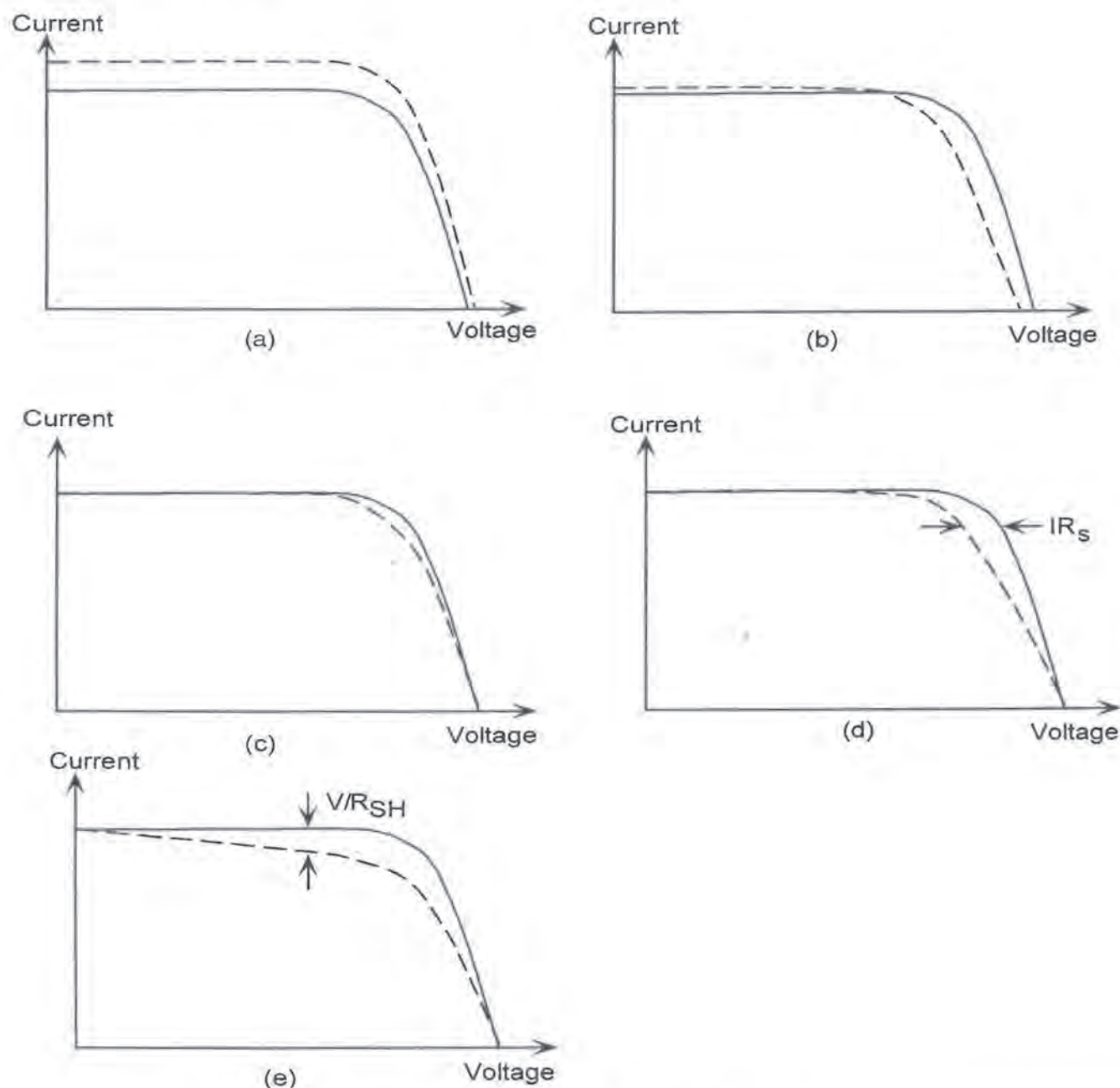


Figure 6.10 Effect of changes in different cell parameters upon output characteristics. Dashed curves show the effects of: (a) increased illumination (I_L); (b) increased cell temperature; (c) increased cell ideality factor (case where I_{sc} and V_{oc} fixed); (d) increased series resistance, R_s ; (e) decreased shunt resistance, R_{SH} .

To maximize both I_{sc} and V_{oc} , and hence energy conversion efficiency, the surface recombination velocities S_n and S_p should be as small as possible while the diffusion lengths L_n and L_p should be as large as possible. This is achieved by using high quality surface 'passivation' and the highest possible bulk material quality, respectively. While the surface recombination velocities appear to be able to be made arbitrarily small, an infinite carrier diffusion

length is not possible, even in principle (since this would imply infinite open-circuit voltage and extraction of the photogenerated current at a voltage above the semiconductor bandgap, which would violate energy conservation).

Early attempts to estimate energy conversion efficiency limits, in essence, made optimistic extrapolations of demonstrated material quality to calculate likely upper bounds (Loferski, 1956). In 1961, Shockley and Queisser (Shockley and Queisser, 1961) took a fundamentally different approach that made use of the reciprocity between light absorption and light emission – any cell that can absorb light must also emit light! This new approach provided a technique for calculating intrinsic limits on efficiency and highlighted some of the characteristics required for a perfect solar cell.

6.4 ENERGY CONVERSION EFFICIENCY LIMITS

6.4.1 Detailed balance: light absorption and emission

Shockley and Queisser realized that, for any light absorption process creating an electron–hole pair, there was a corresponding reverse electron–hole recombination process involving light emission. The highest possible energy conversion efficiency would be demonstrated when all defect-related recombination paths had been removed so that this radiative light emission process was the one limiting recombination in the semiconductor.

An interesting ‘photon recycling’ effect occurs in this case. During the radiative recombination process, a photon is created to take away the energy lost during the recombination process. The energy of the photon is therefore above the threshold for absorption by creating an electron–hole pair. This photon can be reabsorbed at a different location in the semiconductor! If this happens, in effect, there has been no nett recombination event but something more akin to the very rapid transport of an electron–hole pair. In the ideal case where other recombination processes are absent, the only recombination events that produce the loss of an electron–hole pair will be those where the photon emitted during the radiative recombination process escapes from the cell. Rather than trying to keep track of these photon recycling events within the cell, Shockley and Queisser concentrated on the light emitted by the cell, resulting from these internal recombination events.

In thermal equilibrium with its surrounding at, for example, room temperature, a cell with ideal black-body properties will emit radiation described by Planck’s radiation law for that temperature. Radiation of energy above the bandgap will originate mainly from band-to-band recombination processes, while that below the bandgap will originate mainly from other processes, e.g., light emitted during changes of electrons in energy position within a single band or even light entering the cell from the ambient and being re-emitted without absorption. Maximum energy conversion efficiency can be obtained if this natural demarcation is sharpened and all light of

energy above the bandgap threshold is attributed to band-to-band processes and none below the bandgap threshold is attributed to such processes.

By making this sharp demarcation, the number of band-to-band recombination events within the semiconductor leading to the escape of a photon is readily calculated by integrating the standard Planckian black-body formula for the number of photons emitted, over energies larger than the bandgap threshold. The result of this integration gives the number of effective or nett recombination events within the whole volume of the cell.

If the cell is now disturbed from thermal equilibrium by applying a voltage across it, the amount of light emitted will increase above thermal equilibrium values. This is because internal carrier concentrations increase above their equilibrium values, increasing their product as given by Equation 6.8. The rate of radiative recombination is proportional to this product, at least to first order.

In a normal solar cell, the electron and hole quasi-Fermi levels, E_{Fn} and E_{Fp} (and their difference) would vary throughout the cell to accommodate internal current flows, as given by Equations 6.9 and 6.10. This means that the externally emitted light will have a distribution that would be quite difficult to calculate, depending on a range of cell design parameters.

Fortuitously, the best device performance can be shown to be obtained in a situation where this calculation is greatly simplified. If we assume carrier mobilities are large, quasi-Fermi level changes across the cell will become small. In fact, these levels will be constant in the limit of infinite mobilities, with their separation also constant and equal to qV , where V is the applied voltage. This infinite mobility case can be shown to give maximum energy conversion efficiency from thermodynamic arguments, since finite mobility gives rise to entropy production within the cell (Luque and Marti, 1997). (It is easy to show that this infinite mobility assumption leads to maximum I_{sc} , since any finite value would lead to excitation of carrier concentrations above thermal equilibrium to support short-circuit current flows, giving rise to recombination that decreases the short-circuit current.)

With constant quasi-Fermi level separation equal to qV , the electron-hole product increases uniformly throughout the cell. It follows that radiative recombination processes are also uniformly enhanced, exponentially by the factor $\exp(qV)$, similarly enhancing the photon emission rate from the cell. The dark current that must flow to service this recombination will also increase exponentially, giving rise to a current-voltage characteristic essentially identical to that of an ideal p-n junction diode (Equation 6.15) with unity ideality factor.

A very significant difference, however, is that the dark saturation current, I_o , no longer depends on material parameters as in Equations 6.16 and 6.17, but depends only on the radiative absorption properties of the cell. In the limit for a process with a threshold E_G , I_o is given by:

$$I_o = qA \int_{E_G}^{\infty} n_{ph}(E, T) dE \quad (6.24)$$

where

$$n_{\text{ph}} = (2\pi f^2/c^2)/[\exp(hf/kT) - 1] \quad (6.25)$$

and where A is the absorbing area of the cell, n_{ph} is the Planckian photon distribution function (Shockley and Queisser, 1961), T is the cell temperature and $E = hf$ is photon energy. For the usual case where $E_G > kT$, the integration in Equation 6.24 can be made tractable using the expansion:

$$1/(1 - x) = 1 + x + x^2 + \dots \quad (6.26)$$

where $x = \exp(-hf/kT)$. This gives the precise result:

$$I_o = qA \left(\frac{2\pi kT}{h^3 c^2} \right) \sum_{m=1}^{\infty} [E_G^2/m + 2E_G(kT)/m^2 + 2(kT)^2/m^3] e^{-mE_G/kT} \quad (6.27)$$

where, generally, only the first term of the series expansion needs to be retained for reasonable accuracy (i.e., $E_G^2 \exp[-E_G/kT]$).

Since, in such an ideal cell, there is no increase in recombination above thermal equilibrium rates at short-circuit, it follows that there is no loss of photogenerated carriers by recombination in this special case. Each photon of sunlight of energy above the bandgap threshold, therefore, will be absorbed in the cell and will contribute to the short-circuit current. Hence, to calculate I_L for an ideal black body cell (equal to I_{sc} in this ideal case), one has merely to calculate the total number of sunlight photons of energy above E_G striking the cell surface.

Since solar cell energy conversion efficiency depends strongly on the sunlight spectral composition and intensity, as well as cell temperature, cell performance is normally referenced to a set of standard test conditions (STC). This set includes a standard Air Mass 1.5 solar spectrum, in the form of a table of energy content versus wavelength (Hulstrom *et al.*, 1985), with cell output scaled to 1 kW/m² of incident light intensity (of this standard spectral distribution) and with the cell temperature held at 25°C.

The limiting cell performance as a function of bandgap calculated under these standard test conditions is shown in Figure 6.11 (Tiedje *et al.*, 1984). (The results shown here can be readily calculated by hand; I_L and I_{sc} are found by integrating the standard spectrum over energies higher than the given energy value, with results included in some tabulations (Green, 1995); this can be scaled to an incident light intensity of 1 kW/m², if required; I_o can be found from Equation 6.27 which then gives V_{oc} from Equation 6.23; fill factor can be calculated from Equation 6.20; the efficiency is then calculated as the ratio of the cell power output from Equation 6.19 divided by the total power in the incident sunlight (1 kW/m² for STC)).

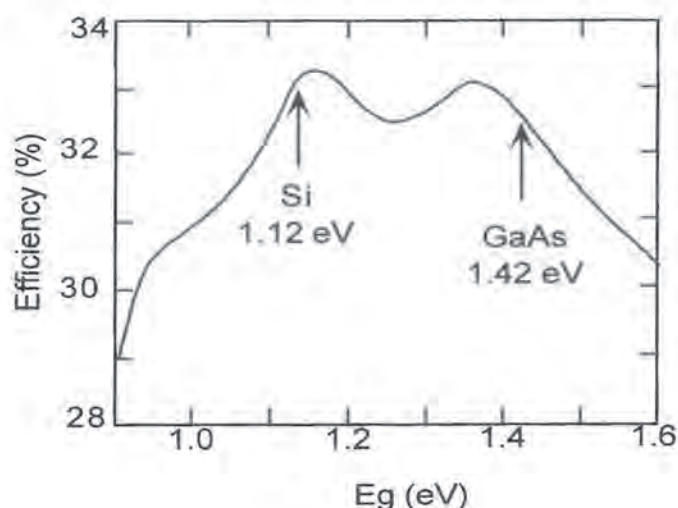


Figure 6.11 Limiting solar cell efficiency for an ideal solar cell made from semiconductor of the bandgap indicated under standard test conditions under the assumptions made in the text.

Note that peak energy conversion efficiency of around 33% is obtained for semiconductor material with bandgaps of 1.15 eV and 1.37 eV, with near peak performance over the 1.1–1.4 eV range (the double peak is due to a strong atmospheric water vapour absorption band centred at 1.3 eV photon energy that marginally mitigates against the performance of cells with a corresponding bandgap). The semiconductors used in all the cells that have demonstrated efficiency above 20% experimentally, silicon, GaAs and InP, have bandgaps in the above range at room temperature (1.12, 1.42 and 1.34 eV, respectively).

The maximum in performance occurs as a compromise between current and voltage outputs. The limiting efficiency is low mainly because each photon gives one electron, regardless of how much energy it has in excess of the semiconductor bandgap!

Any actual cell (apart from those not meeting the assumptions of the above analysis, as discussed below) will have lower efficiency than these limits. One limitation for any practical device will be optical; no practical device will absorb all incident photons of appropriate energy due to reflection at the point of incidence or obscuration by metal contacts to the cell. Another limitation relates to the electronic quality of the semiconductor material. Apart from radiative recombination processes, which must be present in any material that absorbs light, a range of non-radiative recombination processes are possible in any actual piece of semiconductor material. Some of these recombination processes are related to defects in the material and at material interfaces. Although most defects can be completely eliminated, in principle, some, such as vacant atom sites and additional atoms lodged between normal crystal sites, have an equilibrium density at any given temperature and are not avoidable, even in principle. Other non-radiative recombination processes that do not

depend on defects, such as Auger recombination (Green, 1995), will occur in parallel with radiative processes even in ideal material.

Two types of semiconductors can be distinguished that have widely different optical properties. One class, known as 'direct bandgap' semiconductors absorb light quite strongly and, by the reciprocity between absorption and light emission, have quite high rates of radiative recombination. GaAs is a prime example. This class of semiconductors makes good lasers and light emitting diodes. Although no solar cells at the time of writing have been reported using such materials where radiative recombination is the dominant recombination process within the cell, technological capabilities are at the level where this is possible.

The second class is formed from what are known as 'indirect bandgap' semiconductors. Silicon, technologically the most important semiconductor, is the prime example. For a photon near the bandgap energy to create an electron-hole pair in this material, an additional particle, a phonon, a quantized element of crystal vibration, also has to be involved in the process. This reduces the probability for light absorption, hence the rate of radiative recombination, making it likely that detrimental non-radiative recombination processes will be more efficient. In silicon, Auger recombination (an unavoidable process whereby an excited electron or hole recombines by either participant giving the pair's energy to a neighbour, rather than emitting it as light) limits the efficiency bound to 28.8% rather than the radiative value of 33% (Green, 1995).

6.4.2 Approaches for exceeding previous limits

Even though the limits in the previous section are calculated very generally, they are not strictly thermodynamic limits. Two assumptions, in particular, have a large impact on these calculated efficiency limits. One is that there is semiconductor of only a single bandgap involved in the conversion process, a second is that each incident photon creates, at most, only a single electron-hole pair. A third assumption is that the cell needs to be able to absorb light coming from all possible directions.

As previously mentioned, one reason why the limits of the previous section are low is that the surplus energy of a photon of energy above the bandgap is wasted. Monochromatic light can be converted much more efficiently than spectrally broad bandwidth sunlight, if the semiconductor bandgap is chosen to match the targeted wavelength (Luque and Marti, 1997).

If sunlight were split into narrow bandwidth packets and these packets sent to different cells designed to convert the particular wavelengths involved, much higher efficiency is therefore possible. Figure 6.12(a) shows an experimental approach that has been used for doing this for directional light using spectrally sensitive mirrors. However, Figure 6.12(b) shows a much better way of achieving the same result, relying on the fact that semiconductors are largely transparent to light of energy below their bandgap.

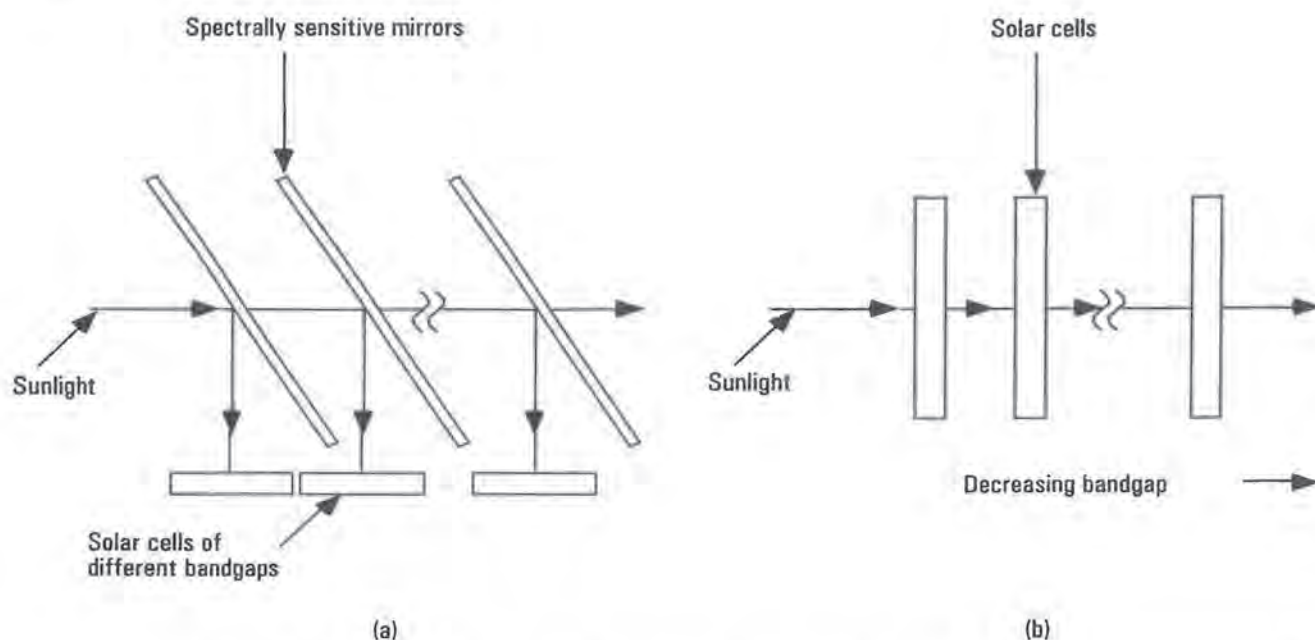


Figure 6.12 Multigap-cell concepts: (a) spectrum-splitting approach; (b) tandem-cell approach.

By stacking cells on top of one another with the highest bandgap uppermost, light is automatically filtered in the desired way as it passes through the stack. The uppermost cell absorbs and converts the highest energy photons, with the rest of the light passing through to the next, where the process repeats itself.

For highest efficiency, each cell is operated as a separate unit with separate electrical connection to each. An enormous simplification without significant loss of performance can be obtained if the bandgaps of the cells are constrained additionally so that approximately the same number of photons are absorbed in each cell, allowing their current outputs to be matched. Then the multiple cells can be connected in series with only two external connections required as in a standard cell. Tandem cells designed in this way are now used in high cost applications on spacecraft and also for low cost terrestrial use, as discussed later.

Another way efficiency could be improved would be if the excess energy of high energy photons were not wasted. Such an energetic photon will excite an electron from deep in the valence band to an energy high in the conduction band. This corresponds to the creation of an electron-hole pair, with both the electron and hole having a high energy in excess of that of carriers at the band edge. Normally, this excess energy is quickly lost in collisions with the atoms in the crystal, in multiple small packets (phonons). Very quickly, these originally energetic carriers are indistinguishable from those created by much lower energy photons.

A more desirable possibility is for the excess energy to be given off in a single packet by exciting an extra electron-hole pair across the gap (this

could occur sequentially as implied by the above description, or simultaneously during the original photon absorption process).

By creating multiple electron-hole pairs in this way, the extra energy of high energy photons need not be wasted and much higher energy conversion efficiency is possible in principle (Werner *et al.*, 1995, Würfel, 1997). However, none of the common semiconductors are sufficiently efficient at this process for it to impact cell performance (careful measurements are required even to detect its presence amongst the more efficient phonon loss processes previously described). This does not mean, however, that it may not be possible to find or engineer a material with much better properties in this area in the future.

Another way, in principle, of improving the cell performance is by noting that direct sunlight comes from only a small section of the sky (the sun subtends an angle of only 0.267° at the Earth's surface). To convert the direct light, there is no need for a solar cell to accept light from all directions, as a black-body does, but only from this very much smaller range of directions. Such an 'angularly selective black-body' cell can have a much higher efficiency since such selectivity also restricts light emission, hence reducing I_0 from the value given by Equation 6.24, increasing V_{oc} and efficiency.

I_0 is reduced by the ratio of the solid angle subtended by the whole sky to that subtended by the Sun (46 200 times!). A cell with such angular selectivity would therefore have much higher conversion efficiency, but would have to track the Sun's position quite closely and would not be able to convert the diffuse component of sunlight. Essentially, systems that use lenses or mirrors to concentrate sunlight onto a cell take advantage of this apparent performance gain. A note of caution is required here in that, even though the quoted efficiency of such systems (and similar efficiencies for solar thermal electric systems) can seem quite high, what is being quoted is the efficiency of conversion of direct sunlight rather than that of the available sunlight (direct plus diffuse)!

Other less commonly known approaches for improving photovoltaic conversion efficiency have been described elsewhere (Green, 2000).

6.5 HETEROJUNCTIONS, METAL-SEMICONDUCTOR CONTACTS, TUNNELLING JUNCTIONS

6.5.1 Heterojunctions

The junctions described in Section 6.3 are formed between p-type and n-type regions of the same semiconductor material and are known as 'p-n homojunctions'. Many solar cells described in the following sections use junctions formed between p-type material of one semiconductor and n-type material of a different semiconductor. Such 'p-n heterojunctions' have properties quite similar to homojunctions.

The thought experiment conducted when explaining Figures 6.5 and 6.6 can be repeated for semiconductors of different bandgap with similar results (Figure 6.13). The constancy of the common Fermi level is the overriding factor. However, there is an additional degree of freedom in determining the alignment between the band edges on either side of the junction (perfect alignment is a justifiable assumption for homojunctions).

A number of theories have been put forward to explain exactly what determines band alignment in junctions between different semiconductors (Böer, 1990). The actual situation appears quite complex, with alignment depending upon interfacial strain, interfacial chemistry and interfacial dipole layers. Although reasonable estimates can be made for any given system using these theories, this is a case where experiment is definitely the final arbitrator. From the point of view of deducing solar cell properties, experimental values of band offsets can be used in a straightforward manner.

The theory of the current–voltage characteristics of p–n heterojunctions parallels that of homojunctions for well behaved cases. For example, Equations 6.15–6.17 still apply but with appropriate material parameters for each side of the junction. The intrinsic carrier concentration, n_i , is usually the most important of these parameters. This makes the current–voltage characteristics and solar cell properties, in general, depend mainly on the properties of the lower bandgap material in the heterojunction, since this has the larger value of n_i as well as determining the threshold for photon absorption.

However, additional complications can arise when energy ‘spikes’ are created in one of the bands right at the heterojunction such as in the valence band edge in Figure 6.13. These spikes can create a problem not present in homojunctions, specifically, a difficulty in transporting the relevant carriers through the depletion region due to the spike. Such spikes are generally undesirable because of this.

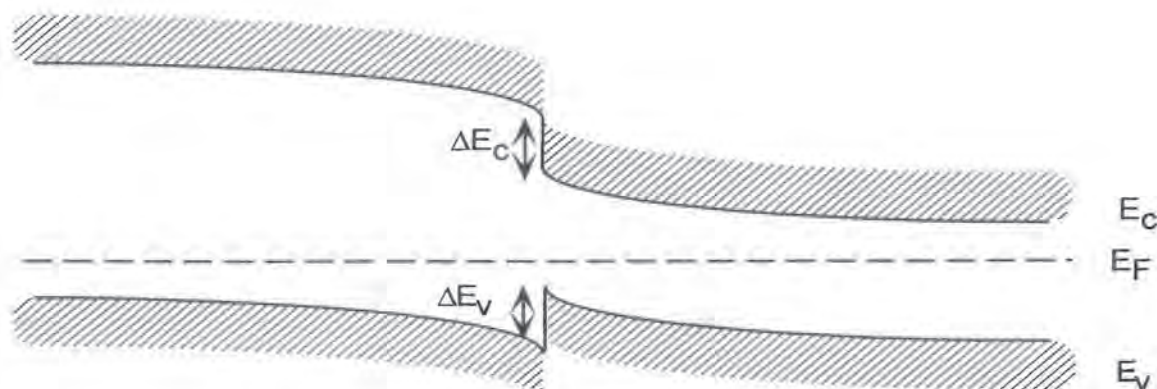


Figure 6.13 A heterojunction solar cell formed from p-type and n-type material of different bandgap. In general, a discontinuity in the energy of each band edge will occur near their interface.

6.5.2 Metal–semiconductor contacts

Solar cells generally are connected to the outside world using metal contacts. Similar issues apply to energy alignments at a metal–semiconductor contact as to the case of semiconductor heterojunctions. Experimentally, most metal contacts are found to cause carrier depletion in the underlying semiconductor as shown in Figure 6.14, creating a barrier at the surface and nonlinear, rectifying characteristics for this junction (such junctions can be used as solar cells in their own right, although fundamentally less efficient than an ideal semiconductor homo- or heterojunction).

The depletion of carriers near the contacts generally poses a problem for standard homo- or heterojunction cell designs since the resulting junction opposes the photovoltaic action of the main cell. The practical approach to overcoming this problem is to ensure that the semiconductor material is heavily doped whenever contact is made as in Figure 6.14(b). This reduces the width of the depletion region under the contact so that carriers flow across it by quantum-mechanical ‘tunnelling’ processes. Essentially, carriers, due to their wavelike nature, do not notice the barrier once it becomes very thin, allowing very low resistance contact between the metal and semiconductor material, ‘shorting-out’ any photovoltage generated at the contact.

6.5.3 Tunnelling junctions

Similar ‘tunnelling’ occurs if both sides of a p–n junction are very heavily doped (Figure 6.15). Carriers can tunnel directly between the conduction and valence band across the junction depletion region as indicated. This shorts-out the normal photovoltage generated by the junction. Such heavily

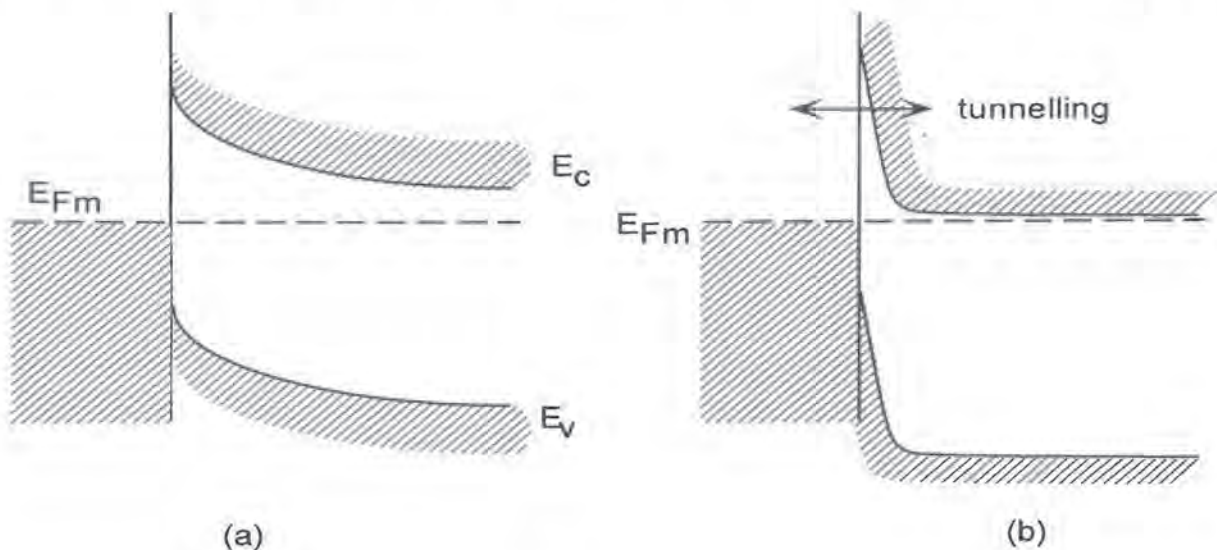


Figure 6.14 Metal–semiconductor contacts: (a) contact to lightly doped semiconductor; (b) tunnelling through the contact region in the case of heavily doped semiconductors.

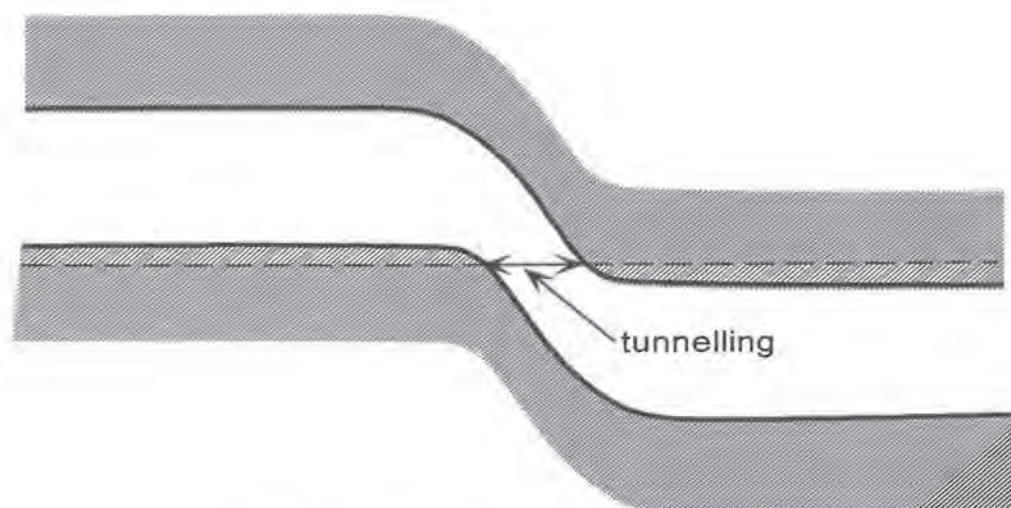


Figure 6.15 Heavily doped p-n junctions showing tunnelling between conduction and valence bands in junction region.

doped tunnelling junctions are used to advantage to connect the cells stacked on one another in tandem cell designs discussed in subsequent sections.

6.6 SILICON SOLAR CELLS

6.6.1 Advantages of silicon

Silicon is an ideal material for solar cells. Not only is silicon non-toxic, but it is also the second most abundant element in the Earth's crust (after oxygen) posing minimal environmental or resource depletion issues if used on a large scale. Silicon also has a well established technological base due to its predominant commercial position in microelectronics.

In view of the above, particularly the latter, it is perhaps not too surprising that the overwhelming majority of commercial solar cells fabricated to date have been based on silicon in one of three forms, crystalline, multicrystalline (large grain polycrystalline) and amorphous. As shown in Figure 6.16, polycrystalline material consists of abutting grains where, within each grain, atoms have the periodic arrangement of crystalline material, but the grains are misaligned at the boundaries between them. In amorphous material, although the local environment resembles that of an atom in crystalline material, slight deviations in bond angles and bond lengths cause the loss of long range order. Without the 'template' provided by perfect periodicity, there is the tendency for this imperfect arrangement to cause a high density of defects, such as dangling bonds. To produce adequate electronic quality in the amorphous form, silicon is alloyed with hydrogen at about the 10% atomic level. This results in material with properties distinctly different from the elemental crystalline counterpart.

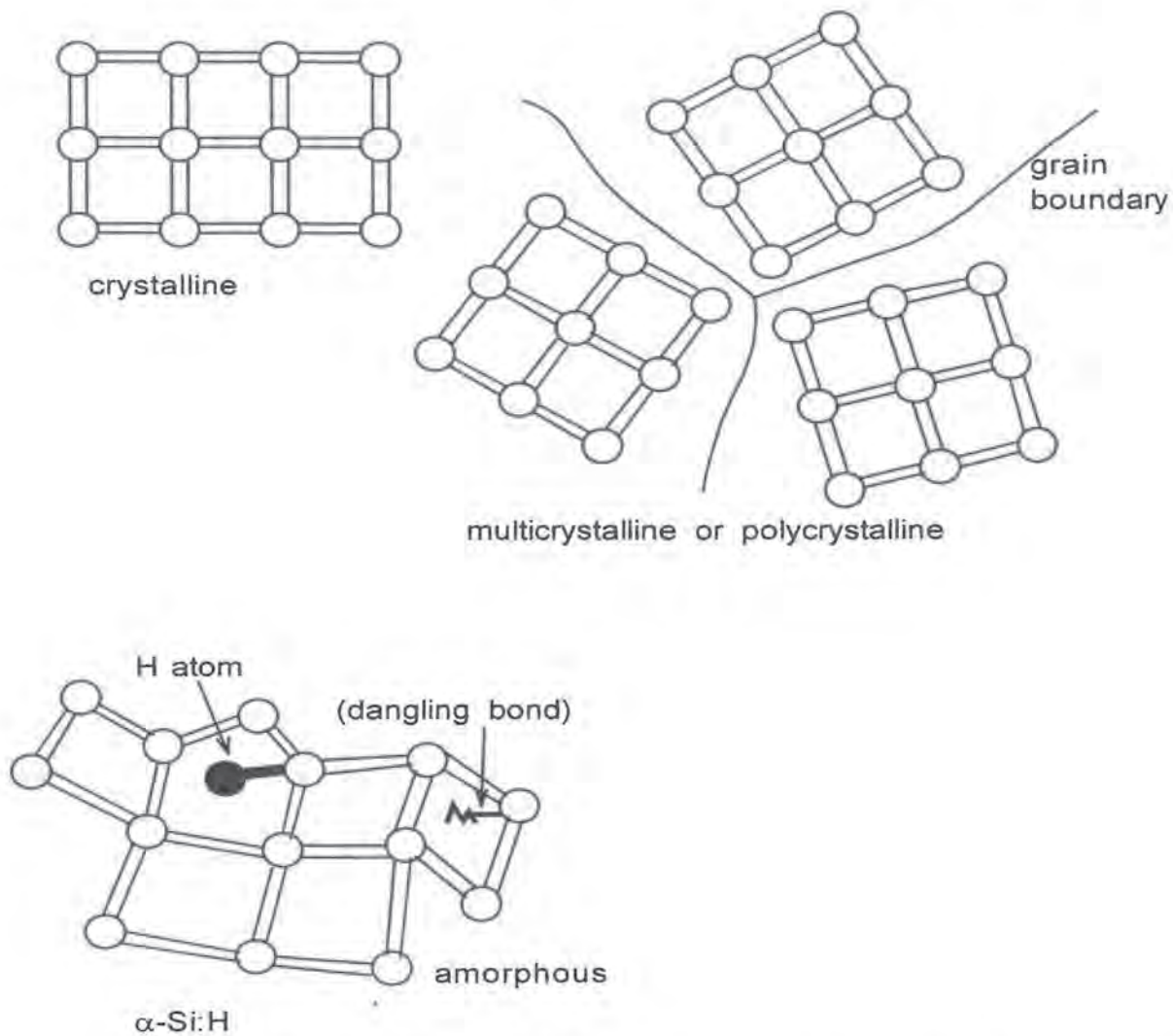


Figure 6.16 The structure of crystalline, multicrystalline, polycrystalline and amorphous silicon (multicrystalline silicon differs from polycrystalline silicon only in the size of the crystalline regions between 'grain boundaries').

The following sections briefly describe the history of each silicon cell type, present cell designs and directions in which the different technologies are heading.

6.6.2 Crystalline silicon cells

Evolution of cell design (Green, 1995)

The first silicon cells were described in 1941 (Ohl, 1941) and were multicrystalline. The first crystalline cells were reported in 1954. The evolution of laboratory cell performance from these early beginnings is shown in Figure 6.17. As shown in this figure, from the mid-1950s until the early 1960s, there was a very rapid evolution in cell performance stimulated by applications on spacecraft. Performance stabilized in the 1960s, with some

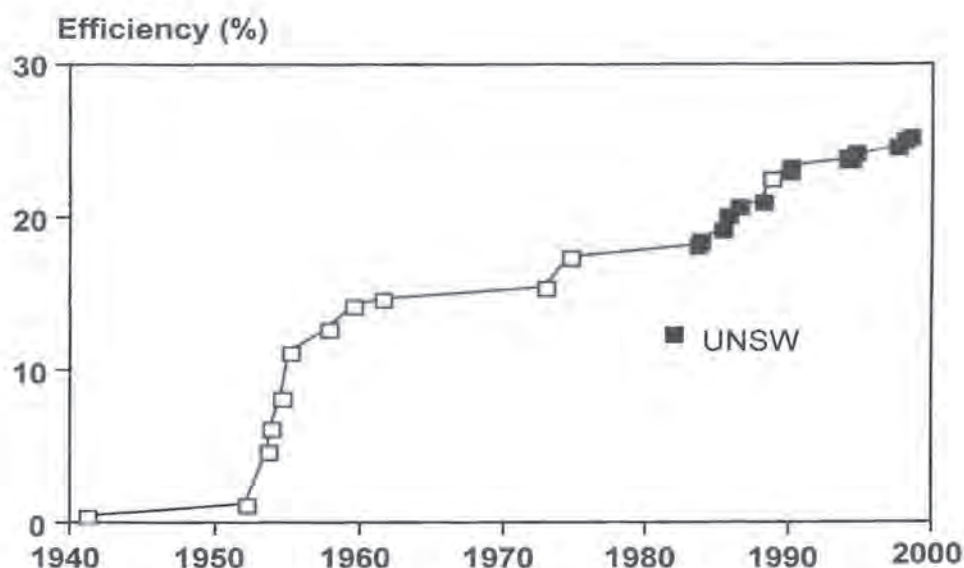


Figure 6.17 Evolution of silicon laboratory cell efficiency.

significant improvements in the early 1970s. Since the early 1980s, there has been a period of sustained improvement in the performance of research devices although, until recently, commercial silicon solar technology remained based largely upon technology of the 1970s.

The structure of a standard commercial silicon cell as used in space is shown in Figure 6.18. These space cells are processed using processing similar to that used in microelectronics. The substrates are prepared from crystalline cylindrical ingots grown by the Czochralski (CZ) method and sliced into wafers by inner diameter sawing (McGuire, 1988, Green, 2002). The ingots are doped with boron during growth to give p-type material. The p-n junction is formed by lightly diffusing phosphorus into the top cell surface. The surface is heavily doped with phosphorus (just below solid solubility limits) but the depth of phosphorus diffusion is quite small ($\sim 0.25 \mu\text{m}$ junction depth). Such a shallow diffusion, traditionally known as the 'emitter' diffusion, allows carriers photogenerated between the junction and the surface to have a better chance of being collected by the junction, i.e., these carriers are more likely to travel from the point of generation to the junction than recombine at the surface or in transit. Thin emitter regions with good properties in this respect are often referred to as being 'transparent' to minority carriers. The high doping near the surface improves tolerance to poor surface properties by suppressing surface minority carrier concentrations and hence their recombination rates.

The p^+-p junction at the rear of the cell is usually formed by the alloying of a layer of evaporated Al. This 'high-low' junction feature is often known as a 'back surface field' (BSF) due to the electrostatic field arising from the dopant gradient at this junction. Although this nomenclature is universally accepted, it is not entirely appropriate since it is fundamentally the suppression of the minority carrier concentration near the rear contact by the p^+

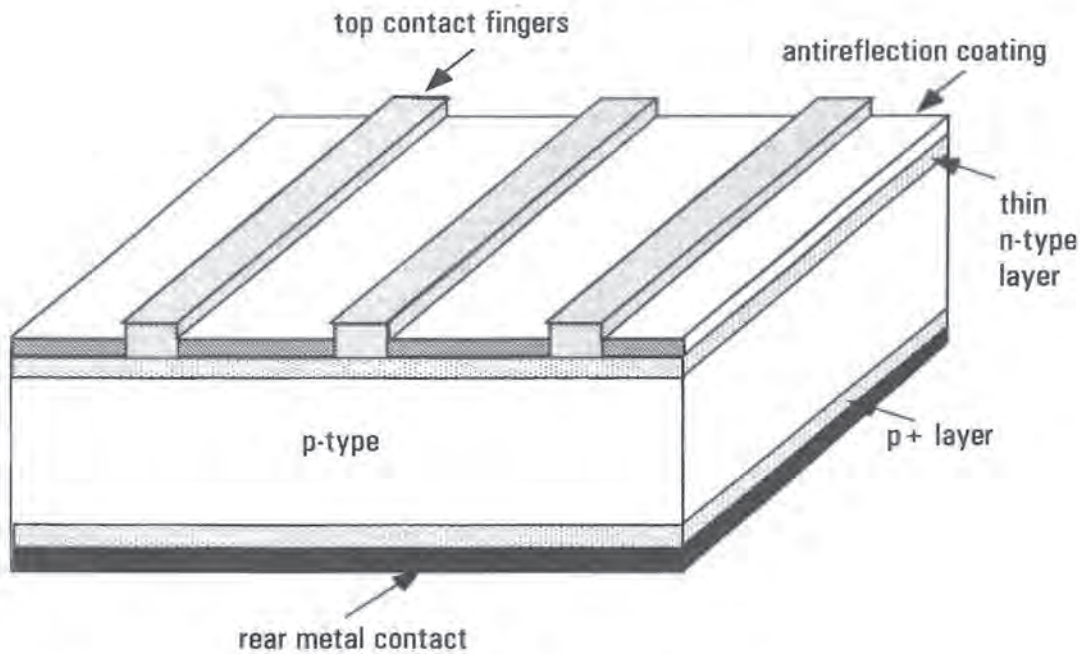


Figure 6.18 Conventional silicon space cell.

region that makes this region effective, rather than the previous field. The effect of the p^+ region is usually characterized by assigning an effective surface recombination velocity along the p - p^+ interface. This velocity is a lot lower than along a silicon-metal interface. The reduction in surface recombination velocity has beneficial effects upon both the I_o of the cell as per Equations 6.16 and 6.17 and also upon the prospects for collecting carriers generated in the p -type region near the rear of the cell. The introduction of a BSF therefore improves both V_{oc} and I_{sc} .

A Ti/Pd/Ag multilayer metallization scheme is universally used as cell metallisation in silicon space cells. The Ti is deposited first by vacuum evaporation to ensure good adhesion of the multilayer and low resistance contact to the underlying silicon. The Ag is deposited last, either by vacuum evaporation or by electrolytic plating, and imparts high conductivity to the trilayer. The intermediate Pd layer acts as a barrier that eliminates a detrimental reaction between the Ti and Ag in the presence of moisture. For the rear contact, an Al layer is often evaporated before the Ti layer to improve the rear surface reflectance. Such an enhanced reflectance rear contact is referred to as a back-surface reflector (BSR).

To reduce reflection from the top surface of the cell, either a single layer antireflection (SLAR) coating of TiO_2 or Ta_2O_5 is evaporated onto this surface or a higher performance, double layer (DLAR) coating of TiO_2 followed by Al_2O_3 is used.

The performance of space cells fabricated in this way is quite modest by the standards of the best cells of Figure 6.17. A DLAR/BSF/BSR silicon space cell has an energy conversion efficiency of about 14.5–15% under Air Mass Zero (AM0) space radiation, and a higher efficiency of about

16–17% under AM1.5 terrestrial radiation due to the more favourable (redder) spectrum of the latter. However, initial or beginning-of-life (BOL) performance is not the most important parameter for a space cell. In space, cells are exposed to damaging high energy particles (electrons, protons, etc.) present in the Earth's radiation fields (Markvart, 1990), from which ground based cells are protected by the Earth's atmosphere. The cell design also determines the end-of-life (EOL) performance after such damaging exposure during the life of the space mission (Markvart, 1990).

The other important cell feature is the thermal performance in space. Since thermal radiation is the main heat loss mechanism in the vacuum of space, thermal performance is determined both by how much light the cell absorbs as well as by the cell's emissivity at the infrared wavelengths where it re-radiates absorbed energy. BSR cells have a good thermal performance since infrared light in the solar spectrum is reflected out of the cell, rather than being absorbed.

The space cell design of Figure 6.18 was developed in the early 1970s. There have been two important directions in which cell design has evolved subsequently. One is towards lower cost fabrication for terrestrial use and the other is towards higher efficiency devices for research and specialised high performance applications. Although, at first sight, these might seem to be completely different directions, there has been considerable interchange between developments in the two areas.

The structure of a 24.7% efficient PERL (passivated emitter rear locally-diffused) cell is shown in Figure 6.19. These and cells with almost identical structure have been made in reasonable quantities for specialised applications where performance is at a premium, such as in solar car racing. Compared with the standard space cell of Figure 6.18, several performance enhancing features are apparent. Perhaps the most striking is the use of a texture on the top surface of the cell, in this case taking the form of 'inverted pyramids'.

These pyramids are formed by using anisotropic etches to expose slowing-etching (111) crystallographic planes in the crystalline silicon substrate, originally chosen to be of (100) orientation. All four (111) equivalent planes are exposed by this surface etching, intersecting to form the distinctive pyramidal features. The surface of PERL cells is selectively masked by a patterned oxide to define the pyramid location. The bases of the pyramids are about 10 μm wide.

One role of the inverted pyramids is to reduce reflection of light incident on the top surface of the cell. Light incident perpendicularly to the cell will strike one of the inclined (111) equivalent planes obliquely. Most will be refracted obliquely into the cell at this point. Since the (111) planes are at an angle of 54.7° to the original surface of the cell, the remaining reflected light is reflected downwards, giving at least one more chance of being coupled into the cell (Green, 1995). Even without antireflection coatings, only about 30% reflection occurs at each point of incidence on a silicon

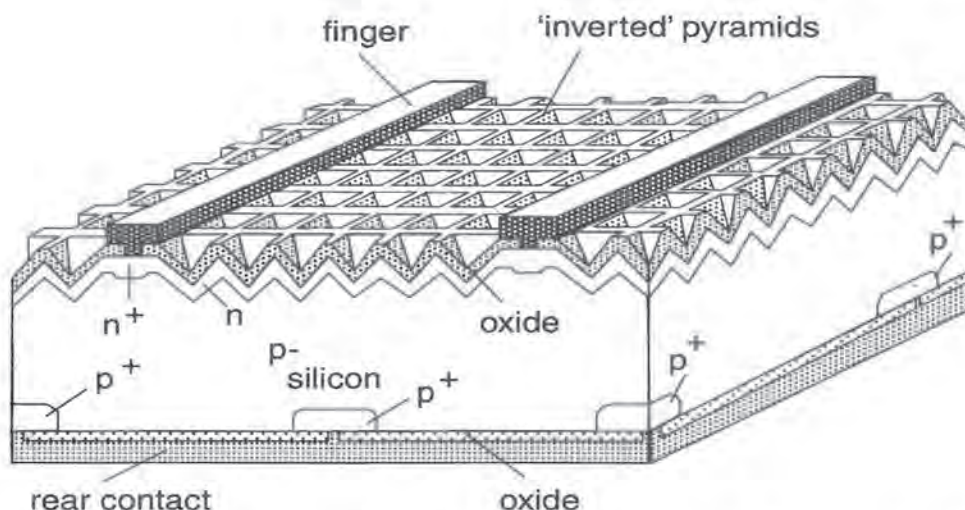


Figure 6.19 PERL cell (Passivated Emitter, Rear Locally Diffused).

surface. Hence, after two reflections, about 9% of the light would remain unabsorbed (30% of 30%). With antireflection coatings, reflection at the first point of incidence can be kept below 10% over a reasonable wavelength range, reducing reflection to around 1% after two 'bounces'.

Since the pyramids cause light refracted into the cell to travel obliquely across the cell, a second advantage of the surface texture is that it causes light to be absorbed closer to the active top junction of the cell. A third benefit arises for light that is so weakly absorbed that it passes across the entire cell thickness without absorption. The rear contact of the PERL cell is separated from the silicon by an intervening oxide layer. This gives much better reflectance than if in intimate contact (around 97% versus about 85% for the lowermost Al layer in the standard BSR rear contact multilayer). Hence, most of the weakly absorbed light reaching the rear is reflected and heads internally back towards the front surface. This light can hit any one of three faces of the pyramids internally. If it hits the face oppositely inclined to the face that originally coupled the light in, the light is coupled out of the cell without further ado! About half the light travels this route. For light from the rear striking the other two faces, the angle of incidence is such that it is totally internally reflected, possibly even more than once, and heads back towards the rear of the cell. Since the light must strike the silicon surface within an angle of 16° or so of the perpendicular to escape [$\sin^{-1}(1/n)$ where n is the refractive index of silicon], only a small fraction of light escapes after each subsequent double pass across the cell as the direction of light is increasingly diversified [$1/n^2$ or 9% for completely randomized light directions (Yablonovitch and Cody, 1982)].

By increasing the optical pathlength for weakly absorbed infrared wavelengths in this way, the current output of the cell can be increased substantially. A pathlength enhancement of weakly absorbed light of $4n^2$ (about 50) is possible by such 'light trapping' approaches (Yablonovitch and Cody, 1982). This factor, in principle, can be increased even further for cells, such

as those in concentrator systems, that only have to accept light from well defined directions (Section 6.4.2). Since light trapping increases the absorbance of a cell, it may not always be a desirable feature for a space cell since it may increase operating temperatures, with the resulting loss in output voltage offsetting the increased current output (Figure 6.10).

Another important feature is the almost complete enshrouding of the PERL cell by a thin layer of thermally grown oxide. High levels of surface passivation provided by such oxides give low surface recombination rates along the cell surfaces without having to have surfaces heavily doped, increasing design options. Contact to the n-type region is made through slots in this passivating oxide, while that to the p-type region is made through small holes. The regions immediately under the contacts in the contact regions are heavily doped to suppress minority carrier concentrations and hence recombination rates at the contacts.

The cell is finished by adding a DLAR coating. For this to be optically effective, the final thickness of the underlying passivating oxide has to be less than about 20 nm. This oxide is grown separately from the rear passivating oxide, since the latter is most effective when grown 10–20 times thicker.

Highest performance is obtained if these devices are fabricated on either float-zoned (FZ) or magnetically confined Czochralski grown (MCZ) silicon of 1–2 Ω cm resistivity. This is because the high minority carrier lifetimes possible with such material can be retained throughout cell processing. Carrier lifetimes in the 1–10 ms range are routinely obtained in such devices, quite close to the value of 30 ms that appears to be the highest ever measured for silicon (Yablonovitch *et al.*, 1986). Good, but slightly poorer results have also been reported for cells fabricated with the PERL structure using conventional CZ substrates.

Although PERL cells were developed primarily for research purposes, they have found applications as advanced space cells and in solar car racing. Features such as oxide passivation and the use of heavily doped regions to passivate contact areas have found their way into low cost cell production via the buried contact cell, discussed later. PERL cells are also very efficient at converting narrow band or monochromatic light with efficiencies approaching 50% demonstrated (Green *et al.*, 1992). This makes such cells of interest for laser beamed energy transmission concepts or for thermophotovoltaic energy conversion (Chubb, 1990). PERL cells can also convert concentrated sunlight with high efficiency of up to about 50 Suns' concentration. Above this concentration level, a different silicon cell design approach, discussed below, has given best results.

Rear contact cells

The rear contact solar cell (Swanson, 1986, Partain, 1995, Green, 1995) of Figure 6.20 introduces a number of different features including the placement of both p- and n-type contacts on the rear cell surface in the form

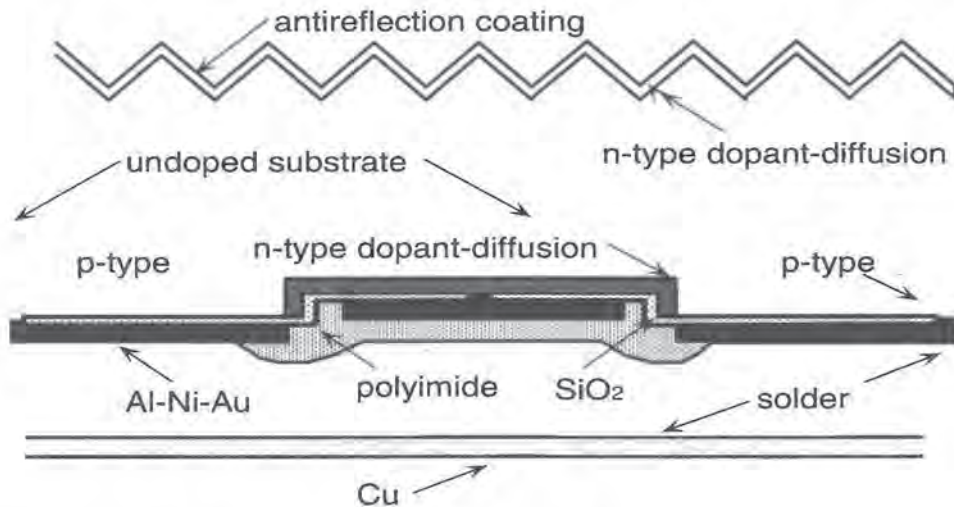


Figure 6.20 Rear contact solar cell.

of interspersed stripes. Since most carriers are photogenerated within a few microns of the top cell surface in sunlight, these have to diffuse to the rear of the cell to be collected. The cell therefore has to be very thin (usually less than $150\text{ }\mu\text{m}$) and to have very large carrier lifetimes, to reduce carrier loss by recombination during the journey to the rear. Extremely good quality surface passivation is required along the front illuminated surface of the cell to reduce carrier recombination there. Although this can be obtained by growing oxide directly onto the lightly doped n-type substrates normally used in these devices, it was found that such a surface was unstable under ultraviolet (UV) radiation. This is presumably due to the injection of 'hot' carriers generated in the silicon by this light into the oxide. Doping the surface with a phosphorus diffusion greatly improves this stability, as does adding a UV absorbing layer on top of the cell, such as provided by a TiO_2 SLAR coating (Gruenbaum *et al.*, 1990).

As opposed to the PERL cells, which operate at relatively low levels of minority carrier injection, these rear contact cells are designed to operate under 'high level injection' (Swanson, 1986). Under operation at high sunlight intensities, the bulk n-type regions are flooded by approximately equal quantities of electrons and holes, overriding the carrier contribution from the low concentration of dopants. This largely eliminates the resistive losses that might be expected from a lightly doped region if it remained in low level injection (Swanson, 1986). Placing both contacts on the rear not only eliminates the shading losses that occur in conventional designs, but also allows a much larger fraction of the cell area to be dedicated to extracting current from each polarity contact. As seen from Figure 6.20, considerable care has been taken in the design of the rear metallisation to allow low resistance electrical and thermal connections to the cell while providing electrical isolation between the two contact polarities.

The cells of this and similar type have been used in a number of concentrated sunlight demonstration systems. Over 7000 were fabricated for

one-sun use for a solar car, the 'Honda Dream', which won the 1993 World Solar Challenge across Australia (Verlinden *et al.*, 1994). These cells were used in an 8 m² solar array which was probably the first ever of this size to exceed 20% energy conversion efficiency.

Screen printed commercial cells (Green, 1995)

For more general terrestrial use, the interest is in reducing cell costs as much as possible usually, but not always, at the expense of performance. The most common fabrication approach is based on technology developed for thick film hybrid microelectronics, to produce the cell structure shown in Figure 6.21.

Starting material is again usually a boron doped silicon wafer. These wafers are often either 'off-specification' for microelectronics, recycled from the microelectronics industry, or grown from polysilicon source material that is 'off-specification'. The cylindrical CZ grown ingot is often 'squared off' prior to wafering to give 'quasi-square' wafers. The ingot is cut into wafers using inner diameter or continuous wire saws to give a wafer thickness of 200–400 μm . After etching in NaOH solution to remove saw damage, the wafers are generally 'textured' in a weaker, anisotropically etching NaOH solution to give the random layout of upright pyramids shown in Figure 6.21, ideally of 5–10 μm pyramid base dimension.

Next the wafers are diffused, either in a conventional tube furnace, or in a belt furnace as commonly used in hybrid microelectronics. The top and rear contacts are then applied by screen-printing silver paste, again a hybrid microelectronics approach. For the top contact, the construction of the wire mesh used in the screen limits the width of the lines which can

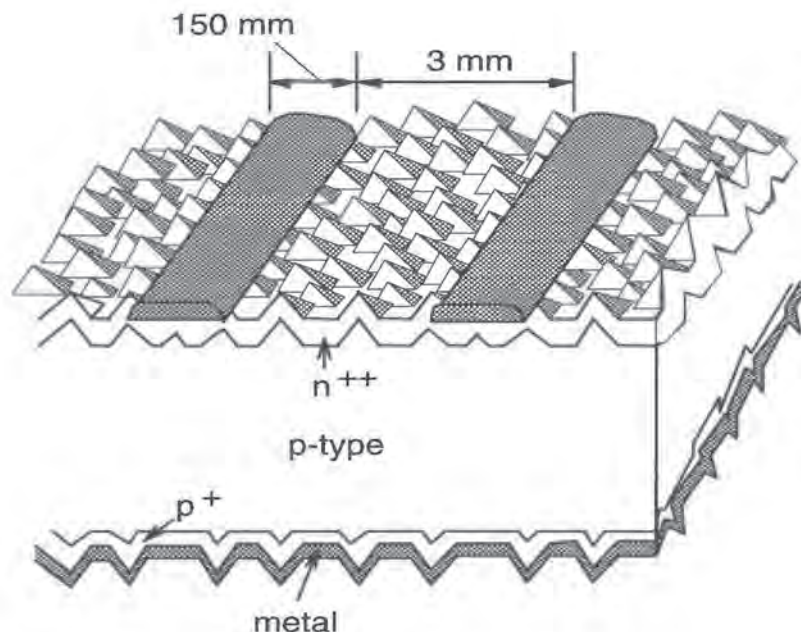


Figure 6.21 Screen printed silicon solar cell (not to scale).

be economically produced to about 150 μm . The low aspect ratio (height/width ratio), the relatively broad linewidth achieved by these devices and the relatively poor conductivity of the fired silver fundamentally restricts performance (Green, 1995). Another restriction is that, to ensure sufficiently low contact resistance, the diffused top layer in the cell has to be quite thick and heavily doped. This is not an ideal situation as apparent from the earlier discussion of silicon space cells. Carriers generated near the surface are not collected causing a poor response to blue wavelengths that are absorbed quickly in silicon. Phosphorus is often added to the top surface paste to help reduce contact resistance.

A variety of approaches are used for the rear contact. In the simplest case, some manufacturers directly screen-print silver paste, as for the top contact. Others add Al to the Ag paste in an attempt to form a BSF simultaneously by Al alloying during the paste firing. Yet others first screen and fire an Al paste to produce the BSF layer, and then screen and fire an Ag paste. The Ag and Al can interact giving rise to additional processing variants to address this issue.

An inexpensive antireflection coating, generally TiO_2 , can then be added to the front surface. This improves cell performance by about 8% in air, but only by about 4% after encapsulation under glass or material of a similar refractive index.

Cells are generally either round and of 10–12 cm diameter or quasi-square and 10–12 cm along each side. Energy conversion efficiency in the 11–15% range is generally produced by this screen printing approach. When encapsulated into modules, module efficiency is in the 10–13% range.

This technology for making cells was first demonstrated in the early 1970s and had become the commercial standard by the early 1980s. As apparent from Figure 6.17, there have been quite substantial improvements in silicon laboratory cell performance since this time. Some of these improvements are now finding their way into commercial production as described below.

Buried-contact solar cells (Wenham et al., 1994, Green, 1995)

It has proved difficult to modify the screen printing approach to increase cell efficiency due to the particular requirements imposed by the very simple metallization approach. Most success has come by pursuing a completely different route, with the most successful commercial alternative so far being the buried contact cell of Figure 6.22. This device was first commercialized by BP Solar in the early 1990s as the company's 'Saturn' product line, and has been produced in increasing production volumes since that time.

As previously noted, performance from the screen-printed cell approach is sacrificed to the processing simplicity offered by the screen-printing approach used for the cell contacts. The key to overcoming these limitations proved to be finding an equally simple way of metallising cells but one that did not demand the same performance compromise. In the buried contact approach, the cell is metallised by the electroless deposition of a

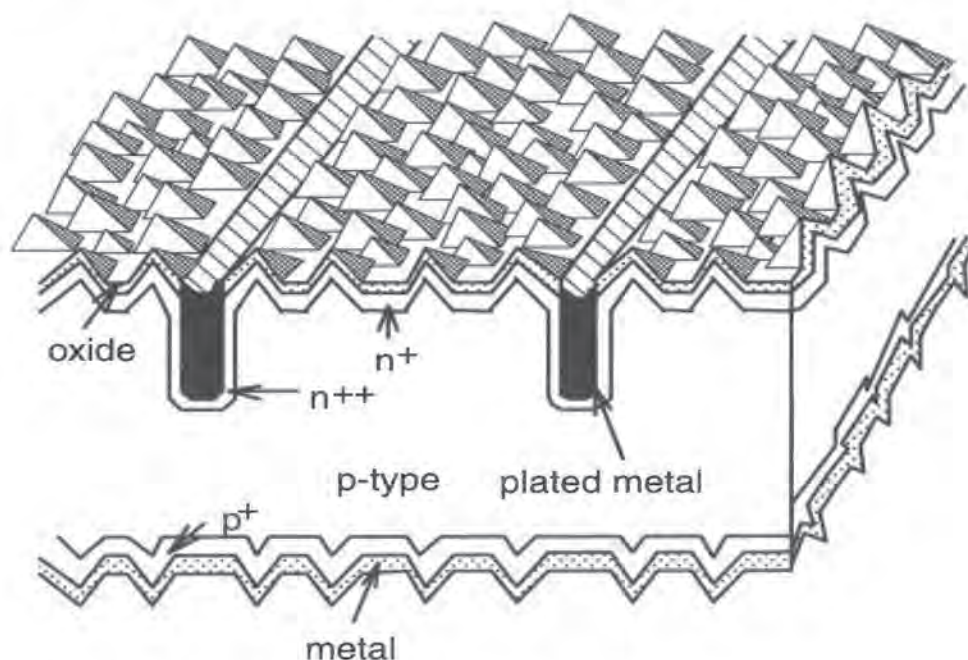


Figure 6.22 Buried contact solar cell.

Ni/Cu/Ag multilayer from appropriate chemical solutions. This is inherently a much less expensive metallisation step than screen-printing and also gives much better electrical performance, in terms of metal conductivity and contact resistance.

The disadvantage of this metallisation approach previously had been that there was no simple technique for defining the pattern of the deposited metal. The buried contact approach solves this difficulty in a particularly elegant way. Buried contact cell processing starts identically to that for a screen printed cell. In-coming wafers are etched to remove saw damage and then chemically textured. The top junction of the cell is then formed by diffusion (much lower doping level than in the screen-printed cell case) and an oxide is thermally grown along the diffused surface or, alternatively, silicon nitride deposited.

A laser is used to cut deep grooves through the resulting dielectric layer and part of the underlying silicon. After cleaning these grooves, the cells undergo a second diffusion, much heavier than the first. Since all but the grooved regions are covered by dielectric, blocking diffusion in these areas, the diffusion is automatically localized to the grooves. Aluminium is then deposited onto the rear surface and sintered to give a rear BSF. The cell is next placed in the electroless plating solutions that selectively deposit metal on conducting areas, namely the grooves on the top surface, since the rest of the top surface is still protected by dielectric, and the entire rear surface.

The buried contact approach allows a number of high efficiency features to be incorporated into the cell. The key to this is the multiple ways in which the top surface dielectric is used. It is not only used as both a diffusion and a plating mask during processing, but serves as both top surface passivation and antireflection coating in the completed device.

High efficiency features, in approximate order of importance, are the nearly ideal top surface diffusion and surface passivation, since these features can be optimized independently of contact shading and contact resistance constraints. Because of this, buried contact cells respond almost ideally to the rapidly absorbed blue wavelengths giving an estimated 15–20% contribution to the performance advantage over a screen-printed cell. A large performance improvement component also comes from the reduced shading loss by the top contact metal since the metal lines can be much narrower than screen printed lines. This accounts for another 5–10% advantage, depending upon cell design. An additional advantage arises from the much superior metal conductance possible. Not only is the conductivity of the plated metal (mainly Cu) about three times that of screen-printed silver but the grooves also can be very deep, giving scope for large cross-sectional areas. An additional advantage is much lower contact resistance. The above resistance improvements combined give a further 5% performance advantage. Additional advantages that are more difficult to quantify arise from the ability of each of the laser grooving, the heavy phosphorus groove diffusion and the rear Al BSF formation steps to provide very effective gettering of impurities from bulk regions of the cells (Green, 1995).

On the standard CZ silicon used in production, the relative cell efficiency advantage is in the 25–30% range (Wenham *et al.*, 1994). The buried contact sequence produces cells in the 16–18% efficiency range on the same substrates that give efficiency in the 11–15% range for screen printing (BP Solar, 1994). Costings based on several years of production experience suggest that the costs of making these improved cells is the same per unit area as screen printed cells (Wenham *et al.*, 1994), giving a pronounced advantage in cost per unit power output and additional advantages in installation costs.

Further developmental work is concentrating on replacing the rear Al BSF step by a grooving approach similar to that used on the top surface (Green, 1995). This gives a structure which is conceptually very similar to the PERL cells described earlier, the highest efficiency silicon cells yet demonstrated. Combining this or related approaches with thinner wafers, a cell efficiency of 20% in commercial production on CZ substrates may eventually be reached.

6.6.3 Multicrystalline and ribbon wafers

The requirements upon material quality for photovoltaics are less demanding than for microelectronics allowing a relaxation in the quality of the starting substrate, without major performance loss. This has prompted the search for alternatives to CZ ingot growth plus wafering for the preparation of silicon solar cell substrates.

Rather than the crystalline ingots produced by CZ growth, large grain polycrystalline (multicrystalline) ingots can be produced by technologically

less demanding processes involving the solidification of a melt in a crucible as shown in Figure 6.23(a), such as casting (Ferrazza, 1996). These more robust processes reduce ingot costs since much larger ingots can be produced, with much higher throughput per unit investment in growth equipment. The ingots can be sawn to smaller units as in Figure 6.23(b), before slicing into wafers. Offsetting these advantages has been the much larger size and maturity of the microelectronics industry, which means there is a supply of 'off-specification' wafers and secondhand CZ crystal growers, for example, which allow much lower prices than for mainstream product.

The most desirable process would be one which produced silicon directly in the form of large area sheets. The closest to achieving this ideal are two ribbon growth processes (Eyer *et al.*, 1990): the edge-defined film-fed growth (EFG) method and the dendritic web approach. The first approach is based on the use of a graphite die to define the shape of the growing ribbon (Figure 6.24) while the second relies on close control of temperature in the solidification zone.

All the above customized approaches produce substrates with many features in common, but differing from CZ substrates. The substrate quality is invariably poorer and more variable due both to higher levels of chemical contamination and the presence of crystallographic defects, the most severe being grain boundaries or twinning planes. The surface generally is not of the (100) orientation required for crystallographic texturing to reduce reflection loss. Because of these differences, changes in processing are required to extract good performance from these materials.

Since crystallographic texturing is not generally possible, some other way of controlling reflection is required. In production, quarter wavelength antireflection coatings are used, usually employing either TiO_2 or Si_3N_4 . The

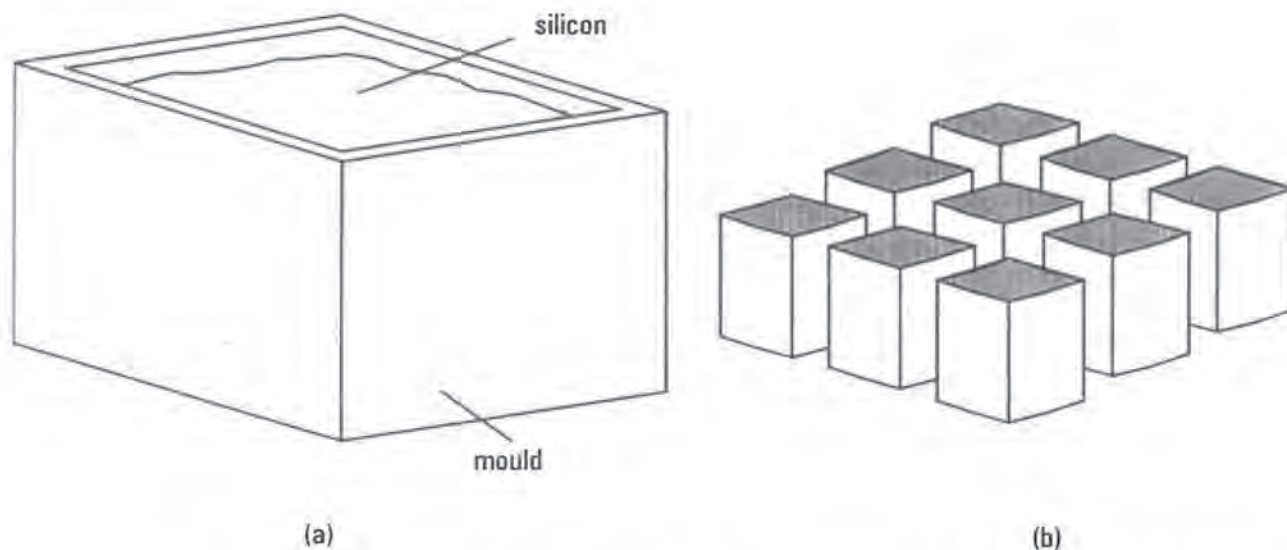


Figure 6.23 (a) Solidification of multicrystalline ingot in a crucible; (b) sawing of ingot into multiple blocks.

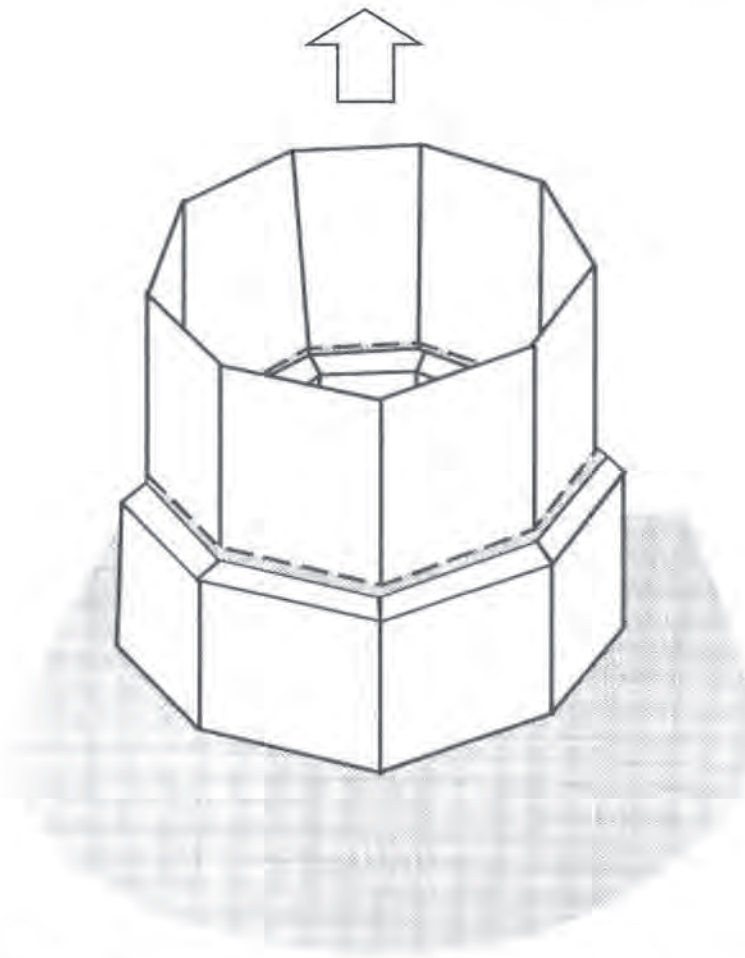


Figure 6.24 Growth of a nonagonal, tubular ribbon of silicon using the edge-defined, film-fed growth (EFG) method.

former is used because of its almost ideal refractive index for this application and its ease of deposition, being able to be sprayed or deposited by other atmospheric pressure deposition approaches. Si_3N_4 is more difficult to deposit, with silane (SiH_4) generally used as the silicon precursor. The hydrogen produced by the dissociation of silane is incorporated into the film and substrate, with beneficial results.

Grain boundaries in silicon tend to be very active electronically, acting as undesirable recombination sites, particularly when decorated by impurities. For reasonable cell performance, grains in silicon wafers have to be of at least several millimetres in size. The variability in grain properties between wafers introduces variability in performance. If hydrogen is introduced into the wafer in atomic form, it is able to neutralise some of the electronic activity at the grain boundary and at other crystallographic and chemical defects, for example, by attaching itself to dangling chemical bonds or otherwise complexing with defected regions. This improves cell performance, particularly the performance of the poorest cells, tightening the production spread.

One way of introducing the hydrogen, commercially, is by the use of an Si_3N_4 antireflection coating as previously noted, although quite a complex processing sequence is involved. Another way used in pilot production is by bombardment by hydrogen ions towards the end of cell processing (Johnson *et al.*, 1985).

The chemical contamination of the material also produces different processing requirements from CZ substrates. The material often benefits from lower processing temperatures than the CZ counterpart and also benefits more from gettering treatments. Heavy phosphorus diffusion and Al BSF treatments are particularly effective gettering steps that appear at least partly complementary in their effect (Pasquinelli *et al.*, 1991). Sometimes, adding additional impurities can improve performance. Cu is reputed to improve the performance in a way similar to hydrogen, while a high oxygen content is known to improve the quality of EFG ribbon, possibly by complexing with carbon incorporated from the graphite die used in this approach.

Most commercial sequences for processing multicrystalline and ribbon material tend to be variations of the screen printing approach described for CZ silicon. The chemical texturing step is usually excluded since, although texturing can at least partially reduce reflection loss for multicrystalline material by texture etching those grains not too far from (100) orientation, texturing can cause steps at grain boundaries jeopardizing the continuity of the screen printed metallization fingers. The temperatures used during processing are often different from those used for CZ material, for reasons previously noted. An antireflection coating of TiO_2 is generally added towards the end of processing as an essential feature, rather than as an option as in the case of CZ material. Overall, performance is lower than demonstrated by CZ material due to the poorer material quality. However, since wafers are generally manufactured with a square or rectangular shape, cells can be packed more densely in the final module package than those based on CZ wafers. This geometrical advantage at the module level largely offsets the efficiency disadvantage at the cell level.

In terms of higher performance cell processing sequences, the buried contact sequence can be applied to such substrates with good effect. Mechanical texturing of the cell surface has been demonstrated at the laboratory level and can give an additional boost to cell performance. Over recent years, there have been promising improvements in the quality of multicrystalline silicon, in particular, with the best laboratory cell on such material demonstrating efficiency close to 20% (Zhao *et al.*, 1998).

6.6.4 Polycrystalline silicon thin film cells

From the early 1970s, there has been a strong interest in trying to reduce the costs of silicon solar cells by depositing the cells in thin film form onto a foreign supporting substrate. One class of approach involved applying

silicon in molten form onto a substrate able to withstand high temperatures such as ceramic, a second class investigated lower temperature deposition approaches such as physical vapour deposition onto low temperature substrates such as Al sheet (Ghosh *et al.*, 1980).

Exciting developments in the mid-1970s with hydrogenated amorphous silicon (Section 6.6.5) dampened enthusiasm for these approaches. It was not until the mid-1980s that interest in polycrystalline silicon thin films was revitalised. Several developments during the intervening period were responsible for this reawakening of interest.

One was the development of light trapping theory (Yablonovitch and Cody, 1982, Green, 1995) and the appreciation of how effective this could be in improving the performance of thin films made from a weakly absorbing semiconductor such as silicon. Essentially, a good light trapping scheme could make the silicon optically appear to be up to fifty times thicker than its physical thickness. A second development was the improved bulk silicon cell efficiency which led to a re-evaluation of limiting silicon cell efficiency, highlighting the good performance possible, in principle, from very thin silicon cells (Tiedje *et al.*, 1984, Green, 1995). The third was the growing interest in silicon-on-insulator technology and in the use of thin polycrystalline films of silicon for active matrix liquid crystal displays (Im and Sposile, 1996).

Although commercial product with films thinner than 50 μm thickness is not available at the time of writing, recent progress suggests that this situation is evolving quickly. Some recent highlights have been the fabrication of simple cells of 2 μm thickness of above 10% energy conversion efficiency (Green, 2002). Another development has been the invention of structures particularly suited to low quality silicon such as the parallel multilayer cell concept (Green and Wenham, 1994). The completed cell and module structure with this approach is shown in Figure 6.25. The presence of several junctions connected in parallel in the cell structure reduces the distance photogenerated carriers have to travel before being collected by any one junction, relaxing material quality requirements. An approach similar to that used in the buried contact cell is used to contact the layers of the multilayer stack and to connect adjacent cell regions together in series. It appears feasible to fabricate these devices directly onto a glass superstrate with efficiencies up 15% projected for completed modules.

6.6.5 Amorphous silicon solar cells

Historical development

Pure amorphous silicon has poor electronic properties. However, in the late 1960s, it was found that amorphous silicon formed by the decomposition of silane in a glow discharge showed more interesting properties. This was ultimately linked to the incorporation of substantial quantities of hydrogen (about 10% atomic). The resulting alloy (a-Si:H) exhibited significant photoconductivity and could be doped n-type or p-type, by incorporation of the

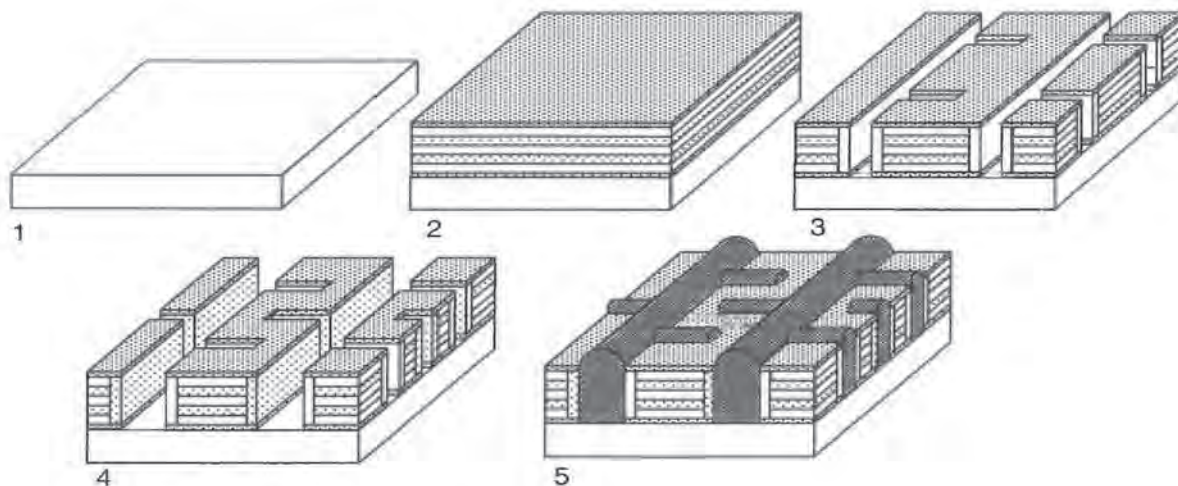


Figure 6.25 Fabrication of multilayer cells: (1) glass superstrate; (2) multilayer deposition; (3) first polarity groove; (4) second polarity groove; (5) metallization.

appropriate dopant containing gases (PH_3 and B_2H_6) into the discharge (Carlson and Wagner, 1993).

By the mid-1970s, the first operational cells had been reported (Carlson and Wagner, 1993). By the early 1980s, cell performance had been improved to about 10% conversion efficiency by improvements such as the use of a wider bandgap a-SiC:H 'window' layer on the top surface of the cell and the incorporation of light-trapping. The first commercial product was on the market, and was an instant success. This product used small arrays of cells in consumer products such as pocket calculators and digital watches. Such consumer product applications have dominated commercial solar cell sales of the material to date, although other non-solar applications of a-Si:H have proved even more significant. The material is used in large volumes as a photoreceptor coated onto photocopier drums and in active matrix liquid crystal displays (LeComber, 1988).

For larger outdoor 'power' modules, progress has been less rapid than originally expected due to stability issues. The beneficial effect of the hydrogen upon the amorphous silicon properties deteriorates under illumination. Such 'Staebler–Wronski' degradation typically causes a steady drop in solar module output over the first few months in the field, with output then stabilising (Carlson and Wagner, 1993). Amorphous silicon based power modules have become available in reasonable quantities since the late 1990s and are generally rated by manufacturers in terms of such 'stabilised' output.

Material properties and cell design

The glow discharge approach remains the preferred method for the deposition of a-Si:H and its alloys. This deposition approach produces material of

acceptable performance although of quite poor quality compared with that of the more established crystalline semiconductors (Bube, 1998). In particular, carrier mobilities are small ($\sim 1 \text{ cm}^2/\text{V s}$ compared with $\sim 1000 \text{ cm}^2/\text{V s}$ in crystalline silicon) as are minority carrier diffusion lengths ($\sim 0.1 \mu\text{m}$ compared with $\sim 200 \mu\text{m}$ in crystalline silicon). Moreover, there is a continuous distribution of electron states lying at energies within the normally 'forbidden' gap between the valence and conduction bands of the semiconductor. Although the material can be doped as for the material's crystalline counterpart, not all dopants are electronically active and the material quality reduces significantly as the doping level increases (Bube, 1998).

The combination of hydrogen and disorder in the material increases the bandgap of the material significantly above that of crystalline silicon, to about 1.7 eV. The disorder within the amorphous material also relaxes the momentum selection rules that cause crystalline silicon to be such a weak absorber of light. However, the a-Si:H material is still not as strongly absorbing as some of direct bandgap materials to be discussed later. Layers about $0.5 \mu\text{m}$ thick are required to capture a reasonable fraction of available sunlight.

The cell design that has proved most suited to take advantage of the above material properties is the p-i-n cell structure of Figure 6.26. The doped layers are generally kept very thin (less than 50 nm in thickness), since very few of the carriers generated in these layers contribute to the collected photocurrent. These doped layers, however, do establish an elec-

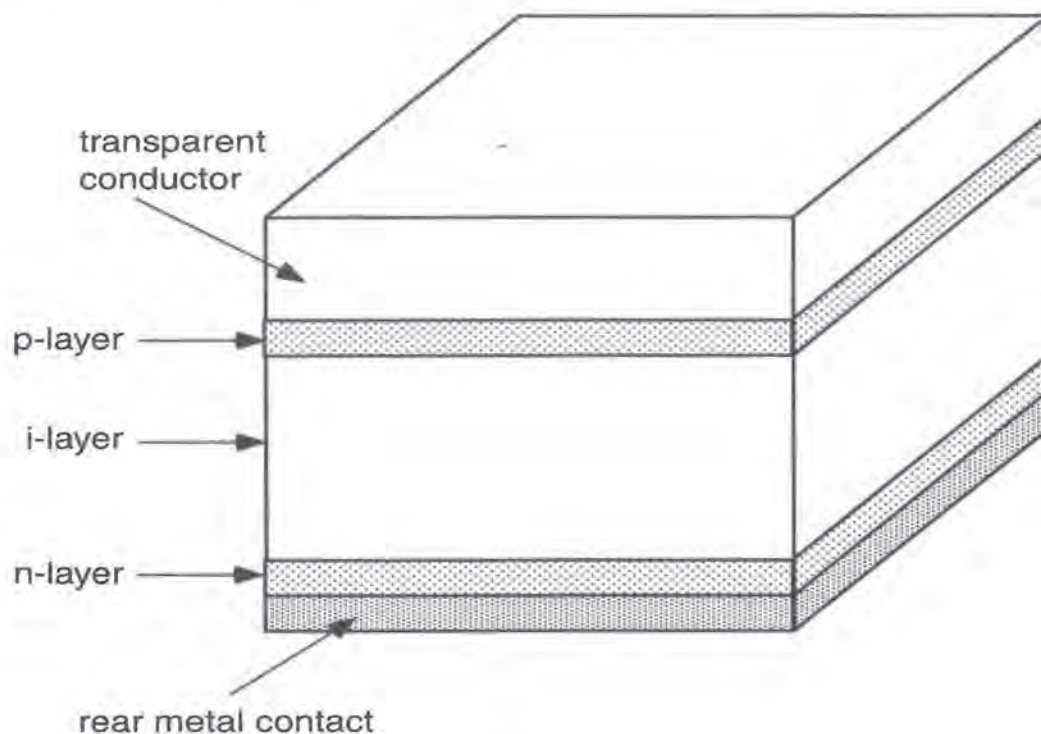


Figure 6.26 Amorphous silicon p-i-n solar cell structure.

tric field in the better quality i-layer that aids the collection of carriers generated in this region. This field allows carriers to be collected over distances longer than a minority carrier diffusion length.

The important parameters in determining carrier collection from this region is the material quality as reflected by the drift length given by the 'mobility-lifetime' product multiplied by the strength of the electric field in the i-layer. The latter depends on the 'built-in' voltage across the i-layer, established by the doped layers terminating this region, and the i-layer thickness. The strength of this field reduces as the output voltage across the cell increases. This gives rise to an effect not seen to any extent in crystalline cells. The light generated current component, I_L , is not constant as in a crystalline cell, but reduces with increasing voltage across the cell. This results in inherently lower fill factor for these devices, with the value limited by the ratio of the collection length to the total cell thickness (Fraughnan and Crandall, 1984).

The material degradation under light exposure also reduces carrier collection from the i-layer. The i-layer thickness therefore has to be chosen for stabilised material quality rather than for that of as-deposited material.

The lateral conductivity of the doped layers in the cell is small since these layers are thin and have low carrier mobility. To conduct the generated current laterally, conducting contacts are required on both cell surfaces. Generally that on the surface exposed to sunlight is a transparent conductor, usually the degenerately doped semiconductor SnO_2 . That on the opposite surface is generally metallic and also acts as a rear reflector for the cell.

Commercial cell designs

The first large amorphous silicon installation was a 400 kW system installed at Davis, California (Shugar, 1994). The strategy adopted in this installation was to produce the amorphous silicon power modules as inexpensively as possible per unit area, with quite modest stabilised efficiency (only 4–5%). The negative impact such low efficiencies would normally have upon area related 'balance-of-systems' costs (such as mounting structures and wiring costs) was neutralised in this case by the use of innovative support structures and installation techniques (Shugar, 1994). This installation set new standards for such 'balance-of-system' costs.

The basic cell structure used in the modules for this installation is shown in Figure 6.27 (MacNeil *et al.*, 1991). A layer of SiO_2 followed by a transparent conducting layer of the large bandgap, degenerately doped semiconductor, SnO_2 , was deposited onto a glass sheet of 1.55 m $\times$ 0.78 m in size and patterned using a split-beam laser. The SnO_2 was deposited under conditions that create a surface texture that improves 'light-trapping' in the final cell. Forty-eight of these substrates were then simultaneously coated by a p-i-n junction stack of amorphous silicon by the decomposition of silane in a radio frequency (RF) plasma discharge system. For good material quality, the deposition rate has to be slow (below 5 Å/s).

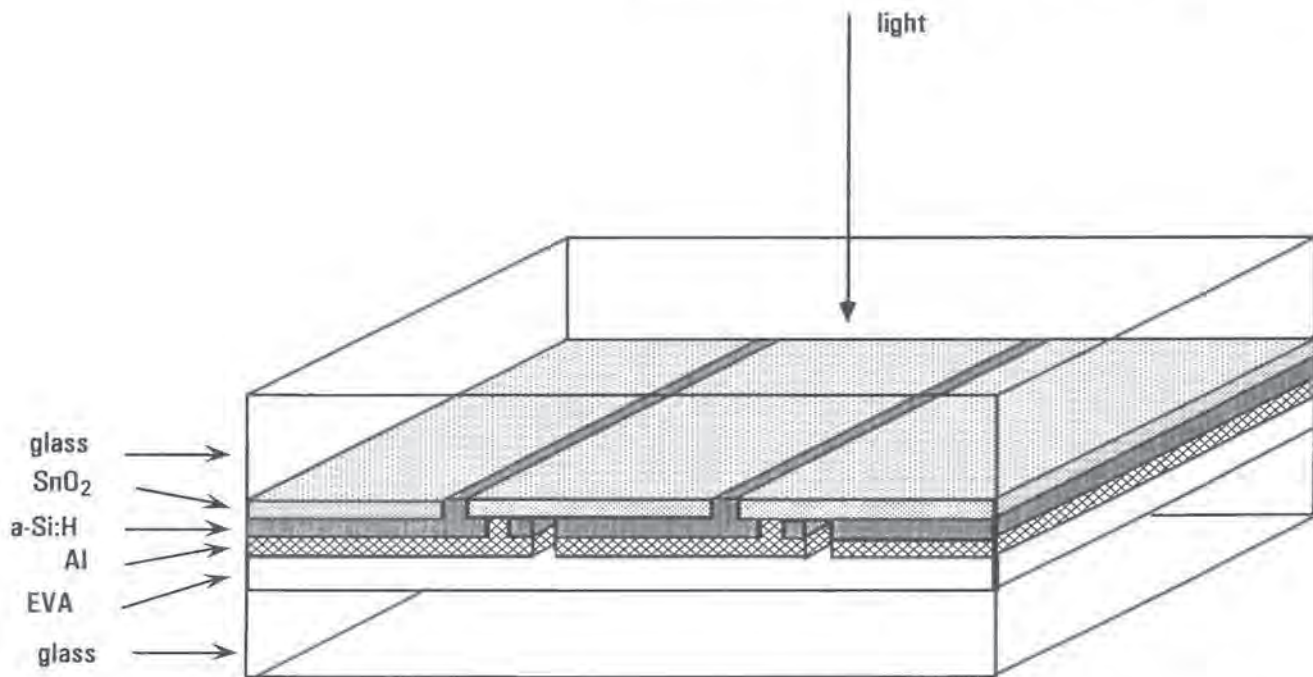


Figure 6.27 Series interconnected a-Si solar cells deposited onto a glass sheet.

Fortunately, only a thin, $0.3\ \mu\text{m}$ thick layer of a-Si is required. After deposition, the a-Si layers were patterned using a second laser system. A layer of Al was then sputtered onto the rest of the silicon and this layer also patterned by laser. In this way a series of interconnected cells were formed as shown in Figure 6.27. Modules were formed by laminating a backing layer of glass onto the rear of the cells as shown.

The large area modules made in this way show energy conversion efficiency in the 4–5% range after stabilisation by outdoor exposure. Minor performance improvements would be expected rather simply by improving light trapping by using a transparent conductor such as ZnO or SnO_2 to contact the rear of the device and then applying the Al layer over the top. This increases the reflectance for light reaching the rear of the cell. Replacing the Al by Ag can further boost this reflectance.

Further improvements can be obtained by stacking two cells, one on top of the other, to produce a tandem cell configuration (Section 6.4.2), as indicated in Figure 6.28. The top cell responds to the strongly absorbed blue wavelengths while the bottom cell responds to the longer wavelength red light. Owing to the marginal quality of the amorphous silicon after stabilisation of its properties, this tandem approach can improve the performance of stabilised devices, even if the bottom cell is made from the same material as the top!

One reason the tandem cell approach works so well for amorphous silicon is that it is very easy to produce the necessary shunting of the reverse polarity p-n junction interposed between the top and rear cell. This shunting is required so this junction does not generate a photovoltage opposing that

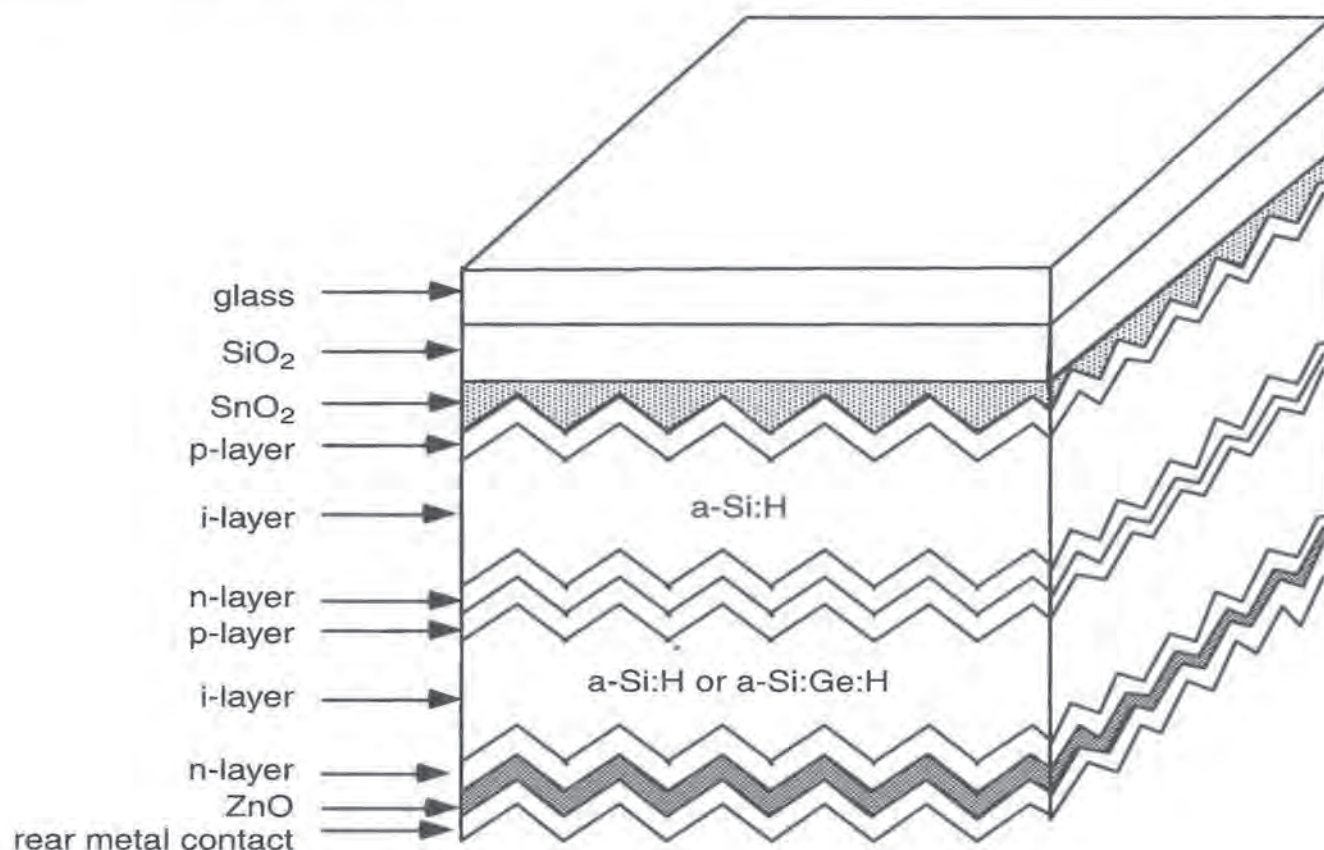


Figure 6.28 Tandem a-Si:H solar cell.

generated by the other two junctions of Figure 6.28. This reverse polarity junction is formed between two heavily doped regions in which it is difficult to obtain the normal rectifying p-n junction characteristics, due to the poor electronic quality of these regions, even without the tunnelling effects mentioned in Section 6.5.3.

Best performance from this tandem approach can be obtained if the semiconductor material used in the top and rear cell are different, with the wider bandgap material used as the top cell. In this way, the tandem is able to respond to a wider range of wavelengths than a single cell of intermediate bandgap. Alloying with C increases the material's bandgap while alloying with Ge reduces the gap. Also microcrystalline material, consisting of a mixed phase intermediate between amorphous and polycrystalline, has a lower bandgap and weaker absorption than the amorphous phase. This gives considerable flexibility in the design of amorphous silicon based tandem cells (Yamamoto *et al.*, 1999).

A commercial process has been developed producing a cell structure similar to that of Figure 6.28 with the standard a-Si:H used as the material for the uppermost cell and a-Si:Ge:H alloy as the lowermost cell. This process has produced stabilised efficiency for large area modules approaching 8% (Arya *et al.*, 1994), although the efficiency of the commercial product is presently somewhat lower.

By stacking three cells, one on top of the other, higher performance is possible, in principle. The first a-Si:H research module with stabilised efficiency above 10% was based upon such a triple junction approach. The top cell consisted of a layer of a-Si:H. The bottom two cells were of increased thicknesses and contained increasing percentages of germanium (Yang *et al.*, 1994). In this case, the triple cell is deposited bottom cell first onto a stainless steel sheet. Although this approach is well suited to continuous production of the cells, the stainless steel sheet has to be cut to give individual cells that are then interconnected within the module, negating some of the potential benefits of a thin film approach. Again, commercial module efficiency with this approach is quite modest at 6.4% (USSC, 1998).

Areas of present activity address production issues such as improving material deposition rates while maintaining acceptable cell performance and increasing the utilisation of the silicon content of the source gases. Other work addresses incremental improvements to cell performance such as by an improved trade-off between the transmittance and sheet resistance of the transparent conducting oxide used in these cells or improved rear contact reflectance. Yet other areas of activity are directed at improved understanding of material properties or ways of overcoming deficiencies of present materials, such as by new deposition approaches; for example, 'hot-wire' deposition where the silane source material is dissociated by the high temperature associated with a resistively heated wire (Bube, 1998).

6.7 COMPOUND SEMICONDUCTOR CELLS

6.7.1 III-V crystalline cells

Historical outline (Bube, 1998)

The earliest semi-empirical analyses of cell efficiency limits predicted an optimum semiconductor bandgap of around 1.4 eV, somewhat higher than silicon's 1.1 eV (Loferski, 1956). This stimulated the fabrication of the first GaAs cells in 1956, giving devices of about 4% efficiency (Jenny *et al.*, 1956). The development of GaAs technology through the 1960s for semiconductor lasers and light emitting diodes produced rapid improvement in device performance. The first solar cells of performance around 20% were produced in the mid-1970s (James and Moon, 1975). One feature was the use of a largely transparent $\text{Al}_x\text{Ga}_{1-x}\text{As}$ window layer on the top surface of the cell, exploiting the formidable properties of the III-V alloy system. Since that time, the best GaAs based cells have maintained a slight efficiency advantage over the best Si cells [the present lead is only 0.4% absolute (Green *et al.*, 2000)]. The application of metal organic chemical vapour deposition (MOCVD) techniques in the early 1980s instead of the earlier liquid phase epitaxial (LPE) techniques produced a marked jump in efficiency. The use of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ as the window layer produced the first 25%

efficient devices in the late 1980s, a result that remains unsurpassed for single-junction devices.

About the same time, progress was made in implementing III–V tandem cells. By suitable choice of III–V alloy, a lattice-matched crystalline device can be deposited onto a substrate by first depositing a low bandgap cell, followed by a tunnelling junction (Section 6.5.3) and a higher bandgap top cell, connected in series with the lower cell by the tunnelling junction. Monolithic tandem cells of this type first exceeded the performance of the simpler single junction towards the end of the 1980s and produced a 30% efficient device in 1996 (Green *et al.*, 2000).

Owing to the higher cost of III–V technology compared with silicon, these high performance crystalline III–V devices have not been suitable for low-cost terrestrial applications. Attempts to produce thin-film polycrystalline III–V cells have been notably disappointing, attributed to the high electronic activity of grain boundaries in these materials. Some interest has been shown in thin-film crystalline devices, produced by chemically removing the thin active layer from a potentially reusable substrate (Hardingham *et al.*, 1994). Good experimental devices have been demonstrated, with efficiencies approaching the best bulk devices, but producing 100 000 m²/year of such cells, as produced by some terrestrial cell manufacturers, would pose serious challenges in scaling-up this approach.

III–V cells, however, have found a market niche in providing electrical power for spacecraft. Here the higher cost of the cells is offset by a lower launch weight, due to their higher efficiency. The performance advantages in space applications are improved compared with terrestrial applications due to a higher tolerance to the damaging high energy radiation found in space. A feature of this space application has been the fabrication of the GaAs based cells upon Ge substrates, rather than upon the GaAs substrates used for the best laboratory devices. This allows the better mechanical and thermal properties of Ge substrates to be used to advantage, while sacrificing little in electrical performance. Although these are single junction devices, the presence of the lower bandgap Ge also offers the prospects for performance increase by producing a lower GaAs/Ge tandem cell, as discussed in the Section on tandem III–V cells, below.

Another III–V compound, InP, also appears promising for space applications due to its exceptionally high tolerance to the damaging space environment (Iles and Yeh, 1995). Great interest has also been shown in the use of III–V cells for terrestrial systems based on concentrated sunlight, where the high cost is offset by the smaller area required for a given power output. However, only the tandem devices have opened up any appreciable performance advantage over inherently much less expensive silicon concentrator cells, making the use of single junction III–V concentrator cells very unlikely.

A newer potential application for III–V cells is the use in thermophotovoltaic energy conversion (Chubb, 1990, Iles and Chu, 1994). In this case,

conventional fuels are used to heat an emitter material to a high temperature, with this emitter chosen to emit energy by luminescence in a narrow wavelength range. This energy can be very efficiently converted to sunlight by a solar cell of appropriate bandgap. Overall conversion efficiency of over 40% has been projected even for small generators that might be of interest in spacecraft.

GaAs cells

The structure of a typical GaAs space cell is shown in Figure 6.29. Starting with an n-type Ge substrate, a heavily doped layer of GaAs is grown, which acts as a BSF in the completed device. This is followed by the growth of a more lightly doped GaAs region that forms the main body of the cell. Since GaAs is a direct bandgap semiconductor that absorbs sunlight strongly, this region need be only a few microns thick to capture most of the incident sunlight. Then follows the growth of a p-type GaAs emitter layer followed by a thin, p-type AlGaAs window layer. Since contact to AlGaAs is difficult, a patterned layer of heavily doped p-type GaAs is grown on top of this layer to improve the reliability of the overlying top metal contact (alternatively, the p-type AlGaAs layer can be patterned to allow contact directly

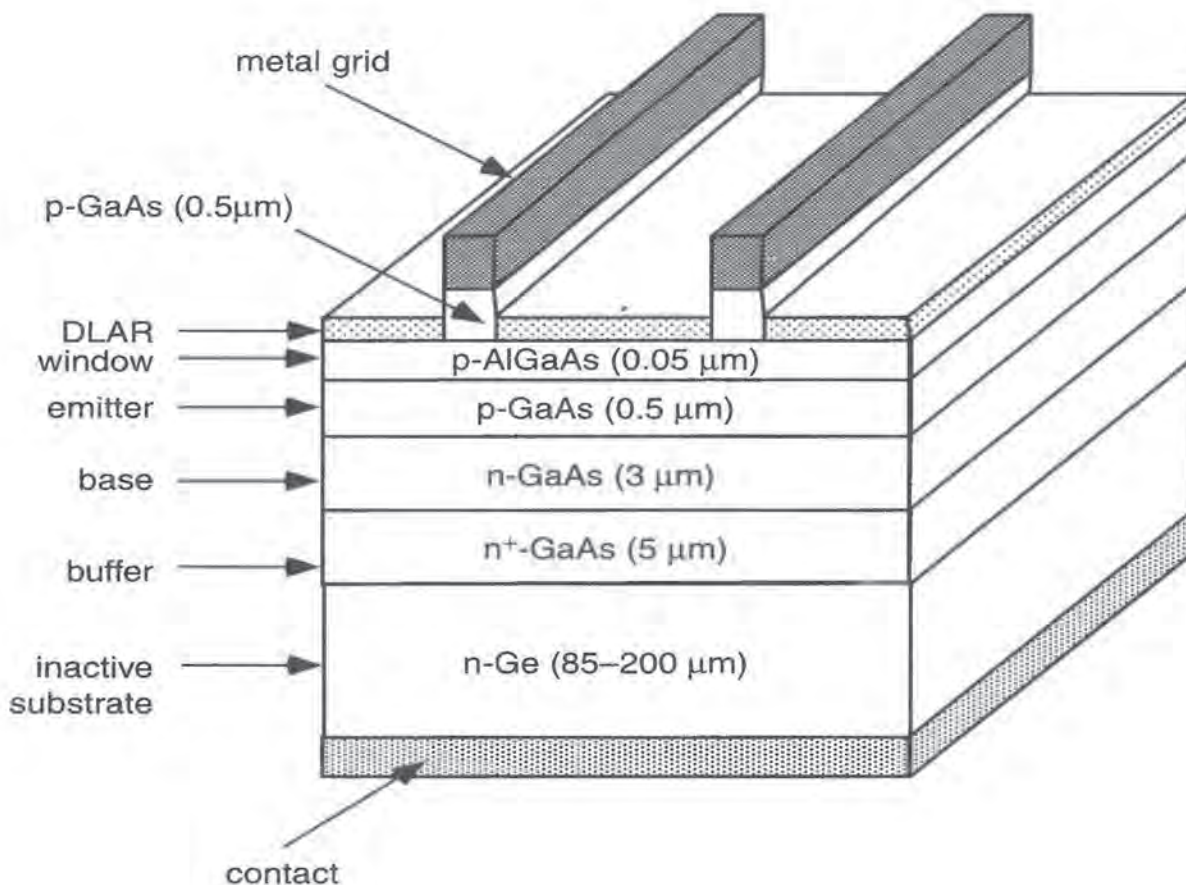


Figure 6.29 GaAs space cell.

to the underlying p-type GaAs layer). Finally a double layer anti-reflection coating of $\text{TiO}_2/\text{Al}_2\text{O}_3$ is applied. Such cells typically display 18% AM0 conversion efficiency, corresponding to efficiencies of about 20% under terrestrial sunlight.

Major differences from silicon devices are apparent in several areas. The AlGaAs window, rather than thermal oxide, is used for passivation of the top surface. It is less ideal since it is not as effective in producing low surface recombination velocity and it is absorbing, reducing the blue response of cells. Owing to the strong light absorption in GaAs, light trapping schemes do not produce the same benefits as in the case of Si. Also, due to the narrower bandwidth of the GaAs cell response and the low refractive index of AlGaAs, there is reduced reflection loss from the top surface of a planar cell, reducing the benefits of surface texturing.

InP cells (Iles and Yeh, 1995)

InP cells appear promising for space-applications since they are very resistant to the damaging high energy radiation encountered in space. However, one disadvantage is that the lattice constant of InP is not well matched with that of the semiconductors produced in higher volume that might be used as substrates (Si, Ge, GaAs). Another disadvantage is that, although there are higher bandgap semiconductors that might appear suitable for use as window layers on the grounds of lattice match, these have performed poorly in practice (Lammasniemi *et al.*, 1994). The best performance has been demonstrated by simple homojunction devices grown by MOVPE on expensive and mechanically fragile InP substrates.

Highest performance is obtained when the top n^+ layer is thin ($0.1\ \mu\text{m}$). There is no deliberate passivation of the surface apart from that provided by the deposited antireflection coating. Terrestrial energy conversion efficiency above 20% has been demonstrated, despite a relatively poor blue response of the cells, caused by the less than ideal nature of the surface passivation. Alternatively, cells have been fabricated with a deposited ZnO layer forming the top surface emitter. Rather than providing a high quality lattice matched window layer, this is a fine grained polycrystalline layer deposited at low temperature. Performance demonstrated by this approach has been lower than for homojunction cells.

Tandem III-V cells

The wide choice of material with the same lattice constant within the system formed by the III-V compound semiconductors and their alloys has made this system ideal for the production of lattice matched crystalline tandem cells. Early work in this area concentrated on the AlAs/GaAs alloy system. Subsequent work has been more diversified with good performance also demonstrated for monolithic tandem cells based on GaInP/GaAs and InP/GaInAs.

For crystalline devices, a major challenge has been the development of the tunnelling junctions required to connect the cells. By having both sides

of this junction heavily doped, the resulting tunnel currents effectively short-out the normally rectifying junction characteristics, preventing an opposing photovoltage being developed across this junction (Section 6.5.3). Since this tunnelling region acts as a plane of very high effective surface recombination velocity, thin layers of the heavily doped tunnelling regions are required. These can serve as a BSF region for the upper cell and a front surface field (FSF) for the lower cell, respectively.

Alternatively, separate contacts could be made to this tunnelling junction region to give a monolithic three-terminal device or two different cells could be mechanically stacked, one on top of the other, to give a four-terminal device. The advantage in both cases is that the current outputs of the top and bottom cells do not have to be matched, increasing both design flexibility and the resulting performance levels. The disadvantage is that a separate circuit has to be set up for each cell type, adding to circuit complexity. Schemes which rely on parallel connection of the two circuits to match the voltage output from small subsets of the cells appear the most promising way of dealing with this complexity (Fraas, 1995) (e.g., connecting four of the lower bandgap cells in parallel with three of the higher bandgap cells).

Since monolithic two-terminal tandem devices have performance levels about 15–20% above the best single junction devices but are estimated to cost only a similar amount more than a III–V single junction device, they would appear a better choice in specialised high performance systems, such as for high concentration terrestrial systems or in space.

Tandem cells have been in production since the late 1990s for use on spacecraft. The structure of one such production device is shown in Figure 6.30, emphasizing the evolution of this technology from the well established GaAs/Ge single junction production technology. By 1999, two companies had triple junction cells in production for space use, formed by making the Ge substrate an active component in the cell stack.

6.7.2 Polycrystalline thin-film compound semiconductor cells

Introduction

Although the III–V compound semiconductors can be strong absorbers of light and hence optically ideal for fabricating very thin devices, the performance from polycrystalline thin film III–V devices has been disappointing. This is attributed to the high level of electronic activity at grain boundaries in III–V material.

There is, however, an enormous range of other compound semiconductors and their alloys with a suitable bandgap for efficient energy conversion. Although bandgaps of such materials can be reasonably reliably predicted, other properties that determine the suitability of the material for use in photovoltaics, such as grain boundary activity and the ease of producing

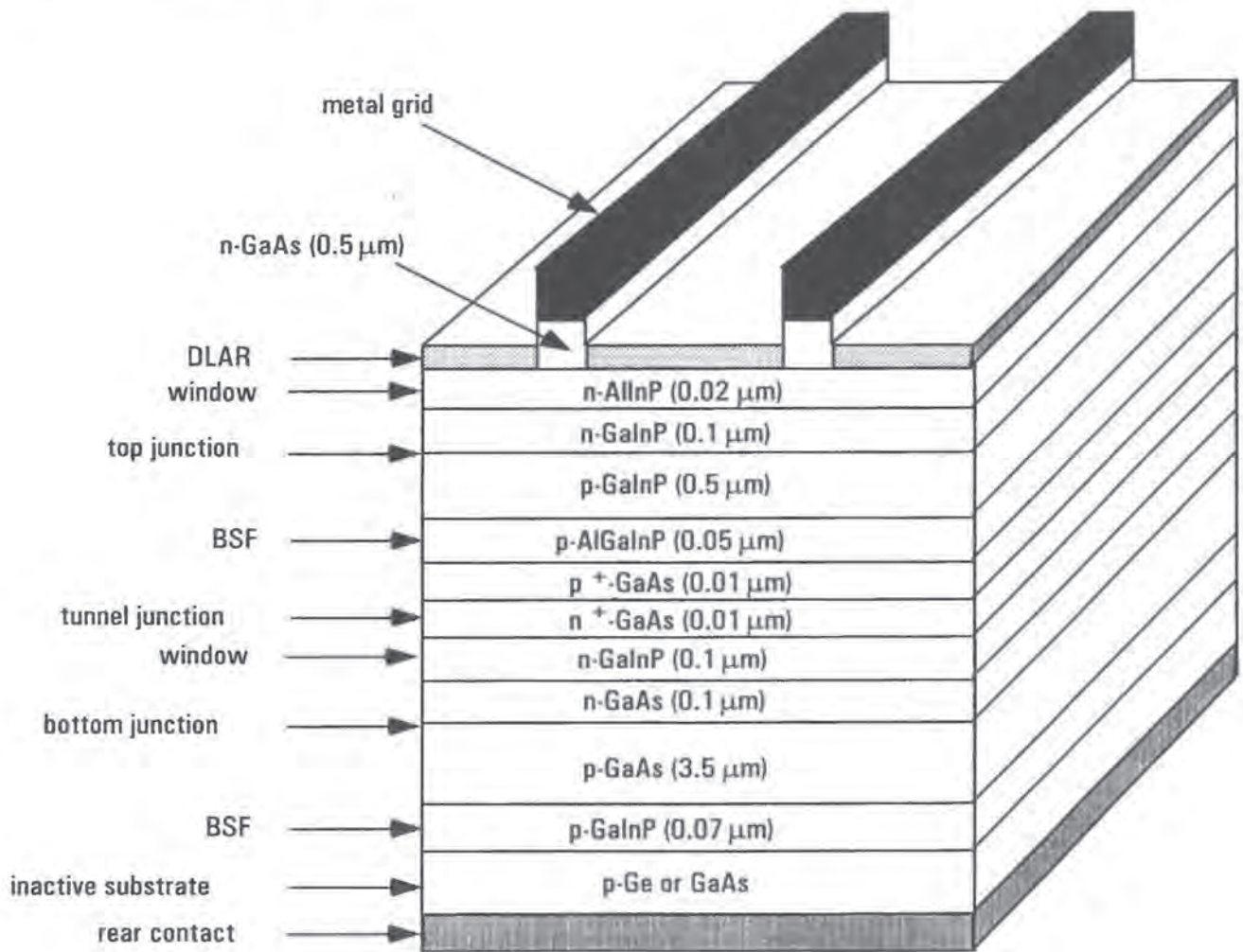


Figure 6.30 Monolithic tandem space cell.

reasonable grain size, are not so readily forecast. This means that extended experimental evaluation is the only reliable method for determining the suitability of any given photovoltaic material candidate when in polycrystalline form, in particular.

From the limited evaluations of this type which have been conducted to date (Bube, 1998), two compound semiconductors have shown excellent potential in thin film form. One is the II–VI compound semiconductor, CdTe, while the other is based on the I–III–VI₂ compound, CuInSe₂ (CIS), and its related alloy system, CuIn_xGa_{1–x}(Se_yS_{1–y})₂.

The strengths of CdTe arise from its robustness in terms of the range of preparation techniques that have given good cell results, including very crude techniques such as electroplating. A weakness relates to an uncertainty as to the environmental acceptability of deploying large areas of such material, given that special precautions are considered likely to be required for its final disposal due to the toxicity of its constituents.

In the case of CIS and its alloys, major strengths relate to the ease with which large grains can be grown during deposition and with which grain

boundaries can be rendered inactive electronically, the material's relatively high tolerance to deviations from perfect stoichiometry (ratio of Group I, III and VI constituents), and the design flexibility imparted by being able to vary the alloy composition. A possible weakness relates to challenges in manufacturing, with a longer term issue relating to the limited supplies of materials such as In, Ga and Se.

CdTe cells (Zweibel, 1995, Chu and Chu, 1995, Meyers and Birkmire, 1995)

CdTe cells were originally investigated due to the nearly ideal bandgap of CdTe for efficient conversion and the fact that, unlike several other compound semiconductors, this material could be doped both n-type and p-type. Subsequently, it was found that the material could be prepared by a range of simple techniques and still give good properties (Bube, 1998). This is attributed to the ability of post-deposition treatments to increase the grain size and to reduce the activity of grain boundaries in this material.

A variety of device structures have been investigated with this material including the p-n homojunction and a variety of heterojunctions including junctions with Cu_2Te , SnO_2 and various II-IV compounds (Chu and Chu, 1995). However, best results have been obtained with the CdTe/CdS/ SnO_2 heterojunction structure of Figure 6.31.

The deposition of the transparent conducting oxide (TCO) layer of SnO_2 onto the glass substrate is followed by the deposition of a thin layer of CdS. This layer is usually heat treated in a reducing atmosphere or in CdCl_2

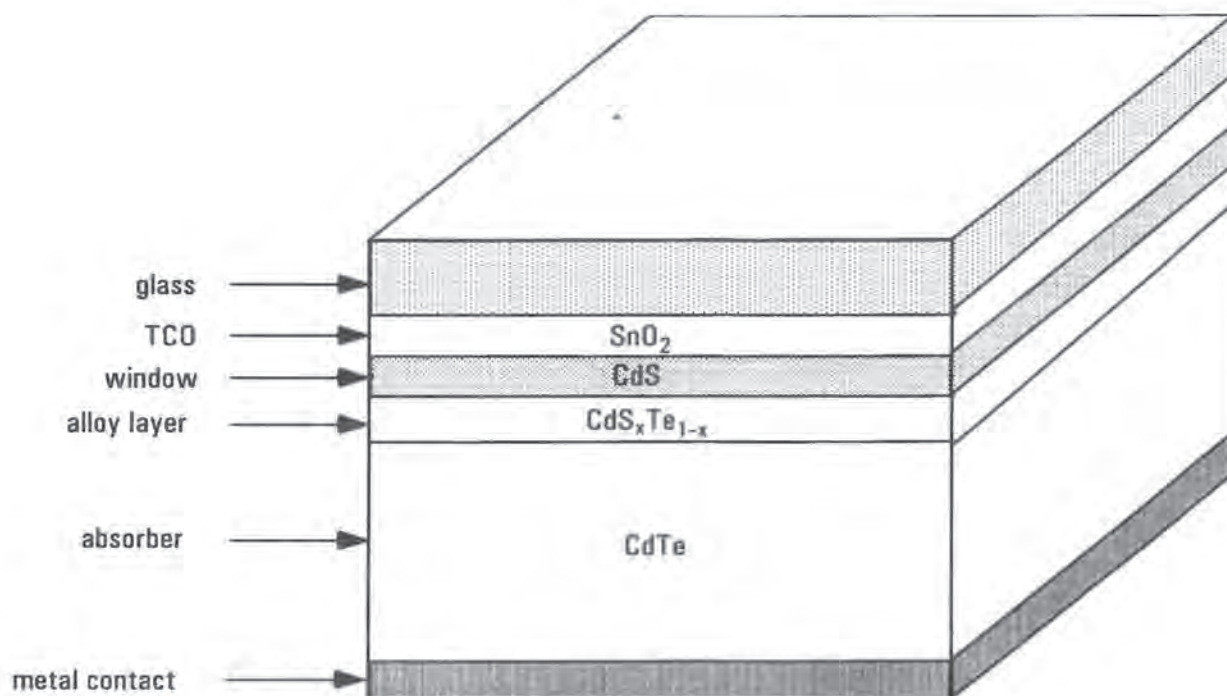


Figure 6.31 CdTe cell structure.

to increase grain size and reduce defect density (Chu and Chu, 1995, Meyers and Birkmire, 1995). Next, the CdTe layer is deposited by one of a variety of techniques, followed by a heat treatment in CdCl_2 or another chlorine containing compound. The heat treatment not only increases grain size and reduces defect density, as for the earlier CdS treatment, but also results in the interdiffusion of the CdS and CdTe layers. The junction thereby moves into the CdTe, rather than remaining at the original metallurgical interface, an effect that is thought to improve the junction quality. A variety of approaches has been used to make rear contact to the CdTe (Chu and Chu, 1995, Meyers and Birkmire, 1995). These are based on a two-layer approach, with the first layer being a heavily doped layer making good electrical contact vertically with the CdTe, while the second layer is metallic and provides good lateral conductivity. Most fabrication procedures include (Chu and Chu, 1995, Meyers and Birkmire, 1995): an etch or surface preparation step, which may produce a Te-rich surface layer; creation of the primary layer, either by deposition of a p^+ layer of SnTe–Cu, HgTe or PbTe or by modification of the CdTe surface by supplying a p-type dopant such as Cu, Hg, Pb or Au; a subsequent heat treatment above 150°C , and application of the secondary contact by sputtering, vacuum evaporation or screen-printing.

As for a-Si cells, the first CdTe cells to be produced in any volume were for pocket calculators. These were fabricated using the simple screen-printing sequence whereby the CdS window layer is screen printed onto a borosilicate glass substrate as a paste consisting of CdS, CdCl_2 and a binder (propylene glycol) (Chu and Chu, 1995). The paste is fired at 120°C and then sintered in a nitrogen ambient at about 700°C in a belt furnace. The CdCl_2 flux encourages grain growth within the CdS films, resulting in grain sizes in the 20–30 μm range in films also of 20–30 μm thickness. The CdTe paste consists of a mixture of Cd and Te, together with the same flux and binder. The paste is fired, then sintered at around 600°C . The Cd and Te react during this sintering step with subsequent grain growth encouraged by the CdCl_2 flux. Considerable alloying occurs in the CdS/CdTe interfacial region, which improves the properties of this interface. The back contact is subsequently screen-printed in the form of a carbon paste, containing a small amount of Cu, and the entire device annealed.

The performance of such screen printed CdTe cells is quite modest, due mainly to the thick CdS window layer. Absorption in this layer and in the alloyed interfacial region results in a very poor response to any wavelengths shorter than 500 nm. The narrower bandgap in the CdTe side of the alloyed interfacial region results in response to photons of energy below the CdTe bandgap. The thickness of the layers used in these devices would exacerbate concerns over the toxicity and sustainability of this technology, if this screen-printing approach were used in any volume.

The first CdTe cells to reach 15% energy conversion efficiency used more sophisticated processing, although still relatively simple compared with other

photovoltaic technologies. A very thin CdS window layer was deposited by a solution growth, chemical bath technique (Bube, 1998). This approach gives thin films of good stoichiometry, but the films are porous and the surface is contaminated by absorbed impurities such as hydroxides (Chu and Chu, 1995). Prior to the deposition of the CdTe, the CdS film is heated in hydrogen to remove oxygen-containing species and to densify the film. The CdTe film is then deposited by close-spaced-sublimation (CSS).

In the CSS process (Chu and Chu, 1995), a heated CdTe source dissociates into its Cd and Te constituents in gaseous form. These recombine on the cooler substrate surface to reform CdTe. The deposition rate can be controlled in the 0.1–10 $\mu\text{m}/\text{min}$ range by varying parameters such as the temperatures of the source and substrate, their separation, the deposition chamber ambient and its pressure. The microstructure of the deposited films is determined by the substrate temperature and the source–substrate temperature gradient. Generally, the grain size increases with increasing source temperature and with increasing film thickness, with average grain size typically in the 2–5 μm range and generally of random orientation. The electrical resistivity of the p-type CdTe films can be controlled by using Cd-deficient or Sb-doped source materials.

For the first 15% efficient CdTe cells, the CdS layer was about 70 nm thick while the CdTe layer was 4–5 μm thick. A 100 nm thick MgF_2 antireflection coating layer was deposited onto the illuminated glass surface.

The CSS approach has also been the focus of a commercial sequence for fabricating large area modules (Chu and Chu, 1995). In this case, both CdS and CdTe are deposited sequentially onto a SnO_2 coated glass substrate by a modified CSS technique. After a post-deposition heat treatment, electrical contact is made to the CdTe by deposition of a Ni/Al bilayer contact. Laser scribing is used at various stages during processing to pattern the SnO_2 layer, the CdS/CdTe active layers and the rear contact layer to provide automatic series interconnection of cells within a module, identical to the approach previously described for a-Si (Figure 6.27). Efficiencies up to 8% were demonstrated in the early 1990s for large area modules processed in this way, a figure recently increased to above 10% (Green *et al.*, 2000).

Environmental issues stemming from the toxicity of Cd and its compounds have slowed the introduction of this CdTe based technology (Meyers and Birkmire, 1995). Issues arise during manufacture, during deployment in the field and after disposal at ‘end-of-life’.

Manufacturing hazards can undoubtedly be controlled. Hazards during deployment stem mainly from incidents such as fire which could cause the release of toxic vapours. Owing to the potential for leaching of Cd into groundwater, special attention may have to be given to the final disposal of these modules. Some manufacturers believe the Cd based materials can be recycled, although collection of product dispersed into widely different cultural and geographical regions would pose significant challenges.

Copper indium diselenide and its alloys (Chu and Chu, 1995, Bloss et al., 1995)

Copper indium diselenide (CIS) is a direct bandgap semiconductor with a bandgap of 1.04 eV at room temperature. A small cell of a reported efficiency of 12% was made by the evaporation of CdS onto a CuInSe₂ single crystal in 1974. Soon after, the first thin-film cells were reported (Kazmerski *et al.*, 1975). In the early 1980s, efficient thin film cells were made with this material using co-evaporation of the Cu, In and Se elemental constituents (Mickelsen and Chen, 1982). By the late 1990s, thin-film cell efficiency approaching 20% (Contreras *et al.*, 1999) had been demonstrated by incorporating CuGaSe₂ into CuInSe₂ to increase the bandgap of the material (CuInS₂ is another candidate for such purposes that has also given good results).

The generic structure of such a thin-film alloy cell is shown in Figure 6.32. A molybdenum back contact is deposited onto a glass substrate by sputtering or electron beam evaporation. After deposition of the main Cu(In,Ga)(S,Se)₂ absorber layer by techniques to be described, a thin CdS or Cd_{1-x}Zn_xS window layer is deposited by evaporation or, for best results, by solution growth. This is followed by the deposition of ZnO, by RF sputtering or by chemical vapour deposition. In the best devices, a two-step process is used whereby about 50 nm of lightly doped ZnO is deposited followed by 300 nm of Al-doped material, to reduce lateral resistance. Ni/Al contacts are applied to contact the ZnO. In the best laboratory devices, a

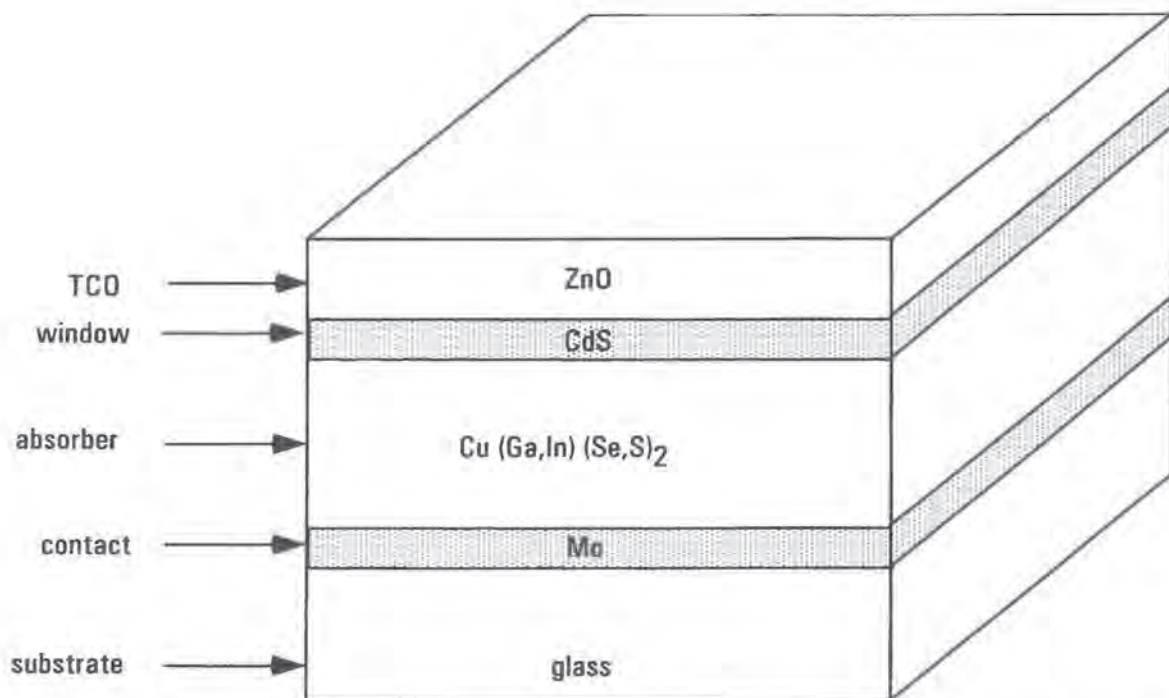


Figure 6.32 Solar cell based on copper indium diselenide and related alloys.

MgF₂ antireflection coating is added to the top of the ZnO (Contreras *et al.*, 1999), although this would not be effective in an encapsulated device.

Three techniques have been used to deposit the Cu(In,Ga)(S,Ge)₂ absorber layer (Contreras *et al.*, 1999) for cells which display over about 16% efficiency (Bloss *et al.*, 1995):

- (a) co-evaporation of the elements onto a heated substrate,
- (b) selenisation of sputtered or evaporated Cu/In precursors in a H₂Se or Se atmosphere, and
- (c) diffusion of Cu and Se into (In,Ga)₂Se₃ precursors.

For the highest performance devices, attempts are made to control composition and hence the alloy bandgap across the thickness of the absorber layer. Not all aspects are well understood. With excess Cu concentration, large crystallites are grown, an effect believed to be promoted by the segregation of a copper chalcogenide phase to the surface of the films. This phase can be removed by subsequent chemical treatment (with KCN) or converted to a more desirable compound. The surface composition of grains also depends on the material composition. In indium rich material, a stable CuIn₃Se₅ phase has been observed on film surfaces, having a larger bandgap than bulk regions (Bloss *et al.*, 1995). It has been proposed that layers of this type are located at the interface with the CdS window layer. Furthermore, Na outdiffusion from soda-lime glass substrates is found to have beneficial effects upon cell performance, by increasing carrier concentrations in the absorber layer! Such material complexities may be responsible for reported difficulties in attempts to commercialize this material in the late 1980s (Zweibel, 1995). Module efficiencies above 12% have been reported in associated pilot production activities (Green *et al.*, 2000).

The completed devices use the glass layer as a substrate rather than a superstrate as for the a-Si and CdTe technologies earlier described (Figure 6.27). The same laser patterning steps can be used, however, for the CIS-based cells as for these other thin film technologies, although conducted in the reverse order from that shown in Figure 6.27. The very high efficiencies already obtained with this material in thin film polycrystalline make it a very strong candidate for a future, low-cost photovoltaic product. Small commercial modules (5 W and 10 W rating) were first reported to be in manufacture in mid-1998 (Siemens Solar, 1998), with higher rating modules now available.

6.8 OTHER PHOTOVOLTAIC APPROACHES

6.8.1 Basic requirements for photovoltaics

Although the technologies described in the previous sections have been based on the use of semiconductors and the use of p-n homojunctions or heterojunctions, these may not be essential requirements for photovoltaics. All that is

required, in principle, is an excited state or set of states into which a carrier can be excited from a ground state or states by photon absorption and some means of extracting or supplying carriers to or from these states. Doped semiconductors allow these functions to be integrated elegantly into a single material.

Nanocrystalline dye cells provide an example of a cell that is simple to fabricate but has these separate functions more clearly partitioned. In these cells (Figure 6.33), the photoabsorption occurs in a dye module, similar to the absorption process in photosynthesis. These cells will be discussed in more detail in Section 6.8.3, following discussion of photoelectrochemical cells, intermediate between conventional cells and the cells of Figure 6.33.

6.8.2 Photoelectrochemical cells

Photoelectrochemical cells are based on junctions formed between liquids and semiconductors as shown in Figure 6.34(a). In such a cell, the liquid

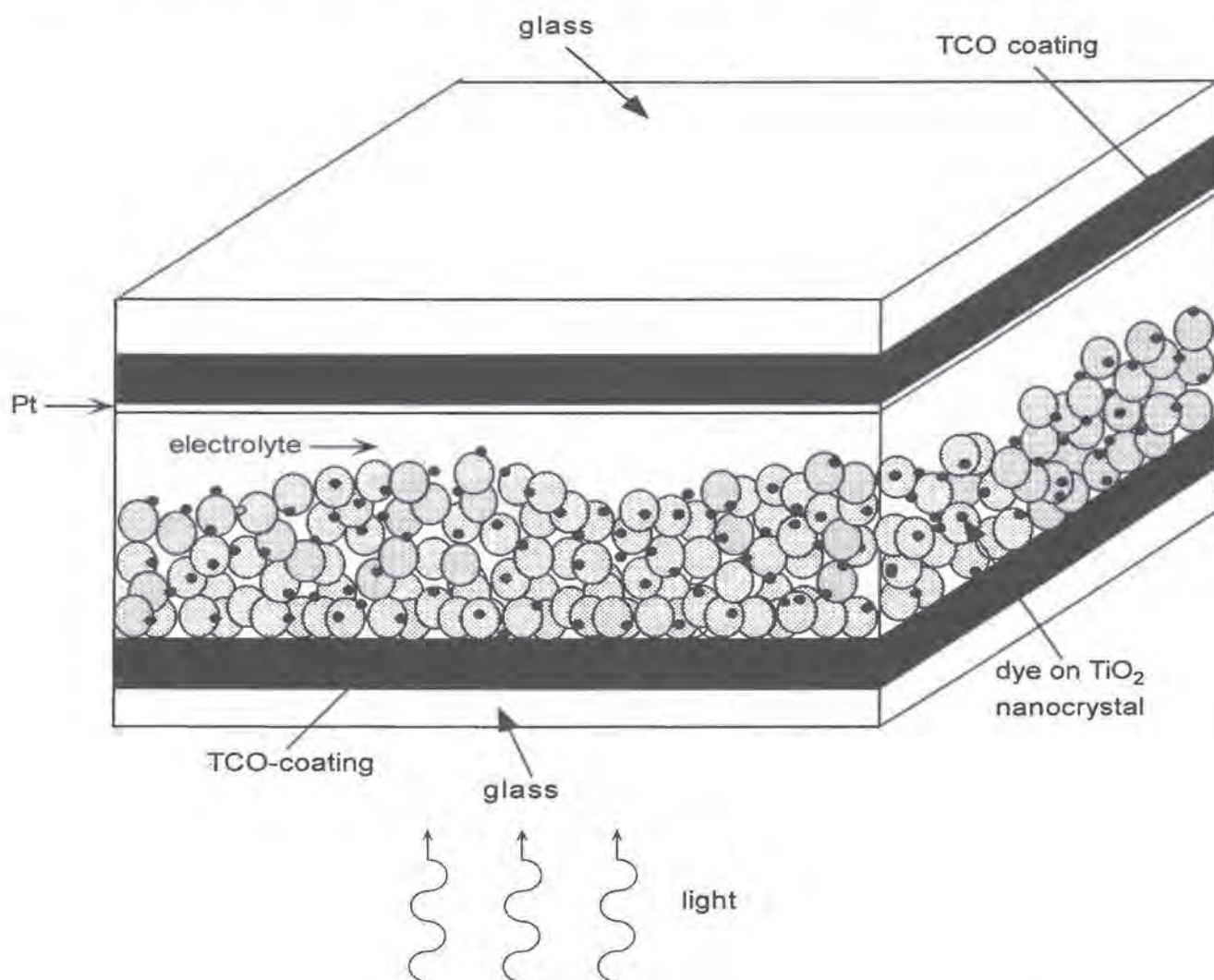


Figure 6.33 Nanocrystalline TiO_2 dye sensitized solar cell.

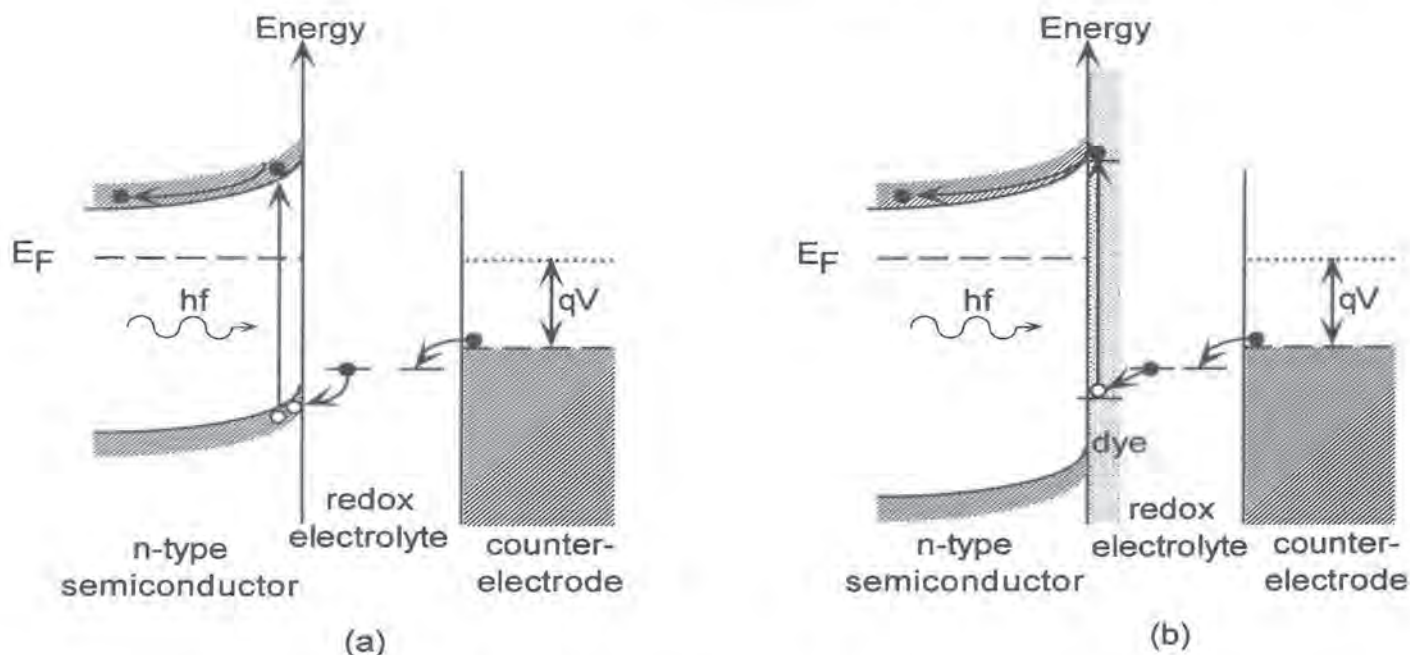


Figure 6.34 (a) Energy relationships in photoelectrochemical solar cell; (b) in a nanocrystalline dye cell in region where the semiconductor is coated by the dye.

induces a barrier in the semiconductor much as in the same way as does a metal (Section 6.5.2). The liquid contains a species known as a redox couple with two charge states. The species changes from an oxidised to a reduced state if it accepts an electron, or undergoes the opposite process of oxidation if it gives up an electron. Light is absorbed in the semiconductor, creating an electron-hole pair, as in a standard cell.

For the case of an n-type semiconductor, shown in Figure 6.34(a), the electron in the pair flows through the semiconductor, the contact to the semiconductor and the load to the counter-electrode. Here it reduces the redox couple within the liquid by this couple accepting an electron. The reduced species moves to the semiconductor interface where it is oxidised by giving up an electron (equivalent to accepting a hole). Charge is transferred across the liquid electrolyte by the motion of the oxidised and reduced species.

One advantage of this approach is the minimal device processing required. A modified approach also allows the direct production of fuel (hydrogen) by the photoelectrolyte decomposition of water. The disadvantage is the difficulty in sealing such a device over required operational lifetimes and the susceptibility of the semiconductor to photo-enhanced corrosion.

6.8.3 Nanocrystalline dye cell

In 1991, a new solar cell was reported that bears some similarity to a photoelectrochemical cell but that more closely mimics photosynthesis in its operation (O'Reagan and Grätzel, 1991). Rather than the sunlight being

absorbed in a semiconductor, the cell absorbs light in dye molecules containing ruthenium ions. These dye molecules are coated onto nanocrystals of the wide-bandgap semiconductor, TiO_2 as indicated in Figure 6.33.

Light causes excitation of an electron in the dye (not the semiconductor in this case, since its bandgap is quite wide) to an energy where it is injected into the conduction band of the adjacent n-type TiO_2 . The electron is transported through the TiO_2 to the transparent conducting oxide at the front side of the cell, through the load, to the counter-electrode. Here, it reduces tri-iodide to iodide, which then diffuses to the photo-oxidised dye molecules to reduce these molecules back to their original state (Deb *et al.*, 1997).

The cells are very simple to prepare (Lauermann *et al.*, 1997). The starting point is a sheet of glass coated by transparent conductive oxide (TCO). TiO_2 is prepared in nanocrystalline form, applied to the TCO coated glass and sintered. It is then soaked in a solution containing the dye, which results in the impregnation of the dye into the porous TiO_2 resulting in a large interfacial area, maximizing prospects for photoabsorption in the dye and electron injection into the TiO_2 .

The counter electrode is again a sheet of TCO coated glass, coated with a thin layer of Pt to catalyse the reduction reaction of this electrode. After sealing, the electrolyte is introduced through holes that are then resealed. The electrolyte consists of a solution of methyl-hexiglimidazolium iodide and t-tert-butylpyridine in acetonitrile.

Quantitative modelling of the performance of these devices (Stangl *et al.*, 1997) suggests that one of the key loss processes is the loss of photoexcited electrons in reducing the electrolyte in areas of TiO_2 not covered by the dye. With the standard ruthenium based dyes, which have peak absorption at 550 nm, energy conversion efficiency up to 8.5% has been confirmed for small area (0.25 cm^2) cells. With a new 'black' dye, this efficiency has been increased to 11.0% (Green *et al.*, 2000). This is quite a remarkable result given both the relatively short history of development and the simplicity of the approach.

However, there are some disadvantages which may be overcome with further work (Lauermann *et al.*, 1997). One is the use of a liquid electrolyte and the difficulty of reliably sealing such an electrolyte. Solid electrolytes are being investigated but efficiencies with such solid electrolytes are presently below 1% (Bell, 1999). Another disadvantage is that organic materials such as the ruthenium dye or electrolyte components can be subject to degradation, particularly under the harsh and hot outdoor conditions to which cells are exposed. Another disadvantage is that some materials used in present cells such as acetonitrile are flammable and toxic. A further is that, although these cells are probably the simplest to fabricate in the laboratory, this does not necessarily transfer to the lowest possible costs in high volume production. For example, present nanocrystalline dye cells require processing of two glass sheets to form the module (coating of glass by TCO plus one other layer), rather than the single sheet used in other thin-film

technologies, as well as the use of more complex cell interconnection approaches.

Regardless of these challenges, dye sensitized cell technology is already finding commercial applications in consumer products such as digital watches and bathroom scales. Unique features such as the ability to produce 'transparent' modules based on infrared absorbing dyes also make the technology of considerable longer-term interest.

6.9 CONCLUSION

With on-going improvements, photovoltaics is expected to provide an attractive way of large-scale electricity generation for the 21st century. The technology's key strengths are its environmental friendliness, deployability, modularity and potential for low cost.

Historically, the technology proved its merits in terms of reliability and durability in the space programmes of the 1960s. Since then, the costs for terrestrial use have reduced quite markedly, even though the mainstream product, at the turn of the millennium, remained based on the same crystalline silicon wafer product of previous decades.

At the start of the new millennium, the industry finds itself in a period of very rapid growth (over 30% per annum). Increased production volumes and the bringing into production of inherently lower cost thin-film photovoltaic technology are expected to cause prices to continue to decrease, possibly at an increased rate. Such price reduction is essential for effective penetration of the large-scale markets for which the technology is otherwise well suited.

Several thin-film technologies based on different semiconductors have the potential for photovoltaic module production at low cost. In all probability, the thin-film technology that proves dominant will match or possibly even exceed its crystalline wafer silicon predecessor in terms of energy conversion efficiency, reliability, durability, and lack of toxic or scarce constituents, while offering much lower cost.

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