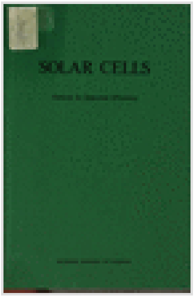

Solar Cells: Outlook for Improved Efficiency (1972)

Ad Hoc Panel on Solar Cell Efficiency; Space Science Board; National Research Council

Pages
81

Size
5 x 9

ISBN
0309345847

c.1

SOLAR CELLS

Outlook for Improved Efficiency

Ad Hoc Panel on Solar Cell Efficiency
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D. C. 1972

NOTICE: The study reported herein was undertaken under the aegis of the National Research Council, with the express approval of the Governing Board of the NRC. Such approval indicated that the Board considered that the problem is of national significance, that elucidation of the problem required scientific or technical competence, and that the resources of the NRC were particularly suitable to the conduct of the project. The institutional responsibilities of the NRC were then discharged in the following manner.

The members of the study group were selected for their individual scholarly competence and judgment with due consideration for the balance and breadth of disciplines. Responsibility for all aspects of this report rests with the study group, to whom sincere appreciation is expressed.

Although the reports of study groups are not submitted for approval to the Academy membership or to the Council, each report is reviewed by a second group of appropriately qualified individuals according to procedures established and monitored by the Academy's Report Review Committee. Such reviews are intended to determine, *inter alia,* whether the major questions and relevant points of view have been addressed and whether the reported findings, conclusions, and recommendations arose from the available data and information. Distribution of the report is approved, by the President, only after satisfactory completion of this review process.

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OTHER CONTRIBUTORS

ARVIN SMITH, Thermo Electron Corporation (formerly NASA Headquarters Liaison Representative), *Consultant*
ERNST COHN, *NASA Liaison Representative*

Preface

This is the report of a study convened by the Space Science Board of the National Academy of Sciences at the request of the National Aeronautics and Space Administration's Office of Aeronautics and Space Technology (formerly the Office of Advanced Research and Technology) to consider the technical feasibility of increasing the efficiency of solar cells in terms of possible benefits to the space program.

The study was conducted through a series of meetings beginning in 1970 and continuing through 1971. The study group, under the chairmanship of Paul Rappaport, consisted of eight participants, who represented a broad range of experience and competence in the various photovoltaic processes and in practical solar-cell-device design. This report has been reviewed by the Space Science Board and by the Academy's Solid State Sciences Committee.

The Space Science Board is grateful to those who participated in this study and to William C. Bartley of the Board's staff, who served as Executive Secretary of the study. The Board also acknowledges with appreciation the support of the National Aeronautics and Space Administration under Contract No. NSR 09-012-903.

Charles H. Townes, *Chairman*
Space Science Board

I THE PANEL'S REPORT

CHAPTER

1 Report and Recommendations

The solar cell has been one of the critically important devices in the space program. To date, over 600 U.S. and some 400 Soviet spacecraft[1] of varying type and function have used solar cells as the primary source of electrical power. Less than 10 of the U.S. unmanned spacecraft have used radioisotope thermoelectric generators for primary power, the only alternative long-life power source available for satellites.

During the period 1958–1969, about 10 million solar cells were purchased for use in the U.S. space program (at an estimated cost of \$50 million[2] plus an additional \$100 million for protective cover glass, support structure, and solar-cell assembly and test). It has been suggested that the use of the solar cell as a space power source would expand greatly, with resulting savings, if its conversion efficiency could be appreciably increased. While considerable engineering work has gone into developing reliable solar power supplies, very little effort has been applied during the past five or six years to increasing the efficiency of the cells beyond their present 10–13 percent.

In response to a request from the National Aeronautics and Space Administration, the Space Science Board, in cooperation with the Solid State Sciences Committee of the National Research Council, brought together this panel of scientists and engineers to study the question of improving the efficiency of solar cells. The panel has reexamined the theory of the photovoltaic effect and the technology of conventional silicon cells. Photovoltaic materials such as II–VI (cadmium sulfide) and III–V (gallium arsenide) semiconductor compounds and organics have also been reviewed, and other possibly

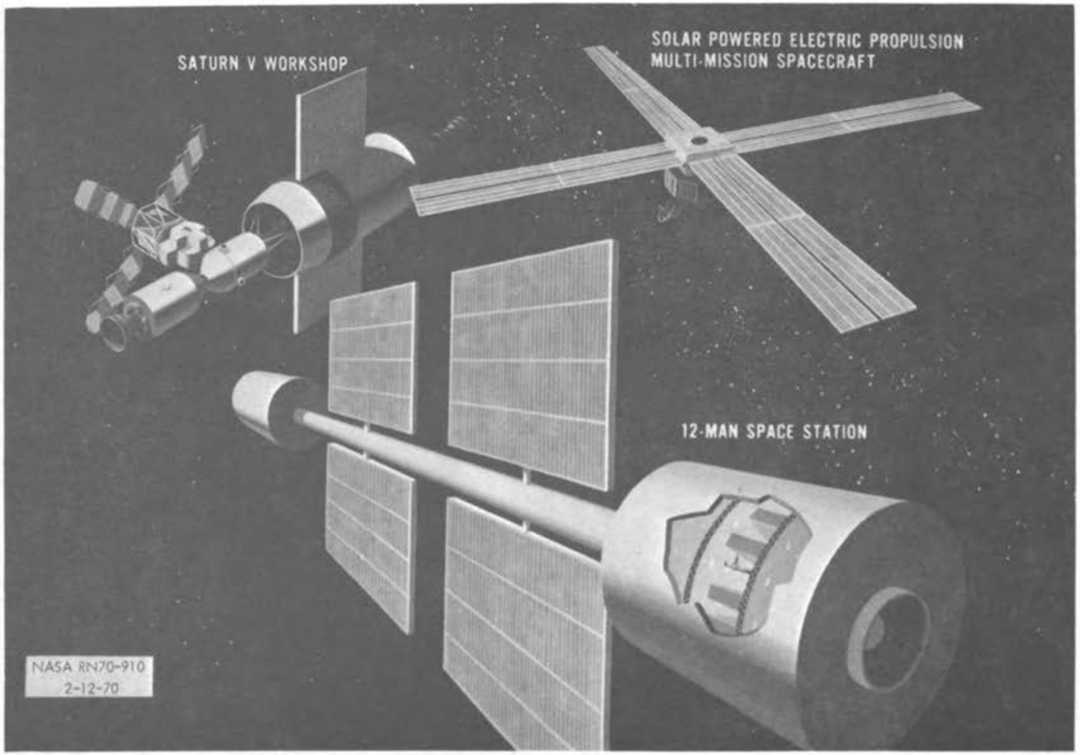

FIGURE 1 Major potential future applications of large-area solar-cell arrays.

relevant phenomena such as photosynthesis have been studied. Thin-film polycrystalline cells were not considered in detail because high efficiency is not probable with this technique.

It is the opinion of this panel that, with sufficient effort, increased solar-cell efficiency of up to 20 percent is feasible and that a 50 percent improvement in present efficiency (11 percent to about 16 percent) is probable with a reasonable improvement of material parameters. A summary of the panel's considerations, conclusions, and recommendations comprises the remainder of this chapter. Chapters in Part II contain more detailed technical presentations, for those who are concerned with the detailed reasons for these conclusions.*

Benefits of Increased Solar-Cell Efficiency

Many of the space missions proposed for the next decade involve large spacecraft. As an example, the Skylab A manned space station scheduled to be launched in 1972 will obtain its electrical power (up to 25,000 W) from over 500,000 silicon solar cells mounted on six structural wings for a total area of about 2500 ft^2. A number of studies for manned space stations beyond Skylab are under way; one configuration of a 12-man station using solar power is illustrated in Figure 1. Its four-wing array, providing 10,000 ft^2 of solar cells (slightly over 2 million equivalent 2 × 2-cm cells), is designed to permit rotation of the station to provide artificial gravity. Initial, nominal output from the array, while oriented to intercept maximum solar energy, would be approximately 100 kW (140 mW/cm^2, 55°C). With reasonable battery and power conditioning efficiencies, the array would be adequate to provide a well-regulated and well-filtered continuous output of 50 kW (to spacecraft loads) at the beginning of its lifetime. This provides a substantial design margin (and derating) to ensure the availability of 25 kW at the end of the mission.

Unmanned spacecraft are also larger, with greater power demands. The original Early Bird communication satellites used only 75 W of solar power, while INTELSAT 4 has a 600-W power capability. The current ATS-F and -G satellites carry 700-W systems, but ATS-H proposed for launch in 1976 or 1977 will carry a 4.5-kW solar array. The

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*See also Reference 3 in which the history and status of the solar cell to 1968 are reviewed by NASA.

High Energy Astronomical Observatory (HEAO) is the first of a new generation of very large unmanned scientific satellites that weigh over 10 tons, the first of which is scheduled for launch in 1974. Each of these spacecraft will depend on solar cells to power over 600 W of x-ray, gamma-ray, and cosmic-ray experiments.

Estimates[2] of spacecraft launches being planned by NASA, DOD, and COMSAT indicate a likely requirement for over 10 million solar cells during the 1970's. It is estimated that over \$150 million will be expended through 1979 to design, develop, and procure assembled solar-cell arrays if the efficiency remains at the current 10 to 11 percent air mass zero (25°C, 140 mW/cm^2). Another \$70 million would be required to launch such arrays, assuming 35,000 ft^2 of array area at 0.5 lb/ft^2 and \$4000 per pound launch cost.

If other factors can be held constant while cell efficiency is increased, the reduction in cost as a function of the increase in efficiency is shown in Figures 2 and 3. The additional research required to develop 16 percent-efficient solar cells is estimated at approximately \$5 million (~ 60 man-years) and to develop 20 percent-efficient solar cells, at approximately \$20 million (~ 250 man-years). Availability of 20 percent-efficient solar cells, comparable in other ways to today's 10 percent silicon solar cells, would afford a potential saving in excess of \$110 million (see Appendix) for assembly and launch costs during this decade alone. In addition, major benefits would result from the improvement of the dynamic performance of satellites due to a reduction in array area and weight. These include the following:

(a) Reduced likelihood of dynamic interactions with vehicle attitude-control systems;
(b) Reduced atmospheric drag in low-altitude earth orbits;
(c) Improved view angles for scientific instruments;
(d) Simplified structural integration and packaging;
(e) Simplified drive systems for array orientation.

Finally, a doubling of solar-cell efficiency would be of major importance to proposed planetary missions* using solar-electric propulsion.

It is clear that practical and financial benefits could result from significant advances in solar-cell efficiency. As solar cells become

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*Performance of 30 W/lb for rollout arrays using 10 percent air mass zero solar cells can lead to 60 W/lb with 20 percent air mass zero solar cells.

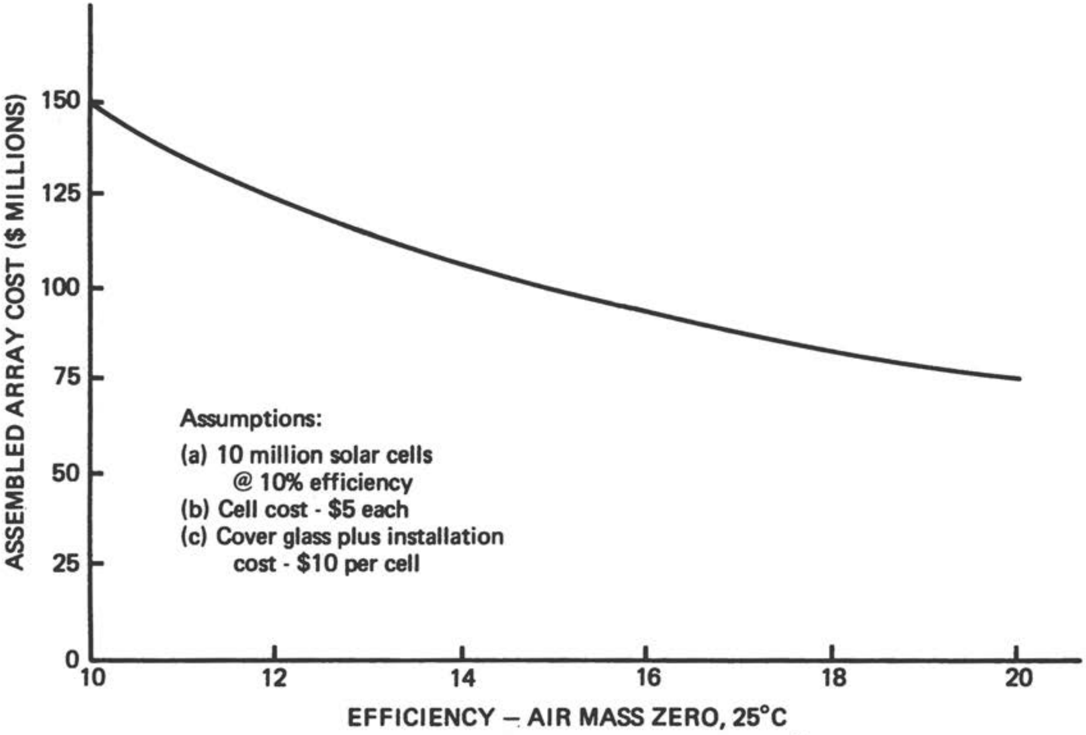
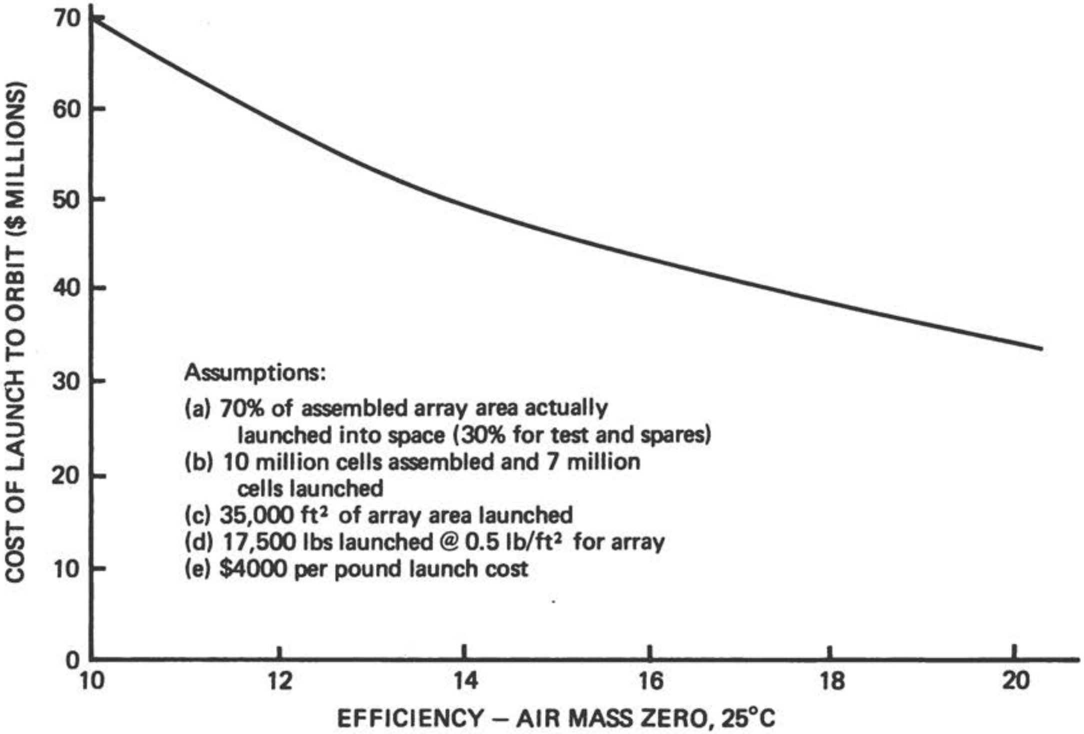


FIGURE 2 Assembled array cost versus solar-cell efficiency.



Assumptions:

(a) 70% of assembled array area actually launched into space (30% for test and spares)
(b) 10 million cells assembled and 7 million cells launched
(c) 35,000 ft^2 of array area launched
(d) 17,500 lbs launched @ 0.5 lb/ft^2 for array
(e) $4000 per pound launch cost

FIGURE 3 Launch cost versus solar-cell efficiency.

more efficient, it is anticipated that systems employing them can be extended to higher power levels, thereby precluding the need to use other, more complex, and more expensive power systems. Missions that cannot be carried out now because of the absence of more efficient solar cells will become feasible.

Although the charge to this study panel was to explore the possibilities of increased efficiencies for photovoltaic devices in the context of advantages to the space program, the panel feels that it should make note of the fact that future use of solar energy conversion for terrestrial power applications may be a far greater justification for developing improved efficiencies. The use of solar cells to generate electric power on a large scale on earth has received relatively little attention to date. To clarify the picture on the future use of solar cells, the panel briefly reviewed the major problem of terrestrial power requirements and the advantages that solar-energy power generation offers over fossil fuel and nuclear power plants.

Solar-energy power plants would be unique in that they would not pollute, either thermally or by particulate or nuclear contamination. The conversion of sunlight into electricity with photovoltaic cells is feasible at very-high-energy levels; however, current costs are high, and practical systems for energy storage and delivery are needed. The development of more efficient solar cells at lower costs (the Appendix presents an analysis of costs) might make this power source both feasible and competitive in price with other fossil fuel and nuclear power plants. Development could follow logically from the space power program. The space power program, in turn, would benefit enormously from the technologies and lower costs developed for terrestrial applications. Because terrestrial uses of solar cells are beyond the mandate of this panel, an extensive discussion of the topic is not appropriate here. Nevertheless, we believe that the field has enormous potential.

Solar-Cell-Efficiency Considerations

The panel concluded that research to accomplish a substantial increase in solar-cell efficiency should concentrate on the silicon solar cell because this cell, of all those considered, appears to have the best potential for large improvement. The rationale for this conclusion can be seen in the following discussion of both silicon and nonsilicon devices.

THE SILICON CELL

The conversion efficiency of solar cells has increased slowly over the last 10 years to a current level of about 11 percent. Of interest is the fact that virtually none of this increase occurred during the last 5 years. The panel believes that this plateau reflects a cessation of research and funding rather than a fundamental limitation in cell efficiency.

The main reason for this stagnation is that there has been very little motivation for technically oriented companies to fund their own R&D for solar-cell improvements. Apparently none of the cell manufacturers has made significant profit in this market. Of the five companies that produced commercial cells [RCA, Texas Instruments Inc., International Rectifiers Corp., Centralab (formerly Hoffman), and Helioteck], only two, Centralab and Helioteck, remain in the business today. The space program has been virtually the only market for solar cells; consequently, production capacity has exceeded the demand. In fact, during the mid-1960's, manufacturers were geared to fabricate 5 to 10 times the demand. Furthermore, the demand was never steady. Lack of standardization in cell specifications has also plagued the industry. A trend toward the more expensive batch type of production developed because user agencies were never able to stockpile cells to smooth over the peaks and valleys of demand. Thus, unlike many other devices in the semiconductor industry, developments in solar cells have had to be supported completely by government funds. This support has been limited mostly to engineering efforts on reliability and array design and to two important research areas, namely, radiation resistance and thin-film cells. Research targeted specifically toward increasing the efficiency of the silicon cells has not been encouraged or supported.

It is interesting to note that the silicon technology from which the solar cell derives is a $100 million R&D technology developed largely by industry. Unfortunately, present-day solar-cell technology does not take advantage of the most sophisticated silicon technology in materials, contacts, or surface treatment, nor do production methods make use of automation, which would probably result in significant cost savings. Solar-cell fabrication has always been largely a hand operation using make-do processes, and production has been a batch processing of each order. A large production line using sophisticated processing was never justified because of the relatively small numbers of cells (typical needs were about 2 million cells per year, split among two to five manufacturers). However, in terms of dollars spent in competing areas of importance to space power, the expenditures were relatively small (about 1 percent of that spent on dynamic and nuclear reactor systems).

What are the technical possibilities for improving the silicon solar cell, and how much improvement can be expected? To understand the problems a brief description of cell operation is required.

In a solar cell two basic processes are taking place, the generation of charge carriers (electrons and holes) by the absorption of solar photons and the collection of these carriers by a *p–n* junction. For high efficiency it is desirable to maximize both these processes. In general the carrier generation processes cannot be improved on once the semiconductor and its geometry are chosen. However, the carrier collection processes depend on materials parameters, and these can be improved considerably.

The generated carriers diffuse in the silicon until one of three processes intervenes. They can recombine with the opposite charge carrier in the volume of the silicon, they can recombine at the surface, or they can flow across the *p–n* junction. Only the last of these processes results in power delivered to a load. By treating the surfaces properly and by using high-lifetime silicon, the carriers' lifetimes are increased, and more are collected at the *p–n* junction. For maximum conversion efficiency this junction should have a potential barrier comparable to the average solar photon energy (about 1.5 eV).

The voltage developed by the cell is determined by the potential barrier of the *p–n* junction. The maximum potential barrier is set by the semiconductor bandgap (1.1 eV in silicon); the higher the doping or conductivity of the *p* and *n* regions, the higher the barrier. Maximum doping is not used in current commercial cells because the lifetime of the carriers is severely reduced in heavily doped silicon, and this would limit the current collection. The maximum room temperature voltage of a present-day silicon solar cell is about 0.6 V. Higher voltages can be obtained from semiconductors with large bandgaps. However, the current would then be lower because fewer photons are absorbed in such materials.

Once the semiconductor is selected, the current in a cell is determined by the carrier collection efficiency of the *p–n* junction. High collection efficiency requires that the lifetimes of the front (*n*-type) and back (*p*-type) regions of the *p–n* junction should be as high as possible. The lifetime is defined as the average time that a photon-generated (excess) carrier remains free. If the collection time is not shorter than the lifetime, the excess carrier will recombine and will not contribute to the cell current. Lifetime depends on doping level (i.e., on conductivity) and can be greater than 1000 μsec in high-resistivity silicon. However, many types of defect in silicon can and do appreciably reduce the lifetime by introducing recombination centers. Defects like dislocations, vacancies, interstitial atoms, composites, and chemical impurities (especially copper and nickel) cause such centers.

The surface recombination rates at the front and rear surfaces should be as small as possible. The carrier loss at a surface can be defined in terms of a velocity flow to the surface. This surface recombination velocity can be as high as 10^5 cm/sec, as is probably the case in existing cells, and as low as 10 cm/sec.

Another factor affecting efficiency is the form of the current voltage characteristic of the *p–n* junction. The junction occupies a finite volume of the cell between the front and back regions. Imperfections in this barrier region can produce "soft" I–V characteristics that reduce the voltage factor (VF) and curve fill factor (CFF) and hence the efficiency.

Theoretical efficiency calculations have been carried out, based on various models. Theoretical efficiencies as high as 26 percent for silicon have been predicted[4] for an outer-space air mass zero solar spectrum. Calculations based on probable material parameter values predict efficiencies of 22 percent for silicon and 25 percent for gallium arsenide.[5] These values are well above the 11 percent that has been achieved[6] in production silicon solar cells.

Possible improvements in silicon solar cells are summarized below. The detailed discussion in Chapter 4 shows that a doubling of efficiency, to the 20–22 percent range, is possible if the properties of the materials can be improved significantly.

1. The initial silicon should be as perfect as possible, free of point defects, defect clusters, dislocations, twins, stacking faults, and unwanted chemical impurities. The dopant should be the only foreign material present. Under these conditions, bulk lifetime would increase markedly, as would the current and voltage of a cell. If a minority-carrier lifetime of 10 μsec were achieved in 0.01-Ω-cm conductivity silicon this would be sufficient to produce cell efficiencies of nearly 20 percent.

2. A decrease in surface recombination velocity to less than 100 cm/sec could result in higher currents largely from the front and in thin cells from the rear portions of the device. This could be especially

important with respect to increasing the response of silicon cells to the blue-violet portion of the spectrum. These photons are absorbed within a few tenths of a micron of the surface and are lost because of the 10^5 cm/sec surface-recombination velocity characteristic of present-day cells.

3. The panel studied schemes to improve the photon utilization of the silicon cell. Among them are a spectral reflector at the rear of the solar cell to reflect the transmitted photons (over 25 percent of photons are lost in this way) back into the cell, and a phosphor on the front surface which would convert the ultraviolet light (less than 20 percent of blue-violet photons are utilized) into lower-energy photons that are more effectively absorbed in silicon. Techniques using cerise-red paint, acriflavin hydrochloride pinacyanol, and other photographic dyes to convert photons and aluminum or silver to reflect photons have not resulted in improvement of cell efficiency. Such potential improvements will be expected to yield small efficiency increases in the 10 percent range and should be kept in mind as new materials and processes become available.

4. Drift fields[7] at the front and rear surfaces of the cell would be effective in reducing the surface-recombination losses.

5. Another suggestion, that of tandem cells,[8] considers stacking two or more cells of different semiconductors. The one facing the sun has the largest energy gap and utilizes the high-energy portion of the solar radiation and transmits all photons below its gap. In principle this idea is workable provided electrical connections take into consideration the severe mismatch of voltage and current from each material. In practice the idea looks less appealing. The additional cells will more than double the cost but will never double the efficiency. Most serious is the problem of lossless transmission of the long-wavelength photons. Reflection losses and free carrier absorption must be reduced.

6. Another possible approach to higher efficiency cells is to construct solar cells with two collecting junctions in the same wafer. Consider the case of an *n*-type silicon wafer in which there are two junctions. The front *p*-region is 0.5 μ thick; the back junction *p*-region is either a thin diffused region or a thick region. In such a cell the response of the front region should be similar to that of a normal cell. The back junction should yield substantial output not realized in normal cells.

J. Capart of the European Space Technology Centre, Noordroyh, Holland, has analyzed such cells.[9] The short-circuit current of such a double-junction cell is substantially higher than that of single-junction cells. The current is 40 percent higher for 200-μ-thick intermediate layers and 61 percent higher for 50-μ-thick layers. Furthermore, the thin double-junction cell has a radiation resistance advantage over the single-junction cell. There is a problem with such cells in that different voltages will be generated at the front and back junctions and power conditioning could be difficult, and there are considerable technological difficulties associated with fabrication of such cells. It does seem, however, that the double-junction cells could indeed exhibit a significant efficiency increase over single-junction devices.

7. It has been suggested that impurities be incorporated into a *p–n* junction space-charge layer in order to utilize the low-energy portion of the solar spectrum. This proposal has recently been shown[10] to be invalid since the impurities in a space-charge layer will degrade efficiencies because of increased recombination.

SOLAR CELLS IN MATERIALS OTHER THAN SILICON

III–V Compounds

Here we discuss single-crystal semiconductors made up of elements from column III and column V of the periodic chart. Such materials, for example, gallium arsenide, indium phosphide, gallium phosphide, aluminum–gallium arsenide, have very interesting properties for photovoltaic energy conversion. They all have energy bandgaps in the proper range for efficient solar-energy conversion. In fact, GaAs with a bandgap of 1.35 eV is very close to the theoretically optimum material.

In the late 1950's and early 1960's, a significant R&D effort was funded for GaAs solar cells. The total expenditure was approximately $3 million. Results on a few cells have shown efficiencies close to those obtained in silicon.[11] Since GaAs is a direct-gap semiconductor it behaves differently from silicon in that the optical absorption edge is very sharp (see Figure 1 of Part II, Chapter 2, "An Introduction to the Physics of Solar Cells") and 1-μm thickness of GaAs is all that is required for almost complete absorption of sunlight. In silicon, an indirect gap semiconductor, several hundreds of microns are required for such absorption. It should be noted that not all III–V compounds are direct; whereas InP is direct, GaP and AlP are not direct.

One of the problems with a direct material such as GaAs is that the surface recombination is very high, and because the carriers are generated so close to the surface a great many of them are lost. In comparison with silicon, very little is known about surface properties of

III–V compounds. However, it should be possible to improve the surface considerably. One idea advanced by a member of the panel is to grow epitaxially an indirect gap material such as AlAs on a GaAs substrate. The AlAs has the wide gap that allows the light to penetrate and to generate carriers at the GaAs *p–n* junction now unaffected by a surface that is relatively far away on the AlAs.

Gallium arsenide solar cells are considerably more expensive than silicon cells and even in production would probably be a factor of 10 more expensive because of the cost of gallium. Indium phosphide, from which 6 to 8 percent efficient cells have been made, would be less expensive in production although the single-crystal material is difficult to grow and would undoubtedly be more costly to make than silicon.

One advantage of gallium arsenide and other large-energy-gap semiconductors is their ability to operate at higher temperatures than silicon. This is important where space missions to Venus, Mercury, or the sun are under consideration or where the use of sunlight concentrators is contemplated.

Work in this country on III–V compounds for solar cells ceased about five years ago. Since that time, however, a great deal of progress in these materials has been made because of interest in lasers, light devices, and microwave devices. New techniques for crystal growth, such as liquid-phase epitaxy,[12] have been devised in recent years; these have improved radiative efficiencies[13] and should be applicable to solar cells. All III–V's are still very impure materials and are probably far from the perfection required for >20 percent efficient solar cells. However, it would be of great interest to see if the progress in these materials has been significant with respect to solar-energy conversion.

There should probably be means to keep up with the state of the art of these materials and to carry out experiments to assess their applicability for highly efficient solar cells. It is estimated, however, that an expenditure of about $20 million would be required to bring the materials know-how of III–V compounds to the state necessary for high-efficiency (15 to 20 percent) solar cells. Such cells would probably be more expensive than silicon in future production and have only limited advantages over silicon.

II–VI Compounds

These are materials such as cadmium sulfide and cadmium telluride made up of elements in column II and VI of the periodic chart. These materials tend to have low lifetimes and cannot be made into good *p–n* junctions. Their electronic properties are dominated by trapping processes. Solar cells made from these materials commonly involve heterojunctions and barrier layer. Efficiencies in single-crystal cells have been reported to be about 8 percent in CdS and CdTe.[3] It is considered quite unlikely that single-crystal cells will show efficiencies approaching those expected from silicon or III–V compounds.

These materials are important to thin-film polycrystalline solar cells. Because of the high degree of ionicity in II–VI compounds, many of the single-crystal properties are preserved even when the material is microcrystalline, as it is when evaporated in thin films. Such cells have shown efficiencies of 6 to 8 percent in large areas of about 60 cm^2. Such cells are lightweight and show promise of high power-to-weight ratio for space applications. Also, because single-crystal material is not required, the cells show promise of low cost—it is hoped a factor of 100 less than present silicon cells. This, of course, is an important factor in possible terrestrial uses of solar cells.

A major problem in the CdS cell is that of reliability. In the presence of humidity the cells have been known to degrade by more than 50 percent. Light and voltage cause degradation due to ion motion in the CdS. Cell operation is not well understood so that improvement has to be empirical. A modest research effort has been under way, much of it in other countries, to better understand the physics of the Cu–CdS cell, and progress is being made slowly.

While the panel did not thoroughly study the CdS cell because of its lack of promise for high efficiency, it recommends that more effort should be devoted to gaining a better understanding of the device rather than to producing devices such as those that are currently possible.

Organic Materials for Solar Cells

Ever since the discovery of semiconductor behavior and weak *p–n* junctions in organic materials, there has been interest in the possibility of making low-cost and easily fabricated devices, including solar cells, with organic materials. Many organic compounds have been investigated and found to have properties of interest to solar-energy conversion. In particular, many of them have activation energies (bandgap) in the range of interest, i.e., 0.5 to 2 eV. While *p–n* junction photovoltaic devices have not been fabricated from these materials, some Schottky barrier cells have been made. Open circuit voltages of 0.5 to 1 V have been observed. These are in the same range as semiconductor devices. However, the currents are much too small to provide efficient energy conversion. This is largely due to the high resistivity of the organic materials. Improvements in resistance and current by a factor of over a million are required before such materials will be of interest for solar cells.

We have, therefore, concluded that organic materials are a long way from providing practical devices. Progress will probably be made by discovering new organic materials or new effects rather than by steady improvement in known materials and effects. Some of our discussion indicated that the combination of photosynthesis and organic materials might lead to fruitful concepts. We do not expect that this field will produce devices that in any way compete with silicon or thin-film (low-cost, large-area) cadmium sulfide solar cells during the next decade. University research at a nominal rate over an extended period of the time should be encouraged here.

Photosynthetic Materials

We felt that it was important to examine the process of photosynthesis in this study. Combining knowledge of *p–n* junctions and photosynthesis might hopefully produce some synergy. The two phenomena have such things in common as the generation of charges, transport, lifetime, and recombination. Unfortunately, the analysis is not optimistic. The maximum efficiency of conversion of solar energy into stored chemical energy via photosynthesis is about 3 percent, and to produce heat and electricity would cause further degradation so that less than 1 percent efficiency can be expected.

Photochemical systems in plants may be more interesting. These systems based on chlorophyll compare with the better organic photovoltaic devices although they are a long way from high-efficiency devices. Some photovoltaic concepts, like the separation of the charges by the potential barrier, should be applied to the photosynthetic process. This kind of research should continue and should be monitored for signs of progress relevant to energy-conversion applications.

Conclusions

1. Solar cells have been a key device in the space program. They will continue to be for the foreseeable future, and their use will increase as the need for space power increases. For example, solar-cell arrays producing 100 kW of electrical power are being contemplated for space stations during this decade. It is estimated that over 10 mil-

lion solar cells will be required during the 1970's. If cells with efficiencies in the 20–22 percent (outer-space air mass zero) range were available, it is estimated that over $100 million could be saved in assembly and launch costs alone. In addition, benefits could also result in the dynamic performance of satellites because the arrays would be considerably smaller and lighter. We therefore conclude that a substantial (50 to 100 percent) increase in solar-cell efficiency could significantly benefit the space program.

2. In considering the various alternative devices, it is clear that the silicon solar cell offers the best opportunity for increased efficiency at lowest cost and shortest payoff time. Air mass zero (outer-space) efficiencies in the 20–22 percent range are deemed feasible. To achieve this efficiency, two major endeavors are required. The first is to substantially improve the initial silicon material from which the cell is made. Silicon is required in the 0.01-Ω-cm range with a lifetime of 10 μsec. The second requirement is improved surface properties. Here, existing silicon technology can be of major assistance. Important work will also be required in processing of silicon so as to maintain the excellent properties throughout the fabrication process.

3. Because ultimate cost savings to the space program are a major justification for this suggested R&D, we should not overlook the fact that savings can be achieved through production methods as well. For example, if a steady production (rather than batch production) of standard solar cells could be achieved over a number of years, the cost would be reduced. The cells could then be stored as needed. Also, more modern, automated production techniques would permit increased production when needed. The same concepts must also be applied to the growth of silicon crystals.

4. The panel feels that it is important to point out that in the past silicon solar-cell technology has relied heavily on the silicon semiconductor industry. However, present-day solar-cell fabrication does not use many of the more sophisticated contact, diffusion, and surface technologies available. To achieve 50–100 percent higher efficiencies, the state of the art of silicon must go beyond that required for present silicon transistor and integrated circuits; significant advances will require special attention to the material quality requirements of silicon solar cells.

5. With respect to work on compound semiconductors such as the III–V's and their alloys, much work on materials development has been done because of the needs of devices in, for example, the laser and high-frequency fields. It would be desirable to have a low-level R&D effort to assess periodically the applicability of this materials

work to solar cells. Major improvements in solar-cell efficiency may be possible here, but it must be borne in mind that the development of production solar cells using such materials may be far more costly than the silicon program we envisage.

6. Work in II–VI compounds, organics, and photosynthetic materials continues at a slow pace in this country. Because attainment of high efficiency in these materials is not expected for a long time, it does not appear that much emphasis should be placed in this area at this time, at least not for the sake of achieving high-efficiency solar cells.

7. Commercial industrial incentive to improve the efficiency of the solar cells has not developed to date. Until it does, such work will have to be funded by government sources.

8. While it was not the primary purpose of the study to consider other than the feasibility of increased solar-cell efficiency in the context of the space program, the panel felt strongly that terrestrial use of solar cells for generating electrical power should be considered, since the space program would benefit from the lower cost that would result from such a commercial application. In this regard the panel feels strongly that, to date, too little consideration has been given to the utilization of solar energy and solar cells for terrestrial power. A few schemes have been suggested based on space technology and are being evaluated. More ideas and creative systems thinking are needed to make direct solar-energy conversion practical for terrestrial power. However, solar power is unique in that it does not pollute, either thermally or by particulate or nuclear contamination, and is therefore particularly attractive.

The Panel urges that studies be undertaken of the technical and economic feasibility of terrestrial uses of solar cells and that an additional study on low-cost energy storage systems be considered. We think it appropriate that Academy groups undertake these tasks. The assessment of the relative merits of solar power for terrestrial use in combination with and as a substitute for alternative energy sources, including fossil fuels, hydro-turbine, geothermal stream, and nuclear and fission systems, will also impact the future use of solar cells in space applications.

Recommendations

1. It is the opinion of this panel that an appreciable improvement in the efficiency of silicon solar cells is technologically feasible. There-

fore, we *recommend* that effort be initiated toward the development of a 20–22 percent (room temperature and air mass zero) efficient silicon solar cell.

2. We believe that the main obstacle to attaining the above goal lies in the quality of silicon attainable. Therefore, we *recommend* that efforts be initiated to increase the diffusion length of highly doped silicon. A goal of 50-μm diffusion length (10-μsec lifetime) in silicon of 0.01-Ω-cm range is feasible. Before this work is carried out, a study of the state of the art of high-quality, single-crystal silicon will be necessary.

3. We *recommend* that development work be initiated in two other areas of importance to high-efficiency silicon solar cells: to improve surface-recombination proerties at the front surface and to better the quality of the junction current-voltage characteristic as measured by the *A* factor. Surface-recombination velocities of 100 cm/sec and *A* factors near unity should be the combined goal of these two efforts.

4. It appears that 20 percent efficiency in other materials such as III–V compounds is theoretically possible. However, there is no promise that the silicon efficiency will be substantially exceeded, and the costs associated with the development of any new material to the stage of producing high-efficiency solar cells will probably be very high. Thin-film photovoltaic cells do not seem to offer the possibility of high-efficiency solar-energy conversion. They do, however, promise a cost advantage over single-crystal cells, and research should be continued on such cells for that reason. We *recommend* support in this area for exploration of promising new ideas and for close surveillance of new developments in ongoing research in these materials.

5. Neither organic semiconductors nor photosynthetic materials offers short-term promise for efficient solar-energy conversion. We *recommend* that low-level support be continued in these areas, with special attention to a combination of the two disciplines.

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Appendix: Cost of Solar Cells

Contrary to the experience with many other semiconductor devices, the cost of solar cells (about $100,000 per kW generating capability) has remained almost unchanged during the past decade. There are a number of factors responsible for this. First, there has been no significant increase in the market for solar cells, whose use is confined almost exclusively to power supplies on satellites. The small market has discouraged introduction of mass production techniques. Second, this particular application sets very stringent requirements on cell reliability. This in turn requires intensive, expensive testing of every cell. Third, limits of area on space vehicles encourage cutting cells to rectangular shapes. This results in additional costs because of the loss of otherwise usable silicon crystal material. The as-grown crystals are circular in shape, and if cells of circular shape were sufficient, savings could be effected. However, power per unit area or weight would be increased.

According to E. L. Ralph,[1] simple changes in shape, etc., would make it possible to produce 11 percent efficient cells at a cost of $15,000 per kW generating capability, a factor of about 6 decrease from present levels. Ralph assumes that the cost of the silicon single crystals will remain unchanged. This cost factor provides a serious ultimate limitation on the cost of the cell. Yet, the ultimate cost is set to a considerable extent by the size of the market. Current U.S. production of single-crystal silicon amounts to about 100 tons per year. The amount of silicon that would be needed to generate enough power to match current U.S. terrestrial electric power needs would be about 2 million tons. (These cells would cover a total area of about 5×10^3 sq miles. This area is comparable with the area of the United States currently covered by structures and roads.) Silicon is an extremely abundant element so that the cost is not based on limited supplies of the raw material. It is reasonable to expect that if the demand for silicon were to increase from the current level to the level required by a large-scale terrestrial market, the price should drop substantially. This has certainly been the case in the history of other materials like aluminum and, more recently, titanium.

Ralph[1] points out that the use of a simple conical "egg carton" concentrator has increased the power produced per cell by a factor of 2.5. The cost of power generated with such a system including the $15,000 per kW solar cell, would further reduce costs to about $6000 per kW. Higher sunlight concentration would reduce costs still further. Ralph estimates that the price could ultimately be reduced to the range of $1000 per kW. He cites the fact that the Odeillo, France, 1000-kW solar furnace was built at a cost of $2000 per kW.[2] A simpler design would be sufficient for large-scale electric power generation.

To date, there has been no attempt to explore the costs of large-scale solar-energy conversion systems; therefore the costs cited here are conjectural.

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II SUPPORTING TECHNICAL PRESENTATIONS

CHAPTER

2 An Introduction to the Physics of Solar Cells

JOSEPH J. LOFERSKI

I. Definition of the Photovoltaic Effect

The photovoltaic effect (PVE) is the generation of an electromotive force as a result of the absorption of ionizing radiation. This definition distinguishes between ionizing and nonionizing radiation. The absorption of nonionizing radiation can lead to a localized temperature increase and this, in turn, can lead to the generation of an emf via thermoelectric effects, which we mean to exclude from this discussion.

In principle, the PVE can occur in gases, liquids, and solids. This discussion will, however, be limited to the PVE in semiconductors with forbidden energy gaps between 1 and 3 eV, because analysis of the effect shows that in the temperature range 100 K to about 500 K acceptable efficiency for conversion of sunlight into electricity occurs only in such materials.[1]

There are two distinct processes involved in the PVE. First, positive and negative charges (holes and electrons) in excess of thermal equilibrium values are generated by absorption of ionizing radiation. Second, the charges of opposite signs are separated at some electrical inhomogeneity in the system. In the most efficient photovoltaic cells (Si, Cu–Cd–S, GaAs, InP, Se, etc.), this inhomogeneity is either a metal-semiconductor barrier or a junction between two regions of a semiconductor having different resistivities, which in cells with the most pronounced PVE, is a *p–n* junction. The *p–n* junction may be a homojunction, i.e., the same semiconductor on each side of the junction. Efficient cells of this type have been made from Si, GaAs, InP, and Ge. It may also be a heterojunction, i.e., a junction between two different semiconductors. Some of the extensively studied heterojunction photocell systems are those involving p-Se–n-CdSe, p-Cu_2S_x–n-CdS, and n-CdTe–p-Cu_2Te_x.

In all these cases, metal-semiconductor as well as junction-type cells, the fabrication process results in the formation of a space-charge region, i.e., a dipole layer, inside the semiconductor. It is the difference in electric potential on the two sides of this region that causes charges to undergo separation. The potential difference between the two ends of the space-charge region sets an upper limit on the magnitude of the emf that can be produced by illumination. Since charge separation occurs at a localized site that may be far from the charge generation site, the charges generated by the light, if they are to contribute to the PVE, must be mobile and must continue in their separated state for a long time compared with the time required to travel to the localized charge separation site. In semiconductor jargon, the diffusion lengths of the free charges must be large compared with the distance between the place where they are generated and the position of the space-charge region.

In what follows, we focus attention on each of the processes—charge generation, migration of free carriers, and charge separation—in order to establish criteria that would lead to optimization of photovoltaic cells. Then we shall review the expressions for current, voltage, and power for photovoltaic cells and show how these expressions are related to material and device parameters.

II. Charge Generation and Light Absorption

The first step in the generation of a photo emf is the generation of excess carriers by the absorption of light in the semiconductor. Consider a monochromatic parallel beam of light incident on a solid. Let the x axis be normal to the plane of constant phase of the incident electromagnetic wave. Then the number of photons/cm^2 $N_{ph}(x)$ remaining in the beam after it traverses a distance x from the reference plane at $x = 0$ is given by

$$N_{ph}(x) = N_{ph}(0)\, e^{-\alpha x},$$

where $N_{ph}(0)$ is the number of photons/cm^2 at the reference plane $x = 0$ and α is the absorption constant. The parameter α is a function of the wavelength of the light or the photon energy $h\nu$.

Figure 1 is a plot of ln *α* versus $h\nu$ for a number of semiconductors of interest for PV solar-energy conversion. These curves are characterized by a threshold for absorption E_G such that for $h\nu < E_G$ the value of *α* is very small ($<1\ \text{cm}^{-1}$), while for $h\nu > E_G$ the value of *α* rises rapidly until it attains a value somewhat in excess of $10^4\ \text{cm}^{-1}$ within an electron volt of the absorption edge.

More than 50 percent of the energy in sunlight is carried by pho-

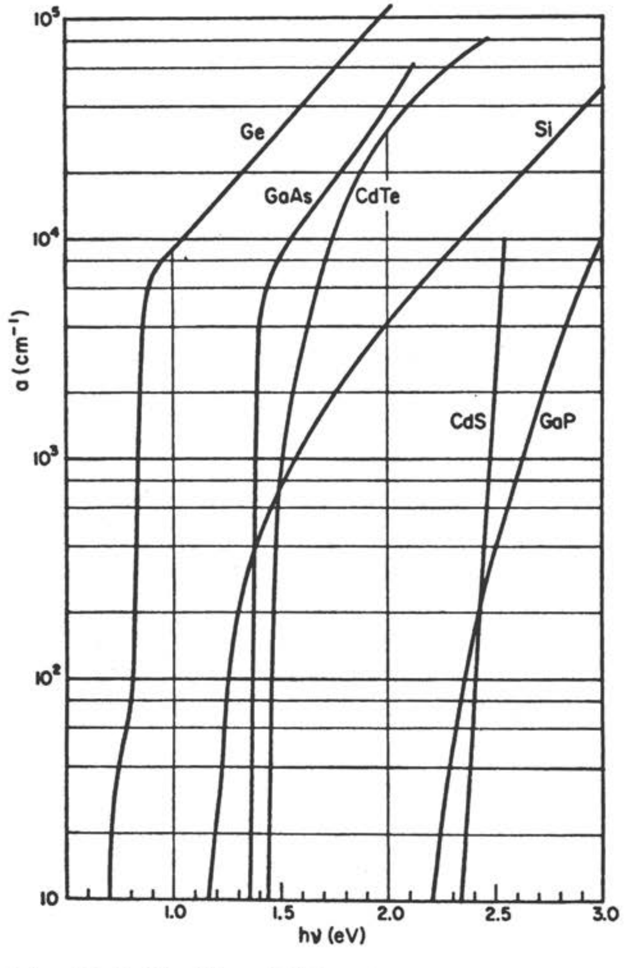

FIGURE 1 Logarithmic plots of the optical absorption constant versus photon energy $h\nu$.

tons whose energies lie between 1.0 and 2.5 eV. For the materials whose ln α versus $h\nu$ curves are shown in Figure 1, most of the solar photons will be absorbed in a thickness of material between 10^{-3} and 10^{-5} cm. This means that from the point of view of nearly total absorption of light, photovoltaic solar cells need not be thicker than a few times 10^{-3} cm. Commercial silicon cells are about an order of magnitude thicker, mainly because of fabrication and handling problems posed by thinner cells. Thus much of a commercial silicon cell is "dead weight" whose elimination could lead to a substantial increase in the power-to-weight ratio.

Figure 1 also shows that the ln α versus $h\nu$ curves of most of these semiconductors rise more rapidly toward high values than does the silicon curve. In fact, one would conclude from Figure 1 that silicon is a poor choice as a photovoltaic material if power-to-weight ratio is an important consideration.

The form of the ln α versus $h\nu$ curves has been explained in terms of the band theory of solids.[2] According to this theory, there is a threshold energy for optical absorption because the generation of a hole–electron pair requires that the electron absorb sufficient energy from the photon to make a transition across the forbidden energy gap E_G between the valence band and the conduction band. The shape of the curve as it rises to higher values of α from the threshold depends on more subtle considerations, according to which semiconductors can be classified as direct- or indirect-gap materials. In direct-gap materials, optically induced transitions from the valence to the conduction band occur in a single step; this leads to a rapidly rising α versus $h\nu$ curve. In indirect-gap materials, optically induced transitions involve interaction among a photon, an electron, and a quantum of lattice vibrational energy, i.e., a phonon. Since there are three entities involved in the act of generating a hole–electron pair, the probability that the event will occur is smaller than for a direct transition, i.e., the absorption constant is smaller. At photon energies sufficiently in excess of E_G, direct transitions begin to dominate even in indirect-gap materials. The direct-type transitions lead to absorption constants in the range 10^4 to 10^6 cm^{-1}.

Thus, on the basis of the ln α versus $h\nu$ curves, it would appear that direct-gap materials would be preferred for PV solar cells, if for no other reason than the fact that cells made from direct-gap materials can be substantially thinner than cells made from indirect-gap materials. This certainly means that the preferred materials for thin-film solar cells are direct-gap materials.

III. Charge Separation in the Photovoltaic Cell

A. HOMOJUNCTIONS

Light absorption results in the generation of pairs of carriers in excess of thermal equilibrium concentrations. Unless the holes and electrons are separated, there can be no current flow. To separate these carriers it is necessary for them to be under the influence of an electric field. The existence of an internal electrostatic field inside a semiconductor implies the existence of oppositely charged regions, i.e., of space-charge regions in the solid. Such regions can be built into the bulk of a crystal by the incorporation of suitable combinations of donor and acceptor impurities, which are ionized at the temperature of interest.

Poisson's equation provides a relation between the electrostatic potential ψ and the charge density ρ. This equation has the form

$$\text{div grad } \psi = -\rho/\epsilon,$$

where ϵ is the dielectric constant. The charge density ρ is composed of free charges (the mobile holes and electrons) and immobile charges (the ionized donors and acceptors):

$$\rho = q(p-n + N_D^+ - N_A^-),$$

where p and n are the densities of holes and electrons, respectively, while N_D^+ is the concentration of ionized donors and N_A^- the concentration of ionized acceptors.

In a semiconductor in which the donors or acceptors are uniformly distributed throughout the volume, $\rho = 0$ since the free charges just compensate the bound charges represented by acceptors or donors. In such a homogeneous material, there is no variation of field with position, i.e.,

$$\text{grad } \psi = -\vec{E} = \text{constant}.$$

If the semiconductor contains a nonuniform impurity distribution, then ψ may vary with position.

The exact form of the variation of ψ with x can be determined by solving Poisson's equation.[3] Figure 2 shows a typical plot of electron energy $(-q)\,\psi$ versus distance through a p–n junction. The following

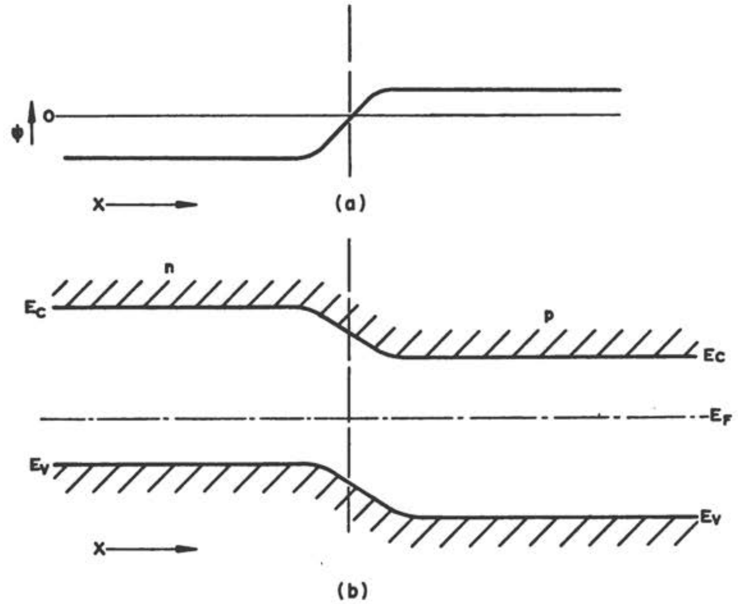

FIGURE 2 Electrostatic potential ψ and electron energy $(-q)\,\psi$ as a function of distance in the vicinity of an unilluminated *p*–*n* junction; E_F is the Fermi energy.

observations concerning this figure are in order. The maximum open-circuit voltage that one can obtain from a conductivity junction is equal to the electrostatic potential difference between the two sides of the junction. This potential difference is determined by the difference in Fermi level on the two sides of the junction. The Fermi level on each homogeneous side is controlled by the impurity concentration. Therefore, the potential difference has its maximum value when the materials on the two sides are heavily doped *n*-material and heavily doped *p*-material. This barrier height argument would lead to the conclusion that the best cell would consist of a junction between degenerate *n*-type material and degenerate *p*-type material. However, if the materials were doped to degeneracy, the diffusion length of the carriers would be drastically reduced, and efficient cells have not been made from such material.

Another point to be considered apropos of the $(-q)\,\psi$ versus x curve is the dependence of ψ on x in the junction region. It is best to have as abrupt a transition as possible because an abrupt transition places the minimum demand on carrier diffusion lengths in the space-charge region. This may not be important in silicon where the diffusion length is usually much greater than the thickness of the space-charge region, but it could be important in materials like GaAs, which have a very small diffusion length. It should also be important in thin-film cells where the space-charge region must be substantially thinner than the film thickness. In commercial silicon cells, one side of the junction (the "base" region) is homogeneous and the impurity forming the *p–n* junction is incorporated by the diffusion process. This process does not lead to an abrupt junction. It does lead to a built-in field in the diffused region. The direction of the field is such that under its influence, minority carriers move toward the junction. This appears to be a desirable arrangement; however, it has not been demonstrated that such a structure will result in a better cell than that associated with an abrupt transition.

To summarize, the best cell design involves a junction between heavily doped *n*-type and heavily doped *p*-type material. This would lead to the highest attainable electrostatic potential difference between the two homogeneous parts of the cell, and this, in turn, should lead to an optimum open-circuit voltage. The presence of impurity gradients in the space-charge region does not appear to have any obvious advantage over abrupt transition regions.

B. METAL-SEMICONDUCTOR JUNCTIONS

Some PV cells incorporate metal-semiconductor barriers. The height of such a barrier and the maximum attainable photovoltage depend on the difference between the work functions of the metal and semiconductor. The potential differences between the metal and the semiconductor can be of the same magnitude as those found in *p–n* junctions. In cells made in this way, the generation of excess hole–electron pairs occurs only in the semiconductor; the metal does not contribute carriers. Any light absorbed by the metal is lost; therefore metal-semiconductor cells should be illuminated on the semiconductor side. This requires, however, that the diffusion length in the semiconductor be large compared with the distance between the illuminated surface and the metal contact. Metal-semiconductor type photovoltaic cells have not been studied intensively in the last decade. In view of modern advances in surface and vacuum technology, MOS devices, for example, it may be desirable to re-examine the metal-semiconductor barrier type of cell.

C. HETEROJUNCTIONS

As we have pointed out, it is possible to make a junction between a *p*-type region of one semiconductor and an *n*-type region of a different semiconductor. The resulting structure is referred to as a heterojunction. The theory of such heterojunctions is in a rudimentary state compared with that of homojunctions. This is because the interface between two materials is not sufficiently understood. The best developed heterojunction-type cell (i.e., the heterojunction on which most research effort has been expended to date) is the CdS–Cu_xS_y cell (the subscripts x and y are used to indicate that there is uncertainty about the composition of the *p*-type copper–sulfur compound in this photovoltaic cell). Because there remain unanswered questions about the nature of the barrier in this cell, it is impossible to predict an upper limit on its solar-energy conversion efficiency. These gaps in understanding the behavior of heterojunctions make it impossible to estimate the ultimate efficiencies attainable in such cells. However, an upper limit on the photocurrent is probably set by the lower bandgap material that controls the fraction of photons absorbed from the solar spectrum.

An important advantage of heterojunction PV cells may be the convenience of fabrication, which, in turn, may result in low fabrication costs. This was true of the Se–CdSe cell, and it is true of the Cu–Cd–S cell.

A few remarks about the Cu–Cd–S thin-film cell are appropriate since it is an important photocell.[4] On the basis of energy-gap considerations alone, this cell ought to attain efficiencies appropriate to the smaller energy-gap constituent, namely, the Cu_xS_y compound. If this compound is Cu_2S, whose energy gap is about 1.1 eV, then the limiting efficiency of a Cu–Cd–S cell would be about the same as that of silicon, i.e., about 20 percent. The fact is, however, that no one has reported a solar-energy conversion efficiency in excess of 8 percent for the Cu–Cd–S cell, and there is no reason to anticipate efficiencies comparable with those that are possible in silicon homojunctions.

As a final comment on heterojunctions, note that a recent (1969) analysis of solar-energy conversion in heterojunctions[5] leads to the conclusion that efficiencies in excess of 20 percent could be obtained in heterojunction cells based on combinations of silicon and III–V compound semiconductors. For example, that paper claims that a *p*-Si–*n*-GaAs heterojunction cell would have an efficiency of 28 percent and that an *n*-InP–*p*-GaAs cell could have an efficiency of 30 percent.

IV. Migration of Light-Generated Carriers

A. RECOMBINATION CENTERS

In order for charge separation to occur, the lifetime of the excess carriers produced by the ionizing radiation must be such that these carriers remain free long enough to reach the charge separation site. There are a number of different lifetimes characteristic of free carriers. In this case we are interested in the lifetime of excess hole–electron pairs that is equal to the minority carrier lifetime in semiconductors used in PV cells.

The concept of lifetime is based on the dynamics of carrier generation.[3] Even in the absence of external excitation, equilibrium concentrations of holes and electrons are maintained in the semiconductor by thermal generation and subsequent recombination. The generation–recombination can involve transition directly across the forbidden energy gap (with or without cooperation of phonons), or they can involve transitions via states in the forbidden energy gap. Excess hole–electron pairs also recombine either directly or through states in the forbidden energy gap.

The upper limit on lifetime is determined by intrinsic recombination processes, i.e., recombination that does not involve states in the forbidden energy gap. In the case of germanium and silicon, this intrinsic recombination time is of the order of seconds because in these semiconductors recombination between electrons in the conduction band and holes in the valence band requires participation of lattice vibrational quanta (phonons). In direct-gap semiconductors, like GaAs, the intrinsic lifetime is considerably shorter (of the order of 10^{-8} sec).

Now energy levels in a semiconductor can be classified as shallow and deep levels. By definition, deep levels are more than a few kT units from one of the band edges. Impurities that introduce shallow levels control conductivity, and their presence is necessary in the PV cell. Defects that introduce deep levels control lifetime. It is therefore one object of solar-cell fabrication technology to exclude the defects that give rise to deep states. These defects may be chemical impurities accidentally incorporated into the lattice, lattice imperfections (vacancies or interstitials), or combinations of these two species. The concentration of such imperfections must be less than about 10^{13}/cc in solar cells that attain 10 percent conversion efficiency.

The origin of these lifetime controlling impurities is not known at this time. Such small concentrations of imperfections could be incorporated as "satellites" of the donors or acceptor impurities required to set the conductivity at the desired level. For example, if the base crystal contains 10^{15}/cc donors, then if the material used to dope the silicon contained a fraction 10^{-2} of an impurity capable of introducing deep states, the satellite impurity concentration would be 10^{13}/cc. Reduction of the concentration of impurities giving rise to deep levels may therefore require higher purity dopants. The diffusion process used to produce the *p–n* junction in silicon PV cells results in donor or acceptor impurity concentrations of 10^{20}/cc, near the surface. After the diffusion process, the lifetime in the surface-diffused region is of the order of 10^{-7} sec, which indicates that there is a very high concentration of imperfections in this region. These imperfections could be satellite impurities carried into the silicon by the dopant used to form the junction.

B. MINORITY CARRIER LIFETIME

The minority carrier lifetime of importance to solar cells is an effective lifetime τ_{eff}. It is a function of both the surface lifetime τ_{surface} and the bulk lifetime τ_{bulk} according to the relation

$$1/\tau_{\text{eff}} = (1/\tau_{\text{bulk}}) + (1/\tau_{\text{surface}}).$$

The recombination centers discussed above control τ bulk; recombination centers on the surface determine τ surface.

It is not always possible to define a carrier lifetime in a semiconductor. If a concentration of free carriers in excess of the equilibrium concentration is produced in the semiconductor by absorption of light, a lifetime can be assigned to the excess carrier populations Δn and Δp only if the relation between generation rate g and Δn and Δp is of the form

$$\Delta n = g\tau_n ; \ \Delta p = g\tau_p .$$

It is only after analysis of a concrete model that the applicability of the carrier lifetime concept to a given semiconductor becomes apparent.

Experience has shown that bulk recombination in solar-cell quality silicon is indirect and that a lifetime can be defined for both low and high injection levels. The injection level is low if the excess carrier populations are small compared with the majority carrier population. (For *n*-type material, this means that $\Delta n, \Delta p << n_o$.) The injection level is high if the excess carrier population is large compared with the majority carrier population. In the case of silicon solar cells at room temperature, illumination at air mass zero intensities is equivalent to a low injection level. If the cells were cooled to, say, 78 K and concentrators were used to increase the illumination intensity, the injection level would be high. Low and high injection level lifetimes are not equal.

Since the report is devoted to the question of higher efficiencies from solar cells at room temperature and under air mass zero illumination, we shall limit the discussion to low injection level lifetime. A model appropriate to this situation has been analyzed by Hall[6] and by Shockley and Read.[7] They treated the case of recombination via a single level in the conduction band. The recombination center was characterized by a capture cross section for minority electrons σ_{cn} and for minority holes σ_{cp} and by an energy E_r within the conduction band. For the case of low injection level, these authors deduced the following expression for bulk lifetime:

$$\tau = \tau_{po} \, [(n_1 + n_o)/(n_o + p_o)] \; + \; \tau_{no} \; [(p_1 + p_o)/(n_o + p_o)] .$$

Here

$$1/\tau_{po} = N_t \, \sigma_{cp} v;$$

$$1/\tau_{no} = N_t \, \sigma_{cn} v;$$

$$n_1 = N_c \exp \left[\frac{-(E_c - E_r)}{kT} \right];$$

$$n_o = N_c \exp \left[\frac{-(E_c - E_F)}{kT} \right];$$

$$p_o = N_v \exp \left[\frac{-(E_F - E_V)}{kT} \right];$$

where N_c and N_v are the effective densities of states in the condition and valence bands, respectively; E_c and E_v are the energies of the edges of the conduction and valence bands, respectively.

Approximate forms for these relations can be derived for specific conditions. For example in an *n*-type material with the recombination center energy in the upper half of the forbidden gap,

$$\tau = \tau_{po} \left\{ 1 + \frac{N_c}{n_o} \exp \left[\frac{-(E_c - E_r)}{kT} \right] \right\}.$$

If $n_o >> n_1$, i.e., heavily doped material,

$$\tau = \tau_{po \cdot l}$$

If $n_o << n_1$,

$$\tau = \tau_{po} \frac{N_c}{n_o} \exp \left[\frac{-(E_c - E_r)}{kT} \right].$$

Figure 3 represents τ versus n_o in *n*-type material for two values of E_r and two values of τ_{po}. The figure also includes two sets of experi-

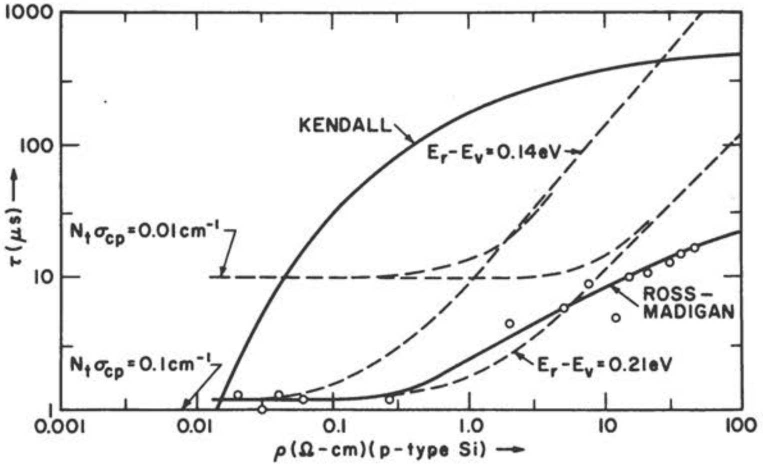

FIGURE 3 ln τ plotted as a function of resistivity in *p*-type Si. The dashed lines are computed on the basis of the Hall-Shockley-Read model. Two values of τ_{po} and two values of $E_r - E_v$ are shown. Solid lines represent the experimental data of Ross and Madigan[8] and Kendall.[9]

mental data on minority carrier lifetime measured in grown silicon ingots for a wide range of donor concentrations. The first set was reported in 1957 by Ross and Madigan[8]; the second set was reported in December 1969 by Kendall.[9] Neither set of data seems to fit the curves generated on the basis of the Hall-Shockley-Read recombination model. The 1957 data resemble the theoretical curves for low-resistivity material. The resistivity dependence of the 1969 data bears little resemblance to the calculated curves. However, over the range of resistivities between 0.1 and 100-Ω-cm, the 1969 data show an improvement of lifetime over the 1957 values by a factor between 30 and 100. The 1969 data do not saturate in low-resistivity materials, as the model predicts.

According to the 1957 data, τ_{po} had a value of about 1 μsec, which corresponds to a value of 0.1 for the $N_t\sigma_{cp}$ product. If σ_{cp} were assigned the reasonable value of 10^{-14} cm^2, this would mean that in the heavily doped material available to Ross and Madigan in 1957, the concentration of recombination centers was about 10^{13}/cc. It would seem therefore that if N_t were reduced by an order of magnitude in the Ross and Madigan low-resistivity material, the lifetime τ_{bulk} would have been increased to about 10 μsec. The increased lifetime shown by the 1969 data indicates a considerable reduction in recombination center concentration, but this apparent decrease is not reflected in the low-resistivity material. This demonstrates the poor state of our knowledge of bulk recombination processes in silicon. In particular, the origin and nature of the recombination centers in the purest silicon available is unknown, and, therefore, upper limits on τ_{po} and τ_{no} are not known.

The surface lifetime τ_{surface} plays a dominant role in controlling τ_{eff} of the diffused skin region of the cell. For a slab of plane-parallel geometry that has the same lifetime on both its faces

$$1/\tau_{\text{surf}} = 2s/W,$$

where s is the surface recombination velocity and W is the thickness of the slab. In treatments of surface effects on the properties of semiconductor devices, the concept of surface recombination velocity s is preferred over that of surface lifetime. The measured values of s for silicon surfaces prepared in various ways range from about 100 cm/sec for carefully etched surfaces to values in excess of 10^7 cm/sec on sandblasted surfaces. Analysis of spectral response curves of commercial silicon cells has shown that in such cells s has a value between

10^5 and 10^6 cm/sec. Such high values probably result from the diffusion process used to make silicon cells. After diffusion, the concentration of diffusant atoms at the surface is of the order of 10^{20}/cc and the defect concentration is very high. Reduction of s would probably require removal of this most heavily doped region.

Systematic studies of surface recombination velocity on heavily doped silicon have not been described in the literature. It is important for solar-cell technology to establish whether values as low as 100 cm/sec on material with resistivities between 0.01 and 0.1-Ω-cm can be achieved on silicon surfaces.

V. A Simple Equivalent Circuit of a *p–n* Junction Photovoltaic Cell[1]

In the preceding sections, the basic processes underlying the photovoltaic effect have been discussed. In the remaining sections of this chapter, the relation between these phenomena and the electrical characteristics of photovoltaic solar cells will be reviewed. A first requirement is an equivalent circuit for the solar cell. The treatment is limited to the *p–n* junction cell.

An unilluminated *p–n* junction has a current-voltage characteristic of the following form:

$$i_j = i_o\,(e^{\Lambda V}-1),$$

where i_j is the current flowing in the junction, i_o is the reverse saturation current, and V is the voltage across the junction. Illumination of the junction results in the generation of a current i_{sc}. If a resistive load is connected across the illuminated junction, the current through the load i_L would be

$$i_L = i_o\,(e^{\Lambda V}-1) - i_{sc}.$$

Figure 4 shows the *i–V* curves of an unilluminated and illuminated photovoltaic cell, and Figure 5 is an equivalent circuit for the illuminated cell. Reflection on the physical structure suggests that the equivalent circuit should include two resistances representing internal loss mechanisms, one in series with the load resistor, the other shunting the junction. The circuit model modified to include these resistances is shown in Figure 6. The relation between load current and load voltage then has the form

$$i_L - [(V_L - i_L R_s)/R_{sh}] = i_o\left\{\exp\,[\Lambda(V_L - i_L R_s)] - 1\right\}.$$

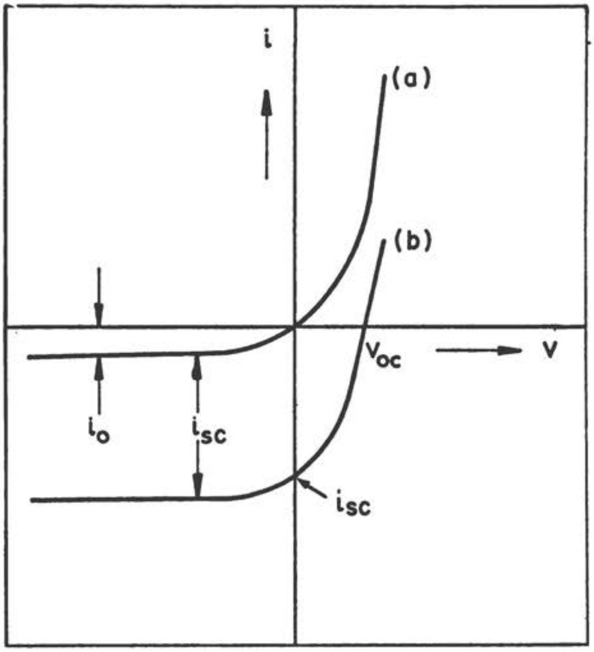

FIGURE 4 Current-voltage curves of a *p–n* junction photovoltaic cell in the dark (a) and under illumination (b). The short-circuit current i_{sc} and open-circuit voltage V_{oc} are indicated.

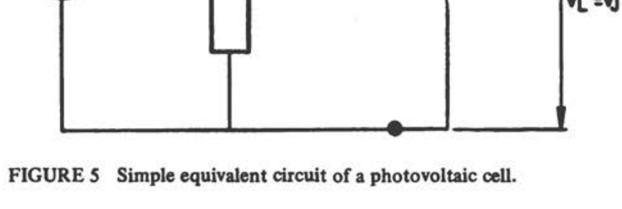

FIGURE 5 Simple equivalent circuit of a photovoltaic cell.

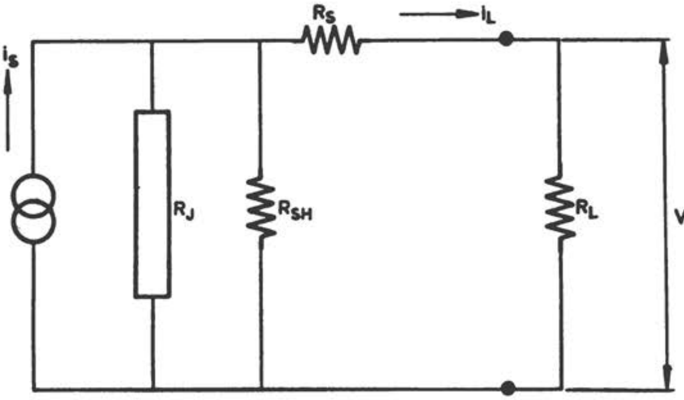

FIGURE 6 Equivalent circuit of a photovoltaic cell including internal series and shunt resistance.

In "good" photovoltaic cells, the internal shunt resistance is so large that its effect is negligible. On the other hand, the internal series resistance cannot be neglected. An optimum cell design aims at minimizing R_s. However, for the present we shall neglect R_s since many features of the behavior of the photovoltaic cell are essentially independent of R_s.

According to the simple equivalent circuit (with $R_{sh} \rightarrow \infty$ and $R_s = 0$), maximum power is delivered to the load when the load resistance matches the dynamic impedance R_j of the diode. An expression for R_j can be derived from the i–V characteristic of the p–n junction. The result is

$$R_j = \partial V_j/\partial i_j = e^{-\Lambda V}/i_o\Lambda.$$

The condition for maximum power transfer has the form

$$R_{Lmp} = R_{jmp} = e^{-\Lambda V_{mp}}/i_o\Lambda,$$

where the subscript *mp* denotes maximum power transfer conditions. The load resistor satisfies Ohm's law, i.e.,

$$i_{Lmp} R_{Lmp} = V_{mp}.$$

Substitution into the $i_L - V_L$ relation for an illuminated junction results in the relation

$$e^{\Lambda V_{mp}}(1 + \Lambda V_{mp}) = (i_s/i_o) + 1.$$

The open-circuit voltage V_{oc}, which is computed from the $i_L - V_L$ relation with $i_L = 0$, is given by the relation

$$e^{\Lambda V_{oc}} = (i_s/i_o) + 1.$$

Figure 7 is a plot of ΛV_{oc} and ΛV_{mp} as functions of $\ln i_{sc}/i_o$. It is

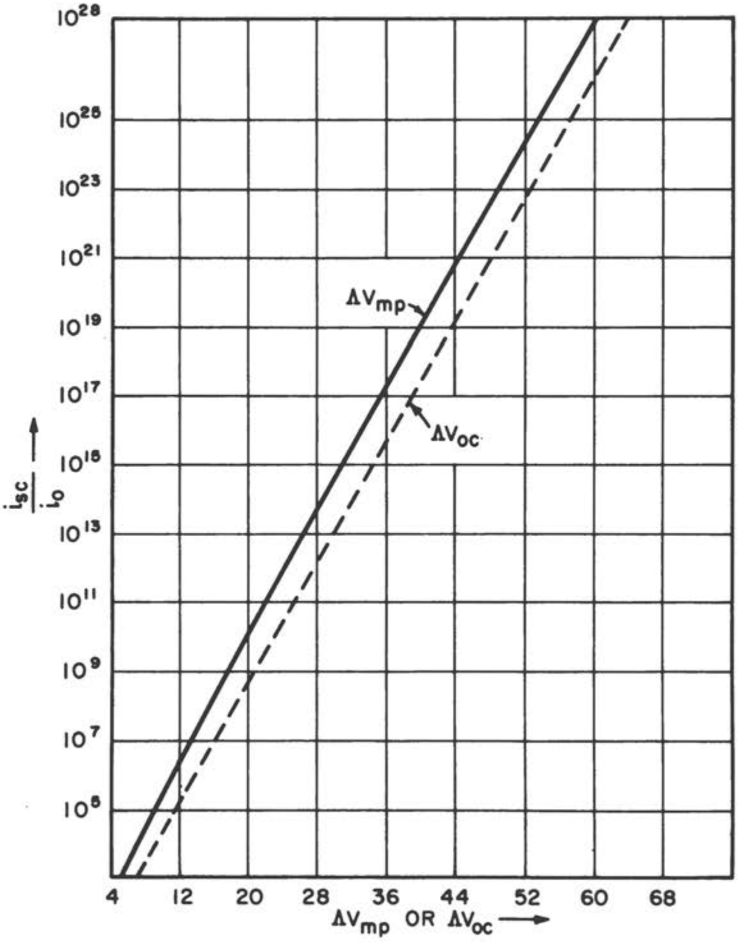

FIGURE 7 Logarithmic plot of i_{sc}/i_o versus ΛV_{oc} and ΛV_{mp}.

evident that V_{oc} and V_{mp} do not differ appreciably. For example, a commercial silicon cell exposed to air mass zero sunlight at 300 K develops $V_{oc} \sim 0.6$ V. The value of Λ that fits the data on such cells is ~ 20. Reference to Figure 7 shows that the value of i_{sc}/i_o that corresponds to this ΛV_{oc} product is about 10^5 and $V_{mp} \sim 0.8\, V_{oc}$.

The value of i_{Lmp} is found to be

$$i_{Lmp} = [\Lambda V_{mp}/(1 + \Lambda V_{mp})]\ (i_{sc} + i_o).$$

The maximum power delivered to this optimum load is

$$P_{\max} = \frac{\Lambda V_{mp}}{1 + \Lambda V_{mp}} \left(1 + \frac{i_o}{i_{sc}}\right) i_{sc} V_{mp}.$$

It was previously shown that $V_{mp} \sim 0.8\, V_{oc}$. For the example given above, $\Lambda V_{mp} \sim 9$, and therefore

$$P_{\max} \sim 0.7\, i_{sc}\, V_{oc}.$$

Since $i_{sc}\, V_{oc}$ is the power that would be delivered to the load if there were no losses, it is evident that a major portion of the power generated in a solar cell is delivered to the load.

In real photovoltaic cells one must take into account series and shunt resistance losses and changes in the i–V characteristics caused by departures from ideal junction behavior. For this reason concepts of voltage factor VF and curve factor CF have proven to be useful and convenient.

The voltage factor is defined by the relation

$$\mathrm{VF} = q V_{oc}/E_G,$$

where E_G is the energy gap of the semiconductor.

The curve factor is defined by the relation

$$\mathrm{CF} = i_{mp} V_{mp}/i_{sc} V_{oc}.$$

In terms of CF and VF, $P_{\max}$ is given by

$$P_{\max} = [(\mathrm{CF})(\mathrm{VF})\, i_{sc} E_G]/q.$$

The maximum efficiency is defined as follows:

$$\eta_{\max} = P_{\max}/P_{in}.$$

These phenomenological relations which describe the operation of a photovoltaic cell contain three parameters characteristic of the junction, namely, i_{sc}, i_o, and Λ. These parameters are in turn related to material parameters, like resistivity, bulk lifetime, and surface recombination velocity as well as junction dimensions and configuration.

VI. Calculation of i_{sc}

The short-circuit current flowing in an illuminated photovoltaic cell is determined by the following integral:

$$i_{sc} = \int_0^{\infty} Q(h\nu) N_{\text{ph}}(h\nu)\,\mathrm{d}(h\nu),$$

where $Q(h\nu)$ is the "collection efficiency" for photons of energy $h\nu$; $N_{\text{ph}}(h\nu)$ is the flux of photons with energies in the interval $h\nu$ to $h(\nu + \mathrm{d}\nu)$.

The collection efficiency $Q(h\nu)$ is the ratio of the number of carriers contributed to i_{sc} by photons of energy $h\nu$ to the number of such photons incident on the surface; Q is a function of the absorption constant a, of the surface recombination velocity s, and of the geometry of the junction. The dependence of Q on these various parameters has been studied by a number of authors in papers dealing with the spectral response of photovoltaic cells.

The dependence of $N_{\text{ph}}(h\nu)$ on $h\nu$ should be that appropriate in air mass zero. The commonly accepted form of this curve is that given by Johnson[10] and is reproduced in Figure 8.

As an indication of the maximum current that can be expected, Figure 9 shows how I_s depends on the forbidden energy gap E_G of the semiconductor under the assumption that $Q(h\nu) = 0$ if $h\nu = E_G$ and $Q(h\nu) = 1$ if $h\nu \geqslant E_G$.[11] The larger the energy gap, the smaller is the value of i_{sc}.

VII. Expressions for I_o and Λ

In general, the $i_j - V_j$ characteristic of a p–n junction can be written in the form

$$i_j = \sum_m i_{om} (e^{\Lambda_m V_j} - 1).$$

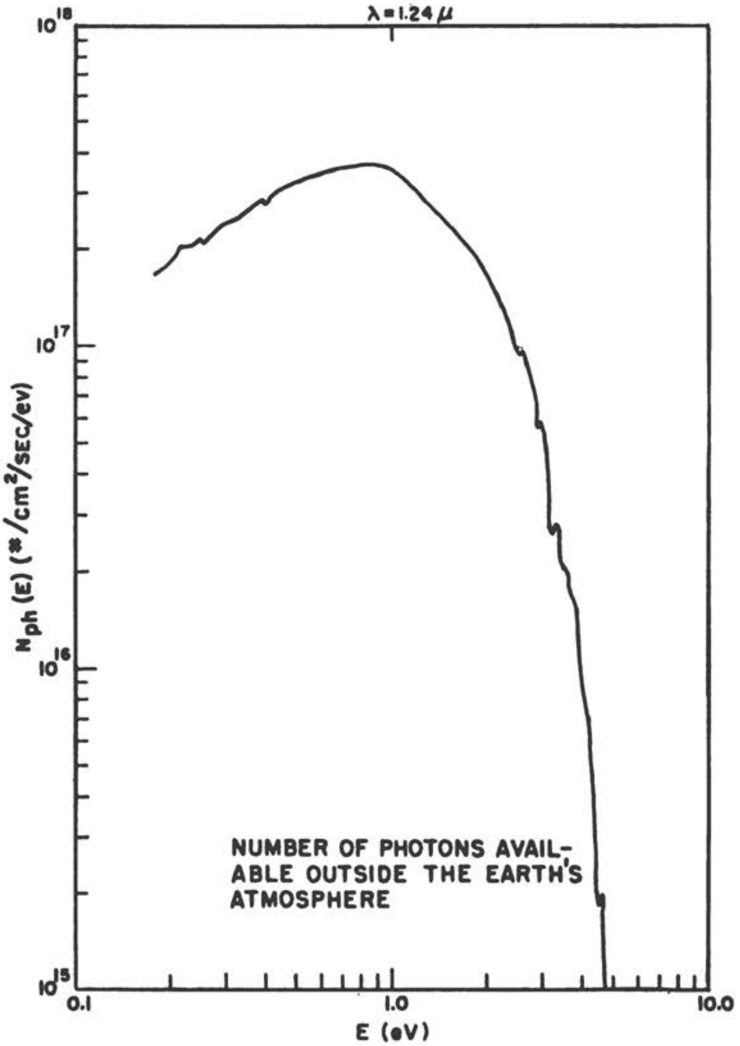

FIGURE 8 Photon flux N_{ph} versus photon energy $h\nu$ for outer-space sunlight, normal incidence.

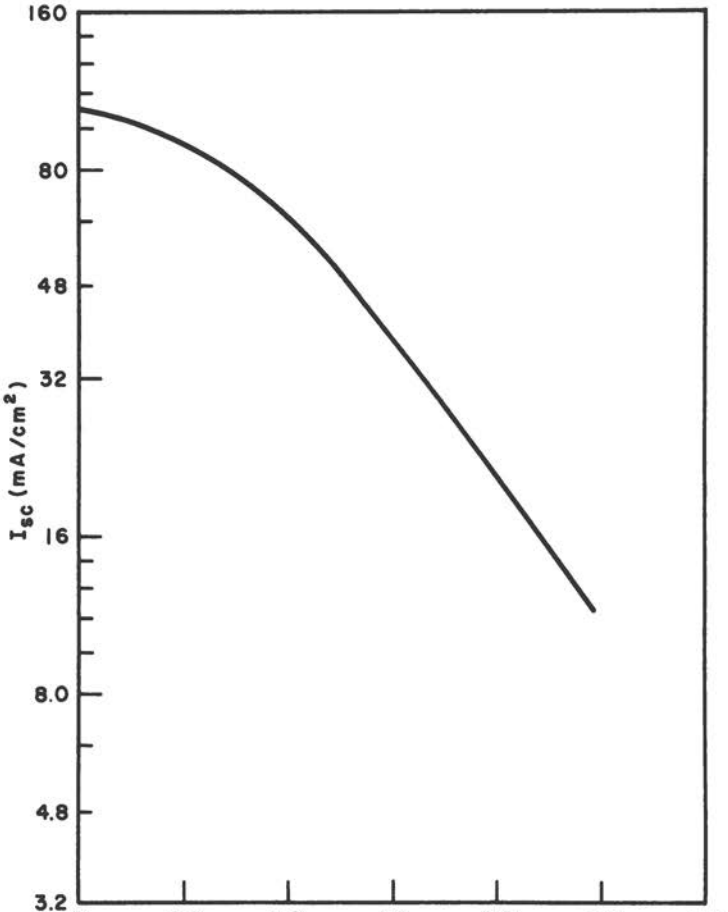

FIGURE 9 Calculated maximum values of i_{sc} versus semiconductor energy gap for air mass zero solar illumination. The assumption is made that $Q(h\nu) = 0$ for $h\nu < E_G$ and $Q(h\nu) = 1$ for $h\nu > E_G$.

Here it is assumed that there are a number of separate physical processes that can affect the i_j–V_j relationship; i_{om} is the reverse saturation current contributed by the process, and $\Lambda_m = q/A_m\, kT$ is a factor associated with the mth process. There are two principal mechanisms that we shall consider.

(a) The first is based on the ideal diode, Shockley model.[3] A crucial assumption is that minority carriers are not generated or recombined in the space-charge region. Analysis leads to the equation

$$i_{j1} = i_{o1}\,(e^{qV/kT} - 1),$$

where

$$i_{o1} = qn_i^2\left[\frac{1}{N_A}\left(\frac{D_n}{\tau_n}\right)^{1/2} + \frac{1}{N_D}\left(\frac{D_p}{\tau_p}\right)^{1/2}\right],$$

$$n_i^2 = N_c N_V \exp(-E_G/kT).$$

Here D_n and D_p are the diffusion constants of minority electrons and holes, respectively; τ_n and τ_p are the minority carrier lifetimes of electrons and holes, respectively; N_c and N_V are the effective densities of states in the conduction and valence bands, respectively. Note that $A_1 = 1$. According to these equations, i_{o1} is a strong function of both E_G and T. This dependence can be shown more clearly by writing i_{o1} in the form

$$i_{o1} = C(T)\exp(-E_G/kT).$$

Carefully made germanium junctions behave as predicted by these relations, but it is only an exceptional, small-area silicon junction that exhibits ideal diode behavior. In fact, no semiconductor with energy gap in excess of 1.0 eV has been reported to behave consistently as predicted by the ideal diode model. Departures from "ideal" behavior consist of a weaker dependence of i_o on energy gap, i.e.,

$$i_o = C(T)\exp(-E_G/BkT),$$

where $B > 1$. In these cases, it is also found the $A > 1$, so that

$$i_j = C(T) \exp(-E_G/BkT)\,[\exp(qV_j/AkT) - 1].$$

(b) A theory that can explain this type of behavior is based on the assumption that minority carriers can be generated and can recombine in the space-charge region. Analysis of this model by Sah *et al.*,[12] resulted in the following expression for i_{j2}:

$$i_{j2} = C_2(t) \exp(-E_G/2kT)\,[\exp(qV/2kT) - 1].$$

VIII. Maximum Efficiency as a Function of E_G[1]

Both i_{sc} and i_o are strong functions of energy gap. This means that V_{mp}, i_{mp}, $P_{\max}$, and the maximum efficiency are also strong functions of E_G. Figure 10 shows the result of calculations of $\eta_{\max}$, where the value of i_{sc} was calculated from the Johnson air mass zero data, i.e.,

$$i_{sc} = q \int_{E_G}^{\infty} N_{\mathrm{ph}}(h\nu)\mathrm{d}(h\nu).$$

Two forms for the relation between i_o and E_G were used. Curve a is based on the assumption that the junction obeys the ideal diode equation, and curve b is for the case $A = B = 2$. In the calculation, all the other semiconductor parameters (μ, τ, σ) were assigned values similar to those observed in silicon. The results show that based on the models we have used, the highest value of $\eta_{\max}$ is about 24 percent, and this occurs for a semiconductor of 1.5-eV bandgap whose i_j–V_j curve is in accord with the ideal diode model. If $A = B = 2$, the highest $\eta_{\max}$ would be about 17 percent. From the curve it is clear that silicon cells with $A = B = 1$ would have $\eta_{\max} \sim 19$ percent; and even with $A = B = 2$, $\eta_{\max}$ should be about 16 percent in silicon. Both these values are substantially higher than the 11 percent efficiency commonly observed in silicon cells.

It should be emphasized here that these calculations are based on present-day silicon materials parameters. Thus the efficiency shown in Figure 10 of 19 percent is lower than the value of 20 percent discussed on page 5 in the first chapter of the report. The 20 percent figure is based on materials parameters that *should be attainable* in silicon.

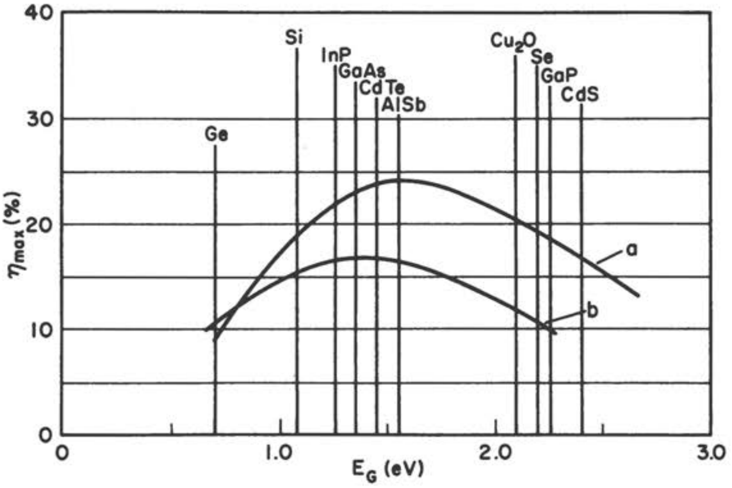

FIGURE 10 Theoretical values of maximum solar energy conversion efficiency η_{max} versus semiconductor energy gap E_G, normal incidence. Curve a, ideal diode model ($A = B = 1$); curve b, nonideal behavior ($A = B = 2$). The vertical lines are drawn at values of E_G appropriate to the indicated semiconductors.

IX. Summary

The physical processes underlying solar-energy conversion through the photovoltaic effect have been examined. The important roles played by bulk and surface recombination have been discussed. The relation between the basic material parameters and the current-voltage characteristics of solar cells were reviewed. The maximum efficiencies for solar-energy conversion that can be expected for a number of semiconductors exceed the best values ever reported for any solar cell by a factor of at least 2. In the case of silicon, there is a considerable gap between the currently encountered 11 percent conversion efficiency and the 16 to 20 percent values predicted by analysis of the photovoltaic effect for that material.

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CHAPTER

3 Theoretical Efficiency Considerations for Photovoltaic Energy Converters

HANS J. QUEISSER

I. Introduction

Here we review the problem of the maximum efficiency of a solar-energy converter that can be predicted by first principles and practical efficiency limits that seem reasonable within the state of the art. *p–n* junctions in inorganic semiconductors are emphasized. We first review the thermodynamic limit and proceed to principal restrictions in approaching this limit. Practical improvements beyond today's technology seem possible, especially for silicon, if our knowledge about hole–electron recombination is increased; this topic is discussed in the following two chapters. Brief comments on a variety of proposals for efficiency increase are compiled in the concluding section of this chapter.

II. Theoretical Limit

The problem of converting solar energy into electrical energy can be treated by basic thermodynamic principles. This was done by Müser,[1] Rose,[2] and Shockley and Queisser.[3] The results of the latter study are summarized in their Figure 6. The best efficiency calculated there for a *p–n* junction cell is about 26 percent for the following assumptions: (1) The sun is a blackbody of 6000 K, (2) the sun subtends a proper solid angle and yields 100 mW/cm^2 incident power, (3) the load is matched, (4) the cell absorbs 90 percent of the incident photons above $h\nu = E_g$, (5) the cell is kept at 300 K, (6) the energy gap E_g is approximately 1.2 eV for the semiconductor comprising the *p–n* junction cell, and finally (7) the only recombination mechanism for hole–electron pairs is that one resulting in photon emission (i.e., radiative recombination).

Of all these assumptions, (7) is by far the most stringent one. As demonstrated in Reference 3 and shown in their Figure 7, the recombination mechanisms completely determine the current-voltage relation of the junction. The restriction to radiative recombinations yields the lowest possible so-called "saturation current." This statement is equivalent to saying that for a given illumination one obtains the maximum open-circuit voltage. All other assumptions are much more realistic than (7). Thus Shockley and Queisser[3] introduced a factor, $f_c < 1$, which gives the ratio of the radiative recombinations to the total (= radiative + nonradiative) recombinations. The best present cells are described by $f_c < 10^{-6}$. This means that most of the recombination does not reversibly return photons but irreversibly leads to heat in the lattice. As a consequence the attainable open-circuit voltage is seriously reduced from its maximum value.

The foregoing considerations are based on a very general idea, the "principle of detailed balance." The theory realistically acknowledges that all photons below the energy gap are not utilized and those above always give a pair at gap energy even though the photon energy may have been higher. It is therefore concluded that the area of improvement lies in upgrading f_c, i.e., reducing the nonradiative recombination rate. Such improvement seems possible because our knowledge of the microscropic mechanism for recombination is poor and they are only substituted by numbers of empirical parameters, such as lifetimes or capture coefficients.

The *p–n* junction with a current-voltage relation of the form

$$I(V) = \text{const} \cdot \exp(qV/kT) - 1 \tag{1}$$

is known[4] to be the ideal rectifier; all other $I(V)$ characteristics are inferior in rectification.

Thus Eq. (1) probably presents an idealized limit for an energy conversion device, too. In particular, a *p–n* junction with generation-recombination in the space-charge layer, having[5]

$$I(V) = \text{const} \cdot \exp(qV/AkT) - 1 \tag{2}$$

with $A > 1$ is inferior to Eq. (1).

It seems that silicon solar cells come closest to this ideal at the present time but still have severe shortcomings. We now discuss these shortcomings as well as the practical reductions of this ideal efficiency.

III. Unattainability of Ideal Limit

We have seen that the assumption 7 of having only radiative recombination ($f_c = 1$) is least fulfilled by silicon solar cells. It seems that no real system can attain $f_c = 1$.

Consider the nature of a system with $f_c \rightarrow 1$. Such a system presents an ideal photon storage. Detailed balance ensures that all photon energies are preserved. There are no nonlinear or anharmonic interactions leading to energy losses. The full frequency bandwidth is maintained. For a semiconductor with $f_c = 1$ we permit losses for all photons having $h\nu > E_g$, leading to a frequency down-conversion but to an otherwise perfect storage of energy in the form of $h\nu = E_g$ excitations only.

The transport of the photon-induced energy, however, is difficult to achieve in such a system. Consider a very dilute gas, such as interstellar hydrogen, with little interaction between particles. Such a system approaches $f_c \rightarrow 1$ if we prohibit Auger transitions and all transitions transferring energy from excited electronic states to vibrational or rotational energy. This model shows that the lack of interaction forbids energy transport into another system. A crystal, however, provides a strongly coupled system permitting a nonuniform structure such as a *p–n* junction to exist with the possibility to separate hole–electron pairs, but at the expense of nonradiative transitions because of electron–lattice interactions.

Molecular crystals, especially organic compounds, show less coupling, thus, probably *a priori*, a higher value of f_c. Table 1 gives a comparison between these crystals and silicon as a representative of the inorganic semiconductors. The Table stresses the differences more than the common features of the two types of solids. In particular, it clearly shows the disadvantages of the loosely coupled system: poor transport of excitation energy, high effective masses equivalent to low carrier mobilities and narrow bands, and sharper absorption bands leading to less efficient intake of radiation. All these points speak against organic semiconductors. The hitherto disappointing experimental results essentially confirm our analysis.

The situation is analogous to the mechanics problem of transferring the potential energy of a lifted body to a distant place: part of the

TABLE 1 Comparison between Crystals with Strong and Loose Coupling for Energy Conversion

Typical Molecular Crystal (Anthracene)	Typical Semiconductor (Silicon)
Weaker electron coupling, stronger electron–photon coupling	Stronger electron–lattice coupling, weaker electron–phonon coupling
Weak coupling → narrow bands, large effective masses	Strong coupling → broad bands, small masses
Photon causes localized excitation absorption: relatively narrow bands (undesirable)	Photon causes crystal-cooperative excitation absorption: continuum above E_q (desirable)
Large masses: low mobility, deep traps (very undesirable) → low current $I \to 0$	Small masses: higher mobility, shallower traps (desirable) → very high current $I \to I_{\max}$
Lifetime limited by radiative recombination (very desirable $f_c \to 1$ → very high open-circuit voltage $V_{op} \to E_g$	Lifetime limited by nonradiative recombination (very undesirable) $f_c < 1$ → reduced open-circuit voltage $V_{op} < E_g$
Losses by re-emission (luminescence efficiency high)	Losses by degradation to heat (luminescence efficiency very low)
Extreme limit: ideal light storage, each photon stored voltage output current → 0	Extreme limit: ideal counter, each photon converted to a low-energy electron at energy → 0
Compromise to improve bad energy transfer: close coupling to other system at less energy (photosynthesis, photography)	Compromise to improve low output voltage: higher doping levels increasing built-in voltage at the expense of mobilities?

potential must be sacrified to overcome the limits in energy transport (friction, in the mechanics analogue). The compromise in organic systems could be achieved by coupling system with successively lower excitation energies, leading to energy transport while degrading the energy. This seems to be the case in photosynthesis and photography.

In an organic solar-energy converter portions of the inherently high open-circuit voltage (or contact potential) must be sacrificed to attain reasonable short-circuit currents. In the other extreme of a strongly coupled system, the current is close to optimum but the open-circuit voltages are much lower than the energy gap; this is obviously the situation of silicon solar cells. The ease of transporting the excitation energy through the crystal makes the nonradiative recombination channels very effective. We must now ask where the best compromise between these two cases lies. It seems that the silicon solar cells comes much closer to this compromise than all other systems at the present state of the art. It seems, however, that too much of the open-circuit voltage V_{op} is sacrificed at present due to the low value of f_c in silicon.

After this general discussion we now turn to a more specific description of solar-cell parameters, which are essential for efficiency improvement.

IV. Possible Improvements of Present Conversion Efficiencies

Here we list the causes for efficiency reductions and try to estimate improvement possibilities. A *p–n* junction structure appears superior to all other devices; therefore we discuss improvements toward an ideal *p–n* junction in silicon.

Silicon solar cells represent a good compromise for energy conversion. The gap energy E_g is almost ideal; mobilities for both electrons and holes are reasonable. Silicon *p–n* junction solar cells are at present the best solar-energy converters.

Improvement must be sought in the area of controlling nonradiative recombination. At present we do not know anything definitive about the very efficient nonradiative recombination. Impurity and/or defect levels in the middle of the forbidden gap, or surface states, may be responsible. Auger effects at neutral donors or acceptors may also be present but have not yet been identified (GaP is a much better understood semiconductor[6]). It is known that today's silicon contains large amounts of nondoping but lifetime-reducing impurities that do not vitally affect transistor performance and therefore have been ignored. Basic materials research with solar-cell applications in mind should be undertaken. Better materials control and process techniques would then lead to cells that tolerate higher doping, thus achieving higher output voltage yet still maintaining long enough lifetimes to keep essentially unity collection efficiency. The *p–n* junction space-charge layer width would be smaller to reduce the number of remaining recombination centers and yet maintain a good reverse characteristic. The quality of these junctions would be apparent by *A*-values tending toward 1 even at low voltages and a low reverse saturation current coming closer to the predictions of theory.

Notice that it is not sufficient to have the minority carrier lifetimes long enough to yield diffusion length greater than cell thickness. This merely ensures good collection efficiency but not optimal voltage output.

We now list some problems and techniques to be studied toward this end in a program of basic research:

(a) Better chemical analysis of nondoping foreign elements in silicon and their relation to lifetime and nonradiative recombination (examples: oxygen, carbon, complexes such as aluminum–oxygen).

(b) Clarification as to whether the doping elements directly or indirectly contribute to recombination channels (Auger effect at neutral dopants, precipitates, complexes with vacancies or dislocations). If, for example, the Auger effect at neutral dopants is effective, this would mean a principal restriction in conversion efficiency. Luminescence efficiency measurements should be useful here.

(c) Process technology for obtaining uniform large-area *p–n* junctions that maintain high crystalline purity and perfection is necessary. Low-temperature processes must be investigated in particular; these techniques (such as liquid phase epitaxy) have proved useful in III–V compounds.

Inherent defects such as vacancies must be investigated for their recombination cross sections; if there are appreciable ways of annealing these defects out to external or internal surfaces, it must be determined which yield the lowest permissible concentration of these inherent defects.

(d) Surface recombination must be controlled and counteracted by drift fields where possible.

At the present time there is no proof that the *practical* limit of conversion efficiency is not 20 percent or higher. Calculations using realistic obtainable parameters should make a 20 percent cell feasible for silicon. These estimates do not violate any principal limitations or conditions and seem reasonable in view of our present knowledge.

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CHAPTER

4 The Fundamentals of Improved Silicon Solar-Cell Performance

MARTIN J. WOLF

I. Introduction

The loss mechanisms in present silicon solar cells have been reexamined and their impact on conversion efficiency in air mass zero and air mass one sunlight analyzed. Attention has been focused on the process-dependent losses that affect collection efficiency, voltage factor, and curve factor. The collection efficiency can be improved by 22 percent by reducing the surface recombination velocity for short-wavelength collection efficiency improvement and by increasing the minority carrier lifetime in thin cells to be combined with a drift field at the back contact for better collection in the long-wavelength range. Voltage factor and curve factor together can yield 56 percent efficiency improvement through reduction of base region resistivity, while maintaining the minority carrier lifetime near present values. Accomplishment of these changes should yield conversion efficiency values near 20 percent in air mass zero sunlight.

Past calculations of theoretical or limit conversion efficiencies were based on a mixture of basic physical principles and experience values of semiconductor material properties. These material data were not derived from known physical limitations but were considered realistic assumptions or extrapolations at the time the calculations were made.

In a different type of approach, ideal conversion efficiencies were arrived at through thermodynamically based theories. The authors using this approach[9-12] agree in introducing radiative recombination into the calculations as a basic physical phenomenon. However, in all known semiconductors, nonradiative recombination introduces additional losses and has therefore, in the mentioned "semiempirical" theories, been considered an unavoidable fact.

II. Analysis of the Power Losses in Present Silicon Solar Cells

To evaluate potential improvement of the silicon solar cell, it is necessary to separate the loss processes into two groups: those that can be influenced by changes in material selection or device fabrication parameters and those that are unalterably determined by basic physical principles. It is further necessary to determine the magnitude of power loss caused by each of these processes and to concentrate improvement efforts on the most effective loss mechanisms.

An accounting of the magnitudes of the various loss processes is shown in Figure 1 in the form of a bar chart for two types of commercial cell, one operating in air mass one, the other in air mass zero sunlight. The bar chart was originally prepared[13] for 1-Ω-cm *p*–on–*n* cells exposed to air mass one sunlight. The two columns of figures on the right side of the bar designate the magnitude of each individual loss factor, while those on the left give the percentage of energy left after application of each of the loss factors.

The two upper blocks in the bar diagram designate the energy loss due to long wavelength photons with insufficient energy for absorption in silicon and energy loss due to the excess energy of the remaining photons, which exceeds the energy gap and can therefore not be utilized in the conversion process. The percentages given relate to the total energy flux in the received sunlight, and the small quantitative differences in the first two blocks are due to the different spectral distributions of the two types of sunlight used. These first two blocks represent basic physical processes that cannot be reduced once the semiconductor is selected. The energy remaining after accounting for these two loss processes is, for silicon, 44 percent for the air mass one spectrum and 43.5 percent for the air mass zero spectrum. The large amount of energy represented by these two blocks cannot be utilized except by methods external to the individual photovoltaic element.

The next four blocks are at least partially determined by material properties and process technology. The largest of these blocks designates the "voltage factor," i.e., the factor by which the open-circuit voltage is smaller than the energy gap. This factor is seen to differ considerably between the two right-hand columns of Figure 1. The main cause of this difference is found in the different base resistivities

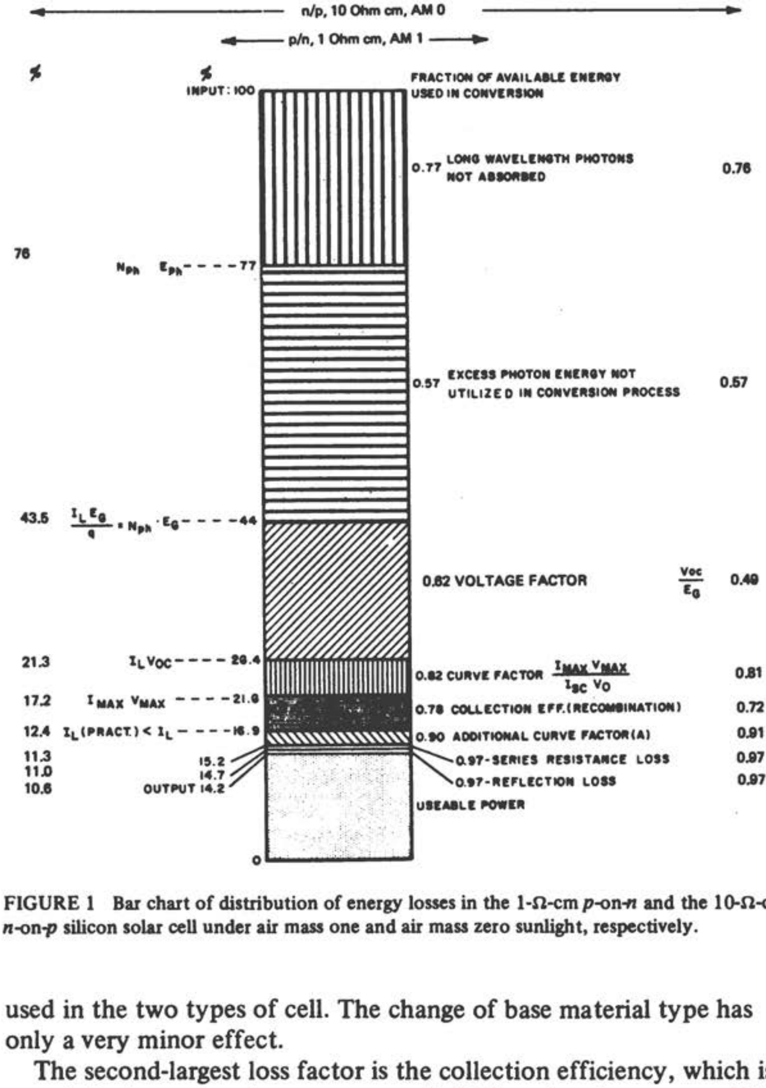


FIGURE 1 Bar chart of distribution of energy losses in the 1-Ω-cm *p*-on-*n* and the 10-Ω-cm *n*-on-*p* silicon solar cell under air mass one and air mass zero sunlight, respectively.

used in the two types of cell. The change of base material type has only a very minor effect.

The second-largest loss factor is the collection efficiency, which is seen to be lower for air mass zero sunlight than for air mass one. This difference in collection efficiency is caused by the larger content of short- and long-wavelength photons in the air mass zero spectrum. Since the collection efficiency is not limited by a basic physical process, it could be set equal to one, at least in theory. This assumption has been made in all previous evaluations of the ideal efficiency of solar cells.

The third-largest loss factor is the "curve factor," which expresses the ratio of the maximum power available from the cell to the product of short-circuit current and open-circuit voltage. Although the curve factor can be influenced by material selection and process technology it has a physical limit, since the solar-cell current-voltage characteristic is always determined by the diode equation. This means that the solar-cell I–V characteristic has to be exponential, with the consequence that any rectangle inscribed under the curve must be smaller in area than an external rectangle.

The next factor is the "additional curve factor (A)," which has an effect on the conversion efficiency through a "softening" of the "knee" of the current-voltage characteristic beyond that caused by the "curve factor." This additional factor is determined by the dimensionless factor A in the exponent of the diode equation:

$$I_D = I_o\ [\exp(qV_D/AkT) - 1], \tag{1}$$

which forms the key element in the simplified solar-cell characteristic equation

$$I = I_D + (V/R_{sh}) - I_L, \tag{2}$$

with

$$V_D = V - IR_s. \tag{3}$$

V and I are the terminal voltage and current, V_D and I_D the voltage across and current through the p–n junction, and R_s and R_{sh} the ohmic series and shunt resistance effects. I_L is the light-generated current, T the device temperature (absolute), and q and k are the electronic charge and the Boltzmann constant, respectively.

The diffusion theory for the p–n junction characteristic[14] predicts a single exponential form of the type in Eq. (1), with $A = 1$. This gives rise to the previously discussed "curve factor." A more complicated characteristic is generally observed, however, which is frequently approximated by a characteristic according to Eq. (1), but with $A \gtrsim 2$ for practical silicon solar cells.

While the curve factor is known to be partially material- and process-determined, the additional curve factor (A), in the absence of any accepted physical theory explaining its origin, has to be considered wholly material- and process-dependent. As Figure 1 indicates, neither the different resistivities used in the two types of cell nor the differing input spectra cause significant differences in the magnitudes of these two loss factors.

Three additional types of loss are entirely process-dependent and are already reduced to the point where significant gains in conversion efficiency cannot be obtained by further efforts in these areas. These losses include the reflection loss, series resistance loss, and shunt resistances loss. The last of these has already been reduced to such an extent that it does not appear on the bar chart.

As a result of the losses discussed above, the useful power output of typical silicon solar cells is 10.6 percent of air mass zero sunlight input (140 mW cm^{-2}) with the 10-Ω-cm *n*-on-*p* cell and 12.2 percent of air mass one sunlight (100 mW cm^{-2}) with the 1-Ω-cm *p*-on-*n* cell. Possibilities for significant improvement in solar-cell conversion efficiency, resulting from this analysis, will be discussed in the following sections.

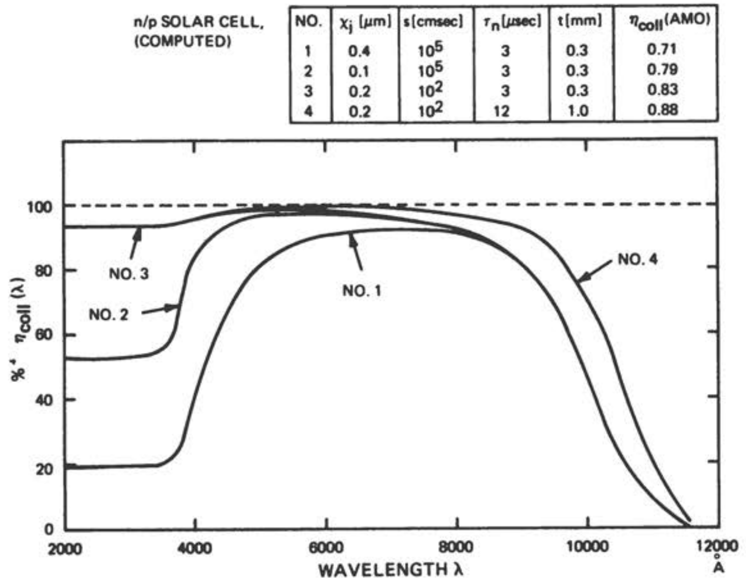
III. Potential Improvement of Collection Efficiency

The first of the material- and process-dependent parameters to be reinvestigated is the collection efficiency. This investigation is carried out by computation, using an exact solution of the transport equation[15] with the physical and material parameters of the device.[16,17]

Figure 2 illustrates the results of such calculations executed with various device parameters. Curve 1 of Figure 2 presents a collection efficiency versus wavelength curve that is characteristic of a typical, present-day *n*-on-*p* silicon cell of 1- to 3-Ω-cm base resistivity.[18] The base region minority carrier lifetime yielding this curve is 3 μsec, the junction depth 0.4 μm, and the wafer thickness 0.3 mm (0.012 in.). The surface recombination velocity (assumed to match the calculated spectral response curve with the measured data) is 10^5 cm sec^{-1}, and the diffused region minority carrier lifetime is 3 nsec. The resultant overall collection efficiency, weighted by the air mass zero sunlight spectrum up to 1.125-μm wavelength, is 0.71.

Both the shape of the collection efficiency versus wavelength curve and the total collection efficiency of 0.71 make it obvious that improvement is desired. Since the solar spectrum peaks in the short-wavelength part of the spectral response curve, increased collection efficiency in this part will be most effective.

Curve 3 of Figure 2 shows the collection efficiency of a cell with



NO.	x_j [μm]	s[cm/sec]	τ_n[μsec]	t[mm]	η_{coll}(AMO)
1	0.4	10^5	3	0.3	0.71
2	0.1	10^5	3	0.3	0.79
3	0.2	10^2	3	0.3	0.83
4	0.2	10^2	12	1.0	0.88

FIGURE 2 Calculated collection efficiency versus wavelength curves for the present silicon solar cell and for several cases of improvement.

0.2-μm junction depth, but with the surface recombination velocity reduced to 10^2 cm sec^{-1}. Curve 3 indicates that collection efficiency values above 0.98 can be achieved in the wavelength range of 0.45 to 0.6 μm. The overall collection efficiency, weighted by the air mass zero sunlight spectral distribution, has been increased to 0.83, or by 17 percent.

Since it would be hardly worthwhile to attempt further improvement in the short-wavelength range, the further investigation is focused next on the long wavelengths where base region minority carrier lifetime and wafer thickness form the limitations. Increasing the base region minority carrier lifetime by a reasonable amount, e.g., to 12 μsec, in addition to the above-mentioned changes in the diffused layer, yields curve 4 of Figure 2. The overall collection efficiency for this case is 0.875, for a total improvement of 23 percent.

It may be noted that increasing the wafer thickness without increasing the minority carrier lifetime in the base region was found to have only a negligible effect on the collection efficiency. In the converse, increasing the minority carrier lifetime to 20 μsec and simultaneously increasing the wafer thickness to 1 mm (0.040 in.) results in a collection efficiency of 0.89, another 2 percent increase in collection efficiency. Nearly the same result can be achieved without increasing the wafer thickness, but instead introducing a drift field (p^+ region) of approximately 2000 V cm^{-1} in the last 1.0 μm before the back contact. As a matter of fact, by this means, the wafer thickness can be reduced to 0.1 mm (0.004 in.), while maintaining a collection efficiency of 0.87 with a minority carrier lifetime of 12 μsec.

The question then arises: How realistic are the assumed material parameters? The first of these material parameters is the surface recombination velocity. While Shockley[14] published surface recombination velocity data for germanium, including 10^4 cm sec^{-1} for a sand-blasted surface, approximately 2×10^3 cm sec^{-1} for an etched surface, and 200 cm sec^{-1} for a specially treated surface, comparable values are not readily found in the literature for silicon. Rosier[19] lists surface recombination velocities of 6 to 7×10^3 cm sec^{-1} for surface state densities of 5×10^{11} cm^{-2} at silicon-to-silicon dioxide interfaces. Revesz and Zaininger[20] list a density of surface states of approximately 3×10^{11} cm^{-2}, achieved after a 6-h anneal following formation of the oxide on the silicon surface. As a result of the recent emphasis on low-threshold voltage MOS devices, considerable development effort has been spent toward the achievement of low surface state densities. Some of the methods presently used toward this goal are ultraclean techniques for applying the SiO_2, followed by proper annealing methods. The use of the (100) crystal orientation in the silicon wafers has been recommended for low surface state densities. It so happens that this orientation is the commonly used one for silicon solar-cell fabrication.

Another device that relies heavily on low surface recombination velocity for achievement of good short-wavelength response is the silicon target vidicon, developed during the last few years at Bell Telephone Laboratories and RCA Laboratories. The target for this vidicon tube is a close-spaced array of photodiodes on a silicon wafer. Besides good minority carrier lifetime, a low surface recombination velocity is imperative for good quantum efficiency of the device at short wavelengths, just as it is in the diffused region of the silicon solar cells. Use of a thin n^+ layer (under 1-μm thick) adjacent to the surface on which the light is incident has been credited with achieving this goal by providing effective surface recombination velocities which are estimated at about 10 cm sec^{-1}.

It would thus appear that methods for the production of low surface recombination velocities are now available as the result of modern silicon device development efforts. What is required for the solar-cell improvement program is a treatment that results in low surface recombination velocity and high minority carrier lifetime in the underlying semiconductor layer and that provides either high transmissivity in the surface layer or absorption by electron–hole pair generation only.

Considerations relative to the increase in base region minority carrier lifetime, as shown to be required for improved long-wavelength response, will be contained in the following section, which explains the possibilities for output-voltage improvement.

IV. Potential Improvement of Voltage Factor and Curve Factor

Both the voltage factor and the curve factor are more strongly influenced by the current-voltage characteristic of the *p–n* junction than by the collection efficiency. Therefore, this section will be concerned primarily with the effects of material parameters, which are also partly process-dependent, on the junction current-voltage characteristic.

The first subject to be investigated in this relation is the interpretation of experimental data. The use of the simplified solar-cell equation Eq. (2)] in attempts to fit the actually measured current-voltage characteristics to a single exponential form by assigning suitable I_o and A values has led to considerable confusion in the past. In particular, in trying to determine ideal conversion efficiencies, workers in the field were left in a quandary about assigning proper values for saturation current and A factor.

It has since been established[21] that, after elimination of the influence of series resistance, the *p–n* junction current-voltage characteristic is best described by two exponential terms (Figure 3). The high injection level region approaches an exponential characteristic with the factor A equal or near to 1 and the saturation current of a magnitude as predicted by the diffusion theory. It was also established that, upon changes in temperature, the factor A remained equal to 1, while the saturation current changed in magnitude according to the diffusion theory. It may be noted that A factors between 2 and 6 have been found for the exponential describing the lower injection region of the i–V characteristic, with saturation currents mostly in the 10^{-6} to 10^{-5} A cm^{-2} region.

Since this type of characteristic has been observed on many solar cells[22] as well as on gallium phosphide diodes,[23] it appears that the observed double exponential characteristic is a rather general phenomenon, although of yet unexplained origin.

As a result of these findings, the observed current-voltage charac-

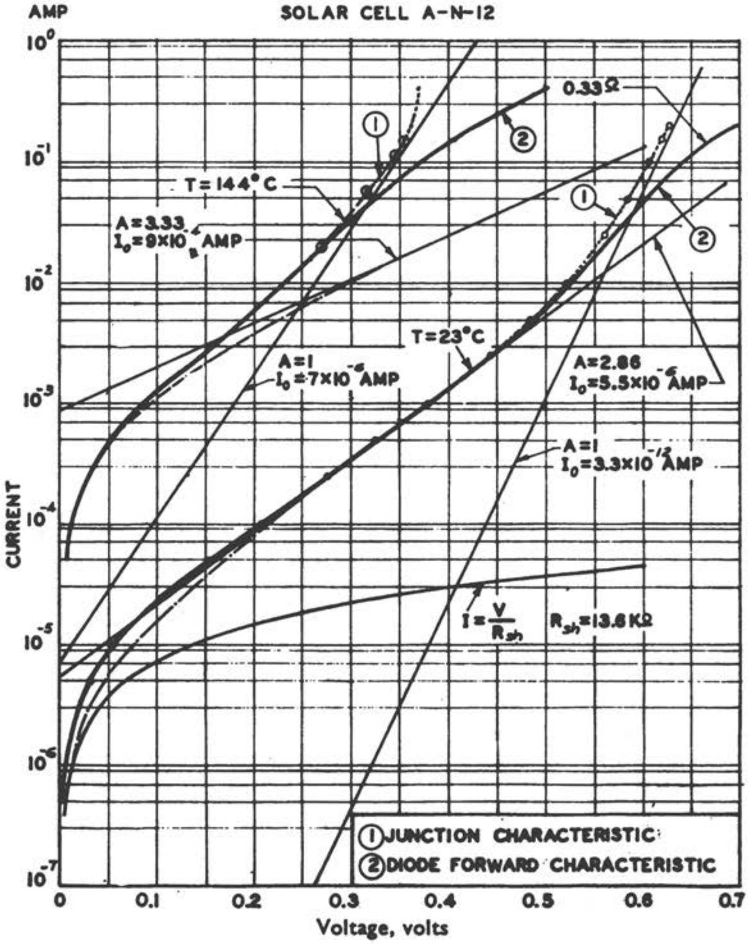


FIGURE 3 Current-voltage characteristic of *p–n* junction [from Figure 11, Wolf and Rauschenbach, Adv. Energy Conversion *3*, 455 (1963)].

teristics of silicon solar cells are best described by a model that contains two conduction mechanisms in parallel, each described by a type of diode equation. One of these obeys the diffusion theory, while the other contains a factor A, generally larger than 2, in the exponent and a saturation current about five orders of magnitude larger than described by the diffusion theory. The latter term dominates the i–V characteristic at low-junction voltages (below 0.4 V), while the diffusion theory term dominates the characteristic above 0.5 V. The maximum power point in normal silicon solar-cell operation falls into the transition region between the two mechanisms. Although no accepted physical explanation exists for the observed current-voltage characteristic at low voltage, it is gratifying to see a well-understood mechanism, described by the diffusion theory, applying in the region where the open-circuit voltage occurs. This fact is of great significance for the prediction of ideal and of realistic conversion efficiencies and for the investigation of methods for the improvement of solar-cell conversion efficiency.

On this basis then, it is appropriate to evaluate the voltage factor by use of the diffusion theory.

The open-circuit voltage is then described by the approximation

$$V_{oc} = (q/kT)\,[\ln (I_L/I_o)]\,, \tag{4}$$

which is practically perfect at I_L values as encountered in normal solar-cell operation.

The predominant term, aside from the light-generated current which is influenced by the collection efficiency, is the saturation current which from Shockley's diffusion theory of the p–n junction is given by

$$I_o = \sqrt{qkT}\, n_i^2 \left(\frac{1}{n_n} \sqrt{\frac{\mu_p}{\tau_p}} + \frac{1}{p_p} \sqrt{\frac{\mu_n}{\tau_n}} \right); \tag{5}$$

for silicon at room temperature, the term in front of the parenthesis equals 1.86. It is seen that the saturation current is dominated by the majority carrier concentrations n_n and p_p and the minority carrier lifetimes τ_p and τ_n in the regions on both sides of the p–n junction.

From Eq. (4) it is clear that small saturation currents are required for large open-circuit voltages. Thus high majority carrier concentrations on both sides of the p–n junction are desirable. However, both the minority carrier mobilities μ_p and μ_n and minority carrier lifetimes τ_p and τ_n included in Eq. (5) are functions of the majority car-

TABLE 1 *n-p*-Silicon Solar Cell, Air Mass Zero

Line	Resistivity, ρ (Ω-cm)	Majority Carrier Concentration, p (cm^{-3})	Minority Carrier Mobility, μ_n (cm^2 V^{-1} sec^{-1})	Minority Carrier Lifetime (Base), τ_n (sec)	Saturation Current Density, j_o (A cm^{-2})	Open-Circuit Voltage, V_{oc} (V)	Voltage Factor, VF	Curve Factor, CF
1	10	4.6×10^{14}	1350	1×10^{-5}	4.7×10^{-11}	0.533	0.48	0.81
2				2.5×10^{-5}	3.0×10^{-11}	0.549	0.50	0.816
3	1	5×10^{15}	1250	3×10^{-6}	7.6×10^{-12}	0.578	0.52	0.82
4				1.2×10^{-5}	3.8×10^{-12}	0.601	0.54	0.825
5	0.1	7.8×10^{16}	800	5×10^{-7}	9.5×10^{-13}	0.627	0.57	0.84
6				1×10^{-5}	2.2×10^{-13}	0.675	0.61	0.842
7	0.01	3.5×10^{18}	175	4×10^{-7}	1.1×10^{-14}	0.745	0.67	0.85
8				1×10^{-5}	2.4×10^{-15}	0.788	0.71	0.86
9	0.0015	5×10^{19}	80	4×10^{-6}	2.8×10^{-16}	0.843	0.76	0.868
10	0.00075	1×10^{20}	80	2×10^{-6}	2×10^{-16}	0.847	0.764	0.869

rier concentration. The dependence of mobility on majority carrier concentration is well established.[24] Also the change of minority carrier lifetime with changes in resistivity due to recombination of minority carriers via recombination centers is well known.[25,26] This type of recombination dominates the recombination process in silicon. However, the magnitude of the recombination rate is less well known. This magnitude is determined by the saturation lifetime, which dominates at low resistivities and which is controlled by the capture cross section of the recombination centers and by their density. Little recent literature seems to be available on the subject of nonradiative recombination. This is probably due to the fact that emphasis in semiconductor device development has lately been on producing fast devices where long minority carrier lifetimes would be a hindrance. Table I of Reference 25 contains a listing of a number of saturation lifetimes measured in *n*-type and *p*-type silicon of different resistivities. These saturation lifetimes vary over nearly two orders of magnitude, rather independently of resistivity. Since the origins of the recombination centers are not fully understood, and since they do not appear to be directly connected with the impurity centers necessary for majority carrier generation, the long-range assumption may be made that the density of recombination centers can be considerably reduced. Such a reduction might ultimately lead to fulfillment of the assumption made in the thermodynamically based theories discussed in the introduction, namely, that all recombination is based on direct, radiative transitions.

Table 1 of this paper presents the results of several sample calculations of saturation current, open-circuit voltage, and resulting curve factor, all based on the diffusion model of the *p–n* junction. Equations (5) and (4), respectively, have been used for the first two quantities, while the curve factor has been determined using Eqs. (1) and (2) together with Eqs. (14) and (15) of Reference 7, the latter in the more easily evaluated form

$$\ln(1 + q/kT\, V_m) = q/kT(V_{oc} - V_m). \tag{6}$$

Lines 1, 3, 5, and 7 of Table 1 present the results of calculation of saturation current, open-circuit voltage, and curve factor, using minority carrier lifetime values from Reference 24. Lines 1 and 3 contain similar calculations representing values close to the best 10-Ω-cm and 1-Ω-cm cells seen. The remaining lines present projections to lower resistivities, with assumption of improved minority carrier lifetimes.

Since the saturation lifetime is primarily process-dependent through the density of recombination centers, and since saturation lifetimes of 4×10^{-6} sec were available 14 years ago, it is not unreasonable to assume that saturation lifetimes of 1×10^{-5} sec should be achievable in the foreseeable future. For the case of 10-μsec minority carrier lifetime (line 8), a saturation current of 2.4×10^{-15} A cm^{-2} was obtained, with a resulting open-circuit voltage of 0.79 V and a curve factor of 0.86. It should be noted that, in the 0.01-Ω-cm case, it becomes necessary to pay attention to the generally much more heavily doped diffused region and its minority carrier lifetime, in order to achieve the listed low saturation current.

The highest carrier concentration that might practically be considered would be 5×10^{19} cm^{-3} on both sides of the junction. This concentration brings the semiconductor to the edge of degeneracy. With the radiative minority carrier lifetime of 4 μsec, an open-circuit voltage of 0.843 V is reached (line 9 of Table 1) and a curve factor of 0.868. Pushing the carrier concentration still higher (line 10 of Table 1), with a radiative minority carrier lifetime of 2 μsec, does not bring a significant improvement of voltage or curve factor. It may be noted that the latter appears to asymptotically approach 0.87 as the resistivity is lowered. This value will in the following be considered as the basic portion of the curve factor with any actual lower value being applied as an additional curve factor due to process-dependent effects.

A further assumption will be made to the extent that the second exponential observed at lower voltages is not based on a basic physical principle but is caused by parameters that can be influenced by material selection and process technology. Therefore, the curve factor will be divided into two parts: one caused by the *p–n* junction characteristic as described by the diffusion theory and one that arises from the action of the second exponential, which is called the "additional curve factor (*A*)."

V. Projected Conversion Efficiency

Figure 4 shows, in a new bar graph, a comparison of the potential performance of an improved silicon solar cell with that of the present 10-Ω-cm cell.

The basic physical limitations are included only in the left-hand chart, which also contains the "basic" portion of the curve factor as explained in the previous paragraph. Remaining after this point are

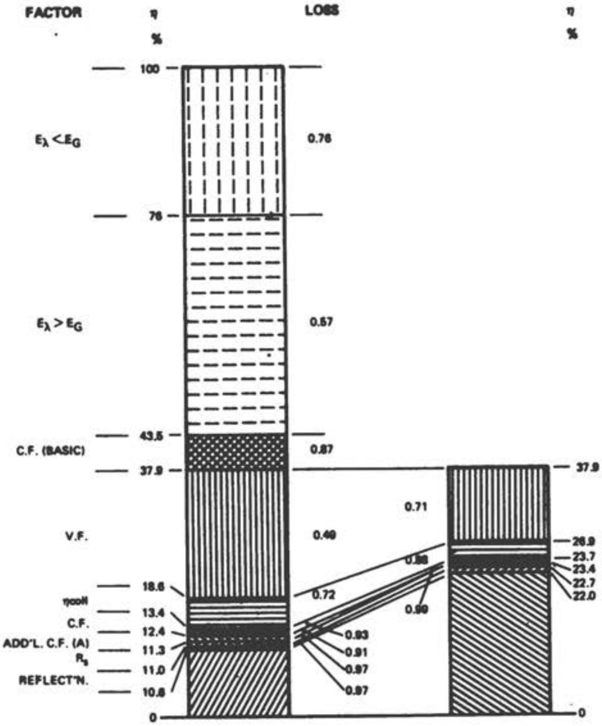


FIGURE 4 Bar chart of distribution of energy losses of the present and the potential improved silicon solar cell.

37.9 percent of the input energy. The remaining items on the chart are then all material selection- and process-dependent. The left bar represents the present-day, 10-Ω-cm *n*-on-*p* solar cell, similar to Figure 1. The process-dependent portion of the curve factor is included here, as well as the additional curve factor (*A*). The right-hand bar graph shows the situation for the projected improved silicon solar cell. The ultimate data of Table 1 have not been used here, but rather the values corresponding to 0.01-Ω-cm base material with 10-μsec minority carrier lifetime, i.e., a voltage factor of 0.71 and a curve factor of 0.86, which is 0.99 times the basic curve factor. An improved collection efficiency of 0.88 has been used, based on the discussion of Section III. Losses due to the additional curve factor (*A*) have been left out on the assumption that they can be eliminated by future work. Finally, losses of 3 percent each due to series resistance and reflection are incorporated just as they exist in the present silicon cell.

Figure 4, then, shows that an improvement in air mass zero conversion efficiency to 22 percent can be realistically expected. Even if the additional curve factor (A) should be found to be a basic problem, the conversion efficiency would still be 20 percent. Thus, a very large performance improvement lies in wait as the reward for a well-conceived and intelligently and diligently executed program.

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CHAPTER

5 Photosynthesis

RODERICK CLAYTON

I. Introduction

Photosynthesis depends on photochemical oxidoreduction in which chlorophyll (chl) acts as sensitizer and, in known cases, as electron donor. Separated electrons and holes, or reducing and oxidizing equivalents, serve as starting points for chemical processes that store energy and afford growth.

Plants have two noteworthy photochemical tricks. One is the use of an "antenna" of chl (and other pigments) to extend the quantum absorption cross section of the photochemical system. Each molecule of chl that is specialized to perform photochemical electron transfer is served by about 100 or more light-harvesting chl molecules. This trick is important in the economy of a plant cell but is unlikely to be useful for artificial photovoltaic (pv) devices.

The second trick, possibly of significance for pv technology, has to do with stabilization of primary + and − against wasteful recombination (i.e., with extension of carrier lifetime). The plant uses some combination of two devices: first, the + and − are apparently deposited on opposite sides of a membrane that is nearly impermeable to ions and to macromolecules. The membrane is about 100 Å thick and is made of lipids and protein. Second, the + and − are not freely diffusible. They are associated with various specific molecules, articulated in a definite sequence so as to promote an orderly chain of electron transfer. In this chain the first step on both the oxidizing and the reducing side acts to separate the primary entities further and to stabilize them against recombination. Part of the stabilization results because each transfer of an electron is attended by a slight loss of energy.

Ultimately the separated + and – components of this pv cell interact, probably across another part of the membrane where the redox energy is converted into chemical bond energy.

Energetics and Efficiency

The maximum efficiency with which solar energy in the field is converted to stored chemical energy, either in higher plants or in tanks of algae, is about 3 percent. If this energy is to be released through combustion of the stored matter it is first necessary to dry the material. The expenditure in terms of heat of vaporization of water offsets about 80 percent of the energy that could be gained, so the overall efficiency (heat out/solar energy in) is less than 1 percent. Furthermore, this method of solar-energy conversion raises the same problems of pollution as does the use of fossil fuels. While plants are useful for converting energy to edible food, and for exchanging CO_2 for O_2, they hold little promise for direct energy conversion.

Viewed as organic pv devices, plants are only a little more interesting. In some ways the "natural" photochemical systems based on chl are like the better artificial organic pv systems. Having significant absorption throughout the visible and near uv, chl at reasonable concentration absorbs most of the solar energy below about 6800 Å (above about 1.8 eV). Because of rapid thermal relaxation, quanta above 1.8 eV are degraded to this level before they are used photochemically. In the photochemical act about 1.0 to 1.2 eV (or less) becomes stabilized as chemical potential. This is near the thermodynamic limit (second law) for a photochemical system in equilibrium with the solar radiation field at the earth's surface. It is also near the practical limit attained with artificial organic pv devices. Probably the photosynthetic pv system, based on chl as sensitizer and electron donor, has no marked advantages or disadvantages in comparison with other pv systems that are being investigated.

Possible Impact on Photovoltaic Technology

The ability of photosynthetic tissues to extend the useful lifetimes of the charge carriers and to conserve them against wasteful recombination is worth special consideration. The study of pv systems should include efforts to separate the positive and negative charges by a barrier, possibly a natural or artificial membrane that contains or supports the sensitizing pigment. Alternatively the construction of multicomponent (and multiphase?) electron transport systems to promote efficient separation of the positive and negative charges with little loss of energy might be studied more intensively. These are the ways in which the lessons provided by nature in the photosynthetic process might best stimulate the improvement of photovoltaic devices.

Fortunately the study of electrochemical processes associated with membranes is enjoying a vogue among biochemists. It should be helpful to bring these approaches more fully to the attention of physical chemists and solid-state physicists and to fund modest efforts in these directions.

Some attention should be paid to research programs in the area of multiphase organic photochemistry, especially in contexts that involve natural or artificial membranes.