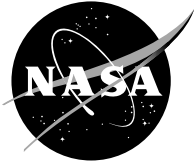


NASA/TM—2005-213341



Inorganic Photovoltaics Materials and Devices: Past, Present, and Future

Aloysius F. Hepp and Sheila G. Bailey
Glenn Research Center, Cleveland, Ohio

Ryne P. Raffaele
Rochester Institute of Technology, Rochester, New York

The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at <http://www.sti.nasa.gov>
- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA Access Help Desk at 301-621-0134
- Telephone the NASA Access Help Desk at 301-621-0390
- Write to:
NASA Access Help Desk
NASA Center for AeroSpace Information
7121 Standard Drive
Hanover, MD 21076

NASA/TM—2005-213341



Inorganic Photovoltaics Materials and Devices: Past, Present, and Future

Aloysius F. Hepp and Sheila G. Bailey
Glenn Research Center, Cleveland, Ohio

Ryne P. Raffaele
Rochester Institute of Technology, Rochester, New York

National Aeronautics and
Space Administration

Glenn Research Center

August 2005

Trade names or manufacturers' names are used in this report for identification only. This usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at <http://gltrs.grc.nasa.gov>

Inorganic Photovoltaics Materials and Devices: Past, Present, and Future

Aloysius F. Hepp and Sheila G. Bailey
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Ryne P. Raffaele
Rochester Institute of Technology
Department of Physics and Microsystems Engineering
Rochester, New York 14623

Abstract

This report describes recent aspects of advanced inorganic materials for photovoltaics or solar cell applications. Specific materials examined will be high-efficiency silicon, gallium arsenide and related materials, and thin-film materials, particularly amorphous silicon and (polycrystalline) copper indium selenide. Some of the advanced concepts discussed include multijunction III-V (and thin-film) devices, utilization of nanotechnology, specifically quantum dots, low-temperature chemical processing, polymer substrates for lightweight and low-cost solar arrays, concentrator cells, and integrated power devices. While many of these technologies will eventually be used for utility and consumer applications, their genesis can be traced back to challenging problems related to power generation for aerospace and defense. Because this overview of inorganic materials is included in a monogram focused on organic photovoltaics, fundamental issues and metrics common to all solar cell devices (and arrays) will be addressed.

1. Introduction

1.1 Recent Aspects of Advanced Inorganic Materials

A variety of different cell types are currently under development for future utility, consumer, military, and space solar power applications. The vast majority of these needs are still currently being met by the use of single crystal silicon (ref. 1). However, a variety of other materials and even solar cell types are vying for the opportunity to replace Si, if not for all applications at least in certain specific ones. Close relatives to single crystal Si such as polycrystalline Si and amorphous Si are receiving much attention (ref. 2). More exotic approaches such as polycrystalline thin film CuInGaSe_2 (ref. 3) or CdTe (ref. 4), dye-sensitized or titania solar cells (ref. 5), and even nanomaterial enhanced conjugated polymer cells (ref. 6) are also garnering much interest. However when it comes to highest efficiency cells, multijunction III-V devices are currently the leader. Of course, it is expected current triple junction GaAs cell technology will give way to quadruple junctions or possible nanostructured approaches. However, the use of ordinary Ge substrates may well give way to Ge on Si substrates. These have the advantages of lower cost, higher strength, and lighter weight. In addition to the traditional lattice-matched multijunction GaAs cells, we may also see the emergence of lattice mismatched or polymorphic cells (ref. 7).

1.2 Focus: Advanced Materials and Processing

There is currently a tremendous amount of research being directed towards a thin film alternative to traditional crystalline cells. Thin film cells are quite attractive due to the fact that many of the proposed fabrication methods are relatively inexpensive and lend themselves well to mass production (ref. 8). These cells can be made to be extremely lightweight and flexible, especially if produced on polymeric substrates. Thin film cells have been investigated for quite some time now. Cu_2S -CdS cells were developed as far back as the mid 1970's. However, even the best results to date have been plagued by low efficiencies and poor stability. The inorganic materials that have received the most attention are amorphous Si, CdTe, and CuInGaSe_2 (refs. 2 to 4). Recently thin film polymeric cells that incorporate inorganic components such as CdSe or CuInS_2 quantum dots have garnered much attention (refs. 6 and 9). Many believe it is these materials that will hold the key to inexpensive, easily deployed, large area, high specific power arrays. This is due in part to the possibility of roll-to-roll processing using low-cost spray chemical deposition or direct-write approaches to producing thin film solar cells on inexpensive lightweight substrates with these materials (refs. 3, 8, and 10).

1.3 Increased Efficiency

Multijunction technology has provided the most dramatic increase in inorganic solar cell technology. Many groups have reported laboratory efficiencies well in excess of 30 percent AM1.5. Industrial lot averages are already above a 28 percent threshold (ref. 11). The move towards a quadruple junction solar cell has been problematic due to lattice constant constraints. However, there are several new programs looking at lattice mismatch approaches to multijunction III-V which can give a better match to the solar spectrum than what is available in an ordinary lattice matched triple junction cell. In addition, there is a considerable amount of attention being paid to the use of nanostructures (i.e., quantum dots, wires, and wells) to improve the efficiencies of III-V devices. Recent theoretical results and experimental advances have shown that the use of such structures may afford dramatic improvement in cell efficiency (refs. 12 and 13).

1.4 Increased Specific Power

When considering specific power, or the power per mass of a solar cell or array, it is clear that crystalline technology will be severely limited by the mass of the substrate on which they are made. In order to achieve the types of specific power that are required to meet portable power needs of consumer or military markets, as well as many large scale space power needs, will require the development of efficient thin film photovoltaics on polymeric substrates. When considering array specific power it is important to note that a cell specific power considerably higher than the array specific power goal will be necessary. The difference in the cell to array specific power must be enough to make up for the interconnects, diodes and wiring harnesses. Roughly speaking the cell mass usual accounts for approximately half the mass of the total balance of systems (refs. 14 and 15).

In addition to improving the cell efficiency or making the cells lighter, gains in array specific power may be made by an increase in the operating voltage. Higher array operating voltages can be used to reduce the conductor mass. A typical array designed for 28 volt operation at several kilowatts output, with the wiring harness comprising ~ 10 percent of the total array mass, yields a specific mass of ~ 0.7 kg/kW. If this array was designed at a 300 V operation it could easily allow a reduction of the harness specific mass by at least 50 percent. This alone would increase the specific power by 5 percent or more without any other modification.

The extremely high specific power arrays that need to be developed for several proposed space programs like solar electric propulsion (SEP) or space solar power (SSP) will require lightweight solar

arrays that are capable of high voltage operation in the space plasma environment. SEP missions alone will require 1000 to 1500 V to direct drive electric propulsion spacecraft (i.e., no voltage step up is required to operate the thrusters). NASA has bench marked a thin film stand-alone array specific power that is 15 times the state-of-the-art (SOA) III-V arrays, area power density that is 1.5 times that of the SOA III-V arrays, and specific costs that are 15 times lower than the SOA III-V arrays (refs. 15 and 16).

2. Overview of Specific Materials

2.1 High-Efficiency Silicon

Silicon solar cells are the most mature of all solar cell technologies and have been used on the vast majority of consumer, military, and space applications. In the early 1960s, silicon solar cells were ~11 percent efficient, relatively inexpensive, and well suited for low power and limited lifetime application. The conversion efficiency of current “standard-technology” silicon ranges from around 12 to 15 percent under standard test conditions. The lower efficiency cells are generally more resistant to radiation (refs. 7, 14, and 17).

There have been many enhancements to silicon cells over the years to improve their efficiency. Textured front surfaces for better light absorption, extremely thin cells with back surface reflectors for internal light trapping, and passivated cell surfaces to reduce losses due to recombination effects are just a few examples. The highest measured efficiency for a large area (i.e., 5 in²) crystalline silicon solar cell stands at 21.5 percent. Currently, high efficiency Si cells approaching 17 percent AM0 efficiency in production lots are available from Japanese and German producers. Tecstar and Spectrolab, the two large U.S. companies that have produced virtually all of the domestic silicon space solar cells, only offer the conventional type of silicon cells with efficiencies around 14.8 percent because they have concentrated their development efforts on GaAs based multijunction cells. The advantage of a high efficiency silicon cell to that of a III-V lies in their relatively lower cost, lower material density, and higher strength (refs. 1, 7, and 17).

2.2 Polycrystalline Silicon

A lower cost alternative, although less efficient, to standard crystalline silicon technology lies in its polycrystalline alternative (ref. 18). This material is manufactured by pouring liquid silicon into a mold. Upon solidification, multicrystallites form with associated grain boundaries. The resulting blocks of material are sliced into suitable wafers. Polycrystalline silicon (p-Si) has been extensively studied over the past decade due to its applications in optoelectronics. The light absorption properties along with its simple manufacture and broadly tunable morphology have made it an attractive photovoltaic material for some time now. Due to the defects associated with the grain boundaries the best polycrystalline Si solar cell efficiencies stand at 19.8 percent, less than its monocrystalline Si counterpart (ref. 19).

2.3 Amorphous Silicon

Silicon based solar cells can also be produced using amorphous thin films that are evaporated onto glass or even polymeric substrates (ref. 2). This approach requires very little active material and thus can relate to tremendous savings in production costs. These types of cells are well suited to large area roll-to-roll processing (ref. 8). Unfortunately this method of manufacture results in high defect densities and thus is even less efficiency than p-Si solar cells. However, this approach does lend itself to multilayer processing and thus multijunction solar cells are possible. This approach has resulted in dramatic

increases in overall amorphous Si solar cell efficiencies. Multijunction amorphous Si solar cell efficiencies as high as 13 percent AM1.5 have been reported (ref. 2).

2.4 Gallium Arsenide and Related III-V Materials

Gallium Arsenide (GaAs) has been a material of interest to the solar cell community for many years (ref. 20). In 1955, an RCA group was funded by the U.S. Army Signal Corps, and later by the Air Force to work on the development of GaAs based cells. GaAs has a nearly ideal direct bandgap of 1.42 eV for operation in our solar spectrum. It also has favorable thermal stability and radiation resistance as compared to silicon. However, it took nearly 30 years of efficiency improvements until the use of GaAs based cells could be argued because of its much higher costs. The arena in which this premium could most easily be justified was in space utilization. In fact, now the vast majority of cells being launched for space solar power are multijunction III-V cells (refs. 14 and 15).

The lattice matched heterojunction cells developed in the early 1970's led to the acceptance of GaAs as a viable photovoltaic material. The Air Force launched the Manufacturing Technology for GaAs Solar Cells or (MANTECH) program in 1982. This program was designed to develop metal organic chemical vapor deposition techniques (MOCVD) necessary for the large-scale production quantities of GaAs solar cells (ref. 21).

The other significant development in GaAs technology was in the use of alternative substrates. In 1986, the Air Force supported work by the Applied Solar Energy Corp. (ASEC) in which they developed GaAs cells grown on Ge substrates. This was possible due to the similarity in the lattice constants and thermal expansion coefficients of the two materials. This resulted in the improvement in the mechanical stability of the cells and a lowering of the production costs.

The development of GaAs-based cells continued throughout the late 1980's with the primary focus being on the development of multijunction approaches to photovoltaic conversion. The initial work was mechanical stacked cells, however this quickly transitioned into epitaxially grown dual-junctions with tunnel junctions in between. Overall cell efficiencies increase dramatically during this time (see fig. 1) (ref. 22).

2.5 Thin-Film Materials

Thin film photovoltaics is an intriguing technology due to flexible lightweight construction, permitting arrays to be "molded" onto non-rigid or uniform structures for innovative power systems. Photovoltaic modules based on ternary chalcopyrite absorber materials, (i.e. I-III-VI₂ - Cu(In:Ga)(S:Se)₂) have been the focus of intense investigation for over two decades (ref. 3). The use of chalcopyrite absorbers is attractive since their bandgaps correlate well to the maximum photon power density in the solar spectrum for both terrestrial (AM 1.5) (ref. 8), and space applications (AM0) (fig. 2) (refs. 14 to 16). Additionally, by adjusting the percent atomic composition of either Ga for In and/or S for Se, the bandgap can be tuned from 1.0 eV to 2.4 eV, thus permitting fabrication of high, or graded bandgaps (refs. 3 and 8).

One of the first thin film cells, Cu₂S/CdS, was developed for space applications. Reliability issues eliminated work on this particular cell type for both space and terrestrial considerations even though AM1.5 efficiencies in excess of 10 percent were achieved. Thin film cells require substantially less material and thus lower mass and promise the advantage of large area, low cost manufacturing (refs. 2 to 4, and 8).

Development of other wide bandgap thin film materials that can be used in conjunction with CIS to produce a dual-junction device is underway. As has already been demonstrated in III-V cells for space use, a substantial increase over single-junction device efficiency is possible with a dual-junction device. NASA and NREL have both initiated dual-junction CIS-based thin film device programs (refs. 3 and 16).

The use of Ga to widen the bandgap of CIS and thus improve the efficiency is already well known. The substitution of S for Se also appears to be an attractive top cell material. The majority of thin film devices developed thus far have been on heavy substrates such as glass; progress is being made in reducing substrate mass through the use of thin metal foils and lightweight flexible polyimide or plastic substrates. A major problem with the use of plastic substrates is the incompatibility with many of the deposition processes. The most efficient thin film cells to date are made by some combination of co-evaporation of the elements and subsequent annealing. AM0 cell efficiencies as high as 7 percent have been measured for $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{S}_2$ (E_g 1.55 eV) thin film devices on flexible substrates (R. Birkmire, personal communication, 2003). The use of such plastic substrates as poly(p-phenylene-2,6-benzobisoxazole) (PBO), Upilex™ or Kapton™ puts an unacceptable restriction on the processing temperatures. The current world records for thin film CdTe and CuInGaSe_2 solar cells AM1.5 efficiencies stand at 16.5 and 19.2 percent, respectively (refs. 3, 4, and 7).

3. Advanced Concepts

3.1 Multijunction III-V Devices

Investigations into further efficiency improvement toward the end of the 20th century turned toward the development of multiple junction cells and concentrator cells. Much of the development of multijunction GaAs-based photovoltaics was supported by a cooperative program funded by the Air Force (ManTech program, Space Vehicles Directorate, and the Space Missile Center) and NASA. This work resulted in the development of a “dual-junction” cell which incorporates a high-bandgap GaInP cell grown on a GaAs low-bandgap cell. The 1.85 eV GaInP converts higher energy photons and GaAs converts lower energy photons. Commercially available dual-junction GaAs/GaInP cells have an AM0 efficiency of 22 percent with a V_{oc} of 2.06 V (refs. 20 to 22).

The highest efficiency solar cells currently available are triple-junction cells consisting of GaInP, GaAs, and Ge (see fig. 3). They are grown in series connected layers and have been produced with a 28.3 percent efficient with a V_{oc} of 2.66 V in production lots, with laboratory cells of 29 percent. Emcore, Inc., and Spectrolab, Inc., currently produce cells that are commercially available in the 25 to 27 percent range. Their high efficiencies are due to their ability to effectively convert a larger portion of the available sunlight. In fact, it is expected as better materials (for triple junction cells) are developed and eventually as quadruple junction cells are developed, cell efficiencies will surpass the 40 percent efficiency barrier (see fig. 4). Hughes Space and Communications Company’s HS601 and HS702 spacecraft currently use multijunction technology as do most other contractors for their high-performance spacecraft (refs. 14, 15, 21, and 22).

Spectrolab, supplier of more than half of the world’s spacecraft solar cells, has reached a milestone of 1400 kW of multijunction cells delivered, with an average ((BOL + EOL)/2) conversion efficiency of 26.3 percent. They are currently producing 1 MW of cells for commercial sales to a variety of array manufacturers (e.g., Hughes Space and Communication Company, Ball Aerospace & Technologies Group, Lockheed Martin, and Boeing). Their high efficiency cells retain 86 percent of their original power after 15 years of operation. There is currently more than 375 kW of Spectrolab multijunction solar cells in operation (ref. 14).

NREL recently announced a new world record conversion efficiency for a multijunction GaAs solar cell at 32.5 percent (ref. 23). The new multijunction III-V cells have allowed a reduction in solar array size and mass over the previously used Si cells to achieve comparable power levels. This is especially important in space applications. Scientists expect the majority of the 800 commercial and military spacecraft launched in the next 5 years to use multijunction technology. This should result in the lower costs for telecommunications, internet, television, and other wireless services. The AFRL recently initiated a 35 percent efficient four-junction solar cell program.

Multijunction III-V cells are relatively expensive to produce. The development of large area arrays using these cells can become cost prohibitive (see section 3.4). One option to reduce the overall cost is to use the cells in solar concentrators, where a lens or mirror is used to decrease the required cell area (ref. 24).

3.2 Nanotechnology—Specifically Quantum Dots

A recent approach to increasing the efficiency of thin-film photovoltaic solar cells involves the incorporation of quantum dots (refs. 6 and 9). Semiconductor quantum dots are currently a subject of great interest mainly due to their size-dependent electronic structures, in particular the increased band gap and therefore tunable optoelectronic properties. To date these nanostructures have been primarily limited to sensors, lasers, LEDs, and other optoelectronic devices. However the unique properties of the size dependent increase in oscillator strength due to the strong confinement exhibited in quantum dots and the blue shift in the band gap energy of quantum dots are properties that can be exploited for developing photovoltaic devices that offer advantages over conventional photovoltaics. Theoretical studies predict a potential efficiency of 63.2 percent for a single size quantum dot cell, which is approximately a factor of 2 better than any SOA device available today. For the most general case, a system with an infinite number of sizes of quantum dots has the same theoretical efficiency as an infinite number of bandgaps or 86.5 percent (refs. 12 and 13).

A collection of different size quantum dots can be regarded as an array of semiconductors that are individually size-tuned for optimal absorption at their band gaps throughout the solar energy emission spectrum. This is in contrast with a bulk material where photons are absorbed at the band gap; energies above the band gap result in less efficient photogeneration of carriers. In addition, bulk materials used in photovoltaic cells suffer from reflective losses for convertible photons near the band gap, whereas for individual quantum dots, reflective losses are minimized. Some recent work has shown that quantum dots may also offer some additional radiation resistance and favorable temperature coefficients.

3.3 Advanced Processing for Low-Temperature Substrates

A key technical issue outlined in the 2001 U.S. Photovoltaic roadmap (ref. 25) is the need to develop low cost, high throughput manufacturing for high-efficiency thin film solar cells. Thus, a key step for device fabrication for thin film solar cells is the deposition onto flexible, lightweight substrates such as polyimides. Current methods for depositing ternary crystallite compounds often include high-temperature processes, often followed by toxic sulphurization/selenization steps (refs. 3, 4, and 8). The high temperature requirements make this protocol incompatible with all presently known flexible polyimides, or other polymer substrates. In addition, the use of toxic reagents is a limiting factor. The use of multisource inorganic/organometallic precursors in a chemical vapor deposition (CVD) process is more appealing due to milder process parameters. However, stoichiometric control of deposited films can be difficult to achieve and film contamination has been reported (ref. 26). A novel alternative approach is the use of ternary single source precursors, (SSP's), which have the I-III-VI₂ stoichiometry "built in" and are suitable for low temperature deposition (fig. 5). Although, a rich and diverse array of binary SSP's are known, characterized, reviewed and tested, the number of known ternary SSP's is limited, as is their use in deposition processes (ref. 27). We briefly summarize the highly promising technique for thin film growth: molecular design of single source precursors for use in a chemical (vapor or spray) deposition process.

Spray CVD has become an often-studied deposition technique; a precursor solution is ultrasonically nebulized, and is swept into a two-zone, hot-wall reactor (fig. 6). The carrier-solvent is evaporated in the warm zone, and the gaseous precursors are decomposed in the hot zone, where film growth occurs as in conventional CVD. Spray CVD maintains the most desirable features of MOCVD and spray pyrolysis,

such as film growth in inert atmospheres, large area deposition, laminar flow over the substrate, and low temperature solution reservoir, while avoiding the major difficulties of each (ref. 28). It minimizes the high volatility and temperature requirements for the precursor, which are essential in MOCVD, by delivering the precursor to the furnace as an aerosol propelled by a fast-flowing carrier gas from a low-temperature precursor reservoir analogous to that employed in spray pyrolysis. The latter feature is an important benefit that can prevent premature precursor decomposition when using thermally labile precursors.

In 1990 Kanatzidis et al., reported the preparation of hetero binuclear complexes consisting of tetrahedrally arranged Cu and In centers, with two bridging thiolato and selenolato groups (see fig. 5 for similar structure) (ref. 29). Pyrolysis studies undertaken revealed that the Se derivative could be converted into CuInSe_2 at 400 to 450 °C, but none of the precursors had been evaluated in a thin-film deposition study. Buhro and Hepp were able to demonstrate that $[\{\text{PPh}_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$ could be utilized in a spray CVD process, for depositing thin-film CuInS_2 below 400 °C (refs. 10 and 30). Thin films were deposited using a dual solvent system of toluene and dichloromethane, (CH_2Cl_2) as the carrier solvent. Single-phase 112 orientated CuInS_2 thin films were successfully deposited at a range of temperatures from 300 to 400 °C; at elevated temperatures (>500 °C), CuIn_5S_8 phase thin films were deposited. Materials analysis showed that the films were free from any detectable impurities and highly crystalline, thus concluding the precursor decomposes cleanly.

In the course of our investigations for improved single source precursors for the spray CVD of chalcopyrite thin-films, for the general semiconductor stoichiometry $\text{Cu}(\text{Ga:In})(\text{Se:S})_2$, we have continued to expand the molecular design of SSP's based on the $[\{\text{LR}_3\}_2\text{Cu}(\text{ER}')_2\text{M}(\text{ER}')_2]$ architecture (ref. 10). Furthermore, the number of "tunable" sites within the complex allows for their utility in preparing a number of ternary chalcopyrites of varying composition, in addition to engineer the SSP's to match a given spray CVD process.

Spray CVD, in conjunction with SSP design, provides a proof-of-concept for a reproducible high manufacturability process. An outlook for further investigation that needs to be undertaken is: (1) **Precursor Design:** Development of more volatile/thermally labile systems. This can be achieved by the incorporation of fluorinated or silylated function groups. Importantly due to the well-known propensity of fluorine to react with silyl moieties, incorporation of both elements in the molecule can serve not only to increase volatility, but also as a "self-cleaning" mechanism should the precursor decompose through an undesired pathway (ref. 31). (2) **Processing Parameters:** Spray CVD has a number of tunable variables, such as droplet size, flow-rate, concentration, solvent polarity, which are advantageous to achieve the desired film characteristics. Thus an in-depth study needs to address these parameters on film composition (ref. 32). (3) **Device fabrication:** working devices from deposited films need to be tested to aid SSP design and spray CVD process parameters; this is the current focus of work on-going at NASA Glenn Research Center (ref. 33). The work summarized here on the molecular design of SSP's for their use in a spray CVD process, although still in its infancy, undoubtedly shows it as a mass producible, cost effective method for fabricating commercial thin film PV devices. Furthermore, we have discovered that single-source precursors are a valuable route to semiconductor nanoparticles (refs. 9 and 31).

3.4 Concentrator Cells

Concentrating solar collectors use devices such as Fresnel lenses and parabolic mirrors to concentrate light onto solar cells (ref. 24). This reduces the area of cells needed and also raising the efficiency of the cells by operating them at higher light concentration. Normally these collectors are mounted onto an axis tracking system to follow the track of the Sun across the sky. Figure 7 shows a point-focus Stirling engine concentrator system. Figure 8 shows a linear concentration system in Austin, Texas.

3.5 Integrated Power Devices

NASA has also been working to develop lightweight, integrated space power systems on small or flexible substrates. These systems generally consist of a high efficiency thin film solar cell, a high energy density solid-state lithium-ion battery, and the associated control electronics in a single monolithic package. These devices can be directly integrated into microelectronic or MEMS devices and are ideal for distributed power systems on satellites or even the main power supply on a nanosatellite. These systems have the ability to produce constant power output throughout a varying or intermittent illumination schedule as would be experienced by a rotating satellite or “spinner” and by satellites in a low earth orbit (LEO) by combining both generation and storage (ref. 34).

An integrated thin film power system has the potential to provide a low mass and cost alternative to the current SOA power systems for small spacecraft. Integrated thin film power supplies simplify spacecraft bus design and reduce losses incurred through energy transfer to and from conversion and storage devices. It is hoped that this simplification will also result in improved reliability (see fig. 9).

The NASA Glenn Research Center has recently developed a microelectronic power supply for a space flight experiment in conjunction with the Project Starshine atmospheric research satellite (see fig. 10) (ref. 35). This device integrates a 7 junction small-area GaAs monolithically integrated photovoltaic module (MIM) with an all-polymer $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ lithium-ion thin film battery. The array output is matched to provide the necessary 4.2 V charging voltage and minimized the associated control electronic components. The use of the matched MIM and thin film Li-ion battery storage maximizes the specific power and minimizes the necessary area and thickness of this microelectronic device. This power supply was designed to be surface mounted to the Starshine 3 satellite, which was ejected into a low-earth orbit (LEO) with a fixed rotational velocity of 5 degrees per second. The supply is designed to provide continuous power even with the intermittent illumination due to the satellite rotation and LEO.

4. Applications

4.1 Terrestrial

The use of photovoltaic power continues to increase steadily in the U.S. and even more so worldwide. Programs to stimulate the use of solar power exist to support homeowners, small businesses, and industry. The government has also expanded programs to support local utility companies, state agencies, and even international developmental projects (ref. 36). Many other nations are supporting similar programs. The UK research council recently funded their largest solar power program to date that will support 6 universities and 7 companies in the UK (ref. 37). Japan’s largest solar power generator was also recently completed in Tsukuba. The system uses 5,600 solar panels and will have the capacity to generate 1 MW of power. Figure 11 shows a 1 MW solar power station installed by BP Solar in Toledo Spain.

4.2 Aerospace

Solar array designs have undergone a steady evolution since the Vanguard 1 satellite. Early satellites used silicon solar cells on honeycomb panels that were body mounted to the spacecraft. Early space solar arrays only produced a few hundred watts of power. Satellites today require low-mass solar arrays that produce several kilowatts of power. Several new solar array structures have been developed over the past forty years to improve the array specific power and reduce the stowed volume during launch. The solar arrays presently in use can be classified into six categories: (1) body-mounted arrays; (2) rigid panel planar arrays; (3) flexible panel array; (4) flexible roll-out arrays; (5) concentrator arrays; and (6) high temperature/intensity arrays.

In addition, several proposed space missions have put other constraints on the solar arrays. Several proposed Earth orbiting missions designed to study the sun require “electrostatically clean” arrays. Inner planetary missions and mission to study the Sun within a few solar radii require solar arrays capable of withstanding temperatures above 450 °C and functioning at high solar intensities. Outer planetary missions require solar arrays that can function at low solar intensities and low temperatures. In addition to the near-sun missions, missions to Jupiter and its moons also require solar arrays that can withstand high radiation levels.

The International Space Station will have the largest photovoltaic power system ever present in space (see fig. 12). It will be powered by 262,400 (8cm x 8cm) silicon solar cells with an average efficiency of 14.2 percent on 8 U.S. solar arrays (each ~ 34 m x 12 m). This will generate about 110 kW of average power, which after battery charging, life support, and distribution, will supply 46 kW of continuous power for research experiments. The Russians also supply an additional 20kW of power to ISS.

5. Summary and Conclusions

Zweibel and Green in a recent editorial (ref. 38) observed that: “... *photovoltaics is poised to progress from the specialized applications of the past to make a broader impact on the public consciousness, as well as on the well-being of humanity . . .*” We as well as Perlin (this volume, Chapter 1 by Perlin) have endeavored to provide a context for the development of organic photovoltaics. While highlighting important applications involving uses on Earth, where price per watt will be a critical driver; the challenges of aerospace and defense have spurred the development of advanced technologies. We have highlighted a number of these in advanced materials, devices, and processing in this overview. It is important to keep in mind the fact that solar cells, regardless the material(s) or device structure, are made to generate electricity. An important lesson to be learned from a more practical consideration of solar cells is that a wide array of power generation applications exist each with its own set of challenges.

These challenges can be addressed by a variety of technologies that overcome specific issues involving available area, efficiency, reliability, and specific power at an optimal cost. The particular application may be in aerospace, defense, utility, consumer, grid-based, off-grid (housing), recreational, or industrial settings. Organic-based photovoltaics will most likely provide solutions in applications where price and/or large area challenges dominate such as consumer or recreational products. Inorganic materials will most likely predominate in aerospace and defense uses: satellites, non-terrestrial surface power, and planetary exploration. As efficiencies, environmental durability and reliability improve for organic photovoltaics, other applications such as off-grid solar villages and utility-scale power generation may well be within reach!

References

1. M.A. Green, *Silicon Solar Cells: Advanced Principles and Practice*, Bridge Printery, Sydney, 1995.
2. S. Guha, J. Yang, A. Banerjee, Amorphous silicon alloy photovoltaic research – present and future, *Prog. Photovolt. Res. Appl.* 8, 141-150 (2000).
3. H.-W. Schock, R. Noufi, CIGS-based solar cells for the next millennium, *Prog. Photovolt. Res. Appl.* 8, 151–160 (2000).
4. D. Bonnet, P.V. Meyers, Cadmium telluride – material for thin film solar cells, *J. Mater. Res.* 13, 2740–2753 (1998).
5. M. Grätzel, Perspectives for dye-sensitized nanocrystalline solar cells, *Prog. Photovolt. Res. Appl.* 8, 171–185 (2000).
6. W. Huynh, J. Dittmer, A.P. Alivisatos, Hybrid nanorod-polymer solar cells, *Science* 295, 2425–2428 (2002).

7. M.A. Green, K. Emery, D.L. King, S. Igari, W. Warta, Solar cell efficiency tables (version 20), *Prog. Photovolt. Res. Appl.* 10, 355–363 (2002).
8. P. Sheldon, Process integration issues in thin-film photovoltaics and their impact on future research directions, *Prog. Photovolt. Res. Appl.* 8, 77–91 (2000).
9. S.L. Castro, S.G. Bailey, R.P. Raffaele, K.K. Banger, A.F. Hepp, Nanocrystalline chalcopyrite materials (CuInS_2 and CuInSe_2) via low-temperature pyrolysis of molecular single-source precursors, *Chem. Mater.* 15, 3142–3147 (2003).
10. K.K. Banger, J.A. Hollingsworth, J.D. Harris, J. Cowen, W.E. Buhro, A.F. Hepp, Ternary single-Source precursors for polycrystalline thin-film solar cells. *Appl. Organomet. Chem.* 16, 617–627 (2002).
11. D.J. Friedman, S.R. Kurtz, K.A. Bertness, A.E. Kibbler, C. Kramer, J.M. Olson, D.L. King, B.R. Hansen, J.K. Snyder, 30.2 percent efficient GaInP/GaAs monolithic two-terminal tandem concentrator cells, *Prog. Photovolt.* 3, 47–50 (1995).
12. R.P. Raffaele, S.L. Castro, A.F. Hepp, S.G. Bailey, Quantum dot solar cells, *Prog. Photovolt. Res. Appl.* 10, 433–439 (2002).
13. A. Martí, L. Cuadra, A. Luque, Quantum Dot Intermediate Band Solar Cell, in *28th IEEE Proceedings of the Photovoltaics Specialists Conference*, Anchorage, AK, September 2000, IEEE, New York, 2000, pp 940–943.
14. P.A. Iles, Future of photovoltaics for space applications, *Prog. Photovolt. Res. Appl.* 8, 39–51 (2000).
15. D.J. Hoffman, T.W. Kerslake, A.F. Hepp, M.K. Jacobs, D. Ponnusamy, Thin-Film Photovoltaic Solar Array Parametric Assessment, in *Proceedings 35th IECEC Conference*, Vol. 1, AIAA (AIAA-00-2919), Washington, D.C., (AIAA-00–2919), 2000, pp. 670–680.
16. A.F. Hepp, M. Smith, J.H. Scofield, J.E. Dickman, G.B. Lush, D. Morel, C. Ferekides, N.G. Dhere, Multi-Junction Thin-Film Solar Cells on Flexible Substrates for Space Power, in *Proceedings 37th IECEC Conference*, EDS (IECEC-2002-20155), Washington, D.C., NASA/TM—2002-211834, 12 pp., October 2002.
17. M. A. Green, The future of crystalline silicon solar cells, *Prog. Photovolt. Res. Appl.* 8, 127–139 (2000).
18. J.C. Zolper, S. Narayanan, S.R. Wenham, M.A. Green, 16.7 percent efficiency, laser textured, buried contact polycrystalline silicon solar cell, *Appl. Phys. Lett.* 55, 2363–2365 (1989).
19. J. Zhao, A. Wang, M.A. Green, 19.8 percent efficient, ‘honeycomb’ textured, multi-crystalline and 24.4 percent monocrystalline silicon solar cells, *Appl. Phys. Lett.* 73, 1991–1993 (1998).
20. H.J. Hovel, *Solar Cells*, vol. 2, Academic Press, New York, 1978.
21. D. Keener, D. Marvin, D. Brinker, H. Curtis, M. Price, Progress Toward Technology Transition of GaInP/GaAs/Ge Multijunction Solar Cells, in *26th Proceedings of the IEEE Photovoltaics Specialists Conference*, Anaheim, CA, August 1997, IEEE, New York, 1997, pp 787–781.
22. M. Yamaguchi, Multi-Junction Solar Cells: Present and Future, in *Proceedings of 12th International Photovoltaics Science and Engineering Conference*, Jeju, Korea, June 11–15, 2001, Kyung Hee Information Printing Co. Ltd., Seoul, Korea, 2001, pp. 291–295.
23. http://www.eere.energy.gov/aro/r_and_d.html#2
24. R.M. Swanson, The promise of concentrators, *Prog. Photovolt. Res. Appl.* 8, 93–111 (2000).
25. http://www.nrel.gov/ncpv/intro_roadmap.html
26. M.C. Artaud, F. Ouchen, L. Martin, S. Duchemin, CuInSe_2 thin films grown by MOCVD: characterization, first devices. *Thin Solid Films*, 324, 115–123, (1998).
27. A.C. Jones, P. O’Brien, *CVD of Compound Semiconductors: Precursors Synthesis, Development & Application*: Wiley-VCH, Berlin, 1997.
28. H. Miyake, T. Hayashi, K. Sugiyama, Preparation of $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ alloys from In solutions. *J. Cryst. Growth* 134, 174–180, (1993).

29. W. Hirpo, S. Dhingra, A.C. Sutorik, M.G. Kanatzidis, Synthesis of mixed copper-indium chalcogenolates. Single source precursors for the photovoltaic material CuInQ_2 ($Q = \text{S}, \text{Se}$), *J. Am. Chem. Soc.* 115, 597–599 (1993).
30. J.A. Hollingsworth, A.F. Hepp, W.E. Buhro, Spray CVD of copper indium disulfide films: control of microstructure and crystallographic orientation. *Chem. Vap. Deposition* 5, 105–108 (1999).
31. K.K. Banger, M.H.-C. Jin, J.D. Harris, P.E. Fanwick, A.F. Hepp, A new facile route for the preparation of single-source precursors for bulk, thin-film, and nanocrystallite I-III-VI semiconductors, *Inorg. Chem.* 42, 7713–7715 (2003).
32. K.K. Banger, J.A. Hollingsworth, M.H.-C. Jin, J.D. Harris, E.W. Bohannon, J.A. Switzer, W.E. Buhro, A.F. Hepp, Ternary precursors for depositing I-III-VI₂ thin films for solar cells via spray CVD. *Thin Solid Films* 431–432, 63–67 (2003).
33. J.D. Harris, K.K. Banger, D.A. Scheiman, M.A. Smith, A.F. Hepp, Characterization of CuInS_2 films prepared by atmospheric pressure spray chemical vapor deposition, *Mater. Sci. Eng.* B98, 150–155 (2003).
34. R.P. Raffaele, A.F. Hepp, G.A. Landis, D.J. Hoffman, Mission applicability assessment of integrated power components and systems. *Prog. Photovolt. Res. Appl* 10, 391–397 (2002).
35. <http://www.azinet.com/starshine/>
36. <http://www.eere.energy.gov/financing/>
37. See the following for news and trends in solar energy: <http://www.solarbuzz.com/>
38. K. Zweibel and M.A. Green, Millennium Special Issue: PV 2000 – And Beyond (Editorial), *Prog. Photovolt. Res. Appl.* 8,1 (2000).

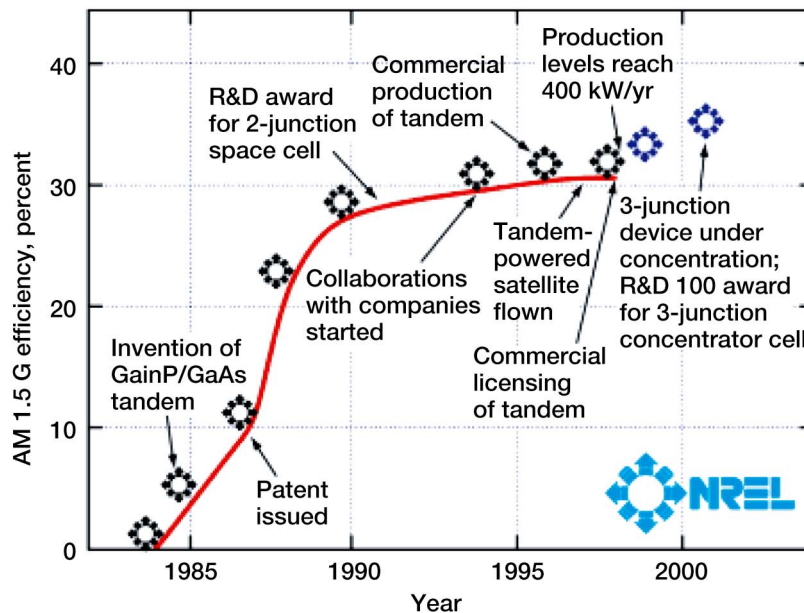


Figure 1.—GaAs-based solar cell development (courtesy of the National Renewable Energy Laboratory).

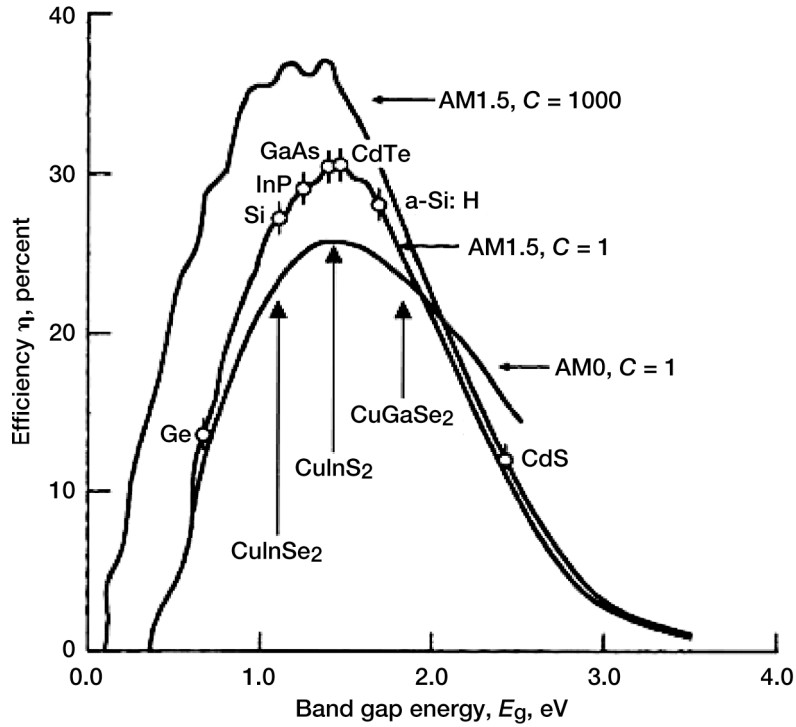
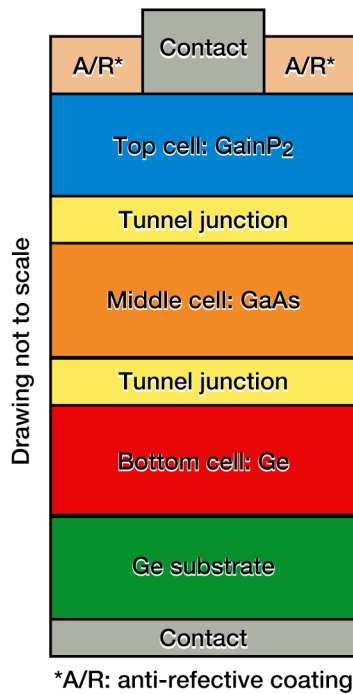


Figure 2.—Predicted efficiency versus bandgap for thin-film photovoltaic materials for solar spectra in space (AM0) and on the surface of the Earth (AM1.5) at 300K compared with bandgaps of other PV materials with unconcentrated ($C = 1$) and high concentration ($C = 1000$) sunlight.



*A/R: anti-reflective coating
 Figure 3.—Multi-junction GaInP/GaAs solar cell structure (courtesy of Spectrolab, Inc.).

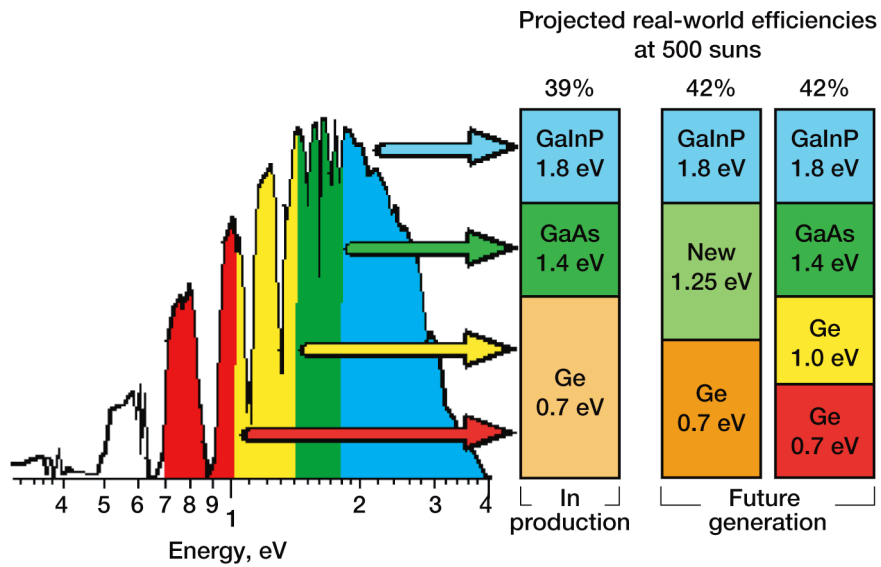


Figure 4.—Diagram showing the potential photoconversion of sunlight using multifunction III-V solar cells (courtesy of Spectrolab, Inc.)

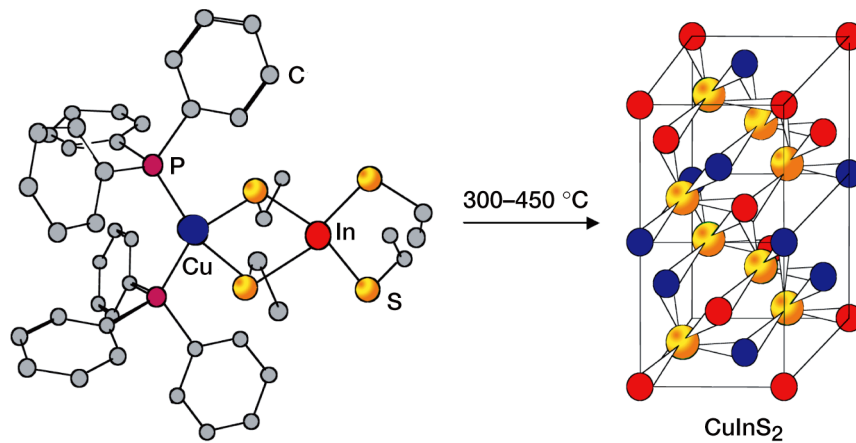


Figure 5.—Pyrolysis of a single-source precursor $[(PPh_3)_2Cu(SET)_2In(SET)_2]$ to produce a semiconductor material, CuInS₂.

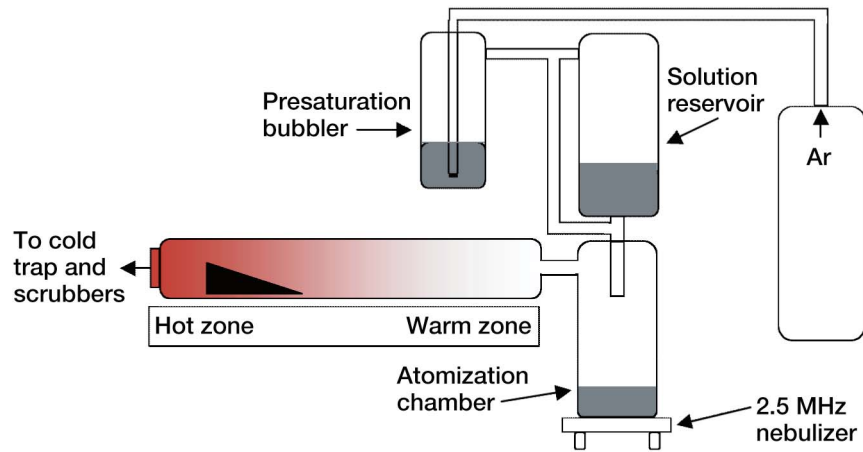


Figure 6.—Schematic for spray CVD apparatus.



Figure 7.—A 5-kilowatt point-focus Stirling engine concentrator system (courtesy of Cummins Power Generation, Inc.).



Figure 8.—A 300-kilowatt linear concentrator system (courtesy of the National Renewable Energy laboratory).

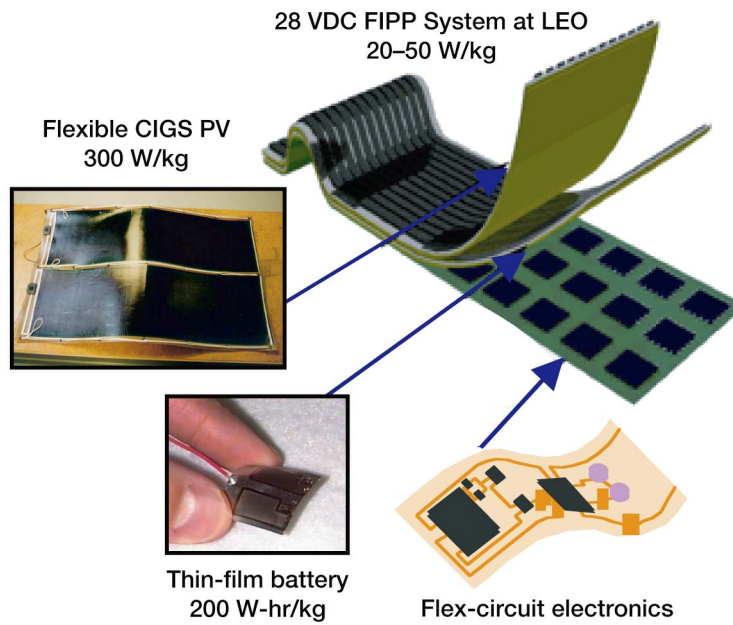


Figure 9.—Flexible Integrated Power Pack (FIPP) (courtesy of ITN Energy Systems).

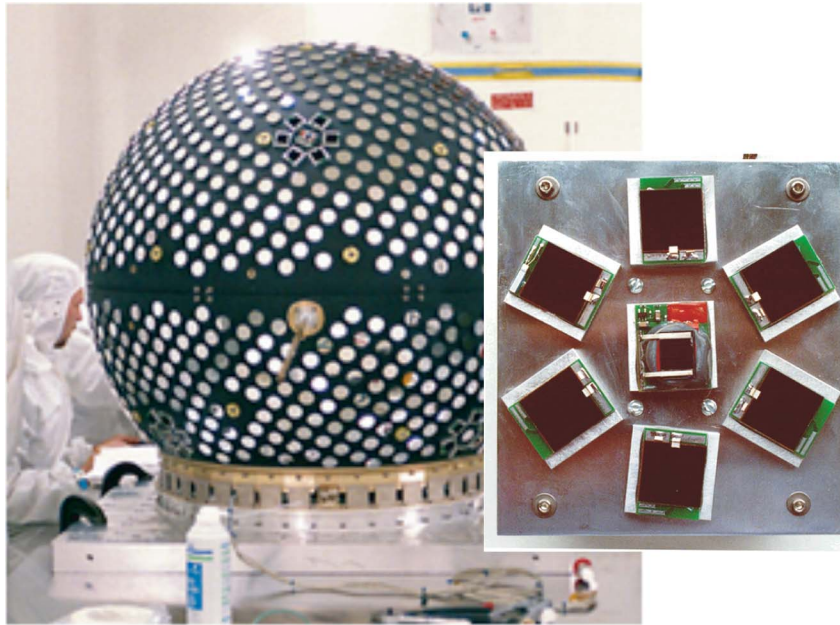


Figure 10.—Starshine 3 satellite (inset: close-up of the IPS surrounded by 6 Emcore triple-junction III-V solar cells).



Figure 11.—Solar power station in Toledo, Spain (courtesy of BP Solar).



Figure 12.—Solar arrays of the International Space Station.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (<i>Leave blank</i>)	2. REPORT DATE August 2005	3. REPORT TYPE AND DATES COVERED Technical Memorandum	
4. TITLE AND SUBTITLE Inorganic Photovoltaics Materials and Devices: Past, Present, and Future		5. FUNDING NUMBERS WBS-22-319-20-A1 WBS-22-319-20-C1	
6. AUTHOR(S) Aloysius F. Hepp, Sheila G. Bailey, and Ryne P. Raffaele			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191		8. PERFORMING ORGANIZATION REPORT NUMBER E-14809	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-2005-213341	
11. SUPPLEMENTARY NOTES Aloysius F. Hepp and Sheila G. Bailey, NASA Glenn Research Center; and Ryne P. Raffaele, Rochester Institute of Technology, Department of Physics and Microsystems Engineering, Rochester, New York 14623. Responsible person, Aloysius F. Hepp, organization code 5410, 216-433-3835.			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Category: 23 Available electronically at http://gltrs.grc.nasa.gov This publication is available from the NASA Center for AeroSpace Information, 301-621-0390.		12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>) This report describes recent aspects of advanced inorganic materials for photovoltaics or solar cell applications. Specific materials examined will be high-efficiency silicon, gallium arsenide and related materials, and thin-film materials, particularly amorphous silicon and (polycrystalline) copper indium selenide. Some of the advanced concepts discussed include multi-junction III-V (and thin-film) devices, utilization of nanotechnology, specifically quantum dots, low-temperature chemical processing, polymer substrates for lightweight and low-cost solar arrays, concentrator cells, and integrated power devices. While many of these technologies will eventually be used for utility and consumer applications, their genesis can be traced back to challenging problems related to power generation for aerospace and defense. Because this overview of inorganic materials is included in a monogram focused on organic photovoltaics, fundamental issues and metrics common to all solar cell devices (and arrays) will be addressed.			
14. SUBJECT TERMS Copper indium selenide; Poly crystalline; Gallium arsenide; High-efficiency solar cells; Inorganic photovoltaic materials; Multi-junction devices; Quantum dots; Silicon solar cells; Amorphous silicon; Thin film(s)		15. NUMBER OF PAGES 23	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT

