Physical problems in solar energy

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A short review is given of the history and current state of physics research on semiconductor solar power generation.

Interest in the physics of semiconductor solar elements is to a certain degree analogous to interest in high-temperature superconductivity and is determined not so much by the physics itself, but by questions of economics and ecology. The principal breakthrough in the development of solar power in recent years has probably been the reduction in cost of electrical energy produced by solar elements. In the United States, the cost of electrical energy produced by solar elements was \$60 per kilowatt-hour in 1970, \$1 in 1980, and 15-20 cents in 1990 (Ref. 1). For comparison, the cost of producing electrical energy by wind generators is about 7 cents per kilowatt-hour in 1990, while the figure is 5 cents for ordinary coal-fired thermoelectric power plants. According to the predictions of Refs. 1 and 2, the cost of ecologically pure energy will decrease and in the next 90 years will be lower than for traditional energy sources. Even today, there are applications where solar elements are economically attractive. One even need not speak of solar batteries on spacecraft ---solar energy power units are cheaper than diesel engines as autonomous energy sources (up to 20 kW) in rural areas.1-3

However, in the present review we will discuss the areas of application of solar elements, technical problems of combining solar elements into blocks and modules in order to obtain sufficient power, currents, and voltages, commutation problems, the shielding of solar elements from external disturbances, and so on. Instead, our brief review concentrates on problems that face physicists.

The most important landmark in the history of solar elements was probably the production of a solar element on a p-n junction in silicon in the early 1950s (Ref. 4). We note that the *internal photoeffect* in semiconductors was itself discovered more than 100 years before, by Becquerel in 1839. The history of the research in this field, as well as questions of practical application, have been discussed in detail in many papers, reviews, and monographs (see Refs. 5–13, for example). The physical basis of the phenomenon has also been studied quite extensively and is covered in textbooks on semiconductor physics.¹⁴ Therefore we recall only the main ideas necessary for an understanding of the logic of development.

BASIC PHYSICAL IDEAS

We will be interested mainly in the photovoltaic effect, which is the production of an emf in a semiconductor as a result of exposure to light. There are several different kinds of photovoltaic effects. A Dember emf is induced in a homogeneous semiconductor by light because of the different mobilities of electrons and holes. In semiconductors with a resistivity gradient we have a so-called volume photoemf and other (usually weaker) effects. As a general rule, the production of an emf and not simply photoexcited carriers (photoconductivity) results from a nonuniform illumination or form an inhomogeneity in the semiconductor.^{14,15}

A photovoltaic emf produced when a diode semiconductor structure is illuminated is the most important for use in power generation.

Pairs of electrons and holes are excited in interband absorption of light in semiconductors. To obtain an emf it is necessary to spatially separate the electrons and holes and prevent them from recombining. Hence the structure of the solar element must ensure spatial separation between the potential-energy minima corresponding to electrons and holes. Sometimes this property is called a built-in electric field.

In principle, there are several ways of accomplishing spatial separation of the potential-energy minima: p-n junctions, Schottky barriers, heterostructures or graded bandgap semiconductors. As an example, Figs. 1-3 show the band diagram of a p-n junction, the simplest structure of a solar element on a p-n junction in silicon, and its volt-ampere characteristic. The quantity $V_{\rm D}$ in Fig. 1 is the height of the potential barrier for the majority carriers and also determines the electric field accelerating the minority carriers. In a solar element on a p-n junction, $V_{\rm D}$ limits the maximum possible photo-emf or zero-load voltage V_{xx} (see Fig. 3). The short-circuit current $I_{\rm sh}$ is determined by the intensity of illumination and is actually proportional to the number of photons in the flux of electromagnetic radiation incident on the semiconductor (more exactly, it is proportional to the number of photons absorbed by the semiconductor).

The volt-ampere characteristic shown in Fig. 3 corresponds to the simplest model of the junction in which curve 1 is described by the equation

$$I = I_{\rm s}(e^{eV/k_{\rm B}T} - 1).$$
(1)

The volt-ampere characteristic of the solar element is obtained by shifting curve I by the magnitude of the photocurrent I_L . Usually $I_L > I_s$ and $I_L = I_{sh}$.

Therefore the photoemf depends on the intensity of the light (let Φ be the flux of light energy incident on the semiconductor per second). The dependence $V_{xx}(\Phi)$ is not nec-



FIG. 1. Band diagram of a p-n junction: E_g is the width of the forbidden band of the semiconductor and V_D is the shift in the chemical potential because of doping.

essarily linear; in fact, to use the solar element as a voltage source it should have the shape shown in Fig. 4. In the model (1) of a p-n junction this dependence is logarithmic. In actuality, it rapidly saturates and $V_{xx} \leq V_D$ over a rather wide range of intensities. In this sense the emf of a solar element is determined by its "construction," i.e. by the built-in electric field.

In a solar element on a p-n junction V_D cannot exceed E_g , the width of the forbidden band of the semiconductor. The emf can be increased by combining solar elements in series in a battery. In an individual solar element in a heterostructure the emf is limited by the maximum value of the energy gap, since the energy gap determines the diode properties of the semiconductor structure and the deviation of the volt-ampere characteristic from Ohm's law (see Fig. 4).

The maximum power P_{max} produced for the optimum load on the solar element is close to the product $I_{\text{sh}} V_{xx}$. The ratio

$$\eta = \frac{P_{\text{max}}}{\Phi} \tag{2}$$

is called the efficiency of the solar element. The efficiency is limited by losses on reflection, thermodynamic absorption of light, the magnitude of the quantum efficiency, recombination of excited carriers, and so on.

EFFICIENCY OF SOLAR POWER GENERATION

The order of magnitude of the power produced by a solar element is determined by the external flux Φ . The quantity of radiant solar energy incident in one second on a square of unit area oriented perpendicular to the rays of the sun and located in space at the distance of the earth from the sun



FIG. 2. Schematic diagram of a solar element based on a p-n junction: 1) grid of electrodes, 2) shielding and illuminated layer, 3) p-layer, 4) n-layer, 5) back contact and reflecting mirror. The main absorbing region is the n-layer; its thickness determines the total size of the solar element and is $10^2-10^3 \mu m$ for crystalline Si.



FIG. 3. 1) Volt-ampere characteristic of a p-n junction in the diode model, 2) volt-ampere characteristic of a solar element.

$$W = 0.1353 \text{ W/cm}^2$$
 (3)

is called the solar constant. The peak flux of light passing through the atmosphere when the sun is directly overhead is, at sea level

$$W_0 = 0.0925 \text{ W/cm}^2.$$
 (4)

The flux obviously varies depending on the time of day, the season, and the location of the solar element on the earth's surface. From the point of view of the designer, the most important characteristic of a solar element is η and the lion's share of research papers have been devoted to ways of increasing η .

For solar elements on p-n junctions the quantity η is a nonmonotonic function of E_g and has a principal maximum in the region $E_g = 1-2$ eV. Of the extensively studied semiconductors, the best material is GaAs with $E_g \approx 1.4$ eV, which almost exactly corresponds to the maximum in the number of photons in the solar spectrum. The total number of photons is

$$N \approx 3 \cdot 10^{17} \text{ photons/cm}^2 \text{sec};$$
 (5)

see Table I. Calculations give for this case¹⁶

$$\eta_{\max}(E_g = 1, 4 \,\mathrm{eV}) \approx 31\%.$$
 (6)

The efficiency drops for materials with $E_g \gtrsim 2$ eV because too small a part of the solar spectrum is being used. For materials with small E_g the excess energy of the photon $(hv - E_g)$ is wasted. Hence suitable materials for solar elements are widely used and have typical "semiconductor" values of the gap. Some examples are listed in Table I.

The efficiency can be increased somewhat by using opti-



FIG. 4. Hypothetical volt-ampere characteristics of solar elements (the dashed lines show the shift as a result of illumination): a) Ohm's law, which is unfavorable for a solar element, b) ideal nonlinear volt-ampere characteristic for a solar element.

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TABLE I. Intensity, photon number, and spectral region distributions of solar radiation and the forbidden band widths $E_{\rm g}$ of some semiconductors. All the values are rounded.

Spectral region, eV	0— 0,5	0,5— 1	1—1,5	1,5— 2	2— 2,5	2,5— 3	3— 3,5	3,5 4	4 4,5	4.5— 5	> 5
Number of photons, 10 ¹⁶ photons/sec	1	5	7	7	5	3	2	0,5	-		-
Intensity, W/m ²	10	80	190	250	250	210	140	100	80	60	30
E _g , eV	0,16 InSb, 0,28 InAs, 0,35 Te	0,68 Ge, 0,81 GaSb	1,12 SI, 1,38 GaAs, 1,04 CuInSe ₂	1,51 CdTe, 1,74 CdSe, 1,80 Se	2,23 AlAs	2,58 CdS	3,58 ZnS				

cal systems to concentrate the light (by 1 to 10^3 times). In this case, however, the heating problem must be solved, since the efficiency of a silicon solar element drops to zero at 300 °C.

Here we concentrate on the physics of the problem and do not touch upon technical problems, which today occupy the lion's share of topical conferences. However, even a purely technical problem can lead to the choice of different materials and to different classes of structures. The different paths of this evolution have already been quite extensively explored (solar elements with and without concentration of light, solar elements for terrestrial or space use, and so on).

The efficiency η can be increased significantly if concentration of light by the optical system is combined with spectral resolution. Each spectral region is then absorbed by an individual solar element with optimum E_g and other characteristics. The first solar element of this kind was made in 1978 using GaAs and Si with $\eta = 28\%$ (Ref. 17).

The principal method of increasing η is the use of layered structures, either by connecting solar elements in series, or by using a compound internal structure of the solar element (see Fig. 2).¹⁸ In the case of solar elements connected in series the upper layer absorbs the shortest wavelength photons and the lowest layer absorbs the long-wavelength photons. Then the total efficiency will be larger than the efficiency of each of the layers and the emfs can simply be added together (neglecting internal resistance). By using a compound internal structure the best conditions for absorption of light and collection of carriers (all of the photoexcited carriers should reach the electrodes) are created. The following results have been obtained so far: an absolute maximum of $\eta = 31\%$ for a solar element on a GaAs heterostructure, 25% for a solar element on a p-n junction in GaAs, 23% for a p-n junction in crystalline Si, and 17% for a solar element on polycrystalline Si (Ref. 11). In addition, thin-film layered solar elements with $\eta = 10-12\%$ have been produced (Cu₂S-CdZnS, CdS-CuInSe₂, CdS-CdTe, and also solar elements on the amorphous silicon structures a-Si:H p-i-n, which will be discussed in more detail below).¹⁹ Thin-film solar elements have a thickness of order 1 μ m. Their small volume of active material, technological effectiveness, and low cost allow them to compete successfully with high-efficiency crystalline solar elements. They

are responsible for the economic "encroachment" of photovoltaic devices.

METHODS OF OBTAINING MAXIMUM EFFICIENCY

Here it is appropriate to point out that the physical problems have not been reduced to simply the highest efficiency at the lowest cost, especially today. Maximizing the efficiency η will therefore be of great interest for a long time to come, regardless of the cost of the solar element. Solid-state technology offers wide possibilities to maximize efficiency. It is probable that in the next decade solar elements will be produced with $\eta \sim 50\%$. Possibilities are solar elements made from three, four, and more semiconductor compounds, heterostructures, superlattices, and systems with spectral resolution.

The problem of maximizing the energy of light absorbed in a semiconductor structure is of great current interest. This problem was considered in the framework of classical electrodynamics in Ch. 13 of Binzburg's monograph;²⁰ see also Ref. 21. The quantum problem (interband absorption of light) is more relevant, however. The theoretical limit $\eta = 72\%$ was obtained in Ref. 16 for an idealized layered system of p-n junctions assuming light concentration by a factor of 10³. It was assumed that photons of each wavelength λ are absorbed and generate electron-hole pairs in the proper semiconductor layer. The limiting value of η , however, will depend strongly on the details of the structure of the solar element. The heterostructures currently used are semiconductors with a staggered variation of the forbidden band width. Graded bandgap semiconductors (Fig. 5) could play a similar role. This idea was advanced at the end of the



FIG. 5. Hypothetical band structure of a graded band-gap semiconductor.

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FIG. 6. Schematic diagram of a doped superlattice solar element: 1) players, 2) n-layers, 3) "electrode" layers.

1950s and large values of η were predicted in a number of calculations, but there have been no practical results up to now.²² From the point of view of current technology, one can propose the analog of a p-i-n structure in which the *i* layer is a graded band-gap semiconductor, such as the solid solution Ga_{1-x} In_xSb_{1-y}As_y (see Fig. 5). The parameters x and y are continuous functions of the coordinate z and both decrease with increasing z.

Another possibility of optimizing the absorption of the solar spectrum is the use of composite semiconductor superlattices (in particular, saw-tooth wells and barriers with variable thickness). In this case the absorption of light energy can be increased by properly choosing the semiconductors, the size and shape of the quantum wells and barriers, and also because of effects of size quantization and the quasitwo-dimensional nature of the carriers.

Furthermore, it can be seen from Table I that there is a large fraction of high-energy photons in the solar spectrum. Absorption of high-energy photons could in principle increase the quantum efficiency by means of collisional ionization, in analogy with avalanche photodiodes.²³

Finally, an idea which was used to produce high-voltage photoelectric generators²⁴⁻²⁶ may be promising. In this case solar elements would be based on a doping superlattice (see Ref. 27, for example), where each period of the superlattice behaves like an individual solar element (Fig. 6). In each period of the superlattice there is a p-n junction and also a layer of metal (or even better, a heavily doped semiconductor). Hence the superlattice is really a battery whose voltage is proportional to the number of periods. The superlattice would be illuminated in the direction perpendicular to the axis of the superlattice and so the absorption length of light and the diffusion length of the carriers would cease to be competing structural parameters; rather, they determine the different geometrical dimensions of the system (the area of the layers and the period of the superlattice).

From the above remarks, it seems to us that the methods of band engineering can be used successfully to maximize the characteristics of solar elements such as η and V_{xx} .

AMORPHOUS MATERIALS

Solid-state solar power engineering is one of the fields of modern physics where one is not only concerned with different kinds of structures, but also with the construction of "artificial" solids, in which each atom is placed in a definite position so that when combined together they have the required properties.

Another branch of modern solid-state physics has

found application in solar power: the study of inhomogeneous disordered materials. As noted above, for terrestrial use one is not only interested in increasing η , but increasing η while reducing the cost of the solar element. A way of doing this is to make solar elements from hydrogenated amorphous silicon (a-Si:H). They are very inexpensive and yet quite efficient. For a laboratory solar element on a-Si:H of area $3 \times 3 \text{ mm}^2$ and total thickness 8000 Å we have:²⁸

$$\eta = 11,4\%, \quad V_{xx} = 0.9 \text{ V}, I_{sh} = 18 \text{ mA/cm}^2.$$
 (7)

The efficiency of solar elements on amorphous silicon can reach 15% (Ref. 29).

Pure academic research on the structure and properties of amorphous materials (at least certain classes of amorphous materials) has a direct payoff for practical application. But the operation of these solar elements have been studied far from completely.

Currently a single amorphous material is used almost exclusively: a-Si:H (work has been done on the fluorination of amorphous silicon³⁰ and also on silicon compounds with carbon and germanium). This is because of a fortunate combination of characteristics. First, hydrogenization of silicon leads to a sharp decrease in the concentration of broken bonds and therefore to a decrease in the density of localized energy levels. Second, localization occurs in the tails of the density of states along the band boundaries, while within the bands the carriers remain mobile and the mobility is quite high for an amorphous semiconductor. Hence a-Si:H is analogous to a straight-band semiconductor with $E_g \approx 1.65$ eV.

Third, although the mobility of the carriers is much lower than for crystalline Si and the rate of recombination is higher, fortunately the absorption coefficient is also significantly higher (at least by an order of magnitude and perhaps two, depending on the technology used to prepare the amorphous film).

The first papers on hydrogenated amorphous silicon appeared in 1969 (Ref. 31). It was shown in the mid-1970s that a-Si:H of 1 μ m is two orders of magnitude smaller than the thickness of a crystalline Si solar element (Fig. 7).

In spite of the fact that a-Si:H solar elements have already been produced industrially, a definitive understanding of the physics of the operation of such solar elements is still lacking. This is the case even for the structure of the amorphous material (for example, it is not clear whether one or two H atoms are required to passivate broken bonds of Si (Ref. 34). Since a-Si:H is metastable, the life of solar elements made from it is limited. A very important degradation



FIG. 7. Schematic diagram of an amorphous silicon solar element (the approximate thicknesses of the layers are indicated below): 1) grid of electrodes, 2) shielding and illuminating cover (~ 100 Å), 3) p-layer (~ 100 Å), 4) i-layer ($\sim 10^4$ Å), 5) n-layer ($\sim 10^3$ Å), 6) back contact and mirror.

was observed in 1977, i.e., a decrease in η with time.³⁵ The rate of decrease depends on the technology, but the decrease itself is due to absorption of light in amorphous semiconductors. It is assumed that the Staebler-Wronski effect³⁵ (a decrease in the dark and photoconductivities in time) is associated with the formation of "new" broken bonds, not passivated by hydrogen. The effect is reversible: upon heating to 150-200 °C the diffusion of hydrogen increases and the conductivity increases to its initial value.

We note that the physical basis of this phenomenon is not well understood. In some cases the opposite effect is observed: under illumination the conductivity first increases and then decreases.³⁶ Or it first decreases and then (the conditions of illumination are constant) the photocurrent not only recovers to its initial value, but exceeds it.³⁷

The construction of amorphous solar elements is also in a rapid state of development. For example, to increase η an attempt is being made to produce a double-layer solar element (a-Si:H-CuInSe₂);³⁸ in this connection it is possible that a search for new materials, including natural materials, will turn out to be useful.

It was shown fairly recently that in certain cases superlattices of amorphous materials can be created.³⁹ The use of an a-SiC (50 Å)-a-Si(25 Å) superlattice as the p-layer of a solar element (see Fig. 7) has been reported.⁴⁰ This superlattice plays the role of a wide-band shielding layer but at the same time it increases the efficiency because of better absorption of short-wavelength photons. We note that these superlattices (and also the superlattice a-Ge:H-a-Si:H are obtained with sharp interfaces, low density of defects, and their properties are described very well by the model of quantum wells⁴¹ (in particular, the edge of optical absorption can be shifted up to 0.25 eV by decreasing the thickness of the layers).

These amorphous materials form a separate class of substances which in many respects is analogous to crystalline semiconductors. The study of their properties and the search for new materials are problems of great current interest.

ALTERNATIVE ENERGY CONVERSION PROCESSES

Methods of using solar energy are not at all limited to those considered above. Here, however, it is not useful to compare photovoltaic devices with biological or photochemical processes of energy conversion or with solar heat collectors. Discussions of the competition between different energy sources can be found in Refs. 1,9–11,13. We only note that the total power consumed on earth is only about 1% of the energy of photosynthesis or $\sim 0.1\%$ of the kinetic energy of the atmosphere and hydrosphere. Therefore in the near future ideas about economic efficiency may change radically.

Instead of discussing new sources of cheap or expensive energy we only note that there is a limitation on the energy consumed on earth. If we are to preserve human life on the planet it will be necessary to radically change most of our technology. In the new reality solar energy will obviously be an irreplaceable component.

Solid-state photoelectric devices can be the basis of both local sources of electrical energy as well as large power installations. We note that this is still the only proven method of using solar energy in deserts, since it does not require water.

Finally, we again turn to physics. There are many different theoretically conceivable methods of converting solar energy into electrical energy, but the photovoltaic effect is known to be the most economical. In any case, the input is a photon and the output must be current carriers separated on different electrodes, which provides a source of emf. It follows from the above discussion that in the photovoltaic effect there are practically no superfluous components. An absorbed light quantum directly gives an electron-hole pair and the structure of the solar element ensures spatial separation of the carriers.

In principle, light absorption can occur because of inhomogeneities in the semiconductor heterostructure, collective excitations of the interfaces, and so on.⁴² But the absorbed energy must still be converted into the energy of the current carriers. In addition, it is usually true that light absorption is a resonance process and therefore monochromatization of the solar radiation is required at the input. The process of interband absorption in semiconductors is a fortunate exception and it is sensitive over a fairly wide region of the spectrum.

Alternative processes to the photovoltaic effect must contain at least two additional components, which would surely lead to additional losses. In the search for the highest efficiency it is difficult to compete with the photovoltaic effect. However, the discovery of a viable alternative process would be an important event in solid-state physics.

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Translated by J. D. Parsons