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Heterojunction solar cells

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This paper gives a qualitative description of semiconductor–semiconductor heterojunction solar cells. The two groups of heterojunctions of greatest economic potential, very highly efficient cells for concentrator applications and moderately efficient thin film cells for flat plates, are described with examples. These examples illustrate the role of heterojunctions in surface passivation, monolithic multijunction devices, devices with semiconductors of only one conductivity type and low-temperature fabrication techniques.

INTRODUCTION

Heterojunction solar cells are composed of two different materials – two semiconductors, a semiconductor and a metal, or a semiconductor and an electrolyte. In this paper we will consider the first of these three types. Semiconductor–metal (Schottky barrier) and semiconductor–electrolyte cells, though frequently similar in device structure, are usually considered to constitute separate classes of solar cells. The reader is referred to texts on solar cells (Hovel 1975) and on heterojunctions (Milnes & Feucht 1972; Sharma & Purohit 1974) for detailed background.

A photovoltaic cell combines two functions that permit conversion of photon flux to electric power: (i) numerous semiconductors efficiently absorb solar radiation; (ii) a space charge can be introduced in a semiconductor when it is made into a diode. This space charge separates the photoexcited electron from the unoccupied ground state, the hole, thus producing a photocurrent while retaining part of the energy of the incoming photon as photovoltage.

All types of solar cells rely on the light absorption properties of semiconductors. The absorption process of interest here takes place through exitation of an electron from the valence to the conduction band. The lowest photon energy for this band-to-band absorption corresponds to the value of the optical band gap. In direct gap semiconductors the absorption coefficient α is high ($> 10^4\ \mathrm{cm}^{-1}$) for all energies above the band gap. Virtually all heterojunction cells under study are based on direct gap semiconductors. The only important indirect gap material is silicon, whose absorption coefficient is small near band gap photon energies.

Band-to-band absorption creates electron–hole pairs with adequate lifetime for efficient spatial separation processes to operate. The light absorption, or charge separation in energy, arises from a bulk property of a given semiconductor. The charge separation in space – resulting in an electric current – depends on the way in which the semiconductor has been made into a diode.

A diode is formed when two semiconductors with different electrochemical potentials of the electron (Fermi levels) are joined. The difference in potentials causes electrons to flow from the semiconductor with the higher Fermi level to that with the lower. The resulting excess positive charge, in the form of ionized impurities, remains as a sheet of space charge adjacent to the junction between the two semiconductors. In the same way, a sheet of negative charge is introduced on the side of the junction with initially lower Fermi level. This space charge induces

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an electric field whose magnitude depends on charge density and position by Poisson's equation. A charge carrier traversing the field either gains or loses an amount of electrostatic energy equivalent to the so-called diffusion or built-in voltage of the diode. The diffusion voltage equals the difference in Fermi levels before junction formation. After junction formation, the Fermi level is equal throughout the device. This, in fact, is the equilibrium condition. The difference in electron concentration between the two partners is exactly balanced by the potential drop across the junction.

A homojunction diode consists of one semiconductor whose Fermi level initially has been brought to two different values by dissolving different types or concentrations of dopant impurities. In heterodiodes, made of two dissimilar semiconductors, doping still plays an important role. However, the diode characteristics are also determined by the different position of the two band gaps with respect to a common reference level. The band gap position is conveniently expressed as the electron affinity, the potential difference between the conduction band edge and the vacuum (reference) level.

Heterojunction solar cells are investigated not merely because they offer another method of diode formation. To list a simple classification, heterojunctions are required for or are the result of:

(*a*) surface passivation and high sheet conductance;
(*b*) monolithic multijunction cells;
(*c*) semiconductors that exhibit only one conductivity type;
(*d*) fabrication at low temperatures.

Although this list is incomplete, a discussion of its items will provide a good overview of typical current heterojunction research.

(*a*) *Surface passivation*

A major advantage of direct gap semiconductors with their high absorption coefficients is the absorption of all incident light within a small distance from the surface. With proper placement of the junction, photogenerated carriers need to travel only short distances to reach the junction. This minimizes the opportunity for electron–hole recombination in the semiconductor. Recombination reduces the external current and thus the cell efficiency. Owing to the strong absorption, however, a substantial fraction of the light is absorbed between the cell surface and the junction, instead of below the junction. The charge carriers generated in the top layer can diffuse to one of two efficient sinks: the junction whose field forces current through the external circuit, or the free surface which efficiently promotes recombination and thereby reduces the photocurrent. The highly defective free surface can be 'passivated' to suppress surface recombination by forming a junction between the absorbing semiconductor and a large gap semiconductor that absorbs little of the incident light. This type of device is called an abrupt heterodiode, as the junction is positioned within or at the edge of the space charge of the diode. An example is the p-InP/n-CdS heterodiode (Wagner *et al.* 1977) depicted in figure 1*a*. Other examples for abrupt cells are p-Cu_2S/n-CdS (Barnett *et al.* 1978), p-GaAs/n-AlAs (Johnston *et al.* 1977), p-InP/n-indium tin oxide (Harsha *et al.* 1977), p-$CuInSe_2$/n-CdS (Wagner & Bridenbaugh 1977), and p-CdTe/n-CdS (Fahrenbruch *et al.* 1976). Two critical but unresolved questions, particularly with abrupt heterojunctions, are those of lattice match and of the interface structure on an atomic scale. Lattice match, the one-to-one correspondence of atomic positions on either side of the interface, is considered a requirement for an interface free of

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those electronic defect levels that could promote undesirable recombination of electron–hole pairs. To date, no abrupt heterojunction has been analysed in sufficient details to determine interphases or very shallow type converted layers. Results of sophisticated surface and thin film analyses are likely to expand the classification scheme for heterojunctions.

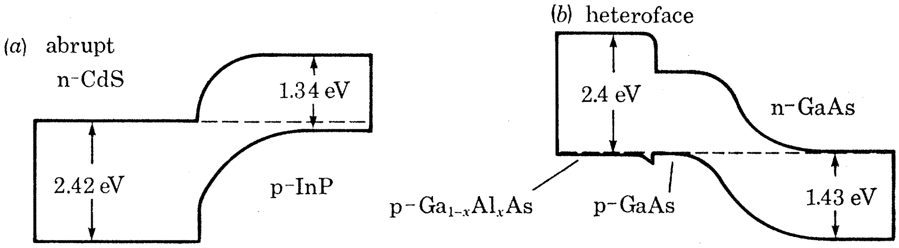

FIGURE 1. Examples of energy band structures for solar cells incorporating an abrupt heterojunction (top) and a heteroface heterojunction (bottom).

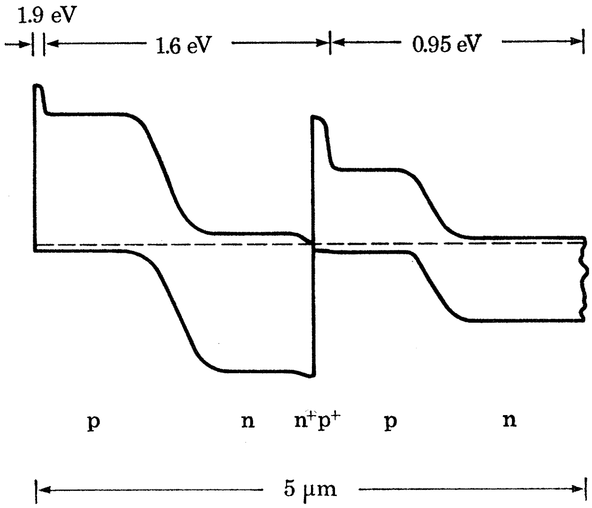

FIGURE 2. Concept of an energy band structure for a multiple junction cell with two heterojunctions, two photoactive homojunctions, and one connecting tunnel homojunction. Illumination is from the left.

Surface passivation with a large band gap 'window' layer can contribute to a reduction of the solar cell series resistance since the window thickness can be increased without impairing its transmittance for sunlight. The photocurrent flows laterally in the layer to reach a contact finger. A thicker top layer offers less resistance to this current.

Heteroface solar cells form a special but very important group of surface-passivated cell. Principal examples are cells based on GaAs with window layers of large band gap $Ga_{1-x}Al_xAs$ alloys (figure 1*b*). The typical cell is a shallow homodiode of p- on n-type GaAs covered with a p-$Ga_{1-x}Al_xAs$ layer (Hovel 1975). The p-GaAs layer is formed during preparation of the cell by liquid-phase epitaxial growth of the p-type window layer on n-type GaAs substrates. During layer growth zinc, the p-type dopant diffuses into the n-GaAs, converting a thin layer of p-GaAs. Because of the exceptional perfection of current GaAs photodiodes and because of adequate surface passivation, cells of this type have reached power conversion efficiencies close to 25%. Since thick window layers can be grown to reduce series resistance, such cells can be employed in concentrators producing photocurrents of 20 A/cm^2 at 1000 Suns.

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(*b*) *Monolithic multijunction cells*

Experience to date has shown that single junction devices are not likely to attain higher than *ca.* 25% efficiency. Current research in high-efficiency cells is directed towards spectral splitting: the cell consists of two active devices, one responding to the short, the other to the long wavelength portion of the solar spectrum. The energy gaps of these devices need to be adjusted such that the currents produced are equal. The semiconductors employed here are alloys of III–V compounds. An example of a proposed multiple (i.e. dual) junction cell involving two active homojunctions and two ancillary heterojunctions is shown in figure 2. To the left, at the surface, a thin large gap (1.9 eV) layer provides surface passivation. A second heterojunction to the right of the n^+p^+ tunnel diodes serves as the contact between the large and the small gap materials. Note the similarity of each half of this device to the heteroface cell depicted in figure 1. The first monolithic multijunction cell has just been demonstrated, albeit not in an optimized form (Bedair & Lamorte 1978). Dual junction cells are expected to reach power conversion efficiencies up to *ca.* 35%.

(*c*) *Semiconductors that exhibit only one conductivity type*

When a semiconductor can be prepared only n- or p-type, fabrication of a homodiode cell is not possible. A number of attractive candidates belong to this group, among them n-CdSe, p-Cu_2S, and p-Zn_3P_2. Heterojunction cells can use such materials. The most prominent example is the p-Cu_2S/n-CdS thin film solar cell that is discussed in more detail in the next section.

(*d*) *Fabrication at low temperatures*

Low processing temperatures are desirable, particularly with polycrystalline thin film cells, to avoid grain boundary diffusion. Diffusion of contact or substrate materials along the grain boundaries of the semiconductor layer frequently leads to shunting or shorting of the cell. Reduction of shunt effects through a thickening of the semiconductor is undesirable as it raises the cell cost. Therefore, fabrication steps that can be carried out at low temperatures are particularly attractive. In general, semiconductors produced at low temperature are more defective than those prepared with conventional methods at high temperatures. Thus, low-temperature processing is usualy not state-of-the-art in conventional semi-conductor technology but is of major interest in thin film solar cell research.

Two examples for cells that are prepared at low temperatures are the p-Cu_2S/n-CdS and the p-CdTe/n-indium tin oxide cells. Both are abrupt heterodiodes between a p-type absorber (p-Cu_2S, p-CdTe) and an n-type semiconductor ‘window’ with a large bandgap (n-CdS, n-ITO).

The Cu_2S/CdS cell can be prepared by several techniques. The ‘conventional’ process consists of evaporation of CdS onto a metallic substrate, e.g. brass, and brief (*ca.* 10 s) dipping of the CdS layer into an aqueous solution of cuprous chloride at 80–90 °C. This dipping is a displacement reaction in which Cu^+ substitutes for Cd^{2+} to transform CdS to Cu_2S. In a third step, the cell is heated in air for *ca.* 2 min at 250 °C to improve its photovoltaic characteristics. Grid metallization (to contact the Cu_2S) and encapsulation follow.

The Cu_2S layer can also be prepared by a displacement reaction in the solid state. Here, Cu_2Cl_2 is evaporated onto CdS and the structure is heated to *ca.* 200 °C to form Cu_2S. Excess Cu_2Cl_2 and $CdCl_2$ then are dissolved before application of contacts.

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In a third process, a 'backwall' Cu_2S/CdS cell is produced by a sequence of spraying and dipping techniques. In a backwall cell, the light enters through the transparent substrate. Contact to the absorbing semiconductor is made by contiguous thus opaque metallization (figure 3). For this backwall cell, a film of conducting glass, usually SnO_2, is first prepared by spraying on aqueous solution of $SnCl_4$ and of a dopant ($SbCl_3$) onto the sheet glass substrate at 400–600 °C. The conducting glass film of SnO_2 in fact is a n-type and degenerate (highly conductive) semiconductor. The n-SnO_2 provides the contact to the n-CdS. Two CdS layers are produced sequentially. First, a solution of $CdCl_2$, $AlCl_3$ and thiourea is sprayed onto the heated SnO_2/glass substrate to form a thin (*ca.* 1 µm) layer of polycrystalline CdS. This layer contains a second phase of aluminium oxide (and probably hydroxide) in its grain boundaries. Next, another 1 µm layer of CdS is applied by spraying a solution free of aluminium compounds. The aluminium oxide provides electrical insulation of the grain boundaries and permits the building of cells with very small total CdS thickness (cells with evaporated CdS use 20–30 µm thick layers). The Cu_2S is produced by the dipping process. After application of a metal contact to Cu_2S, the cell is sealed with a Pb-Sn alloy film.

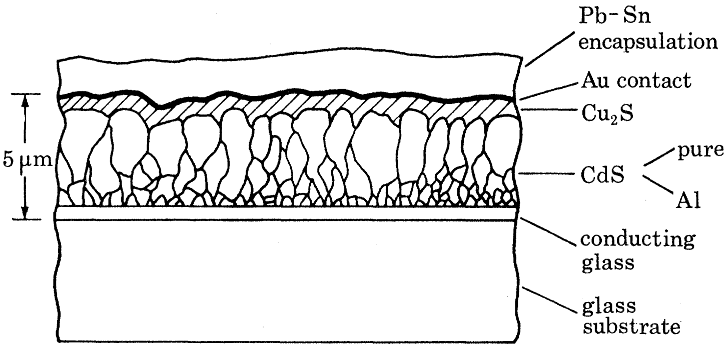

FIGURE 3. Schematic cross section of a thin film p-Cu_2S/n-CdS solar cell. Light falls on this cell from the bottom and is converted in the Cu_2S layer.

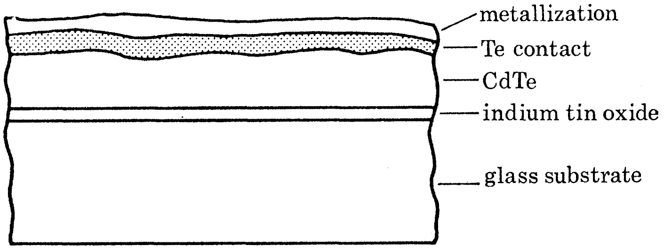

FIGURE 4. Schematic cross section of a thin film p-CdTe/n-indium tin oxide cell. Light is converted in the CdTe layer. Grain boundaries are not shown.

The sprayed cells have power conversion efficiencies of only 3–5 %, as compared with evaporated CdS laboratory cells of *ca.* 1 cm^2 area with up to 9.15 % efficiency. However, the sprayed cell is in a pre-production stage with panel sizes of approximately 40 × 50 cm (G. A. Roderick 1978, private communication).

Another heterojunction cell that is prepared by what could become a mass-production technique is p-CdTe/n-SnO_2 (R. Rod 1968, private communication). This is also a backwall type cell (figure 4) whose first fabrication step is again the deployment of a conducting SnO_2

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film on a sheet glass substrate. Next, a p-CdTe film is deposited by an electrochemical technique from aqueous solution. The electrolyte is a solution of Cd^{2+}, the two counter-electrodes are carbon (the inert electrode for controlling the Cd deposition rate) and Te, an electrode that is made to dissolve continuously to provide Te. The concentration of Te ions in the electrolyte is kept low to prevent CdTe precipitation. A pure Te layer is grown on top of the CdTe film. This p-type semiconductor provides an adequate contact to the p-CdTe. Note that in this cell, contrary to the Cu_2S/CdS cell described above, the diode is formed between the n-SnO_2 contact and the p-CdTe. This cell has shown only 1–2 % conversion efficiency in the laboratory. Nevertheless, it serves as a useful illustration for the new techniques that are introduced to semiconductor technology as a consequence of the need for production of inexpensive thin film solar cells.

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Discussion

H. Tabor. The predictions for reducing the cost of solar cells by 2–3 orders of magnitude, hence leading to cheap solar electricity, contain a hidden trap, namely the cost of storage: except for applications such as water pumping, the user of electricity usually demands firm power. To date, the cost of storage in a solar-cell installation has been trivial compared with the cost of the cells: with the cost reductions now being envisaged, storage becomes the dominant cost item. As an example, the current simplest method of storing electricity (d.c.) is the lead–acid battery. A simple calculation shows that to put 1 kWh into such a battery and take it out again costs in the region of 6 ¢. Some U.S. studies suggest using the electricity grid as equivalent to storage: clearly there are limits to this and the utility companies would need to raise their rates to compensate for lost income. Furthermore, solar electricity, in the early stages at least, would tend to be in isolated areas where, even if there were a grid, it might not be adequate for this purpose. Thus the problem of storage – which we know to be fundamental to the thermal application of solar energy – is even more fundamental in the solar-electric case.

P. T. Landsberg. The speakers have not made any reference to the degradation of solar cells. The study of these degradation processes in cells for space use has been conducted for a number of years (and we are working in this area), but the results of such tests are still far from fully understood. In the case of terrestrial cells the available evidence is sparse, but a comment on the current views in this important area would nonetheless be of interest.

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The double-hetero junction concept noted by Dr Wagner in his interesting contribution can in principle be extended to more cells. One can imagine a split of the solar spectrum into a number of components. Each component can then be incident on a properly optimized cell with a resulting considerable gain in overall efficiency. This leads to the problem of combining the outputs of these cells ('Tandem cells'). A comment on this problem area would also be appreciated.

S. Wagner. No generally accepted accelerated life test has been developed for terrestrial solar cells. However, in the opinion of many workers in the field, the semiconductor portion of silicon pn junction cells has the prospect of remaining stable over 20–30 years. Contact grids and metallic leads appear to be susceptible to degradation due to atmospheric corrosion. Here, inexpensive but adequate packaging, with emphasis on sealing of feedthroughs, will be important. It is too early to speculate about the stability of thin film cells based on polycrystalline or amorphous semiconductors, or of multijunction concentrator cells. With appropriate glazing, power reduction by accumulated dirt, found to be less severe in wet than in dry climates, will probably be of the order of 5%.

A number of calculations have been carried out for the potential conversion efficiency of multiple junction cells (see, for instance, the Record of the 13th IEEE Photovoltaic Specialists' Conference, 5–8 June 1978, Washington, D.C.; The Institute of Electrical and Electronics Engineers, New York, 1978). An achievable efficiency for a device with two active junctions appears to be 35%. Calculated efficiencies for cells with three or more active junctions lie in the 40–50% range. In these cell structures individual junctions always are arranged in series. For maximum efficiency, identical photocurrents must be generated in each junction. The numerous semiconductor alloy layers of such multijunction cells have to be tailored precisely with respect to band gap, lattice parameter, doping, thickness.

F. A. Holland. The energy pay back period for a power generating process is the time taken for the energy generated to equal the sum of the energies used in the production of materials, fabrication, plant construction and process operation, etc. A power producing system is of little value unless its enegy pay back period can be reduced to be a small proportion of its total life. What are the estimates of energy pay back periods for solar cells on the basis of current technology and what are the prospects for the future?

S. Wagner. At present, photovoltaic converters are produced with comparatively cheap energy and are deployed where energy is expensive, for instance in remote terrestrial areas or in Space. Although the energy pay back period may be long, the pay back in energy *value* is acceptable. The energy pay back period for large scale terrestrial applications was of much concern a few years ago until it was realized that competitive photovoltaic electricity implied a short pay back period. It is estimated that when cells reach the cost goal of $0.50 (in 1975 dollars) per peak-watt of generating capacity, the energy pay back period will be about one year.

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