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**MASTER**

HETEROJUNCTION SOLAR CELLS

PREPARED FOR PHILOSOPHICAL  
TRANSACTIONS OF THE ROYAL SOCIETY

BY

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## 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 and Feucht 1972, Sharma and Purohit 1974) for detailed background.

A photovoltaic cell combines two functions that permit conversion of photon flux to electric power. One, numerous semiconductors efficiently absorb solar radiation. Two, 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 excitation 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  $\alpha$  is high ( $>10^4 \text{ cm}^{-1}$ ) 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 to 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. Likewise a sheet of negative charge is introduced on the side of the junction with initially lower Fermi level. This space charge induces 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 that is 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 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.

#### 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. Due 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 the upper half of Fig. 1. Other examples for abrupt cells are p-Cu<sub>2</sub>S/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<sub>2</sub>/n-CdS (Wagner et al. 1977b), 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 those electronic defect levels that could promote undesirable recombination of electron-hole pairs. To date, no abrupt heterojunction has been analyzed 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.

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 top 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<sub>1-x</sub>Al<sub>x</sub>As alloys (bottom of Fig. 1). The typical cell is a shallow homodiode of p- on n-type GaAs



covered with a  $\text{p-Ga}_{1-x}\text{Al}_x\text{As}$  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 to 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 ampères per square centimeter at 1000 suns.

#### Monolithic multijunction cells:

Experience to date has shown that single junction devices are not likely to attain higher than ~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 Fig. 2. To the left, at the surface, a thin large gap (1.9eV) layer provides surface passivation. A second heterojunction to the right of the  $\text{n}^+\text{p}^+$  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 Fig. 1. The first monolithic multijunction cell has just been demonstrated albeit not in an optimized form (Bedair et al. 1978). Dual junction cells are expected to reach power conversion efficiencies up to ~35%.

### Semiconductors that exhibit only one conductivity type:

When a semiconductor can be prepared only n- or only p-type, fabrication of a homodiode cell is not possible. A number of attractive candidates belongs to this group, among them n-CdSe, p-Cu<sub>2</sub>S, and p-Zn<sub>3</sub>P<sub>2</sub>. Heterojunction cells can use such materials. The most prominent example is the p-Cu<sub>2</sub>S/n-CdS thin film solar cell that is discussed in more detail in the next section.

### 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 usually not state-of-the-art in conventional semiconductor technology but it is of major interest in thin film solar cell research.

Two examples for cells that are prepared at low temperatures are the p-Cu<sub>2</sub>S/n-CdS and the p-CdTe/n-indium tin oxide cells. Both are abrupt heterodiodes between a p-type absorber (p-Cu<sub>2</sub>S, p-CdTe) and an n-type semiconductor "window" with a large bandgap (n-CdS, n-ITO).

The Cu<sub>2</sub>S/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 (~10 sec.) dipping of the CdS layer into

an aqueous solution of cuprous chloride at 80 to 90°C. This dipping is a displacement reaction in which  $\text{Cu}^+$  substitutes for  $\text{Cd}^{2+}$  to transform CdS to  $\text{Cu}_2\text{S}$ . In a third step, the cell is heated in air for ~2 min. at 250°C to improve its photovoltaic characteristics. Grid metallization to contact the  $\text{Cu}_2\text{S}$  and encapsulation follow.

The  $\text{Cu}_2\text{S}$  layer can also be prepared by a displacement reaction in the solid state. Here,  $\text{Cu}_2\text{Cl}_2$  is evaporated onto CdS and the structure is heated to ~200°C to form  $\text{Cu}_2\text{S}$ . Excess  $\text{Cu}_2\text{Cl}_2$  and  $\text{CdCl}_2$  then are dissolved before application of contacts.

In a third process, a "backwall"  $\text{Cu}_2\text{S}/\text{CdS}$  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 (Fig. 3). For this backwall cell, a film of conducting glass, usually  $\text{SnO}_2$ , is first prepared by spraying on aqueous solution of  $\text{SnCl}_4$  and of a dopant ( $\text{SbCl}_3$ ) onto the sheet glass substrate at 400 to 600°C. The conducting glass film of  $\text{SnO}_2$  in fact is a n-type and degenerate (highly conductive) semiconductor. The n- $\text{SnO}_2$  provides the contact to the n-CdS. Two CdS layers are produced sequentially. First, a solution of  $\text{CdCl}_2$ ,  $\text{AlCl}_3$  and thiourea is sprayed onto the heated  $\text{SnO}_2/\text{glass}$  substrate to form a thin (~1  $\mu\text{m}$ ) layer of polycrystalline CdS. This layer contains a second phase of aluminium oxide (and probably hydroxyde) in its grain boundaries. Next, another 1  $\mu\text{m}$  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 to build cells with very small total CdS thickness (cells with evaporated CdS use 20 to 30  $\mu\text{m}$  thick layers). The  $\text{Cu}_2\text{S}$  is produced by the

dipping process. After application of a metal contact to  $\text{Cu}_2\text{S}$ , the cell is sealed with a Pb-Sn alloy film.

The sprayed cells have power conversion efficiencies of only 3 to 5%, as compared to evaporated CdS laboratory cells of  $\sim 1\text{cm}^2$  area with up to 9.15% efficiency. However, the sprayed cell is in a pre-production stage with panel sizes of approximately 40x50 cm (Roderick 1978).

Another heterojunction cell that is prepared by what could become a mass-production technique is p-CdTe/n- $\text{SnO}_2$  (Rod 1968). This is also a backwall type cell (Fig. 4) whose first fabrication step is again the deployment of a conducting  $\text{SnO}_2$  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  $\text{Cd}^{2+}$ , 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  $\text{Cu}_2\text{S}/\text{CdS}$  cell described above, the diode is formed between the n- $\text{SnO}_2$  contact and the p-CdTe. This cell has shown only 1 to 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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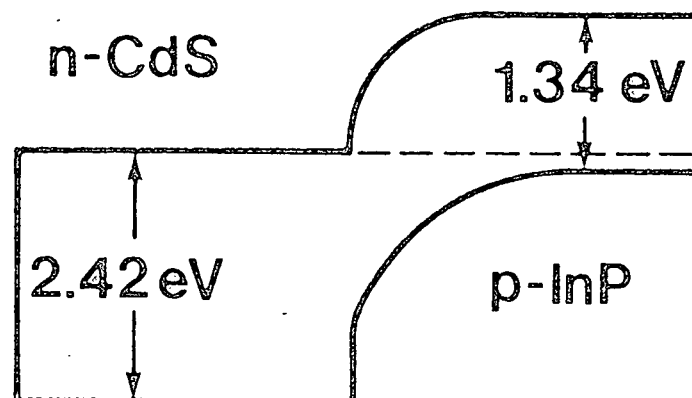
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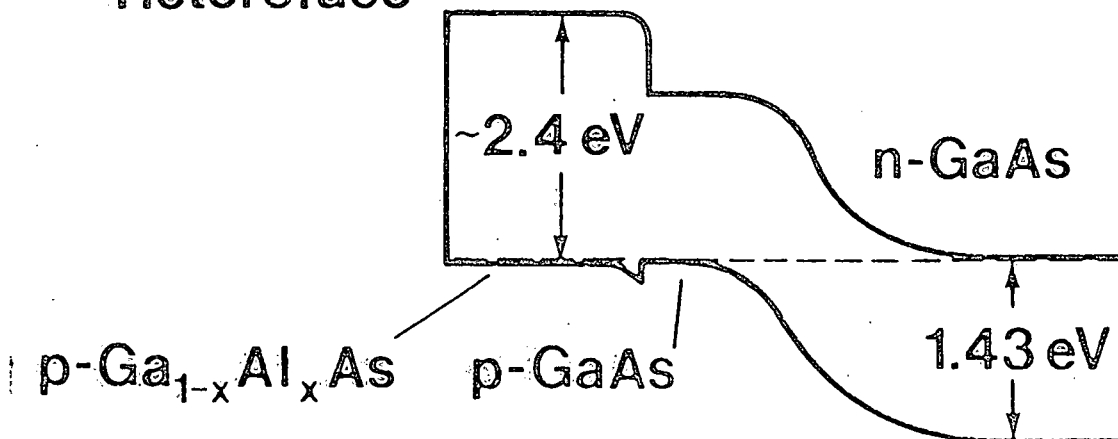
# Types of Heterojunctions

Figure 1

Abrupt



Heteroface





# Multiple Junction Cell

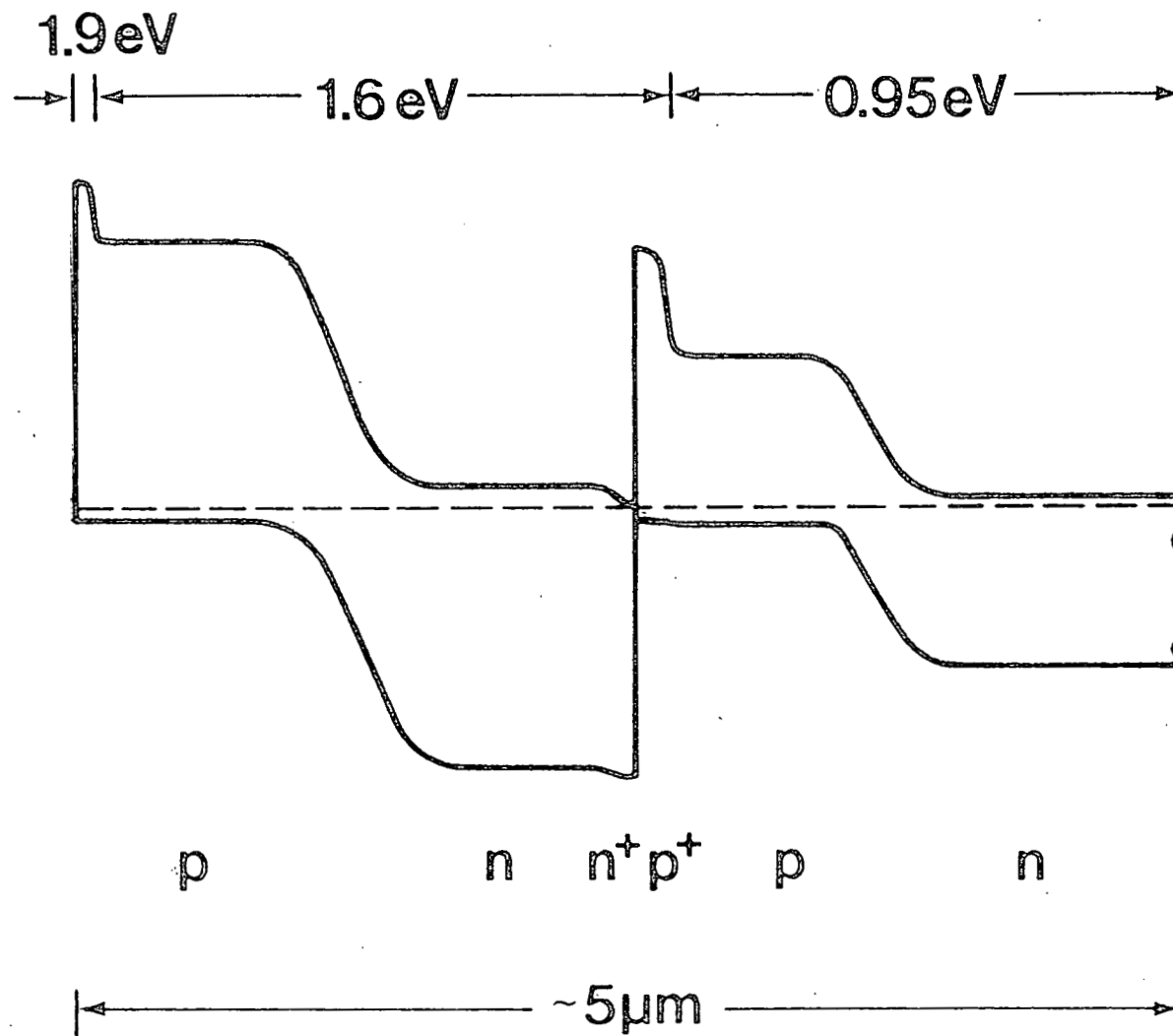


Figure 2

Figure 3

## p-Cu<sub>2</sub>S/n-CdS Cell

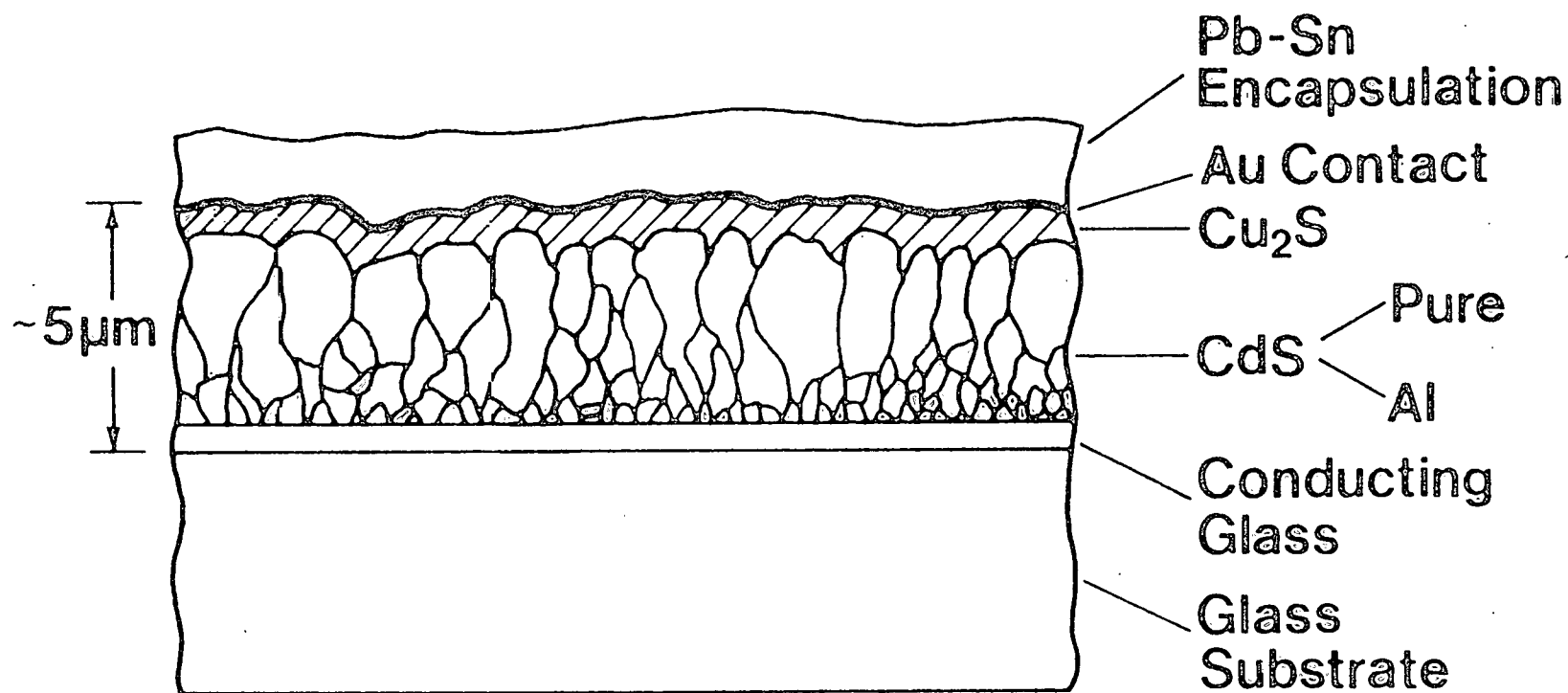


Figure 4

## p-CdTe/n-ITO Cell

