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Photovoltaic principles

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Abstract

The underlying principles of photovoltaic energy conversion are briefly reviewed, with particular reference to solar application. Although most photovoltaic converters to date have been based on semiconductor p–n junctions, more general structures and materials are feasible. The fundamental requirements for photovoltaic conversion are discussed, as is a generic approach for analysing the limiting efficiency different conversion options. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Photovoltaic: adj. *providing a source of electric current under the influence of light or similar radiation* [1].

With such a broad definition, a large range of physical effects qualifies for description as photovoltaic. Bequerel [2] is usually credited as being the first to demonstrate the photovoltaic effect in 1839 by illuminating Pt electrodes coated with AgCl or AgBr inserted into acidic solution, as in Fig. 1 [3].

The next significant development arose when Adams and Day [4] in 1876 were investigating the photoconductive effect in Se. They noted anomalies when Pt contacts were pushed into an Se bar (Fig. 2). This led them to demonstrate that it was *possible to start a current in selenium merely by the action of light*.

This led to the first thin-film Se solar cells being fabricated by Fritts in 1883 [5]. Up until the 1940s,

the most efficient photovoltaic devices used either Se, Cu₂O or Tl₂S as the absorbing layer with a rectifying metal contact as in Fig. 3 [3], a structure very similar to that earlier demonstrated by Fritts.

The first semiconductor p–n junction solar cells were described in 1941 by Russel Ohl of Bell Laboratories [6]. These junctions formed naturally in slowly solidified melts of silicon (Fig. 4). Exploration of their properties led to the understanding of the role of p- and n-type dopants in controlling semiconductor properties and hence to the microelectronics revolution [3,7]. Most photovoltaic solar cells produced to date have been based on silicon p–n junctions, although now relying on junctions formed more controllably by diffusing one polarity dopant into a wafer substrate of opposite polarity. By the late 1970s, design had evolved to that of Fig. 5. One new feature, introduced in 1974, was the use of crystallographic texturing on the top surface, to reduce reflection loss. Other features of the fabrication technology largely have been adapted from the standard or hybrid microelectronics areas.

Another significant development in the III–V compound semiconductor area was the use of

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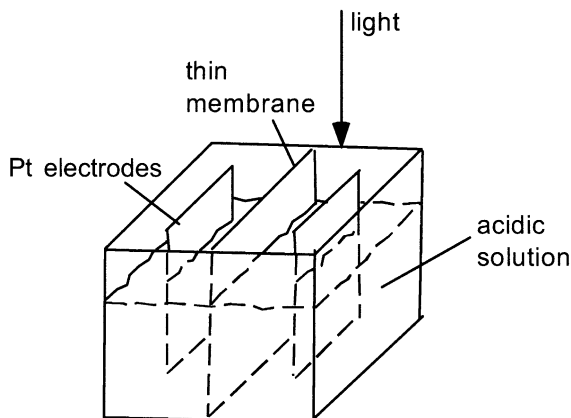


Fig. 1. Diagram of apparatus described by Becquerel [2].

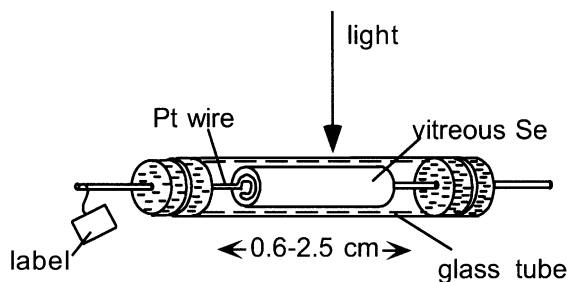


Fig. 2. Sample geometry used by Adams and Day [4] for the investigation of the photovoltaic effect in selenium.

heterojunctions formed from different III–V compounds or their alloys to produce the rectifying junction [8]. This, along with the other attributes of III–V

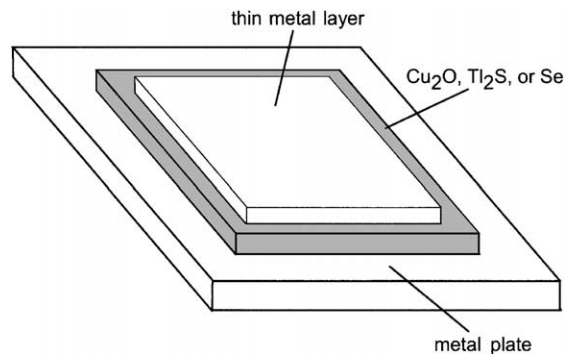


Fig. 3. Structure of the most efficient photovoltaic devices developed during the 1930s.

technology that facilitate ‘band-gap engineering’, has resulted in the most sophisticated photovoltaic devices to date. These are double- and triple-junction devices that allow the monolithic stacking of multiple cells on top of one another, so each efficiently converts a relatively narrow range of photon energies suited to its band gap (Fig. 6).

Other significant developments have been the development of thin-film II–VI and I–III–VI₂ cells [9,10], using CdS deposited by a chemical bath approach as a heterojunction window layer, and the development of heterojunction amorphous Si:C:Ge:H alloy technology [11].

Recent developments that considerably broaden the base of photovoltaics from mainstream homo- or hetero-junction semiconductor approaches include dye-sensitised nanocrystalline semiconductors [12] and organic solar cells [13].

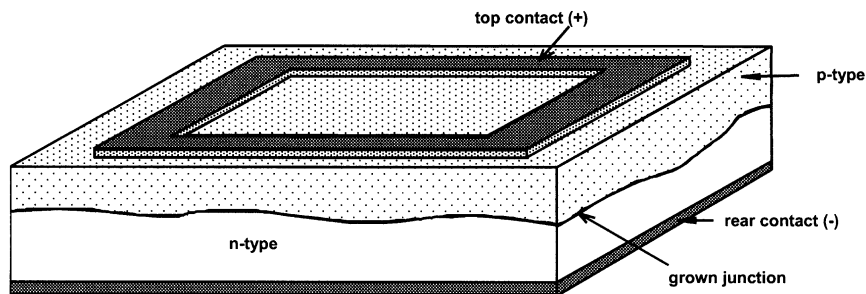


Fig. 4. Silicon solar cell reported in 1941 relying on ‘grown-in’ junctions formed by impurity segregation in recrystallised silicon melts.

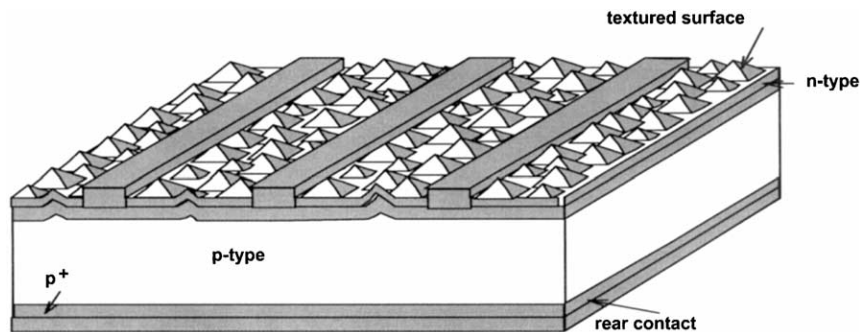


Fig. 5. Standard silicon solar cell structure developed in the 1970s.

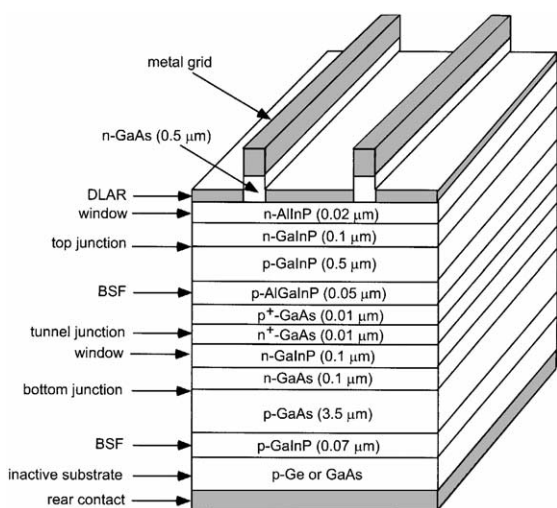


Fig. 6. Monolithic tandem space cell using two stacked p–n junctions connected by a tunnelling junction.

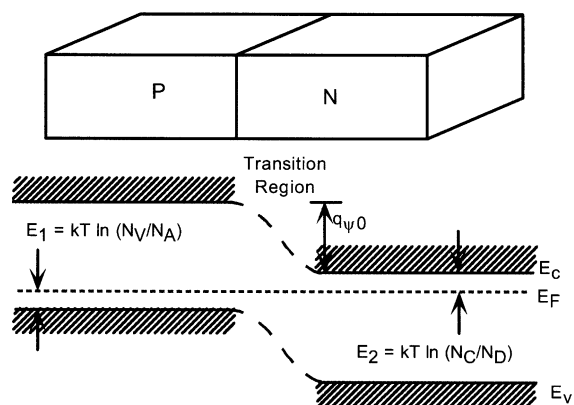


Fig. 7. A p–n junction formed by bringing the isolated p- and n-type regions together. Also shown is the corresponding energy-band diagram at thermal equilibrium.

2. p–n Junction devices

Most photovoltaic devices to date have been formed using a semiconductor p–n junction. The different work function of p- and n-type regions results in a transition region at their interface where this work function difference is accommodated by a built-in electric field (Fig. 7). Elementary treatments of photovoltaics stress the importance of this field in separating charge carriers, although this is not the fundamental mechanism for imparting directionality to carriers in most photovoltaic devices.

Light is absorbed by exciting electrons from the valence band of the semiconductor to the conduction band, throughout the volume of the p–n junction. When operating as a solar cell, the electrons excited to the conduction band flow from the p-type to the n-type side, while the holes left behind in the valence band flow in the opposite direction. Although this flow is in a direction where it is assisted by the field, the field is not the source of directionality, as previously mentioned and later discussed more fully.

The various loss processes in a p–n junction device are shown in Fig. 8. In what I have described as *the most elegant theoretical work in photovoltaics to date*, Shockley and Queisser in 1961 [14] published an analysis that allowed a cap to be placed on

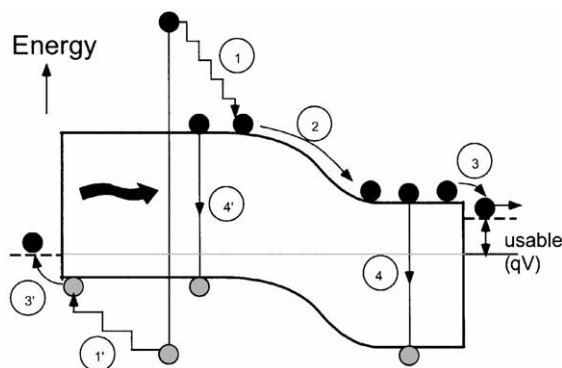


Fig. 8. Efficiency loss processes in a p–n junction solar cell: (1) thermalisation loss; (2) junction loss; (3) contact loss; (4) recombination loss.

p–n junction performance, regardless of likely future improvements in material quality or device design. The analysis notes that any device that absorbs light must emit light. In essence, light emission above the band gap in high-quality p–n junctions can be regarded as black-body Planckian radiation, enhanced by an exponential factor dependent on the diode voltage, as deduced by the following argument.

A diode with zero applied voltage in thermal equilibrium is in equilibrium with encompassing black-body radiation at its temperature. At each wavelength above the band gap, the diode absorbs a fraction of incident black-body radiation given by its spectral absorptance and emits the same fraction, according to Kirchhoff's law. The physical source of this emitted super-band gap radiation is predominantly band-to-band radiative recombination within the diode. Much of the light emitted during this recombination is re-absorbed, internally reflected and so on within the diode, with only a fraction reaching the exterior, balancing the incoming.

If a voltage is now applied to a high-quality diode, the product of the electron and hole concentrations will increase exponentially throughout the diode volume. This exponentially increases the radiative recombination rate throughout. As the same fraction of this is re-absorbed internally, reflected, etc., as before, the emitted light increases exponentially by the same factor. In a perfect device, each emitted photon would correspond to the flow of one electron in the diode terminals, allowing the best-possible product of

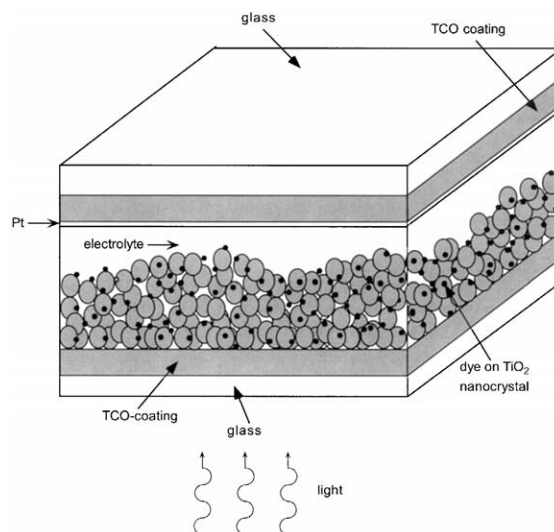


Fig. 9. Nanocrystalline TiO_2 dye-sensitised solar cell.

device current and voltage to be calculated. In this way, a limiting conversion efficiency of 31% is calculated for a p–n junction cell.

The best experimental devices approach this limiting performance. For example, even though silicon is often thought to have poor radiative efficiency, cell design has evolved to the stage where experimental cell efficiency of 25% approaches the Shockley–Queisser limit quite closely. A recent measurement [15] shows that about 10% of the recombination events in such a device are radiative. When used in the reverse mode as light emitting diodes, the performance of these silicon devices is not to much below that of the best III–V devices that have been developed for this application [15].

3. Dye-sensitised cells

In a p–n junction cell, the light absorption and photogenerated carrier transport processes occur side by side throughout the device volume. Dye-sensitised cells [12] exhibit a different mode of operation. Here, absorption occurs at a very specific location at the dye molecules attached to a porous titania medium (Fig. 9).

In the dye-sensitised cell, photoabsorption excites an electron to a high energy within a dye molecule

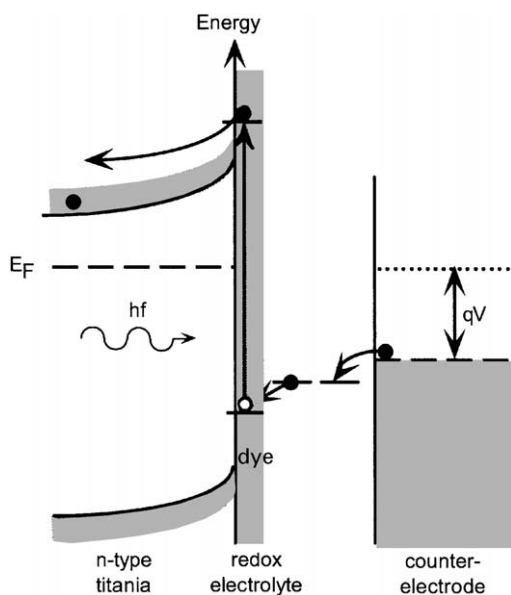


Fig. 10. Energy relationships in a nanocrystalline dye cell in region where the titania semiconductor is coated by the dye.

adjacent to titania (TiO_2), a large band gap n-type semiconductor (Fig. 10). The excited electron quickly drops into the conduction band of the TiO_2 and is transported away from the generation site. The state from which electron was originally excited is replenished by electrons shuttled across a liquid medium. Light absorption prospects are increased by depositing the titania in a porous form that gives a large surface area to be coated with the dye. The liquid solution can also penetrate the pores allowing even the most inaccessible dye molecules to be recharged.

From the point of view of photovoltaic principles, the interesting feature of this conversion process is that the light absorption and charge transport processes are largely decoupled. The presence of semiconductors, both TiO_2 and transparent conducting oxide at the contacts, is largely incidental to the conversion process, suggesting that semiconductors may not be essential components of photovoltaics.

4. Fundamental photovoltaic requirements

The previous examples allow the fundamental requirements for photovoltaics to be formulated (Fig. 11).

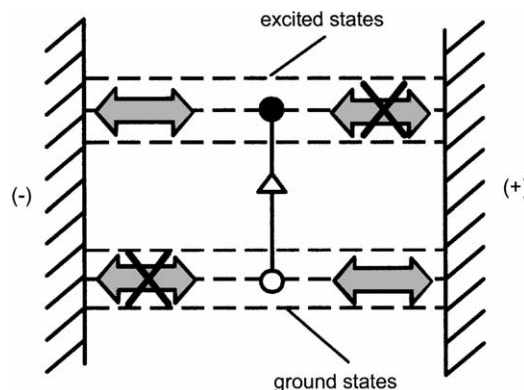


Fig. 11. Essential requirements for photovoltaics.

It seems that an essential requirement should be that the photon be absorbed by exciting electrons from a low-energy state to a high-energy state. Although processes such as the thermoelectric effect are possible where electricity can be produced from light by its heating effects (phonon production), most would not regard such effects as photovoltaic. Perhaps, a qualifier such as *by the direct release of charge carriers* needs to be added to the definition at the beginning of this paper to hint at this difference.

After excitation, some method is needed for extracting the electron from its high-energy state and transporting it to the high electron energy (negative potential) contact and another method for replenishing the vacated low-energy state from the low-energy (positive) contact. An important requirement is that the high-energy contact not be able to supply carriers readily to the low-energy state as this would just waste the energy of the excited electrons. Similarly, the low-energy contact should not be readily able to extract carriers from the high-energy state, for the same reason. The energy selectivity required for the contacts is suggested in Fig. 11.

For the nanocrystalline dye cell, it can be seen that this energy selectivity in contacting the ground and excited states is obtained in different ways for positive and negative contacts. The excited state is contacted by the conduction band of the titania. This lies much higher in energy than the ground state, making relatively poor contact to it, although electron loss due to this contact is the source of much of the loss in the device. The ground state is contacted by the redox

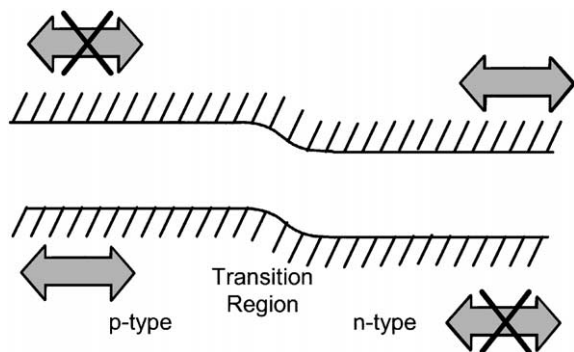


Fig. 12. Essentials of p–n junction solar cell operation.

couple modules. The excited state in the dye lies well above the energy at which this couple can accept and supply electrons.

If we apply this insight to a p–n junction device (Fig. 12), we note that conduction band electrons move freely in n-type materials while holes do not. Similarly, holes move freely in p-type material while electrons do not. This selectivity can be enhanced by design features such as back and front surface fields.

The fundamental reason why a p–n junction works well as a solar cell is not due to the field at the junction. Rather, it is due to the fact that the n-type region allows selective contact to the conduction band (excited states), while the p-type region allows selective contact to the valence band (ground state). The junction field is incidental to the operation. This has been demonstrated by simulation of devices where collected carriers are opposed by all fields in the device [16]. Devices such as amorphous Si:H are strongly reliant on built-in fields to enhance the conversion process rather than to make conversion possible.

In a standard p–n junction, selective contact is made to the whole range of energies corresponding to the conduction band and to those corresponding to valence band energies. An interesting development of this feature applies to ‘hot carrier’ cells [17], where the negative contact has to be made to a single energy in the conduction band and the positive to a single energy in the valence band [18].

5. Advanced approaches

The minimum possible leakage that the selective contacting approach will allow is that determined by

radiative relaxation between the excited and ground states as given by the Shockley–Queisser formulation [14]. Hence, the same limit applies for p–n junction and dye sensitised cells.

The Shockley–Queisser approach was put on a more complete basis in 1980 [19] and extended to the tandem cell (Fig. 2) and hot carrier cells at about the same time [17,20]. It was subsequently extended to approaches where high-energy photons are able to create more than one electron–hole pair [21]. More recently, it was applied to cases where excitations between more than two bands are possible, such as when an impurity band is present, as well as the conduction and valence band [22].

The most recent extension has been to the impurity photovoltaic effect, where excitation is possible via a defect level at intermediate energies between the two main bands [23]. This analysis would also be applicable to enhanced dye-sensitised cells, where the excitation through a series of different excited levels was possible [12]. In principle, it is possible to nearly double the energy conversion efficiency in this way from that of a standard device [23], as for the other approaches mentioned above.

6. Conclusion

Photovoltaics requires the excitation by light of an electron from a ground to an excited state, with some way provided both for selectively extracting excited electrons and for replacing those in the ground state. Reverse radiative recombination processes from the excited to the ground state provide the limits on the conversion efficiency on such a process, although at least double the efficiency of the standard process is possible in principle by extensions to it.

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