THE PHOTOVOLTAIC EFFECT, ITS PRESENT UNDERSTANDING AND REMAINING MYSTERIES*

Karl W. Böer
University of Delaware, Newark, DE 19711
and SES, Inc., Newark, DE 19711

1. PRESENT UNDERSTANDING AND LIMITATIONS

The photovoltaic effect was discovered 140 years ago by Becquerel (1) using liquid electrolytes and just about 100 years ago by Adams and Day (2) in solid selenium.

Today, it is generally accepted that the photovoltaic effect, characterized by the generation of a current by light from a photocell through an external circuit without an externally applied voltage, can be described as caused by minority carrier generation through the light in one part of the cell (we will call this part the emitter as it is able to emit these minority carriers into the junction) and separation of these from the oppositely charged majority carriers by a built-in field (the junction). This built-in field provides a "cliff" towards which the minority carriers (here assumed to be electrons) may diffuse, and, when reaching it, will slide down the cliff and away from their place of origination. When an external circuit provides a path, many of these electrons will use this path to return to their birthplace within the emitter in order to recombine with their majority carrier counterpart, rather than to try to jump backward over the cliff. A photovoltaic current will flow. If the external circuit is an electrical short, this current is called the "short circuit current". However, when no external circuit of sufficient conductivity is available, the region beyond the built-in field (in a p-n junction photovoltaic cell, we will call this part the collector) will be charged-up causing a reduction of the height of the cliff until the current caused by electrons sliding down the cliff is equal to the current in opposite direction for electrons climbing up the cliff. This charging of the collector relative to the emitter can be measured and the potential built-up for no load condition is referred to as the "open circuit voltage".

1.1 Current-Voltage Characteristics

The electrical behaviour is analyzed correctly by calculating the current in the emitter by balancing generation and recombination with leakage to the surface determined by surface recombination and with the current towards the junction determined by the electron density at the emitter-junction interface. The corresponding voltage drop can be obtained by properly integrating transport and Poisson equation through the junction for the same electron density as one of the boundary conditions. This idea, first properly developed for dark p-n diodes by Shockley (3), and in some simplified form applied for photocells by Cummerow (4) and improved by others more recently (5-7) leads to the well-known basic photocell equation

\[ j = j_0 \exp \frac{eV}{KT} - j_L \]  \[ \text{[1]} \]

with \( j_0 = j_{oo} \exp \frac{e\Phi}{KT} \) and \( j_{oo} \) of the form \( eN_{L1}c_{n1}r_{n1} \).

The simplicity of this equation, combined with the suggestive ease to accept current "injection" as cause for this "parallel shift" of the dark characteristic, misguided most researchers into accepting the validity of Eq. 1 at least throughout the entire fourth quadrant and slightly into the third and first quadrant of the photo diode characteristic (Superposition Principle (8)). In fact, however, the validity of Eq. 1 is restricted to the Boltzmann range, in which the total carrier current is small compared to drift and to diffusion current, a range usually only a few \( \frac{KT}{e} \) around \( V_{oc} \), as can be shown by integrating transport and Poisson equations (7).

Proper computer integration of transport and Poisson equations under consideration of the sliding boundary condition \( n_j(j) \) leads to the correct current voltage characteristics. Such integration should replace the present practice to introduce fudge-factors, usually as series and shunt resistance and parallel connection of various diodes in order to...
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achieve improved agreement between theory and experiment. The problem with this practice is, that, even though sometimes there are such parameters as series resistance, etc., which modify the characteristics, while at other times a very similar behaviour may be simulated for totally different reasons with the obvious dangers to be misleading.

Moreover, excellent work was done by Sah, Noyce and Shockley (9) and extended by Choo (10) to include recombination in the junction. However, here again one must be careful to accept linearization, i.e., the simple addition of a current component only near $V_{oc}$.

Proper inclusion of the changes in charge distribution throughout the junction — by trapping, charge release and recombination — into the Poisson equation before integration is essential for an improved analysis. On the other hand, the task to perform such an analysis in each case seems to be excessive, and, for reasons of the many adjustable parameters, the results may be less than convincing. However, there are already some indications that, by systematic mapping, specific segments of the characteristics can be identified which are affected in a specific fashion by certain charge redistributions within the junction, hopefully providing improved, more unambiguous, diagnostic tools.

1.2 High-field Effects

Depending on junction space charges and bias, junction fields are usually in the range from 10 to several hundred kV/cm. These fields are sufficient to cause redistributions of carriers in the junction, e.g., by Frenkel-Poole effect in the lower (11) and by impact ionization or tunneling in the higher field range. Such field-induced changes of the trapped charge distribution provide a needed adjustment mechanism to permit the joining of the two quasi-Fermi levels throughout the junction, a task easily achieved by a simple charge exchange for one Fermi-level (dark-case) but requiring specific changes in generation or recombination kinetics when the cell is illuminated.

A particularly attractive field-related mechanism is that of field-quenching (12, 13), a term related to removing minority carriers by high fields. This mechanism permits utilization of a material of relative low purity which otherwise, by depletion of majority carrier traps in the junction, would build-up excessive fields; however, long before these fields are reached, the minority carrier traps are also depleted by field-quenching, hence reducing the space charge and consequently limiting the field. Copper-doped CdS is probably such a material which is known to be well suited as junction and collector material without requiring excessive purification.

Other materials may behave similarly.

1.3 Heterojunction

Sufficient knowledge of the band interconnection at an (abrupt) heterojunction is prerequisite for any meaningful analysis of such photovoltaic cells. The common practice to use the difference of electron affinities to obtain first estimates about the sign and magnitude of the "discontinuity" of the conduction band (14, 15) is insufficient as it assumes the independence of surface dipole moments from other materials and their structure when brought in contact (or at least cancellation of the changes induced in the two contacting materials) (16-19).

Recently, experimental evidence was obtained that the dipole moment between the Ge and GaAs lattices indeed depend significantly on the crystallographic orientation of the interface (19).

It is, therefore, imminent to reevaluate the band structure at the heterojunction interface. Often, there is substantial lattice mismatch causing a mismatch dislocation network, which is probably charged in partially covalently bond material. Even at only 1% mismatch, this results in a too large layer charge ($-10^{14}$ cm$^{-2}$) with an excessive and uncontrolled field jump. Charge compensation near such dislocation network occurs preferentially within one material, hence producing a double layer with a potential jump (20) up or down depending on the sign sequence of such double layer. This potential jump is of the order of a few tenths of an eV, hence modifies majorly the jump deduced from differences in electron affinities.

Before a better bulk-to-bulk related theory of the ideal band connection is worked out, possibly continuing along the basis given in (18), which may necessitate some corrections to the above introduced step, it may be better to start from the real junction with mismatch dislocations, the density of which is usually well-known, and study origin and solubility of compensating defects to estimate sign and magnitude of the potential jump at the interface.

1.4 Junction or Interface Recombination

Recombination in junctions are usually increased compared to either n- or p-type region since compensation within this junction brings donors and acceptors in closer proximity, and donor-acceptor pairs are known to act as effective recombination centers (21).

In heterojunction, the special geometrical arrangement of compensating defects surrounding each dislocation line in the form of a cut-in-half pipe may provide an increased probability for recombination when this
charge cloud is Coulomb-attractive for the photo-generated minority carriers and lies within the emitter material, so that these carriers can be easily trapped and finally recombine.

In the first case of a homojunction, recombination may extend over a layer of width comparable to the junction thickness. Here, proper accounting of all important transitions and consequent changes in the defect charges within the Poisson equation is essential.

In heterojunctions, however, the double layer due to mismatch dislocations is usually substantially thinner than the junction, hence the characterization of such recombination by one parameter, the interface recombination velocity may be sufficient.

1.5 Various Items in Need for Improved Understanding

In following the outline given in the preceding section, it should be, in principle, a matter of straightforward analytical analysis to describe the photovoltaic effect of any material or material combination, provided their relevant properties are sufficiently known. Except for the mysteries — a few are already identifiable, see Sec. 2 — this may indeed be so, however, in the photovoltaic cell more detailed knowledge of a number of usually not so readily available parameters is requested, as indicated below.

1.5.1 Emitter

Extensive knowledge of the spectral distribution of all optical constants, minority carrier mobility and lifetime as function of the temperature and of typical doping (up to high doping levels) and the surface recombination velocity as function of temperature and for different means of surface passivation are prerequisite to analyze the basics of the emitter operation at various intensities and temperatures.

However, for some cells, other parameters are equally important: For instance, in frontwall cells in which the emitter for achieving sufficient conductivity is heavily doped, sometimes to a degenerated state, the band gap narrowing with doping must be known. The lifetime of minority carriers is known usually only for thermalized carriers. Light with energy larger than gap energy could cause a different lifetime of higher energy minority carriers. Except for some direct gap, frontwall cells with high minority carrier mobility (where diffusion encompasses only few scattering events) and for an analysis of high surface recombination velocity, hot carrier effects are of minor importance. Not so, however, is Auger recombination as a possible limitation for high sunlight concentration-caused minority carrier densities.

1.5.1.1 Driftfields

When properly applied, driftfields can be helpful in emitters to increase the minority carrier collection efficiency. An example for this is the thin p⁺ (Al-doped) layer near the back contact of a p⁺/n⁺ Si solar cell. Here, the driftfield helps to keep the electrons from recombining at the back electrode. Extended regions with driftfields were investigated by Wolf and Rauschenbach (22); however, these carry as penalty a reduction in the open circuit voltage ΔVoc = Fd · d (d = thickness of driftfield layer) and, even though the collection efficiency increases, they may or may not offer advantages for the collectable power.

1.6 Non-Planar Photocells

Texturing of the outer surface is believed to be beneficial as it reduces the intensity of reflected light (velvet effect for pyramidal surface structures typical for etched Si and CdS/Cu₂S solar cells) (22, 24).

However, sometimes a penalty is encountered if the junction itself is also undulated and contains regions where the adjacent emitter receives less light, as e.g. from the Cu₂S extending into the etched-open grooves between the CdS grains. Here the parallel-connection between more or less excited microcells causes a reduction of the open circuit voltage which is typically of the order of 50 mV (7).

1.7 Surface Passivation Layers (Windows)

Especially in frontwall cells, the application of a "window" which shows little interface recombination is of advantage to reduce the surface recombination velocity compared with an emitter with "natural" surface adsorbates (or chemisorption) and slows down degradation via corrosive atmospheric influences. GaₓAl₁₋ₓAs/GaAs (5) and Cu₂O/Cu₂S - CdS (7) are typical examples for such passivation. An extended study beyond some original estimates (5) why the interface recombination velocity is so low in these couples could shine more light onto the selection criteria to be applied for other advantageous window/emitter couples.

2. REMAINING MYSTERIES

There are probably mysteries left not known yet to us and only indicated when more knowledge is assembled. However, these general problems are already identifiable which need substantially more work until a satisfactory answer can be developed.
2.1 How Much of the Junction (and Collector) Needs Optical Excitation?

The answer is seemingly simple if additional recombination in the junction (or interface) can be neglected: Since the open circuit voltage is equal to the difference between the two quasi-Fermi levels in the emitter as long as the minority quasi-Fermi level continues flat into the collector, one needs to avoid collapsing of the two quasi-Fermi levels in the junction before the collector is reached, i.e., before the minority carrier has turned into the majority carrier with only negligible density change due to the photocarriers from the emitter.

However, with additional (minor) minority carrier generation from the collector, the situation is not quite so clear-cut; and enhanced recombination in the junction makes the problem even more complex: It forces true integration of both carrier transport and Poisson equations throughout the junction with substantial increase in complexity, mostly for reasons of some unknown boundary conditions and an almost impossibility to hit the singular point at the other side of the junction when starting with the integration near the singular point at one side of the junction (singular points: \( n = \text{const} \), \( F = \text{const} \) in the n-type and \( p = \text{const} \), \( F = \text{const} \) in the p-type material).

2.2 Band Connection With Interface Recombination

At first view, interface recombination at a heterojunction does not seem to have anything to do with the connection of bands at the interface. However, a simple example convinces us of the opposite: Let us assume a CuS/CdS-type of abrupt heterojunction with no interface dipole layer, i.e., a connection of both conduction bands without a jump (25).

The current from the CuS into the junction is given as electron diffusion current. The electron current, after entering through the interface, remains constant in the CdS (no optical excitation assumed here). Current continuity within the junction is achieved as the (constant) difference between drift and diffusion current, controlling a certain profile \( n(x) \) in CdS.

Now, let us introduce interface recombination. As a result, an additional electron and hole current will flow within the CuS towards the interface; therefore, for the same net current into the CdS, the electron density at the interface in CuS will be lowered. However, in CdS, the current entering and, hence, the difference of drift and diffusion current will remain the same. Since there is no optical carrier generation in CdS, the junction will not recognize the existence of additional recombination centers at the interface (the hole current in CdS is negligible), hence the profile \( n(x) \) in CdS does not depend on interface recombination.

This means that both the conduction bands and the quasi-Fermi level for electrons in CdS, will slide down (without changing its relative distance) until \( E_F \) connects at the interface, leaving, if the resulting current is zero, a jump of the conduction bands of the magnitude equal to the lowering of \( E_F \) at the interface of CuS due to interface recombination (25).

Hence, the interface dipole layer causing such jump must be adjustable by interface recombination.

This example explains the principle involved. Obviously, more complex consideration must be given if an interface dislocation network is involved, and optical excitation occurs also within the CdS.

Another interesting consideration, following similar basic concepts, may be given to increased recombination within a homojunction.

2.3 Current Continuity Through An Interface

Except for interface recombination, electron and hole currents have to be continuous through an interface, e.g. through an abrupt heterojunction interface. With band discontinuities, this poses some additional difficulties as best seen from the following example: Let us again discuss the simplified CuS/CdS heterojunction, however, now including a step of the conduction bands at the interface and assume open circuit condition. Obviously, the electron current across the junction interface must be zero (the hole current across this interface is zero). This means that the current of electrons passing this interface to the right must be equal and opposite in sign to the current to the left. There are electrons which can move above and below (in traps) the conduction bands. The total current can be estimated only by proper integration of all components over all energies. Moreover, an electron transfer from one material into the other needs consideration of the density of states in each material at the given energy. Even an electron transfer from one conduction band into the adjacent one will only be partial, similarly as an electromagnetic wave, when impinging onto the interface between two transparent materials will be partially transmitted and partially reflected. Finally, when electrons are transmitted from the lower edge of the conduction band of one material high into the conduction band of the other, they need several scattering events to thermalize, i.e., their mobility will be different in the first part of the junction.
3. GENERAL CONCLUSIONS

The present understanding of the photovoltaic effect seems to be fairly well advanced, its mathematical description, however, is still cumbersome, since a systematic mapping of the different influences of device parameters on the main output function, the current-voltage characteristic is not yet performed.

In its absence, a rather simplified picture of a current generator in parallel to one or more diodes with a resistive network is presently used by most investigators for guidance of their work. This mathematically rather questionable approach provides nevertheless sometimes quite useful assistance, as indeed presently many devices are still deficient in performance because of excessive series resistance and alike. However, more and more new and different reasons of performance limitations are discovered, and, in order to optimize performance, one needs to approach through a more refined theory.

On the other hand, how many of the present mysteries are still important? Some of them seem to offer modifications which could well disappear in the round-off error; maybe the mobility of hot electrons being one of those. Others — the jump of the conduction bands adjusted by recombination at the interface — may be much more significant.

In conclusion, we feel that a sophisticated theoretical analysis needs more sound and careful research and less of an attitude that the factors involved in understanding the photovoltaic cell and controlling its properties are "rather prosaic and can be treated simply" (26), before we will understand why as examples, CdS/Cu2S solar cells have presently less than 10% efficiency, CdZn1-xS/Cu2S less than 7% and Cu2O solar cells less than 1% efficiency, although we expect much more. Only then will we have a better chance to avoid present obstacles and improve efficiencies significantly, rather than restricting our research to improving photon absorption and engineering our cells by reducing simple losses.

4. REFERENCES

(1) E. Becquerel, Compt. Rend. 9, 561 (1839).