

How the relative permittivity of solar cell materials influences solar cell performance



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ABSTRACT

The relative permittivity of the materials constituting heterojunction solar cells is usually not considered as a design parameter when searching for novel combinations of heterojunction materials. In this work, we investigate the validity of such an approach. Specifically, we show the effect of the materials permittivity on the physics and performance of the solar cell by means of numerical simulation supported by analytical relations. We demonstrate that, depending on the specific solar cell configuration and materials properties, there are scenarios where the relative permittivity has a major influence on the achievable conversion efficiency, and scenarios where its influence can be safely ignored. In particular, we argue that high-permittivity materials should always be the preferred choice as heterojunction partners of the absorber layer when prototyping new materials combinations. When the heterojunction partner has a high permittivity, solar cells are consistently more robust against several non-idealities that are especially likely to occur in early-stage development, when the device is not yet optimized.

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1. Introduction

Within the last few years, impressive power conversion efficiencies have been demonstrated by various heterojunction solar cell technologies. Si-based heterojunction intrinsic thin layer (HIT), CdTe, Cu(In,Ga)Se₂ (CIGS), and metal halide perovskite solar cells have all reached efficiencies above 20% (Green et al., 2016; Jackson et al., 2016) and can be manufactured at a relatively low cost. The earth-abundant and non-toxic absorber Cu₂ZnSn(S,Se)₄ (CZTS) has also been investigated extensively and has reached a promising 12.6% record efficiency (Wang et al., 2013).

Assuming a p-type absorber material, heterojunction solar cells typically feature a moderately doped thin layer (n-type), often called “buffer layer” or “intrinsic layer”, as the immediate heterojunction partner of the absorber layer. This is followed by a layer with heavier doping (n⁺-type), often called “window layer” or “electron transport layer”. Such a solar cell architecture is shown in Fig. 1. Especially for CIGS and CZTS solar cells, there is an ongoing effort to replace the standard CdS buffer layer with another material (Naghavi et al., 2010). The reasons are the toxicity of Cd and relatively low band gap of CdS (2.4 eV), which means that an

appreciable fraction of light is absorbed in this layer, where carrier collection efficiency is low.

Selection of potential candidates as buffer layer materials is typically based on criteria such as (1) wide band gap, (2) natural occurrence of doping of opposite type as the absorber layer, (3) favorable conduction band offset with the absorber layer, (4) lattice matching with the absorber layer, (5) good coverage of the absorber layer, (6) absence of detrimental chemical interdiffusion with the absorber layer. While all the above reasons are valid, efficiency limitations arising from an unfavorable relative permittivity of the buffer layer have not been discussed in detail. In general, the relative permittivity $\epsilon_r(\omega)$ of a material, also known as dielectric constant, depends on frequency ω or, equivalently, on photon energy. It describes how the material polarizes under the application of an electric field. For solar cell applications, two spectral regions are of primary interest. The first is the static permittivity $\epsilon_r(0)$, or simply ϵ_r , which describes polarization under a constant electric field. This is a relevant quantity in the depletion region of a solar cell, where a constant electric field exists due to the presence of a space charge region (Sze and Ng, 2004). The second important spectral region corresponds to the solar spectrum (optical frequencies). In this region, the relative permittivity becomes a complex number and describes the optical phenomena of light absorption and refraction in the solar cell material (Crovetto et al., 2015; Crovetto et al., 2016). Optical optimization of solar

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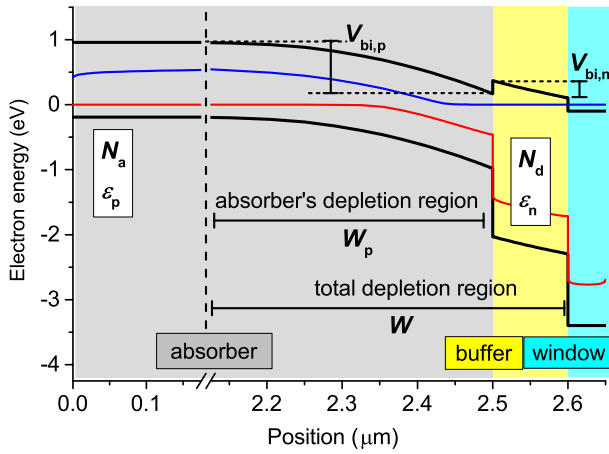


Fig. 1. Simulated band diagram of the baseline solar cell used in this work, under standard AM 1.5 illumination and with no applied voltage. The case of the high-permittivity ratio is plotted ($\epsilon_p = 13.6$ and $\epsilon_n = 20$). The black lines are the valence and conduction band edges. The blue (red) line is the quasi-Fermi level for electrons (holes) under illumination. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cells has already received much attention in solar cell research and will not be treated here. Instead, this work will focus on the static component of the permittivity while the optical component is kept fixed. The static component will be simply called “relative permittivity” or “permittivity” in the following for simplicity.

To study the effect of the materials permittivity on solar cell performance, we will use a generic absorber/buffer/window solar cell architecture inspired by CIGS solar cell technology. This approach follows the recommendation of a reference book on heterojunction solar cell design (Scheer and Schock, 2011). Throughout this work, we will present different scenarios in which the relative permittivity of the solar cell materials affects the power conversion efficiency significantly. We will show which physical mechanisms are responsible for the observed changes in efficiency and we will quantify such changes by device simulation. Based on those results, we will suggest a design rule for the relative permittivity of novel heterojunction solar cell materials. The rule is relatively easy to implement since the relative permittivity of materials is usually known or easily measurable (Tereshchenko et al., 2011).

2. Theory

2.1. Effect on depletion region width

Using standard equations for p-n heterojunctions in the depletion approximation with a p-type absorber and an n-type partner, the effect of the relative permittivity of the two heterojunction materials on device operation can be summarized by two mathematical relations (Sze and Ng, 2004). The first is

$$W = \left[\frac{2V_{bi} \epsilon_n \epsilon_p (N_d + N_a)^2}{e N_d N_a (\epsilon_n N_d + \epsilon_p N_a)} \right]^{1/2} \quad (1)$$

Here W is the total width of the depletion region, ϵ_n and ϵ_p are the static permittivities of the n- and p-type semiconductors, V_{bi} is the built-in voltage in equilibrium, e is the elementary charge and N_a and N_d are the acceptor and donor densities of the p- and n-type material, respectively (Fig. 1). In most practical cases, both light absorption and collection efficiency are low in the n-type heterojunction partner, so it can be more instructive to deal with the part

of the depletion region that lies in the p-type absorber, which has a width

$$W_p = \left[\frac{2V_{bi} \epsilon_n \epsilon_p N_d}{e N_a (\epsilon_n N_d + \epsilon_p N_a)} \right]^{1/2} \quad (2)$$

Eq. (2) predicts that the width of the depletion region increases as the permittivity of the two heterojunction materials increases. Notice that, if one of the two sides of the junction is doped heavily with respect to the other, then it is only the permittivity of the lightly-doped side of the junction that contributes to depletion region widening. Since minority carriers are collected most efficiently within a depth corresponding to the depletion width in the absorber layer plus their diffusion length, widening of the depletion region increases the depth at which the carriers can be efficiently collected. This can noticeably increase the short circuit current density J_{sc} in the cases where the total width of the two above regions is not enough to efficiently collect all photo-generated carriers, especially those due to long-wavelength photons. If, on the contrary, the collection length is large compared to the light absorption depth in the absorber material, the short circuit current is unaffected by the permittivities. The influence of the permittivity on solar cell performance in those two scenarios will be shown in detail in Section 4.5.

2.2. Effect on built-in voltage distribution

The second relation (Sze and Ng, 2004) describing the effect of the materials permittivity on device performance is the following:

$$\frac{V_{bi,n}}{V_{bi,p}} = \frac{\epsilon_p N_a}{\epsilon_n N_d} \quad (3)$$

Here, $V_{bi,n}$ and $V_{bi,p}$ are the built-in voltage drops in the n-type and p-type junction materials, as shown in Fig. 1. This relation is valid for a single heterojunction without interface charge. If there is a high interface charge density the $V_{bi,n}/V_{bi,p}$ ratio is not determined by Eq. (3) anymore, but it is determined by the energy level of the charged state at the interface (“Fermi level pinning”). For intermediate cases with moderate interface charge density, no simple expression exists to calculate the $V_{bi,n}/V_{bi,p}$ ratio, which must therefore be determined by numerical simulation. This will be done in Sections 4.3 and 4.4.

For an ideal heterointerface (i.e., with zero interface recombination velocity), the $V_{bi,n}/V_{bi,p}$ ratio does not affect the efficiency (Scheer and Schock, 2011). However, in the presence of interface recombination, an increase in the $V_{bi,n}/V_{bi,p}$ ratio leads to a decrease in the open circuit voltage V_{oc} (for $0 < V_{bi,n}/V_{bi,p} < 1$) and in the short circuit current J_{sc} (for $V_{bi,n}/V_{bi,p} > 1$), due to trends in the relative abundance of electrons and holes at the interface (Scheer and Schock, 2011). Hence, the ϵ_n/ϵ_p ratio is a key quantity that can in principle be used to tune the built-in voltage drop distribution $V_{bi,n}/V_{bi,p}$ and therefore the efficiency of the solar cell. Specifically, it appears that increasing the ϵ_n/ϵ_p ratio is beneficial for increasing solar cell efficiency. However, this statement must be qualified by several factors. First of all, if the n-type material is much more heavily doped than the p-type material, $V_{bi,n}$ will be very small compared to $V_{bi,p}$ regardless of the permittivity ratio, as permittivities of most semiconductors only vary over one order of magnitude. This renders all buffer-free solar cell architectures – with the absorber in direct contact with a highly doped window – insensitive to the ϵ_n/ϵ_p ratio. On the other hand, if N_d is not much greater than N_a , then the permittivity ratio can significantly influence the voltage drop ratio, as will become evident in Section 4.1. However, even under those conditions, if the lightly-doped buffer layer is thin enough it will be completely depleted, such that

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