Numerical modeling of perovskite solar cells with a planar structure

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Abstract. The paper is devoted to the research and development of high-efficiency solar cells with a planar perovskite n-i-p structure. A numerical model of this solar cell in the drift-diffusion approximation based on Poisson equation and continuity equations provided to determine their photoelectric characteristics and design optimization. The author considers the spectral photogeneration, bulk and surface recombination, transport charge carriers in perovskite and their collection by the electron and hole transport layers. As a result of the simulation, it was obtained efficiency dependence on perovskite absorber material thickness and lifetime (diffusion length) of the charge carriers. It is found that in addition to absorption coefficient optimal perovskite thickness is determined largely by the charge carrier diffusion length, and it has the upper limit in thickness of 500-600 nm.

1. Introduction

Recently, the alternative materials and technologies are actively searching for the production of low-cost and highly efficient solar cells. Research of absorber materials new types has led to the use of perovskite semiconductor in the dye-sensitized solar cell (DSSC) design. Solar cells based on titanium dioxide (TiO₂) / perovskite semiconductor heterojunction showed high power conversion efficiency of 15-20% [1,2]. The organometal perovskite materials with crystal structure ABX₃ similar to the crystal lattice of calcium titanate (CaTiO₃) are useful for photovoltaic applications. The main advantages of perovskite such as the methylammonium lead iodide (CH₃CN₃PbI₃) are the lack of energy-intensive and complex coating processes on various substrates (crystallization temperature 100-150 °C), as well as their inherent band gap (1.5-2.3 eV) with direct transitions, high and balanced charge carrier mobility (0.1-10 cm²·V⁻¹·s⁻¹), relatively long diffusion length (0.1-1.5 µm) and a high absorption coefficient (more 5×10⁴ cm⁻¹) [3].

Simulation is an important and necessary step in the development and manufacture of new semiconductor devices, such as solar cells. The simulation reduces the costs of the experimental researches and the parameters optimization. The operation principle of perovskite solar cells differs from substantially silicon solar cells and DSSC [1-3], and therefore requires the development of new physical and topological models for determination the photoelectric characteristics, research, and design optimization and increase solar cell efficiency. The thickness of perovskite absorber material is one of the most important parameters affecting the solar cell performance. In addition, the charge
carrier diffusion length (perovskite quality) in the n-i-p solar cell structure must be large enough to photogenerated charge carriers effectively collected [4,5].

In this paper, the numerical model based on drift-diffusion system semiconductor equations was proposed. It allows taking into account the solar cell material parameters with photovoltaic behavior. The model can be used for optimization of perovskite absorber material thickness and research of its qualities (charge carrier lifetime and diffusion length) influence on photoelectric characteristics.

2. Development of a numerical model

Research and perovskite absorber material optimization were carried out with the use of the developed physical and topological one-dimensional model of perovskite solar cell with planar n-i-p structure. Figure 1 shows simulated solar cell design, where the absorber material is a relatively widely studied perovskite CH$_3$NH$_3$PbI$_3$ combination with an electron (TiO$_2$) and hole (Spiro-OMeTAD) transport layers [1-3]. As the substrate, we can use glass, sapphire or polyethylene naphthalate (PEN) coated by transparent conductive oxide (TCO). We assumed that the photogenerated charge carriers in perovskite are free electrons and holes, and perovskite semiconductor is intrinsic. Photogenerated electrons and holes diffuse and drift through the perovskite absorber and transport layers n- and p-type. In this case, the electron and hole transport layers are considered as perfect conductors for the major carriers.

![Figure 1. Design (a) and the energy diagram (b) of perovskite solar cell with planar n-i-p structure.](image)

The model is based on drift-diffusion equations semiconductor system with stationary differential equations of continuity for the determination electrons and holes concentrations, and Poisson equation for the potential calculation in perovskite [4,6]:

\[
D_n \frac{d^2n(x)}{dx^2} - \mu_n \left( \frac{dn(x)}{dx} \frac{d\varphi(x)}{dx} + n(x) \frac{d^2\varphi(x)}{dx^2} \right) + G(x) - R(x) = 0,
\]

\[
D_p \frac{d^2p(x)}{dx^2} + \mu_p \left( \frac{dp(x)}{dx} \frac{d\varphi(x)}{dx} + p(x) \frac{d^2\varphi(x)}{dx^2} \right) + G(x) - R(x) = 0,
\]

\[
\frac{d^2\varphi(x)}{dx^2} = \frac{q(n(x) - p(x))}{\varepsilon \varepsilon_0}
\]

where \( n \) and \( p \) is the electron and hole concentrations; \( D_n \) and \( D_p \) are the electron and hole diffusion coefficient; \( \mu_n \) and \( \mu_p \) are the electron and hole mobility; \( x \) is the coordinate on Figure 1; \( \varphi \) is the electrostatic potential within the absorber layer; \( q \) is the elementary charge; \( \varepsilon \) is the perovskite relative permittivity; \( \varepsilon_0 \) is the permittivity of vacuum; \( G \) is the electron and hole photogeneration rate; \( R \) is the electron and hole recombination rate.

The charge carrier photogeneration rate were determined in the spectral range of perovskite absorption on the base of Bouguer-Lambert law [5]:

\[
G = \eta \alpha (1 - t) \Phi e^{-ax},
\]
where $\eta$ is the photons generation of electron-hole pairs coefficient; $\alpha$ is the perovskite absorption coefficient; $t$ is the reflectance from the front surface; $\Phi$ is the photon flux density in the spectral absorption range of perovskite.

Solar spectrum AM1.5 approximation was made by thermal radiation at temperature $5780$ K (Planck's law) [5,7]:

$$F = \int_{2800}^{800} K \left( \frac{R_s}{\phi \lambda} \right)^2 \left( \frac{2\pi c}{\lambda^2} \right) d\lambda,$$

where $\lambda$ is wavelength; $h$ is Planck constant; $c$ is the velocity of light in vacuum; $f$ is the shading factor; $R_s$ is the solar radius; $r_0$ is the average distance between the Sun and the Earth; $T$ is the temperature; $K$ is the Earth's atmospheric mass effect on the solar power density for AM 1.5 spectrum.

We take into account the direct interband recombination (non-radiative recombination) and recombination at impurity centers (bulk and surface recombination), i.e. deep levels located near the middle of the band gap (traps). In perovskite trap recombination (the crystal structure Schottky’s and Frenkel’s point defects [6]) is the dominant mechanism that limits the solar cell performance. Consequently, recombination rate in the perovskite was determined by using the following analytical models:

- the Shockley-Read-Hall model of carrier trap recombination [6]:

$$R_{SRH} = \frac{np - n_i^2}{\tau_n(n + n_i) + \tau_p(p + n_i)},$$

where $\tau_n$ and $\tau_p$ are the electrons and holes lifetime; $n_i$ is the intrinsic carrier concentration;

- the model of the direct interband non-radiative recombination [6]:

$$R_{dir} = C (np - n_i^2),$$

where $C$ is the inter band recombination coefficient.

To determine the generated current density in the drift-diffusion models, it can be traditionally used the following form [4]:

$$J_n(x) = -qD_n \frac{dn(x)}{dx} - q \mu_n n(x) \frac{d\phi(x)}{dx},$$

$$J_p(x) = q D_p \frac{dp(x)}{dx} - q \mu_p p(x) \frac{d\phi(x)}{dx},$$

where $J_n$ and $J_p$ are the electron and hole components of the current density.

The output voltage of the perovskite solar cell defined as the potential difference at the ends of the perovskite, i.e. between the quasi-Fermi level for electrons at $x = 0$ and quasi-Fermi level for holes at $x = L$ (Figure 1):

$$U = E_{F_n} - E_{F_p} = E_g + kT \ln \left( \frac{n(0)}{N_c} \right) + kT \ln \left( \frac{p(L)}{N_v} \right),$$

where $N_c$ and $N_v$ are the effective density of states in the conduction and valence bands.

The solution of model equations system was carried out numerically (finite difference method) using an iterative method Hummel in short circuit, open circuit and operating conditions of the solar cell.

3. Results

The simulation photovoltaic characteristics of perovskite solar cells were carried out. The electrons and holes diffusion coefficients are 0.017 cm$^2$·s$^{-1}$ and 0.011 cm$^2$·s$^{-1}$ [8], respectively, and same lifetime in the range of 0.05-1.3 µs, which corresponds to the diffusion length of 0.29-1.48 µm (characteristic for organometal perovskites). The perovskite absorber should be thick enough to absorb a large quantity of photons, but too thick a perovskite layer creates more recombination centers and prevents of photogenerated charge carrier transport due to the decrease of the electric field in the perovskite. Thus, the optimum perovskite thickness should be in a balance of its absorption length and diffusion length. As a result of the simulation, the dependence of power conversion efficiency from the absorber
perovskite thickness at a different charge carrier lifetime was obtained. Figure 2 (a) it is shown that for solar cells with a lifetime of 0.1 µs the optimum thickness is about 325 nm. If the lifetime increased to 0.3 µs, the optimum thickness is around 500 nm. A further lifetime increase causes a slight increase in the optimum thickness. In the case of a large diffusion length (lifetime is more than 0.3 µs) we can see a slight decrease of efficiency in a thick absorbent layer because it reduces the electric field in the perovskite. When the lifetime is less than 0.3 µs increase in the perovskite thickness leads to an increase of recombination losses and significant efficiency reduction.

Figure 2 (b) shows the optimum perovskite thickness of the lifetime and diffusion length. The optimal thickness of the perovskite is largely determined by the charge carrier lifetime and an upper limit of 500-600 nm with bulk and surface recombination.

![Figure 2](image.png)

**Figure 2.** The efficiency dependence on thickness and lifetime (a). The optimum thickness dependence on lifetime and diffusion length (b).

Thus, in this paper, a numerical model of perovskite solar cell in drift-diffusion approximation was developed. Simulation results show that the absorber perovskite thickness and its quality (lifetime, diffusion length) significantly influence on the solar cell efficiency. It can be obtained efficiency 25-27 % with optimized design of perovskite solar cell (large diffusion length of 1-1.5 µm, the optimal thickness of 500-600 nm). The efficiency corresponds to the best silicon solar cells. The developed model allows us to understand of perovskite solar cells operation mechanism, and it contributes to the further improvement of their efficiency.

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