Solar Energy 137 (2016) 364–370

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Towards nanostructured perovskite solar cells with enhanced efficiency: Coupled optical and electrical modeling

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ARTICLE INFO

Article history:
Received 4 July 2016
Received in revised form 18 August 2016
Accepted 24 August 2016

Keywords:
Perovskite
Solar cell
CuSCN
$CH_3NH_3PbI_3$
Carrier generation
Light trapping

ABSTRACT

Third generation photovoltaic technologies based on perovskites have demonstrated an exceptional progress in solar energy conversion since their first use in 2009. Herein, we investigated the effect of using light trapping nanostructures on the absorption, carrier collection, and overall efficiency of perovskite ($CH_3NH_3PbI_3$) solar cells using three dimensional (3D) finite element method (FEM) technique. A combined optical-electrical model was constructed to full characterize the proposed devices. Upon the use of nanotubular architecture, the optimized active area absorption enhanced by 6% and the total generation rate increased by 7% compared to the planar architecture. Under one sunlight illumination (AM1.5G), with normal incident angle, the solar cells containing nanostructured light trapping architecture showed a drastic enhancement in the short circuit current (J_{sc}), the quantum efficiency (EQE), and the overall efficiency compared to the planar film-based solar cell. The obtained enhancements would open a new route for integrating light trapping nanostructures in $CH_3NH_3PbI_3$ perovskite-based solar cells for better efficiency.

1. Introduction

Third generation photovoltaic technologies based on perovskites have demonstrated an exceptional progress in solar energy conversion since their first use in 2009 (Kojima et al., 2009). These promising results have made perovskites one of the most attractive light absorbing materials for solar energy conversion applications (Im et al., 2011; Etgar et al., 2012). Devices based on $CH_3NH_3PbI_3$ perovskite have large absorption coefficient, high charge carrier mobility and diffusion length (Zhumekenov et al., 2016; Lee et al., 2012; He et al., 2014). In 2014, Grätzel and co-workers reported power conversion efficiency of 12.4% using an effective and cheap inorganic p-type hole-transporting material, copper thiocyanate CuSCN, on lead halide perovskite-based devices using low-temperature solution-process deposition method (Qin et al., 2014). Herein, we propose a new approach to increase the efficiency of $CH_3NH_3PbI_3$ perovskite-based solar cells. Specifically, we investigated the effect of using nanostructures with different shapes and dimensions on light absorption, carrier generation, and carrier collection. To this end, light trapping nanostructures with thin absorbing layer would increase the optical absorption in the active layer and enhance charge carriers collection. Introducing nanostructures would enable the efficient use of many materials with short diffusion length. Moreover, they would reduce time and cost of production due to the use of thin absorbing layers (He et al., 2014).

The integration of light trapping nanostructures in photovoltaics changes the mechanism of light absorption. In bulk semiconductor, light is absorbed exponentially from front to back. In a thin film with a back reflector, incompletely absorbed light can reflect off each interface several times, making multiple light paths through the semiconductor. Optical models are based on the interaction between electromagnetic waves and photovoltaic solar cell materials. Maxwell's equations of light propagation can be used to describe the optical properties:

$$\frac{\partial H}{\partial t} = \frac{-1}{\mu} \nabla \times E \tag{1}$$

$$\varepsilon \frac{\partial E}{\partial t} = -\nabla \times H - \sigma E \tag{2}$$

Here, H is the magnetic field, E is the electric field, μ is the permeability, ε is the permittivity, and σ is the electric conductivity. The optical generation rate (G_{optical}) of electrons per wavelength (λ) can be calculated using Eq. (3) (Deceglie et al., 2012). The optical generation rate is proportional to the intensity of the electric field in the active layer, and the imaginary part of the permittivity (ε'').

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http://dx.doi.org/10.1016/j.solener.2016.08.039
0038-092X/

$$G_{\text{opt}}(\lambda) = \frac{\varepsilon''|E|^2}{2\hbar} \tag{3}$$

Electrical modeling of photovoltaic solar cells is important to calculate the electrical performance of devices. The current-voltage (J-V) characteristics of any photovoltaic solar cell can be described using Eq. (4), where J_{sc} is the short circuit current that is proportional to the generation rate of electrons (G_{Total}), diffusion length of the perovskite material (L_n), and diffusion length of the hole transport material (HTM) (L_p). The term J_{dark} represents the current of photovoltaic cell in the absence of sunlight illumination and it does not depend on the generation rate of electrons. (n) is an ideality factor and it depends on the type of material, (J_0) is the saturation current of the photovoltaic solar cell and can be calculated using Eq. (5), where (N_D) is the donor concentration in perovskite, (N_P) is the hole concentration in HTM, (n_i) is the intrinsic carrier concentration in perovskite and HTM, (τ_n) is the electron lifetime, (τ_p) is the hole lifetime, (D_n) is the diffusion coefficient of electrons, and (D_p) is the diffusion coefficient of holes.

$$J(V) = J_{dark} - J_{sc} = J_0\left(\exp\left(\frac{eV}{nKT}\right) - 1\right) - qG_{Total}(L_n + L_p) \tag{4}$$

$$J_0 = \left(\sqrt{\frac{D_p}{\tau_p}}\frac{n_i^2}{N_D} + \sqrt{\frac{D_n}{\tau_n}}\frac{n_i^2}{N_A}\right) \tag{5}$$

In our mode, the effect of external series (R_s) and shunt (R_{sh}) resistance was considered, as shown in Eq. (6). These parasitic resistances degrade the performance of any solar cell device as will be described later.

$$J(V) = J_{sc} - J_0\left(\exp\left(\frac{eV + J_{sc}R_s}{nKT}\right) - 1\right) - \frac{V + J_{sc}R_s}{R_{sh}} \tag{6}$$

Therefore, to enhance the efficiency of any solar cell, the generation rate of electrons should be enhanced by increasing the absorption of incident sunlight in the active layer. Also, it is necessary to enhance the carrier collection of these electrons by increasing the built in electric field inside the active layer and reducing the carriers recombination. Herein, the optical modeling of perovskite solar cells was performed using different light trapping structures inside the active layer such as thin film, nanotube, nanopyramid, nanorod, and nanocone. In this part, the nanostructure with the largest absorption enhancement and electron-hole pair generation rate enhancement in the active area of solar cell was identified. Then, the calculated generation rate of electrons was used as an input in the electrical model to estimate the enhancement in the overall efficiency of each nanostructured solar cell.

2. Modeling details

The design of the proposed nanostructures is based on photonic and electronic design considerations. Two photonic design considerations were applied on the proposed nanostructures: First, to achieve light trapping by making the photon propagation and carrier transport orthogonal, which could be possible if the propagation of incident photon is normally above the active layer, where nanostructuring may result in $CH_3NH_3PbI_3$/HTM interface being in the normal direction above the active layer, thus transport of carriers between interfaces should be orthogonal to the photon propagation. Light trapping depends also on the distance between repeating patterns of nanostructures. Therefore, to enhance absorption, the nanostructures in the array would be closely packed while increasing the aspect ratio. The second photonic consideration is to increase antireflection. A graded index for optical impedance matching has proven to be an effective antireflection strategy (Wang et al., 2012). There are two geometric requirements for effective antireflection. First, the periodicity of nanostructures needs to be much smaller than the wavelength of incoming light to result in an effectively averaged refractive index. Second, the height of nanostructures needs to be large enough for a smooth transition. Achieving these two requirements should result in enhanced absorption over broad range of wavelengths.

On the other hand, the two separate electronic considerations in designing the nanostructures are: First, is to maximize the collection of generated electron-hole pairs. This could be achieved by using nanostructures with dimensions less than their diffusion length. The electron diffusion length in $CH_3NH_3PbI_3$ perovskite is greater than 1 μm, which is more than four orders of magnitude of the light intensity (Zhao et al., 2014). The second electronic consideration in our approach is to increase the built-in electric field aiming to increase the rate of carrier collection. Therefore, the thickness of our nanostructures should not be less than the thickness of space charge region and should be large enough for increasing the optical absorption.

To construct the model, we started with the optical modeling of the different nanostructures. We calculated optical absorption and generation profiles of electrons within the nanostructures, then we calculated the generation rate of electrons, followed by optimization of the thickness and length of the nanostructures to satisfy the optical considerations mentioned above. The generation rates of electrons obtained from the optical model were used as an input to the electrical model to calculate the short circuit current and carrier collection rates in all nanostructures. Finally, we made another optimization in thickness and length of the nanostructures to satisfy both the optical and electronic considerations at the same time.

The modeled perovskite solar cell consists of (up-to-bottom) air, fluorine-doped tin oxide (FTO) and titanium dioxide (TiO_2) as a transparent conducting oxide, perovskite ($CH_3NH_3PbI_3$) as an n-type layer, holes transport material (CuSCN) as a p-type layer, and silver (Ag) as a back reflector. Five designs have been modeled where different nanostructured light trapping architecture of the perovskite ($CH_3NH_3PbI_3$) layer were simulated: (I) planar, (II) nanotube, (III) nanopyramid, (IV) nanorod, and (IV) nanocone.

The theoretical investigation on the optical and electrical performances of perovskite solar cell has been reported by several groups using transfer-matrix method (Ball et al., 2015) or finite difference time domain method (Zhang and Xuan, 2016). Our optical model simulation was done in three dimension (3D) using finite element method (FEM) simulator COMSOL 4.3b. A plan wave source is placed above air and used as a source of sunlight. AM1.5G was used as the input power of the plan wave, with normal incident angle only. The wavelength simulation range was 300–800 nm with 10 nm resolution. Note that this wavelength range is chosen based on the fact that the investigated perovskite material ($CH_3NH_3PbI_3$) has a band gap of 1.6 eV (Butler et al., 2015) and its extinction coefficient reduces to zero at a wavelength of 800 nm (Lin et al., 2015). Also, AM1.5G spectrum showed a higher incident sunlight energy on the earth surface starting from a wavelength of 300 nm. To reduce simulation time, we modeled a small unit of solar cell and used periodic boundary condition (PBC) on side of all simulated layers except silver. For silver, we used different boundary condition, which is perfect electric conductor (PEC), silver acts as a back reflector and reflects back most of unabsorbed incident sunlight. The used mesh size is ten times smaller than the smallest incident wavelength of the sunlight. The complex refractive indices of Ag, CuSCN, $CH_3NH_3PbI_3$, TiO_2, and FTO were taken from previously measured data (Xing et al., 2014; Pattanasattayavong et al., 2013; Rakhshani et al., 1998; Wang et al., 2013; Rakić et al., 1998). Using the optical model, we calculated the absorption of incident sunlight into the active layer,