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Recommended Citation
Available at: https://uzjournals.edu.uz/semiconductors/vol2/iss6/13

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THIRD-GENERATION SOLAR CELLS BASED ON THE EFFECT OF MULTI-EXCITON GENERATION IN PEROVSKITE

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Abstract. The electron-ion processes in the solar cell combining the properties of perovskite and the multiple exciton generation effect are considered. Attention is focused on the role of a polyatomic organic molecule introducing new features by its phonon spectrum into nonradiative transitions.

Keywords: photovoltaics, perovskite, MEG effect, non-radiative transitions, degradation.

In previous years, two particularly promising directions for the development of third-generation photovoltaic cells were identified \([1]\):

1) elements based on perovskites;

2) elements based on a new photoelectric effect of multiexciton generation in quantum dots of semiconductors.

Of particular interest is the combination of these approaches in a single device, and such experiments have already appeared, however, only for purely inorganic perovskites \([2]\). In this work, an attempt is made to carry out an analysis within the framework of a unified approach, as, for example, in \([3]\), having considered the problem, especially in such a combination, for both inorganic and hybrid (with organic) samples.

Effects at the primary stage of quasiparticle generation. The proposed model considers two types of quantum dots: CsPbI\(_3\) and CH\(_3\)NH\(_3\)PbI\(_3\) (Fig. 1). Let a high energy flux \(\hbar \nu \gg E_g\) fall on each of them, where \(E_g\) is the width of the forbidden zone in the quantum dot. It is obvious that both quantum dots differ significantly in phonon spectra. To estimate the multiexciton generation probability, we use the theory of multiple particle production \([3]\).

In this theory, adapted \([4]\) for photovoltaic cells, all quantum characteristics of the multiple generation process are replaced by thermodynamic and statistical quantities. Then for multiple exciton generation (their number is \(n_{ex}\)), we obtain
\[
\begin{align*}
    n_{\text{ex}} &\leq \frac{1}{3} + \frac{\hbar \nu}{E_g} \ln \left( \frac{2\pi m_{\text{ex}} \hbar \nu}{2\pi \hbar} \right) \Omega \frac{\bar{E}}{E_g} - \frac{P}{2} \left( 1 + \frac{E_{\text{ph}}}{E_g} \right),
\end{align*}
\tag{1}
\]

where \( \Omega \) is the volume of a quantum dot, \( P \) is the number of excited phonons with energy \( E_{\text{ph}} \) each, \( m_{\text{ex}} \) is the exciton mass.

It can be seen from (1) that excited phonons reduce the yield \( n_{\text{ex}} \), but the presence of a term in (1) also \(- \frac{P}{2} \left( 1 + \frac{E_{\text{ph}}}{E_g} \right)\) indicates a more subtle "game": many phonons (\( P \) is much greater than unity) but their small quantum (phonon energy is much less than the band gap), therefore, for the multiplicity of excitons, the role for various types of organic molecules requires specific calculations.

Ultimately, it can be concluded that organics reduce the \( n_{\text{ex}} \) yield.

**Effects at the second stage of quasiparticle production.** An inverse Auger process is considered, when the "fall" of a primarily excited electron into the conduction band causes excitation ("band-band") of additional electrons. The presence of an easily excitable organic molecule (its vibration) is an outflow of energy for the "falling" electron (ie \( E_e - E_c = n_1 \hbar \nu_{\text{ph}} + n_2 E_{\text{ex}} \)) - Fig.2.
In this case, the probability of additional excitation of phonons in an organic molecule is determined by the value of the Franck-Condon factor ($P_{F \rightarrow o, i}$). Finally, the probability of excitation of $n_2 + 1$ electrons into the conduction band will be exactly

$$W = W_{ex}^{(1)} \cdot W_{ex(Auger)}^{(2)} \cdot \prod_{i=1}^{n_2} \Phi(o, i)$$

(here $i$ numbers the number of phonons in an organic molecule). Obviously, it is the large number of small energies of the vibration quanta of the organic molecule that prevents the Franck-Condon factor from being too small ($\leftrightarrow 0$).

We believe that this very circumstance may be the cause of the anomalies noted in [5].

References