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Role of Fractals in Perovskite Solar Cells

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Abstract

The interface engineering plays important role in fabrication of the tandem and perovskite based solar cells. Recent experiments show that the interface effects caused by the coupling of the electron bands and the pairing of geometry of contacting surfaces. In particular, it has been experimentally revealed that the transition from planar to the rough interface improves many photoelectric parameters of the device. It means that the value of the fractal dimension of the interface may be key factor in device performance. It is possible to formulate two problems: firstly, the understanding on simple models why the electrical properties at fractal interfaces are improved, and, secondly, to discuss one of the most promising approaches in modern electronics, namely technology of radiation applications in the creation of rough interfaces. Thirdly, the problem of photodegradation is analyzed in detail in the structures containing the fractal interfaces. On the basis of the constructed models, it was found: i) increase of roughness (fractal) of interface structure can enhance the role of total internal light reflection effect, thereby increasing the effective light path, and therefore, the number of generated e-h-pairs; ii) the curvature of the surface leads to the shift of Tamm levels both to the borders of allowed bands, and to the middle of the band gap; it opens the way of the control of carrier recombination on the interface; iii) surface Tamm orbitals interact differently each with other on the convex and concave areas; it leads to the different probability of defect formation and, consequently, reduces the fractal interface, inhibiting the effect of increasing of the photocurrent associated with the fractal interface (new channel of photodegradation).

1. Introduction

Thin film photovoltaic materials on the basis of polymers and tandem structures have attracted much attention due to their flexibility, environmental safety and low cost. However, to compete with silicon based solar cells, conversion efficiency and stability of organic and tandem solar cells need considerably to be improved. This concerns, in particular, perovskite based solar cells, whose conversion efficiency has been monotonically growing during last 3–4 years [1–3].

Fabrication of highly efficient solar cells (SC) on the basis of organic-inorganic perovskites requires basic studies related to such issues as the physical and chemical aspects of cell morphology [4], the architecture of device structures [5], stability and degradation of photovoltaic materials and devices [6], thermodynamics and electronics of defects [7], homologous composition of perovskites [8], the role of the organic component of perovskites [9], mechanisms of photophysics [10] in organic and tandem structures.

All these issues can be classified as the "problem of interface engineering for photovoltaics" [11]. In this paper we address the problem of rough interfaces in the charge dynamics and conversion efficiency of the perovskite based tandem solar cells. This problem is of special importance for perovskites because of their multi-component nature. Earlier, in the study of similar problem in thin film silicon solar cells, it was found that the surface “landscape” plays important role causing the multiple reflection of the light [12]. Similar effects in organic-inorganic perovskite solar cells was studied in [13], where the cells with rough interface surfaces were fabricated.

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In particular, in [13] additional power conversion efficiency should be gained without increasing the thickness and the complexity of the devices for practical applications. This result has been checked in [13] on 20 samples. A rough interface between perovskite and hole-conducting material (HTM) was fabricated in perovskite solar cells to enhance the light scattering effect and improve the charge transport [13]. The parameters related to the morphology have been systematically investigated by sequential deposition. The control of the roughness degree of the interface was realized by two ways: a) reaction temperature control and b) pre-wetting time control (see Fig. 1). Simultaneous enhancements of short-circuit current and power conversion efficiency were observed in both $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$ devices containing the rough interface, with power conversion efficiencies of 10.2% and 10.8%, respectively, besides the enhance of short-circuit current was more than 13%.

Here it is important to note that the increase of the total surface intrinsic for the fractal interfaces should decrease the current through the device, since the interface has the electron traps. However, it is in contradiction with the experimental results of [13]. This may imply that the fractal structure on the interfaces play important role. Therefore, the theoretical analysis of such structures and their role in photovoltaic conversion is important for deep understanding of the mechanisms for charge carrier generation and dynamics.

These theoretical and experimental results give an efficient and universal way to control the morphology and further optimize perovskite solar cells for devices by sequential deposition with various structures.

2. Light passage through the fractal interface

The interaction of electromagnetic waves with the fractal ("rough") surfaces has attracted much attention earlier within the different models. However, the geometric structures of the rough surfaces considered in these models are very far from that of the perovskite cells studied in [13]. Therefore we consider a simple model of the "perovskite particles/HTM film" interface, which is more close to the interface structures studied by SEM method. Let us assume that the interface contains the tightly contacting perovskite balls with radiuses R and the dense HTM film. The light beam falls vertically on the interface inside perovskite cell from the side of balls (see Fig. 2). It is obvious that there is a distance $\rho^* = Y_0$ measured from the central diameter of the ball (see Fig. 2a), further, which the light beam undergoes the total internal reflection and remains inside the perovskite. From the simplest constructions the following expression for the part of total interactions of parallel rays with the spherical surface of the perovskite ball, when the light rays remain in the ball and cannot transit into the HTM film can be obtained: $F = (1-\eta^2)^{\frac{3}{2}}$ (here $\eta = \sin\alpha^*$ is the light refraction index in the transition from the more dense medium of perovskite into the less dense HTM medium).

Now suppose that the interface is formed from the ellipsoidal perovskite particles (with semi-axes a, b, c = b) and the HTM film (Fig. 2b). The calculations for ellipsoidal particles similar to that for the spherical particles allow ones to obtain the part of rays falling initially parallel to the major axis of the ellipsoid but undergoing the total internal reflection: $\widetilde{F} = \widetilde{Z}^3 / 2(1+\widetilde{Z}^2)^{3/2}$; here $\widetilde{Z} = (a/b) ctg\alpha^*$. It is important to note that in the case of the spherical particles (a = b) the expression for $\widetilde{F}$ transforms into that for F. Therefore, we can conclude that in the case of the surface constructed from the ellipsoids, the probability of total internal reflection of light beams is greater than in the case of spherical particles of perovskites. From this conclusion it follows that the number of electron-hole

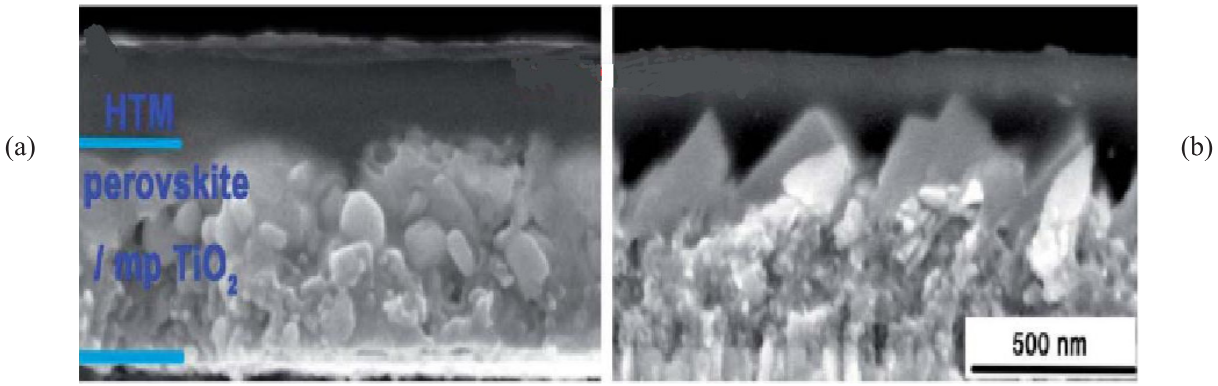

Fig. 1. Scanning electron microscope images of cross-sections of perovskite/HTM interface: a) planar, b) rough relief.

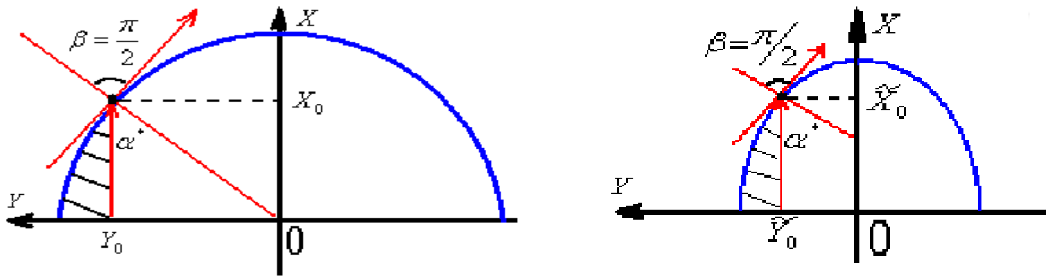

Fig. 2. Schematic representation for the total internal reflection inside the round (a) and ellipsoidal (b) particles of perovskite; in the case (b) the shaded area is greater than in (a) $\left({}^{Y_O}\!/_{R} > {}^{\tilde{Y}_O}\!/_{B} \right)$, which corresponds to the larger number of generated e-h-pairs for the ellipsoidal particles.

pairs generated per one second in the subsurface particles of perovskite increases with the growth of the roughness of the interface. Of course, this leads to the increase of the current through the interface. Note that these results are in agreement with the concept of "true fractal interfaces". Indeed, as the result of technological operations, the large set of perovskite particles with varying degrees of ellipticity (i.e. with different relation ${}^{a}\!/_{b}$) is presented at the interface. If we introduce the idea about the value of the deformability of particles $\tilde{\beta} = 2\frac{a-b}{a+b}$, then at the small degree of deformability we obtain ${}^{a}\!/_{b} \approx 1 + \tilde{\beta}$. In this way, in the expression for $\tilde{F}$ we can introduce the dependence on $\tilde{\beta}$, and then we consider it distributed in agreement with the fractal laws. This case corresponds to the change of the shape of perovskite particles under the influence of some type of technology, but with the preservation of its volume. Thus, we can assume that the growth of the fractal dimension (roughness) of interface causes the decrease of the current due to the enhanced electron-hole recombination at the interface.

3. Influence of surface roughness of interfaces on the passage of the photocurrent

Effect of fractal interface on the electronic photocurrent through it can be interpreted on the basis of two ideas. The first idea is related to the feature of the scattering of the electron de Broglie waves on the fractal interface. The simplest variant takes into account the broadening of interface with increasing of its roughness described by the average variance σ^2. The analysis shows [14] that the coefficient of wave reflection from the barrier decreases with increasing of fractal dimension: ${}^{d(\tilde{R})}\!/_{dD} < 0$. The second idea is related to the interesting effect of the dependence of the depth of Tamm states at the interface from the curvature of the surface [15]. Indeed, for the crystal surface with significant ionic character (for example, the perovskite), the gap between the electron Tamm levels of cation and anion increases with the value of the Madelung surface energy $E_{Sg} = 2V_S$-*const*. In the framework of this approach, the prevailing role have in [13] the concave areas of interface. It is clear that the convex areas corresponding to the deficit of Madelung energy have smaller bands, while concave ones with higher Madelung energies have larger bands. Consequently, there is a tendency for the deep traps on the convex parts of the interfaces to be moved to the middle of the band gap (the ability of enhanced recombination), while the deep levels are shifted to the boundaries of zones on the concave areas and are now the trapping levels (reducing recombination capacity) (Fig.3).

In the case of fractal interface, the total combined effect should be described on the basis of the so-called two-scale multifractal [16], witch takes into account both the different lengths of convex and concave regions and their different curvatures.

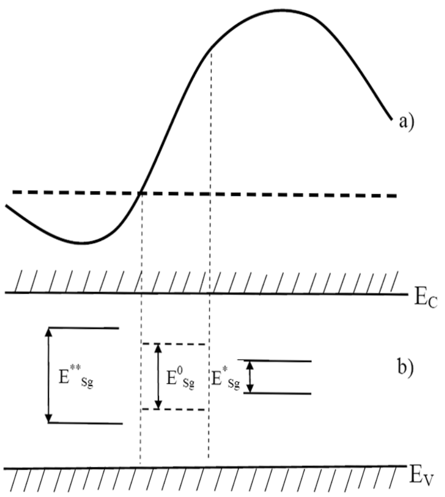

Fig. 3. (a) convex and concave areas of rough (fractal) surface (solid line) and the flat surface (dashed line); (b) scheme of the electronic levels of relevant surface areas.

4. Controlling of the interface fractal structure by radiation

Along with the usual methods of thermodynamic technology in modern micro- and nanoelectronics gives radiation technologies quite a lot of attention also. Therefore, noting the success of the thermodynamic technology perovskite issues, what were referenced above [13], we want to draw the attention of specialists on challenger and radiation technologies to control the degree of "roughness", i.e. fractal perovskite interfaces.

Consider a planar boundary in the characteristic architecture of solar elements based on perovskite (Fig. 4a). We choose as the radiation exposure method of ion bombardment, with such intensity and energy to the maximum formation of radiation defects occurred in the area of the perovskite, adjacent to the flat interface. This creates specific conditions: wide variety of defects (due to multi-component material) and a high degree of non-equilibrium of the open system – all of this radiation is controlled by the selection of parameters. These two conditions allow the manifestation of hope for the widest number of conventional radiation physical processes [17], but also the implementation of a new and very special class effect is called "synergy radiation" [18]. Based on this separation, we will consider here first option of radiation to stimulate the formation of the rough interface.

Consider the interface between the film of hole transporting material (HTM) and perovskites, made in the form of fine particles so that the interface can be considered as quasi-plane (Fig. 4a). Such a "weakly rough" surface may be characterized by the surface height (*Z*) at its different points (with coordinates y) along a certain direction. Then sufficient portion representative surfaces can be characterized by dispersions rough surfaces:

$$\sigma^2 = \{Z^2(y)\} \qquad (1)$$

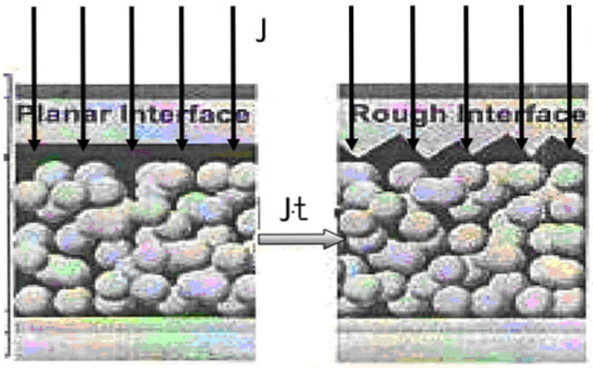

Fig. 4. Diagram of the perovskite solar cells on the planar (left) and rough (right) interface under irradiation *J*.

There brackets denote averaging over the interface area, the reference point on a vertical is chosen so that $<Z(y)> = 0$. An important measure of the statistical properties for the surfaces is the correlation function:

$$C(\Delta y) = \{Z(y + \Delta y)^{*} Z(y)\}, \qquad (2)$$

which may be expressed in terms of «power spectrum» *G* (*f*) by Fourier transformation:

$$C(\Delta y) = \int_{f\,\min}^{\infty} G(f)\exp(2\pi i f \Delta y)\,df \qquad (3)$$

Here *f* is spatial frequency which inversely proportional to the wavelength corresponding to the rough surface; it is clear that $f_{\min} = 1/M_{\max}$, where $M_{\max}$ is the physical length of the entire interface. Obviously, if to choose the "fractal spectrum" of power $\mathrm{G(f)} = \chi/\mathrm{f}^{\alpha}$ (where χ is the coefficient surface irregularity), then

$$\sigma^2 = \langle Z^2(y)\rangle = \int_{f_{\min}}^{\infty} G(f)\,df = \chi M_{\max}^{\alpha-1}/(\alpha-1) \qquad (4)$$

From the Mandelbrot relation [19] α = 7-2D, we obtain the relationship of fractal dimension (*D*) for rough surface with its dispersion:

$$D = 3 - \frac{const}{\sigma^2} \qquad (6)$$

Eq. (6) is valid in the range of $2<D<3$ and was tested on a huge number of surface types (see, e.g., [19]).

Note that the constant in the last formula allows to obtain the correct value of *D* and for extreme cases: perfectly smooth ($\sigma \rightarrow 0$) and absolutely rough ($\sigma \rightarrow \infty$) surfaces; formally, it is sufficient in the upper limit of the integrals used to replace infinity fmax, expressed in terms of the minimum size of a representative portion of the surface. Thus, to verify in the growth of D under the action of radiation (Fig. 4b) it is necessary to prove an increase in the spread of height "hills" on the surface (i.e., increasing its roughness). Let us return to the original formulation of the problem and use the results of Mullins (1959) (see in [20]) to describe the evolution of the groove on the border of the two grains (Fig. 5).

In this work it is shown under the influence of the difference in the chemical potential $\Delta\mu = \gamma_s \Omega \widetilde{K}$ under certain conditions there is a material removal from the contact between two grains (in our case - the two neighboring particles of perovskite) on the border of the groove (here γ_s is the surface tension of the free surface, Ω is the atomic volume, $\widetilde{K}$ is the curvature of the surface). As a result, the groove depth *d* increases with time.

For the case of surface diffusion we obtain

$$d = 2(ctg\theta)(Bt)^{1/4} \tag{7}$$

where $B = {D_S \delta \gamma_S \Omega}/{k_B T}$, D_s is the surface radiation enhanced atom diffusion coefficient, *d* is the width of the surface layer having a high rate of diffusion; θ is the angle of the original groove before its recess (at $t = 0$) - (Fig. 5).

Thus, the value *d* at different points of the surface is determined by the angle θ at a predetermined growth time (*t*).When *q* is increased from 0 to $\pi/2$ rate of groove deepening decreases. The speed of growth is determined by depending on the irradiation parameters and increases with increasing *d* and D_s: managing them, you can change the value of *d*. Obviously, the larger *B*, the difference in the initial increases $\{d\}$, i.e. it increases the degree of roughness and hence the fractal dimension *D*. This qualitative picture can easily be translated into the language of mathematics, if we take into account that the original set of θ has a different fractal distribution, averaging on which allows to give all the necessary statistical values.

5. Photodegradation of solar cells with fractal interfaces

Since the presence of fractal interface leads to its excessive area, the exposure by ionizing light (as such as by any type of ionizing radiation in general), taking into account the semiconductor nature of the perovskite, can lead to the surface radiation-stimulated atomic diffusion. This diffusion takes place by recharge of local electron levels and should lead to the smoothing of the roughness of the interface; this, in turn, should eliminate the extra value of 13% of the photocurrent. The effect of radiation smoothing of fractal has been observed already on the BaF_2 surface [21].

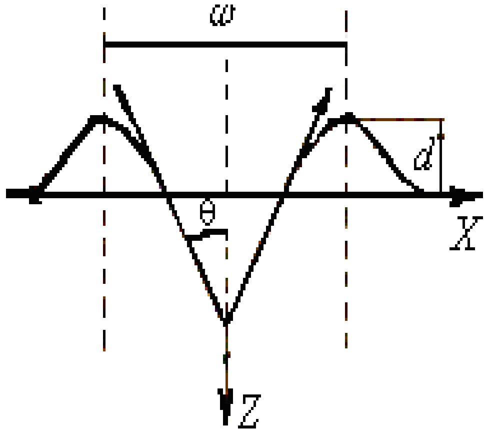

Fig. 5. Profile of "groove" in place of the output of the boundary of two particles on the surface of the interface under irradiation.

However, to realize such surface smoothing by surface diffusion of atoms it is necessary to release them from their regular surface layer of perovskite, i.e. the action of some mechanism for the formation of defects on the surface under exposition of light, UV-radiation (as well as the X- and gamma-rays in the case of work of device in space) must take place. The most important mechanism of the radiation defect may be the so-called mechanism of Dexter-Varley, including his variations in form of Knotek-Feibelman [22]. Its essence is the ionization of deep shell of surface negative ion by X-rays, resulting that the deep-level hole rises to higher levels by Auger transition with "breeding"; the negative ion is converted into the positive one losing electrons (in our case it is $I_S^- \rightarrow I_S^+$). Such a transformation does the ion I_S^+. Coulomb unstable and he leaves his site. This process is probabilistic in nature and is governed by the ratio of the reverse Debye frequency $1/w_D$ and of the time t_e of life of hole on the I_S^+ ion, so that the cross section of the destruction is proportional to $\eta \sim \exp\left(-{1}/{\omega_D \tau_e}\right)$ [22]. Since the surface ions I_S^- form area of Tamm states [23], the delocalization of the holes takes place on Tamm zone, so $\tau_e \approx {\hbar}/{\Delta E_T}$, where ΔE_T is the width of the Tamm zone. Turning to the fractal surface of the interface where the convexes alternate with the cavities (see Fig. 3), we see that electron wave functions overlap on neighboring ions I_S^- in the areas of convexity worse than on a flat surface, whereas in the area of the cavities the situation is inverse. The result is the variation of ΔE_T on the convexes and the cavities, but the time τ_e is higher on the convexes than on the cavities. This, in turn, leads to the conclusion that the probability of destruction of convex domains is greater. Consequently, under the X-rays (and under the corresponding UV-radiation) the smoothing of the relief takes place that reduces the fractal dimension of the interface and leads to the degradation of the device as lost an additional 13% found in [13].

6. Conclusion

In this paper we proposed a model which explains experimentally established effect of enhancement of the photovoltaic parameters of the perovskite based solar cells in the transition from the planar to the rough interface. The model is based on the assumption that the surface perovskite interface has the fractal structure that may cause the increasing of the mobility of the electrons. The rigorous analysis the problem can be done by modeling of the interaction of the waves of different nature with fractal surfaces. The above model can be used for the comprehensive description of the problem of charge carrier generation, separation and transport in perovskite based tandem solar cells.

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