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Impact of grain boundary defect on performance of perovskite solar cell

S.M. Iftiquar*, Junsin Yi*

College of Information and Communication Engineering, Sungkyunkwan University, Natural Sciences Campus, 2066 Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do 16419, South Korea

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ABSTRACT

Methyl ammonium lead halide ($MAPbI_3$) perovskite is a crystalline material. It shows interesting properties that are suitable for absorber layer of solar cell. An optimized solar cell requires 200–400 nm thick absorber layer. However, the thin absorber layer inevitably contains grain of crystallites and hence grain boundary (GB) defects. The GB defects affect device performance. Therefore, we theoretically investigated the effects of GB defects on performance of solar cells. In this simulation studies, we kept total mid-gap defect density (N_d) as constant at 4×10^{17} cm^{-3} but varied the GB defect density (GB_{dd}) from 3×10^{12} cm^{-3} to 3×10^{22} cm^{-3}, because of which, the observed short circuit current density (J_{sc}) of the cells remain nearly unchanged, but the open circuit voltage (V_{oc}) and power conversion efficiency (*PCE*) decreased steadily, while the fill factor (*FF*) shows a different trend of variation in a region (*Region-X*, say) where the GB_{dd} and the N_d were nearly equal. A further investigation reveals that in the *Region-X*, a transition happens from defect mediated recombination to GB mediated recombination, where the reverse saturation current density (J_0) and diode ideality factor (n) of the solar cells, reduce sharply from 3.46×10^{-13} A cm^{-2} to 2.65×10^{-19} A cm^{-2} and 1.9 to 1.1, respectively for a cell with 200 nm thick absorber layer. For 400 nm thick absorber layer, reduction of these parameters was 1.96×10^{-13} A cm^{-2} to 1.20×10^{-17} A cm^{-2} and 1.8 to 1.2 respectively.

1. Introduction

Methyl ammonium lead iodide ($MAPbI_3$) is an attractive organic-inorganic halide material for solar cell [1]. Recent works and reports show that significantly high photovoltaic conversion efficiency (*PCE*) is achievable [2] (for example 13 – 17% *PCE* were reported in [3–7]) with such an absorber material. A sharp improvement in PCE was reported from the year 2009 (3.8%) to 2015 (20.1%) [8]. One of the interesting features of this material is that it can be prepared easily and in a relatively low-cost technique, like solution processing [9], spin coating on a substrate [10,11], evaporation [12,13] etc, yet the solar cells exhibit superior performance [3–7]. It was estimated that cost of electricity from the perovskite solar cell can be 3.5 – 4.9 US cents/kWh [14], which is low and encouraging to adapt such a technology. Therefore, a considerable interest is drawn to investigate this material and related devices.

The $MAPbI_3$ perovskite has low defects density [15–17], high carrier mobility ($\sim$ 20 cm^2 V^{-1} s^{-1} [18–21]), longer carrier diffusion length ($\sim$175 μm [22]); these are the characteristic features that are remarkably different from other low cost semiconductors. Results show that the method of preparation has an influence on material characteristics and device performance [23], which is an expected trend. One of the most important characteristics is found to be the crystallite grain size [24–28], that was reported to vary from 50 to 300 nm [23], 1 μm to 180 μm [29], or 100 nm to 2 mm [30]. It was observed that solar cells, fabricated with materials of lower grain size show relatively lower *PCE* [29,31,32]. Therefore, the popular attempt is to prepare the perovskite materials with a larger grain size [24–28]. However, when this material is prepared in solution processing and evaporation techniques, and in the form of a few hundreds of nanometer film thickness, the possibility of having grain boundary (GB) defects is unavoidable. Therefore, several investigations reported about the role of GB to material or device characteristics [23,29,30,32,33]. In the $MAPbI_3$ perovskite material, the photoexcited electron-hole pairs are expected to have a high diffusion length, that may be even longer than average grain size. In that situation most of the charge carriers will reach grain boundary before being collected at the electrodes or lost by gap-state defect-mediated recombination. Therefore, the carrier transport is expected to degrade. In a solar cell the effect of this modified carrier transport will subsequently influence the *PCE*, open-circuit voltage (V_{oc}), fill factor (*FF*) etc.

Effect of crystallite grains were investigated and reported earlier, both theoretically [33] as well as experimentally [32]. Experiments with conductive atomic force microscopic measurement show that a

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* Corresponding authors.
E-mail addresses: iftiquar@skku.edu (S.M. Iftiquar), junsin@skku.edu (J. Yi).

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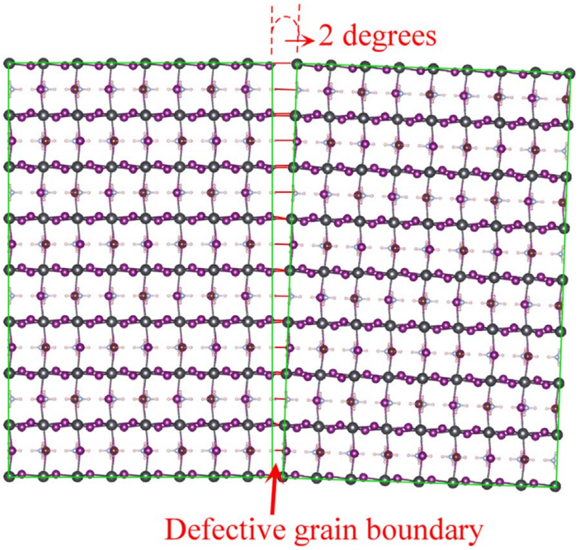

Fig. 1. Two-dimensional projection of two perovskite crystallites, having a defective grain boundary. The green outline to the crystallites indicate the boundary of the crystallites, that are mutually distorted from each other by a 2 degree angle. This distortion creates a strain in the bonds at the grain boundary. The stressed bonds at the grain boundary are shown as a red-colored line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)

band bending occurs at the crystallite grain boundary [23], indicating that the GB defects indeed play a significant role in carrier transport.

Although it is understandable that the density of GB defects depends upon average crystallite grain size, however, a definitive role of the GB defect on the device performance is not very clearly understood. As it appears from the above discussion that the crystallite size has a significant influence on material and device performance, so we investigated the effect of such crystallite grain size or GB defects on device performance.

Usually the GB defects arise due to the presence of randomly oriented crystallites within the film. The randomness of the crystallites can vary from small distortion of lattice points to a completely broken bond at the surface of a crystallite. Although these GB defects exists at the surface of crystallites, but effectively the defect in the volume of the film is introduced. Here we investigate the effects of GB defects based on the average grain size. We assume here that the lattice distortion is the only contributing factor to the GB defect, and exclude the broken bonds. Therefore, these defects do not form mid gap defects, but stays near valence and conduction band tails [33]. A schematic diagram of lattice orientation is given in Fig. 1, to demonstrate the type of GB defect investigated here.

2. Grain boundary defect density (GB_{dd})

A typical two dimensional projection of a 2×2 unit cell of a perovskite crystal can be as shown in Fig. 2(a). In a thin film, it is expected that this kind of crystals or crystallites will be formed with a varying degree of randomness in orientation and sizes. For simplicity of the theoretical analysis, we assume that the crystallites are of equal sizes (length of each side as x_1), and of cubical in shape as shown in Fig. 2(b), but of varying sizes from one sample to another.

Therefore volume of the crystallite will be x_1^3 and its surface area will be $6x_1^2$. Total volume of the film material will be WLd, where W is film width, L length and d as film thickness. If there are N number of crystallites in the film, then

$$Nx_1^3 = WLd \tag{1}$$

or

$$N = WLd/x_1^3 \tag{2}$$

It indicates that the number of crystallites in the film depends upon size of the crystallites, if thickness and surface area of the films remain constant. As mentioned above, size of the crystallites can vary to a great extent on the deposition conditions; it can be within 50–300 nm [23], 1–180 µm [29], or 100 nm to 2 mm [30]. In our model, we consider such a variation by changing the x_1.

We further assumed that an insignificant or constant volume of non-crystallite material exists between the neighboring crystallites, in other words, variation in the films are due to a variation in size of the crystallites. Although the assumption of insignificant amorphous phase is another simplification for the analysis, yet the defect contribution by non-crystallite phase will be higher than that of the situation when the film is completely filled up by crystallites. However, as we kept mid-gap defect density (N_d) as constant at 4×10^{17} cm^{-3}, implying that all the contributions to mid-gap defects, including that coming from amorphous phase remains unchanged. In reality, there are significant variations in number density of broken bonds at the GB. These broken bonds will contribute to gap state defects. As the energy of formation of a chemical bond is higher than the broken or unfilled or distorted bond at the grain boundary so the energy level of these defects will be within the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states.

Now, total surface area of the crystallite grains within the perovskite film can be expressed as

$$S = 6Nx_1^2 = 6WLd/x_1 \tag{3}$$

If N_{ds} is the average surface-defect density of the crystallites, then total surface defects (S_{def}) due to the crystallites will be

$$S_{def} = 6WLdN_{ds}/x_1 \tag{4}$$

Here it is to be noted that the surface defects indicate defects at the surface of crystallites, not at the surface of the films. These defects correspond to the tail states [33], and will contribute to the existing total volume defects within the films. Then the part of the volume defect density coming from GB defect (V_{def}), can be expressed as

$$V_{def} = (6WLdN_{ds})/(x_1Nx_1^3) \quad = 6N_{ds}/x_1 \tag{5}$$

This contribution of the grain boundary defects towards the volume defect density is proportional to the density of surface defects and inversely proportional to the size of the crystallites. This implies that when the crystallites are larger in size then material is expected to have less GB defects.

Length of energy-minimized MAPbI$_3$ unit cell is 0.52 nm, width is 0.42 nm, surface area is 1.3304 nm^2. It corresponds to a maximum of 8 defects (if all the bonds with H and I are strained). So maximum surface density of defects, N_{ds}, can be 6.01×10^{14} cm^{-2}.

Lets assume the minimum possible N_{ds} as 2.5×10^6 cm^{-2}, and maximum size of cubical crystallite grain as 200 nm (for a 200 nm thick film). Then for a variation of x_1 from 1 nm to 200 nm, the V_{def} will change as follows:

$$(V_{def})_{min} = 6N_{ds}/x_1 = 7.5\times10^{11} cm^{-3}, \quad \text{for} \quad x_1 = 200 \ \text{nm} \tag{6}$$

$$(V_{def})_{min} = 6N_{ds}/x_1 = 1.44\times10^{14} cm^{-3}, \quad \text{for} \quad x_1 = 1.04 \ \text{nm} \tag{7}$$

When $N_{ds} = 6.01 \times 10^{14}$ cm^{-2}, and maximum size of cubical crystallite grain as 200 nm. Then for a variation of x_1 from 1 nm to 200 nm, the V_{def} will change as follows:

$$(V_{def})_{max} = 6N_{ds}/x_1 = 1.8\times10^{20} cm^{-3}, \quad \text{for} \quad x_1 = 200 \ \text{nm} \tag{8}$$

$$(V_{def})_{max} = 6N_{ds}/x_1 = 3.47\times10^{22} cm^{-3}, \quad \text{for} \quad x_1 = 1.04 \ \text{nm} \tag{9}$$

Therefore, the defect density within the HOMO and LUMO can vary between 7.5×10^{11} cm^{-3} to 3.47×10^{22} cm^{-3}; the lower limit of V_{def} can be reduced further if we assume the minimum possible N_{ds} as less