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Impact of the trap–assisted recombination in the perovskite solar cells

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***Abstract*—To achieve the highest performance using perovskite solar cells it is necessary to understand all the dominant mechanisms which affect the operation of solar cell. Here, we have investigated the bulk and interface trap–assisted recombination processes in the solar cells with p–i–n architecture. These studies are based on the numerical and experimental methods to get better understanding of these physical processes. The following results are useful for optimization of the performance of perovskite solar cells.**

***Index Terms*—perovskite solar cell, trap-assisted recombination, interface and bulk processes**

I. INTRODUCTION

The organometal trihalide perovskite materials have gained a lot of attention since they have started to be used as an absorption layer in the photovoltaic cells. The continuous studies on perovskite solar cells (PSCs) lead to achieve a power conversion efficiency (PCE) with a value of 24.2% [1]. However, the best performing PSCs are still far from the final optimization. The theoretical simulations show that PSCs could operate with an efficiency around 31% [2]. There are already studies showing PSCs reaching its maximum short–circuit photocurrent (J_{sc}) [3]. However, the losses in a fill–factor (FF) and an open–circuit voltage (V_{oc}) are still observed. These losses are mostly related to the parasitic recombination processes. Thus, more studies are needed to define the dominant recombination mechanisms and their impact on the operation of perovskite solar cells.

In the operation of PSCs, a radiative recombination does not play a dominant role in comparison to a non–radiative mechanism [4], [5]. In general, the non–radiative recombination occurs when the electron (or hole) is trapped in the defect state located within the band–gap where it recombines with a hole (or electron). The traps concentration could be either accumulating at the bulk grain boundaries of the perovskite layer [6] or at the interface between the perovskite material and a transporting layer [7]. It is likely that both of the trap accumulation takes place and influences the operation of PSCs [4], [8]. In this work we study the role of both of these recombination bulk processes.

The concept of interface recombination is explored using the idea of a highly defected dead recombination layer which is present at the interface of Cu:NiO$_x$/CH$_3$NH$_3$PbI$_3$. It has been observed that the layer influences J_{sc} and V_{oc}, and as a result, the efficiency of PSCs. In addition, it is presented that a chemical modification of Cu:NiO$_x$ with PTAA material leads to deacreasing of the parasitic effect in the absorber layer. The trap-assisted bulk recombination processes is shown using the effect of different source of bromine atoms which affect the operation of Cs$_{0.18}$FA$_{0.82}$Pb(I$_{0.94}$Br$_{0.06}$)$_3$ perovskite solar cell. Therefore, each perovskite layer is prepared using only PbBr$_2$, FABr, CsBr compounds as the source of bromine atoms. There are assumed to be no other differences, therefore the investigated solar cells are called Pb–Br, FA–Br and Cs–Br, respectively.

In order to qualitatively study the recombination processes on the operation of PSC, the results obtained from experiment with different illumination conditions are applied. Also, for the modeling purposes, the drift–diffusion simulation tool is used [9], [10].

II. RESULTS

Fig. 1 shows the photocurrent–voltage characteristics of the PSCs measured under 1 sun light intensity. The measured sample structure is composed of Cu:NiO$_x$ and Cu:NiO$_x$/PTAA

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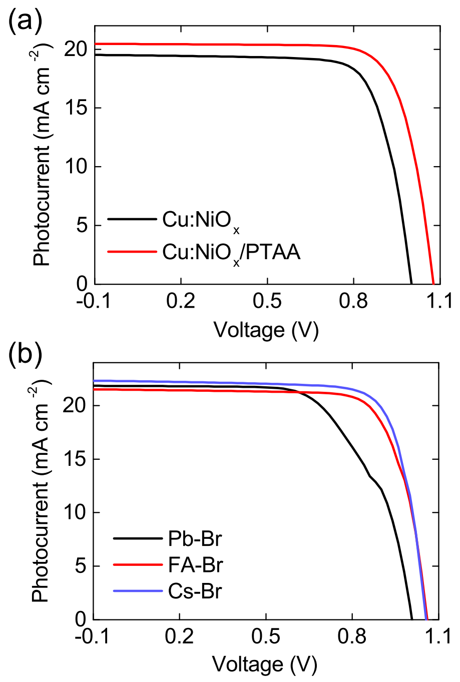

Fig. 1. The J–V characteristics for forward (solid line) and reverse (dashed line) scans for PSCs. a) Red and black lines represent Cu:NiO$_x$ with and without PTAA layer, respectively, b) black, red and green lines represent perovskite solar cells with Pb–Br, FA–Br and Cs–Br bromide source, respectively.

layers, see Fig. 1(a). It is observed that solar cells without PTAA layer are performing by about 2–3% lower in efficiency. This is mostly due to J$_{sc}$ and V$_{oc}$ losses that are equal to 1 mA cm^{-2} and 100 mV, respectively. There are no changes in FF for both types of PSCs. Therefore, the losses are most likely related to interface recombination in $CH_3NH_3PbI_3$ perovskite and HTL. As the only modification appears at the Cu:NiO$_x$ material. Sherkar et al. [8] has already observed similar effect for perovskite solar cells. However, such a high J$_{sc}$ and V$_{oc}$ losses would be only possible for very high surface recombination and that would also lead to a drop of FF. The most likely explanation is related to the concept of a dead layer, where trap states are very concentrated [11]. This theory should be capable of explaining all the observed losses with a small impact on FF.

The results of photocurrent–voltage characteristics for the bulk trap-assisted recombination using a double–cation perovskite material are shown in Fig. 1(b). There is observed a drop of 3% efficiency in Pb–Br comparing to FA–Br and Cs–Br samples. The differences in efficiency are mostly affected by FF and V$_{oc}$. The three types of perovskite solar cells have approximately the same photocurrent. In Fig. 1(b) it is seen that losses of FF are approximately 6% to 5% and about 70 mV if comparing Pb–Br samples to FA–Br and Cs–Br ones, respectively. This clearly shows the impact of bromine atom source on the electrical properties of the perovskite solar cell.

To increase the accuracy of the modeling results, we apply light intensity variations by using light filters from 1 sun to 0.001 suns, as shown in Fig. 2. Fig. 2(I) illustrates the results of calculations and experiment for the interface recombination between Cu:NiO$_x$ and perovskite layer. The simulation results show that the thickness of the dead layer is equal to 5 nm. Also the surface recombination velocities are equal to 3.75×10^3 and 3.75×10^4 m s^{-1} for electrons and holes, respectively. It has been observed that the recombination is higher for holes within the dead layer. This is due to a location of the recombination area in between perovskite and HTL, where mostly holes are drifting. The operation of solar cell at its maximum power is described using FF in function of light intensity. This parameter is very sensitive in simulation of solar cells. Therefore, it gives a high accuracy of the model if it is fitted properly. The shape of FF as a function of light intensity suggests that there are two dominant loss mechanisms competing each other in the analyzed PSCs, see Fig. 2(I.a). The monotonically increase of FF at high light intensities is mostly related to series resistance, but also to bimolecular or surface recombination mechanisms. However, at low light intensities the FF drop is most probably related to a trap–assisted recombination or a shunt resistance [4]. We conclude that, in general, the losses of FF are both interface and bulk recombination assisted. In Fig. 2(I.b), we can see the relation of V$_{oc}$ in the function of light intensity which allow us to calculate the ideality factor (n$_{id}$). The simulation results are well fitted for both FF and V$_{oc}$ which means that we have chosen correctly the rates of dominant recombination processes. Studies of Tress et al. [12] show that the interface recombination is the dominant one if the n$_{id}$ is approaching 1 kT/q in perovskite solar cells. As we observe, the PSC with only Cu:NiO$_x$ has the ideality factor equal to approximately 1.4 kT/q and that means the domination of interface recombination. The flattening of V$_{oc}$ in the high light intensity region is also associated with a high defect density at the dead layer. However, the passivation with PTAA layer leads to reduction of the surface recombination. It is also visible that the ideality factor is increased to 1.7 kT/q for the PSC with PTAA layer. Also, the higher ideality factor is appearing for the bulk trap–assisted recombination. Modeling with the same electrical parameters but without the recombination layer leads to results that show a very good agreement with the experiment. This clearly confirms the presence of the dead layer at the Cu:NiO$_x$.

Fig. 2(II.a), shows the results for FF in a light intensity function demostrated for different bromine atoms. The results suggest once again a competition of two dominant recombination mechanisms. However, most importantly the use of a different source of bromide shows the decrease of the FF at its peak value. This is mainly related to the bulk recombination process. Fig. 2(II.b) illustrates V$_{oc}$ in function of a light illumination intensity. The calculated ideality factor for Pb–Br is equal to 2.516 kT/q. This can be explained with the trap distributions that gives a very high bulk recombination [12]. Also, it is observed that the ideality factor for FA–Br and Cs–Br PSCs is slightly smaller but still around 2 kT/q. This clearly suggests that the trap–assisted recombination is the dominant

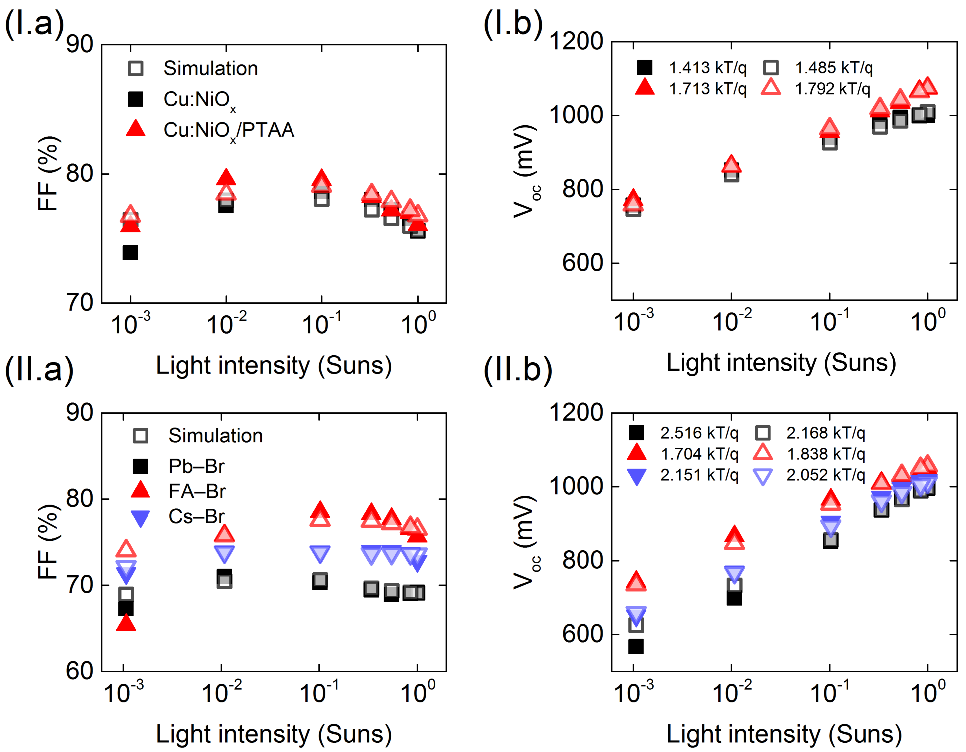

Fig. 2. Photovoltaic experimental (full symbol) and simulation (open symbol) results for different light illuminations. I.a) FF and I.b) V$_{oc}$ for Cu:NiO$_x$ (square symbol) and Cu:NiO$_x$/PTAA (up triangle symbol) HTL layer. II.a) FF and II.b) V$_{oc}$ for Pb–Br (square symbol), FA–Br (up triangle symbol) and Cs–Br (down triangle symbol) bromide source.

recombination mechanism for the different source of bromide samples.

The simulation results show a very good agreement with the experimental values for all three PSCs, see Fig. 2(II). The small discrepancy at 0.001 suns illumination is a result of leakage current or a shunt resistance which are not included in the modeling and have the highest impact on the cell at low light intensity [13]. The simulation results for Pb–Br give the rate of trap–assisted recombination (8.16×10^{27} m^{-3} s^{-1}) about three orders of magnitude higher than a value of radiative recombination rate (1.49×10^{24} m^{-3} s^{-1}) and about ten orders higher than the value of Auger recombination rate (9.34×10^{17} m^{-3} s^{-1}) at SC. Therefore, the trap–assisted recombination has been found to be the most dominant recombination process that also explains the differences between different bromide source of atoms in the PSCs.

The further studies of precursors and complex layer show that the observed effect is related to the presence of different complex compounds in each bromide source layer. Thus, we have suggested the explanation that using a different source of bromide it impacts the formation of complexes which are nucleation seeds during the crystallization of the layer. This leads to formation of a higher density of trap states which influences the trap–assisted recombination rate and lowers the operation efficiency of the devices.

III. SUMMARY

The studies presented here are concerning two trap–assisted recombination problems which appear in the PSCs. Firstly, the interface recombination has been studied using different hole transporting layers with Cu:NiO$_x$ and Cu:NiO$_x$/PTAA. The experimental results for Cu:NiO$_x$ has shown a significant recombination losses. It has been related to 1 mA cm^{-2} and 100 mV losses of a photocurrent and open–circuit voltage, respectively. The modeling results has shown the presence of a highly defected dead layer which appears at the interface between Cu:NiO$_x$ and perovskite. Secondly, the bulk recombination studies are demostrated for perovskite materials with Pb–Br, FA–Br and Cs–Br bromide sources. The experimental measurements have shown that Pb–Br perovskite solar cells are approximately 3% worse in efficiency if compared to FA–Br and Cs–Br samples. It has been found out experimentally that using different bromine source of atoms it affects the formation of complexes in the solution. This leads to formation of defect states during the crystallization process of the perovskite layer which changes the trap–assisted recombination rate in the PSCs.

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