Modelling of slow transient processes in organo-metal halide perovskites

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Abstract—**We have modelled the effect of ionic motion in MAPbI$_3$ cells, deepening the understanding of how these mobile species can result in current-voltage hysteresis. In addition, we present a quantitative model for photo-deactivation of carrier traps to explain the observed increase in photoluminesence efficiency upon light-soaking.**

I. Introduction

Organo-metal halide perovskites (OHPs) have been shown to possess many attractive characteristics for a photovoltaic material including a large absorption coefficient, long carrier diffusion lengths and a high tolerance to defects, enabling their facile synthesis. Nonetheless, there is mounting evidence that defects are responsible for a variety of unusual properties in OHPs such as current-voltage hysteresis[1], the possibility of anion and cation interconversion[2], degradation, and photochemical reactions[3], all of which can be observed on a slow timescale of seconds to several minutes. The majority of work to date on these issues has been experimental, aimed at discovering how to mitigate the undesirable properties by making alterations to the processing or device structure. Here we present some insights gleaned from our modelling of two slow processes in OHPs: the well-known current-voltage hysteresis, and PL efficiency enhancement upon light-soaking.

OHP cells are notorious for their hysteretic behaviour, which can have a strong influence on reported device performance and efficiencies. Key cell parameters such as the open-circuit voltage are found to depend on the biasing history as well as on scan-rates when measuring I-V curves. As a potential cause for this behaviour, mobile ions are expected to occur in high densities as native defects in MAPbI$_3$ films due to their low formation energies and significant diffusion coefficents as predicted by ab initio calculation[4]. A number of recent papers (e.g. [5]) have investigated the effect of mobile ions on photovoltaic behaviour with a range of device models and concluded that these could explain the observed hysteresis. Here we present our own device-scale simulations which reinforce the findings of ref. [5] as well as providing new insights.

MAPbI$_3$ films have also been observed to exhibit a PL efficiency which grows with prolonged light-soaking on a similar timescale to the hysteresis, making it possible for both effects to be at play in a single observation. The presence atmospheric oxygen has been shown to play a crucial role in the PL enhancement, motivating the proposal that a photochemical reaction occurs between oxygen and non-radiative recombination centers in the MAPbI$_3$ films during light-soaking. Deactivated traps are also observed to reactivate after a period in the dark, implying that the reaction with oxygen is at least partially reversible. We report a numerical model incorporating both trap deactivation by photogenerated electrons and trap regeneration which demonstrates good agreement with light-soaking experiments, giving quantitative evidence in favour of the theory.

II. Results and Discussion

A. Slow-moving ions and hysteresis

A model was developed to simulate a *p-i-n* cell with mobile ions in its intrinsic region by combining SCAPS[6] to solve the semiconductor equations with MATLAB's in-built *pdefun* to solve the drift-diffusion equation for ionic motion. At each timestep an electric field was obtained from SCAPS to update the ion distribution, which would be input as a dopant concentration into SCAPS for the next timestep. In this way the ions move in response to the internal electric field within the intrinsic layer, accumulating at the *p* and *n* interfaces and screening the bulk electric field. At the high ionic concentrations of $N_i \approx 1 \cdot 10^{19} \mathrm{cm}^{-3}$ predicted by theory these accumulation regions have narrow widths of order of 1nm. At equilibrium the ions therefore affect the bulk primarily by screening the internal field, which can change the distribution of carriers significantly. In normal operation without ions, the built-in electric field caused by the difference in electron and hole contact work-functions assists in the separation of photogenerated carriers causing electrons to drift towards the electron transport layer and holes to drift in the opposite direction. When the cell is left in the dark or near short-circuit condition in the light, the internal field is such that ions will move to nullify this effect, decreasing carrier separation and increasing recombination. This mechanism has been pointed out by other investigators and goes most of the way towards explaining experimentally observed hysteresis curves.

In addition to screening the bulk field, we find that the accumulation of ions at the *i-n* and *p-i* boundaries also affects the junction properties at these interfaces, a fact which has received less attention. For example, after biasing at $V < V_{oc}$
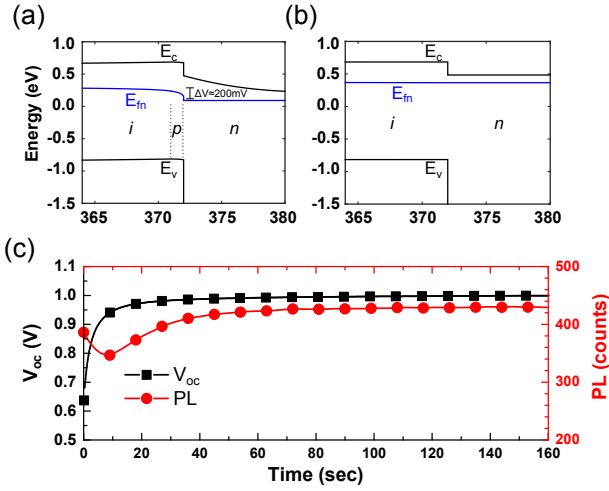
Fig. 1. (a) Band structure at the *i-n* interface (electron contact) with ions in their equilibrium position for short-circuit bias, measured at V_{oc} and (b) without ions. (c) Measurements of V_{oc} and PL intensity after biasing at short-circuit condition.

Fig. 2. (a) PL intensity of a partially encapsulated $MAPBI_3$ film measured as a function of time after exposure to 572nm laser light at an intensity of $80\,\mathrm{W\,cm^{-2}}$ with spot size $\approx 750\,\mathrm{nm}$. (b) Measured PL intensity shown at different radii. (c) Simulated PL intensity.

negative ions are accumulated at the *i-n* interface to form what is effectively an *i-p-n* junction. This narrow region of high p-doping causes a depletion of electrons which drastically reduces the electron conductivity near the interface, visible as a drop-off in the electron quasi-fermi level (Fig. 1(a)). There is also significant depletion and band-bending on the *n* side, even though this region is highly doped ($N_D = 8 \cdot 10^{18}\mathrm{cm^{-3}}$), which is a likely cause of capacitive behaviour. We note that a similar effect may occur at the *p-i* interface.

Ordinarily, a reduction in open-circuit voltage would indicate a decrease in the quasi-fermi level splitting within the absorber and would manifest as an exponential reduction in PL efficiency. Measurements of V_{oc} after biasing a planar $MAPbI_3$ cell at short-circuit defy this expectation as shown in Fig. 1(c). This may be explained by a sharp drop carrier quasi-fermi levels at the selective contacts as in Fig. 1(a) which are not accompanied by a similar reduction in splitting throughout the bulk, leaving the PL measurements relatively unaffected.

B. Photochemically active defect model

We have employed the semiconductor module of COMSOL Multiphysics to check the viability of defect deactivation as a theory for explaining the light-soaking behaviour observed in our labs (Fig. 2(a)). It is assumed that the photochemically active defects are the dominant source of SRH recombination in the film and that charging effects can be neglected. The defect concentration u is taken to follow the equation

$$\frac{\partial u}{\partial t} = u(-R_{dt}n + 1/\tau_{reg}) \tag{1}$$

which captures the processes of deactivation by photogenerated electrons with a rate constant R_{dt} and reactivation on a timescale τ_{reg}, respectively. Diffusion of traps was also modelled as a possible explanation for the results in Fig. 1(a) but was ruled out as a significant process by further experiments. The simulation consisted of two steps in which equation
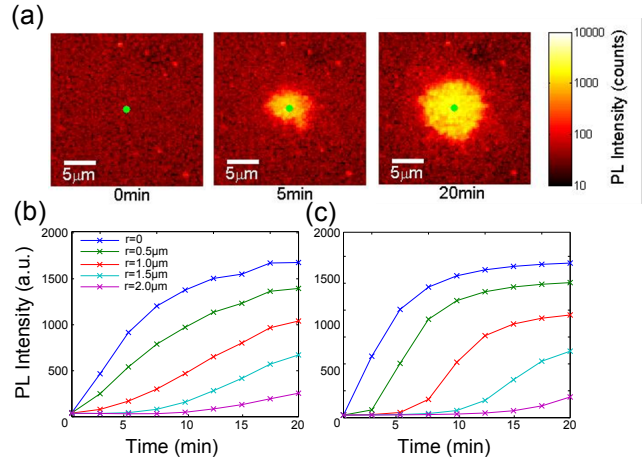
(1) was first used to simulate the evolution in trap density under illumination at $r = 0$ with an axissymmetric model, followed by a measurement step in which the resulting profiles were used to simulate PL measurements taken at different radii in a two-dimensional model. With some adjustment the simulation was able to match experiment in terms of both the net enhancement (≈ 60 fold after 20 minutes) as well as the approximate variation with distance from the central spot and in time.

III. CONCLUSION

We have succeeded in modelling two slow processes in organo-metal halide perovskites: the well-known current-voltage hysteresis, and the enhancement in PL efficiency after light-soaking. Our work provides further evidence in favour of the theory that mobile ions are primarily responsible for hysteresis in perovskite cells, and has provided new insights into the relationship between their internal distribution and measured properties such as open-circuit voltage and PL efficiency. We have also developed a quantitative model for the theory of photoinduced defect deactivation which is shown to be a viable explanation for the unusual light-soaking behaviour in $MAPbI_3$ films.

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