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Modeling the degradation/recovery of open-circuit voltage in perovskite and thin film solar cells

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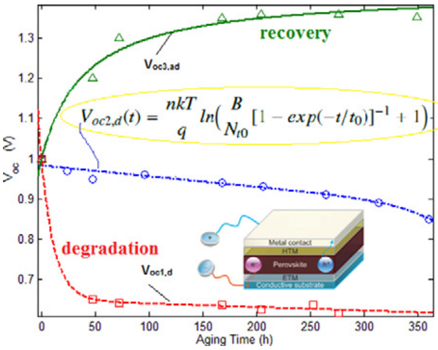
HIGHLIGHTS

- Eight different time-dependent models of V_{oc} degradation/recovery were modeled.
- V_{oc} changes by defect increment within depletion region under stress condition.
- Defect generation profile (linear/exponential) roles out the V_{oc}(t) trend.
- V_{oc}(t) models were fitted for various CdTe, CIGS, CZTS and perovskite solar cells.

GRAPHICAL ABSTRACT



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ABSTRACT

Developing theories behind the degradation/recovery of polycrystalline perovskite and thin film solar cells is essential in promoting the stability of such devices under stress conditions. Here we propose a novel approach to model the variation of open-circuit voltage by time, $V_{oc}(t)$ for perovskite, CdTe, CIGS and CZTS-based solar cells. Several time-dependent equations have been derived and fitted with the experimental data on degradation/recovery of V_{oc} under stress of light, bias, moisture and temperature. Any stress condition will change the defect density across the absorber layer of a solar cell. This will in turn effect on the saturation current density, depletion width and finally on the V_{oc} of a device. A good fit has been obtained between these proposed models and the data reported in the literature on degradation rate of V_{oc}. In some cases more than one model is required to fit with the data as urges by the non-crystalline nature of perovskite and thin film materials and specific influence of every stress condition (i.e. prolonged irradiation, elevated temperature or air humidity) on materials properties and defect profile across the device. Therefore, the distribution of defects may change by time depend on the intensity, type of the stress or recovery process. Different than previous believes, we showed that V_{oc}, as a measure of recombination rate and carrier collection efficiency of a device, may follow 8 different time-dependent models.

1. Introduction

Concerted efforts are currently being made to understand (and to limit) the degradation mechanisms in polycrystalline solar cells made of chalcogenide or perovskite materials. The device parameters of CdTe, CIGS, CZTS and perovskite-based thin film flexible

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photovoltaics go under sever degradation under the stress (aging) of prolonged irradiation, elevated temperature, long term bias, and air moisture exposition. Many of known degradation mechanisms are interrelated, creating additional complications in understanding the overall degradation process and kinetics. Generally, degradation is assigned to the electrodes or photo-absorbing material. Here we focus on the materials degradation as polycrystalline nature of thin film and perovskite materials is critically the source of many device instability [1,2]. The photo-degradation of open-circuit voltage over time has been experimentally investigated for thin film Si devices, including a:Si [3]. It was proposed that degradation kinetics depends only weakly on time but more on deposition conditions. However, several Potential-Induced Degradation, *PID*, and recovery analysis of thin film solar cells have shown to be significantly effective on device stability [4,5]. Also, a combinated aging tests (thermal and light-soaking) resulted in even more drastic effect on device stability. Therefore, modeling the degradation behavior of thin film solar cells is essential to gain more insight into device response to aging conditions. Majority of the degradation models reported in the literature are based on fitting functions created by taking the ratio of initial and final values of the device parameters before and after degradation period [6,7]. Only a few models were proposed based on the device physics and degradation kinetics and by using the optical and electrical properties of the materials [8–11]. Proposing a time-dependent model for the degradation of such devices is basically complicated because of a non-crystalline or slightly random reaction of such materials to the level and type of stress condition [12–15]. Nardone proposed a time-dependent numerical simulation based on defect creation/annihilation kinetics in thin film solar cells by dividing the CdTe layer to several thinner layers and assuming a *simultaneous* generation of shallow and deep defect in vicinity of junction [8]. A different approach was developed by Principato et al. where they assumed that the electric field in the absorber layer is time-dependent as the defect density increases exponentially by time in a fully depleted CdTe device [9,10]. Although these approaches provide a time-dependent model for device metrics, they are mostly based on many assumptions which makes the generalization of the model difficult; defect increment is supposed to follow a single power law or exponential profile, the defects are to be generated only in the depletion width, and only a single model to fit with the degradation trend of all device parameters for the whole aging time. Here we propose several different time-dependent models for the degradation of open-circuit voltage of various thin film solar cells based on two main defect generation profiles: linear and exponential. We focused on V_{oc} as a representative parameter for the recombination rate of the solar cells [5]. Moreover, we used the basic theories to relate V_{oc} to aging time for both inside and outside of depletion width such as when the depletion width is narrow and when it is widely extended to the back region of the device. These were important to be separately discussed since in the prior case, the carrier transport is by drift and diffusion whereas the latter case only the drift component is the dominant. The presented modeling procedure provides a road to model the V_{oc} of various semiconductor devices only by finding the proper time-dependent trap density profile. We note that this ideal model, considers only the degradation mechanisms due to changes in electronic defects and does not consider more realistic macroscopic “engineering” related defects like metallic shunting, film delamination, hot spots.

2. Theory

Generally, the open circuit voltage, V_{oc}, of a solar cell is given by [16]

$$V_{oc} = \frac{nkT}{q}\ln\left(\frac{J_{sc}}{J_0}+1\right) \tag{1}$$

where kT/q ≈ 26 meV, and $n = 1{,}2$ is the ideality factor. The ideality factor $n = 1$ corresponds to the case where the bimolecular (direct) recombination is the dominant whereas $n = 2$ is attributed to the case with Shockley-Read-Hall, SRH, trap-assisted recombination dominant. In Eq. (1), if we assume $J_{sc} = J_{ph}$, which is usually between 25–35 mA/cm^2 for the thin film and perovskite solar cells. The time-dependent parameter in this equation is the dark saturation current, J_0, via it's dependence on the defect density, N_A. N_A is variable under stress at elevated temperature, prolonged irradiation, bias or moisture [9,10]. J_0 is slightly different for the thin and thick depletion width [16],

$$J_{01}(t) = \frac{qn_i^2}{N_A}\sqrt{\frac{D_n}{\tau_n}}, \quad W \quad thin, \tag{2}$$

$$J_{02}(t) = \frac{qn_iW}{\tau_n}, \qquad W \quad thick \tag{3}$$

where N_A is the acceptor density, D_n is the diffusion coefficient, the intrinsic carrier density is $n_i^2 = N_cN_v \cdot exp(-E_g/kT)$ where $N_{c,}v$ are the valence and conduction band density of states and E_g is the band gap. In Eq. (2), W is thin compared to absorber layer thickness, thus both drift and diffusion mechanisms are involved in current conduction. This applies to most of solar cells with absorber layer thickness of >1.5 μm i.e. CdTe, Cu(In,Ga)(Se,S)$_2$ and Cu(Zn,Te)(S,Se$_2$) (CZTS) based devices. In contrast, when W is thick has a comparable thickness to absorber layer (i.e. fully depleted device), the drift component is the dominant carrier transport mechanism and the diffusion component has negligible effect in carrier collection.

In above equations, τ_n is carrier recombination lifetime which is related to defect density by,

$$\tau_n = \frac{1}{V_{th}\cdot\sigma_n\cdot N(t)}. \tag{4}$$

V_{th} is electrons thermal velocity, σ is the minority carrier's capture cross section, and $N(t)$ is the trap density. It is well known that the trap density changes by time under the stress. Light induced defects, ion migration, etc. will effectively increase the trap density as the major reason for the degradation of solar cells [17]. This time-dependent variation has been investigated in the literature and some time-dependent functions have been suggested for $N(t)$ in different thin film and perovskite solar cells or even for IR photo-detectors. This time-dependency trend was mainly proposed to have the following forms for shallow and deep level trap density, respectively [8,10],

$$N_{ts}(t) = N_{t0}(1+t/t_0)^{1/\theta} \quad \theta = 2,3 \tag{5}$$

$$N_{td}(t) = N_{t0}\,(1-\exp(-t/t_0)) \tag{6}$$

In Eq. (5), N_{t0} is the trap density at $t = 0$ and t_0 is degradation time constant as calculated in Refs. [8,12] for the CdTe thin film solar cells. Principato et al. presented a time dependent approach for deep acceptor increment with time [10] as given by Eq. (6) where t_0 is hole de-trapping time. Several other time-dependent profiles were also suggested for $N(t)$ in the literature, but they do generally follow a linear or exponential trend similar as Eqs. (5) & (6) [18,19]. Therefore, we limit our calculation to the above two time-dependent functions of N_A(t). The other proposed N_A(t) profiles can be considered using the same approach developed in the following.

Now, we drive the time-dependency of V_{oc} by inserting Eq. (4) in Eq. (2) or (3) and inserting the latter in Eq. (1). After some simple

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