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Modeling the time-dependent characteristics of perovskite solar cells

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ABSTRACT

We proposed two different time-dependent modeling approaches for variation of device characteristics of perovskite solar cells under stress conditions. The first approach follows Sah-Noyce-Shockley (SNS) model based on Shockley–Read–Hall recombination/generation across the depletion width of pn junction and the second approach is based on thermionic emission model for Schottky diodes. The connecting point of these approaches to time variation is the time-dependent defect generation in depletion width (W) of the junction. We have fitted the two models with experimental data reported in the literature to perovskite solar cell and found out that each model has a superior explanation for degradation of device metrics e.g. current density and efficiency by time under stress conditions. Nevertheless, the Sah-Noyce-Shockley model is more reliable than thermionic emission at least for solar cells.

1. Introduction

Time dependent models have been rarely developed for current–voltage (JV) characteristics of optoelectronic devices. Time-dependent models have much more realistic approaches to device function and provide the observation possibility to determine the degradation/recovery behavior of a device operating under stress conditions such as long term reverse biasing (e.g. in solar cell, sensors, and photodetectors) (Alsari et al., 2018; Turturici et al., 2014). The currently available models are presented mainly in static mode which ignores materials and structural changes in the device such as defect generation and intermix of the adjacent layers or in-diffusion of the metallic contacts towards the junction. These are the detrimental process that happen by time and cause degradation in device performance. A comprehensive model must be able to trace the device characteristics by time. We have previously developed several time-dependent theories to model the characteristics of solar cells under stress conditions (Darvishzadeh et al., 2017a; Darvishzadeh et al., 2017b). There are few other publications in the literature which propose time-dependent models for current conduction mechanisms in various devices (Turturici et al., 2017). Turturici et al. have proposed a time dependent modeling for the forward current and reverse biased currents of a photodetector based on p-CdTe (Turturici et al., 2014; Turturici et al., 2017). We will partially use their modeling approach in this paper to develop from a static JV analysis to a time dependent JV curves or at least a current vs. time approach. In their modeling, Turturici et al. have assumed that the defect generation follows an exponential trend by time in the p-type layer and negatively impacts on carrier collection at reverse biases. Although this modeling approach is partly able to explain the current density variation by time, the direct role of electric field at the metal/p-type junction is not clear. A rather parametric model is required to understand how the electron, hole, acceptor, donor defects are involved in the carrier collection under the electric-field in the depletion width of a device. We have previously applied a strong modeling approach to CdS/CdTe solar cells which devices the carrier collection to drift and diffusion currents in within and outside of depletion width, respectively (Darvishzadeh et al., 2017a; Darvishzadeh et al., 2017b). Here, we propose the model in time-dependent form for pn junction and photodetectors based on graphene. We use graphene based devices it has attracted the attention of many researchers not only for solar cell application but also for sensors, photodetectors, LEDs, etc. over 100 papers have been published last year on graphene application in perovskite solar cells (Son et al., 2017; Singh et al., 2018). The recent review on these hybrid devices shows a power conversion efficiency between 10% and 15% for graphene and inorganic semiconductor-based hybrid heterojunction solar cells, and 15.6% for graphene-containing perovskite cells. Graphene or carbon nanolayers will act as a supressing layer for shunting process. Bi et al. have designed a

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nanostructured carbon layer to impede the diffusion of ions into perovskite layer which have significantly suppressed the degradation process (Bi et al., 2017).

We will develop two time-dependent approaches to model the instability of current–voltage characteristics of perovskite solar cells (with graphene contact) under stress conditions of elevated temperature, long term bias or prolonged irradiation. We will fit the model with experimental data reported in literature and will show that our simple but strong modeling can explain the defect generation impact on device characteristics. The modeling is based on a fundamentally different approach than the other theories like transient current and will simply start from Shockley–Read–Hall recombination or Thermionic emission theories.

2. Modeling approach

We present two different modeling approach based on SNS theory for the generation/recombination within depletion width and thermionic Schottky emission for a fully depleted cell. This theory was well developed by Kosyachenko's group (Kosyachenko et al., 2009; Kosyachenko et al., 2016) and also by our group recently (Aldosari et al., 2016). Both theories have the electric field or depletion width in their formulation which provides us a way to connect them to time and the change in defect density by time. The models provide time-dependent current density (J_{sc}) and current–voltage characteristics which could lead us to calculate the efficiency variation by time ($\eta(t)$) through solar cell's principal theory (Kosyachenko, 2011).

2.1. Time-dependent Sah-Noyce-Shockley theory

The current–voltage characteristics of a pn junction is best described by modeling approach developed by Kosyachenko et al. (2009). The model is based on known Shockley–Read–Hall (SRH) recombination described by Sah-Noyce-Shockley (SNS) theory for the depletion width or as so called space charge region of a pn junction (Kosyachenko et al., 2016),

$$U(x,\,V) = \frac{n(x,\,V)p(x,\,V) - n_i^2}{\tau_{po}[n(x,\,V) + n_1] + \tau_{no}[p(x,\,V) + p_1]} \tag{1}$$

where $n(x,\,V)$ and $p(x,\,V)$ are defined as minority and majority carriers in the p-type layer,

$$n(x,\,V) = N_c exp\left(-\frac{E_g - \Delta\mu - \varphi(x,\,V) - qV}{kT}\right), \tag{2}$$

$$p(x,\,V) = N_v exp\left(-\frac{\Delta\mu + \varphi(x,\,V)}{kT}\right). \tag{3}$$

where $\Delta\mu$ is the distance between Fermi level and valence band (conventionally given as: E_f-E_v) as shown in Fig. 1. The thermionic emission is not introduced here because the barrier for carrier transport, $\Phi = \varphi_{bi} + \Delta\mu$, (characteristic of thermionic emission) does not appear in Eqs. (1)–(3). n_1 and p_1 are determined by SRH theory by supposing that a single defect level (E_t) is located in the band gap,

$$n_1(x,\,V) = N_c exp\left(-\frac{E_g - E_t}{kT}\right),\ \ where\ N_c = 2(m_n kT/2\pi\hbar^2)^{3/2} \tag{4}$$

$$p_1(x,\,V) = N_v exp\left(\frac{-E_t}{kT}\right),\ \ where\ N_v = 2(m_p kT/2\pi\hbar^2)^{3/2}. \tag{5}$$

By integrating over $U(x,\,V)$, the generation current is obtained under reverse bias and recombination current is obtained under forward bias over the SCR (from 0 to W) (Kosyachenko et al., 2009),

$$J_{gr} = q\int_0^W U(x,\,V)dx. \tag{6}$$

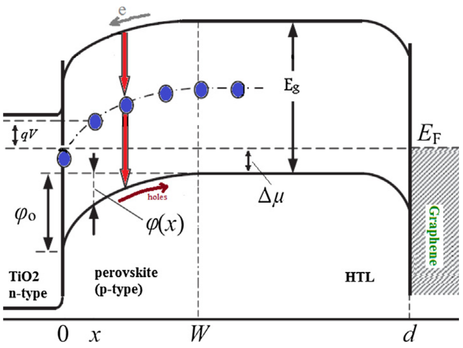

Fig. 1. The energy band diagram of the perovskite solar cell under forward bias. Carrier transport through generation/recombination current, I_{gr}, and over-barrier current, I_n, depletion width, W, band bending $\varphi(x)$, and Fermi levels are indicated (Kosyachenko et al., 2009; Darvishzadeh et al., 2017a). Note that, the back barrier will be neglected for a fully depleted device as TiO_2/perovskite/HTL layer are thin enough compared to the depletion width ($W > d$). Therefore, this diagram changes to a band diagram of a, for example, photodetector with metal/semiconductor/metal structure.

where W is the depletion region of the device where the main recombination and generation of carriers occurs and the drift current is dominant by a strong electric field. The depletion width is conventionally given by Shockley barrier theory,

$$W = \sqrt{\frac{2\,\epsilon(\varphi_0 - qV)}{q^2(N_a - N_d)}}, \tag{7}$$

where ϵ is the dielectric constant of the p-type layer and N_a and N_d are acceptor and donor density in depletion region. Note that the term under the root allows modeling both reverse and forward bias ranges only by changing the + sign to − in $\varphi_0 - qV$. The static nature of the modeling for current–voltage characteristics comes from this point where W is taken constant. However, the generation/recombination mechanism is not a static process but a dynamic one which can slightly or significantly change under prolonged irradiation, elevated temperature and ever moisture ingression to the junction (Chen et al., 2016). Therefore, a time-dependent process might be introduced for a real-time analysis of device under operation or at certain times of operation under real conditions. A time-dependent depletion width was introduced by Turturici et. al. for photo-detectors with Al/p-CdTe/Pt structure (Turturici et al., 2014). They proposed that the depletion width becomes a time-dependent parameter when the defect density exponentially increases in the region,

$$W(t) = \sqrt{\frac{2\,\epsilon(\varphi_0 - qV)}{q^2 N_{a0}(1 - e^{\frac{-t}{\tau}})}}, \tag{8}$$

where τ and N_{a0} are hole detrapping time and deep trap acceptor density at t = 0 before the voltage is applied to the photodetector. The time dependent profile of acceptor trap density is given by $N^-(t) = N_T(1 - e^{\frac{-t}{\tau}})$ (Turturici et al., 2014). Although we have previously introduced a different defect changing profile to be in form of quadratic or even linear form elsewhere (Darvishzadeh et al., 2017a). By inserting Eq. (8) into Eq. (6) one can calculate a time-dependent photocurrent density for a pn junction device or for a photodetector with a metal/semiconductor/metal structure if the semiconductor thickness (L) is smaller than the depletion width (L < W) at all voltages. Finally, Eq. (6) must rewritten in the form of a time-dependent equation,

$$J_{gr}(t,\,x,\,V) = q\int_0^{W(t)} U(x,\,V)dx. \tag{9}$$

Note the above is a time, position and voltage dependent equation which makes the modeling quite close to reality.