Tunneling-enhanced recombination in Cu(In,Ga)Se_2 heterojunction solar cells

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This letter presents an analytical model for tunneling-enhanced recombination current in the space charge region of semiconductor junctions. We investigate current–voltage characteristics of different types of Cu(In, Ga)Se_2-based heterojunction solar cells in a temperature range from 100 to 340 K. The temperature dependence of the saturation current and of the diode ideality factor of these devices are well described by the closed form expressions derived by the present approach. © *1999 American Institute of Physics.* [S0003-6951(99)05101-3]

Trap assisted tunneling or tunneling enhanced recombination in the space charge region (SCR) is an important electronic transport mechanism in highly doped bipolar semiconductor devices.[1–3] Here, the recombination of electron hole pairs via trap states, normally described by the classical Shockley–Read–Hall (SRH) recombination rate,[4] is enhanced by tunneling of free carriers into the recombination centers.[2,3] Recombination in the SCR is the dominant loss mechanism of polycrystalline thin film solar cells based on Si[5] and Cu(In, Ga)Se_2.[6,7] An increase of the doping density, in principle, could minimize this loss mechanism by minimizing the width of the SCR. However, it has been recognized that the gradual increase of the tunneling probability going hand in hand with the increased built-in field in the junction limits this benefit. The competing effects of decreasing the width of the effective SRH recombination zone and increasing the tunneling current define an optimum doping density.[8] Optimizing the solar cell performance by optimizing the electrical field in the junction requires simulation of the electrical transport of those devices *as well as* a careful analysis of the electronic transport mechanism of the finished devices. Recently, theoretical approaches for the tunneling enhancement of recombination currents have been developed for the purpose of numerical device simulation.[2,3] However, no simple tool is available for the quantitative analysis of experimentally obtained data of practical devices working just at the threshold between classical and tunneling enhanced recombination.

In this letter we introduce a simple equation for the recombination current resulting from tunneling enhanced recombination in the SCR of biplor devices (details of the mathematics will be given elsewhere).[9] We demonstrate that the temperature dependence of various Cu(In, Ga)Se_2 based heterojunction solar cells is well described by our theory. Hurkx and co-workers[2] find for the recombination rate of tunneling assisted recombination

$$R=\frac{np-n_i^2}{\gamma_p(n+n^*)+\gamma_n(p+p^*)}, \tag{1}$$

where n and p are the number of free electrons and holes, kT the thermal energy, n_i is the intrinsic carrier concentration, $n^*=N_C\exp[(E_T-E_C)/kT]$ and $p^*=N_V\exp[(E_V-E_T)/kT]$ with N_C and N_V as the effective density of states in the conduction and in the valence band and E_T being the trap energy. The quantities $\gamma_{n/p}$ are defined by $\gamma_{n/p}=\tau_{n/p}[1+\Gamma]^{-1}$ where $\tau_{n/p}$ are the lifetimes of trapped electrons and holes and Γ is a correction factor for the enhancement of recombination by tunneling. For a parabolic band bending we rewrite the original expression derived in Ref. 2 by

$$\Gamma=2\sqrt{3\pi}\sqrt{\frac{qV_b(x)}{3kT}\frac{E_{00}^2}{(kT)^2}}\exp\left(\frac{qV_b(x)}{3kT}\frac{E_{00}^2}{(kT)^2}\right), \tag{2}$$

where $V_b(x)$ is the local band bending dependent on coordinate x and $E_{00}=(q\hbar/2)(N_A/m^*\epsilon_s)^{1/2}$ the well known characteristic tunneling energy.[10] Here, N_A is the net doping density, m^* the effective tunneling mass, and ϵ_s the semiconductor's dielectric constant. Equations (1) and (2) describe a continuous modification of the SRH recombination rate by an increasing contribution of tunneling with increasing E_{00} or decreasing temperature T. Therefore, we prefer to use the term *tunneling enhanced recombination* instead of trap assisted tunneling.

Following the idea of Walter *et al.*[6] we use a distribution of recombination centers with an exponential decay of the trap density from the band edge in order to describe recombination in Cu(In, Ga)Se_2-based devices, i.e., we assume a trap density $dN_t(\eta)\propto\exp(-\eta/kT^*)d\eta$ where kT^* is the characteristic energy of the distribution and $\eta=E_T-E_V$ in the case where the distribution has its maximum at the edge of the valence band. Integration of Eq. (1) over the distribution dN_t yields[9]

$$R(T^*)=(np)\frac{(\gamma_p n+\gamma_n p)^{T/T^*-1}}{(\gamma_n N_V)^{T/T^*}}\frac{\pi T/T^*}{\sin(\pi T/T^*)}. \tag{3}$$

It is straightforward to integrate the recombination rate $R(T^*)$ across the width of the SCR of a single-sided junction (e.g., a Schottky contact or a n^+p heterojunction).[9] We find for the case of the *standard* SRH recombination (i.e., $\Gamma\ll 1$)

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$$j_r = j_{00} \exp\left(\frac{-E_g}{AkT}\right) \exp\left(\frac{qV}{AkT}\right) \tag{4}$$

with

$$j_{00} = \frac{kT}{F_m} \nu^{1/2} \theta^{T/2T^*} \Lambda(T/T^*,1) \tag{5}$$

and $\nu = (N_C N_V)/(\tau_n \tau_p)$, $\theta = (\tau_p N_C)/(\tau_n N_V)$. The quantity F_m denotes the magnitude of the electrical field at the location of maximum recombination and A is the diode ideality factor with

$$\frac{1}{A} = \frac{1}{2}\left(1 + \frac{T}{T^*}\right). \tag{6}$$

The function $\Lambda(\vartheta,\xi)$ entering in Eq. (5) and later in Eq. (9) is defined by

$$\Lambda(\vartheta,\xi) := \frac{\pi\vartheta}{\sin(\pi\vartheta)} \int_0^\infty \frac{(u+u^{-1})^{\vartheta-1}}{u^\xi} du. \tag{7}$$

The expression for the ideality factor of Eq. (6) as derived earlier in Ref. 6 explains ideality factors which are between one and two for temperatures $0 < T < T^*$. The temperature dependence of the ideality factor of $Cu(In,Ga)Se_2$ solar cell devices in a limited range around room temperature is well described by Eq. (6).[6,7] However, at lower temperatures the tunneling contribution becomes more and more significant and deviations from Eq. (6) are expected.

Let us now integrate Eq. (3) for the case of a considerable tunneling contribution to the recombination (i.e., $\Gamma \gg 1$). We find[9]

$$j_r = j_{00} \exp\left(\frac{-E_g}{AkT}\right) \exp\left(\frac{qV}{AkT}\right) \tag{8}$$

with

$$j_{00} = 2\sqrt{3\pi}\, \frac{kT}{F_\Gamma} \nu^{a_t/2} \theta^{T/2T^*} \left(\frac{p_0}{\tau_p}\right)^{1-a_t} \Lambda(T/T^*,a_t), \tag{9}$$

where p_0 is the equilibrium hole concentration in the neutral zone of the semiconductor, F_Γ is a characteristic field strength defined in Ref. 2, and $a_t = 1 - E_{00}^2 (kT)^{-2}/3$. The ideality factor A for tunneling enhanced recombination in the SCR reads

$$\frac{1}{A} = \frac{1}{2}\left(1 - \frac{E_{00}^2}{3(kT)^2} + \frac{T}{T^*}\right). \tag{10}$$

Equation (10) describes the diode ideality factor which results from tunneling enhanced recombination of electron hole pairs via an exponential distribution of recombination centers. In the limit ($T^* \to \infty$) we obtain a one parameter equation which holds for tunneling enhanced recombination via midgap states whereas in the limit ($E_{00} \to 0$) Eq. (6) is recovered. Thus, our theory, much like the theory for thermionic field emission at Schottky contacts,[10] represents a continuous transition of the diode ideality factor A between one and two at high temperatures T to that dominated by tunneling towards lower T where A can be also larger than two.

In the following we present investigations of the temperature dependence of current voltage (I–V) characteristics of different $ZnO/CdS/Cu(In,Ga)Se_2$ heterojunction solar cells. For the evaluation of these experimental data we take advantage of the fact that according to Eq. (8) the saturation current density can be rewritten by $A \ln j_0 \propto E_g/kT$. Thus, a *modified* Arrhenius plot $A \ln j_0$ vs $1/T$ should yield a straight line, with the slope corresponding to the band gap energy E_g. In Fig. 1 we display such modified and the unmodified Arrhenius plots of the saturation currents I_0 derived from the different solar cells. The $Cu(In,Ga)Se_2$ absorbers of samples A and B were prepared by rapid thermal processing (RTP) of stacked elemental layers as described in Ref. 11 whereas curve C stems from a cell with a $Cu(In,Ga)Se_2$ absorber layer prepared by coevaporation.[12] The activation energies of the modified curves A' and B' are 1.04 eV which is the band gap energy of pure $CuInSe_2$ despite of the Ga content of 17% in these samples. This finding is compatible with the fact that almost all Ga in solar cells prepared by RTP is situated close to the back contact and, consequently, the band gap in the SCR is that of pure $CuInSe_2$. The activation energy of 1.21 eV found for of sample C corresponds to the Ga content of approximately 28% in this sample.

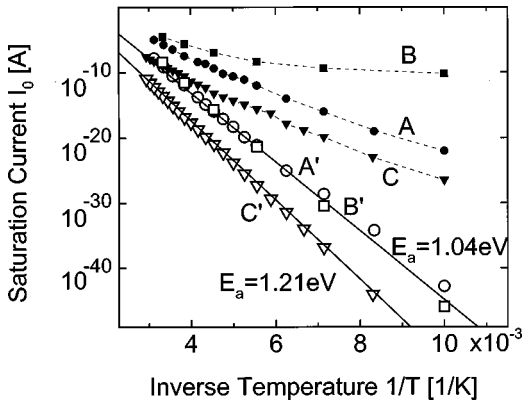

FIG. 1. Semilogarithmic plot of the unmodified (full symbols) and modified (open symbols) saturation currents of the ZnO/CdS/$Cu(In,Ga)Se_2$ heterojunction solar cells A (squares), B (circles), and C (triangles) vs the inverse temperature. The slopes of the *corrected* plots A',B',C' yield the band gap energies of the absorber material of the devices (1.04 eV for A' and B', 1.21 eV for C').

The difference between the corrected and the uncorrected Arrhenius plots in Fig. 1 according to Eq. (8) are simply due to the different temperature dependencies of the ideality factors of the different samples. The inverse $1/A$ of the ideality factors of samples A–C are shown in Fig. 2 together with fits to Eq. (10). From these fits we obtain the following parameters: $A - E_{00} = 3.9$ meV, $kT^* = 95$ meV, $B - E_{00} = 13.8$ meV, $kT^* = 134$ meV, $C - E_{00} = 6.5$ meV, $kT^* = 74$ meV. It is interesting to compare the E_{00} values of samples A and B, because these solar cells are prepared with the same process except that the Na content of sample B was intentionally increased by a factor of 10 with respect to sample A.[13] As it is known that Na increases the net doping density of $Cu(In,Ga)Se_2$[13,14] it is not surprising that E_{00} of sample B is increased by a factor of $3.5 \approx \sqrt{10}$ when compared to sample A. The low open circuit voltage V_{OC} of 360 mV of device B compared to $V_{OC} = 434$ meV of device A is then understood by the fact that tunneling significantly enhances the recombination already at room temperature. The I–V data obtained from the solar cell with the coevaporated

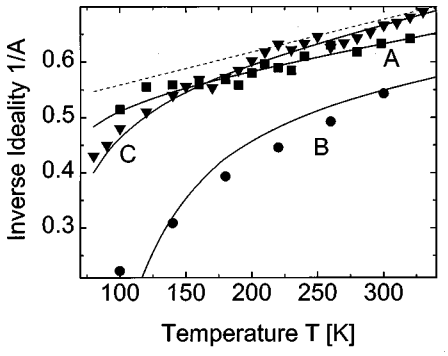

FIG. 2. Temperature dependence of the inverse diode idelity factor of the solar cells A–C. The solid lines are fits to Eq. (10) with the parameters: $A-E_{00}=3.9$ meV, $kT^*=95$ meV, $B-E_{00}=13.8$ meV, $kT^*=134$ meV, $C-E_{00}=6.5$ meV, $kT^*=74$ meV. The straight, dashed line corresponds to Eq. (6) with $kT^*=74$ meV.

absorber is fitted with $E_{00}=6.5$ meV, a value between the extremes provided by the two RTP samples. The higher open circuit voltage $V_{OC}=640$ mV of device C compared to A and B is partly due to the higher band gap of the absorber material but might be also a consequence of the more optimized doping which decreases the width of the SCR without increasing too much the tunneling contribution to the recombination current.

In summary, we have proposed a new closed form expression for tunneling enhanced recombination currents via trap states in the SCR of single-sided semiconductor junctions. The temperature dependence of $I-V$ curves of $Cu(In, Ga)Se_2$-based solar cells is well described by this model. The analysis of more electrical data together with a careful tuning of the doping density in $Cu(In, Ga)Se_2$-based solar cells could help to improve the open circuit voltage of future devices.

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