Bulk Recombination in Organic Bulk Heterojunction Solar Cells under Continuous and Pulsed Light Irradiation

Kazuhiro Seki, Kazuhiko Marumoto, and Masanori Tachiya

1 National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan
2 Division of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Received March 12, 2013; accepted April 16, 2013; published online May 9, 2013.

We study bulk recombination under both steady-state and time-resolved conditions by using the multiple trapping (MT) model. The MT model incorporates charge trap states with a distribution of trapping energies. Charge densities under the continuous excitation are shown to obey the power law as a function of light intensity, and the exponent is related to that obtained from the transient decay of charge densities in time-resolved experiments. The theory is applied to analyze charge densities in bulk heterojunction photovoltaic cells measured by light-induced electron spin resonance (LESR) under both continuous and pulsed light irradiation. © 2013 The Japan Society of Applied Physics.

In order to improve power conversion efficiency, it is important to suppress the electron–hole recombination and promote efficient charge separation.15 Electron–hole recombination has been studied extensively under time-resolved conditions in which the sample is irradiated with a short pulse of the excitation light. Several groups measured the decay kinetics of carriers after they are generated by a short pulse. If the electron–hole recombination occurs following an ordinary bimolecular reaction, the decay of carriers should be proportional to $1/t$, where $t$ is the time after the pulse. The observed data followed a power law $1/t^\beta$ but $\beta$ was much less than unity.2–10

By using light-induced electron spin resonance (LESR), electron–hole recombination has also been studied under steady-state conditions in which the sample is continuously irradiated with an excitation light.8–10 The dependence of the carrier density on the light intensity has been measured. If the electron–hole recombination occurs following an ordinary bimolecular reaction, the carrier density should be proportional to $I^0\gamma$, where $I$ is the light intensity. The observed data followed a power law $I^\gamma$ but $\gamma$ was less than 0.5.8–10

In the present paper, we explain the above two types of experimental result on the basis of the multiple trapping (MT) model.8,11–15 The MT model was presented and applied to time-resolved kinetics of charge recombination in organic solar cells by using the analytical solution.15 In the MT model, charge trap states are assumed to be distributed with different trapping energies, and charges perform transitions among trap states of different energies. In time-resolved experiments, the distribution of carriers among trap states with different trapping energies changes with time. This changes the detrapping rates of carriers. We have shown theoretically in Ref. 15 that the total density of carriers decays with time as $t^{-\beta}$ with $\beta$ less than unity instead of $t^{-1}$. A similar explanation was also given by other approaches.16,17

In this work, the MT model is developed to introduce the generation rate of charges under steady-state conditions. If the total density of carriers is changed in a steady-state experiment by changing the light intensity, it changes the distribution of carriers among trap states with different trapping energies. This changes the detrapping rates of carriers. We show theoretically that the total density of carriers depends on the light intensity as $I^\gamma$ with $\gamma$ much less than 0.5 instead of $I^0$.

Under the continuous irradiation with light, the excitons are generated. The electron–hole pairs are strongly bound in excitons. The excitons can be dissociated into a hole and an electron at the interface between a donor phase and an acceptor phase in a bulk heterojunction. The charge generation rate, $G$, is proportional to the light intensity, $I$,

$$G = k_g I.$$  \hfill (1)

The charges are initially produced in the free state. The motion of charges in bulk heterojunction solar cells has been described using the MT model.18–21 In the model, charges are trapped in the trap sites. We assume that if the detrapping rates of electrons and holes are different, charges with the lower detrapping rate are always trapped but those with the higher detrapping rate (hereafter, called carriers) are partly trapped and partly free.

We assume that electron–hole recombination occurs once carriers are detrapped. Therefore, the recombination rate depends on the detrapping rates of carriers. The detrapping rate constant is expressed as

$$k_d(E) = \nu_3 \exp\left(-\frac{E}{k_BT}\right).$$  \hfill (2)

where $E$ is the trapping energy of a carrier relative to the free mobile state, and $\nu_3$ is the detrapping frequency. We use $\nu_4$ to normalize rates and introduce the dimensionless energy defined by $\epsilon = E/k_BT$. By thermal excitation, carriers can be detrapped to the free state. The carriers in the free state can either be trapped by vacant trap sites or recombine with trapped counter charges.

We denote the trapping energy distribution by $g(\epsilon)$. Let $f(\epsilon)$ denote the number density of carriers trapped at trap sites with trapping energy $\epsilon$. In the steady-state, the distribution $f(\epsilon)$ obeys

$$0 = G \frac{k_d[N g(\epsilon) - f(\epsilon)]}{k_r(n - N + k_r n) + k_i n} - e^{-\epsilon} f(\epsilon)$$

$$+ k_i \frac{N g(\epsilon) - f(\epsilon)}{k_r (N - n) + k_i n} \int_0^\infty e^{-\epsilon} f(\epsilon) \, d\epsilon,$$  \hfill (3)

where the number density of trap sites is denoted by $N$, $n$ is the total number density of carriers and related to the number density of carriers trapped with energy $\epsilon$ by

$$n = \int_0^\infty f(\epsilon) \, d\epsilon.$$  \hfill (4)
The density numbers of holes and electrons are the same. \( k_i \) and \( k_t \) are the rate constants of a carrier in the free state for trapping and for recombination, respectively. \( G, k_i \), and \( k_t \) are normalized by \( \nu_0 \) as mentioned above.

The first term on the right-hand side represents the generation rate of carriers with trapping energy \( \epsilon \). The probability that a carrier in the free state will be trapped in a trap state with trapping energy \( \epsilon \) is proportional to \( k_t \). Therefore, the probability that a carrier in the free state will recombine with a trapped counter charge is proportional to the recombination rate multiplied by the number density of counter charges, \( n \). Therefore, the probability that a carrier in the free state will be trapped into a site with trapping energy \( \epsilon \) can be written as

\[
\frac{k_i [N g(\epsilon) - f(\epsilon)]}{k_t \int_0^\infty [N g(\epsilon) - f(\epsilon)] d\epsilon + k_t n} = \frac{k_i [N g(\epsilon) - f(\epsilon)]}{k_t N + (k_t - k_i)n}.
\] (5)

This factor is multiplied by a carrier generation rate in the free state, \( G \), to obtain the generation rate of carriers with trapping energy \( \epsilon \) by detrapping. The third term represents the increase in the carrier distribution due to trapping and can be derived in the following way.\(^\text{[13-15]}\) The number density of carriers detrapped from all traps per unit time is given by \( \int_0^\infty e^{-f(\epsilon)} d\epsilon \). The carriers detrapped into the free state are subsequently either re-trapped into trap sites or recombine with trapped counter charges. The former probability is given by Eq. (5). The third term is obtained by combing these factors.

By integrating Eq. (3) over \( \epsilon \), the fraction of trap sites occupied by carriers, \( \rho = n/N \), is shown to satisfy

\[
1 - \rho = \exp(\epsilon_F) \int_0^\infty d\epsilon \exp(-\epsilon) \frac{f(\epsilon)}{N},
\] (6)

where \( \int_0^\infty g(\epsilon) d\epsilon = 1 \) is used. \( \epsilon_F \) is given by

\[
\epsilon_F = \ln \left( \frac{k_i}{k_t} \right) + \ln \left( \frac{N \nu_0}{G} \right).
\] (7)

In the steady-state, the number density of carriers trapped with trapping energy \( \epsilon \) is obtained by introducing Eq. (6) in Eq. (3) as

\[
f(\epsilon) = \frac{N g(\epsilon)}{1 + \exp(-\epsilon - \epsilon_F)}.
\] (8)

Equation (8) indicates that the number density of carriers obeys a Fermi distribution as in equilibrium, and \( \epsilon_F \) represents the quasi-Fermi energy of a carrier relative to the energy of the free state. Since \( \epsilon_F \) is given by Eq. (7), \( \epsilon_F \) depends on the fraction of trap sites occupied by carriers, \( \rho = n/N \), and the light intensity through \( G \).

In the following, we derive the relation between \( \rho \) and \( G \). The density of occupied sites is given by Eq. (8) regardless of the form of the trapping energy distribution. By substituting Eq. (8) in Eq. (4) and noting \( \rho = n/N \), we obtain

\[
\rho = \int_0^\infty d\epsilon \frac{g(\epsilon)}{1 + \exp(-\epsilon - \epsilon_F)}.
\] (9)

Now, we assume that \( g(\epsilon) \) decreases exponentially with increasing trapping energy, \( g(\epsilon) = (1/E_0) \exp(-\epsilon/E_0) \), where \( E_0 \) is a parameter indicating characteristic trapping energy. The trapping energy distribution can be expressed in the dimensionless unit as

\[
g(\epsilon) = \alpha \exp(-\alpha \epsilon).
\] (10)

\( \alpha = k \nu_0/E_0 \) is a key quantity in the MT model. \( \alpha \) is called the dispersion parameter and given by the ratio of thermal energy to the characteristic trapping energy of trap sites. A small \( \alpha \) compared with unity indicates that the thermal energy is small compared with the typical trapping energy of trap states. Thermally assisted detrapping is suppressed when \( \alpha \) is small.

By expanding the exponential term in the integrand, Eq. (9) can be expressed as

\[
\rho = \frac{\pi \alpha}{\sin(\pi \alpha)} \left( \frac{N k_t}{G k_i} \right)^{-\alpha}.
\] (11)

Equation (12) can be rewritten as a relation between the number density, \( \rho \), and the charge generation rate, \( G \),

\[
\rho \approx \frac{\pi \alpha}{\sin(\pi \alpha)} \left( \frac{N k_t}{G k_i} \right)^{1/(\alpha + 1)}.
\] (13)

Since the charge generation rate is proportional to the light intensity [Eq. (1)], the number density of carriers obeys the power law as a function of the light intensity and the exponent is given by \( \alpha/(\alpha + 1) \). Equation (13) is valid under the condition \( \exp(\epsilon_F) \gg 1 \). By using Eq. (7), we can show that this condition is equivalent to

\[
\frac{\pi \alpha}{\sin(\pi \alpha)} \frac{k_t}{k_i} \frac{N}{G} \gg 1.
\] (14)

The power law dependence of \( \rho \) on the excitation light intensity, Eq. (13), is related to the transient decay kinetics of the total number density of carriers. When the light irradiation is switched off, the carrier density decays to its value under the dark condition. We have analyzed such a transient kinetics. When the recombination rate constant is much lower than the trapping rate constant, the fraction of trap sites occupied by carriers, \( \rho = n/N \), is shown to satisfy\(^\text{[5]}\)

\[
\rho(t) = \frac{\rho(0)}{[1 + (\epsilon_4/\alpha) \rho(0)]^{1/\alpha} \sin(\pi \alpha)} \exp(-c_\alpha t),
\] (15)

with \( \epsilon_\alpha = [\sin(\pi \alpha)/\alpha]^{1/\alpha} \). Despite the ratio between the trapping rate and the recombination rate, the asymptotic time dependence is derived as\(^\text{[5]}\)

\[
\rho(t) \sim 1/t^\alpha,
\] (16)

where \( \alpha \) is again the dispersion parameter. The value of \( \alpha \) in Eq. (16) should be equal to that in Eq. (13).

The charge carrier density in the composite of regioregular poly(3-hexylthiophene) (RR-P3HT) and 6,6-phenyl-C_{61}-butyric acid methyl ester (PCBM) has recently been measured by LESR under the continuous irradiation with
light. LESR has been applied to probe the holes on the polymer and fullerene radical anions. In Fig. 1, the hole density measured by LESR is shown against excitation light intensity for different PCBM concentrations. We analyzed these results by using the power law dependence on the excitation light intensity. As shown in Fig. 1, the values of \( \alpha \) estimated by using Eq. (13) are within the range of 0.26–0.35. These values can be assessed by analyzing the transient kinetics.

As shown in Fig. 2, the decay of the hole density in time-resolved experiments obeys the power law and we obtained \( \alpha = 0.3 \) for 5 mol% PCBM by using Eq. (16). This value is consistent with \( \alpha = 0.31 \) estimated from Fig. 1 by using Eq. (13). The difference between the fit with \( \alpha = 0.31 \) and the best fit with \( \alpha = 0.3 \) is small as shown in Fig. 2. The results indicate the applicability of the MT model to interpret the experimental data under both the steady-state and time-resolved conditions.

Unfortunately, detailed data on the temperature dependence are not available for this sample. Thus, we analyze the temperature dependence for other samples, where the acceptor was fullerene, and the length of alkyl chains was changed. Figure 3 shows the typical results on the hole density as a function of the excitation light intensity of continuous light for RR-poly(3-octylthiophene) (P3OT)/fullerene at 60 K measured by LESR. The value of \( \alpha \) estimated by using Eq. (13) is 0.38. The decay kinetics is analysed by using Eq. (15) and \( \alpha = 0.32 \) is extracted. In Fig. 5, we compare \( \alpha \) values obtained from the kinetic measurements at various temperatures. The two exponents are consistent. By using \( \alpha \) values extracted from the kinetic measurements, \( \alpha \) can be approximated by a linear function of temperature and is almost proportional to temperature. This is again consistent with the MT model that incorporates an exponential trapping energy distribution. It predicts \( \alpha = k_B T / E_0 \). The results support
E500 and EMX X-band spectrometers equipped with a microwave cavity with optical windows using an Oxford ESR900 gas-flow cryostat under 100-Torr He-exchange-gas conditions. In Figs. 1–2, the excitation light was provided by a laser diode with the wavelength of 670 nm at power levels up to 3 mW cm\(^{-2}\) with an optical fiber delivery. In Figs. 3–5, a JASCO SM-5 light source with a 300 mW xenon lamp was used to provide excitation for 700 nm at power levels up to 1 mW cm\(^{-2}\) with an optical fiber delivery.

In conclusion, we have analyzed the recently observed power law dependence of the charge density on the intensity of excitation light by using the MT model. Previously, the exponent \(\gamma\) smaller than 0.5 was explained by assuming quadrimolecular recombination among holes and electrons. By using the MT model, we have successfully explained the experimental results of \(\gamma < 0.5\). To be more precise, the exponent is given in terms of the dispersion parameter \(\sigma\) as \(\gamma = \alpha/(1 + \alpha)\) and \(\sigma\) should be smaller than 1 when the deep trap levels inside the band gap are described by an exponential trapping energy distribution. The value of the exponent is consistent with that obtained from the independent experiment on the transient decay of charge density. Analysis of the temperature dependence of the exponent shows that the temperature dependence is consistent with the MT model.

---

1) C. Deibel and V. Dyakonov: Rep. Prog. Phys. 73 (2010) 096401.
2) A. F. Nogueira, I. Montanari, J. Nelson, J. R. Durrant, C. Winder, N. S. Sariciftci, and C. J. Brabec: J. Phys. Chem. B 107 (2003) 1567.
3) S. Yamamoto, H. Ohkita, H. Benten, and S. Ito: J. Phys. Chem. C 116 (2012) 14804.
4) H. Ohkita, S. Cook, Y. Astuti, W. Duffy, S. Tierney, W. Zhang, M. Heeney, L. Mc Culloch, J. Nelson, D. D. C. Bradley, and J. R. Durrant: J. Am. Chem. Soc. 130 (2008) 3030.
5) T. M. Clarke, J. Peet, P. Denk, G. Demmler, C. Lungen schmied, and A. J. Mouez: Energy Environ. Sci. 5 (2012) 5241.
6) M. P. Eng, P. R. F. Barnes, and J. R. Durrant: J. Phys. Chem. Lett. 1 (2010) 3096.
7) T. Kobayashi, Y. Terada, T. Nagase, and H. Naito: Appl. Phys. Express 4 (2011) 126602.
8) H. Tanaka, Y. Yokoi, N. Hasegawa, S. Kuroda, T. Iijima, T. Sato, and T. Yamamoto: J. Appl. Phys. 107 (2010) 083708.
9) H. Tanaka, N. Hasegawa, T. Sakamoto, K. Marumoto, and S. Kuroda: Jpn. J. Appl. Phys. 46 (2007) 5187.
10) K. Marumoto, Y. Muramatsu, and S. Kuroda: Appl. Phys. Lett. 84 (2004) 1317.
11) J. Nelson: Phys. Rev. B 59 (1999) 15374.
12) J. Nelson: Phys. Rev. B 67 (2003) 155209.
13) A. V. Barzykin and M. Tachiya: J. Phys. Chem. B 106 (2002) 4356.
14) A. V. Barzykin and M. Tachiya: J. Phys. Chem. B 108 (2004) 8385.
15) M. Tachiya and K. Seki: Phys. Rev. B 82 (2010) 085201.
16) A. Zaban, M. Greenshtein, and J. Bisquert: ChemPhysChem 4 (2003) 859.
17) A. Foerstig, A. Baumann, D. Raub, V. Dyakonov, and C. Deibel: Appl. Phys. Lett. 95 (2009) 052104.
18) F. W. Schmidlin: Phys. Rev. B 16 (1977) 2362.
19) A. I. Rudenko and V. I. Arkhipov: Philos. Mag. B 45 (1982) 177.
20) V. I. Arkhipov and A. I. Rudenko: Philos. Mag. B 45 (1982) 189.
21) A. I. Rudenko and V. I. Arkhipov: Philos. Mag. B 45 (1982) 209.
22) M. Abramowitz and I. A. Stegun: Handbook of Mathematical Functions (Dover, New York, 1972).