Extraction technique of trap states based on transient photo-voltage measurement

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This article puts forward a technique for extracting the density of trap states (DOS$_T$) distribution based on the transient photo-voltage (TPV) measurement result. We prove that when the TPV result is linear, the DOS$_T$ distribution is exponential type and vice versa. Compared to the approach based on the space charge limited current measurement, the method given in this paper has the advantage of requiring less calculation. The results obtained by our method provides a guidance for preparing less trap states solar cells.

In order to improve the photo-voltaic performance of perovskite solar cells (PSCs), we need to further explore the mechanism such as carrier mobility$^{1-3}$, ion migration$^{4-8}$, density of trap states (DOS$_T$) distribution$^{9-13}$, carrier recombination$^{14-18}$ and so on. The DOS$_T$ distribution is a crucial factor that determines the photovoltaic performance of PSCs$^{19-33}$. According to the literatures in recent years$^{19-23}$, current density–voltage ($J$–$V$) hysteresis is caused by the ion migration and trap assisted carrier recombination. The DOS$_T$ distribution affects the carrier recombination$^{24-27}$, influences the open circuit voltage$^{28-30}$, and hinders the enhancement of power conversion efficiency (PCE)$^{31-34}$. The DOS$_T$ distribution cannot be obtained by experimental measurement directly. There are only few methods for the extraction of DOS$_T$ distribution. The space charge limited current (SCLC) method uses the deconvolution to extract the DOS$_T$ distribution$^{35-40}$, based on the measured $J$–$V$ data at different temperatures. Walter et al.$^{41-45}$ put forward the impedance spectroscopy (IS) method to extract the DOS$_T$ distribution. They extract the DOS$_T$ distribution based on the plot of equivalent chemical capacitance versus frequency given by IS measurement$^{41-45}$. They regard the capture and de-capture of carrier by the trap states in the PSCs as charging and discharging of the equivalent chemical capacitance$^{41}$. They put forward the formula

$$\text{DOS}_T(E_\omega) = \left(\frac{V_{bi}}{eW}\right)\frac{dC}{d\omega}\left(\frac{\omega}{k_B}\right)$$

Here, $C$ is the equivalent chemical capacitance. $\omega$ is the angular frequency of the ac signal. $V_{bi}$ is the built-in electric voltage. $W$ is the depletion width. $k$ is the Boltzmann constant. $e$ is the elementary charge. The corresponding energy level is calculated by the formula $E_\omega = \frac{k}{T}\ln(\omega_0/\omega)$, where $T$ is the ambient temperature and $\omega_0$ is the attempt-to-escape frequency$^{41-45}$. Wang et al.$^{46}$ proposed a transient photo-voltage (TPV) method for DOS$_T$ distribution extraction. Based on the hypothesis of exponential type DOS$_T$ distribution$^{46-49}$, multiple-trapping model$^{46,50-52}$, and the zero-temperature approximation$^{46,52}$, they find that when the DOS$_T$ distribution is exponential type, the logarithm of carrier lifetime and the photo-voltage satisfy linear relation. They use this relation to extract the DOS$_T$ distribution based on the TPV result$^{46-48}$. Because of the hypothesis of exponential type distribution$^{46-49}$, their method is effective only when the TPV result is linear. The DOS$_T$ distribution extracted by their method is an exponential type distribution$^{46-48}$.

However, according to the TPV experiments reported in recent years$^{46-48}$, the majority of TPV results are non-linear. In these cases, the method of Wang et al. is not effective to extract the DOS$_T$ distribution. In this article, we put forward a new technique for extraction of DOS$_T$ distribution based on the TPV measurement result. We give up the hypothesis of exponential type DOS$_T$ distribution$^{46-49}$ and zero-temperature approximation$^{46,52}$. The method given in our work is based on the single hypothesis of multiple-trapping model$^{46,50-52}$. Our method is effective for arbitrary TPV results and can be used to extract general type DOS$_T$ distribution.

Results and discussion

Establishment of theory and method. In this section, we establish the equation for the extraction of DOS$_T$ distribution based on the TPV result.
Because of the trap states in the perovskite absorber layer, the behavior of trapping and de-trapping of carrier by the trap states determines the recombination rate, which can be described by the multiple-trapping model. According to the multiple-trapping model, the relation of carrier lifetime $\tau_n$ and the free carrier lifetime $\tau_f$ satisfies:

$$\tau_n = (\partial n / \partial n_c) \tau_f. \quad (1)$$

Here $n = n_t + n_c$ denotes the sum of electron density in trap states $n_t$ and electron density in conduct band $n_c$. Therefore, we have

$$\tau_n = (1 + \partial n_t / \partial n_c) \tau_f, \quad (2)$$

which can be rewritten as

$$\tau_n = \left(1 + \frac{\partial n_t / \partial E_{Fn}}{\partial n_c / \partial E_{Fn}}\right) \tau_f. \quad (3)$$

The density of electron in trap states satisfies:

$$n_t = \int \rho_t(E) f(E) dE. \quad (4)$$

Here $\rho_t(E)$ denotes the DOS$_T$ distribution. $f(E) = \frac{1}{\exp\left(\frac{E - E_{Fn}}{k_B T}\right) + 1}$ denotes the Fermi–Dirac distribution.

Therefore, we have

$$\frac{\partial n_t}{\partial (E_{Fn})} = \frac{1}{k_B T} \int \rho_t(E) f(E) (1 - f(E)) dE. \quad (6)$$

We rewrite Eq. (6) as

$$\frac{\partial n_t}{\partial E_{Fn}} = \frac{1}{k_B T} \int \rho_t(E) f(E) (1 - f(E)) dE. \quad (7)$$

The carrier density in conductor band satisfies:

$$n_c = N_c \exp\left(\frac{E_{Fn} - E_c}{k_B T}\right). \quad (8)$$

Here $N_c$ is the density of effective states in conduction band. $E_c$ is the conduction band energy level position.

Therefore, we have

$$\frac{\partial n_c}{\partial E_{Fn}} = \frac{n_c}{k_B T}. \quad (9)$$

According to Eqs. (3), (7), and (9), we have

$$\tau_n = \left(1 + \int \frac{\rho_t(E) f(E) (1 - f(E)) dE}{n_c}\right) \tau_f. \quad (10)$$

We rewrite Eq. (10) as

$$\int \rho_t(E) f(E) (1 - f(E)) dE = \left(\frac{\tau_n}{\tau_f} - 1\right) n_c. \quad (11)$$

Substituting the Fermi–Dirac distribution into Eq. (11), we have

$$\int \frac{\rho_t(E)}{\exp\left(\frac{E_{Fn} - E}{k_B T}\right) + 1} \left(1 - \frac{1}{\exp\left(\frac{E_{Fn} - E}{k_B T}\right) + 1}\right) dE = \left(\frac{\tau_n}{\tau_f} - 1\right) n_c. \quad (12)$$

We rewrite Eq. (12) as

$$\int \frac{\rho_t(E)}{\exp\left(-\frac{(E_{Fn} - E)}{k_B T}\right) + 1} \left(1 - \frac{1}{\exp\left(-\frac{(E_{Fn} - E)}{k_B T}\right) + 1}\right) dE = \left(\frac{\tau_n}{\tau_f} - 1\right) n_c. \quad (13)$$

We define a derivation factor
to solve the equation for DOST distribution.

\[ f = \frac{1}{\tau} \]

The free carrier lifetime \( \tau \) can be measured or can be calculated according to the equation

\[ \tau = \frac{1}{C_n} \text{Vph} \]

Equation (18) is the fundamental equation for DOST distribution extraction of intrinsic perovskite. Similarly, we obtain the DOST distribution using numerical deconvolution function in MATLAB. The parameters used for calculation are list in Table 1.

\[ \text{Table 1. Parameters used for DOS}_T \text{ distribution calculation}^{27,35}. \]

| Sym | Description | Value             |
|-----|-------------|-------------------|
| \( \varepsilon \) | Elementary charge | \( 1.60 \times 10^{-19} \text{ C} \) |
| \( k_B \) | Boltzmann constant | \( 1.38 \times 10^{-23} \text{ JK}^{-1} \) |
| \( E_c \) | Conduction band minimum | \( 4.18 \text{ eV} \) |
| \( E_g \) | Band gap | \( 1.52 \text{ eV} \) |
| \( E_{\text{F0}} \) | Fermi energy level | \( -4.3 \text{ eV} \) |
| \( T \) | Ambient temperature | 300 K |
| \( N_t \) | Conduction band DoS | \( 1 \times 10^{24} \text{ m}^{-3} \) |
| \( C_n \) | Electron trap coefficients | \( 1 \times 10^{-15} \text{ m}^{-3} \) |
| \( N_t \) | Electron trap concentration | \( 1 \times 10^{19} \text{ m}^{-3} \) |

In this section, we explore the exponential type DOS\(_T\) distribution. Wang et al.\(^{46}\) find that for the exponential type DOS\(_T\) distribution, the logarithm of carrier lifetime is proportional to the photo-voltage (TPV result). The proof of this relation is shown as follows.

The exponential type DOS\(_T\) distribution satisfies\(^{46-49}\)

\[ \rho_T(E) = \frac{N_T}{E_B} \exp \left( \frac{E - E_c}{E_B} \right). \]
Here, $E_B$ is the characteristic energy and $N_T$ is the total density of the trapped state. Substituting formula (19) into formula (4), and taking zero-temperature approximation, we have

$$ n_T = N_T \left( \exp \left( \frac{E_{F_n} - E_c}{E_B} \right) - \exp \left( \frac{E_p - E_c}{E_B} \right) \right). $$ (20)

Making the approximation of $n \approx n_T$, we rewrite the multiple-trapping model as

$$ \tau_n = \left( \frac{\partial n_T}{\partial n_c} \right) \tau_f, $$ (21)

which is equivalent to

$$ \tau_n = \frac{\partial n_T}{\partial V_{ph}} \frac{\partial n_c}{\partial V_{ph}} \tau_f. $$ (22)

The electron density in conductor band satisfies

$$ n_c = N_c \exp \left( \frac{E_{F_n} - E_c}{k_B T} \right). $$ (23)

According to Eqs. (20), (22), and (23) and from the relation of $E_{F_n} = E_{F_p} + eV_{ph}$, we have

$$ \ln \tau_n = \left( \frac{e}{E_B} - \frac{e}{k_B T} \right) V_{ph} + \ln A. $$ (24)

Here $A = \frac{N_c k_B T}{N_e} \exp \left( \frac{E_{F_p} - E_c}{k_B T} \right) \tau_f$.

We write Eq. (24) as linear mathematical form $\ln \tau_n = a V_{ph} + b$.

Here, $a = \frac{e}{E_B} - \frac{e}{k_B T}$, $b = \ln A$.

Therefore, we finish the proof of this relation. Note that for the intrinsic perovskite, Eq. (24) can be written as

$$ \ln \tau_n = \left( \frac{e}{2E_B} - \frac{e}{2k_B T} \right) V_{ph} + \ln A. $$ (25)

Here $A = \frac{N_c k_B T}{N_e} \exp \left( \frac{E_{F_p} - E_c}{k_B T} \right) \tau_f$. We write Eq. (25) as linear form $\ln \tau_n = a V_{ph} + b$. Here, $a = \frac{e}{2E_p} - \frac{e}{2k_B T}$, $b = \ln A$.

Similarly, we can also prove that when TPV result is linear, the extracted DOS$_T$ distribution is exponential type. Details of the proof are given in the supporting information. We can use this relation to extract the DOS$_T$ distribution when the TPV result is linear. Below, this method is called analytic method.

We can use the analytic method to verify the validity of our numerical method. We use both our numerical method and the analytic method to extract the DOS$_T$ distribution and make a comparison. In Fig. 1a–c, we set...
the \( b = -5 \) and the slope parameter \( a \) as \(-1.5\), \(-2.0\) and \(-2.5\), respectively. Using the analytic method, we derive \( E_b \) and \( N_T \) (see Table 2). Figure 1d–f shows the extracted DOS\(_T\) distributions from Fig. 1a–c using our numerical method. As expected by the analytic method, the DOS\(_T\) distribution is exponential type. In order to compare with the DOS\(_T\) distribution extracted by analytic method, we use the exponential fitting \((f(E) = c\exp(dE))\) to calculate the \( E_b \) and \( N_T \) (see Table 2). As shown in Table 2, the \( E_b \) and \( N_T \) calculated by our numerical method are consistent with the \( E_b \) and \( N_T \) calculated by the analytic method, indicating that the numerical algorithm to do the deconvolution in our calculation is reliable. We explain the slight deviation of \( E_b \) and \( N_T \) extracted by the two methods as follows. The analytic method is established based on the three hypothesis of multiple-trapping model\(^{46,50–52}\), zero-temperature approximation\(^{46,52}\), and exponential type DOS\(_T\) distribution\(^{46–49}\). Our numerical method is established based on the unique hypothesis of multiple-trapping model\(^{46,50–52}\). Therefore, the slight deviation of \( E_b \) and \( N_T \) extracted by the two methods is attributed to the zero-temperature approximation and the fitting error.

### Non-exponential type DOS\(_T\) distribution.

In this section, we investigate the non-exponential type DOS\(_T\) distribution. We take the TPV data in Ref.\(^{47}\) as an example. As shown in Fig. 2a,b, the TPV result is non-linear. Hence, we cannot use the analytic method to extract the DOS\(_T\) distribution.

To overcome this difficulty, Wang et al.\(^{47}\) made a linear fitting in the subintervals of 0.05–0.6 V and 0.6–0.91 V (see Fig. 2a). They used formula (24) to get two values of \( E_b \) in these two subintervals, respectively\(^{47}\). They explained these two \( E_b \) as two types of exponential type DOS\(_T\) distribution (They called them as deep trap type and shallow trap type)\(^{47}\). However, there are some difficulties in their method. (1) Equation (24) is derived from

![Figure 2](https://example.com/fig2)

**Figure 2.** Plots of carrier lifetime versus photo-voltage given by TPV measurement\(^{47}\). The black lines represent the result of TPV measurement. The red lines represent linear fitting in the subintervals. (a) shows the linear fittings of TPV in two subintervals, respectively. (b) shows the linear fittings of TPV in three subintervals, respectively.

| Coefficients Example 1 | Example 2 | Example 3 |
|------------------------|-----------|-----------|
| Chosen parameters      |           |           |
| \( a \)                | \(-1.5\)  | \(-2.0\)  | \(-2.5\)  |
| \( b \)                | \(-5\)    | \(-5\)    | \(-5\)    |
| Exponential fitting    |           |           |
| \( c \) (exponential fitting) | \(1.525 \times 10^{14}\) | \(7.536 \times 10^{13}\) | \(3.666 \times 10^{13}\) |
| \( d \) (exponential fitting) | \(-2.542 \times 10^{20}\) | \(-2.466 \times 10^{20}\) | \(-2.388 \times 10^{20}\) |
| R-square               | 1         | 1         | 1         |
| Calculation result     |           |           |
| \( E_b \) (analytic method) | \(28.0 \text{ meV}\) | \(28.8 \text{ meV}\) | \(29.7 \text{ meV}\) |
| \( E_b \) (our method)  | \(24.6 \text{ meV}\) | \(25.3 \text{ meV}\) | \(26.1 \text{ meV}\) |
| \( N_T \) (analytic method) | \(7.305 \times 10^{13} \text{ cm}^{-3}\) | \(7.5158 \times 10^{13} \text{ cm}^{-3}\) | \(7.7392 \times 10^{13} \text{ cm}^{-3}\) |
| \( N_T \) (our method)  | \(5.9992 \times 10^{13} \text{ cm}^{-3}\) | \(3.0560 \times 10^{13} \text{ cm}^{-3}\) | \(1.5352 \times 10^{13} \text{ cm}^{-3}\) |

**Table 2.** Exponential fitting coefficients, distribution coefficients calculated from Fig. 2.
one exponential type DOS$_T$ distribution, not the two types of DOS$_T$ distribution (deep trap state type DOS$_T$ distribution and shallow trap state type DOS$_T$ distribution). We cannot derive Eq. (24) based on these two types of distribution. (2) There is no clear boundary for deep and shallow trap. So the definition of deep and shallow trap is ambiguous. (3) It is more accurate to take linear fittings in three subintervals, respectively (see Fig. 2b). According to the differential theory, we can divide the photo-voltage interval into infinite differential subintervals and use Eq. (24) to calculate the $E_B$ in these differential subintervals, respectively. These $E_B$ cannot be explained

by the concept of deep and shallow trap.

Our method is effective for arbitrary TPV results, which can be used to extract general type DOS$_T$ distribution. Using our method, we extract the DOS$_T$ distribution (as illustrated in Fig. 3). It can be seen that the extracted DOS$_T$ distribution is not an exponential type distribution. Compared to the method given by Wang et al., our method is more accurate and it can give the fine structure of DOS$_T$ distribution.

We make the exponential, double exponential and Gauss fittings for the extracted DOS$_T$ distribution, respectively (see Fig. 3). The R-square (Coefficient of determination) of these fittings are given in Table 3. It can be seen that the R-square of double exponential fitting is larger than the exponential fitting and Gauss fitting, indicating that the DOS$_T$ distribution is more consistent with the double exponential type distribution than with the exponential type distribution. Therefore, when the TPV result is non-linear, the extracted DOS$_T$ distribution is non-exponential type.

**Calculation example.** In this section, we give some examples of DOS$_T$ distribution extraction using our method. We take the TPV data in Ref. 47 as an example. Figure 4a–c shows the TPV results for meso-structured perovskite solar cells with large, middle and small size of perovskite grain, respectively. Using our method, we extract the DOS$_T$ distributions from Fig. 4a–c, respectively, (as shown in Fig. 4d–f).

For comparing, we plot the extracted DOS$_T$ distributions in Fig. 5. Using the formula $T_{total} = \int \rho(E)dE$, we calculate the total amount of trap states for three solar cells. We derived $T_{total} = 5.4431 \times 10^{20}$ cm$^{-3}$ (large size), $T_{total} = 5.9096 \times 10^{20}$ cm$^{-3}$ (middle size) and $T_{total} = 4.5628 \times 10^{20}$ cm$^{-3}$ (small size). It can be seen that the solar cell with small size of perovskite grain has the least amount of trap states. This result could give a guidance for preparing perovskite solar cells with less trap states.

**Comparison to SCLC method.** SCLC measurement gives the relation of current density and voltage at different temperatures ($j = j(U, T)$). For SCLC method, we extract the DOS$_T$ distribution adopting the equations listed as follows

$$E_a = - \frac{d \ln j}{d(k_B T)^{-1}},$$

(26)
Here $j$ denotes the current density. $U$ denotes the voltage. $E_a$ is the activation energy. $m, B, C$ are the parameters for calculation. $L$ is the thickness of perovskite absorber layer. $e$ is the elementary charge. $\varepsilon$ is the dielectric permittivity. $d$ is the thickness of perovskite absorber layer.

$$m = \frac{d(lnj)}{d(lnU)},$$  \hspace{1cm} (27)

$$B = -\frac{dm}{d(lnU)}/[m(m-1)(2m-1)],$$  \hspace{1cm} (28)

$$C = \frac{B(2m-1) + B^2(3m-2) + d(ln(1+B))/d(lnU))}{(1 + B(m-1))},$$  \hspace{1cm} (29)

$$\int \rho_s(E)f(E)(1-f(E))dE = \frac{1}{k_B T} \frac{\varepsilon U}{\varepsilon d L^2} \frac{2m-1}{m^2} (1 + C).$$  \hspace{1cm} (30)

Figure 4. (a)–(c) TPV results for meso-structured perovskite solar cells with large, middle and small size of perovskite grain. (d)–(f) DOS$_v$ distributions extracted by our method from (a)–(c), respectively.

Figure 5. DOS$_v$ distributions for meso-structured perovskite solar cells with large, middle and small size of perovskite grain extracted by our method given in this paper.
constant of perovskite absorber layer. Based on the SCLC measurement result, we need to calculate $E_a$, $m$, $B$, $C$ and finally use Eq. (30) to extract the DOS of by deconvolution. The calculations of $E_a$, $m$, $B$, $C$ are complicated. For our method, we only need to use formula (18) to extract the DOS distribution by deconvolution. Therefore, our method takes less computation.

Conclusion
In conclusion, this article presents a new technique for DOS distribution extraction based on the TPV measurement result. The approach given in this paper is effective for extraction of general type DOS distribution. We prove that when the TPV result is linear, the DOS distribution is exponential type and vice versa. Our method needs less computation than the SCLC method. The obtained results provide a guidance for preparing perovskite solar cells with less trap states.

Methods
The transient photo-voltage measurement is an effective technique for the study of carrier recombination. Figure 6a shows the typical TPV measurement result. Figure 6b shows the mechanism of TPV experiment. Photo-voltaic device is held under open circuit. At the start of the TPV experiment, we use a steady-state bias light to illuminate the device until the equilibrium between generation and recombination is established. The steady-state bias light produces a bias photo-voltage $V_{ph}$. As a result, the Fermi energy level $E_F$ changes to electron quasi Fermi energy level $E_{Fn}$ and hole quasi Fermi energy level $E_{Fp}$. Thereafter, we apply an additional small light pulse to the device. With the perturbation of small light pulse, the photo-voltage increases to $V_{ph} + \Delta V$. The electron quasi Fermi energy level $E_{Fn}$ shifts to $E_{Fn}'$ and the hole quasi Fermi energy level $E_{Fp}$ to $E_{Fp}'$. After switching off the small light pulse source, due to carrier recombination, the photo-voltage decays exponentially until it reaches the bias value $V_{ph}$. The electron quasi Fermi energy level comes back to $E_{Fn}$ from $E_{Fn}'$, and the hole quasi Fermi energy level comes back to $E_{Fp}$ from $E_{Fp}'$. The carrier lifetime $\tau_n$ is defined as the time taken for the photo-voltage to decay from $V_{ph} + \Delta V$ to $V_{ph} + \Delta V/e$. Here, $e$ is the natural constant. By tuning the intensity of steady-state bias light $I$, we get the relation between the photo-voltage $V_{ph}$ and carrier lifetime $\tau_n$, which is written as $\tau_n = \tau_n(V_{ph})$ (TPV result).

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