

Defect identification based on first-principles calculations for deep level transient spectroscopy

Darshana Wickramaratne,^{1,a)} Cyrus E. Dreyer,^{2,3} Bartomeu Monserrat,⁴ Jimmy-Xuan Shen,⁵ John L. Lyons,⁶ Audrius Alkauskas,⁷ and Chris G. Van de Walle¹

¹Materials Department, University of California, Santa Barbara, California 93106-5050, USA

²Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794-3800, USA

³Center for Computational Quantum Physics, Flatiron Institute, 162 5th Avenue, New York, New York 10010, USA

⁴TCM Group, Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom

⁵Department of Physics, University of California, Santa Barbara, California 93106-9530, USA

⁶Center for Computational Materials Science, US Naval Research Laboratory, Washington, DC 20375, USA

⁷Center for Physical Sciences and Technology (FTMC), Vilnius LT-10257, Lithuania

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Deep level transient spectroscopy (DLTS) is used extensively to study defects in semiconductors. We demonstrate that great care should be exercised in interpreting activation energies extracted from DLTS as ionization energies. We show how first-principles calculations of thermodynamic transition levels, temperature effects of ionization energies, and nonradiative capture coefficients can be used to accurately determine actual activation energies that can be directly compared with DLTS. Our analysis is illustrated with hybrid-functional calculations for two important defects in GaN, which have similar thermodynamic transition levels and shows that the activation energy extracted from DLTS includes a capture barrier that is temperature dependent, unique to each defect, and, in some cases, large in comparison to the ionization energy. By calculating quantities that can be directly compared with the experiment, first-principles calculations thus offer powerful leverage in identifying the microscopic origin of defects detected in DLTS. *Published by AIP Publishing.*

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Point defects and impurities are present in all semiconductors. They can act as recombination centers that lower the efficiency of optoelectronic devices or as carrier traps in electronic devices such as transistors. Microscopic identification of the detrimental defects is crucial in order to mitigate their impact. Deep level transient spectroscopy (DLTS) is a powerful technique for determining the properties of defects; from an analysis of electrical measurements on a *pn* junction or Schottky diode, properties such as the position of the defect level within the bandgap, electrical nature (donor or acceptor), density, and carrier capture cross section of specific defects can be obtained.^{1–3}

Translating this wealth of information to a microscopic identification of a given defect requires comparison with theoretical or computational models, and first-principles calculations based on density functional theory (DFT) have proven very helpful.^{4–8}

One of the key quantities measured in DLTS is the activation energy for carrier emission from a defect, ΔE_a . Defect identification is often based on comparing ΔE_a with the values of the defect ionization energy ΔE_i determined from zero-temperature first-principles calculations. However, the underlying theory of DLTS^{2,3} makes clear that ΔE_a and ΔE_i are distinct, and the use of ΔE_i can affect the correct identification of a defect.

In the present study, we describe a first-principles approach to explicitly determine the activation energies

measured in DLTS. Recent advances have enabled the quantitative prediction of defect levels in the bandgap⁹ and the ability to accurately describe nonradiative carrier capture.¹⁰ We will show that ΔE_a can significantly differ from ΔE_i for some defects, demonstrating the need to explicitly calculate the activation energy in order to correctly identify defects detected by DLTS. Our analysis is general but will be illustrated with examples of deep defects in GaN, a material of high technological relevance because of its applications in solid-state light emitters and power electronics.

Let us consider a defect that acts as a single deep acceptor. A standard DLTS measurement relies on a *pn* junction or Schottky diode that is reverse biased, which establishes a depletion region that is free of mobile carriers. The band diagram is illustrated in Fig. 1(a).¹¹ A forward-bias injection pulse is applied, which decreases the width of the depletion region [Fig. 1(b)]. Holes from the valence band are captured nonradiatively into the acceptor level during the injection pulse. After the pulse is turned off, the depletion width increases to its reverse-bias value and the holes captured into the acceptor level are re-emitted into the valence band, which results in a transient change in the capacitance. Using the “double boxcar” technique,¹¹ the difference in the capacitance, ΔC , is measured at two different times, t_1 and t_2 , after the injection pulse is turned off [schematically illustrated in Fig. 1(c)]. The times t_1 and t_2 within which the capacitance measurement occurs set the emission rate window.¹¹ The change in the capacitance for a given emission rate window is measured as a function of temperature T . From Fig. 1(c) it

^{a)} Author to whom correspondence should be addressed: darshana@ucsb.edu

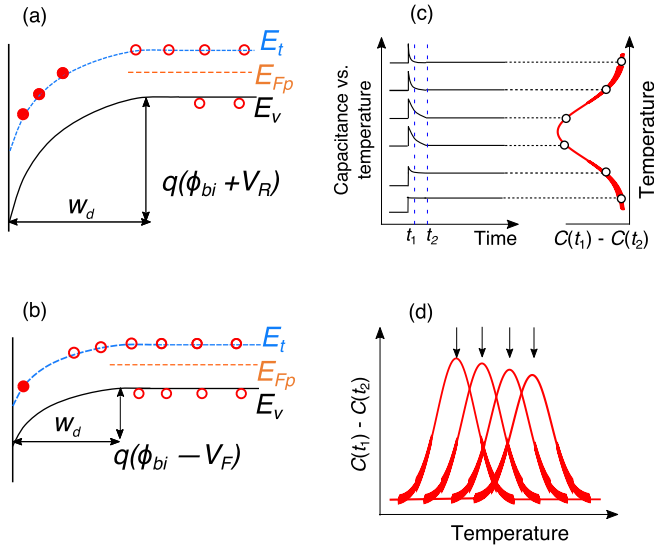


FIG. 1. Schematic illustration of the DLTS measurement process for a *p*-type Schottky junction with a single deep acceptor level at an energy E_i . E_{Fp} is the quasi-Fermi level for the junction under bias, and E_v is the valence-band maximum. The band diagram is shown under (a) reverse bias, V_R , and (b) forward bias, V_F . ϕ_{bi} is the built-in potential at the Schottky junction. (c) Capacitance measurement as a function of temperature within the DLTS rate window. (d) Resulting hole emission spectra as a function of temperature obtained for different rate windows. Panel (c) is adapted with permission from Fig. 6 of D. V. Lang, *J. Appl. Phys.* **45**, 3023 (1974). Copyright 1974 AIP Publishing.

is clear there is a peak in the transient change in the capacitance for a given choice in the rate window; this peak serves as one data point in a plot of the emission rate e_p versus $1/T$. Therefore, repeating this measurement with a variety of rate windows, as shown in Fig. 1(d), yields measurements of e_p versus T .

Under equilibrium conditions, the principle of detailed balance requires that the rate of hole capture into the acceptor level is equal to the emission rate of holes into the valence band. Therefore, e_p can be written in terms of the hole capture cross section σ_p as¹¹

$$e_p(T) = \frac{\sigma_p(T) \langle v_p(T) \rangle N_v(T)}{g_v} \exp\left(-\frac{\Delta E_i(T)}{k_B T}\right), \quad (1)$$

where $\langle v_p \rangle$ is the average thermal velocity of holes in the valence band, N_v is the effective density of states of the valence band, g_v is the valley degeneracy, and $\Delta E_i(T)$ is the ionization energy of the defect. For the case of the deep acceptor, $\Delta E_i(T)$ is the energy difference between the valence-band maximum, E_v , and the acceptor level.

To obtain the ionization energy and capture cross section from the emission rate versus T data obtained by the procedure in Fig. 1, the temperature dependence of the various quantities in Eq. (1) must be specified. The thermal velocity $\langle v_p \rangle$ is given by $\sqrt{\frac{3k_B T}{m_h}}$, where m_h is the hole mass. Assuming parabolic bands, the valence-band density of states is defined as $N_v = 2g_v \left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2}$, where m_h^* is the density-of-states effective mass of holes ($1.50 m_0$ for GaN).^{12,13} Therefore, $\langle v_p \rangle N_v \propto T^2$. The standard procedure in DLTS analysis is to assume that σ_p is independent of temperature and plot $\ln(e_p(T)/T^2)$ versus $1/T$ and then fit to an Arrhenius expression to extract an activation energy ΔE_a .¹¹

This activation energy would coincide with the 0 K ionization energy of the defect if ΔE_i and the prefactor of Eq. (1) were independent of temperature.

However, in reality, σ_p can have a strong temperature dependence and therefore a significant contribution to the slope obtained from a $\ln(e_p(T)/T^2)$ versus $1/T$ plot.³ This contribution must be clarified in order to extract the activation energy from these plots. In addition, ΔE_i , i.e., the position of the thermodynamic transition level with respect to the band edge, is also temperature dependent.^{14,15} Both effects are addressed here from first principles.

We perform DFT calculations based on the generalized Kohn-Sham scheme using the projector-augmented-wave method with the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE)¹⁶ as implemented in the VASP code.^{17,18} We use a mixing parameter of 0.31 which results in lattice parameters ($a = 3.19 \text{ \AA}$ and $c = 5.17 \text{ \AA}$) and a bandgap (3.495 eV) which are close to the experimental $T = 0 \text{ K}$ lattice parameters¹⁹ and bandgap^{20,21} of GaN. The defect calculations are performed using a 96-atom supercell, a plane-wave basis set with a 400 eV cutoff, and a $(2 \times 2 \times 2)$ Monkhorst-Pack k -point grid to sample the Brillouin zone. Spin polarization is explicitly included. All atomic relaxations are performed consistently with the HSE functional. Defect formation energies and thermodynamic transition levels are calculated using the standard formalism⁹ with charge-state corrections applied to account for the periodic supercells.²²

Capture coefficients and their temperature dependence are evaluated using the formalism in Ref. 10. In order to discuss the temperature dependence of the capture cross section, we prefer to consider the capture coefficient, $C_p(T) = \sigma_p(T) \langle v(T) \rangle$, which is a more general quantity since it can be calculated without assuming a thermal velocity for the carriers.

To determine the temperature dependence of $\Delta E_i(T)$, we calculate the temperature dependence of the band edges and the thermodynamic charge-state transition level. Two mechanisms contribute to the temperature dependence of the band edges. The contribution due to electron-phonon interactions was evaluated by using the methodology of Refs. 23 and 24, on a $4 \times 4 \times 4$ q -point grid. To determine the contribution due to thermal expansion, we used experimental thermal expansion coefficients¹⁹ to determine the lattice expansion at a given temperature and absolute deformation potentials²⁵ to determine the resulting shift in the band edges. We verified that the calculated cumulative change in the bandgap agrees with experimental measurements,²¹ but we emphasize that our procedure allows us to assess the shifts in the individual band edges (valence band versus conduction band).

To determine the temperature dependence of the defect levels, we calculate the zone-center vibrational frequencies of each defect in its different charge states using HSE with 216-atom supercells using the $T = 0 \text{ K}$ HSE lattice parameters. The vibrational frequencies were determined for a set of atoms within 4 \AA around the defect while the remaining atoms were kept fixed at their equilibrium positions. Details of the calculations are provided in the supplementary material. The vibrational frequencies were used to evaluate the vibrational free energy for a given charge state within the harmonic approximation [cf. Eq. (17) in Ref. 9]. The difference in vibrational free energy between the two charge states

was used to determine the temperature dependence of the transition level.

We will determine the implications of the T dependence for two examples of defects in GaN which have very similar thermodynamic transition levels but different temperature dependences of their capture coefficient: carbon on a nitrogen site, C_N ,²⁶ and a gallium vacancy complex, $V_{Ga}-O_N-2H$.²⁷ One-dimensional configuration coordinate diagrams (see Ref. 10) are shown in Fig. 2. C_N is a deep acceptor, with a (0/−) transition level 1.02 eV above E_v . $V_{Ga}-O_N-2H$ is a complex based on a gallium vacancy that exhibits a (+/0) transition level 1.06 eV above E_v .²⁷

For purposes of determining the capture coefficient, the initial state of the system consists of a hole in the valence band and a negatively charged acceptor; see the potential energy surface labeled $C_N^- + h^+$ in Fig. 2(a). Capture occurs when the system traverses to the potential energy surface corresponding to the neutral acceptor, C_N^0 . The difference in energy of the minima of the two curves is the thermodynamic charge-state transition level referenced to E_v and corresponds to the ionization energy ΔE_i from Eq. (1). At high temperatures, the capture process occurs by surmounting the “classical” barrier, ΔE_b , obtained from the intersection point of the curves in the configuration coordinate diagram; at low temperatures, the transition rate is dominated by quantum-mechanical tunneling.¹⁰ The classical barrier ΔE_b is 490 meV for C_N and 49 meV for $V_{Ga}-O_N-2H$.

The large difference in these classical barriers is reflected in our results for the temperature dependence of the hole capture coefficients in Fig. 3(a) (dashed lines). We focus on the temperature range up to 600 K; DLTS measurements on GaN are limited to this temperature to prevent degrading of the metal contacts. The hole capture coefficient of C_N changes by two orders of magnitude as the temperature increases from 0 K to 600 K, while for $V_{Ga}-O_N-2H$, the temperature dependence is much more modest. The results shown in dashed lines in Fig. 3(a) assume that ΔE_i are fixed to their $T = 0$ values. These ΔE_i values correspond to charge-state transition levels obtained from static-lattice calculations of a zero-temperature DFT calculation. Both dashed curves have an Arrhenius form at high T and have a weak temperature dependence as $T \rightarrow 0$.¹⁰ In reality, the distance between E_v and the defect level shrinks as T increases, and so $\Delta E_i(T)$ is reduced, as shown in Fig. 3(b).

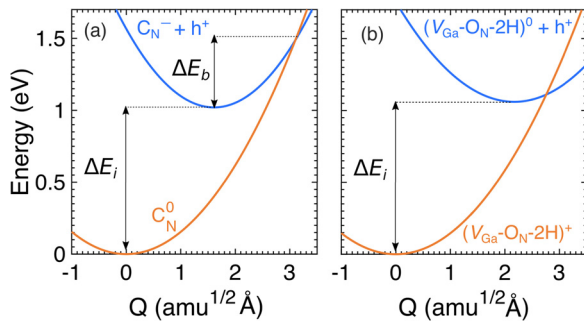


FIG. 2. One-dimensional configuration coordinate diagrams describing hole capture due to (a) C_N and (b) $V_{Ga}-O_N-2H$ in GaN. In (a), the initial state of the defect is C_N in a negative charge state and the final state is C_N in a neutral charge state. In (b), the initial state is $(V_{Ga}-O_N-2H)^0$ and the final state is $(V_{Ga}-O_N-2H)^+$. ΔE_i is the energy difference between the minima of the potential energy surfaces at $T = 0$ K, and ΔE_b is the classical barrier for the nonradiative capture process.

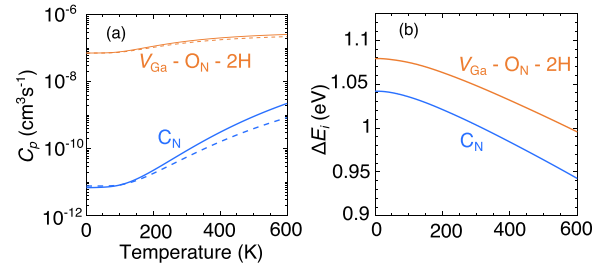


FIG. 3. (a) Hole capture coefficient versus temperature for C_N and $V_{Ga}-O_N-2H$ in GaN. The dashed lines are based on constant $T = 0$ K values for ΔE_i . The solid lines take the temperature dependence of ΔE_i , as shown in (b), into account. (b) Variation in the ionization energy of C_N and $V_{Ga}-O_N-2H$ as a function of temperature, as described in the text.

Inclusion of this additional effect enhances the dependence of C_p on T , as shown by the solid curves in Fig. 3(a).

It is commonly assumed³ that the capture coefficient has a temperature dependence given by $C_p = C_\infty \exp(-\Delta E_b/k_B T)$. Our results in Fig. 3(a) show that the description in terms of a temperature-independent classical barrier is too simple to capture the actual temperature dependence of C_p . At low temperatures, the Arrhenius form would imply that C_p goes to zero as $T \rightarrow 0$ K, but in reality, C_p remains finite because of quantum-mechanical tunneling. At high T , the behavior is also non-exponential, caused by the temperature dependence of ΔE_i . Hence, in a quantum-mechanical treatment of nonradiative capture of carriers by defects, one should consider an effective barrier to describe the temperature dependence of such processes.¹⁰ Unlike the classical capture barrier ΔE_b , the effective barrier $\Delta E'_b(T)$ is temperature dependent, resulting in C_p deviating from purely exponential behavior.

We now use our values of C_p [Fig. 3(a)] to calculate the emission rate based on Eq. (1). We mentioned before that the common practice in DLTS analysis is to plot $\ln(e_p/T^2)$ versus $1/T$, based on a lack of information about the temperature dependence of σ_p and the fact that $\langle v_p \rangle N_v \propto T^2$. Therefore, in Fig. 4, we plot $\ln(e_p/T^2)$.

When plotted over this large temperature range, the calculated emission rates (black solid lines in Fig. 4) clearly deviate from linearity, reflecting the non-Arrhenius behavior of C_p and the temperature dependence of ΔE_i . It is important to note that even if $\ln(e_p/T^2)$ would be linear, the slope still does not correspond to the ionization energy, as it includes the capture barrier.

DLTS measurements are carried out over a limited temperature range, typically about 50 K, and the data are then fitted to an Arrhenius expression. Based on the data as plotted in our Fig. 4, we fit to an expression

$$e_p/T^2 = e_0^{\text{fit}} \exp(-\Delta E_a^{\text{fit}}/k_B T). \quad (2)$$

We can thus determine the activation energy ΔE_a^{fit} that would be extracted from a typical DLTS measurement by fitting over a finite temperature range similar to the one probed in experiments (dashed curves in Fig. 4). We find that for C_N , the fitted activation energies increase from 1.162 eV to 1.394 eV, depending on the temperature range for which the fit is performed [Fig. 4(a)]. For $V_{Ga}-O_N-2H$, the explicit calculations are much closer to a simple Arrhenius behavior, and hence, there is little variation in the activation energies extracted over different temperature ranges [Fig. 4(b)].

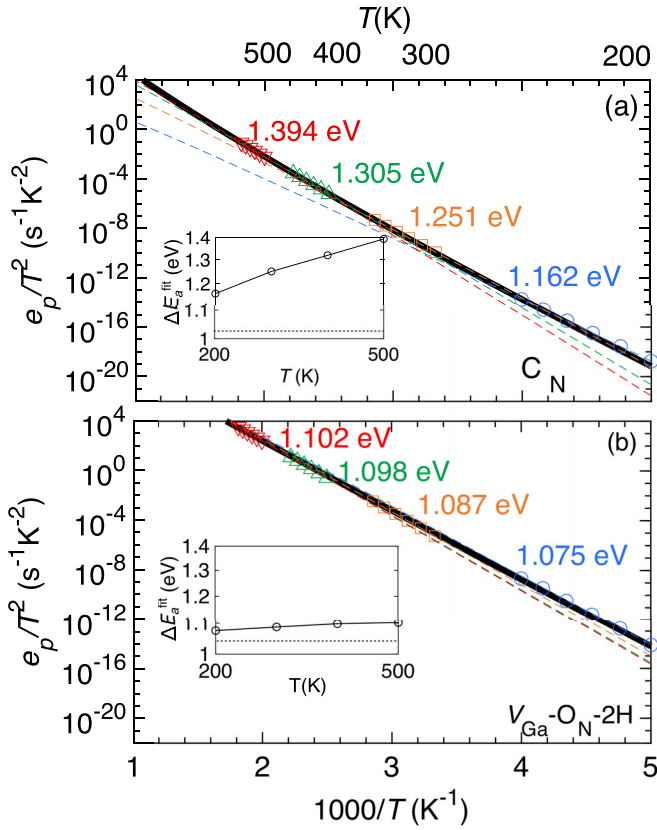


FIG. 4. Calculated hole emission rates for (a) C_N and (b) $\text{V}_\text{Ga}-\text{O}_\text{N}-2\text{H}$ in GaN (solid lines). The dashed lines are least-squares fits to Eq. (2), with the thick band of symbols indicating the temperature ranges over which the fit was performed: 200–250 K, 300–350 K, 400–450 K, and 500–550 K. Extracted activation energies ΔE_a are shown alongside each fit and plotted as a function of temperature in the inset. The zero-temperature ionization energy for each defect is illustrated with a horizontal dashed line.

The activation energy is temperature dependent, and the deviation between the ionization energy and activation energy is pronounced at higher temperatures. Our calculations highlight that the difference between the activation energy and the ionization energy can be large: up to 0.4 eV for C_N . The activation energy obtained from an Arrhenius analysis of the emission rate differs from the 0 K ionization energy of the defect for two reasons: first, because the activation energy also includes a capture barrier, and second, because the ionization energy itself is temperature dependent, due to the temperature dependence of the band edges and of the defect transition level. Activation energies extracted from DLTS should therefore not be simply interpreted as ionization energies, and simple comparisons with first-principles ionization energies could lead to incorrect identification of defects.

As mentioned above, the typical procedure (which we have followed in this paper) is to plot the results of DLTS experiments as $\ln(e_p/T^2)$ and perform an Arrhenius analysis assuming that σ_p has a temperature-independent prefactor [see Eq. (1)]. It has been shown, however, that at high temperature, the preexponential factor in σ_p has a $1/T$ dependence [cf. Eq. (28) in Ref. 2 and Eq. (61a) in Ref. 28]. At high temperature, one should therefore perform an Arrhenius analysis of $\ln(e_p/T)$, and this would be important to recover the value of the classical barrier ΔE_b . Indeed, we find that

including this $1/T$ dependence when fitting our first-principles calculations of capture coefficients at high temperatures ($T > 1200$ K) results in $\Delta E'_b \rightarrow \Delta E_b$ (the classical barrier at fixed ΔE_i , see Fig. 2), as expected. However, the typical temperature range over which DLTS experiments are performed does not reach this “high-temperature” limit, and therefore, $\ln(e_p/T^2)$ is an acceptable approximation.

In summary, we have shown DLTS activation energies are temperature-dependent and should not be compared directly with first-principles calculations of ionization energies of defects. Using first-principles calculations, we determined the temperature dependence of nonradiative carrier capture and the ionization energy of defects in GaN and demonstrated how they yield activation energies that can differ greatly from the 0 K ionization energy of the defect. The C_N and $\text{V}_\text{Ga}-\text{O}_\text{N}-2\text{H}$ defects we considered in this study are examples of positive- U defects where we determined the activation energy due to thermal emission from a single thermodynamic transition level. Our conclusions on the temperature dependence of activation energy will also apply in the case of more complex situations such as defects with two thermodynamic transition levels that are amenable to ionization in DLTS. In the case of a positive- U center, thermal emission due to both thermodynamic transition levels would be observed in a DLTS measurement. Our formalism can be applied to determine the activation energy of both transitions separately. In the case of a negative- U center, the DLTS transient is determined by the slower of the two carrier emission process. Thus, one would observe a single peak with an activation energy that corresponds to the slower emission process, to which our analysis is equally applicable. Hence, our analysis of these quantities is general and can be applied to accurately determine defect activation energies when comparing to DLTS measurements.

See supplementary material for the details of calculations of the vibrational properties of defects and a comparison between the calculated and the experimental temperature dependence of the bandgap of GaN.

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