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Role of excited states in Shockley-Read-Hall recombination in wide-band-gap semiconductors

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Defect-assisted recombination is an important limitation on efficiency of optoelectronic devices. However, since nonradiative capture rates decrease exponentially with energy of the transition, the mechanisms by which such recombination can take place in wide-band-gap materials are unclear. Using electronic structure calculations we uncover the crucial role of electronic excited states in nonradiative recombination processes. The impact is elucidated with examples for the group-III nitrides, for which accumulating experimental evidence indicates that defect-assisted recombination limits efficiency. Our work provides new insights into the physics of nonradiative recombination, and the mechanisms are suggested to be ubiquitous in wide-band-gap semiconductors.

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Defect-assisted recombination is a process that limits the efficiency of many electronic and optoelectronic devices. The classic Shockley-Read-Hall (SRH) recombination picture considers a defect with a single energy level in the band gap,^{1,2} as illustrated in Fig. 1 for a defect with charge states 0 and -1 . A complete recombination cycle requires capture of an electron by the neutral defect, followed by capture of a hole at the negatively charged defect. The overall recombination rate is thus governed by the *slower* of the two processes. Radiative capture rates are typically too small (an issue discussed in more detail below), and nonradiative capture rates decrease roughly exponentially with the energy of the transition³; this trend would lead one to conclude that defect-assisted recombination becomes unimportant in wide-band-gap materials.

However, evidence is mounting for the occurrence of SRH recombination in materials with band gaps of 2.5 eV or larger.⁴⁻⁶ Strong motivation for these studies has been provided by the technological importance of group-III nitride semiconductors as the key materials for light emitters in the green and blue spectral regions.⁷ With band gaps of 3.5 eV for GaN and 0.7 eV for InN,⁸ InGaN alloys can cover the entire visible spectrum. Progress in nitride growth currently allows producing materials with dislocation densities $<10^6 \text{ cm}^{-2}$, and there is a consensus that it is point defects that cause SRH recombination in such materials.^{6,9,10} However, the microscopic origin and mechanism of SRH recombination in nitrides has remained elusive. This is a serious handicap for improving device efficiencies.

In this work we show that intra-defect excited states can play a key role in enabling carrier capture required for SRH recombination. These excited states are derived from defect-related orbitals, as opposed to the shallow hydrogenic states that have been previously invoked to explain carrier capture at some charged centers in, e.g.,

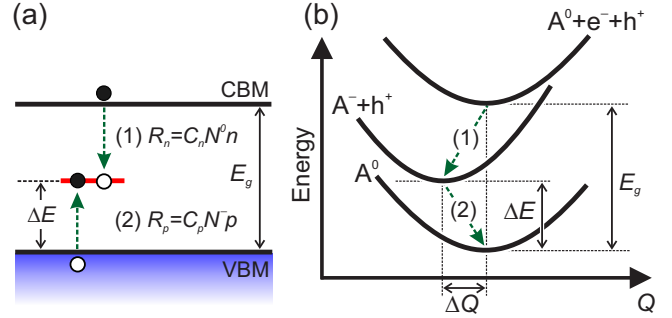


FIG. 1: (Color online) Shockley-Read-Hall recombination at a defect with a level at energy ΔE above the valence-band maximum (VBM), in two different representations: (a) energy level diagram; (b) configuration coordinate diagram. Electron and hole capture rates R_n and R_p are expressed as a function of capture coefficients C_n and C_p , carrier densities n and p , and defect concentrations in charge states N^0 and N^- .

Si or GaP.^{11,12} The wider the band gap of the material, the greater a role these excited states are likely to play. We demonstrate this for the highly relevant case of gallium vacancy complexes in nitride semiconductors, where processes involving excited states increase nonradiative recombination rates by many orders of magnitude. Such mechanisms play a key role in turning specific defects into efficient nonradiative centers, solving the problem of the bottleneck in SRH recombination in wide-band-gap materials.

Our analysis is bolstered by first-principles calculations performed within the framework of density functional theory (DFT) using the VASP code.¹³ We used the Heyd-Scuseria-Ernzerhof (HSE) functional¹⁴ with a fraction of screened Fock exchange $\alpha=0.31$ to provide an accurate description of the electronic structure of GaN—a requirement for obtaining reliable results for defect levels.^{15,16} Interaction between ions and valence electrons

were treated with the PAW approach.¹³ Wavefunctions were expanded in plane waves (using 400 eV for the kinetic energy cutoff), and the Brillouin zone was sampled at $k = (1/4, 1/4, 1/4)$. Formation energies and charge-state transition levels of defects¹⁵ were calculated using 96-atom supercells. The Freysoldt correction was applied for charged systems.¹⁷

We consider nonradiative processes that occur via multiphonon emission.³ We calculate nonradiative capture coefficients $C_{\{n,p\}}^{nr}$ (units: cm^3s^{-1}) within the static approach,¹⁸ using an effective one-dimensional approximation for phonons^{19,20} (for alternative formulations, see Refs.21,22). The special phonon mode is not an eigenmode of the system, but it represents all vibrations that couple to the change of defect's geometry caused by carrier capture. Capture coefficients are given by¹⁹:

$$C_{\{n,p\}}(T) = Vf\eta_{sp}g\frac{2\pi}{\hbar}W_{if}^2\sum_{m,n}w_m(T) \times |\langle\chi_{im}|Q + \Delta Q|\chi_{fn}\rangle|^2\delta(\Delta E + m\hbar\Omega_i - n\hbar\Omega_f). \quad (1)$$

V is the supercell volume, f is the scaling (Sommerfeld) factor needed to describe capture by charged defects,^{18,19} g is the degeneracy of the final state, W_{if} is the electron-phonon coupling matrix element.¹⁹ η_{sp} accounts for spin-selection rules: $\eta_{sp} = 1$ when the initial state is spin-singlet and the final state is spin-doublet, $\eta_{sp} = 1/2$ when the initial state is spin-doublet and the final is spin-singlet, etc. ΔE is the energy difference between the two states, $\Omega_{\{i,f\}}$ are effective vibrational frequencies in the initial and the final state, and Q is the effective one-dimensional phonon coordinate, with $Q = 0$ corresponding to the equilibrium geometry of the initial state. Potential energy minima in the two electronic states are offset by ΔQ ,^{19,20} as shown in Fig. 1(b). The sum runs over vibrational states in the excited (χ_{im}) and ground (χ_{fn}) electronic states. $w_m(T)$ is the thermal occupation factor. δ -functions in the sum are replaced by Gaussians with widths $\sigma = 0.8\hbar\Omega_f$.¹⁹ Matrix elements W_{if} are calculated as in Ref. 19.

Cation vacancies have been flagged as important defects in nitrides, and invoked as nonradiative recombination centers.²³ However, isolated gallium vacancies (V_{Ga}) have high formation energies and are thus unlikely to form; complexing with donor impurities such as oxygen significantly lowers the formation energy.²⁴ Indeed, mobility²⁵ and positron annihilation²⁶ studies indicate that there are at least $N = 10^{16} \text{ cm}^{-3}$ gallium-vacancy related defects in GaN. We will use this number as a conservative estimate for the defect concentration. However, as mentioned in the introduction, the precipitous decrease in capture rate with increasing transition energy seemingly renders these defects ineffective SRH centers in materials with larger band gaps.

We now demonstrate that capture into electronic excited states can provide an extremely efficient recombination channel. To illustrate this mechanism we will focus on a specific complex, $V_{\text{Ga}}\text{-O}_\text{N}$, which we will refer to

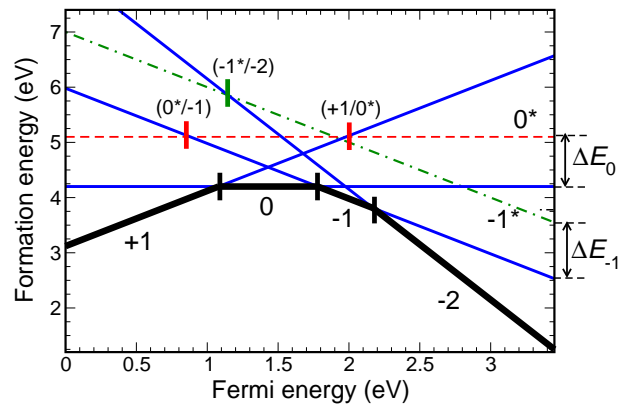


FIG. 2: (Color online) Formation energy of the $V_{\text{Ga}}\text{-O}_\text{N}$ complex in bulk GaN in different charge states as a function of Fermi energy, under Ga-rich conditions. Blue solid lines correspond to the lowest-energy configuration for each charge state; the black lines highlight the charge state with the lowest ground-state energy for a specific Fermi-level position. Red (dashed) and green (dash-dotted) lines correspond to excited states of the neutral and negatively charged state, respectively. ΔE_0 and ΔE_{-1} are intra-defect excitation energies for the neutral and the negatively charged defect. Charge-state transition levels that involve excited states and that are important for SRH recombination are explicitly marked.

as the VO center. All subsequent discussion also applies to the $V_{\text{Ga}}\text{-H}$ defect which has a very similar electronic structure to that of VO.²⁷ However, this defect has a larger formation energy and is less likely to form than the VO center. The calculated formation energies²⁸ for the different charge states of the VO center in GaN are shown in Fig. 2. The $(+/0)$, $(0/-)$, and $(-/-2)$ charge-state transition levels occur at 1.08, 1.78, and 2.17 eV above the valence-band maximum (VBM), respectively.

For a defect with a single energy level in the gap (Fig. 1) and assuming that carrier re-emission is negligible (entirely justified for deep levels in wide-band-gap semiconductors), the SRH recombination rate is^{1,2}

$$R = N \frac{C_n C_p n p}{C_n n + C_p p}. \quad (2)$$

where $N^0 + N^- = N$ is the total defect density. If photo-generated or injected carrier densities are much larger than the background carrier density, then $n \approx p$ and R can be written as $R = An$, where A (units: s^{-1}) is the SRH coefficient:

$$A = NC_{tot}; C_{tot} = \frac{C_n C_p}{C_n + C_p}. \quad (3)$$

This equation makes clear that the *slower* of the two processes determines the overall rate. For a defect such as the VO center [Fig. 2] with multiple levels in the gap, one might think that the closer positioning of the $(+/0)$ and $(-1/-2)$ transition levels to the respective band edges would be an advantage; in reality, such additional

transition levels reduce the efficiency of SRH recombination. For the defect with multiple charge states one can derive^{27,29} a SRH coefficient $A = NC_{tot}$, where

$$C_{tot} = \frac{1}{G} \left(C_n^{+1} + \frac{C_n^{+1}C_n^0}{C_p^0} + \frac{C_n^{+1}C_n^0C_n^{-1}}{C_p^0C_p^{-1}} \right); \quad (4)$$

$$G = 1 + \frac{C_n^{+1}}{C_p^0} + \frac{C_n^{+1}C_n^0}{C_p^0C_p^{-1}} + \frac{C_n^{+1}C_n^0C_n^{-1}}{C_p^0C_p^{-1}C_p^{-2}}.$$

The superscripts indicate the charge state, the subscripts specify the carrier type. We exclude the consideration of radiative capture processes, which are characterized by coefficients $C_{rad} = 10^{-14} - 10^{-13} \text{ cm}^3\text{s}^{-1}$ [Ref. 30]. Assuming $N = 10^{16} \text{ cm}^{-3}$ this yields A coefficients three-four orders of magnitude smaller than the values of $A \approx 10^7 \text{ s}^{-1}$ experimentally determined for InGaN.⁴

We calculated²⁷ all capture coefficients appearing in Eq. (4). We assumed $T=120^\circ\text{C}$, a typical internal temperature of operating LEDs.³¹ Explicit calculations for InGaN alloys are computationally prohibitive. Based on calculations at select alloy compositions we have found that the variation in defect properties is predominantly determined by the change in the lattice parameters between GaN and InGaN; explicit interactions with In atoms affect defect levels by less than 0.1 eV. We therefore determined charge-state transition levels of the VO defect in GaN supercells with lattice parameters expanded to match the volume of InGaN with 5, 10, and 20% In. The resulting transition levels are then positioned within the InGaN band gap by (i) aligning the average of the top three valence bands in the expanded cell to that of unstrained GaN using the absolute valence-band deformation potential of GaN³²; (ii) aligning band edges of unstrained GaN and unstrained InGaN using band offsets from Ref.33. The dependence of transition levels on band gap is given in Ref.27.

Our calculations reveal that the capture coefficient C_{tot} [Eq. (4)] is smaller than $10^{-19} \text{ cm}^3\text{s}^{-1}$ for band gaps 2.20 – 3.45 eV. The reason for these negligibly small coefficients is that the defect gets stuck in the “extreme” charge states +1 and –2. This follows from Eq. (4) in the following way^{27,29}: the total recombination coefficient C_{tot} is a sum of coefficients corresponding to pairs of charge states with charges differing by one. For each pair the recombination rate is given by Eq. (2), with N now representing the concentration of defects in those particular two charge states.²⁹ Let us take the (+1,0) pair of charge states as an example. In steady state, the number of defects in each of the charge states is constant, and detailed balance gives $N^{+1}C_n^{+1} = N^0C_p^0$, and thus $N^{+1}/N^0 = C_p^0/C_n^{+1}$. The (+1/0) charge-state transition level is much closer to the VBM than to the CBM. Consequently, $C_p^0 \gg C_n^{+1}$, and therefore $N^{+1} \gg N^0$. Similar reasoning for the (–1,–2) pair leads to $N^{-2} \gg N^{-1}$. Thus almost all defects are in either the +1 or –2 charge states. The +1 state captures electrons very inefficiently, while the –2 state captures holes very inefficiently, leading to the overall low SRH recombination rate.

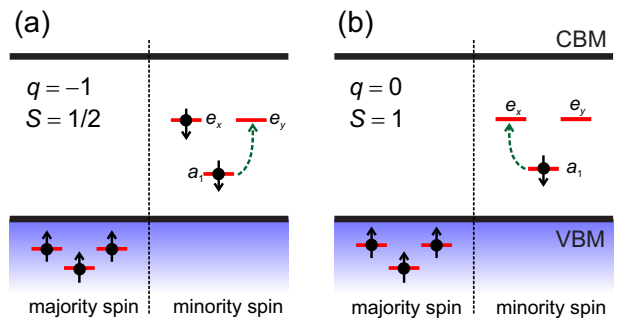


FIG. 3: (Color online) Single-particle states of the VO defect for charge states $q = -1$ (a) and $q = 0$ (b). Intra-defect excitation occurs by promoting an electron from the a_1 state to the e state.

Our considerations so far did not take *excited* electronic states into account. We will show that such states exist for the –1 and 0 charge states. Single-particle defect states at the VO center arise from the interaction of dangling bonds on three N atoms. The lower-lying state results from a symmetric combination, while the two higher-lying states result from an anti-symmetric combination. Were the symmetry of the center C_{3v} , these single-particle states would belong to a_1 and e irreducible representations; we will retain these labels also for lower symmetries. In charge state $q=-2$ all levels are filled, and no excited states are possible. For $q=-1$ (spin $S=1/2$) the electronic configuration is $a_1^1e^2$ in the majority-spin channel, and $a_1^1e^1$ in the minority-spin channel. The excited state is an excitation from the a_1 state to the e state, as shown in Fig. 3(a). For charge state $q=0$ ($S=1$) the electronic configuration is $a_1^1e^0$ in the minority-spin channel, and again, an excitation can occur by promoting the a_1 electron to the e state [Fig. 3(b)]. In the ground state of the $q=+1$ charge state ($S=3/2$) all defect states are filled in the majority-spin channel, and empty in the minority-spin channel, and thus there are no spin-conserving excited states.

DFT is a ground-state theory, and in order to describe excited states one has to go beyond DFT. One way to do this is to approximate total energy differences by differences in single-particle Kohn-Sham eigenvalues in the spirit of the generalized Koopmans theorem.^{34–36} For transitions for which actual comparison could be made we have explicitly verified²⁷ that this approach is very accurate for the VO defect when calculations are performed with the HSE hybrid functional. By mapping ground-state and excitation energies along the relevant configuration coordinates³⁷ we can determine potential energy surfaces in the excited states.²⁷ We obtain intra-defect excitation energies $\Delta E_0 = 0.90 \text{ eV}$ and $\Delta E_{-1} = 1.02 \text{ eV}$, as shown in Fig. 2.

Excited states drastically change the dynamics of SRH recombination. Let us again consider the (+1, 0) pair of charge states (which will turn out to be the most important for SRH recombination at VO defects). Without

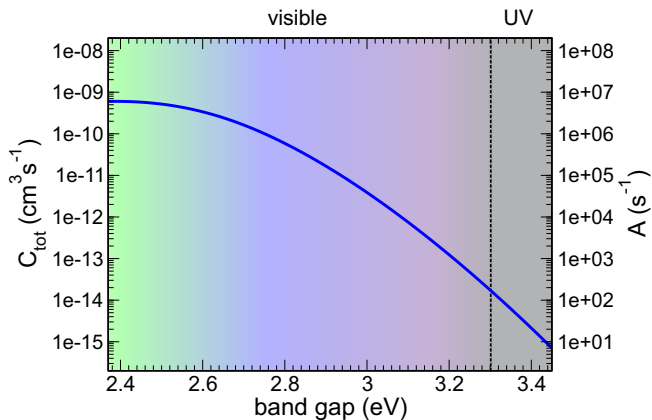


FIG. 4: (Color online) Calculated total capture coefficient C_{tot} (left vertical axis) and SRH coefficient $A = NC_{tot}$ (right vertical axis) as a function of band gap for gallium-vacancy complexes with oxygen. We assumed a defect concentration $N = 10^{16} \text{ cm}^{-3}$.

excited states recombination via this pair is slow: almost all defects are in the +1 state, which captures electrons inefficiently since the (+1/0) transition is far from the CBM (2.37 eV in GaN). When excited states are taken into account, capture of an electron into the 0^* state can occur (the phrase “capture into” refers to the final state of the process). The (+1/0 *) transition [vertical red bar in Fig. 2] is closer to the CBM by an amount ΔE_0 ; i.e., the (+1/0 *) level is $2.37 - 0.90 = 1.47$ eV below the CBM, resulting in much more efficient electron capture. After this capture process occurs, the system quickly relaxes from 0^* to 0 via intra-defect relaxation.²⁷ Once in the 0 charge state, the defect captures a hole very efficiently, closing the recombination cycle.

Also important for the SRH recombination is hole capture by the -2 state into the -1^* state. In GaN the ($-2/-1$) charge-state transition level is 2.17 eV from the VBM, resulting in negligibly slow hole capture. The presence of the -1^* state reduces this separation by $\Delta E_{-1} = 1.02$ eV, resulting in a substantial increase in hole capture. Equally important is hole capture by the -1 state: the presence of the 0^* state makes this process orders of magnitude more efficient, because the ($-1/0^*$) transition level is much closer to the VBM than the ($-1/0$) level [Fig. 2]. Calculations show that the latter two processes are responsible for removing defects from charge states -2 and -1 , and most recombination proceeds via states +1 and 0.

Analysis of Fig. 2 would seem to suggest that electron capture by the 0 charge state (configuration $a_1^1 e^0$) into the (-1^*) charge state (configuration $a_1^0 e^2$) should also be beneficial for SRH recombination. However, this is actually an Auger process, because it requires that one electron is captured from the conduction band to the e state, while the other at the same time is promoted from a_1 to e . Such four-state processes are expected to be slower³ and are not taken into account in our analysis.

Quantitatively, the total capture coefficient in the presence of excited states is given by an equation analogous to Eq. (4), with C_n^{+1} , C_p^{-1} , and C_p^{-2} replaced by coefficients that describe capture into the respective excited states. The overall capture coefficient is shown in Fig. 4. C_{tot} is equal to $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for InGaN alloys emitting in the blue (band gap 2.75 eV) and $6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for InGaN emitting in the green (2.40 eV). For defect concentration $N = 10^{16} \text{ cm}^{-3}$, this gives SRH coefficients $A = NC_{tot} = 1 \times 10^6 \text{ s}^{-1}$ and $A = 6 \times 10^6 \text{ s}^{-1}$, respectively. For the blue InGaN the determined A coefficient is very close to the ones found in actual LEDs.⁴

We are now in a position to determine the impact of SRH recombination on efficiency of LEDs. At low injected carrier densities, when third-order processes can be ignored, the internal quantum efficiency is given by $\eta = Bn/(A + Bn)$. We take $n = 10^{18} \text{ cm}^{-3}$, a typical carrier density in operating LEDs.⁴ Since $B \approx 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$,³⁸ we find that $N = 10^{16} \text{ cm}^{-3}$ VO centers would decrease the quantum efficiency of blue LEDs by $\sim 2.5\%$ and green LEDs by 13%. A defect concentration of $N = 10^{17} \text{ cm}^{-3}$ would decrease efficiencies of blue LEDs by 20%, and those of green LEDs by as much as 60%. Note that in the latter case, where most of the recombination is nonradiative, the presence of defects modifies the charge-neutrality condition and we can no longer take $n = p$, an assumption used in deriving Eqs. (3) and (4). Still, these equations provide a reasonable estimate of the SRH coefficient. Our analysis shows that gallium-vacancy complexes are an important source of efficiency loss in nitride light emitters.

In conclusion, we have found that electronic excited states can play a crucial role in Shockley-Read-Hall recombination in wide-band-gap semiconductors. Our example for gallium vacancy complexes in nitride semiconductors demonstrated that inclusion of excited states enhances nonradiative recombination rates by many orders of magnitude. We suggest that such mechanisms should be ubiquitous in wide-band-gap materials. Excited states similar to the ones considered in this work can occur at cation vacancies and their complexes not only in nitrides, but also in oxides as well as carbide materials. More generally, excited states of defects can also affect recombination mechanisms other than the multiphonon emission process considered in this work. For example, in the so-called impurity Auger process³ the recombination rates also decrease exponentially when the band gap of the material increases, seemingly making such processes unimportant for wide-band-gap materials. Inclusion of excited states of defects could drastically change the impact of this mechanism as well.

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