

Multiscale Explanation of the Missing Gallium Vacancy in Gallium Arsenide

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Irradiation of gallium arsenide (GaAs) produces immobile vacancies and mobile interstitials. Yet, after decades of experimental investigation, the immobile Ga vacancy continues to evade detection, raising the question: where is the Ga vacancy? Static first-principles calculations predict a Ga vacancy should be readily observed. We find that short-time dynamical evolution of primary defects is the key to explaining this conundrum. Using a dynamical multiscale atomistically informed device engineering (AIDE) method, we discover that during the initial displacement damage, the Ga vacancy ($3-/2-$) defect level pins the Fermi level near the midgap, producing oppositely charged vacancies and interstitials. Driven by Coulomb attraction, fast As interstitials preferentially annihilate Ga vacancies. The Ga vacancy population plummets below detectable limits—and the now unpinned Fermi level recovers—before being experimentally observed. This dynamical model solves the mystery of the missing Ga vacancy and reveals the importance of a multiscale approach to explore the dynamical chemical behavior in experimentally inaccessible short-time regimes.

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Atomic defects play a significant role in semiconductor properties. Understanding their chemical behavior has been a central theme in several investigations [1–4]. Defect physics in gallium arsenide (GaAs) has been intensively studied for many decades [5–8]; however, despite the progress, several issues remain unresolved [9]. Irradiation of GaAs by energetic particles—through deliberate ion implantation (to controllably dope a material), exposure to high-energy electrons, or to ions in radiation environments (e.g., satellite electronics)—displaces atoms from their lattice positions, leaving behind immobile vacancies and mobile interstitials. Identifying and characterizing these atomic defects and their subsequent chemical evolution (annealing), through defect reactions, is essential to developing the comprehensive understanding necessary to enhance and improve the longevity of semiconductor devices. Currently, our understanding of these processes in GaAs remains incomplete and insufficient.

A provisional assignment of GaAs defects has been established through a series of experimental and theoretical studies. Theory was pivotal in definitively identifying the technologically crucial EL2 in as-grown GaAs as the

arsenic antisite As_{Ga} (As atom occupying a Ga site) [10,11]. Deep-level transient spectroscopy (DLTS) experiments on irradiated n-GaAs revealed a collection of defect levels, denoted E1, E2, E3, E4, and E5 [6], at or above midgap. With limited theoretical support and capability, defect identification proved to be challenging for several decades. However, using density functional theory (DFT) modeling, Schultz and von Lilienfeld provided predictions for intrinsic point defects and defect levels in GaAs (Fig. 1) [8]. Theory, now equipped with this Rosetta Stone of GaAs defects, was instrumental in identifying several defects, including the primary E1–E2, two distinct transitions of the same defect near the conduction band edge (CBE) [6,12–14], as the divacancy ($v_{\text{Ga}}v_{\text{As}}$) [15], and the E3 center as the As vacancy (v_{As}) [8,15]. The E4 and E5 centers, located

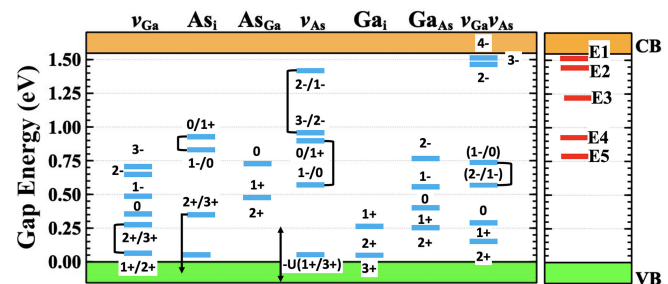


FIG. 1. DFT-computed defect levels were extracted from Ref. [8], where the LDA-LMCC (local density approximation [16]-local moment countercharge [17,18]) approach was used. Solid lines connect levels that exhibit -U behavior. Conduction (CB) and valence (VB) bands are orange and green.

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near midgap among a zoo of defects, remain unidentified and are likely due to a complex of point defects.

Recently, a Laplace DLTS study [19] resolved the E3 peak into three distinct components—E3a, E3b, and E3c. The E3a (principal component) and E3c were identified as v_{As} [8] and the vacancy-Si pair [20], respectively. The E3b (CBE – 0.38 eV) has not been theoretically identified but was determined to be intrinsic [19]. None of the defect identifications included the Ga vacancy (v_{Ga}). Despite theory predicting v_{Ga} , like v_{As} and $v_{Ga}v_{As}$, to be stable [21–24], immobile [25], and have multiple charge states [8,21–24], no experimental measurement has unambiguously observed the v_{Ga} .

The absence of v_{Ga} is a crucial missing link in understanding radiation damage in GaAs. It remains unclear whether this gap is due to a failure in understanding the nature of the initial displacement damage (as Frenkel pairs), some undiagnosed blindness of experimental probes to v_{Ga} , or a failure in the theoretical and experimental interpretation of v_{Ga} stability and mobility. This understanding has eluded investigators for decades.

Our primary motivation is to confront this fundamental puzzle: where is the missing v_{Ga} ?

Theory has reached a consensus that v_{Ga} exists in a 3- charge state above midgap [8,21]. Meanwhile, neither DLTS nor any other experimental technique has witnessed any firm indication of v_{Ga} , inferring that any transition levels must lie near or below midgap. This provides the first essential clue needed to explain the observational absence of v_{Ga} : it exists as a 3- defect above midgap.

The conceptual model of irradiated n-type (Si-doped) GaAs begins with standard displacement damage: energetic particles displace mobile interstitial atoms (Ga_i and As_i) from their lattice sites, leaving behind immobile vacancies (v_{Ga} and v_{As}) and divacancies ($v_{Ga}v_{As}$). The *fastest* process, immediately following the primary displacement damage, is electron flow between defects. Mediated by charge carriers, electrons fill the defect states deepest in the band

gap until establishing an equilibrium Fermi level—charge equilibration (CE).

The Ga vacancy assumes a 3- charge state at midgap (Fig. 1). The irradiation event generates sufficiently many Ga vacancies—each capturing three electrons—to collapse the Fermi level from the Si-doping level to midgap, where it is pinned by the v_{Ga} (3-/2-) defect level. This Fermi level shift to midgap alters all defect charge states, producing negatively charged vacancies and positively charged interstitials [Fig. 2(a)].

The *next-fastest* process is defect diffusion. Theory predicts that As_i is positively charged at the pinned midgap Fermi level ($E_F = 0.76$ eV). This prediction is significant because both experimental [7] and theoretical [8] studies have asserted that As_i undergoes fast, athermal diffusion [26] as a positive ion: a fast As_i dominates the first stage of defect reactions. The As_i^{1+} are attracted by all negatively charged vacancies, but the strongest Coulomb attraction is from v_{Ga}^{3-} . The As_i^{1+} preferentially annihilates v_{Ga}^{3-} to form As_{Ga}^0 ($As_i^{1+} + v_{Ga}^{3-} \rightleftharpoons As_{Ga}^0 + 2e^-$), causing its population to plummet. With v_{Ga}^{3-} eliminated, the Fermi level becomes unpinned and recovers, rising so that As_i^{1-} becomes its dominant charge state. The As_i^{1-} interaction with all negatively charged vacancies becomes repulsive, shutting down any further annihilation by As_i . This annihilation, consistent with experimental observations, suggests that only As-site vacancies (v_{As} and $v_{Ga}v_{As}$) survive [Fig. 2(c)]. The declining v_{Ga} population—and recovery of the unpinned Fermi level—occurs too quickly to be experimentally observed.

While this conceptual model presents a plausible chain of events inferred from the DFT data, it invokes kinetic processes whose effects cannot be assessed with stationary-static DFT calculations. To account for the kinetic processes, we developed an atomistically informed device engineering (AIDE) method, which uses defect properties from DFT and experimental observations and measurements.

The multiscale AIDE method is very powerful and encompasses the necessary dynamical physical phenomena to explain why v_{Ga} is invisible to experimental probing.

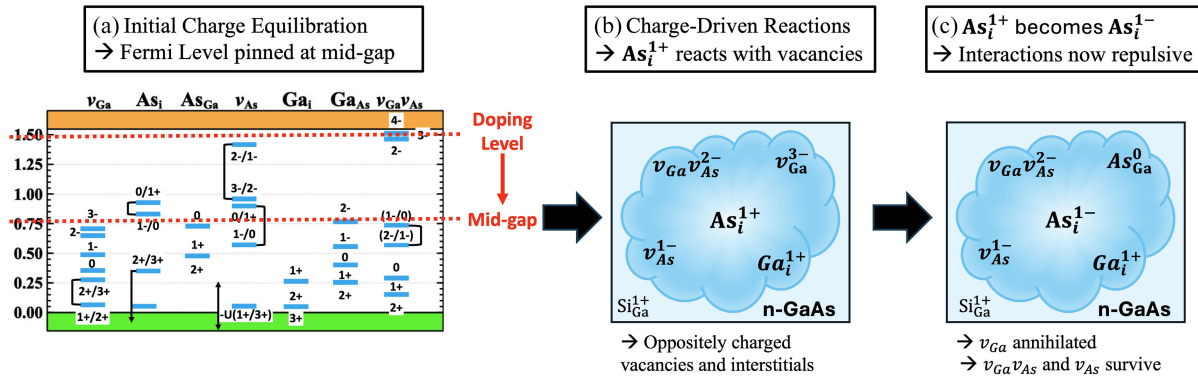


FIG. 2. An illustrative description of the conceptual model used in this Letter showing (a) the initial charge equilibration (i.e., Fermi level stabilization at midgap), (b) the most populated charge state for each defect causing charge-driven reactions, and (c) the dominant charge state of the surviving defects after the Ga vacancy is annihilated.

Device model—Using the Radiation Effects in Oxides and Semiconductors (REOS) software package [27], the dynamical nature of defects in irradiated GaAs was studied at 300 K. Unlike standard commercial device simulation codes, REOS is populated with DFT-calculated defect levels and available experimental data, creating a physically accurate treatment of dynamical systems. An important advantage is its ability to probe regimes—early-time behavior and extremely low populations—that are inaccessible to current experimental techniques.

A one-dimensional slab of thickness 2.1×10^{-4} cm was used in the device simulations. The DFT-predicted effective band gap (1.54 eV, experimental value 1.52 eV [28]) was used and populated with the computed defect levels (Fig. 1 [8]). In addition to the simple intrinsic defects predicted by DFT, a Si dopant was added to the GaAs sample at a concentration of 1.00×10^{15} cm $^{-3}$, with two charge states, $\text{Si}_{\text{Ga}}^{1+}$ and Si_{Ga}^0 , consistent with typical experimental doping concentrations ranging from 10^{15} to 10^{16} cm $^{-3}$ [19]. After irradiation, the initial defect concentrations were chosen as follows: $\text{As}_i = \text{Ga}_i = 1.24 \times 10^{15}$, $v_{\text{As}} = v_{\text{Ga}} = 6.10 \times 10^{14}$, and $v_{\text{Ga}}v_{\text{As}} = 6.30 \times 10^{14}$ cm $^{-3}$ (criteria in End Matter).

Charge equilibration—After primary displacement damage, the fastest processes occur during CE [Fig. 2(a)], where electrons rapidly migrate throughout the system, filling the lowest-energy defect states first, until Fermi level stabilization. This produces negatively charged vacancies and positively charged interstitials [Figs. 2(a) and 2(b)]. In agreement with our conceptual model, the Fermi level collapses from the Si-doping level to midgap ($E_F \approx 0.76$ eV), pinned by the v_{Ga} (3-/2-) defect level. To confirm this shift, defect species populations were calculated for each defect and compared to one another; all dominant charge states must correlate with the same Fermi level. In Fig. 3, species densities for all v_{Ga} and As_i charge states are shown. The model, consistent with

DFT-predicted defect levels, identifies As_i^{1+} and v_{Ga}^{3-} as the dominant charge states. Not shown here, the model also correctly identifies v_{As}^{1-} , Ga_i^{1+} , and $v_{\text{Ga}}v_{\text{As}}^{2-}$ as the dominant defect charge states. Additionally, the calculated charge-state ordering for all defects agrees with the DFT-predicted levels, including those below measurable limits.

Despite being able to predict each defect's dominant charge state from the defect level diagram (Fig. 1), performing CE dynamically with REOS served as an additional metric to ensure the simulation's physical accuracy. To enhance the physical realism of the CE process, specifically to achieve faster equilibration, an initial condition was implemented, lowering the CE time from 1 to $> 10^{-12}$ s (Supplemental Material [29], Fig. S1). This initial condition produced identical results and was used for the remainder of this Letter.

Charge-driven reactions—After the fast electron migration, the Fermi level—pinned by v_{Ga}^{3-} —stabilized near midgap and established three negatively charged vacancies (v_{As}^{1-} , $v_{\text{As}}v_{\text{Ga}}^{2-}$, and v_{Ga}^{3-}) and two positively charged interstitials (As_i^{1+} and Ga_i^{1+}) as the most populated defect species. The next-fastest process involves defects diffusing throughout the material. Coulomb attraction between oppositely charged species triggers a sequence of defect-defect reactions that leads to the formation of (i) new defects, (ii) point defect complexes, and/or (iii) healed lattice sites via recombination. Like-charged species, conversely, repel one another. Since defect-defect reactions involve several possible outcomes, it is expected that charge state population sizes will change throughout this process and, in response to charge flow, cause the Fermi level to shift once again. Therefore, during this stage of our conceptual model [Fig. 2(b)], two reaction types ensue: charge carrier capture reactions and charge-driven defect-defect reactions (diffusion-driven reactions).

Diffusion-driven reactions are governed by the diffusion coefficient in which the migration barrier energy (E_m) is essential for species diffusion in the simulation. In GaAs, vacancies are immobile [8,30,31]; consequently, any chemical evolution must be mediated by the mobile As and Ga interstitials. However, As_i^{1+} has a lower thermal migration barrier ($E_m^{\text{As}_i^{1+}} = 0.50$ eV [7] vs $E_m^{\text{Ga}_i^{1+}} \approx 1.0$ eV [8,32,33]) and diffuses athermally via the Bourgoin-Corbett mechanism [26]. Any initial defect chemistry in GaAs will be dominated by the very fast As_i^{1+} athermal diffusion.

Athermal processes (Bourgoin-Corbett), while conceptually understood, remain a challenge to quantitatively model [34] and integrate into simulations. Athermal processes were not simulated directly in REOS. While some have treated it as an additive term to the thermal diffusion coefficient [35], we adopt an alternate approach and mimic the fast athermal diffusion effects by reducing the As_i^{1+} thermal migration barrier (0.50 eV [7]) by 20% to 0.40 eV.

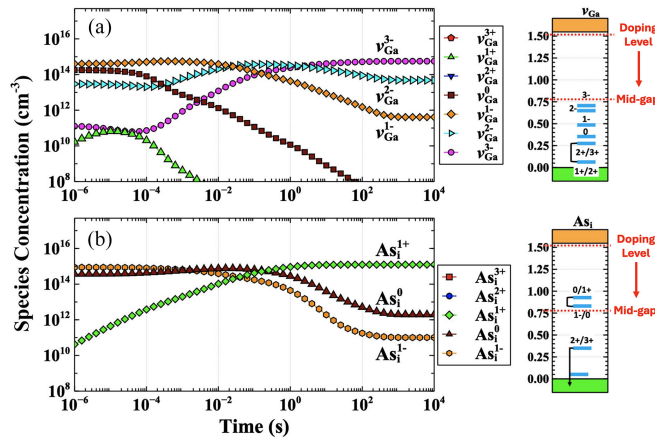
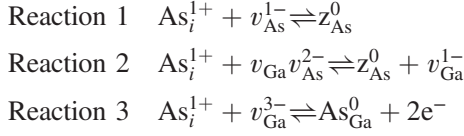


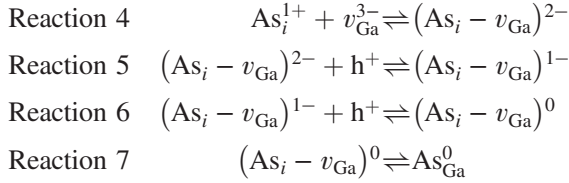
FIG. 3. Calculated species concentration for (a) v_{Ga} and (b) As_i charge states during charge equilibration. Charge states not shown exist below 10^8 cm $^{-3}$. (c) Defect levels of v_{Ga} and As_i with Fermi level shift to midgap ($E_F \approx 0.76$ eV).

Each reaction considered yields a final product defect that DFT predicts to be stable (Fig. 1), ensuring its physical presence in the material. Limiting our Letter to As_i^{1+} -type reactions— As_i^{1+} is the fastest diffusing interstitial—and adhering to the stability prerequisite limits the number of possible reactions and products formed. From weakest to strongest Coulomb attraction, the three reactions and their products are



where Reaction 1 results in a healed As-lattice site (z_{As}), Reaction 2 produces z_{As}^0 and v_{Ga}^{1-} , and Reaction 3 forms As_{Ga}^0 with $2e^-$ released into the system. Reaction 3 is expected to form $As_i^{1+} + v_{Ga}^{3-} \rightleftharpoons As_{Ga}^{2-}$; however, according to our defect stability prerequisite, As_{Ga}^{2-} is predicted by DFT to be absolutely unstable [8] and cannot be a forming product.

Currently, the mechanism of Reaction 3—emission of multiple electrons in a single step—is represented, in REOS, as a sequence of intermediate charge-conserving reactions that involve the emission of a single electron:



where $(As_i - v_{Ga})^{2-}$, $(As_i - v_{Ga})^{1-}$, and $(As_i - v_{Ga})^0$ are short-lived intermediates formed during the process. Reactions 4–6 occur rapidly, serve only to aid our simulation, and produce thermodynamically unstable product defects. These intermediate steps ensure (i) the formation of a stable As_{Ga}^0 and (ii) the release of $2e^-$ into the system. Physically, Reaction 7 has a separate mechanism in which As_i must overcome an energy barrier before hopping into vacancy sites. Formation of a complex and overcoming of an energy barrier is true for all As_i^{1+} -vacancy reactions (see End Matter and Supplemental Material [29]).

Simulated reactions include Reactions 1, 2, and 4–7. Notably, the Coulomb attraction for each reaction is different, with v_{Ga}^{3-} attracting As_i^{1+} more than the other vacancies. To account for the increasing Coulombic attraction between As_i and the vacancy types, effective reaction radii were set to 1.0×10^{-10} , 1.0×10^{-8} , and 1.0×10^{-6} cm for Reactions 1, 2, and 4, respectively.

In Fig. 4, the $As_i^{1+} + v_{Ga}^{3-}$ reaction is shown. After charge equilibration, the strong Coulomb attraction (Region I) results in the v_{Ga}^{3-} population collapsing below 10^{11} cm $^{-3}$ after 5 s and below 10^9 cm $^{-3}$ after 60 s (Region III), where

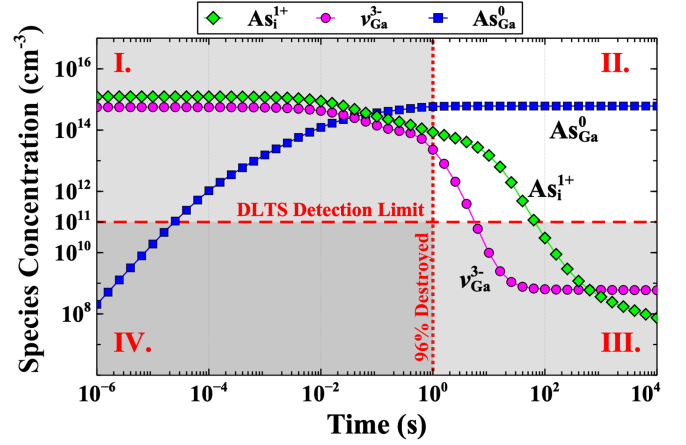


FIG. 4. Species concentration for $As_i^{1+} + v_{Ga}^{3-}$ reaction. Red lines indicate DLTS concentration limit (dashed: 10^{11} cm $^{-3}$) and when 96% of v_{Ga}^{3-} is annihilated (dotted: 1 s). Intermediate steps are rapidly occurring, and only As_{Ga}^0 is shown.

its population flattens. Flattening occurs because as the v_{Ga}^{3-} population declines, its probability of reacting with As_i^{1+} gets overtaken by the largely more populated $v_{Ga} v_{As}^{2-}$. The As_i^{1+} also experiences a diminishing population because, unlike v_{Ga}^{3-} , it is consumed by v_{Ga} reactions and charge re-equilibration, causing its charge state to change to 1-. Formation of As_{Ga}^0 , denoted by an increasing population (increasing slope), reaches its peak after about 5 s, where its slope flattens in Region II. This rapid v_{Ga}^{3-} decline provides a direct explanation for its invisibility to experimental probing.

Despite DLTS revealing several defects in GaAs, none have been identified as the Ga vacancy. Generally, DLTS includes filling active defects with a voltage pulse and measuring gradual changes in capacitance, recording capacitance transients. Conventional DLTS setups have concentration detection limits described by $N_{\text{defect}}/N_{\text{doping}} \approx \delta C_{\text{max}}/C_0$, where N and C denote concentration and capacitance, respectively [36]. For our system (Si doping = 1.00×10^{15} cm $^{-3}$), conventional DLTS sensitivity ($\delta C/C_0 \approx 10^{-5}$ – 10^{-4} [37]) is expected to be $N_{\text{defect}} = (\delta C_{\text{max}}/C_0)N_{\text{doping}} \approx 10^{11}$ cm $^{-3}$ (red dashed line in Fig. 4). This limit is roughly 100 times larger than our predicted v_{Ga} density ($< 10^9$ cm $^{-3}$), making it impossible to detect through DLTS. Including a high-sensitivity bridge improves this sensitivity to $\approx 10^9$ cm $^{-3}$ ($\delta C/C_0 \approx 10^{-6}$) [38], still not sensitive enough to see the Ga vacancy. Moreover, inclusion of omitted (slower) Ga_i^{1+} -vacancy reactions, with Coulomb interactions similar to As_i^{1+} , would reduce the v_{Ga}^{3-} population further. Defect populations existing in Regions III or IV will not be seen by experimental probes.

The v_{Ga} is increasingly difficult for DLTS to observe because its population is nonconstant and rapidly changing

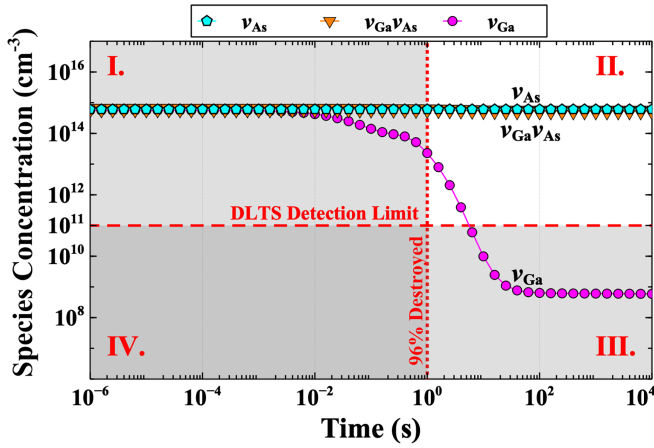


FIG. 5. Total species concentrations for v_{As} , $v_{\text{Ga}}v_{\text{As}}$, and v_{Ga} . Red lines indicate DLTS concentration limit (dashed: 10^{11} cm^{-3}) and when 96% of v_{Ga} is annihilated (dotted: 1 s).

as it plummets below detectable limits—it is effectively invisible. Therefore, any chemical behavior, such as v_{Ga} population decline, which saw roughly 96% annihilated after 1 s (red dotted line in Fig. 4), will not be observed under current detection capabilities. The v_{Ga} exists, predominately, in the immeasurable regimes (Regions I and III) of the DLTS technique.

Total populations (sum of all defect charge states) for each vacancy type (v_{Ga} , $v_{\text{Ga}}v_{\text{As}}$, and v_{As}) are plotted over the duration of As_i^{1+} -vacancy reactions in Fig. 5. The total v_{Ga} population experiences a collapse resembling that of its 3- charge state. Most of v_{Ga} exists as v_{Ga}^{3-} , the source of the midgap Fermi level pinning. In contrast to v_{Ga} , $v_{\text{Ga}}v_{\text{As}}$ and v_{As} populations do not collapse; instead, their populations remain largely unaffected and survive. Recall that $v_{\text{Ga}}v_{\text{As}}$ and v_{As} have been observed as E1 and E2 [15] and E3a [20], respectively. Also, E1, E2, and E3 do not anneal until temperatures above 490 K [6,19], suggesting that at room temperature, $v_{\text{Ga}}v_{\text{As}}$ and v_{As} should maintain substantial populations and survive any early-time defect chemistry. In agreement with observations, our simulation predicts that $v_{\text{Ga}}v_{\text{As}}$ and v_{As} survive the Coulomb-driven wave of As_i reactions. Their survival provides further reassurance of the simulation's physical accuracy and confirms v_{Ga} preferential annihilation.

As_i^{1+} becomes As_i^{1-} —Simulations in Figs. 4 and 5 were allowed to run for 10^4 s. During this time, the v_{Ga} population is exhausted and As_i^{1+} becomes As_i^{1-} , which then repels all negatively charged vacancies [Fig. 2(c)]. This concludes the initial, fastest (athermal) stage of defect reactions after irradiation. The next-fastest dynamical stage (not considered here) would be reactions mediated via thermally activated As_i and Ga_i . The extended time-scale demonstrates the AIDE method's potential and aptitude for exploring experimentally inaccessible regimes.

In summary, the physical explanation to the long-standing mystery of the missing v_{Ga} in irradiated GaAs is simple and is resolved once dynamical effects are deliberately considered in a multiscale atoms-to-devices analysis. This innovative approach reveals that v_{Ga} is not observed because it has been preferentially annihilated—below detectable levels—by highly mobile As_i in a rapid initial wave of defect reactions. This confirms the hypothesized stability of a v_{Ga}^{3-} deep in the band gap and validates the DFT-predicted ionization of As_i into a positive ion at midgap. Interestingly, the lack of experimental evidence for v_{Ga} is, in fact, evidence for its absence. It is not due to some undiagnosed experimental blindness (v_{Ga} is not there to be seen), nor to errors in DFT predictions (deducing the fate of v_{Ga} depends on DFT defect level calculations being accurate), nor the result of some unknown, unusual kinetic processes—the initial annealing kinetics can be modeled effectively in a defect device model using well-established defect physics.

In addition to providing an explanation for the experimentally invisible v_{Ga} , the AIDE method provides insight into the rich defect physics of regimes that are inaccessible to experimental probing. The AIDE method serves as a virtual experiment to bound estimates for difficult-to-measure quantities such as capturing cross sections and diffusion activation energies.

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Data availability—The data supporting this study's findings are available within the article.

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End Matter

The REOS suite is a device theory simulation package capable of implementing and running damage models by solving the classical continuum semiconductor transport equations [39,40] for a collection of species in an idealized device structure. The suite obtains the electrical response of the one-dimensional sample connected to an electrical circuit. In this Letter, the one-dimensional slab of thickness 2.1×10^{-4} cm (simulation space) is composed of imperfections (defect and dopant species) and charge carriers (e^-/h^+).

Defect population size criteria—Experimentally reported defect concentrations for radiation-induced GaAs defects are sparse and never comprehensive. Defect populations were chosen by considering experimental and theoretical observation and intuitive reasoning. The criteria were as follows. (1) Single vacancy populations should be equal ($v_{\text{Ga}} = v_{\text{As}}$). (2) The divacancy population must be larger than single vacancies, $v_{\text{Ga}}v_{\text{As}} > v_{\text{Ga}} = v_{\text{As}}$, because the experimentally reported E1 and E2 are larger than E3 [5]. (3) Based on the manner in which these defects are created—an interstitial leaves behind a vacancy [41]—the total number of vacancies should be roughly equal to the number of interstitials ($v_{\text{Ga}} + v_{\text{As}} + 2v_{\text{Ga}}v_{\text{As}} = \text{As}_i + \text{Ga}_i$ or $v_{\text{As}} + v_{\text{Ga}}v_{\text{As}} = \text{As}_i$ and $v_{\text{Ga}} + v_{\text{Ga}}v_{\text{As}} = \text{Ga}_i$). (4) Fermi level pinning implies that there are equal (or more) available states for dopant electrons (e), i.e., the number of available negatively charged vacancy states must be equal (or greater) than the number of Si-dopant electrons $e^{v_{\text{Ga}}} + e^{v_{\text{As}}} + e^{v_{\text{Ga}}v_{\text{As}}} > e^{S_{\text{Ga}}}$. (5) The Ga vacancy consumes the majority of the available electrons ($e^{v_{\text{Ga}}} > e^{v_{\text{As}}}, e^{v_{\text{Ga}}v_{\text{As}}}$).

Using these criteria, defect population sizes were chosen to be $\text{As}_i = \text{Ga}_i = 1.24 \times 10^{15}$, $v_{\text{As}} = v_{\text{Ga}} = 6.10 \times 10^{14}$, and $v_{\text{Ga}}v_{\text{As}} = 6.30 \times 10^{14} \text{ cm}^{-3}$.

Increasing (decreasing) the number of interstitials increases (decreases) the probability that As_i^{1+} will react with vacancies, accelerating (decelerating) the reaction. Slightly increasing (decreasing) the number of vacancies shifts the Fermi level deeper (shallower) in the band gap, resulting in more (fewer) As_i^{1+} interstitials accelerating (decelerating) the reaction. Too many vacancies shift the

Fermi level deeper, changing the dominant defect charge states, which results in new favorable defect reactivity.

Reactions description—The reactive-transport equation (RTE) governs the temporal evolution of chemical species $c_i(\mathbf{r}, t)$ as they participate in chemical reactions (e^-/h^+ capture-emission reactions and defect-defect reactions). The RTE is given by

$$\frac{\partial c_i(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \left(q_i c_i \frac{D_i}{k_B T} \right) \nabla \Phi_i + \sum_j \nu_{ij} r_j, \quad (\text{B1})$$

where the first term on the right-hand side describes transport (drift-diffusion) and is composed of the diffusion coefficient $D_i = D_{0i} e^{-E_{mi}/k_B T}$ where D_{0i} , E_{mi} , k_B , and T are the diffusion prefactor, migration barrier, Boltzmann constant, and temperature, respectively. The second term describes the reaction rate r_j for reaction j at a stoichiometric coefficient ν_{ij} . The electrochemical potential is defined by $\Phi_i = q_i \phi + \mu_i$, where q_i is the species charge, ϕ is the electric potential calculated from the Poisson equation, and μ_i is the chemical potential. The D_i and r_j are highly important and will be for charge carrier reactions and defect-defect reactions.

Charge equilibration—To investigate the Fermi level shift, an initial defect population was given to each neutral defect (initial populations were set to charge state zero) and allowed to distribute throughout the system, via e^-/h^+ capture and emission (charge carrier) reactions, until achieving equilibrium. Charge carrier reactions enable charge flow while also maintaining charge neutrality via the charge-conserving reactions $a^{1-} + h^+ \rightleftharpoons a^0$ and $a^0 + e^- \rightleftharpoons a^{-}$, where a is a generic defect. Charge equilibration depends only on charge carrier reactions—no defect-defect reactions—and occur rapidly because e^- and h^+ (diffusion coefficients of 207 and 11 cm^2/s , respectively [42]) diffuse much faster than defects. The reaction rate for the generic h^+ capture reaction discussed above is given by

$$r_j^{a^{1-}} = v_{\text{th}} \sigma_j \{ -[a^{1-}] n_h e^{-E_f/kT} + N_V [a^0] e^{-E_r/kT} \}, \quad (\text{C1})$$

where v_{th} , σ , n_h , are the thermal velocity, capture cross section, and number of holes, respectively. The E_f and

E_r are activation energies for the forward and reverse reactions—DFT-predicted defect levels. With minor changes, a similar equation can be written for e^- capture. As seen in Fig. 1, the defects exist in positive, neutral, and negative charge states, creating an imminent Coulomb interaction between charge carriers and defect charge states. Since it is generally accepted that Coulombic interactions change the size of capture cross section [43], cross sections were set to range from 10^{-11} to 10^{-18} cm² for attractive and repulsive Coulomb interactions, respectively. For capture by a neutral defect species, cross sections were set to 10^{-15} cm². Chosen values for each reaction are given in the Supplemental Material, Tables 1–7 [29]. There is substantial uncertainty in the capture cross sections with widely ranging reported values. However, these values agree with a range of experiments for charged (attractive or repulsive) and neutral interactions [19,44,45]. This representation is both of the correct order and reflects the varying Coulomb interactions.

Defect-defect reactions: Diffusion controlled—The As_i dominated all defect-defect reactions. The determination of its parameters had immense importance in this Letter. The diffusion prefactor is known to vary widely among materials and material defects [46]. Here, $D_0 = 10^{-2}$ cm²/s, similar to other device simulations [35,47], was nominally chosen. The As_i^+ diffuses athermally via the Bourgoin-Corbett mechanism; i.e., its motion through the lattice occurs by changing its charge state by alternating capture of electrons and holes [26]. Its thermal migration barrier was set to 0.40 eV (20% lower than 0.5 eV) to mimic this athermal behavior. Using only the thermal barrier 0.5 eV—instead of 0.40 eV—produced similar results, with v_{Ga} density plummeting to immeasurable scales after ≈ 200 s instead of ≈ 5 s. Interestingly, even with the thermal migration barrier, v_{Ga} would still be difficult to experimentally observe. Diffusion coefficients for all immobile species were set to zero. The Ga_i diffusion coefficient was also set to zero, since the reactivity in our simulation is dominated by As_i .

Defect-defect reactions take the form $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$, where A , B , C , and D are generic

defects and α , β , γ , and δ are their coefficients. The forward reaction rate for j diffusion-controlled reactions (r_{jf}^d) takes the form

$$r_{jf}^d = k_{jf}^d [A_j]^{\alpha_j} [B_j]^{\beta_j}, \quad (\text{D1})$$

$$k_{jf}^d = 4\pi R_{\text{eff}} [D_A + D_B], \quad (\text{D2})$$

where R_{eff} is an effective reaction radius of reaction j and D_A and D_B are diffusion coefficients of reactant defects A and B . Forward reaction radii were used to simulate the Coulomb attraction between As_i^{1+} and the negatively charged vacancies. Reaction radii are difficult to determine, and they were set on the order of a lattice constant 10^{-8} cm: 1.0×10^{-10} , 1.0×10^{-8} , and 1.0×10^{-6} cm for Reactions 1, 2, and 4, respectively. Reverse reactions were not included in this Letter and are not discussed.

Defect-defect reactions: Transition-state controlled—For each reaction, a complex forms before As_i hops into a vacancy site, i.e., As_i must overcome an energy barrier (E_b) before occupying the vacancy site. This transition state must be included, as it occurs after diffusion-controlled (Coulomb-driven) reactions. The forward transition-state reaction rate (r_{jf}^{ts}) is given by

$$r_{jf}^{ts} = \frac{kT}{h} e^{-E_b/kT}, \quad (\text{E1})$$

where h is the Planck constant. For the energy barrier (E_b), physically reasonable values of 0.75, 0.50, and 1.00 eV were chosen for Reactions 1, 2, and 4. Note that when all energy barriers are set to 1 eV, nearly identical results persist. Further details are provided in the Supplemental Material [29].

Several parameters used in device simulations are not well known, e.g., capture cross sections, diffusion rates, and reaction radii, both experimentally and theoretically. The chosen parameters were physically reasonable and produced results that agree with well-established defect physics.

Further details on the methods used in the REOS suite will be provided in a separate work.