

Electrically and optically active charge carrier traps in silicon-doped few-layer GaSe

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Understanding defects in atomically thin van der Waals (vdW) semiconductors is essential for advancing their use in next-generation optoelectronic and photovoltaic devices. Here, we apply a combination of various impedance spectroscopy techniques to two-dimensional (2D) vdW GaSe doped with silicon (Si) to reconstruct deep trap states across the full bandgap. Deep-level transient spectroscopy reveals three distinct deep states, 0.33, 0.68, and 0.24 eV, below the conduction band edge. Complementary deep-level optical spectroscopy and photocapacitance measurements identify two deep states at 1.4 and 1.8 eV below the conduction band edge and one at 2.0 eV above the valence band edge, with thermal admittance spectroscopy providing additional verification and further resolving two trap states at 0.16 eV above the valence band edge and at 0.26 eV below the conduction band edge. By comparing the experimentally extracted ionization energies with the predictions of density functional theory, our results attribute these trap states primarily to Si-related defects and metal vacancies. This work presents a comprehensive defect map of Si-doped GaSe, providing critical insights into carrier trapping mechanisms that are essential for optimizing the design of 2D material-based devices for industrial applications.

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I. INTRODUCTION

The performance of semiconductor-based (opto)electronic devices is very strongly influenced by deep levels that act as charge traps or recombination centers. These defects, while potentially detrimental to device efficiency, can also serve as functional components in emerging technologies. For example, deep levels can enhance the catalytic activity of two-dimensional (2D) materials for the hydrogen evolution reaction, but can also operate as spin-active color centers with potential applications in

spin-photon interfaces or for quantum metrology [1–4]. As the field of 2D van der Waals (vdW) materials continues to expand, understanding and characterizing electrically active midgap defects within this class of semiconductors has become crucial for the advancement of 2D-based devices. Among the diverse 2D vdW materials, the post-transition metal monochalcogenide (PTMC) GaSe [5] has garnered significant attention due to its promising electronic and optoelectronic properties. GaSe transistors exhibit high on-off current ratios, exceptional photoresponse, and promising (photo)electrochemical capabilities [5–9], making the materials system attractive for next-generation technologies.

Few-layer GaSe is of particular interest since its valence band lies at the transition between a conventional parabolic dispersion and a caldera-like, ring-shaped dispersion, yielding near-flat bands and a van Hove singularity at the valence band maximum (VBM) [10–12]. These result in a low carrier group velocity and a strongly enhanced density of states (DOS), which amplifies many-body interactions such as excitonic or correlation effects.

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These same electronic features, combined with the intrinsically low thermal conductivity, also lead to enhanced Seebeck coefficients, higher power factors, and improved thermoelectric performance [13,14]. For example, theoretical calculations of a GaSe/SnS₂ van der Waals heterostructure predict very high thermoelectric performance, with a figure of merit zT reaching 2.99 at 700 K for n -doped GaSe [15]. However, the nature of the PTMC band structure also makes these materials highly sensitive to disorder: even weak defect potentials can strongly modify carrier transport, thereby degrading mobility, optical response, and thermoelectric performance [16,17].

Realizing specifically doped GaSe devices, or complementary p - n junctions for photovoltaics, LEDs, and photocatalytic applications, requires reliable n - and p -type doping. However, achieving such doping in atomically thin materials is notoriously challenging due to their high surface-to-volume ratio and their strong sensitivity to structural damage. In conventional III-V semiconductors such as gallium arsenide, silicon can incorporate on both cation and anion sites, acting either as a donor or an acceptor depending on its lattice position [18–21]. This amphoteric behavior can lead to compensation effects, underscoring the importance of understanding dopant-related defects. In contrast, for GaSe, studies on Si incorporation and its associated defect configurations remain scarce, and understanding these dopant-induced defects is essential for assessing their impact on carrier dynamics and device performance.

Defect characterization in semiconducting 2D materials relies on techniques with varying trade-offs. Photoluminescence, Raman, and x-ray photoemission spectroscopies are noninvasive and device-compatible but often provide only qualitative or indirect information [22–24]. Scanning tunneling and transmission electron microscopies offer atomic resolution but require complex sample preparation and can be destructive [25,26]. In contrast, capacitance-based spectroscopic techniques, such as deep level transient spectroscopy (DLTS), are a highly sensitive and nondestructive approach to probing electrically active states. DLTS has proven its utility in bulk [27] and single-layer [28] transition metal dichalcogenide semiconductors by providing quantitative information on energy levels and capture cross sections. However, shallow traps and minority carrier bands have not been accessible. Similarly, deep level optical spectroscopy (DLOS) is a powerful and quantitative approach to accessing deep-level defect states across a wide energy range [29,30], enabling the investigation of traps near both band edges.

In this study, we employ a combination of impedance spectroscopy techniques, including DLTS, DLOS, and temperature- and frequency-dependent capacitance-voltage profiling, to investigate defect states in exfoliated Si-doped few-layer GaSe. By systematically exciting GaSe electrically and optically, we reconstruct a comprehensive

picture of electrically active defect states within the GaSe bandgap. The experimentally derived trap ionization energies are then compared with density functional theory (DFT) calculations to identify the specific defects responsible for the observed states. These insights not only elucidate the defect landscape of silicon-doped GaSe and its impact on carrier dynamics but also establish a robust framework for defect characterization in other doped 2D vdW semiconductors.

II. RESULTS

Modulation of trap occupancy in monolayer 2D semiconductors is challenging due to the atomic-scale thickness, which prevents the formation of a significant vertical depletion width in a Schottky diode, the conventional device geometry for DLTS measurements. By contrast, a metal-insulator-semiconductor (MIS) structure allows for the tuning of the surface Fermi level via a back-gate voltage, enabling the filling and emptying of defects over a wider range of biases. Studies on monolayer MoS₂ show DLTS in MIS geometries where trap filling is gate modulated, overcoming the limitations of vertical Schottky devices [28]. Moreover, using hBN as the insulator in MIS structures reduces interface state densities substantially due to its atomic flatness and van der Waals bonding [31]. Based on this, we prepared the GaSe-based MIS capacitor as depicted in Fig. 1(a). The device stack consists of a rectangular Pt (7.0 nm) top gate, a 15.0-nm hBN dielectric, a 7.1-nm GaSe layer, and a thin graphite bottom contact running across the GaSe to achieve a more homogeneous potential distribution. The vdW heterostructure is assembled using a PDMS/PC stamp (polycarbonate film on polydimethylsiloxane), which is then aligned and transferred onto a sapphire substrate. Afterward, the Pt gate and electrical contacts are defined and evaporated on top. The sapphire substrate is advantageous for suppressing background-related charges, thereby minimizing parasitic effects and reducing electrical noise arising from capacitive coupling. The doping of GaSe was confirmed by secondary ion mass spectrometry (SIMS), which revealed a Si concentration of approximately 10^{20} cm^{-3} (see Fig. S1 in Supplemental Material [32]). Figure 1(b) shows typical room-temperature CV curves recorded at 500 Hz and 700 kHz, by sweeping the back-gate voltage from -8.5 to $+6$ V and back, while applying a 50-mV ac signal. At low frequencies, leakage currents restricted the usable gate voltage range to -8 to $+5$ V, whereas this effect was suppressed at higher frequencies. As expected for MIS devices, three operating modes can be distinguished in the profile, such as inversion, depletion, and accumulation [33]. The strong gate-voltage dependence of the capacitance confirms the efficient Fermi-level modulation, and the absence of noticeable frequency dispersion in the strong accumulation regime indicates low series resistance at the contacts. From the CV response, the

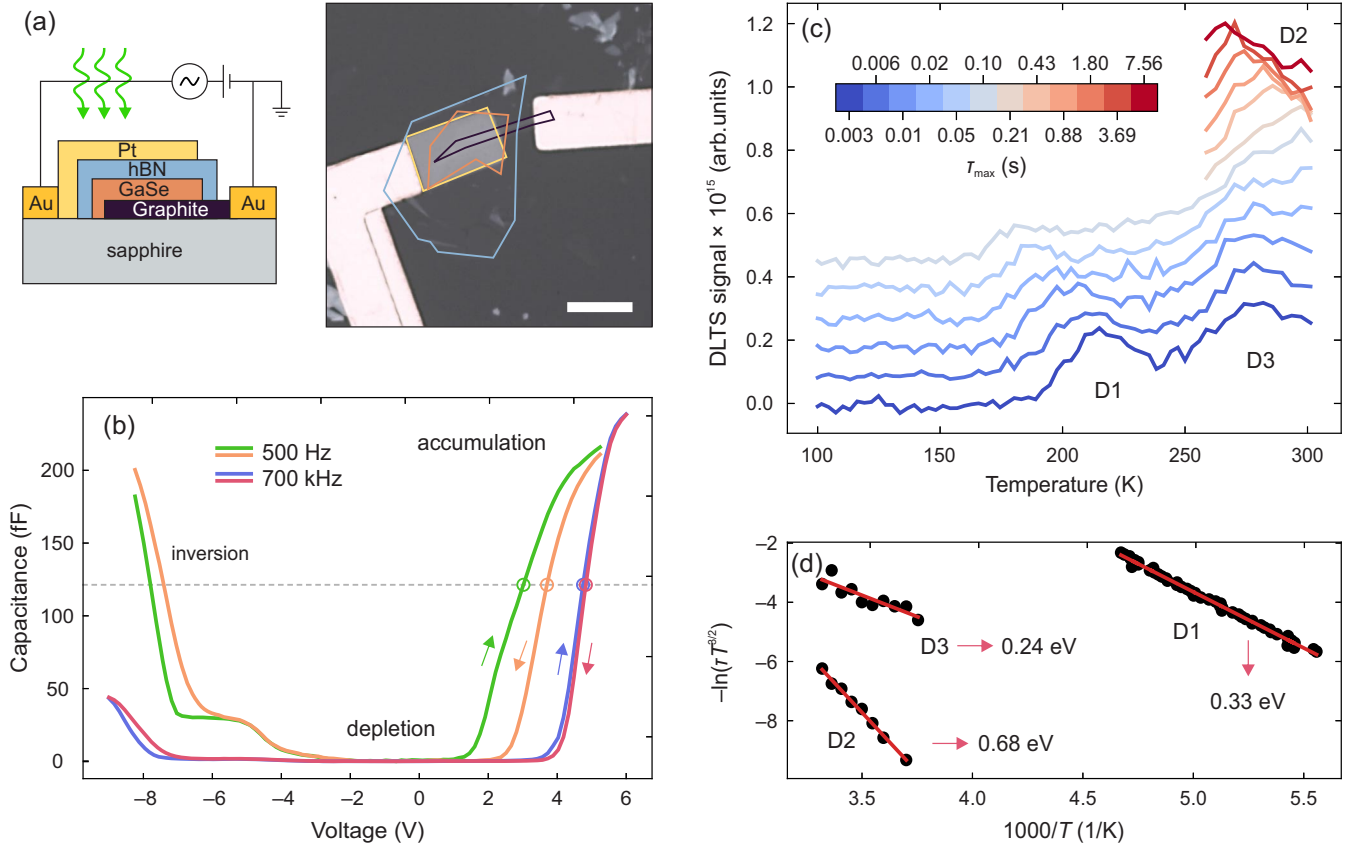


FIG. 1. (a) Schematic (left) and optical micrograph (right) of the GaSe metal-insulator-semiconductor (MIS) device. Scalebar: 18 μm . (b) Forward and backward capacitance-voltage (CV) sweeps at 500 Hz and 700 kHz (room temperature). The gray dotted line indicates the position of half the geometric capacitance. (c) DLTS spectra as a function of temperature for different rate windows τ_{max} between 100 and 300 K and (d) Arrhenius plot (black points) of the temperature-dependent lifetime τ of the identified defects with respective fits (red lines). To limit measurement duration, temperatures below 257 K were limited to measured lifetimes of a maximum of 100 ms.

device clearly exhibits n -type behavior, consistent with the successful Si incorporation into the GaSe lattice [34]. Notably, despite the high Si doping, the device is depleted at 0 V, indicating that it is not in the degenerate regime and that the chemical potential remains within the bandgap. The inversion capacitance is suppressed at high frequencies, as expected, since minority carriers cannot be generated or transported quickly enough to follow the ac modulation. The forward and backward hysteresis, measured at room temperature at half of the geometric capacitance in the weak accumulation regime, is 0.73 and 0.08 V for 500 Hz and 700 kHz, respectively (0.10 and 0.03 V at 70 K), indicating a low density of long-lived traps. In the following sections, further frequency- and temperature-dependent studies will be discussed to extract trap signatures and quantify defect-related states.

DLTS measurements on a few-layer GaSe MIS device were performed at the onset of the accumulation regime. The populating voltage pulse of 25 ms was set to 4.6 V, and the transients were recorded at 3.8 V. Figure 1(c) shows the heatmap of the DLTS signal constructed from the

temperature-dependent capacitance transients (see Supplemental Material for details on optimization of the measurement and the algorithm used for signal extraction [32]).

Note, however, that in a 2D system, the measured capacitance transient is not governed by a modulation of the depletion width, as in conventional DLTS of bulk materials, but by the time-dependent shift of the chemical potential induced by variations in the total stored charge and the resulting change in the quantum capacitance. Within a small-perturbation approximation around the operating point and at constant applied bias V_0 , the capacitance change can be expressed as

$$\delta C(t) \propto \frac{1}{C_{\text{geom}}} \frac{dC}{dV} \bigg|_{V_0} \Delta q_i(t), \quad (1)$$

where C_{geom} is the geometric capacitance and $\Delta q_i(t)$ is the time-dependent trap-charge variation. This relation provides a direct link between the DLTS signal and the local

slope of the measured CV characteristic. The voltage dependence of the capacitance arises from the quantum capacitance C_q , such that

$$\frac{1}{C} = \frac{1}{C_{\text{geom}}} + \frac{1}{C_q[\mu(V)]}.$$

To the best of our knowledge, such an analytical expression for 2D-DLTS has not been explicitly formulated in the literature. The full derivation, together with additional features specific to 2D-DLTS, is provided in Note S1 in Supplemental Material [32].

Each feature in the DLTS spectrum corresponds to a defect state with a characteristic emission lifetime that depends on temperature. The emission rate $1/\tau$ of an electron deep-level state follows the expression [35]:

$$\frac{1}{\tau} = \sigma_n v_{\text{th},n} N_C \exp\left(-\frac{\Delta E}{kT}\right), \quad (2)$$

where σ_n is the capture cross section, $v_{\text{th},n} = \sqrt{\frac{2k_B T}{m_n^*}}$ the thermal velocity of electrons in 2D, $N_C = \frac{4\pi m_n^* k_B T}{h^2}$ the effective density of states in the 2D conduction band, ΔE the activation energy of the trap, k_B the Boltzmann constant, and T the absolute temperature (note that within the 2D formalism [28], some quantities are reduced in dimensionality relative to standard DLTS; see Notes S1 and S3 in Supplemental Material for further details [32]). An analogous expression holds for hole emission. The activation energies and capture cross sections of the identified defect states can be determined using a linear fit to the Arrhenius plot after extracting the maxima positions of the DLTS signal for each feature through Gaussian fitting of the signal peaks (Fig. 1(d) and Fig. S6 in Supplemental Material [32]). The DLTS analysis reveals three distinct defect energy levels at 0.33 ± 0.01 eV (D1), 0.68 ± 0.02 eV (D2), and 0.24 ± 0.04 eV (D3) below the conduction band minimum (CBM, E_c). By assuming a 2D thermal velocity, an effective electron density of states [28] (see Supplemental Material [32]), and employing an in-plane electron effective mass $m_n = 0.2m_0$ [36,37], we determine a capture cross section for D1, D2, and D3 of $(4.69 \pm 1.00) \times 10^{-10}$, $(7.06 \pm 5.97) \times 10^{-8}$, and $(6.39 \pm 11.50) \times 10^{-14}$ cm, respectively. Note that capture cross sections extracted from Arrhenius intercepts often carry considerable uncertainties and should therefore be regarded as order-of-magnitude estimates. Nevertheless, the extracted values fall within the range commonly associated with localized point defects. Also note that within the 2D formalism [28], the capture cross section has units of cm rather than cm^2 . Within the 2D-DLTS model introduced above, the signal amplitude can be related to the defect density. In the small-perturbation limit, the maximum DLTS signal follows Eq. (24) in

Supplemental Material [32]. Assuming that the entire flake contributes to the response, we obtain defect densities of 7.5×10^{15} , 2.0×10^{16} , and $1.5 \times 10^{16} \text{ cm}^{-3}$ for D1, D2, and D3, respectively. These values are lower than the impurity concentrations obtained from SIMS (approximately $10^{19} - 10^{20} \text{ cm}^{-3}$), consistent with only a fraction of impurities forming electrically active deep levels. Furthermore, since in 2D systems, the DLTS signal scales with the local slope of the CV characteristic, $S \propto \frac{dC}{dV}|_{V_0}$, the measurement conditions that maximize the signal do not coincide with complete trap emptying, which may lead to an underestimation of the absolute trap density.

To investigate deep levels near the VBM and construct a clearer picture of the defect landscape, we used DLOS with monochromatic photons with energies approximately 1.3 to 2.6 eV. DLOS replaces the temperature sweep with an optical source, allowing the detrapping process to be driven by light. This enables probing a broader range of defect states across the bandgap, depending on the wavelength used (see Fig. S2 and Note S4 in Supplemental Material [32]). Since the measurement records capacitance transients during optical excitation after all defects have been filled with electrons via a voltage pulse, it exclusively probes electron emission from traps relative to the CBM, without contributions from trap-to-trap transitions or optically driven metastable charge capture by defects. The DLOS spectrum is shown in Fig. 2(a). The data were fitted with two curves based on Lucovsky's model [38] for localized traps, which assumes no lattice relaxation (i.e., neglects the Franck-Condon relaxation energy, which should be kept in mind when comparing the optical onset energies extracted here with the thermal activation energies obtained from DLTS), and an Urbach-like exponential distribution of traps close to the VBM and CBM. The best fit is characterized by two trap states below the CBM at 1.38 ± 0.02 and 1.84 ± 0.01 eV, respectively. The signal increases up to the band edge of few-layer GaSe at 2.16 eV, after which the contribution from band-to-band transitions dominates the spectrum. The exponential fit of the signal close to the band edge returns an Urbach energy of 63.10 ± 4.90 meV. To validate the DLOS results, we also performed steady-state photocapacitance (SSPC) measurements [see Fig. 2(b)], which record the total capacitance change under monochromatic illumination once steady-state conditions are established. Since the steady-state signal reflects a dynamic equilibrium between photo-excitation (detrapping) and optically driven recapture (retrapping) processes, the measured capacitance corresponds to the net trap occupancy. A step in the SSPC as a function of excitation energy indicates the activation of a new defect state. SSPC spectroscopy confirms the states close to 1.39 and 1.85 eV below the CBM observed in DLOS. The constant slope [see the gray curve in Fig. 2(b)] close to the band edge is consistent with an increasing share of defects being excited, compatible with the Urbach

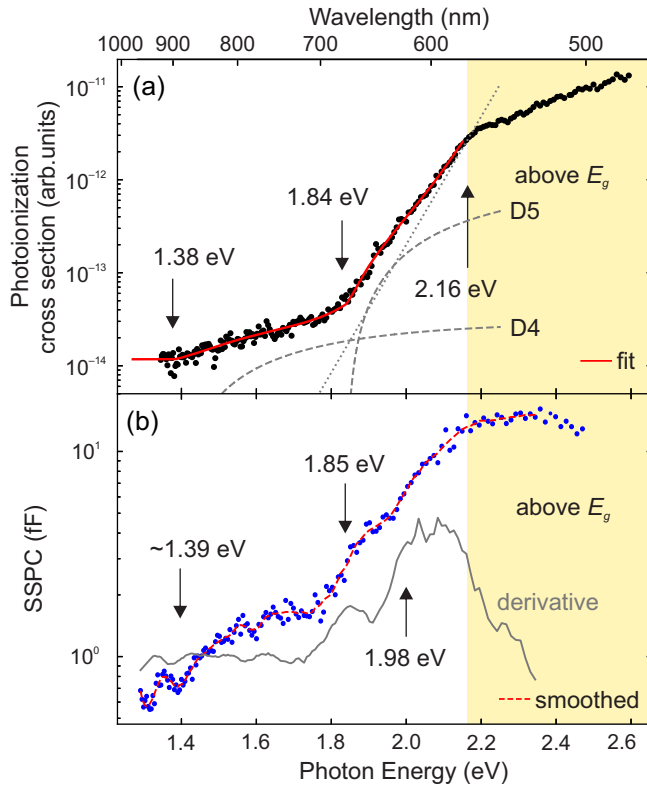


FIG. 2. (a) DLOS and (b) SSPC of the GaSe MIS device. The black dashed lines in (a) show the fitting results using Lucovsky's model. The gray line in (b) represents the derivative function used to determine the transitions.

tail seen in the DLOS measurement. An additional feature not evident in the DLOS spectrum appears at 1.98 eV. This discrepancy arises because, as previously mentioned, under the present initialization and transient readout, DLOS selectively probes photoemission of electrons from prefilled traps into the conduction band, while SSPC, operating in steady state, also probes charge transfer between traps or from the valence band to traps. We therefore attribute the observed kink at 1.98 eV to a defect state located 0.18 eV below the CBM. Finally, the onset energies extracted from both DLOS and SSPC spectroscopy are consistent with a bandgap of approximately 2.16 eV, in good agreement with reported values for GaSe. [11,39,40].

We continue to investigate the temperature and frequency dependence of the *CV* characteristics in detail to probe the dynamic behavior of the defects. Figure 3(a) shows the room-temperature *CV* curves, measured from -8.5 to 6 V, for a range of frequencies from 20 Hz to 700 kHz. A pronounced frequency dispersion is observed in the weak accumulation regime, which cannot be attributed to series resistance effects, as the strong accumulation regime exhibits negligible frequency dispersion [41]. Furthermore, a clear capacitance peak emerges at negative gate voltages but weakens and eventually

vanishes as the measurement frequency increases. This is a characteristic signature of trap states with emission rates that are too slow to follow the ac probing signal at higher frequencies [42,43].

To elucidate the origin of these trap states, temperature-dependent *CV* measurements were carried out. Since the emission rate of trap states is thermally activated, changing the temperature shifts the frequency at which these states can respond, resulting in an Arrhenius-type dependence of the cutoff frequency. Figure 3(b) presents a false color image of the temperature-dependent *CV* curves measured at 500 Hz. The capacitance peak at negative voltages vanishes below a certain temperature (approximately 175 K), consistent with the expected behavior of discrete trap states whose emission rates fall below the probing frequency. In contrast, the dispersion observed at positive gate voltages does not disappear at a single temperature but rather diminishes gradually over a range of temperatures, depending on the applied bias. This behavior indicates the presence of a distribution of defect states across a range of energies within the bandgap, such as those associated with an Urbach tail. It is significant to note that the onset of accumulation occurs at lower gate voltages for higher temperatures.

To further investigate the origin of the frequency-dependent capacitance features and understand the role of minority carriers in the trap emission rates, thermal admittance spectroscopy (TAS) measurements [44] were performed under different gate bias conditions. TAS yields defect energy levels and capture cross sections by tracking the demarcation ac frequency, ω_0 , at which a given defect feature vanishes as temperature changes (see Supplemental Material for details [32]). As the temperature decreases, the defect emission rate, $1/\tau(T)$, falls toward the probing frequency, ω_{ac} . In the limit that

$$\omega_0(T) = \frac{1}{\tau(T)} < \omega_{ac},$$

the defect can no longer respond to the ac modulation and ceases to contribute to the total capacitance. By identifying the temperature at which each feature disappears, we reconstruct the temperature dependence of the defect lifetime. An Arrhenius analysis of $\omega_0(T)$ then allows extraction of the defect activation energy and capture cross section, in direct analogy to the DLTS procedure [see Figs. 1(c) and 1(d)]. Notably, both the inversion capacitance and the capacitance peak disappear simultaneously as either the temperature is lowered or the probing frequency is increased, indicating a common, kinetically limited origin. This behavior is consistent with a trap-mediated, thermally activated emission process that supplies minority carriers to the inversion charge. We exclude a transport-limited minority-carrier response: in 2D MIS capacitors, a high channel resistance and the associated

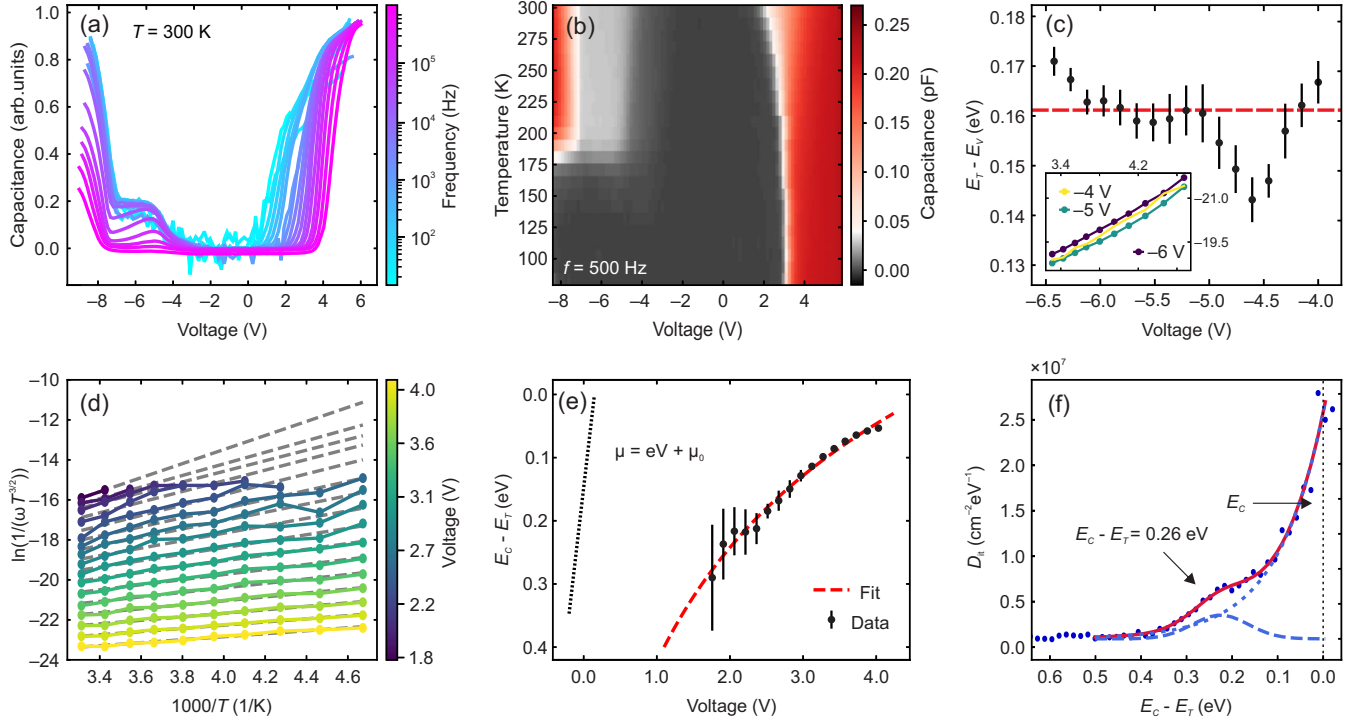


FIG. 3. (a) CV measurements taken at frequencies ranging from 20 Hz to 700 kHz. (b) Temperature-dependent CV profiling at 500 Hz. (c) Trap energy as a function of voltage, as extracted from the thermal admittance spectroscopy (TAS) measurement in the inversion regime. The inset shows the Arrhenius plot of the detrapping lifetime for -4 , -5 , and -6 V, plotted as $1000/T$ vs $\ln(1/\omega T^{3/2})$. (d) Arrhenius plots of the detrapping lifetime at various voltages in the accumulation regime. (e) Trap energy as a function of voltage, as extracted from (d). The dashed red line is a fit of the voltage-dependent chemical potential $\mu(V)$. The dotted black line indicates $\mu(V)$ for a semiconductor with no gap states. (f) Defect density close to the conduction band. The energy position ($\mu(V)$) is computed from the fit in (e). The red line is a fit using the sum of an exponential function and a Gaussian.

lateral potential drop can lead to frequency dispersion in the CV characteristics [41]. In our device, no cutoff frequency is observed in accumulation, indicating sufficiently low channel resistance [Fig. 3(a)]. Similarly, a lateral depletion region would be expected to modify the effective RC time constant and produce a bias-dependent cutoff frequency, as its width varies with the applied gate voltage. As shown in Fig. 3(c) (inset), however, the cutoff frequency does not vary with bias. The absence of such a trend, together with the observed Arrhenius-type temperature dependence, is consistent with thermally activated Shockley-Read-Hall emission from defect states within the bandgap, which serve as a local supply of minority carriers.

Figure 3(c) presents the trap energy, $E_T - E_V$, as a function of various negative gate voltages. We identify a trap level located at 0.16 ± 0.02 eV above VBM, with a large corresponding capture cross section of $(2.41 \pm 1.24) \times 10^{-6}$ cm (see Supplemental Material for the derivation [32]). Note that for 7.1-nm-thick GaSe (eight monolayers), the valence band evolves from a parabolic shape to a caldera-like, ring-shaped structure, coinciding with the emergence of flat bands and a van

Hove singularity near the VBM [10,11]. The trap energy and capture cross-section values reported here are based on the implicit assumption of parabolic bands. As such, they are expected to represent effective values that may deviate significantly from their actual values. Notably, the extracted capture cross section should be interpreted as an effective parameter of the model, since it depends on the thermal velocity and the band-edge density of states. In few-layer GaSe, where the valence band is strongly non-parabolic, the resulting value should therefore be treated with caution. For the calculation, an effective hole mass of $m_p = -1.9m_0$ was employed [45].

The same analysis was applied to the weak-accumulation regime. Figure 3(d) shows the Arrhenius plots of the demarcation frequency, ω_0 , for different gate voltages, and Fig. 3(e) displays the resulting trap energy relative to the CBM. We observe that, as the gate voltage increases, the extracted trap energy shifts closer to the CBM, consistent with a continuum of band-tail states. Consequently, raising the chemical potential enables probing of traps at progressively higher energies, providing an indirect measure of the chemical potential as a function of the applied voltage.

By assuming an exponential band-tail DOS, we obtain for the voltage dependence of the chemical potential μ ,

$$V = \frac{\mu - \mu_0}{e} + \frac{eD_0E_0}{C_{\text{geom}}} \exp\left(\frac{\mu}{E_0}\right),$$

where μ_0 is the chemical potential at 0 V, e the elementary charge, D_0 and E_0 the amplitude and characteristic energy of the exponential band tail, and C_{geom} the geometric capacitance (see Note S6 in Supplemental Material [32]). The dashed red line in Fig. 3(e) shows the fit to this model, while the dotted black line represents the ideal $\mu(V)$ for a gap without band-tail states. From the fit, we extract a charge-neutrality Fermi-level position of $\mu_0 = -0.79 \pm 0.29$ eV relative to the CBM and an Urbach characteristic energy $E_0 = 0.27 \pm 0.09$ eV.

Finally, the interface trap density, $D_{\text{it}}(V)$, is computed from the measured low- and high-frequency capacitances, $C_{\text{lf}}(V)$ and $C_{\text{hf}}(V)$ [42,43], using

$$D_{\text{it}} = \frac{1}{q} \left[\frac{C_{\text{geom}} C_{\text{lf}}}{C_{\text{geom}} - C_{\text{lf}}} - \frac{C_{\text{geom}} C_{\text{hf}}}{C_{\text{geom}} - C_{\text{hf}}} \right].$$

By mapping V to energy through the relation for $\mu(V)$ introduced above, we plot $D_{\text{it}}(E)$ in Fig. 3(f). The trap distribution is well described by the sum of an exponential tail (Urbach-like) with a characteristic energy of 0.10 ± 0.01 eV and a Gaussian peak centered at 0.26 ± 0.02 eV, indicating a discrete electron trap superimposed on a band-tail background. These values are in reasonable agreement with the fit in Fig. 3(e), with the remaining difference ascribed to the assumption of 0 K and the omission of the Gaussian peak contribution in the first fit, which, when neglected, artificially broadens the exponential tail. Notably, the electrical values differ from the Urbach energy of 63.10 meV determined via DLOS. This discrepancy is a known artifact of comparing optical and electrical characterizations [46]. While voltage-dependent electrical techniques probe deeper traps than optical methods, they are also highly susceptible to device-specific transport limitations (e.g., high internal series resistance), which often lead to an overestimation of the characteristic disorder energy.

Our results demonstrate that few-layer GaSe doped with Si hosts multiple energy levels within the band gap. DLTS measurements identified defect states at 0.33, 0.68, and 0.24 eV below the CBM, while TAS revealed a trap at 0.16 eV above the VBM and an Urbach-like band-tail density of states near the CBM, together with another trap at 0.26 eV below the CBM. Optical techniques, including DLOS and SSPC, detected defect levels at 1.4 and 1.8 eV below the CBM, an additional transition at 1.98 eV above the VBM, and the bandgap at 2.16 eV. While these measurements provide a comprehensive experimental

TABLE I. Calculated defect transition levels relative to band edges.

	This work	Literature [47]
Charge- transition level	2.02 eV	2.26 eV
Ga _i (+/0)	$E_C - 0.39$	$E_C - 0.2$
V _{Se} (-/2-)	...	$E_V + 1.6$
V _{Se} (0/-)	$E_V + 1.61$	$E_V + 1.1$
Ga _{Se} (0/-)	$E_V + 0.45$	...
Se _{Ga} (0/-)	$E_V + 0.25$	...
V _{Ga} (0/-)	$E_V + 0.04$	$E_V + 0.1$
Se _i	Inactive	Inactive
Si _{Ga} (+/0)	$E_C - 0.39$	$E_C - 0.7$
Si _i (0/-)	$E_V + 1.63$	...
Si _{Se} (0/-)	$E_V + 1.20$	...
O _{Ga} (0/-)	$E_V + 0.17$	...
O _{Se}	Inactive	...
O _i	Inactive	...

picture of the defect landscape in our materials, they do not yet clarify the microscopic origin of the observed states. Moreover, the influence of silicon doping on these defects remains largely unexplored in the literature. To address these open questions, we performed *ab initio* calculations using density functional theory (DFT) with the HSE06 hybrid functional (see Theoretical Methods in Sec. V). These calculations focused on a range of point defects, including gallium and selenium vacancies, oxygen-passivated vacancies, and silicon-related substitutional or interstitial defects. A summary of the calculated defect energy levels is presented in Table I and Fig. 4.

Figure 4 highlights the overall good agreement between our DFT calculations and the defect levels observed experimentally, confirming the correspondence between theoretical predictions and DLTS measurements. In particular, the defect levels detected in DLTS align well with those predicted for silicon-related defects. It should be noted that the calculations were performed for bulk GaSe, leading to deviations of up to 0.14 eV (see Figs. S8–S10 in Supplemental Material [32], and the high-temperature DLTS of bulk GaSe in Fig. S11 in Supplemental Material [32]) from the experimental values. These deviations are ascribed to confinement-induced changes in the band structure of few-layer GaSe, as well as to the use of plain DFT. However, Fig. S10 in Supplemental Material [32] shows that the charge-transition levels rapidly converge toward the bulk limit with increasing layer number, indicating that bulk bandgap values provide a reasonable reference for the 7-nm film. Interestingly, the calculations indicate that oxygen-passivated selenium vacancies and interstitial oxygen atoms are electrically inactive.

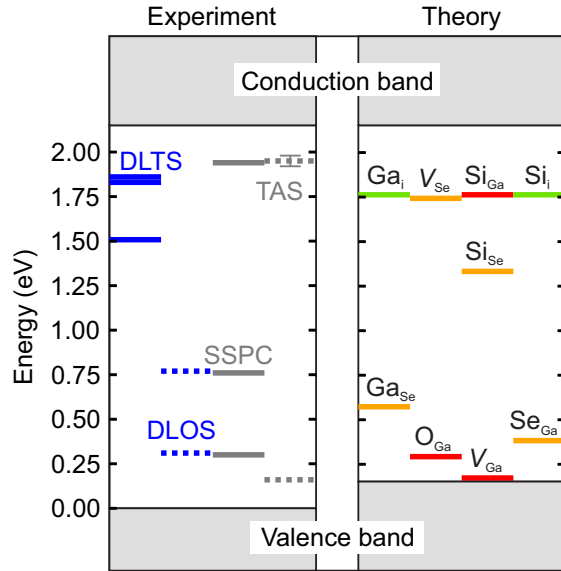


FIG. 4. Comparison between experimentally measured (left) and DFT-calculated (right) midgap states and band-edge positions relative to the CBM. Left: deep levels detected experimentally by DLTS (continuous blue), DLOS (dotted blue), SSPC (continuous gray), and TAS (dotted gray). Right: defect levels for various point defects calculated by DFT. The color of each marker indicates the defect site: green for interstitial positions, yellow for selenium sites, and red for gallium sites. Solid black lines indicate the CBM and VBM.

III. DISCUSSION

A defect level at approximately 0.2 eV above the VBM has been consistently reported in GaSe across multiple studies, regardless of the doping type [48–55]. This defect is commonly attributed to Ga vacancies, which act as acceptor levels. Structural studies using annular dark field-scanning transmission electron microscopy imaging have shown that Ga vacancies are indeed one of the predominant defects in atomically thin GaSe [56]. Our TAS measurements reveal a defect level at 0.16 eV above the VBM, in good agreement with the reported values for Ga vacancies. However, this is in contrast with the theoretically obtained values, placing the defect transition level of V_{Ga} at 0.04 eV above the VBM (see Table I).

The energy calculated by DFT for Si-based defects is in good agreement with our DLTS and TAS results. The experimentally observed defect levels at 0.33, 0.24, and 0.68 eV (DLTS) and 0.26 eV (TAS) below the CBM, as well as 1.98 eV (SSPC) above the VBM (which corresponds to a shallow level 0.18 eV below the CBM given the 2.16-eV bandgap), are compatible with Si_{Ga} and Si_i (both predicted at 0.39 eV below the CBM), which act as a donor and acceptor, respectively, and with Si_{Se} (predicted at 0.82 eV), which acts as an acceptor. However, the applied experimental techniques do not allow unambiguous determination of whether Si occupies Ga sites,

interstitial positions, or both. The small offset between the DLTS/TAS and SSPC values is tentatively ascribed to the contribution of a small Franck-Condon relaxation energy, which causes the optical SSPC transition to appear at higher energy than the adiabatic charge-transition level measured by DLTS and TAS [30]. To assess the likelihood of formation for the different Si-based defects, we computed their formation energy (see Fig. S12 in Supplemental Material [32]), and we found that Si_i exhibits a considerably higher formation energy under any growth condition. In contrast, Si_{Ga} and Si_{Se} have comparable and lower formation energies, enabling us to exclude Si_i and assign the observed defect levels D3 and D2 to Si_{Ga} and Si_{Se} . It is worth noting that according to our calculations, interstitial Ga introduces a donor gap state at the same energy as Si_{Ga} and Si_i , albeit with a formation energy slightly higher than that of Si_{Ga} (see Figs. S8 and S12 in Supplemental Material [32]). Considering the high silicon doping and the presence of Ga vacancies, we attribute the observed state primarily to Si-related defects.

Selenium vacancies have previously been associated with acceptor levels in bulk GaSe at approximately 0.5 eV below the CBM [57,58]. Our calculations place V_{Se} at 0.41 eV below the CBM, overlapping with the energy range of the silicon-related defects. Given that chalcogen vacancies are among the most commonly reported intrinsic defects in two-dimensional chalcogenide materials, D1 is tentatively attributed to a selenium vacancy, V_{Se} . V_{Se} may compete with the low formation energy of the electronically inactive O_{Se} defect, but the coexistence of both defects is consistent with previous structural studies on atomically thin GaSe, which reported the observation of both Se vacancies and O substituting Se sites [56]. Also note that the oxidation of V_{Se} appears to be the primary process driving the degradation of GaSe under dark conditions [59]. The defect observed in both DLOS and SSPC spectroscopy, approximately 1.8 eV below the CBM, is consistent with the calculated energy levels of an O-passivated Ga vacancy O_{Ga} or Se_{Ga} . The former would be in line with the high oxygen content and the presence of Ga vacancies. However, the formation energy for O_{Ga} is much higher than Se_{Ga} , making it less probable to form. A definitive distinction could be achieved by correlating the DLOS signal with controlled oxygen exposure, which lies beyond the scope of the present work and is left for future studies. In contrast, the defect located at approximately 1.4 eV below the CBM, as detected by DLOS and SSPC, is energetically consistent with Ga_{Se} . In addition to these point defects, extended defects, such as trigonal defects and metallic inclusions, have been reported in GaSe [56,60]. While we cannot exclude the presence of large traps, the wide variation in size would lead to a correspondingly broad distribution of defect energetic positions and capture cross sections. Note that while we also cannot exclude a possible contribution from

deep defects in the hBN dielectric, their involvement in the observed signal appears unlikely. First, charge trapping in hBN would require tunneling from the GaSe layer, as hBN does not support mobile carriers that can be trapped. This interpretation is consistent with the absence of measurable leakage current within the investigated DLTS and DLOS voltage range. Second, such a tunneling process would significantly increase the effective capture and emission times, resulting in substantially slower dynamics than those typically associated with deep traps in the semiconductor itself. Finally, considering the relatively high doping density and the large, extracted trap densities, it is reasonable to conclude that the dominant contribution to the measured signal originates from defects within the GaSe layer rather than from the dielectric environment. Finally, the observed Urbach tails at the band edges indicate the presence of shallow, distributed defect states. These are typically associated with defect continua arising from interfacial defects, dielectric defects, or extended defects within the GaSe layers, and their identification is correspondingly more challenging. A comprehensive analysis of these defects is left for future studies.

IV. CONCLUSIONS

In this study, we systematically investigated the defect landscape of few-layer silicon-doped GaSe using a combination of electrical, optical, and temperature-dependent spectroscopies, which reveal defect energies and capture cross sections consistent with DFT calculations and previous reports. Using these complementary techniques, we identify multiple electrically active defects in silicon-doped GaSe. Specifically, we observe five acceptors: four deep levels located at approximately 0.33 eV (V_{Se}), 0.68 eV (Si_{Se}), 1.4 eV (Ga_{Se}), and 1.8 eV (O_{Ga}/Se_{Ga}) below the CBM, and one acceptor at approximately 0.16 eV above the VBM, attributed to V_{Ga} . In addition, we identify a donor state at approximately 0.2 eV (0.23 and 0.26 eV from DLTS and TAS, and 0.18 eV from SSPC) below the CBM, consistent with Si_{Ga} . Our results highlight the critical role of silicon in creating states inside the bandgap and suggest that gallium and selenium vacancies remain among the dominant electrically active defects.

We further introduce a 2D-DLTS formalism that accounts for the absence of a vertical depletion region in low-dimensional materials and explicitly includes quantum capacitance effects.

These findings underline the importance of controlling defect chemistry in 2D-GaSe to tailor its electronic properties for next-generation devices. Looking ahead, as scalable, large-area epitaxy of van der Waals PTMCs becomes mature [61–64] and device architectures continue to be refined [65,66], defect control will be a determining factor in achieving reproducible electronic and

optoelectronic performance. In this context, the integration of complementary characterization techniques, as demonstrated here, provides a robust framework for systematic optimization of PTMC material properties and represents an essential step toward integration-ready 2D materials technologies.

V. EXPERIMENTAL SECTION

A. Crystal growth

GaSe bulk crystals were prepared by direct reaction from elements in a quartz ampoule. Gallium (99.9999%, Wuhan Xinrong New Materials Co., China) and selenium (2–4 mm, 99.9999%, Wuhan Xinrong New Materials Co., China) corresponding to 25 g of GaSe were placed in a quartz ampoule (25 × 100 mm, quartz purity over 99.99%) and melt-sealed with an oxygen-hydrogen welding torch under high vacuum ($<1 \times 10^{-3}$ Pa using an oil diffusion pump with LN_2 cold trap). The ampoule was placed in a muffle furnace and heated to 900 °C using a heating rate of 1 °C/min. After 5 h at that temperature, the furnace was cooled to 500 °C using a cooling rate of 5 °C/h and finally freely cooled to room temperature. The ampoule was opened in an argon-filled glovebox.

B. Sample fabrication

The few-layer flake (7.1 nm thick, corresponding to approximately 8 monolayers; see Fig. S15 in Supplemental Material [32]) of gallium selenide was mechanically exfoliated from bulk crystals. The flake was electrically contacted using a few-layer graphite electrode and subsequently transferred onto a c-plane sapphire substrate. To protect the sample from oxidation, a 15.0 nm hexagonal boron nitride (hBN) encapsulation layer was used, which also served as the gate dielectric. A 7.0-nm platinum (Pt) layer was then evaporated onto the top surface to serve as a transparent top electrode.

C. Impedance and optical measurements

CV curves and transient signals were recorded using a Zurich Instruments MFIA Impedance Analyzer, capable of measuring capacitance across frequencies from 1 mHz to 5 MHz and on timescales as short as 10 μ s. The samples were mounted on a sample holder in direct contact with the cryostat cold finger to ensure stable thermal conditions. Optical excitation was provided by a NKT Photonics SuperK Fianium laser coupled with a VIS HP8 tunable bandpass filter, offering continuous wavelength tuning from 400 to 1000 nm (<2.5 meV bandwidth). Temperature- and time-dependent capacitance measurements were conducted over the range of 75–300 K, with a temperature precision of ± 500 mK. DLOS and SSPC data were acquired at 17 K using monochromatic light with wavelengths ranging from 400 to 1000 nm.

D. Theoretical methods

Density functional theory (DFT) *ab initio* calculations were employed to identify defects observed via DLTS. Calculations were performed using the Vienna *Ab initio* Simulation Package [67] with the projector-augmented wave method [68]. The cutoff for wave-function expansion was 400 eV. We took van der Waals interactions into account by the Tkatchenko-Scheffler method [69]. Defect states were modeled in a supercell with lattice vectors ($4a$, $2a + 4b$, c), where a , b , and c are the primitive unit vectors. We took a $2 \times 2 \times 2$ Γ -centered k -point set. The structure optimization was performed with the exchange-correlation energy functional by Perdew *et al.* [70] and the total energy calculations were carried out by use of an HSE hybrid functional [71] with the fraction of exact exchange 0.3. Total energy of the charged system was corrected by the SLABCC code [72]. The formation energy was evaluated following the method in Ref. [73]. The equilibrium position of Ga_i is between two layers, and, on the other hand, Se_i occupies a puckered bond-center interstitial site between a pair of Ga atoms. In the system with V_{Ga} , the neighboring Ga atom relaxes to the middle of the layer (see Fig. S14 in Supplemental Material [32]). For other defects, only small rearrangements of the neighboring atoms were seen. These positions are consistent with other calculations [47]. Si_i and O_i also occupy a puckered bond-center interstitial site between a Ga pair.

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The authors declare no conflict of interest

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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