Radiation-induced Electron and Hole Traps in Ge$_{1-x}$Sn$_x$ ($x = 0-0.094$)

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Radiation-induced electron and hole traps in Ge$_{1-x}$Sn$_x$ ($x = 0$–0.094)

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ABSTRACT

The band structure of germanium changes significantly when alloyed with a few percent concentrations of tin, and while much work has been done to characterize and exploit these changes, the corresponding deep-level defect characteristics are largely unknown. In this paper, we investigate the dominant deep-level defects created by 2 MeV proton irradiation in Ge$_{1-x}$Sn$_x$ ($x = 0.0, 0.020, 0.053, 0.069, \text{and } 0.094$) diodes and determine how the ionization energies of these defects change with tin concentrations. Deep-level transient spectroscopy measurements approximate the ionization energies associated with electron transitions to/from the valence band (hole traps) and conduction band (electron traps) in the intrinsic regions of p-i-n diode test structures. The prominent deep-level hole traps may be associated with divacancies, vacancy–tin complexes, and vacancy–phosphorous complexes ($V_2$, $V$–Sn, and $V$–P, respectively), with the presumed $V$–P hole trap dominating after room temperature annealing. The ionization energy level of this trap (approximated by the apparent activation energy for hole emission) is close to the intrinsic Fermi level in the 0% and 2% Sn devices and decreases as the tin concentration is increased, maintaining an approximately fixed energy spacing below the indirect conduction band edge. The other hole traps follow this same trend, and the dominant electron trap ionization energies remain roughly constant with changes in tin concentrations, indicating they are likewise pinned to the conduction band edge. These results suggest a pattern that may, in many cases, apply more generally to deep-level defects in these alloys, including those present in the “as-grown” materials.

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I. INTRODUCTION

Recent progress in Ge$_{1-x}$Sn$_x$ nonequilibrium growth techniques, with the demonstration of a direct energy gap for tin concentrations around 7%, promises significant near-mid-infrared (IR) optoelectronic performance that is similar to III–V and HgCdTe semiconductors but is also compatible with complementary metal oxide semiconductor (CMOS) manufacturing technology with much lower costs.$^{1,2}$ Ge$_{1-x}$Sn$_x$-based photodetectors, light emitting diodes, and optically pumped lasers have been fabricated by several techniques.$^{3-5}$

In order to realize the promise of these materials, however, native defects, impurities, and defect–impurity complexes must be better understood and controlled. Deep-level defects, in particular, decrease the detector signal-to-noise ratio and radiative efficiency of optoelectronic and photonic devices via Shockley–Read–Hall (SRH) generation or recombination of electron–hole pairs. Substantial knowledge has been gained about defect properties in pure germanium, due to intensive studies in the mid-20th century and a resurgence of interest in recent decades, motivated by the usefulness of SiGe alloys in strain engineering of silicon CMOS transistors. Because interstitials and vacancies in germanium are mobile well below room temperature, defects that are relatively stable at room temperature can be assumed to involve complexes of these primary point defects with one another (e.g., divacancies and trivacancies) and/or impurities (group-V and oxygen impurities being significant).$^{6-8}$ Comprehensive studies of radiation-induced deep-level defects in germanium have reported deep-level transient spectroscopy (DLTS) signatures for electron traps$^{7,9,10}$ and hole traps.$^{8,11}$ The specific defect complexes that dominate the measured DLTS spectra are primarily determined by the as-grown material characteristics (e.g., intentional doping and unintentional impurities) and secondarily by the type, energy, and flux of radiation used.
to create the atomic displacements. Defect complexes related to two or more primary defects are more likely to form when a large concentration of primary defects are present at the same time, as occurs with irradiation by heavy ions or a high flux of lighter particles.

Radiation-induced deep-level defects associated with Sn-doped germanium have been studied using DLTS and IR absorption, in which complexes between vacancies and tin were found to form readily at room temperature. There have been a few reports on deep-level defect properties in germanium–tin alloys, but almost nothing has been confirmed about the dependence of these defect properties on tin concentrations. In the present paper, we report the results of a comprehensive deep-level transient spectroscopy (DLTS) study of dominant radiation-induced electron and hole traps in Ge$_{1-x}$Sn$_x$ ($x = 0.0, 0.020, 0.053, 0.069, and 0.094$), using p-i-n diode test devices.

II. EXPERIMENT

Ge$_{1-x}$Sn$_x$-based light emitting diodes were fabricated at the Arizona State University. The devices were grown by chemical vapor deposition (CVD) upon Si (100) using ultralow temperature deposition of highly reactive Ge and Sn hydrides. This growth method yields Ge$_{1-x}$Sn$_x$ layers 300–800 nm thick that are mostly relaxed of misfit strains, with the highest compressive strain (in the $x = 0.094$ Ge$_{1-x}$Sn$_x$ layer) corresponding to 75%-77% strain relaxation. Cross-sectional transmission electron microscopy (XTEM) images reveal relatively benign edge-type dislocations and short stacking faults at the i-n$^-$ interface, which extend downward into the n$^-$ region. The Sn concentration, $y$, in the p$^+$ region is equal to the Sn concentration, $x$, in the intrinsic region for $x < 0.069$ devices and held fixed at $y = 0.05$ for $x ≥ 0.069$ to improve light extraction and promote carrier confinement in the intrinsic region. In all cases, the p$^+$ layer was grown fully strained to the i layer, resulting in a p$^-$i interface largely free of extended defects.

Active device areas were defined in circular mesas 360 μm and 580 μm in diameter, and Cr/Au metallization was deposited for ohmic contacts to the p$^+$ and n$^-$ regions (Fig. 1), which were doped with $2 \times 10^{19}$ cm$^{-3}$ boron and phosphorous atoms, respectively. A thin passivation layer of SiO$_2$ was deposited on the outer surfaces of the device mesa.

The intrinsic regions of these devices are unintentionally doped at concentrations around $10^{16}$–$10^{17}$ cm$^{-3}$, with the germanium ($x = 0$) sample being n-type and the $x > 0$ samples being p-type. The source of this unintentional p-type doping in GeSn is unclear, but it is generally supposed to consist of multivacancy complexes, which form shallow acceptorlike states. The properties of the intrinsic regions of these devices are listed in Table I. The carrier concentrations were estimated based on capacitance–voltage (C–V) measurements, and the part of the intrinsic region being probed by standard DLTS pulse/measurement bias parameters was also estimated from the C–V data. As seen in Fig. 2, reverse biasing the 0% and 2% Sn devices expands the depletion regions over a 100 nm range deep in the intrinsic region. The depletion region extends inward from the i-p$^+$ interface in the 0% Sn devices and from the i-n$^-$ interface in the 2.0%–9.4% Sn devices. The devices with higher Sn concentration also exhibit higher unintentional p-type doping, and reverse biasing those devices expands their depletion regions over a 40 nm range to a distance 100 nm from the i-n$^-$ interface. Thus, the regions probed by conventional DLTS are expected to contain significant concentrations of phosphorus before and after irradiation in the 2.0%–9.4% Sn devices and after irradiation in the 0% Sn devices.

Temperature-dependent electrical characterization was performed from 24 to 220 K before and after irradiation using a Semetrol DLTS, C–V, and I–V characterization system. DLTS measurements were performed in the conventional fashion and in current injection mode for detection of dominant majority and minority carrier traps.

The 2 MeV proton irradiations were conducted at the Edwards Accelerator Laboratory, Ohio University. SRIM Monte

<table>
<thead>
<tr>
<th>Sn conc. (mol. %)</th>
<th>Carrier conc./type (cm$^{-3}$)</th>
<th>Thickness (nm)</th>
<th>Strain (%) $\sim-/+$ compressive/tensile</th>
<th>Bandgap at 295 K (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$5 \times 10^{16}$/n-type</td>
<td>790</td>
<td>+0.11</td>
<td>0.66</td>
</tr>
<tr>
<td>2.0</td>
<td>$2 \times 10^{16}$/p-type</td>
<td>530</td>
<td>−0.14</td>
<td>0.62</td>
</tr>
<tr>
<td>5.3</td>
<td>$1 \times 10^{17}$/p-type</td>
<td>440</td>
<td>−0.16</td>
<td>0.57</td>
</tr>
<tr>
<td>6.9</td>
<td>$2 \times 10^{17}$/p-type</td>
<td>400</td>
<td>−0.22</td>
<td>0.54</td>
</tr>
<tr>
<td>9.4</td>
<td>$2 \times 10^{17}$/p-type</td>
<td>300</td>
<td>−0.32</td>
<td>0.46</td>
</tr>
</tbody>
</table>
Carlo simulations of the proton–target interactions were used to confirm that energy was deposited uniformly throughout the device intrinsic regions and to calculate the initial (instantaneous) vacancy concentration produced per unit proton fluence in each device. These simulations show that approximately 0.13 vacancies/μm/proton are deposited uniformly in the intrinsic region of each device, with only 5% fewer displacements in the 9.4% Sn devices due to reduced energy transfer to the higher mass Sn target atoms as compared to the lower mass Ge atoms. Thus, the amount of initial displacement damage per unit fluence is approximately the same in each device. The beam current was selected to ensure devices remained within a few degrees of room temperature throughout the irradiation. Proton fluence up to $4 \times 10^{14}$ cm$^{-2}$ ($\sim 5 \times 10^{17}$ initial vacancies/cm$^3$) was applied over a period of 5–20 min, and the devices were then placed in liquid nitrogen storage to ensure they were subjected to no more than 2 h of room temperature annealing prior to the first post-rad DLTS measurements.

III. RESULTS

As shown in Fig. 2 the 2.0%–9.4% Sn devices exhibit no significant decrease in the carrier concentration profiles after being exposed to the highest proton fluence of $4 \times 10^{14}$ cm$^{-2}$. The 0% Sn device profile, however, reflects a reduction in n-type carrier concentration that can be attributed to a net increase in acceptor-type trap concentration after irradiation. Several vacancy-related acceptor-type defects can be formed in germanium doped with tin, and accordingly, as-grown GeSn layers usually exhibit p-type conduction. It is reasonable to suppose that acceptor-type defects (shallow and deep) dominate in the irradiated Ge and GeSn materials, and the results in Fig. 2 are consistent with that supposition.

A. Hole traps

Prior to irradiation, DLTS spectra magnitudes were generally below $10^{-3}$ ΔC/C, with associated deep-level defect concentrations up to $5 \times 10^{14}$ cm$^{-3}$ in the devices of higher Sn concentration and no more than $1 \times 10^{13}$ cm$^{-3}$ in the 0% and 2% Sn devices. Electron trapping generally dominated in the as-grown and $4 \times 10^{13}$ cm$^{-2}$ proton fluence DLTS spectra under conventional and current injection pulse/measurement bias parameters. Following $4 \times 10^{14}$ cm$^{-2}$ proton irradiation, however, hole trapping clearly dominated over electron trapping, and the representative DLTS spectra are shown in Fig. 3. In this figure, 545 s$^{-1}$ DLTS spectra are shown for 0%, 2%, 6.9%, and 9.4% Sn devices. Hole traps are observed as majority carrier traps (yielding negative capacitance transients) in the 2.0%–9.4% Sn devices and as minority carrier traps (yielding positive capacitance transients) in the 0% Sn devices. Corresponding DLTS spectra are graphed as positive values in both cases for ease of comparison. All the observed peaks overlap to a greater or lesser degree with adjacent peaks, so a Gaussian peak fitting method was primarily used to infer the individual peak temperatures and magnitudes. These fitting results showed consistency at different rate windows and, in most cases, dozens of different DLTS data sets for each device. The regions probed by conventional DLTS in the 5.3%–9.4% Sn devices are proximate to edge-type dislocations and short stacking faults. A variety of interaction processes can take place between point defects and extended defects, potentially increasing uncertainty in the extracted DLTS parameters relative to completely isolated point defects.

A dominant hole trap, labeled H1, is observed in each of the devices. Based on the apparent activation energy, capture cross section, and “annealing-out” temperature, as well as consideration of likely impurities in these devices, we attribute this hole trap to the (−0) transition of the vacancy–phosphorous (V–P) complex. Most studies of this and other E-centers have been conducted on intentionally doped n-type Ge$^{25}$ and SiGe$^{23,24}$ in which the concentration of group-V donors is unambiguous and the monovacancies are in a negative charge state, and thus strongly attracted to the positively charged donors. Nevertheless, E-centers have been reported in p-type germanium$^{25}$ and the vacancies are expected to be negatively charged when the Fermi level is above about 0.2 eV from the valence band edge$^{26}$. This latter condition does not hold at room temperature for the p-type Ge$_{1-x}$Sn$_x$ devices in this study, but we note that the excess electron–hole pairs generated by proton bombardment would have raised the quasi-Fermi level toward the middle of the bandgap during irradiation. In a similar way, light–based photoionization was used to generate E-centers in p-type germanium codoped with antimony.$^{26}$

FIG. 2. Carrier concentration profiles inferred from C–V measurements at 150 K before and after $4 \times 10^{14}$ proton cm$^{-2}$ irradiation conducted at room temperature. The depletion width on the x-axis is measured from the i+p$^+$ interface for the n-type 0% Sn device and from the i+n$^+$ interface for the p-type 2.0–9.4% devices. Except for the 0% Sn device, there was little change between the pre-rad data (black) and post-rad data (red). The 0% Sn plot reflects a reduction in n-type carrier concentration due to a net increase in acceptor-type trap concentration.
In the 0% Sn devices, the H1 peak was not initially dominant, but it increased in magnitude with isochronal annealing up until 110 °C. This annealing response was one of several instances in which the presumed V−P complex appeared to grow in magnitude in the 30–80 °C anneal temperature range, perhaps as additional vacancies were released from less stable defect complexes.12

In the 0% and 2% Sn devices, the H1 peak was little affected by neighboring peaks, and the apparent hole trap activation energy, $E_{pa}$, was readily deduced from Arrhenius fitting. The actual ionization energy (i.e., Gibbs free energy) is given by

$$E = E_{gibbs} - E_{pa} - T\Delta S,$$

(1)

where $E_{gibbs}$ is the activation energy for hole capture, $T$ is the temperature, and $\Delta S$ is the difference in entropy after the charge transfer. The values of $E_{gibbs}$ and $\Delta S$ have not been reported for hole trapping at the first acceptor level of any E-center in germanium, so the extent to which the apparent ionization energy overestimates the actual ionization energy is unknown. In devices with higher Sn concentration, the Arrhenius fitting technique was applied to the H1 peak that resulted from a 2 or 3 Gaussian peak deconvolution algorithm in the Semetrol analysis software. This procedure entailed greater uncertainty in the extracted values of $E_{pa}$ for the higher Sn concentration samples. These extracted DLTS parameters are shown in Table II for devices at five different Sn concentrations.

In the 2% Sn devices, a prominent hole trap peak, labeled H3, is clearly discernable, and this peak also appears to be present (though less clearly) in the 5.3%, 6.9%, and 9.4% Sn devices. Based on the apparent activation energy, peak temperature in the DLTS spectrum, anneal-out temperature, and apparent absence of this peak in the 0% Sn devices, this hole trap can likely be attributed to the $(2/-)$ transition of the vacancy−tin (V−Sn) complex. The V−Sn complex was previously only reported for germanium doped with tin.12,13 A decrease in the magnitude of the H3 peak is discernable after just a few hours annealing at 25 °C, and this decrease is roughly anticorrelated with the increase in the magnitude of H1 discussed above. This observation is similar to that observed in Ref. 12, where the authors surmised that V−Sn complexes dissociated in the 50–100 °C range, and the resulting monovacancies formed stronger bonds with phosphorus atoms, resulting in V−P complexes. In comparison with the samples of Ref. 12, the concentration of tin in our 2% Sn devices is three to four orders of magnitude higher, and the concentration of phosphorus is two to three orders of magnitude higher. Furthermore, the unintentional p-type doping of these devices results in different charge states (and likely diffusivities) of some deep-level defects compared to the n-type samples of Ref. 12.

A recent IR absorption spectroscopy study of germanium, doped with Sn and Sb and irradiated by 5 MeV electrons at low temperature, found the divacancy (V2) was dominant in the complex with tin, such that V2−Sn was formed below 243 K.14 This complex then diffused and transformed into more stable V2−Sn−Sb at temperatures greater than 243 K. These IR absorption spectroscopy measurements have not been correlated with DLTS measurements, so it is unclear how the comparable V2−Sn−P complex might be evidenced in the DLTS spectra of Fig. 3. In a different...
study of germanium doped with Sn and P and irradiated by 6 MeV electrons at room temperature, it was suggested that V–Sn–P arises when V–P pairs diffuse (at anneal temperatures over 100 °C) and form complexes with Sn that are stable up to at least 275 °C.27 The hole trap associated with this complex exhibited a 0.21 eV activation energy for hole emission to the valence band. The stability of the V₂–Sn–Sb complex in Ref. 14 was not reported above 300 K, adding to the difficulty of comparing that work with the results of Ref. 13 and those reported here.

The 0% Sn DLTS spectrum was obtained using current injection DLTS, in which electrons and holes can be trapped in the measured region, and standard DLTS analysis can be applied only if either one or the other type of trapping dominates. For this device, the valleys in the spectrum (inverted as peaks in Fig. 3) were indistinct until annealing, when the H₁ hole trapping started to dominate, and thus the 110 °C data from this device are used for comparison with the post-rad hole traps in the other devices. Also of note in the 0% Sn DLTS spectrum is a broad continuum of more shallow hole traps that grow in with elevated temperature annealing.

The H₂ peaks in Fig. 3 are obscured by neighboring peaks, so DLTS parameter extraction and identification are somewhat tentative. Based on the \( E_{pa} \) value of 0.22 ± 0.03 eV for H₂ in the 0% Sn device and the peak temperature around 140 K (545 s⁻¹ rate window), this trap likely corresponds to the lattice divacancy, \( V_2^- \), which is expected to have a significant presence in these alloys.25,27 The \( \Delta S \) for V–Sn and \( V_2^- \) in germanium has been reported as 6.5 k and 7.4 k, respectively,15 so the values of \( E_{pa} \) in this study may overestimate the true ionization energies of these two traps by up 0.06 eV.

Annealing studies were conducted on several of the irradiated devices. Figure 4 is representative of the results seen in the 2% Sn devices, where the annealing behavior is more evident than in other devices. Here, the H₃ hole trap, which is dominant within the first 2 h following irradiation, diminishes considerably after two days at room temperature. The remaining trap concentration continues to decrease at elevated temperature isochronal (30 min) annealing steps. The energetically shallow hole trap, H₄, is less stable than H₃, disappearing by the end of the two-day room temperature anneal. The magnitudes of all the hole trap peaks are shown vs annealing steps in Fig. 5. The H₁ peak magnitude is roughly anticorrelated with the H₃ and/or H₄ peaks in the room temperature and 50 °C annealing steps, and above 50 °C, the H₁ peak continues to be dominant, though slowly decreasing in magnitude at higher annealing temperatures. A reduced yet significant residual concentration of H₀, H₁, and H₂ hole traps remains after the 200 °C anneal step. If the assignments of H₁ to the divacancy and H₂ to the V–P complex are correct, the corresponding peaks might be expected to anneal out entirely by the 200 °C anneal step.25,27 The fitting method of Fig. 5 assumes fixed peak temperatures, allowing the peak amplitudes to vary for the best fit. Moderate changes in the apparent activation energies and capture cross sections may not be discernible, especially above 110 °C. Keeping this in mind, we suggest that the microscopic defects corresponding to the peaks labeled H₁ and H₂ in Figs. 4(g) and 4(h) are likely different from the defects corresponding to peaks having those same labels in Figs. 4(a)–4(e).

A positron annihilation spectroscopy (PAS) study found, for example, that annealing the V–P complex in germanium above 130 °C leads to the formation of \( V_2^- \)–P complexes.28 It is currently unknown by how much the hole trap characteristics of \( V_2^- \)–P and V–P differ.
FIG. 4. DLTS spectra (545 s$^{-1}$ rate window) of a 2% Sn device at successive annealing stages following $4 \times 10^{14}$ cm$^{-2}$ proton fluence. The room temperature anneal was applied for two days, whereas the elevated temperatures were each applied for 30 min. The bias parameters are $V_{\text{forward}} = 0$ V, $V_{\text{meas}} = -0.6$ V, and $t_{\text{pulse}} = 1$ ms.
B. Electron traps

Electron trapping was also studied via DLTS, using the conventional voltage pulse technique for the 0% Sn devices and the injection current technique for the 2.0%–9.4% Sn devices. At the lower irradiation fluence of $4 \times 10^{13}$ protons cm$^{-2}$, electron trapping clearly dominated over hole trapping in most devices, and the representative DLTS spectra are shown in Fig. 6. In this figure, 545 s$^{-1}$ rate windows are shown for 0%, 2%, and 6.9% Sn devices. Electron traps are observed as majority carrier traps (yielding negative capacitance transients) in the 0% Sn devices and as minority carrier traps (yielding positive capacitance transients) in the 2.0%, 6.9%, and 9.4% Sn devices. Corresponding DLTS spectra are graphed as negative values in both cases for ease of comparison.

In the 0% device, a large peak around 160 K dominates the spectrum. This peak is composed of two closely spaced overlapping peaks (labeled GE0a and GE0b). This inference is drawn from Gaussian peak deconvolution and the observation of a small, yet distinct, difference in thermal stability. The apparent activation energy and "anneal-out" temperature of GE0b closely match those reported for the $(2-/-)$ transition of the vacancy–oxygen complex ("A-center") in germanium.8-6 The concentration of this complex suggested by the DLTS peak heights is $\sim 2 \times 10^{15}$ cm$^{-3}$. We do not know if the oxygen impurity content is high enough to produce such a concentration of A-centers. The $(2-/-)$ transition of the V–P complex could also possibly be linked to either GE0a or GE0b, with the reported anneal-out temperature most closely matching the 140 °C observed for GE0a.7 GE0a and GE0b are dominant in freshly irradiated 0% Sn devices. It is unclear whether these electron traps are also present in the 2.0%–9.4% Sn devices, but they are certainly not dominant there. It has been argued that the primary mechanism of disappearance of both the V–O and V–P complexes upon thermal annealing is their migration as a unit to sinks (likely to be Sn atoms in the 2.0%–9.4% Sn devices).26-27 If GE0b is associated with the V–O complex, such a mechanism might explain its
apparent absence in the 2.0%–9.4% Sn devices. Assignment of GE0a to the V–P complex, however, would be incompatible with the assignment of H1 to that same complex because the annealing of GE0a and H1 are roughly anticorrelated in the 0% Sn device.

The electron traps labeled E1 and E3 have characteristics similar to those with the same labels in the 2.0%–9.4% Sn DLTS spectra, consistent with the supposition (discussed in Sec. IV) that these trap energy levels maintain a fixed spacing relative to the conduction band edge. Employing this supposition, the electron trap labeled E2 in these DLTS spectra is noticeably absent from the 0% Sn spectrum. Thus, the defect complex corresponding to this electron trap is likely to involve tin. The measured DLTS parameters for these defects are shown in Table III.

### IV. DISCUSSION

Central to this study is the question of how defect ionization energy levels change relative to the conduction and valence band edges when Sn concentration is changed. In Fig. 7, the ionization energy levels for the dominant H1 hole trap, \( E_{iH1} \) (approximated by \( E_{pa} \)), are shown relative to the intrinsic Fermi level, \( E_i \), at each Sn concentration. Here, the 300 K bandgaps are taken from previously reported empirical fitting, and the intrinsic Fermi levels are one-half the bandgap energy plus a small term resulting from the hole effective mass being nearly twice greater than that of the electron in germanium. The bandgap energies decrease with Sn concentrations, and the \( E_{iH1} \) levels decrease to a greater extent than the corresponding \( E_i \) levels. In order to investigate this trend more closely, the change in \( E_{iH1} \) was plotted vs the change in bandgap at the indirect (L) and direct (Γ) points in momentum space. Figure 8 shows these energy level changes compared to the 0% Sn values. It is seen that the H1 level changes roughly as if pinned to the indirect conduction band edge, although the 5.3%, 6.9%, and 9.4% Sn values show some deviation from this generalization. The ionization energy levels of electron traps associated with the V–P complex \(^{23}\) and V–Sb complex \(^{24}\) in Si\(_{1-x}\)Ge\(_x\) were reported to show similar behavior as the bandgaps decreased with composition and strain. In another study of irradiated Si\(_{1-x}\)Ge\(_x\), conducted over a wider composition range \((x = 0–0.5)\), the E-center ionization energy level moved toward the valence band by a greater amount than the corresponding decrease in the bandgap. Furthermore, trap ionization energy levels associated with the divacancy, A-center, and others also exhibited a movement toward the valence band in Si\(_{1-x}\)Ge\(_x\) as the bandgap narrowed with increasing x.\(^{31}\)

### TABLE III. Measured DLTS parameters of radiation-induced electron traps. Valley temperatures are cited for 545 s\(^{-1}\) rate windows. Annealing temperatures indicate steps where considerable changes in defect concentration (40% or greater) are observed. Apparent capture cross sections are generally uncertain by a factor of 10.

<table>
<thead>
<tr>
<th>Sn conc. (%)</th>
<th>Defect label</th>
<th>( T_{\text{peak}} ) (K)</th>
<th>( E_{\text{in}} ) (eV)</th>
<th>( \sigma_{\text{in}} ) (cm(^2))</th>
<th>Annealing</th>
<th>Defect attribution</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>GE0a</td>
<td>162</td>
<td>-0.27 ± 0.01</td>
<td>1 × 10(^{-14})</td>
<td>( \downarrow )140°C</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>GE0b</td>
<td>153</td>
<td>-0.26 ± 0.01</td>
<td>2 × 10(^{-14})</td>
<td>( \downarrow )110°C</td>
<td>A-center ?</td>
<td>8 and 6</td>
</tr>
<tr>
<td></td>
<td>E1</td>
<td>133</td>
<td>-0.19 ± 0.02</td>
<td>6 × 10(^{-16})</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>E3</td>
<td>53</td>
<td>-0.06 ± 0.01</td>
<td>7 × 10(^{-17})</td>
<td>( \downarrow )140°C</td>
<td>I(_{\text{Ge-O}}) 2</td>
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</tr>
<tr>
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<td>E0</td>
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<td>...</td>
<td>...</td>
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<td>...</td>
</tr>
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<td>8 × 10(^{-16})</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<tr>
<td></td>
<td>E2</td>
<td>96</td>
<td>-0.12 ± 0.01</td>
<td>4 × 10(^{-16})</td>
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<td>...</td>
</tr>
<tr>
<td></td>
<td>E3</td>
<td>60</td>
<td>-0.06 ± 0.01</td>
<td>7 × 10(^{-17})</td>
<td>...</td>
<td>I(_{\text{Ge-O}}) 2</td>
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</tr>
<tr>
<td>6.9</td>
<td>E0</td>
<td>153</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>E1</td>
<td>122</td>
<td>-0.18 ± 0.01</td>
<td>5 × 10(^{-16})</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>E2</td>
<td>91</td>
<td>-0.12 ± 0.02</td>
<td>2 × 10(^{-16})</td>
<td>...</td>
<td>Sn related</td>
<td>...</td>
</tr>
<tr>
<td>9.4</td>
<td>E1</td>
<td>116</td>
<td>-0.17 ± 0.03</td>
<td>...</td>
<td>Unmeasured</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>E2</td>
<td>79</td>
<td>-0.12 ± 0.03</td>
<td>...</td>
<td>Unmeasured</td>
<td>Sn related</td>
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</tbody>
</table>

V–P complex \(^{25}\) and V–Sb complex \(^{24}\) in Si\(_{1-x}\)Ge\(_x\) were reported to show similar behavior as the bandgaps decreased with composition and strain. In another study of irradiated Si\(_{1-x}\)Ge\(_x\), conducted over a wider composition range \((x = 0–0.5)\), the E-center ionization energy level moved toward the valence band by a greater amount than the corresponding decrease in the bandgap.\(^{31}\) Furthermore, trap ionization energy levels associated with the divacancy, A-center, and others also exhibited a movement toward the valence band in Si\(_{1-x}\)Ge\(_x\) as the bandgap narrowed with increasing x.\(^{31}\)
It seems that the trend observed for the H1 (V–P) hole trap can apply to other deep-level defects in these devices, as evidenced in Fig. 9. Here, trap energy levels are shown for 0%, 2.0%, 6.9%, and 9.4% Sn devices, with each of the conduction band edges aligned. Plotted in this way, trap energy levels pinned to the conduction band edge should occupy the same vertical position across the figure, as appears to be the case for these traps. The $E_v + 0.19$ eV level measured by Markevich et al.\textsuperscript{12} and attributed to the V–Sn complex in germanium is included to show consistency with the trend. The hole trap, H2, likely corresponding to the divacancy, is not included in the figure because values of $E_{pa}$ could not be accurately determined from these DLTS measurements. Nevertheless, the peak temperature of the H2 traps decreases consistent with the trend observed for H1, suggesting the energy level may likewise be pinned to the conduction band edge. Using the reported value of $E_v + 0.19$ eV,\textsuperscript{11} the trend would predict values for the divacancy in the 2% and 6.9% devices to be $E_v + 0.15$ eV and $E_v + 0.06$ eV, respectively. Continuation of the trend in 9.4% Sn would push the energy level into the valence band, which would not be consistent with the assignment of this defect to the 57 K “H2” peak in the 9.4% Sn DLTS spectrum of Fig. 3. As noted above, that assignment is in fact somewhat tentative, but there is no reason to assume the observed trend continues unchanged as the defect energy transitions from deep to shallow.

![Figure 8](https://example.com/fig8.jpg) **FIG. 8.** Change in direct and indirect bandgap energies and H1 trap (V–P) apparent activation energies in Ge$_{1-x}$Sn$_x$ as a function of Sn concentration relative to germanium (0% Sn). The bandgap energies and associated error bars are taken from the empirical fit expressions in Ref. 21. The H1 apparent activation energies are determined from the DLTS measurements in this study. The devices in this study are largely relaxed of strain, and no strain corrections are applied to the bandgap values.

![Figure 9](https://example.com/fig9.jpg) **FIG. 9.** Electron and hole trap ionization energy levels (approximated by $E_{na}$ and $E_{pa}$) relative to 125 K band edges at different Sn concentrations. These trap levels exhibit fixed energy spacing relative to the conduction band edge. The devices in this study are largely relaxed of strain, and no strain corrections are applied to the bandgap values.
According to the theory, the rate of SRH recombination or generation mediated by a given trap is maximized when the trap energy level, $E_T$, is equal to the intrinsic Fermi level, $E_i$ (near midgap). If the intrinsic carrier concentration, $n_i$, is large compared to both the electron and hole concentrations (e.g., in the “i” region of a p-n diode under reverse bias), the SRH generation rate decreases exponentially as $|E_i - E_T|$ increases.\textsuperscript{26} Thus, under low carrier injection conditions, none of the hole traps discussed above should contribute significantly to SRH recombination/generation in Ge$_{1-x}$Sn$_x$ devices at high tin concentrations (≥6.9%). On the other hand, the energy level of the electron trap E1 moves closer to the intrinsic Fermi level as tin concentration increases, so E1 could be an important SRH center in Ge$_{1-x}$Sn$_x$ optoelectronic devices operating in the mid-IR range.

V. SUMMARY

Displacement damage from 2MeV proton irradiation of these Ge$_{1-x}$Sn$_x$ devices results in deep-level hole traps, which can possibly be attributed to $V_2$, V–Sn, and V–P (E-center) defect complexes; the presumed V–P defect is the most dominant of these complexes after room temperature annealing. The (~0°) ionization energy level of this defect (approximated by $E_{ion}$) is close to the intrinsic Fermi level in the 0% and 2% Sn devices, indicating it may be an important center for undesired SRH recombination/generation in optoelectronic device applications. In the 5.3%, 6.9%, and 9.4% Sn devices, this energy level shifts closer to the valence band, indicating a trend whereby the defect energy level remains approximately fixed relative to the indirect conduction band edge. The apparent activation energies and peak temperatures in the DLTS spectra for the other identified hole traps and for three electron traps are roughly consistent with those of the authors and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the United States Government.

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