FORMATION ENERGIES OF NATIVE POINT DEFECTS IN STRAINED-LAYER SUPERLATTICES (POSTPRINT)

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12 September 2017
Interim Report

Distribution Statement A.
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1. REPORT DATE (DD-MM-YY)
12 September 2017

2. REPORT TYPE
Interim

3. DATES COVERED (From - To)
11 September 2013 – 31 May 2017

4. TITLE AND SUBTITLE
FORMATION ENERGIES OF NATIVE POINT DEFECTS IN STRAINED-LAYER SUPERLATTICES

5a. CONTRACT NUMBER
FA8650-11-D-5800-0008

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62102F

5d. PROJECT NUMBER
4348

5e. TASK NUMBER
0008

5f. WORK UNIT NUMBER
X0TW

6. AUTHOR(S)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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Menlo Park, CA 94025

8. PERFORMING ORGANIZATION REPORT NUMBER
AFRL/RX
Wright Patterson Air Force Base
Dayton, OH 45433

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750

Air Force Materiel Command
United States Air Force

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/RXAN

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-RX-WP-JA-2017-0440

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Statement A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES
PA Case Number: 88ABW-2017-4378; Clearance Date: 12 September 2017. This document contains color. Journal article published in AIP Advances, Vol. 7, 5 Jun 2017. © 2017 AIP Publishing. The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work. The final publication is available at https://doi.org/10.1063/1.4985136

14. ABSTRACT (Maximum 200 words)
We develop a theoretical approach that employs first-principles Hamiltonian, tight-binding Hamiltonian, and Green’s function techniques to obtain energy levels arising from native point defects (NPDs) in InAs-GaSb and InAs-InAs$_{1-x}$Sb$_x$ strained layer superlattice (SLS) systems. In particular, we consider 4 types of NPDs — anion vacancy, cation vacancy, anion anti-site, cation anti-site, isoelectronic substitution at anion sites (Sb at As site and As at Sb site) — in the InAs, GaSb compound regions, and additional three types of defects — cation at the second anion site, second anion at the cation site, and second anion vacancy — in InAs$_{1-x}$Sb$_x$ alloy region of the SLS. For a selected few designs, we study NPDs both in the bulk region and near the interfaces of the SLS. We have considered 12 designs of InAs-GaSb systems and 2 designs of InAs-InAs$_{0.7}$Sb$_{0.3}$ systems lattice matched to GaSb substrate. The calculated defect levels not only agree well with available measurements but also reveal the connection between mid-gap levels and specific NPDs. We further calculate defect formation energies both in compounds and for all superlattices considered above.

15. SUBJECT TERMS
Hamiltonian; Green’s function; InAs/InAs$_{0.7}$Sb$_{0.3}$ strained layer superlattice (SLS); GaSb; anion; cation; alloy region

16. SECURITY CLASSIFICATION OF:
a. REPORT Unclassified
b. ABSTRACT Unclassified
c. THIS PAGE Unclassified

17. LIMITATION OF ABSTRACT: SAR

18. NUMBER OF PAGES
7

19a. NAME OF RESPONSIBLE PERSON (Monitor)
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The two most desired properties for photo-detection using a strained-layer superlattice (SLS) are high native point defect (NPD) formation energies and absence of mid-gap levels. In this Letter we use first-principles calculations to study the formation energies of NPDs. First we validate the numerical method by comparing the calculated defect formation energies with measured values reported in the literature. Then we calculate the formation energy of various NPDs in a number of InAs-GaSb SLS systems. From the calculated defect formation energies in SLS relative to that in constituent bulk material, the probability of defect presence in SLS can be inferred if we know the growth conditions of SLS with respect to those of the bulk material. Since the defects with much higher formation energy in SLS will be difficult to form, their energy levels in the SLS mini-gap will have little effect on device performance, even if the defect states lie in mid-gap. Together with our calculated defect energy level results, we can identify promising SLS designs for high-performing photodetectors. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Strained-layer superlattice (SLS) systems have been proposed for the next generation infrared detection materials to replace the widely used HgCdTe alloys because of the promised great wavelength tunability and long carrier lifetimes. However, the measured carrier lifetimes in SLSs for infrared (IR) detection are extremely short, owing to strong Shockley-Read-Hall (SRH) recombination facilitated by native point defects (NPDs). Because the NPDs give rise to large dark currents that are detrimental to device performance, it is desirable to identify SLS structures in which NPDs are intrinsically few (i.e., their formation energy is large), or where the NPDs do not produce any mid-gap states, which are particularly damaging to carrier lifetime.

Formation energy of NPDs in GaAs, GaSb, and InAs has been studied extensively—both theoretically and experimentally. However, very little or no information is available for the formation energy of NPDs in SLS systems, mainly because a reliable calculation requires a very large supercell and the experimental determination is obscured by a multitude of material and extrinsic variables. Recently we developed a hybrid approach, which uses the Green’s function of a perfect SLS obtained with long-range tight-binding Hamiltonian together with the defect potentials obtained from first principles based on SIESTA to calculate the defect energy levels. These calculations, which employ only a minimal basis set of sp³ orbitals, predicted SLS defect levels in good agreement with measurements. While these calculations predicted more defect states to have a GaSb origin, consistent with the observation in Ga-free systems, the likelihood of defect formation was not addressed. Defect formation energy calculations are useful to help narrow the choice of design, since a large formation energy would suggest that the NPD is unlikely to be present in the SLSs. The successful use of the minimal basis set in SIESTA enables us to study defect formation energy with very large supercells as required for SLS systems.
In this Letter we report the defect formation energy in InAs-GaSb SLS, relative to InAs and GaSb, calculated by using SIESTA with minimal basis. The relative values give the information about the likelihood of the defect formation in SLS compared to that in the bulk material. Since defect formation in bulk materials has been extensively studied, we can draw reliable conclusions on NPD formation in SLS systems. This information, combined with recent calculations of defect levels,\textsuperscript{13} can help identify desired SLS systems with no damaging defect levels.

In the calculations we use the atomic basis set in SIESTA to be consistent with that used for energy-level calculations. In this basis, the defect potential is found to die off after two atomic layers away from the defect. We use local density approximations and the conjugate-gradient scheme to find relaxed atomic structures in the presence of an NPD.

First, we calculate the total energy $E_0$ of a large supercell of the perfect lattice (Fig. 1a). Then we calculate the total energy $E_1$ of the same supercell, but with an NPD (Fig. 1b). Ideally the formation energy is $\Delta E = (E_1 + E_2 - E_0) - T(S_1 + S_2 - S_0)$, where $T$ is the temperature, $S_0$ and $S_1$ are, respectively, the entropies of the ideal and defective supercell, and $E_2$ and $S_2$ are, respectively, the final state energy and entropy of the atomic defect (Fig. 1c). Since the entropy difference between the ideal and defective SLS, due mainly to phonons, is small, we can approximate $\Delta E = (E_1 - E_0)$ as the free energy difference between the ideal and defective lattice. The free energy of atomic defect, $E_2 - T S_2$, depends on the growth condition. For example, in the case of In-vacancy, final state energy of the removed In atom depends on overpressure conditions, such as In-rich or As-rich, and the structure of the In solid. However, these conditions and energies would be the same whether the In is removed from bulk InAs or from the InAs-GaSb SLS. We calculate $\Delta E$ in bulk and SLS, respectively, and denote their values as $\Delta E_{\text{bulk}}$ and $\Delta E_{\text{SLS}}$.

To ensure the reliability of our results for the SLS study, first we calculate $\Delta E$ for various NPDs in bulk GaAs, where many theoretical and experimental values are available in the literature. To calculate the formation energy of an NPD in a bulk compound, we need to evaluate the chemical potential for Ga and As. For example, to antisite $\text{As}_{\text{Ga}}$, we calculate the total energy of a large structure with such a defect and its energy difference from that of the defect-free structure. In addition, we must calculate the chemical potential of solid Ga and solid As. For the formation energy in the As-rich environment, the chemical potential of As is set as the value of solid As, and the chemical potential for Ga is the difference between chemical potentials for GaAs and As. Similarly, in the Ga-rich environment, the chemical potential of Ga is set as the value of solid Ga, and the chemical potential for As is the difference between chemical potentials GaAs and Ga. As shown in Table I, we see that the calculated values for four NPDs in GaAs agree very well with those obtained by other accurate methods.\textsuperscript{5,7} Here both the experimental and theoretical values

**TABLE I.** Calculated defect formation energies in bulk GaAs under two extreme growth conditions, compared with corresponding values from Refs. 6-10. Also given are the literature values for GaSb and InAs. Energies are in eV.

<table>
<thead>
<tr>
<th>Defect</th>
<th>GaAs As-rich</th>
<th>GaAs As-rich</th>
<th>GaAs Ga-rich</th>
<th>GaAs Ga-rich</th>
<th>GaSb Sb-rich</th>
<th>GaSb Ga-rich</th>
<th>InAs In-rich</th>
<th>InAs In-rich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Refs. 6-10</td>
<td>This work</td>
<td>Refs. 6,15</td>
<td>Ref. 12</td>
<td>Ref. 12</td>
<td>Ref. 14</td>
<td>Refs. 13,14</td>
</tr>
<tr>
<td>$a_c$</td>
<td>1.664</td>
<td>1.4-1.51</td>
<td>3.29</td>
<td>3.7</td>
<td>1.83</td>
<td>2.76</td>
<td>2.12</td>
<td>1.25-1.33</td>
</tr>
<tr>
<td>$c_a$</td>
<td>3.265</td>
<td>3.74-4.1</td>
<td>1.639</td>
<td>1.9</td>
<td>2.3</td>
<td>1.37</td>
<td>1.75</td>
<td>2.49-2.63</td>
</tr>
<tr>
<td>$V_A$</td>
<td>3.209</td>
<td>3.2-4.1</td>
<td>2.396</td>
<td>2.5-2.9</td>
<td>3.5</td>
<td>3.03</td>
<td>2.1</td>
<td>2.60-2.64</td>
</tr>
<tr>
<td>$V_c$</td>
<td>3.547</td>
<td>2.75-3.2</td>
<td>4.36</td>
<td>4.3</td>
<td>2.5</td>
<td>2.97</td>
<td>–</td>
<td>2.7 [Ref. 13]</td>
</tr>
</tbody>
</table>
used for comparison with our calculations are for neutral defects. Since our Green’s function-based
defect-level calculations are limited to neutral defects, we focused only on charge-neutral defects
here.

Having confirmed that our method of calculating NPD formation energies yields reasonable
agreement with previous elaborate calculations, we extend our study to the NPD formation in SLSs.
We consider supercells made of as many as 4032 atoms containing 36 cells of the chosen superlattice
and calculate the total energy. Then we consider the same supercell but with an NPD and calculate
the total energy. Table II lists the energy differences, $\Delta E_{\text{SLS}}$, for eight NPDs—anion (As or Sb) vacancy ($V_a$), cation (Ga or In) vacancy ($V_c$), anion antisite ($a_n$) and cation antisite ($c_n$) — in a number of InAs ($n$ mL)-GaSb ($m$ mL) SLS systems (denoted as $n/m$), where $n$ and $m$ are the number of monolayers (MLs). All energies are in eV. The actual formation energy can be calculated from the values of Table II by subtracting the free energy of atomic defect, ($E_\text{f}-TS_\text{f}$), appropriate for a given growth condition.

For the case of bulk materials, the energy and the entropy of an atomic defect are determined
by whether the growth is in anion-rich, cation-rich, or partial vapor pressure conditions. For the SLS
growth, the choice is complicated and is not clear because of the presence of four (Ga, In, As, and Sb)
different atoms. So, instead of calculating the formation energies under various growth conditions,
we calculate the energy difference, ($\Delta E_{\text{SLS}} - \Delta E_{\text{bulk}}$), for each SLS design. This energy difference is
closely related to the difference in defect formation energies between the SLS and the bulk material.
If the SLS and the bulk compound are grown under identical growth conditions, the formation energy
in SLS is simply the sum of ($\Delta E_{\text{SLS}} - \Delta E_{\text{bulk}}$) and the formation energy of that defect in the bulk
(given in Table I for GaSb and InAs for anion and cation rich conditions). Table III lists the calculated
difference energy, ($\Delta E_{\text{SLS}} - \Delta E_{\text{bulk}}$), for eight NPDs in a number of SLSs. We see that the formation
energy difference depends on both the NPD type and the SLS structure and its value can be as high
as a few eV. A negative value in the table indicates that the defect in the SLS is easier to form
than in the bulk, under identical growth conditions. Conversely, a positive value indicates that the
defect in the SLS is more difficult to form than in the bulk. For example, the formation of $A_{\text{Sn}}$ is
easier in InAs (6 ML)/GaSb (4 ML) SLS than in bulk InAs by $\sim0.15$ eV. The comparison across
the columns gives the likelihood of a defect in one SLS versus the other under the same growth
condition.

<table>
<thead>
<tr>
<th>InAs (n ML)/GaSb (m ML)</th>
<th>6/4</th>
<th>8/8</th>
<th>8/16</th>
<th>16/8</th>
<th>17/8</th>
<th>18/8</th>
<th>24/4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{Sn}}$</td>
<td>−0.15</td>
<td>−0.66</td>
<td>−3.03</td>
<td>−1.23</td>
<td>−1.15</td>
<td>−0.52</td>
<td>−0.1</td>
</tr>
<tr>
<td>$V_{\text{In}}$</td>
<td>0.96</td>
<td>0.37</td>
<td>−1.98</td>
<td>−0.25</td>
<td>1.58</td>
<td>0.48</td>
<td>1.02</td>
</tr>
<tr>
<td>$S_{\text{bg}}$</td>
<td>0.27</td>
<td>−0.5</td>
<td>−2.68</td>
<td>−1.21</td>
<td>−1.2</td>
<td>−0.5</td>
<td>−0.9</td>
</tr>
<tr>
<td>$V_{\text{Ga}}$</td>
<td>−0.82</td>
<td>−1</td>
<td>−2.25</td>
<td>−1.56</td>
<td>−1.44</td>
<td>−0.91</td>
<td>−1.02</td>
</tr>
<tr>
<td>$I_{\text{As}}$</td>
<td>1.18</td>
<td>0.49</td>
<td>−1.88</td>
<td>0.078</td>
<td>−0.11</td>
<td>0.5</td>
<td>0.95</td>
</tr>
<tr>
<td>$V_{\text{As}}$</td>
<td>2.34</td>
<td>1.73</td>
<td>−0.64</td>
<td>1.01</td>
<td>1.03</td>
<td>1.71</td>
<td>1.93</td>
</tr>
<tr>
<td>$G_{\text{As}}$</td>
<td>−1.22</td>
<td>−1.34</td>
<td>−3.14</td>
<td>−2.09</td>
<td>−1.64</td>
<td>−1.4</td>
<td>−1.57</td>
</tr>
<tr>
<td>$V_{\text{Sb}}$</td>
<td>−0.42</td>
<td>−0.6</td>
<td>−2.98</td>
<td>−1.31</td>
<td>−1.04</td>
<td>−0.61</td>
<td>−0.75</td>
</tr>
</tbody>
</table>
We emphasize that the strains are relatively weak in the system—InAs-GaSb SLSs lattice-matched to GaSb—a studied here. The lattice constants of GaSb and InAs are 6.096 and 6.058 Å and SLS structure along the growth direction is allowed to relax to achieve a minimal stress. For the values listed in Tables II–IV, the defects are located in the middle of the each compound region, i.e., have the largest distance from interfaces. We did not study defect format at the interfaces because the defects form chemical bonding with two different compound materials and the reference bulk energy for formation-energy deviation is not well-defined.

We make the following observations:

1. The change in formation energy in the GaSb region is more negative in SLSs with thick GaSb layers. For example, in InAs (8 ML)/GaSb (16 ML), the difference in formation energy is -2.09 eV for GaSb, -2.25 eV for VGa, -2.68 eV for SbGa, and -2.96 eV for VSB. These large negative values indicate that these defects are more likely to form in SLS. They become less negative when the GaSb thickness decreases, as in the case of InAs (24 ML)/GaSb (4 ML), where the corresponding deviations are -1.57 eV, -1.02 eV, -0.09 eV, and -0.75 eV. This indicates the preference to SLS with thin GaSb layers to reduce GaSb-originated defects.

2. The presence of GaSb, however, does not always decrease the NPD formation energy. In fact, the GaSb layer increases the formation energy of NPDs in the InAs region and makes these NPDs unlikely to form. For example, in InAs (24 ML)/GaSb (4 ML), the formation-energy deviation is -0.1 eV for AsIn, 1.93 eV for VAs, 0.95 eV for InAs, and 1.02 eV for VIn. Except for AsIn, the other NPDs will be much harder to form.

3. For all InAs-GaSb SLSs considered in Table III, the change in formation energy for GaSb and AsIn antisites are both negative, indicating that they are easier to form in SLS than in bulk. Noting from Table I that antisites in bulk GaSb are easy to form, we conclude the antisites are most likely defects in these SLSs as well.

4. In general, the deviation for GaSb is more negative than for AsIn. Thus based on the formation energy alone, GaSb is the most damaging NPD in SLSs. From the results listed in Table III, SLS structures with a thinner GaSb layer is better than those with a thicker GaSb layer because the latter have more negative change in formation energy.

Recently we calculated defect levels of a variety of InAs-GaSb SLSs using the hybrid approach and have listed these values in Table IV for the systems considered here. We note:

(a) Among these structures, the right four columns have fewer defect levels than the left four columns. In the right four structures, the defect levels have GaSb-origin—mainly VGa, GaSb, and VSB. Since GaSb is the easiest to form, we should use a structure with the largest possible formation energy for the GaSb defect. Hence, after adding the formation energy values in the bulk material (Table I) to the corresponding defect formation energy in Table III, we find 18/8 SLS has the largest formation energy of the GaSb defect.

(b) The 18/8 SLS is additionally a good candidate because of the higher formation energies of VGa, and VSB.

TABLE IV. Defect levels of SLS NPDs. All energies, in meV, are with respect to the SLS valence band.

<table>
<thead>
<tr>
<th>InAs (n ML)/GaSb (m ML)</th>
<th>6/4</th>
<th>8/8</th>
<th>8/16</th>
<th>16/8</th>
<th>17/8</th>
<th>18/8</th>
<th>24/4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eg</td>
<td>350</td>
<td>300</td>
<td>320</td>
<td>120</td>
<td>97</td>
<td>97</td>
<td>120</td>
</tr>
<tr>
<td>AsIn</td>
<td>–</td>
<td>255, 298</td>
<td>311</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>VIn</td>
<td>–</td>
<td>43, 67</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SbGa</td>
<td>91</td>
<td>2, 132</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>VGa</td>
<td>29, 49</td>
<td>9, 76, 106,</td>
<td>127</td>
<td>10</td>
<td>22</td>
<td>8</td>
<td>10, 15</td>
</tr>
<tr>
<td>VAs</td>
<td>205, 211</td>
<td>285, 296</td>
<td>5, 57, 311</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>GaSb</td>
<td>8, 13</td>
<td>53</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>16, 25</td>
</tr>
<tr>
<td>VSB</td>
<td>257, 313</td>
<td>2</td>
<td>278</td>
<td>–</td>
<td>–</td>
<td>10, 12</td>
<td>0</td>
</tr>
</tbody>
</table>

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(c) We see that 16/8 SLS and 17/8 SLS have very similar defect level distributions. However, 17/8 has higher formation energies for $V_{Ga}$, $Ga_{Sb}$, and $V_{Sb}$ defects, which makes the 17/8 design more desirable than the 18/8 SLS.

(d) Sb$_{Ga}$ and $V_{Ga}$ produce mid-gap states (shown in bold in Table IV) in 8/8 SLS and 24/4 SLS, respectively, and the corresponding formation energies of 2.26 eV and 1.97 eV are moderate enough to create a sizable density of defects. We can expect the lifetimes in these designs to be highly limited by SRH mechanism.

In summary, we have studied the formation energies of NPDs in a number of SLSs with gaps in mid-wave and long-wave IR spectral regions. The formation energy of an NPD in SLSs is quite different from its value in compound semiconductors. This design-dependent deviation can be exploited to select a design with fewer of the defects that are known to produce undesired mid-gap energy levels. The calculated formation energy, together with the results on defect levels, is helpful in designing an SLS structure for photodetectors.

This work was supported by the United States Air Force under Contract FA8650-11-D-5800/TO 0008) through a Universal Technology Corporation subcontract (#14-S7408-02-C1).

4. R. N. Hall, Phys. Rev. 83, 228 (1951); 87, 387 (1952).