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

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Formation energies of native point defects in strained-layer superlattices

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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. [http://dx.doi.org/10.1063/1.4985136]

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.[1] However, the measured carrier lifetimes in SLSs for infrared (IR) detection are extremely short,[2,3] owing to strong Shockley-Read-Hall (SRH) recombination[4,5] 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,[6–10] GaSb,[11,12] and InAs[13–15] 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,[16] 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,[17] 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[18] to calculate the defect energy levels. These calculations, which employ only a minimal basis set of *sp*^{3} orbitals, predicted SLS defect levels in good agreement with measurements.[19] While these calculations predicted more defect states to have a GaSb origin, consistent with the observation in Ga-free systems,[20] 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.

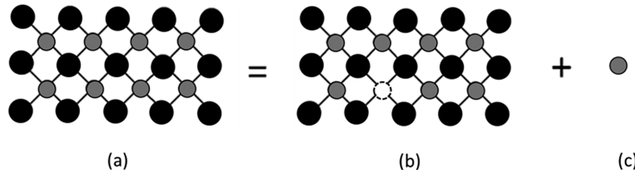

FIG. 1. The initial (a) perfect lattice state transforms to (b) lattice with a vacancy (dotted circle) and (c) final state of the removed atom.

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,[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 $[(E_1 + E_2 - E_0) - T (S_1+S_2-S_0)]$, 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-TS_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 ΔE in bulk and SLS, respectively, and denote their values as $(\Delta E)_{bulk}$ and $(\Delta E)_{SLS}$.

To ensure the reliability of our results for the SLS study, first we calculate ΔE 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 As_{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.[6,7] 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.

Defect	GaAs As-rich This work	GaAs As-rich Refs. 6–10	GaAs Ga-rich This work	GaAs Ga-rich Refs. 6,15	GaSb Sb-rich Ref. 12	GaSb Ga-rich Ref. 12	InAs In-rich Ref. 14	InAs As-rich Refs. 13,14
a_c	1.664	1.4-1.51	3.29	3.7	1.83	2.76	2.12	1.25-1.33
c_a	3.265	3.74-4.1	1.639	1.9	2.3	1.37	1.75	2.49-2.63
V_a	3.209	3.2-4.1	2.396	2.5-2.9	3.5	3.03	2.1	2.60-2.64
V_c	3.547	2.75-3.2	4.36	4.3	2.5	2.97	–	2.7 [Ref. 13]

TABLE II. Calculated total energy difference between a 6x6 perfect supercell and the supercell with an NPD.

InAs (*n* ML)/GaSb (*m* ML)	6/4	8/8	8/16	16/8	17/8	18/8	24/4
As_{In}	121.23	120.73	118.35	120.16	120.23	120.86	121.28
V_{in}	289.05	288.46	286.12	287.84	289.67	288.58	289.11
Sb_{Ga}	−89.94	−90.71	−92.88	−91.42	−91.41	−90.7	−90.3
V_{Ga}	62.07	61.89	60.64	61.33	61.45	61.98	61.88
In_{As}	−123.36	−124.05	−126.42	−124.47	−124.66	−124.05	−123.59
V_{As}	164.84	164.23	161.87	163.52	163.53	164.22	164.44
Ga_{Sb}	91.82	91.7	89.9	90.95	91.41	91.64	91.47
V_{Sb}	154.28	154.1	151.72	153.39	153.66	154.09	153.95

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, ΔE_{SLS}, for eight NPDs—anion (As or Sb) vacancy (V_a), cation (Ga or In) vacancy (V_c), anion antisite (a_c) and cation antisite (c_a) — 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_2-TS_2), 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, (ΔE_{SLS} - ΔE_{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 (ΔE_{SLS} - ΔE_{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 energy difference, (ΔE_{SLS} - ΔE_{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 As_{In} is easier in InAs (6 ML)/GaSb (4 ML) SLS than in bulk InAs by ~ -0.15 eV. The comparison across the columns gives the likelihood of a defect in one SLS versus the other under the same growth condition.

TABLE III. Deviation of formation energy SLS NPDs from its bulk value.

InAs (*n* ML)/GaSb (*m* ML)	6/4	8/8	8/16	16/8	17/8	18/8	24/4
As_{In}	−0.15	−0.66	−3.03	−1.23	−1.15	−0.52	−0.1
V_{in}	0.96	0.37	−1.98	−0.25	1.58	0.48	1.02
Sb_{Ga}	0.27	−0.5	−2.68	−1.21	−1.2	−0.5	−0.09
V_{Ga}	−0.82	−1	−2.25	−1.56	−1.44	−0.91	−1.02
In_{As}	1.18	0.49	−1.88	0.078	−0.11	0.5	0.95
V_{As}	2.34	1.73	−0.64	1.01	1.03	1.71	1.93
Ga_{Sb}	−1.22	−1.34	−3.14	−2.09	−1.64	−1.4	−1.57
V_{Sb}	−0.42	−0.6	−2.98	−1.31	−1.04	−0.61	−0.75

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 A 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 Ga_{Sb}, -2.25 eV for V_{Ga}, -2.68 eV for Sb_{Ga}, and -2.96 eV for V_{Sb}. 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 As_{In}, 1.93 eV for V_{As}, 0.95 eV for In_{As}, and 1.02 eV for V_{In}. Except for $As_{In,}$ 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 Ga_{Sb} and As_{In} 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 Ga_{Sb} is more negative than for As_{In}. Thus based on the formation energy alone, Ga_{Sb} 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[13] using the hybrid approach[11] 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 V_{Ga}, Ga_{Sb}, and V_{Sb}. Since Ga_{Sb} is the easiest to form, we should use a structure with the largest possible formation energy for the Ga_{Sb} 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 Ga_{Sb} defect.

(b) The 18/8 SLS is additionally a good candidate because of the higher formation energies of V_{Ga}, and V_{Sb}.

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

InAs (*n* ML)/GaSb (*m* ML)	6/4	8/8	8/16	16/8	17/8	18/8	24/4
Eg	350	300	320	120	97	97	120
As_{In}	–	255, 298	311	–	–	–	–
V_{in}	–	43, 67	–	–	–	–	–
Sb_{Ga}	91	2, **132**	–	–	–	–	–
V_{Ga}	29, 49	9, 76, 106, **127**	10	22	8	10, 15	39, 44, **66**
In_{As}	–	–	–	–	–	–	–
V_{As}	**205**, 211	285, 296	5, 57, 311	–	–	–	–
Ga_{Sb}	8, 13	53	10	10	0	–	16, 25
V_{Sb}	257, 313	2	278	–	–	10, 12	0

(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 the18/8 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.

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