

## AFRL-RX-WP-JA-2017-0440

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

Zhi Gang Yu

Washington State University

S. Krishnamurthy

**SRI International** 

12 September 2017 Interim Report

> Distribution Statement A. Approved for public release: distribution unlimited.

© 2017 AIP PUBLISHING

(STINFO COPY)

AIR FORCE RESEARCH LABORATORY MATERIALS AND MANUFACTURING DIRECTORATE WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750 AIR FORCE MATERIEL COMMAND UNITED STATES AIR FORCE

REPOR		Form Approved OMB No. 0704-0188							
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. <b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS</b> .									
1. REPORT DATE (DD-MM-YY)		2. REPORT TYPE		3. DATES COVERED (From - To)					
12 September 2017	7	Inter	im	11 Septemb	ber 2013 – 31 May 2017				
4. TITLE AND SUBTITLE	•			5a. CONTRACT NUMBER					
FORMATION ENERGIE	S OF NAT	TIVE POINT DEF	ECTS IN	FA8650-1	1-D-5800-0008				
STRAINED-LAYER SUP	ERLATT	ICES (POSTPRIN	JT)	5b. GRANT NUN	IBER				
				<b>5c. PROGRAM ELEMENT NUMBER</b> 62102F					
6. AUTHOR(S)				5d. PROJECT NUMBER					
1) Zhi Gang Yu –	2	) S. Krishnamurth	iy –	4348					
WSU		SRI Internationa	.1	5e. TASK NUMBER 0008					
				5f. WORK UNIT NUMBER					
				X0TW					
7. PERFORMING ORGANIZATION N	IAME(S) AN	D ADDRESS(ES)		8. PERFORMING	GORGANIZATION REPORT NUMBER				
1) Washington State Univer	rsity 2	) SRI Internation	al	AFRL	/RX				
410 E Spokane Falls Blv	d.	333 Ravenswoo	od Ave.	Wrigh	t Patterson Air Force Base				
Spokane, WA 99202		Menlo Park, CA	A 94025	Daytor	n, OH 45433				
9. SPONSORING/MONITORING AG	ENCY NAMI	E(S) AND ADDRESS(E	ES)	10. SPONSORING/MONITORING AGENCY ACRONYM(S)					
Air Force Research Laborato	ry			AFRL/RX	AN				
Materials and Manufacturing	Directorate	F	11. SPONSORIN	G/MONITORING AGENCY					
Wright-Patterson Air Force Base, OH 45433-7750				REPORT NU	MBER(S)				
United States Air Force	1		AFRL-RA	K-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 word	ds)	1 0 1							
We develop a theoretical appr tachniques to obtain energy lo	roach that e	mploys first-princip	les Hamiltonian,	tight-binding H	amiltonian, and Green's function				
superlattice (SLS) systems. In	n particular.	we consider 4 types	of NPDs –anion	i mAs-Gaso and	n vacancy, anion anti-site, cation				
anti-site, isoelectronic substitu	ution at ani	on sites (Sb at As sit	e and As at Sb si	(te) - in the InA	As, 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 InAs1 $_{x}$ 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 lettice metabol to GaSb substrate. The coloulated defect levels not only agree will with swellable metabolic states in the levels of the second states in the seco									
the connection between mid-gap levels and specific NPDs. We further calculate defect formation energies both in compounds									
and for all superlattices consid	dered above	e.							
15. SUBJECT TERMS									
Hamiltonian; Green's function	on; InAs/In/	As <sub>0.7</sub> Sb <sub>0.3;</sub> strained la	yer superlattice (	SLS); GaSb; an	ion; cation; alloy region				
16. SECURITY CLASSIFICATION OI	<u></u>	18. NUMBER	19a. NAME OF	RESPONSIBLE PERSON (Monitor)					
a. REPORT b. ABSTRACT c. T	HIS PAGE	SAR	7	Joseph B	urns NE NUMBER (Include Area Code)				
	C1455111CU	~	,	(937) 24	55-9594				



## Formation energies of native point defects in strained-layer superlattices

Zhi-Gang Yu<sup>1</sup> and Srini Krishnamurthy<sup>2</sup> <sup>1</sup>ISP/Applied Sciences Laboratory, Washington State University, Spokane, Washington 99202, USA <sup>2</sup>Applied Optics Laboratory, SRI International, Menlo Park, California 94025, USA

(Received 23 January 2017; accepted 24 May 2017; published online 5 June 2017)

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/). [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.<sup>1</sup> However, the measured carrier lifetimes in SLSs for infrared (IR) detection are extremely short,<sup>2,3</sup> owing to strong Shockley-Read-Hall (SRH) recombination<sup>4,5</sup> 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,<sup>6–10</sup> GaSb,<sup>11,12</sup> and InAs<sup>13–15</sup> 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,<sup>16</sup> 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,<sup>17</sup> 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<sup>18</sup> 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.<sup>19</sup> While these calculations predicted more defect states to have a GaSb origin, consistent with the observation in Ga-free systems,<sup>20</sup> 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.

2158-3226/2017/7(6)/065203/5

7,065203-1







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,<sup>13</sup> 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 lattice. The free energy of atomic defect,  $E_2$ -TS<sub>2</sub>, 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  $(\Delta E)_{bulk}$  and  $(\Delta E)_{SLS}$ .

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 As<sub>Ga</sub>, 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.<sup>6,7</sup> 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 <sub>c</sub>	1.664	1.4-1.51	3.29	3.7	1.83	2.76	2.12	1.25-1.33
ca	3.265	3.74-4.1	1.639	1.9	2.3	1.37	1.75	2.49-2.63
Va	3.209	3.2-4.1	2.396	2.5-2.9	3.5	3.03	2.1	2.60-2.64
Vc	3.547	2.75-3.2	4.36	4.3	2.5	2.97	-	2.7 [Ref. 13]

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

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

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,  $\Delta E_{SLS}$ , for eight NPDs—anion (As or Sb) vacancy (V<sub>a</sub>), cation (Ga or In) vacancy (V<sub>c</sub>), anion antisite (a<sub>c</sub>) and cation antisite (c<sub>a</sub>) — 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<sub>2</sub>-TS<sub>2</sub>), 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,  $(\Delta E_{SLS} - \Delta E_{bulk})$ , 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  $(\Delta E_{SLS} - \Delta E_{Bulk})$  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, ( $\Delta E_{SLS} - \Delta E_{bulk}$ ), 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  $\sim$  -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.

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

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

We emphasize that the strains are relatively weak in the system— InAs-GaSb SLSs latticematched 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 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.
- The presence of GaSb, however, does not always decrease the NPD formation energy. In fact, (2)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<sub>In</sub>, 1.93 eV for V<sub>As</sub>, 0.95 eV for In<sub>As</sub>, and 1.02 eV for V<sub>In</sub>. Except for As<sub>In</sub>, 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<sub>Sb</sub> and As<sub>In</sub> 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<sub>Sb</sub> is more negative than for As<sub>In</sub>. 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 SLSs13 using the hybrid approach<sup>11</sup> and have listed these values in Table IV for the systems considered here. We note:

- Among these structures, the right four columns have fewer defect levels than the left four (a) 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<sub>Sb</sub> 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<sub>Sb</sub> defect.
- (b) The 18/8 SLS is additionally a good candidate because of the higher formation energies of V<sub>Ga</sub>, and V<sub>Sb</sub>.

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 <sub>In</sub>	-	255, 298	311	-	-	-	_
V <sub>in</sub>	-	43, 67	_	-	-	-	_
Sb <sub>Ga</sub>	91	2, <b>132</b>	_	-	-	-	_
V <sub>Ga</sub>	29, 49	9, 76, 106, <b>127</b>	10	22	8	10, 15	39, 44, <b>66</b>
In <sub>As</sub>	_	-	-	-	-	-	_
V <sub>As</sub>	<b>205</b> , 211	285, 296	5, 57, 311	-	-	-	_
Ga <sub>Sb</sub>	8,13	53	10	10	0	-	16, 25
V <sub>Sb</sub>	257, 313	2	278	-	-	10, 12	0

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

- (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<sub>Ga</sub>, Ga<sub>Sb</sub>, and V<sub>Sb</sub> defects, which makes the 17/8 design more desirable than the18/8 SLS.
- (d) Sb<sub>Ga</sub> and V<sub>Ga</sub> 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).

- <sup>1</sup> D. L. Smith and C. Mailhiot, J. Appl. Phys. 62, 2545 (1987); J. Vac. Sci. Tech., A7, 445 (1989).
- <sup>2</sup> J. Pellegrino and R. DeWames, Proc. SPIE, **7298**, 72981U (2009).
- <sup>3</sup> D. Rhiger, R. E. Kvaas, S. F. Harris, and C. J. Hill, Infrared Physics & Technology 52 304 (2009).
- <sup>4</sup> R. N. Hall, Phys. Rev. **83**, 228 (1951); **87**, 387 (1952).
- <sup>5</sup> W. Shockley and W. T. Read, Phys. Rev. 87, 835 (1952).
- <sup>6</sup>H.-P. Komsa and A. Pasquarello, J. Phys.: Condens. Matter 24, 045801 (2012).
- <sup>7</sup> P. A. Schultz and O. A. von Lilienfeld, Modell. Simul. Mater. Sci. Eng. 17, 084007 (2009).
- <sup>8</sup> P. A. Schultz, Sandia Report, SAND2012–2675 (2012).
- <sup>9</sup> J. E. Northrup and S. B. Zhang, Phys. Rev. B 47, 6791 (1993).
- <sup>10</sup> J. I. Landman, C. G. Morgan, J. T. Schick, P. Papoulias, and A. Kumar, Phys. Rev. B 55, 15581 (1997).
- <sup>11</sup> M. Hakala, M. J. Puska, and R. M. Nieminen, J. Appl. Phys. **91**, 4988 (2002).
- <sup>12</sup> V. Virkkala, V. Havu, F. Tuomisto, and M. J. Puska, Phys. Rev. B 86, 144101 (2012).
- <sup>13</sup> P. A. Schultz, Sandia Report, SAND2013–2477 (2013).
- <sup>14</sup> A. Hoglund, C. W. M. Castleton, N. Gothelid, B. Johansson, and S. Mirbt, Phys. Rev. B 74, 075332 (2006).
- <sup>15</sup> S. T. Murphy, A. Chroneos, R. W. Grimes, C. Jiang, and U. Schwingenschlogl, Phys. Rev. B 84, 184108 (2011).
- <sup>16</sup> E.-G. Wang and D.-S. Wang, J. Phys. Cond. Matter 4, 1311 (1992).
- <sup>17</sup> S. Krishnamurthy, D. van Orden, and Z.-G. Yu, J. of Electron. Mater. 45, 4574 (2016).
- <sup>18</sup> http://www.icmab.es/dmmis/leem/siesta/; see also, J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordej on, and D. Sanchez-Portal, J. Phys. Condens. Matter 14, 2745 (2002).
- <sup>19</sup> S. Krishnamurthy and Z. G. Yu, Appl. Phys. Lett. 110, 021113 (2017).
- <sup>20</sup> S. P. Svensson, D. Donetsky, D. Wang, P. Maloney, and G. Belenky, Proc. SPIE **7660**, 76601V (2010).