Supporting Information for: Quantum Confinement in Group III-V Semiconductor 2D Nanostructures

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1. Atomic connectivity at the surface layers

The (110) surface of the group III-V semiconductors was studied at the DFT/HSE06 level[1,2] of theory as implemented in CRYSTAL17 code.[3]

In Figure S1 is shown a schematic representation of the surface layer upon full geometry optimization of the slabs, and in Table S1 we report the calculated values describing the atomic connectivity for all the materials. We see that the local coordination of atoms of the surface layer is different from that of inner slabs. The values are compared with available previous theoretical data obtained with comparable thickness of the surface models, see Table S2.

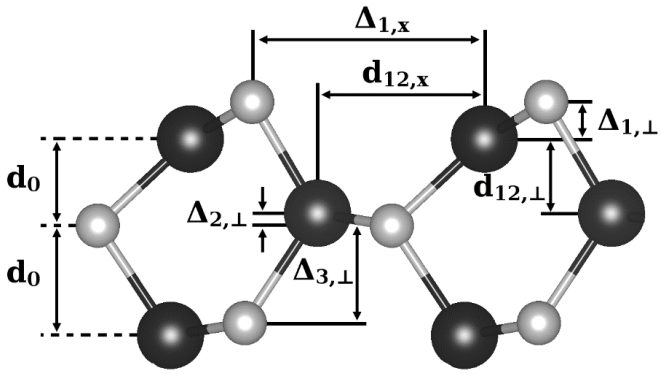

Figure S1. Surface termination of the relaxed (110) surfaces in the group III-V semiconductors. Black dots represent the III-group elements and grey dots the V-group elements.

Table S1. Geometrical parameters of 12-atomic layers thick group III-V (110) surfaces layers at the relaxed geometry. Values are in Å.

material	$\Delta_{1,x}$	$\Delta_{1,\perp}$	$\Delta_{2,\perp}$	$\Delta_{3,\perp}$	$d_{12,x}$	$d_{12,\perp}$
AlP	4.31	0.58	0.10	1.99	3.09	1.45
AlAs	4.48	0.69	0.12	2.08	3.26	1.45
AlSb	4.85	0.81	0.14	2.24	3.56	1.52
GaP	4.33	0.63	0.11	2.01	3.13	1.43
GaAs	4.49	0.72	0.13	2.09	3.27	1.45
GaSb	4.82	0.81	0.15	2.24	3.54	1.55
InP	4.66	0.68	0.14	2.16	3.36	1.54
InAs	4.81	0.75	0.16	2.24	3.50	1.57
InSb	5.14	0.88	0.21	2.40	3.77	1.60

Table S2. Geometrical parameters of the group III-V (110) surfaces, 11 atomic layers thick taken from the Literature. Values are in Å.

material	$\Delta_{1,x}$	$\Delta_{1,\perp}$	$\Delta_{2,\perp}$	$\Delta_{3,\perp}$	$d_{12,x}$	$d_{12,\perp}$
AlAs	4.46[a]	0.71[a]	0.11[a]	1.94[a]	3.26[a]	1.41[a]
GaP	4.26[a,b]	0.58[a], 0.61[b]	0.08[a], 0.10[b]	1.88[a]	3.06[a,b]	1.44[a], 1.37[b]
GaAs	4.38[a], 4.41[b]	0.67[a,b]	0.10[a,b]	1.95[a]	3.18[a], 3.19[b]	1.47[a], 1.42[b]
InP	4.62[a], 4.52[b]	0.66[a], 0.67[b]	0.11[a], 0.12[b]	2.04[a]	3.34[a], 3,22[b]	1.57[a], 1.44[b]
InAs	4.77[a], 4.66[b]	0.74[a], 0.75[b]	0.13[a,b]	2.09[a]	3.48[a], 3.40[b]	1.57[a], 1.45b

See references as: a[4] (non-local pseudopotential level) and b[5] (8 atomic layers at LDA level).

We see that our result are in good agreement with the previous works,[4–8] where it was suggested that the top anions move outward in favor of an s^2p^3 bonding with three neighboring cations, while the cations move inward favoring a sp^2 bonding with three anions neighboring in the surface plane.[4,8]

We now want to look at the impact of model's thickness to the surface structural effects. To do so, we compare results arising from difference slabs thickness (4, 8, 12, and 40 atomic layers) for some selected case as InP, InAs.

Table S3. Geometrical changes on the In-V (110) surfaces as a function of layers number (L).

material	$\Delta_{1,x}$	$\Delta_{1,\perp}$	$\Delta_{2,\perp}$	$\Delta_{3,\perp}$	$d_{12,x}$	$d_{12,\perp}$
InP 4L	4.62	0.74	0.24	2.18	3.32	1.47
InP 8L	4.65	0.69	0.15	2.16	3.35	1.54
InP 12L	4.66	0.68	0.14	2.16	3.36	1.54
InP 40L	4.66	0.68	0.13	2.16	3.36	1.54
InAs 4L	4.73	0.82	0.30	2.27	3.43	1.50
InAs 8L	4.79	0.75	0.17	2.25	3.49	1.58

InAs 12L	4.81	0.75	0.16	2.24	3.50	1.57
InAs 40L	4.82	0.74	0.16	2.24	3.50	1.57

From Table S3 we observe that when taking sufficiently thick models significant geometric changes are not present with the increase of surface thickness. Indeed, when taking 8 atomic layers or more, we do not see significant variation in the atomic connectivity, while we see significant changes in the geometry properties – around 0.05 Å for every bond length in the case of thinner slabs.

2. Thickness dependence

The impact of (110) slabs thickness to the structural and electronic properties of the materials has been investigated. Lattice parameters, band gaps, and band edges positions have been taken from optimized structures. The surface energy has been calculated as reported in Equation S1, where E_{slab} is the total energy of the optimized slab, E_{bulk} is the bulk's total energy, and n is the coefficient equal to the ratio between the number of atoms contained in the slab and bulk models. For semiconductors with indirect band gaps and heavy electron mass (GaP, AlP, AlAs, AlSb), we observed that after 8 atomic layers (~ 3nm) the surface properties are nearly converged. However, with semiconductor that have direct band gap and light electron mass (GaAs, GaSb, InP, InAs, and InSb) a higher thickness is necessary to reproduce the bulk band gaps. For the materials with indirect band gaps, contribution in the band gaps due surfaces states was accounted.

$$E_s = \frac{E_{slab} - nE_{bulk}}{2A} \quad \text{Eq. (S1)}$$

a) AlP

In Table S4, the Structural and electronic properties are reported as a function of the slab thickness. In the case of AlP (110) surfaces, we observed the contribution of surface states ~0.35 eV.

Table S4. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of AlP (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

layers	Thickness (Å)	a (Å)	b (Å)	γ (°)	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	6.26	3.8351	5.3500	90	2.41	20.52	1.21	6.26
8	13.92	3.8572	5.4240	90	2.44	20.92	1.23	6.22
12	21.63	3.8639	5.4375	90	2.44	21.01	1.24	6.22
16	29.36	3.8674	5.4425	90	2.46	21.05	1.25	6.21
bulk		3.8659	5.4671		2.52			

b) AlAs

In Table S5, the Structural and electronic properties are reported as a function of the slab thickness. In the case of AlP (110) surfaces, we observed the contribution of surface states ~0.50 eV.

Table S5. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of AlAs (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

n	Thickness (Å)	a (Å)	b (Å)	γ (°)	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	6.62	3.9649	5.5322	90	2.04	21.93	0.98	5.45
8	14.55	3.9961	5.6260	90	2.25	22.48	0.99	5.46
12	22.56	4.0065	5.6395	90	2.28	22.59	1.00	5.47
16	30.57	4.0117	5.6446	90	2.28	22.64	1.01	5.48
bulk		4.0122	5.6741		2.38			

c) AlSb

In Table S6, the Structural and electronic properties are reported as a function of the slab thickness. In the case of AlSb (110) surfaces, we observed the contribution of surface states ~0.70 eV.

Table S6. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of AlSb (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

layers	Thickness (Å)	a (Å)	b (Å)	γ	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	7.26	4.2796	5.9479	90	2.03	25.45	0.82	4.53
8	15.77	4.3210	6.0882	90	2.10	26.31	0.83	4.57
12	24.43	4.3335	6.1020	90	2.12	26.44	0.83	4.58
16	33.10	4.3398	6.1068	90	2.14	26.50	0.84	4.59
bulk		4.3392	6.1365		2.19			

d) GaP

In Table S7, the Structural and electronic properties are reported as a function of the slab thickness. In the case of GaP (110) surfaces, we observed the contribution of surface states ~0.46 eV.

Table S7. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of GaP (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

layers	Thickness (Å)	a (Å)	b (Å)	γ	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	6.35	3.8465	5.4145	90	2.32	20.83	0.94	5.60
8	14.05	3.8720	5.4639	90	2.32	21.16	0.96	5.57
12	21.80	3.8809	5.4706	90	2.36	21.23	0.97	5.58
16	29.56	3.8853	5.4734	90	2.37	21.27	0.98	5.59
bulk		3.8829	5.4913		2.46			

e) GaAs

In Table S8 are reported all the electronic and geometrical properties of GaAs (110) as a function of the thickness.

Table S8. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of GaAs (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

layers	Thickness (Å)	a (Å)	b (Å)	γ	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	6.70	4.9920	5.5793	90	1.66	22.27	0.73	4.86
8	14.68	4.0251	5.6620	90	1.54	22.79	0.74	4.85
12	22.73	4.0357	5.6731	90	1.54	22.90	0.75	4.86
16	30.79	4.0406	5.6767	90	1.55	22.94	0.76	4.87
20	38.86	4.0439	5.6783	90	1.49	22.96	0.77	4.86
30	59.03	4.0479	5.6795	90	1.42	22.99	0.79	4.85
40	78.81	4.0448	5.6969	90	1.39	23.04	0.80	4.86
bulk		4.0354	5.7070		1.29			

f) GaSb

In Table S9 are reported all the electronic and geometrical properties of GaSb (110) as a function of the thickness.

Table S9. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of GaAs (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

layers	Thickness (Å)	a (Å)	b (Å)	γ	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	7.29	4.2992	5.9714	90	1.26	25.67	0.65	4.09
8	15.83	4.3366	6.0914	90	1.18	26.42	0.66	4.10
12	24.49	4.3474	6.1009	90	1.14	26.52	0.66	4.10
16	33.16	4.3527	6.1041	90	1.10	26.57	0.66	4.11
20	41.87	4.3555	6.1045	90	1.01	26.59	0.67	4.08
30	63.57	4.3595	6.1068	90	0.90	26.62	0.68	4.08
40	84.75	4.3618	6.1293	90	0.84	26.73	0.70	4.10
bulk		4.3419	6.1406		0.8			

g) InP

This semiconductor represents the first example of In-based materials. In Table S10 are reported all the electronic and geometrical properties of GaSb (110) as a function of the thickness.

Table S10. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of InP (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

layers	Thickness (Å)	a (Å)	b (Å)	γ	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	6.85	4.1418	5.8484	90	2.16	24.22	0.75	5.46
8	15.16	4.1687	5.8866	90	2.03	24.54	0.76	5.43
12	23.51	4.1768	5.8918	90	1.92	24.61	0.77	5.44
16	31.87	4.1811	5.8930	90	1.86	24.64	0.78	5.44
20	40.23	4.1836	5.8943	90	1.82	24.66	0.79	5.44
30	61.14	4.1874	5.8961	90	1.75	24.69	0.81	5.43
40	82.06	4.1904	5.8979	90	1.71	24.71	0.82	5.43
bulk		4.1810	5.9128		1.68			

h) InAs

In Table S11 are reported the lattice parameters and electronic properties of InAs (110) as a function of the thickness.

Table S11. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of InAs (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

layers	Thickness (Å)	a (Å)	b (Å)	γ	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	7.20	4.2866	6.0021	90	1.82	25.73	0.61	5.45
8	15.78	4.3204	6.0759	90	1.32	26.25	0.62	5.42
12	24.41	4.3304	6.0908	90	1.12	26.38	0.63	5.42
16	33.07	4.3357	6.0948	90	1.01	26.43	0.63	5.42
20	41.73	4.3391	6.0938	90	0.93	26.44	0.64	5.41
30	63.38	4.3441	6.0954	90	0.81	26.48	0.67	5.38
40	84.99	4.3436	6.1005	90	0.75	26.50	0.68	5.38
bulk		4.3308	6.1247		0.68			

i) InSb

Finally, in Table S12, we shown the computed values of the surface properties properties of InSb (110) as a function of the thickness.

Table S12. Lattice vectors (*a* and *b*, in Å), lattice angle (γ), band gap (E_g, in eV), surface area (A, in Å²), surface energy (E_s, in J/m²), and ionization potential (ϕ, in eV) of InSb (110) slabs as a function of the thickness. In the last row are reported the bulks lattice parameters and band gap for comparison.

layers	Thickness (Å)	a (Å)	b (Å)	γ	E_g (eV)	A (Å²)	E_s (J/m²)	ϕ (eV)
4	7.78	4.5582	6.3540	90	1.40	28.96	0.51	4.11
8	16.87	4.6039	6.4763	90	1.07	29.82	0.52	4.11
12	26.87	4.6171	6.4906	90	0.85	29.97	0.52	4.11
16	35.32	4.6236	6.4957	90	0.73	30.03	0.53	4.11
20	44.57	4.6286	6.4949	90	0.65	30.06	0.53	4.10
30	67.06	4.6318	6.4984	90	0.52	30.10	0.53	4.08
40	90.74	4.6353	6.4953	90	0.45	30.11	0.54	4.08
bulk		4.6185	6.5316		0.37			

3. The surface energy and ionization potential

In Tables S13 and S14, we compare the surface energy and ionization potential of the semiconductors with available theoretical and experimental data. Our values are taken from the highest dimensional model investigated.

Table S13. Surface energy of the semiconductors (E_s, in J/m²)

	E_s (J/m²)								
	AlP	AlAs	AlSb	GaP	GaAs	GaSb	InP	InAs	InSb
This work	1.25	1.01	0.84	0.98	0.80	0.70	0.82	0.68	0.54
LDA-CAPZ[9]	0.75	0.66	0.61	0.67	0.58	0.55	0.61	0.55	0.52
Exp_1[10]	---	---	---	1.96	0.86	---	---	---	---

Table S14. Ionization potential of the semiconductors (ϕ, in eV) compared with available data.

	ϕ (eV)								
	AlP	AlAs	AlSb	GaP	GaAs	GaSb	InP	InAs	InSb
This work	6.21	5.48	4.59	5.59	4.86	4.10	5.49	5.38	4.08
Exp_1[11]	6.18	5.77	4.85	5.71	5.24	4.47	5.38	5.03	4.44
Exp_2[12]	---	---	---	6.01	5.56	4.91	5.85	5.42	4.90

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