Stability and Electronic Structure of Superlattices $(IIIV)_n/(IV_2)_n$

D. Casagrande and A. C. Ferraz

Instituto de Física da Universidade de São Paulo

Caixa Postal 66318, 05389-970, São Paulo, SP, Brazil

Theoretical investigations of atomic relaxation and electronic states have been made for ultrathin superlattices $(GaP)_n/(Ge_2)_n$, $(GaP)_n/(Si_2)_n$, $(InP)_n/(Ge_2)_n$ and $(InP)_n/(Si_2)_n$, with period $n \leq 3$ in growth directions (001) and (110). The calculations were performed within the momentum-space formalism of the self-consistent ab-initio pseudopotential method and the molecular dynamics approach as proposed by Car and Parrinello. The structures were found to be unstable with respect to the phase separation into the constituent bulk materials. The results for the enthalpy show a metastability as increasing the superlattice period n. The density of nonoctet *"wrong-bonds"* play an important role to determine the stability of the structures.

I. Introduction

Recently it has increased the study of semiconductor heterostructures mainly of III-V/IV type to construct heterojunction bipolar transistors[1-4] (HBT's) with better performance than the conventional III-V HBT's. On that way, Ito et al.[5] and Ohno et al.[6] observed that the $(GaAs)_1(Ge_2)_1$ superlattice (SL), grown on (001) direction, exhibit a metallic behavior correlated to the band structure anomaly induced by the Ge-As nonoctet bond at the interface. In these possible junction devices, interface electronic properties may play an important role.

In this paper we study the electronic properties of $(GaP)_n/(Si_2)_n$, $(GaP)_n/(Ge_2)_n$, $(InP)_n/(Si_2)_n$ and $(InP)_n/(Ge_2)_n$ SL's, with $n \leq 3$, grown in the nonpolar (110) and in the polar (001) directions. The stability of the structures was analyzed considering the charge transfer between the bonds at the interface. A self-consistent first principles method is used in our calculations in order to be able to accurately describe the electronic charge rearrangement that occurs near the interface. The equilibrium atomic geometries were found by using the "ab initio" molecular dynamics method.

II. Method of calculation

Our calculations are performed in the framework of density-functional theory within the local-density approximation[7]. We have used nonlocal, norm-conserving pseudopotentials in the separable form as suggested by Kleinman and Bylander[8] following the prescriptions of Gonze et al.[9] and tabulated by Stunpf, Gonze and Scheffler[10]. The Ceperley-Alder form of the exchange and correlation energy as parametrized by Perdew and Zunger[11] was used. The wave functions are expanded in plane waves with kinetic energy up to 22 Ry. In order to determine the equilibrium atomic positions the geometry was relaxed according the calculated total energy and forces following the Car-Parrinello[12] approach for bringing the wave functions to self- consistency together with the atomic displacements. This method involves integrations over the Brillouin zone which are carried out using four special k points[13] within the irreducible wedge of the Brillouin zone for the SL structure.

The tetragonal unit cells used for (001) and (110) superlattices are depicted in Fig. 1. The lattice mismatched SL's were coherently constrained to a substrate chose to be the average of the equilibrium lattice

constant of the constituents. To obtain a value for the

formation enthalpies of the full relaxed SL's,

$$\Delta H(n) = E[(III - V)_n (IV - IV)_n, \bar{a}, R^{eq}_{(III-V)}, R^{eq}_{(IV-IV)} -$$

$$-\frac{1}{2}\{E[(III - V)_n (III - V)n, \text{ bulk}] + E[(IV - IV)_n (IV - IV)_n, \text{ bulk}]\}$$
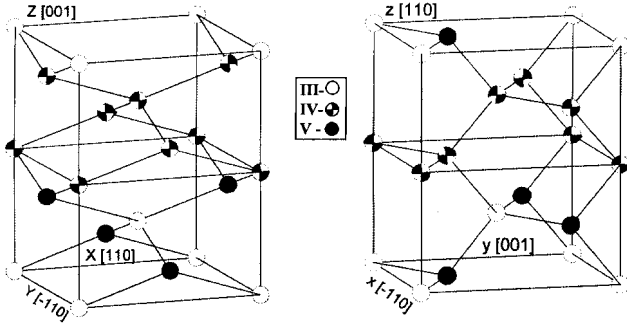

Figure 1. Unit cells of the (001) and (110) oriented (III-V)$_2$ (IV-IV)$_2$ superlattices.

one must have consistent values for bulk III-V and IV-IV total energies so that can be compared with the SL total energy. To minimize errors associated with k-point sampling and plane-wave expansions, the bulk calculations are performed in the SL's geometries.

III. Results and discussion

We calculate equilibrium lattice constants of 5.353, 5.666, 5.620 and 5.380 Å for pure GaP, InP, Ge and Si respectively. The experimental values[13] are 5.451, 5.869, 5.657 and 5.431 Å. The theoretical lattice mismatch are 4.99, 0.50, 0.82 and 5.31 for the SL's GaP/Ge, GaP/Si, InP/Ge and InP/Si respectively.

Table I gives our calculated bond-length at the interface for *the n = 1, 2 and 3* SL's along (001) direction, while Table II gives the obtained values along (110) direction. Since a III-IV bond as a deficiency of 1/4 electron and a IV-V bond as an excess of 1/4 electron, these are expected to behave as acceptor and donor states respectively, giving rise in uncompensated systems to partially occupied localized interface states. In nonpolar (110) SL's each interface contains both donor and acceptor bonds, the charge transfer occurs within a given interface and complete charge transfer can be expected. In polar (001) SL's, each of the two interfaces

contains a single type of nonoctet bond, and compensation thus involves inter-interface charge transfer.

From Table II, (110) SL's direction, we verify that after relaxation the bond-length of pure materials (Ga-P, In-P, Ge-Ge, Si-Si) near the interface show the deep trend to restore the covalent-bond character, getting close their bonds to the values as pure materials. All SL's along (110) direction exhibit bigger change when the period goes from $n = 1$ to $n = 2$ pointing out a more effective transference of charge at the interface for the SL's with $n = 2$. For the bond-length of the pure materials there is a trend to stability from $n = 2$ to $n = 3$. The nonoctet bond (III-IV, IV-V) approach to the sum of their covalent radii when $n = 2$.

On the other hand, in polar (001) SL's (Table I) the behaviour is quite different except for $n = 1$ where the results are the same for both directions. The bond-length of pure materials (III-V, IV-2) near the interface expand when increasing the SL period. The nonoctet bonds V-IV, with excess of 1/4 electron in one of the interfaces, sustain the bond-lengths near the average value. At the other interface, the nonoctet bonds III-IV, with a deficiency of 1/4 electron have their bond-lengths near the III-V bond- length for $n = 1$ and $n = 2$. For all SL's the III-IV bond-length have a strong reduction when the SL period increase from $n = 2$ to $n = 3$.

The bond-length change is associate to the ionic character of the bond. The charge transfer between the bonds within the interface in (110) SL's, or inter-interface in (001) SL's, is also related to that ionicity. Fig. 2(a) shows, for the $(GaP)_n(Ge_2)_n$ prototype SL's, the total charge distribution along the bonds. Figs. 2b and 2c show the positive and negative charge-density difference between the un-relaxed and full-relaxed SL structure. On that way we can determine which region respectively, received or lose electronic charge. For all SL's the phosphorus atom with Ge-P bond lose electronic charge that goes to Ge-Ge or Ga-P bonds. The

amount of concentrated charge at the bonds IV- IV and III-V is almost proportional to their ionicity. As the charge transference for (001) SL'sis inter-interface, when we increase the SL period there will be a reduction of the charge compensation. We also can see that for (110) SL the charge transfer is much more effective because it happens between donor and acceptor bonds at the interface. This reflects the fact that (110) SL has lower electrostatic energy than (001) SL, and reduced stress, favoring the stability.

Our calculated SL formation enthalpies are given in Table III. All ΔH's are positive, hence these SL's are unstable thermodynamically towards phase separation. (110) SL's are more stable than (001) SL's reflecting a more effective charge transfer at the interface between the bonds. Our results for GaP/Si SL's agree very well with the obtained by Dandrea et al.[2]. All the structures have a trend to become more stable with increasing the period n. When we increase the period of the SL's, there is a reduction of the nonoctet bond density and the energy related to the charge distribution around the nonoctet bond is the main term to the SL stability. Finally, the lower values of ΔH for bigger SL's on (110) direction can be seen as a trend to metastability.

References

1. A. Munoz, N. Chetty and R. Martin, Phys. Rev. **B 41**, 2976 (1990).

2. R. G. Dandrea, S. Froyen and A. Zunger, Phys. Rev. **B 42**, 3213 (1990).

3. M. Peressi, S. Baroni, R. Resta and A. Baldereschi, Phys. Rev. **B 43**, 7347 (1991).

4. G. Bratina, L. Sorba, A. Antonini, G. Biasiol and A. Franciosi, Phys. Rev. **B 45**, 4528 (1992).

5. T. Ito, A. Taguchi and T. Ohno, Solid State Comm. **69**, 869 (1989).

6. T. Ohno, Solid State Comm. **74**, 7 (1990).

7. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

8. L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

9. X. Gonze, P. Kackell and M. Scheffler, Phys Rev. **B 41**, 12264 (1990).

10. R. Stumpf, X. Gonze and M. Scheffler, Fritz Haber Institute Research Report, Berlim, 1990.

11. D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J.P. Perdew and A. Zunger, Phys. Rev. **B 23**, 5048 (1981).

12. R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

13. Numerical Data and Functional Relationships in Science and Technology, Landolt-Börnstein, News Series Group III, vol. 22a, edited by O. Madelung (Springer, New York, 1987).

TABLE I: Optimized bond-lengths of atomic pairs near the interface in (001) superlattices. The values are given in Å.

(001) DIRECTION

INTERFACE A

Covalent Bonds

	GaPGe	InPGe	GaPSi	InPSi	GaPGe	GaPSi	InPGe	InPSi
n	Ge-Ge	Ge-Ge	Si-Si	Si-Si	Ga-P	Ga-P	In-P	In-P
1x1	2.399	2.408	2.310	2.318	2.355	2.341	2.470	2.462
2x2	2.402	2.426	2.318	2.338	2.357	2.348	2.473	2.469
3x3	2.411	2.433	2.326	2.344	2.366	2.357	2.476	2.473

Nonoctet Bonds

	GaPGe	InPGe	GaPSi	InPSi
n	P-Ge	P-Ge	P-Si	P-Si
1x1	2.399	2.425	2.320	2.341
2x2	2.396	2.417	2.317	2.334
3x3	2.401	2.418	2.323	2.334

INTERFACE B

Covalent Bonds

	GaPGe	InPGe	GaPSi	InPSi	GaPGe	GaPSi	InPGe	InPSi
n	Ge-Ge	Ge-Ge	Si-Si	Si-Si	Ga-P	Ga-P	In-P	In-P
1x1	2.399	2.408	2.310	2.318	2.355	2.341	2.470	2.462
2x2	2.406	2.421	2.319	2.332	2.365	2.345	2.471	2.469
3x3	2.432	2.437	2.346	2.344	2.391	2.376	2.482	2.470

Nonoctet Bonds

	GaPGe	InPGe	GaPSi	InPSi
n	Ga-Ge	In-Ge	Ga-Si	In-Si
1x1	2.352	2.463	2.310	2.452
2x2	2.352	2.477	2.310	2.454
3x3	2.242	2.414	2.198	2.385

TABLE II: Optimized bond-lengths of atomic pairs near the interface in (110) superlattices. The values are given in Å.

(110) DIRECTION

Covalent Bonds

	GaPGe	InPGe	GaPSi	InPSi	GaPGe	GaPSi	InPGe	InPSi
n	Ge-Ge	Ge-Ge	Si-Si	Si-Si	Ga-P	Ga-P	In-P	In-P
1x1	2.399	2.408	2.310	2.318	2.355	2.341	2.470	2.462
2x2	2.410	2.436	2.326	2.350	2.351	2.335	2.463	2.456
3x3	2.408	2.434	2.323	2.351	2.358	2.337	2.462	2.453

Nonoctet Bonds

	GaPGe	InPGe	GaPSi	InPSi	GaPGe	GaPSi	InPGe	InPSi
n	P-Ge	P-Ge	P-Si	P-Si	Ga-Ge	Ga-Si	In-Ge	In-Si
1x1	2.399	2.425	2.320	2.341	2.352	2.310	2.463	2.452
2x2	2.351	2.348	2.264	2.258	2.405	2.373	2.544	2.520
3x3	2.367	2.363	2.273	2.267	2.387	2.347	2.510	2.481

TABLE III: Calculated formation enthalpies of reconstructed heteropolar superlattices (in units of eV/4-atoms).

SL's	n	(001) ΔH (eV/4at.)	(110) ΔH (eV/4at.)
$(GaP)_n /(Ge_2)_n$	1	0.54	0.54
	2	0.37	0.19
	3	0.30	0.11
$(GaP)_n /(Si_2)_n$	1	0.47	0.47
	2	0.32	0.12
	3	0.26	0.11
$(InP)_n /(Ge_2)_n$	1	0.78	0.78
	2	0.47	0.24
	3	0.39	0.26
$(InP)_n /(Si_2)_n$	1	0.85	0.85
	2	0.52	0.22
	3	0.44	0.25

001

110

1×1

1×1

2×2

3×3

3×3
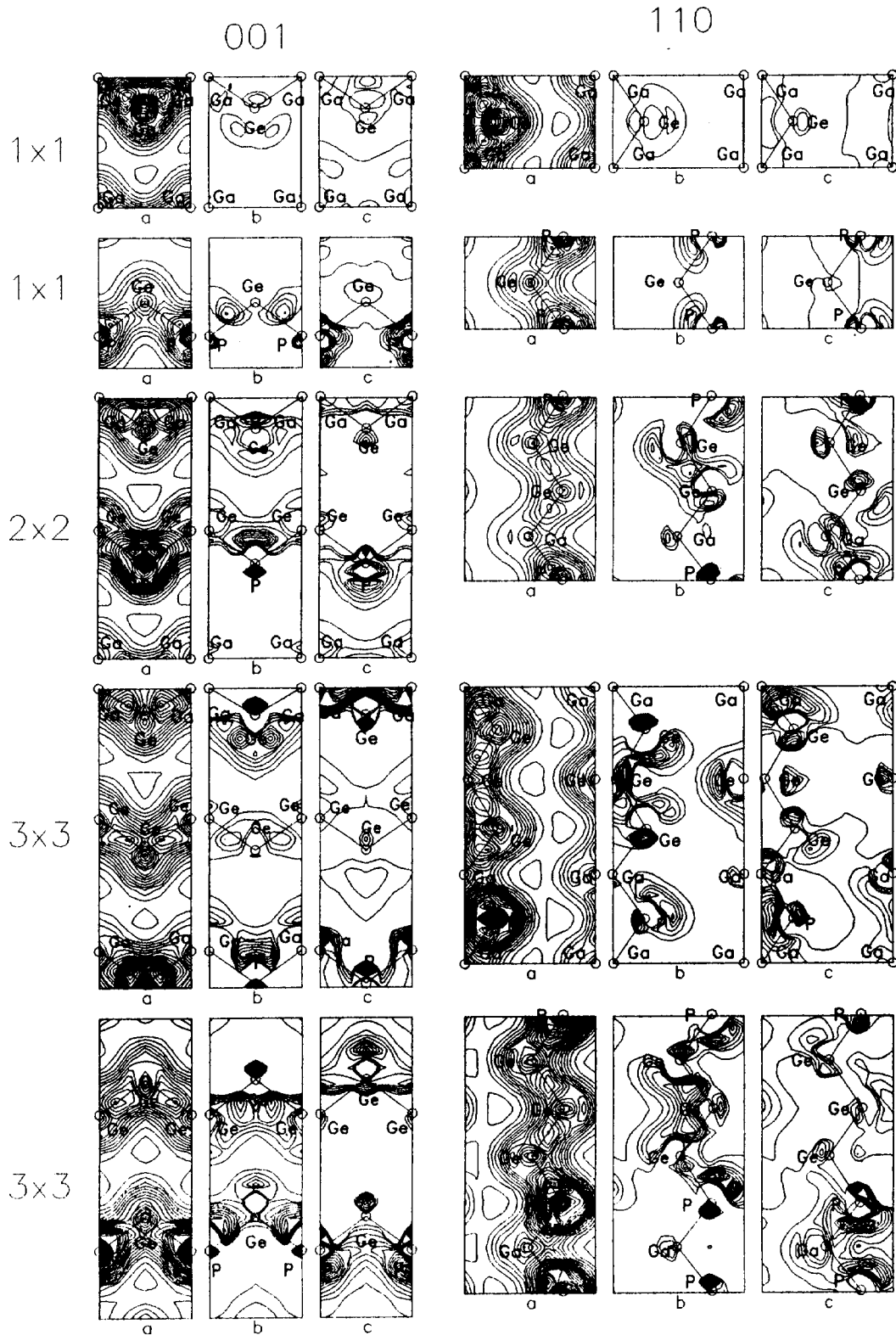

Figure 2. Electron charge density for $(GaP)_n$ $(Ge_2)_n$ (001) and (110) superlattices along the bonds: a) total valence charge densities, b) and c) are the positive and negative charge-density difference between the un-relaxed and relaxed structure.