Surface states in GaAs-GaP (001) semi-infinite superlattices

1993 J. Phys.: Condens. Matter 5 5429

(http://iopscience.iop.org/0953-8984/5/31/007)

J. Phys.: Condens. Matter 5 (1993) 5429–5436. Printed in the UK

Surface states in GaAs–GaP (001) semi-infinite superlattices

J Arriaga, F García-Moliner and V R Velasco

Instituto de Ciencia de Materiales, CSIC, Serrano 123, 28006 Madrid, Spain

Received 8 April 1993, in final form 22 June 1993

Abstract. We study the surface states at the $\bar{\Gamma}$ point of (001) GaAs/GaP semi-infinite superlattices by using an empirical tight-binding (ETB) Hamiltonian together with the surface Green function matching (SGFM) method. The strain due to lattice mismatch is explicitly included in the calculations. We study the effects of the period length and the layer forming the surface on the energy value and attenuation of the surface state.

1. Introduction

When a superlattice is grown on a substrate one can have Tamm-like states at the end of the semi-infinite superlattice terminating in a well slab followed by a thick barrier, the substrate. Currently, there is growing interest in the interface between the superlattice and the substrate. Thus Tamm states have been experimentally observed [1, 2] by means of a combination of photoluminiscence, photoluminiscence excitation and photocurrent spectroscopies. The first theoretical calculations of these states are based on very simple models [3–6], as are the calculations of surface states for the free surface of a semi-infinite superlattice [7–9].

It would seem desirable to have a computational technique which is sufficiently elaborate to handle with ease more realistic models for this type of problem and, while the substrate–superlattice interface is the ultimate goal, the study of the free surface constitutes an interesting subject to set up and test the technique with the full complexity of an elaborate model suitable for realistic calculations. Quite recently we studied the ideal semi-infinite superlattices [10] by means of an ETB Hamiltonian, which gives a good description of the electronic properties of bulk semiconductors and infinite superlattices, together with the SGFM method [11]. The method was then applied to the study of the ideal semi-infinite (001) AlAs–GaAs superlattices. In this case there is good lattice matching of the two constituent crystals, but there is another situation which is the subject of increasing attention in which there is sufficient lattice mismatch that one must account for lattice distortions. We shall study here the semi-infinite (001) GaAs–GaP superlattices, which not only constitute a relevant case of strained layer superlattices but also differ from GaAs–AlAs in that they have a common cation instead of a common anion. The constituent slabs will be assumed to have the system of strains experimentally found for GaAs–GaP superlattices [12], but otherwise the free surface will be ideally terminated. Our study will be concentrated on the energy positions of the surface states and on the penetration of these states. The superlattice can be terminated in either of the two constituent materials and, in each case, the terminal slab may or may not contain the same number of atomic layers as a slab of the same material in the bulk superlattice. This fact can have its importance in the study of the Tamm states at the interface with the substrate. In the case of the semi-infinite superlattices one may

0953-8984/93/015429+08$07.50

expect this to have some influence on the attenuation of the surface states but not much on the position of the surface states.

In section 2 we briefly discuss the theoretical framework and some formal aspects of the calculations. In section 3 we present the results of our calculations for several semi-infinite (001) GaAs/GaP superlattices. Conclusions are presented in section 4.

2. Theoretical aspects

Our calculations are performed with an ETB Hamiltonian with a sp^3s^* orbital basis [13], and interactions up to nearest neighbours only, including spin-orbit splitting [14], using the SGFM method. The geometry, notation, size of the matrices and numerical algorithms to calculate the Green functions are the same as those previously used for the infinite superlattices [15]. We shall employ the concept of *principal layer*, which is defined so that it interacts only with nearest-neighbour principal layers, and this accounts for all interactions in the crystal. With the model employed here a principal layer consists of two atomic layers, one of anions and one of cations.

The Green function one obtains off-hand for the infinite superlattices [15], which we shall denote by G_{SL}, depends on κ (wavevector parallel to the interfaces), E (energy), n, n' (layer indices) and q, the 1D wavevector associated with the superperiodicity of the superlattice. This means that $G_{\overline{SL}}(n, n'; q)$ is the *structural Green function* of the superlattice and thus q must be eliminated in order to study the semi-infinite superlattice [10] which no longer has supertranslation symmetry.

It has been shown [16] that the correct Green function needed to study the semi-infinite superlattice is

$$G_{\overline{SL}}(\kappa, n, n') = \frac{1}{2\pi L}\int_{-\pi}^{\pi} G_{SL}(\kappa, n, n'; qL)\,\mathrm{d}(qL). \tag{1}$$

This Green function can then be used to study the semi-infinite superlattice, exactly as the ordinary Green function of a crystal is used to study the semi-infinite crystal [10].

Now consider a semi-infinite superlattice and let $n = 1$ denote the surface layer, $\mathcal{I}$ the surface projector and $\mathcal{G}_s$ the surface projection of the Green function G_s of the semi-infinite superlattice and in this space we define the Hamiltonian H_s, which describes the atoms constituting the semi-infinite superlattice and their interactions. We define G_s in the same space by

$$(EP - H_s)PG_s = P \tag{2}$$

whence the surface projection

$$\mathcal{G}_s^{-1} = E\mathcal{I} - \mathcal{I}H_sPG_s\mathcal{G}_s^{-1}. \tag{3}$$

We define

$$H_s = PHP \tag{4}$$

as an *ideally truncated* Hamiltonian (H is the Hamiltonian of the bulk infinite superlattice). It is important to notice that an actual H_s need not be given by (4), as discussed in [10]. It can be shown [10, 11] that we finally obtain the following *matching formula*

$$\mathcal{G}_s^{-1} = (E - \mathcal{H}_s)_{11} - H_{12}G_{\overline{SL}}(2, 1)\mathcal{G}_{\overline{SL}}^{-1}(1, 1) \tag{5}$$

yielding $\mathcal{G}_s$ in terms of H and $G_{\overline{SL}}$ of the infinite superlattice, which we are supposed to know. So far the formal aspects are completely analogous to those of the standard semi-infinite crystal. For a standard crystal $G(2,1)\mathcal{G}^{-1}(1,1)$ is simply the transfer matrix T of the bulk crystal [16, 17] but this is not true for superlattice. In this case the product of the last two factors of (5) must be explicitly evaluated from the elements $G_{\overline{SL}}(2,1)$ and $G_{\overline{SL}}(1,1)$ and these are obtained by first evaluating $G_{\overline{SL}}(2,1)$ and $G_{\overline{SL}}(1,1)$ by the standard SGFM formulae [11] for the infinite superlattice and then performing the integration indicated in (1).

In the semi-infinite superlattice the terminal slab may or may not contain the same number of layers as the slab of the same material in the bulk. Consider a bulk superlattice (N_A, N_B) and assume it is terminated in material A. We label the A layers by $n = 1, 2, \ldots, N_A$ from left to right. Formula (3) is general, while formula (5) corresponds to the case in which the terminal A slab contains also N_A layers. But this could have, say, one layer less. Then we say formally in (3) that the terminal layer is $n = 2$, and the adjacent one is $n = 3$, with consequent changes in (5). In general, as the number of layers in the terminal slab decreases, the label n of the surface layer increases, and the matching formula for the inverse of the surface projection of the Green function of the semi-infinite superlattice is

$$\mathcal{G}_s^{-1} = (E - \mathcal{H}_s)_{nn} - H_{n,n+1}G_{\overline{SL}}(n+1,n)G_{\overline{SL}}^{-1}(n,n) \tag{6}$$

in each case the surface projection $\mathcal{G}_s$ is obtained by inversion of the matrix in (5) or (6) and then the diagonal matrix elements of G_s, for the semi-infinite superlattice, are obtained from the corresponding $\mathcal{G}_s$ by means of standard SGFM formulae [15]. These diagonal elements are then used to obtain the local density of states. Thus we can study the surface states as the surface layer of terminal slab is $n = 1, 2, \ldots$, and, in each case we can study their penetration into the bulk of semi-infinite superlattice, as measured by the LDOS starting from the surface layer and moving inwards.

In the integration in (1) we have employed a Simpson rule method. For very accurate results about 100 points are required depending on the energy range, but substantially fewer points are needed to reliably obtain some key features like the position of surface states.

3. Results

We shall consider several (001) semi-infinite GaAs/GaP superlattices and study the region near the gap between the top of the valence band (VB) and the bottom of the conduction band (CB) at the centre of the 2D Brillouin zone (the $\overline{\Gamma}$ point), as in the case of the (001) semi-infinite GaAs/AlAs superlattices [10]. The effects of the strain are included in the same way as in the infinite superlattices [18, 19]. We use the following reference energy in our calculation $E_V(\text{GaP}) = 0.0$ eV, $E_C(\text{GaP}) = 2.9$ eV, $E_V(\text{GaAs}) = 0.9$ eV, and $E_C(\text{GaAs}) = 2.45$ eV. This band-offset was used in previous calculations [18, 19] and was able to explain the experimental data available. As discussed in [19] an uncertainty in this value exists, but will not modify in a substantial way the qualitative picture that will be presented now. It is also known [20] that the band-offset can be strongly affected by the strain. Our values for the strain are taken from the experiment [12] in which the superlattice was grown on a GaAs substrate. The empirical tight-binding parameters are those employed in the infinite superlattice calculations [18].

We shall consider the effects on the surface states of terminating in the AsGa or PGa slab, and also of reducing the thickness of the terminal slab. We study the position of the surface state in the gap and the attenuation of the surface state in the different cases.

We shall consider a (6,6) GaAs/GaP superlattice, which according to experimental information has the strain shared by both slabs: GaAs having a 1.4% compressive strain and GaP a 2.3% tensile strain [12]. We start with the superlattice terminated at the $n = 1$ layer of a AsGa slab, so the terminal slab has six layers, and then increase n, corresponding to a decreasing number of AsGa layers in the terminal slab. In each case we study the LDOS at the atomic layers of the surface layer (a) and of the contiguous subsurface layer (b). Figure 1 gives the results when there are six layers in the terminal slab. The band edges $E_V = 0.81$ eV and $E_C = 2.50$ eV are those of the infinite superlattice and are indicated by the vertical arrows appearing in all the figures. The gap and band edges are, in all figures, those of the infinite (6,6) superlattice.

The surface state at 1.85 eV is mostly concentrated in the surface layer (figure 1(a)) and, within it, mainly in the anion layer. The picture is qualitatively similar to that of the AlAs/GaAs case. The surface state is very quickly attenuated, as can be seen on moving into the subsurface layer (figure 1(b)).

The same information is given in figure 2 for the case when the terminal slab has five AsGa layers. The surface state peak stays basically at the same energy and is equally strongly attenuated. These trends persist as the number of AsGa layers in the terminal slab decreases. The extreme case is reached when the terminal slab has only one AsGa layer (figure 3). The surface state peak shows a small shift in this case, and moves to 1.77 eV.

The next three figures present the results of the same study when the terminal slab consists of PGa layers, with figures 4, 5 and 6 corresponding to figures 1, 2, 3 respectively. The position of the surface state changes from 1.1 eV (figure 4) to 1.28 eV (figure 6) but otherwise its behaviour, as well as that of the LDOS in the continuum, is similar in both cases.

Figure 7 shows the results for the case in which the terminal slab consists of six GaP layers, while figure 8 shows the results for the case in which the terminal slab consists of six GaAs layers. In both cases the outermost atomic layer of the surface state is one of cations (Ga). The position of the surface state is 1.4 eV in figure 7 and 1.6 in figure 8. The surface states show strong attenuation and have spectral strength in the cation layer and in the anion layer. It can be seen (figures 4 and 7), by looking at the surface states in the main gap for the GaP and PGa terminations, that the surface state associated with the cation terminated layer is somewhat higher in energy than the one associated with the anion terminated layer, while the opposite behaviour is observed for the GaAs and AsGa terminations (figures 1 and 8). We note that the same situation holds for AlAs/GaAs superlattices, where AlAs and AsAl terminations behave in this respect like GaP and PGa terminations while of course GaAs and AsGa terminations behave as in the GaP/GaAs superlattice. Furthermore, we have studied free GaP and free GaAs surfaces and found the same situation as when these materials form the terminal slab of the superlattice. In this respect it might be relevant to note that GaP and AlAs both have indirect gap, unlike GaAs which has direct gap. Thus, although the energy differences are not too large, there appears to be a systematic pattern and it seems plausible to associate this with structural features of the terminal slabs, rather than local properties of the terminal ions.

We have concentrated on the main gap because, as in the case of the semi-infinite crystals, this is the most important one. We have also considered some other gaps at the $\overline{\Gamma}$ point, but we have not seen any important feature. The nearest gaps are quite narrow and no surface state is present there. We have also studied the behaviour of the surface state

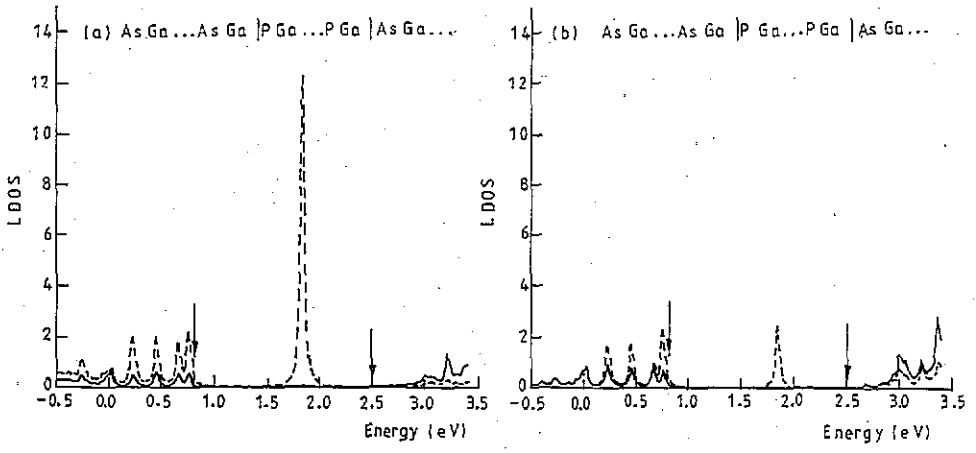

Figure 1. (*a*) LDOS in arbitrary units projected at the surface AsGa principal layer, (*b*) LDOS in a.u. projected at the next principal layer. Continuous line indicates projection in cation layers and dashed line indicates projection in anion layers.

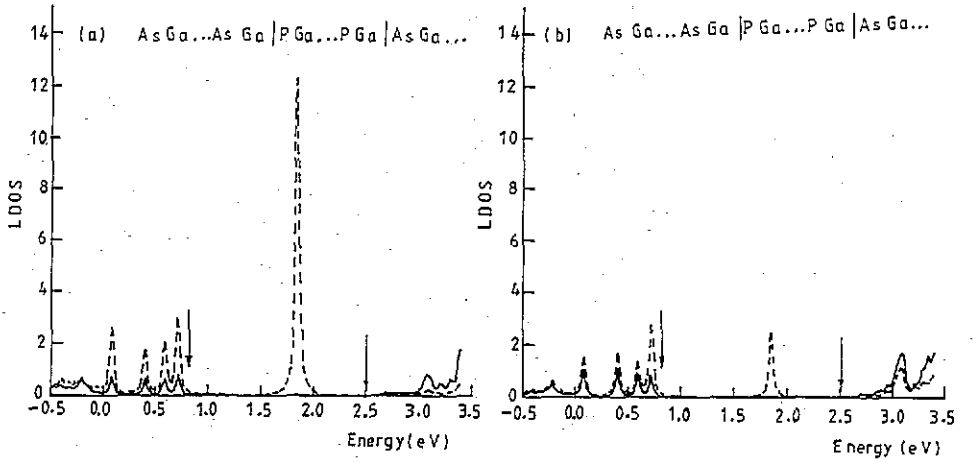

Figure 2. As in figure 1 for the surface AsGa second principal layer.

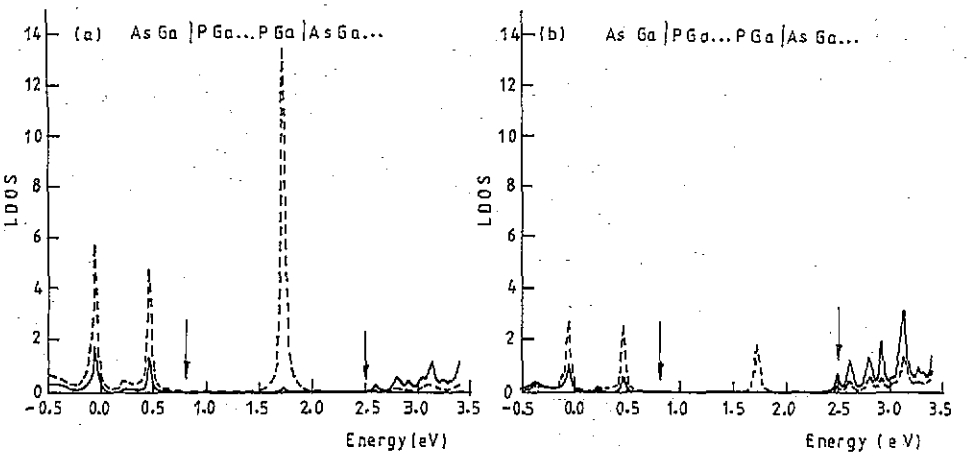

Figure 3. As in figure 1 for the surface AsGa sixth principal layer.

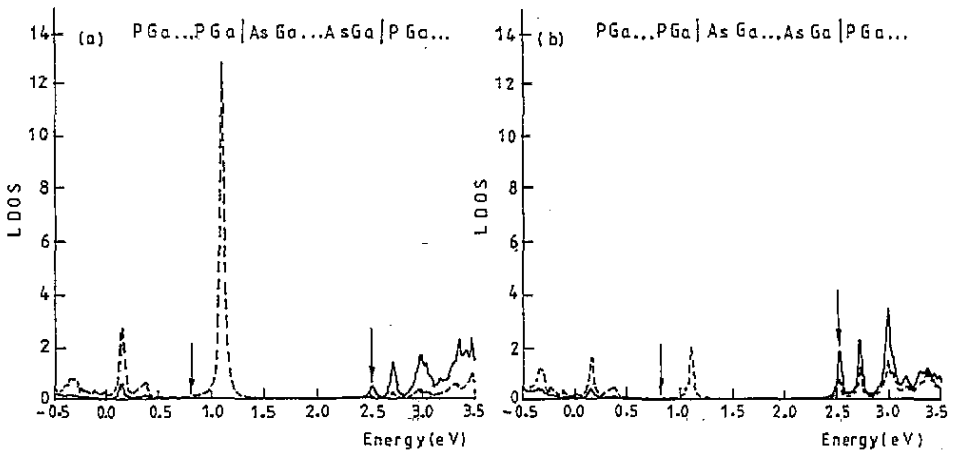

Figure 4. (*a*) LDOS in arbitrary units projected at the surface PGa first principal layer, (*b*) LDOS in a.u. projected at the next principal layer. Same conventions as in figure 1.

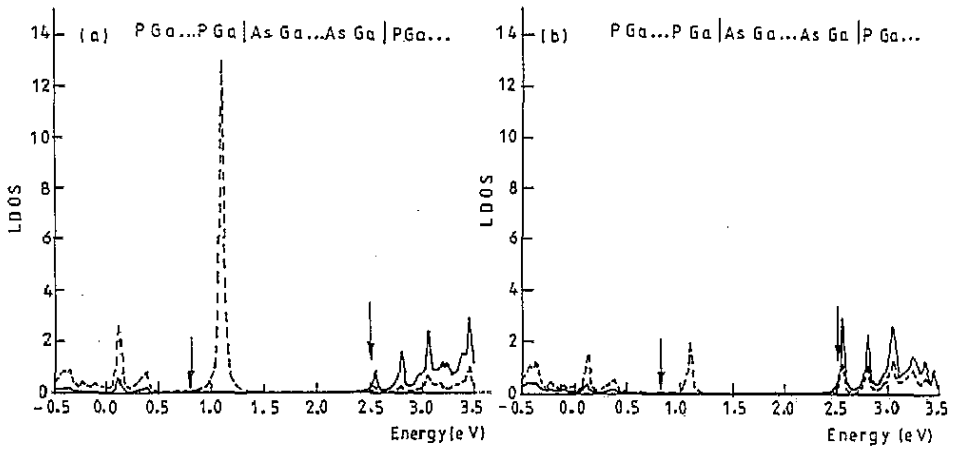

Figure 5. As in figure 4 for the surface PGa second principal layer.

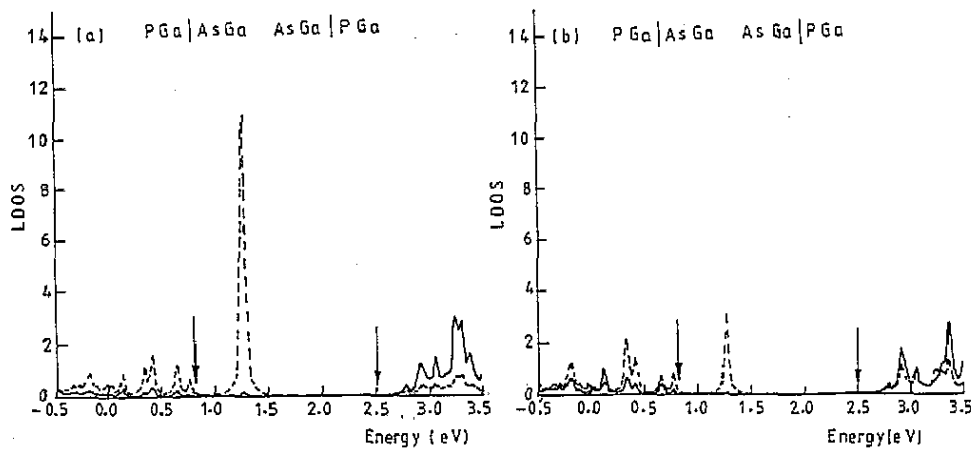

Figure 6. As in figure 4 for the surface PGa sixth principal layer.

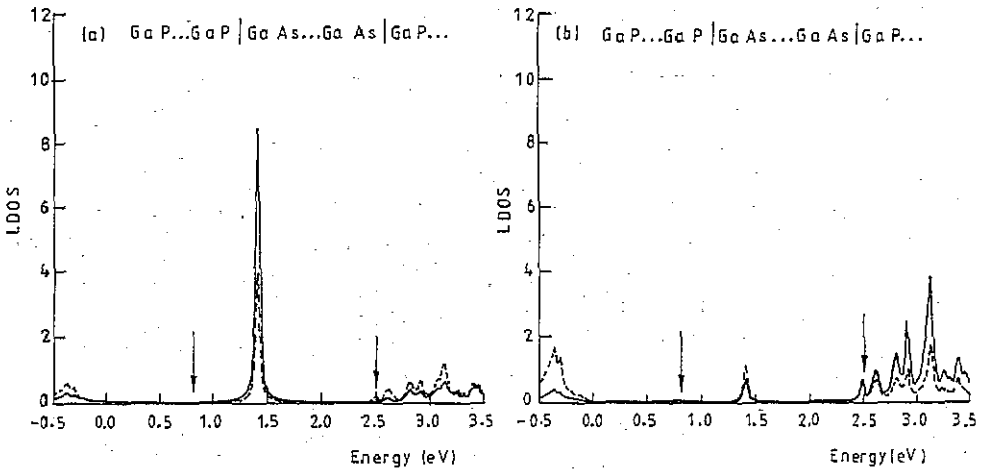

Figure 7. (*a*) LDOS in arbitrary units projected at the surface GaP first principal layer, (*b*) LDOS in a.u. projected at the next principal layer. Same conventions as in figure 1.

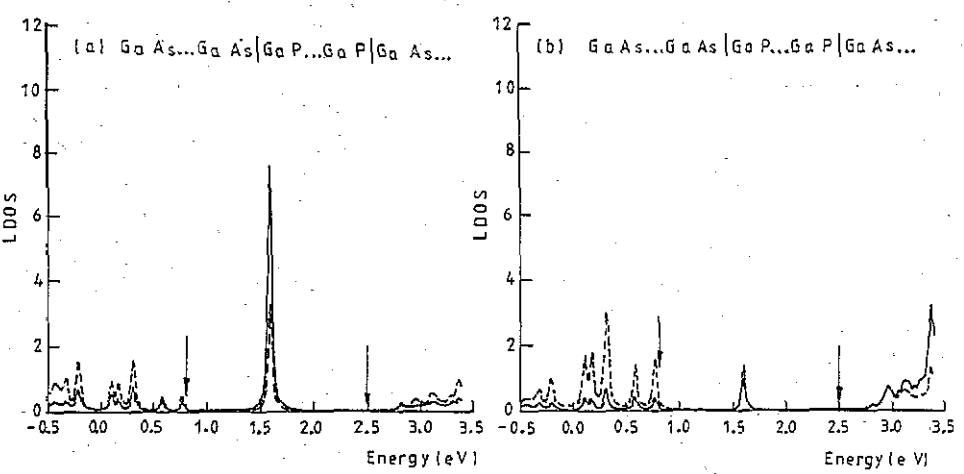

Figure 8. (*a*) LDOS in arbitrary units projected at the surface GaAs first principal layer, (*b*) LDOS in a.u. projected at the next principal layer. Same conventions as in figure 1.

in the main gap at κ points along the [1,0] direction, but we have found no changes in the behaviour of the surface state. In some cases [7–9] some surface states have been reported in gaps near the main one. The models employed in these calculations are very simple and they cannot give the indirect gap of AlAs and GaP, so their value is only qualitative.

It can be argued that the elimination of layers in the surface slab can modify the strain ratio in that region. There is no information on this subject and we have kept the values of the infinite superlattices in all our calculations. These effects could be introduced in any case in the calculation by modifying the ideally truncated Hamiltonian. This could modify slightly the position of the surface state peaks, but would not substantially alter the qualitative picture drawn here. The same is true for the possible effects of employing a different valence band offset.

4. Conclusions

We have studied the electronic structure in the region near the VB top and the CB bottom at the $\overline{\Gamma}$ point of (001) GaAs/GaP semi-infinite superlattices. We have found surface states in the gap for both cation and anion terminated surfaces. The attenuation rate of the surface states is always strong and for anion (P, As) terminated semi-infinite superlattices the spectral strength of the surface state is practically concentrated in the anion layers.

In the Ga terminated semi-infinite superlattice the spectral strength of the surface state is distributed between the anion and cation layers. This behaviour of the LDOS is similar to that shown for the AlAs–GaAs semi-infinite superlattices [10]. The position of the surface state remains practically unchanged and there is only a small shift when the number of layers in the terminal slab is reduced to one, like in the AlAs–GaAs case [10]. This reflects the fact that the surface states are associated to the dangling bonds, and they are only slightly affected when the chemical environment is more strongly modified as in the case of only one principal layer in the terminal slab.

The method here employed to study the free surface of a semi-infinite superlattice can easily be extended to the case of the interface. Work on this problem is in progress in our laboratory.

Acknowledgments

This work was partially supported by the Spanish CICYT, under Grant MAT91-0738. One of the authors, J Arriaga, is indebted to the Spanish Ministry of Education and Science for the award of a Postdoctoral Fellowship.

References

[1] Ohno H, Mendez E E, Brum J A, Hong J M, Agulló-Rueda F, Chang L L and Esaki L 1990 *Phys. Rev. Lett.* **64** 2555
[2] Ohno H, Mendez E E, Alexandrou A and Hong J M 1992 *Surf. Sci.* **267** 161
[3] Huang F Y 1990 *Appl. Phys. Lett.* **57** 1669; 2199
[4] Bloss W L 1991 *Phys. Rev.* B **44** 8035
[5] Kucharczyk R and Steślicka M 1992 *Solid State Commun.* **81** 557
Kucharczyk R and Steślicka M 1992 *Solid State Commun.* **84** 727
[6] Zhang J and Ulloa S E 1988 *Phys. Rev.* B **38** 2063
[7] Steślicka M, Kubarizyk R and Glasser R L 1990 *Phys. Rev.* B **42** 1458
[8] Jaskólski W 1992 *Phys. Rev.* B **45** 4398
[9] Masri P, Dobrzynski L, Djafari-Rouhani B and Idiodi J O A 1986 *Surf. Sci.* **166** 301
[10] Arriaga J, García-Moliner F and Velasco V R 1993 *Prog. Surf. Sci.* at press
[11] García-Moliner F and Velasco V R 1989 *Theory of Single and Multiple Interfaces* (Singapore: World Scientific)
[12] Armelles G, Recio M, Meléndez J, Ruiz A, Briones F, Khirouni K and Barrau J 1989 *Japan J. Appl. Phys.* **28** L1495
[13] Vogl P, Hjalmarson H P and Dow J D 1983 *J. Phys. Chem. Solids* **44** 365
[14] Chadi D J 1977 *Phys. Rev.* B **16** 790
[15] Muñoz M C, Velasco V R and García-Moliner F 1989 *Phys. Rev.* B **39** 1786
[16] García-Moliner F and Velasco V R 1991 *Phys. Rep.* **200** 83
[17] López Sancho M P, López Sancho J M and Rubio J 1984 *J. Phys. F: Met. Phys.* **14** 1205
[18] Arriaga J, Muñoz M C, Velasco V R and García-Moliner F 1991 *Phys. Rev.* B **43** 9626
[19] Arriaga J, Muñoz M C, Velasco V R and García-Moliner F 1992 *Phys. Scr.* **46** 466
[20] van de Walle C G and Martin R M 1986 *Phys. Rev.* B **34** 5621