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PSEUDOPOTENTIAL CALCULATION OF THE ELECTRONIC STRUCTURE AT THE CLEAVAGE SURFACE OF GaP

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We present a self-consistent calculation of the surface states of GaP using pseudopotential method and a large plane wave basis set. Surface states at high symmetry points of the two dimensional Brillouin zone are analyzed for different surface geometries and compared with previous tight binding results. It is confirmed that filled surface states are removed from the gap by surface atom relaxation, while the empty surface band is still present inside the gap.

1. Introduction

It is now well established that relaxation of the outermost layers of the cleavage surface of III-V compounds is essential in the determination of the electronic surface structure [1,2]. In particular theoretical calculations performed assuming different atomic geometries have shown that relaxation is responsible of the removal of surface states from the gap in agreement with experimental results [3]. Appropriate surface geometries can be found which reproduce both LEED data [4] and the symmetry sequence of the surface states as determined by polarization dependent angular resolved photoemission [5].

Among III-V compounds GaP is a relevant exception being the only material where empty surface states have been found inside the gap both experimentally and theoretically. On the experimental side measurements of Fermi level pinning [6], photoemission yield spectroscopy [7] and external differential reflectivity [8] give evidence of the presence of empty surface states between the conduction band minimum and midgap, while no evidence is found of the presence of filled surface states. On the theoretical side semi-empirical tight binding calculations have shown that the most common relaxed geometries do not remove empty surface states from the gap [9].

In this paper we present the first theoretical calculation of the electronic structure of the (110) surface of GaP based on a pseudopotential method.

2. Theoretical Framework

Following a well known procedure [10] we consider an artificially periodic system of GaP slabs. Each slab has a (110) surface exposed on both sides and it is separated from neighbouring slabs by a large region of vacuum. In our calculation we examine a nine layers slab of GaP surrounded by six layers of vacuum. By introducing this artificial periodicity normal to the surface we can perform a surface band structure calculation as in a bulk solid. Choosing plane waves as basis functions the standard procedure of bulk calculations and the useful reciprocal space representation can be used, the only disadvantage being the large number of plane waves to be considered due to the small size of the reciprocal unit cell.

The effective single particle potential is partitioned in a bare pseudopotential and in a screening potential, that is a functional of the self-consistent pseudo-charge density:

$$V_{eff}(\underline{r}) = V_b(\underline{r}) + V_H(\underline{r}) + V_{xc}(\underline{r}) \quad ,$$

where V_H is the Hartree term, V_{xc} is the exchange and correlation potential. The bare pseudopotential V_b was calculated from the potential of Ga^{3+} and P^{5+} ions as given by Frensley and Kroemer [11] shown in Fig.(1). The use of a local form for V_b does not produce the highly accurate description of bulk properties of non-local calculations, particularly for the lowest valence band, but for the purpose of establishing the existence of surface states in the gap it should prove satisfactory. As to V_{xc} we take the usual Hartree-Fock-Slater form with alpha equal to one. Doing the self-consistent procedure one has to evaluate the Fourier transforms of the screening potential from the Fourier coefficients of the pseudo-charge density. To this end we evaluated the charge density throughout the real space unit cell and we got the screening potential using Fast Fourier Algorithm.

In order to reduce the size of the secular problem symmetry adapted combinations of plane waves were used. The matrix we diagonalized were of the order of 300x300. In addition to the plane waves treated directly, we included approximately 1000 additional plane waves via Lowdin's perturbation technique.

As a first step we performed a fully self-consistent calculation of bulk GaP band structure getting a screened pseudopotential to be used as starting potential for the surface calculation. In order to perform the calculation for the periodically repeated GaP slab we need the Fourier transform of the screened pseudopotential at small reciprocal lattice vectors not involved in bulk calculations. They were obtained by relating the difference between average bulk and average vacuum potentials to the known value of the work function. A self-consistent procedure was then set up for the surface, the screening potential at each step being determined from the calculated charge density. The instabilities of the iterative procedure arising from the small $\underline{G}$ Fourier coefficients of the effective potential were treated as in [10].

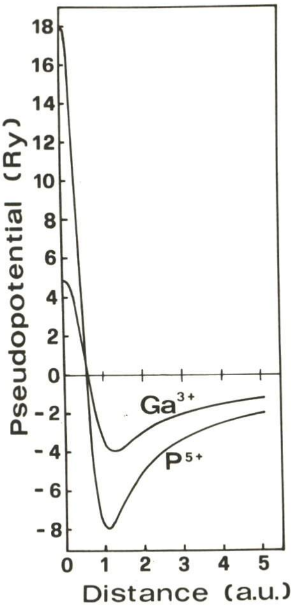

Fig.1 Ionic pseudopotentials for Ga^{3+} and P^{5+}

3. Results and Discussion

In order to indicate the accuracy of our self-consistent procedure we display in Fig.(2) the laterally averaged "input" and "output" potentials at the last iteration of the calculation for the ideal surface plotted as a function of the

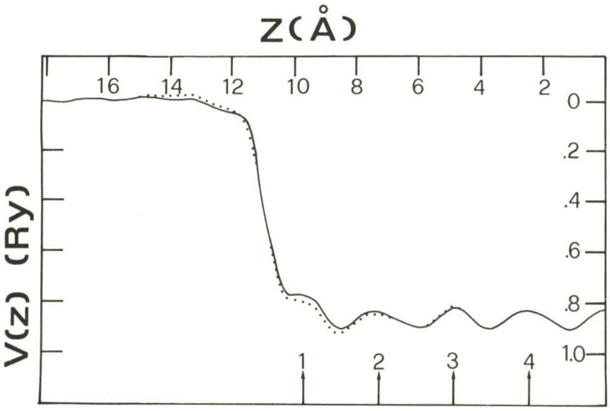

Fig.2 Total laterally averaged potentials for the GaP ideal (110) surface

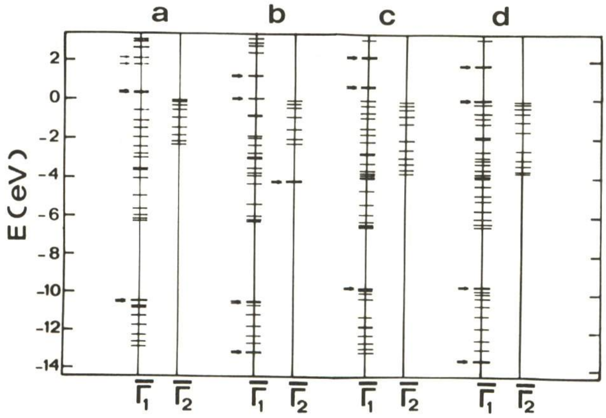

Fig.3 Band structure at $\bar{\Gamma}$ point. (a-c) ideal, (b-d) relaxed geometry for pseudopotential and tight binding calculations respectively. Energies are referred to the valence band maximum

distance from the slab centre. Notice that the small changes in the profile of the potential near the surface shown in the figure do not alter the location of the surface states.

We performed calculations for both ideal and relaxed geometries. We considered a model of surface relaxation where both atoms move from ideal positions keeping constant the nearest neighbours distances. The bond rotation angle involved was the maximum one i.e. θ=34.8°. This is one of the possible surface distortions which preserve 1x1 surface periodicity proposed for GaAs. Since the details of the atomic displacements leading to relaxation depend on the nature of the chemical interaction, the choice of this geometry for GaP can be only approximate.

Figure (3) shows our results for the two geometries at the centre of the two dimensional Brillouin zone. For comparison the results of tight binding calculations are also given. The electronic structure for the ideal surface shows the dangling bond states in the gap and a surface state near the lower edge of the ionic gap, arising from s-phosphorus orbitals. These features are present in the tight binding calculations also and appear in the electronic structure of the ideal (110) surface of other III-V materials. Notice that, in spite of the difference in the description of the bulk bands, there is a close agreement between tight binding and pseudopotential calculations about the position of the surface states relative to the band edges.

The main effect of relaxation is to shift surface states to lower energies, changing their orbital composition. The filled P-dangling bond state becomes degenerate with the valence band maximum while the empty Ga-dangling bond state is moved deeper into the gap. The P-s-derived state near the lower edge of the ionic gap is not appreciably altered, but a new surface feature appears near the bottom of $\bar{\Gamma}_1$ band. All these results are in agreement with the outcomes of tight binding calculations, although the displacement of the Ga-derived state to lower energy is less pronounced. As to $\bar{\Gamma}_2$ symmetry pseudopotential calculation shows a strong surface feature at about -4 eV below the top of the valence band, which is not found in the tight binding results. It is unlikely that the use of a different tight binding parametrization can introduce this feature in the surface electronic structure, so that this state appears to be present only when the profile of the potential near the surface is accurately described as in pseudopotential calculations.

Similar results were obtained for the other symmetry points of the Brillouin zone. In all cases we found that relaxation does not remove the empty surface states from the gap, although the shift of the Ga-dangling bond states with respect to the location in the ideal surface is somewhat different than at $\bar{\Gamma}$. As to filled states we found that the P-dangling bond states lie close to the edge of the projected valence band, nearly 1 eV below the valence band maximum. Except for minor details these results agree with previous tight binding calculations [9].

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