

Proceedings of the XX International School of Semiconducting Compounds, Jaszowiec 1991

INFLUENCE OF CHEMISTRY ON THE ENERGY BAND STRUCTURE: AlAs VERSUS GaAs

P. BOGUSŁAWSKI

Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warszawa, Poland

AND I. GORCZYCA

High Pressure Research Center, Polish Academy of Sciences, Warszawa, Poland

Energy band structure of AlAs and GaAs is analyzed in terms of the energy structure of the constituent atoms. Conduction band wave functions are projected on *s*-, *p*-, and *d*-symmetry atomic orbitals. The resulting information is combined with the eigenenergies of Al and Ga atoms, in order to discuss the character of the band gaps, and the sign of deformation potentials.

PACS numbers: 71.25.Tn, 71.10.+x

Our goal is to interpret energy band structure of semiconductors in terms of the energy structure of the constituent atoms. We choose AlAs and GaAs, since the near lattice matching of these materials eliminates effects induced by the difference of lattice constants. Here, we consider first the character of the fundamental band gap, which is direct for GaAs and indirect for AlAs. Second, we discuss the changes of the band gaps induced by the hydrostatic pressure. Our results demonstrate an important role of the excited *d* states.

Energy band structure was calculated using the atomic *ab initio* pseudopotentials [1]. They were consistently used also to calculate energy levels of isolated atoms. Due to the common anion, differences between AlAs and GaAs stem from the differences in atomic terms of cations, which are:

$$\begin{array}{lll} \epsilon_s(\text{Al}) = -12.20, & \epsilon_p(\text{Al}) = -6.70, & \epsilon_d(\text{Al}) = -1.40, \\ \epsilon_s(\text{Ga}) = -14.05, & \epsilon_p(\text{Ga}) = -6.95, & \epsilon_d(\text{Ga}) = -1.05, \end{array}$$

where all values are in eV. We see that the energies of the *s* states differ by as much as 1.75 eV, while ϵ_p and ϵ_d are close to each other.

In order to analyze the orbital content of electron states, conduction band wave functions ψ_{ck} were projected on s -, p -, and d -symmetry orbitals of an atom located at a lattice site τ . Projection coefficients P , normalized to 100%, are [3]

$$P_{lm}(\tau, k) = C \int_0^R r^2 dr \langle \psi_{ck} | Y_{lm} \rangle \langle Y_{lm} | \psi_{ck} \rangle, \quad (1)$$

where R is the Wigner-Seitz radius, Y_{lm} is the spherical harmonic, and C is the normalization constant. The results are shown in Fig. 1 and in Table.

TABLE
Energies and projection coefficients on s -, p -, and d -symmetry orbitals of the first conduction band of AlAs and GaAs for two values of lattice constant a .

AlAs								
State	$a(\text{\AA})$	$E(\text{eV})$	$s(\text{Al})$	$p(\text{Al})$	$d(\text{Al})$	$s(\text{As})$	$p(\text{As})$	$d(\text{As})$
Γ_{1c}	5.65	2.5	43			57		
	5.20	4.3	31			69		
X_{1c}	5.65	1.3		32	29	8		31
	5.20	0.8		25	34	8		33
GaAs								
State	$a(\text{\AA})$	$E(\text{eV})$	$s(\text{Ga})$	$p(\text{Ga})$	$d(\text{Ga})$	$s(\text{As})$	$p(\text{As})$	$d(\text{As})$
Γ_{1c}	5.65	1.2	49			51		
	5.20	3.4	40			60		
X_{1c}	5.65	1.4		33	26	10		31
	5.20	0.8		25	32	11		32

We begin by considering the decomposition of the lowest conduction band of GaAs as a function of the wave vector along the Γ - X direction. Energy band structure is shown in Fig. 1a, and projection coefficients on the Ga and As states in Fig. 1b and 1c, respectively. The results agree with rules given by group theory [5]. Complex dependencies of the projection coefficients on the wave vectors reflect a strong coupling of the Δ_{1c} level with other states. The initial increase of the contribution of p orbitals stems from the Γ_{1c} - Γ_{15v} interaction, which in the $k \cdot p$ picture determines the effective mass of conduction electrons. Two anticrossings of Δ_{1c} with higher-lying levels are clearly visible. The first one, with the Γ_{15c} -derived level, occurs at $\sim (0.25, 0, 0)$ ($2\pi/a$). The anticrossing at $\sim (0.9, 0, 0)$ ($2\pi/a$) close to the zone boundary is with the state derived from Γ_{12c} (with $E(\Gamma_{12}) = 10.8$ eV in Fig. 1a). Accordingly, the $d_{3x^2-r^2}(\text{As})$ orbital contributes by as much as 31% to X_{1c} . The lowest conduction state at X has a X_{1c} symmetry (we fix the origin on As). This agrees with Ref. [6], but is in contradiction with the X_{3c} symmetry found in Ref. [3] within the empirical pseudopotential method.

The most important difference between energy band structures of AlAs and GaAs is the character of the band gap, indirect for AlAs and direct for GaAs. This difference results from two facts, namely (i) the lowering of Γ_{1c} level from 2.5 eV

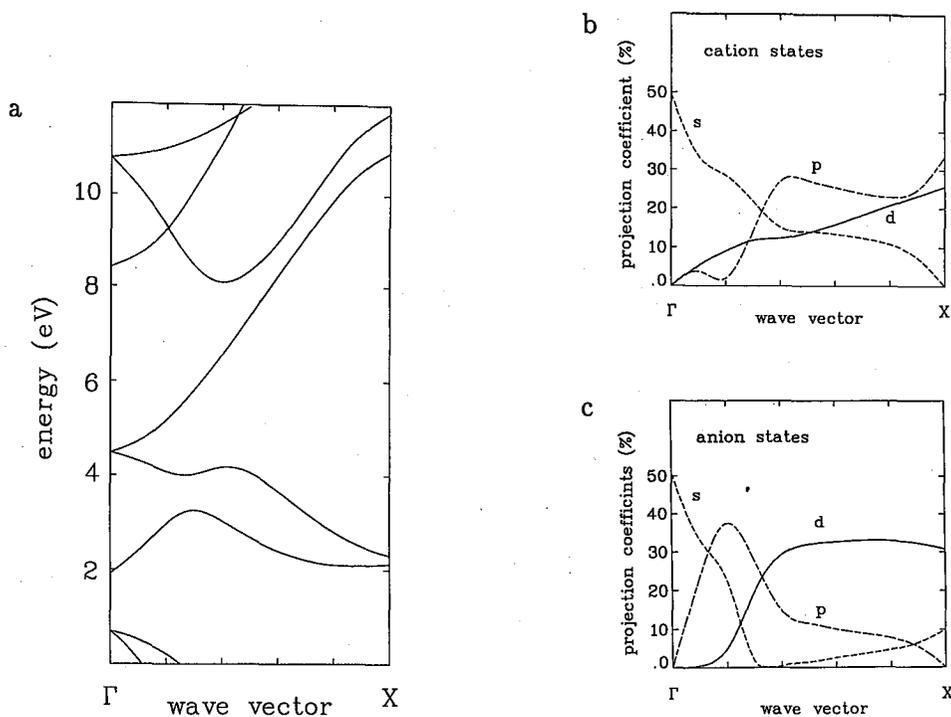


Fig. 1. (a) Energy band structure of GaAs and coefficients of projection on (b) Ga and (c) As states along the Γ -X direction.

in AlAs to 1.2 eV in GaAs, and (ii) similar energies of the lowest conduction bands X_{1c} , amounting to about 1.4 eV in both crystals. Since the Γ_{1c} states are built up of s orbitals only, see Table, the lowering of $E(\Gamma_{1c})$ level stems from the fact that $\epsilon_s(\text{Al}) > \epsilon_s(\text{Ga})$. On the other hand, the cation s states do not contribute to X_{1c} level, which therefore has a similar energy in both crystals. The energy of X_{1c} is lower in AlAs than in GaAs by 0.1 eV. The difference is small, but it may be understood basing on Table and the values of atomic terms ϵ_p and ϵ_d (we have $P_p(\text{Al}) < P_p(\text{Ga})$ and $\epsilon_p(\text{Al}) > \epsilon_p(\text{Ga})$, and opposite relations for d orbitals).

On the other hand, changes of the energy band structure induced by hydrostatic pressure in AlAs and GaAs are similar. First, the direct Γ - Γ band gap opens due to the increase of bonding-antibonding splitting. This is accompanied with an increase of contribution of $s(\text{As})$ to the wave function, see Table. We also find the deformation potential constant $C_1 = 7.5$ eV for both materials.

In contrast to the direct gap, the indirect Γ -X gap is reduced by the pressure, with the deformation potential constant -1.9 eV for both AlAs and GaAs. This behavior cannot be understood in terms of sp^3 model, which predicts the opening of the gap. We propose that the reduction of the indirect gap results from the

contribution of the bonding combination of excited d states. As it follows from Table, this contribution increases with pressure. Due to its bonding character, it tends to lower energy of X_{1c} , which dominates the bonding-antibonding splitting.

References

- [1] G.B. Bachelet et al., *Phys. Rev. B* **26**, 4199 (1982). Plane wave basis with the energy cut-off of 12 Ry was used. Local Density Approximation used in our calculations is known to underestimate energy band gaps of semiconductors. However, wave functions [2] (and thus their orbital compositions) are given with sufficient accuracy.
- [2] M.S. Hybertsen, S.G. Louie, *Phys. Rev. B* **34**, 5390 (1986).
- [3] S.L. Richardson, M.L. Cohen, S.G. Louie, J.R. Chelikowsky, *Phys. Rev. B* **33**, 1177 (1986). This procedure turned out to be very helpful in analysis of the electronic structure of ordered alloys [4]. It reverses the order of the LCAO approach, because the orbital composition of the wave functions is given as output, and not as input of calculations.
- [4] P. Bogusławski, A. Baldereschi, *Solid State Commun.* **70**, 1085 (1989).
- [5] F. Bassani, in *Semiconductors and Semimetals*, Eds. R.K. Willardson, A.C. Beer, Academic, New York 1966.
- [6] G.B. Bachelet, N.E. Christensen, *Phys. Rev. B* **31**, 879 (1985).