

Bond energy in III-V group of Semiconductors

Kalyan Singh¹, V.K. Singh², Deepak Sharma³

^{1,3}Deptt. of Applied Science, IIMT College of Engineering, Greater Noida
²D.S. College, Aligarh

Abstract: Semiconductors are presenting periodic table of group III-V, in this paper, we have calculated values of bond energy of III-V group of semiconductors. The value of bond energy found corresponding with bond orbital parameter (V_2 , V_3), average s-p splitting (V_1^s) and polarity (α_p) used as input data.

Keywords: Semiconductors, bond orbital parameters, s-p splitting and polarity.

Introduction: We have investigated bonding properties such as bond energy for III-V group of semiconductors, by using bond orbital parameter based on tight binding theory with universal parameters. We have reviewed and discussed theoretical formulations for the bond energy. Various optoelectronic properties and bond energy describing the structural behaviour have been studied for the III-V group of semiconductors. Some useful relationships have been obtained by making some theoretical assumptions for s-p splitting of the anion and cation, in the tight binding theory with universal parameters, which yield consistent results for bonding properties of III-V group of semiconductors.

Theory: The bonding properties and bond length distortion of III-V group of semiconductors studied by Kalyan Singh et al. [1] and optoelectronic properties of III-V group of semiconductors studied by V.K. Singh et al. [2-4]. The term bond energy was used by Pauling [5] such that the sum of all bond energies is the energy to separate the system into isolated atoms. In the bond orbital model [6] for polar semiconductors, the bond energy can be approximated by calculating the four major components in the energy as

$$E_{\text{bond}} = E_{\text{pro}} + E_{\text{sig}} + E_{\text{over}} + E_{\text{met}} \quad \dots (1)$$

where E_{pro} is promotion energy, E_{sig} is the bond formation energy, E_{over} is the overlap energy and E_{met} is the metallization energy. There are two aspects to the bond orbital approximation. First is the neglect of coupling between two hybrids on the same atom, but directed into different bonds. Second is the neglect of coupling between one hybrid and a hybrid on a neighbouring atom, but directed into a different bond.

A general sp-hybrid is a normalized sum of an S and P state which can be written,

$$|h\rangle = \cos\beta|S\rangle + \sin\beta|P\rangle \quad \dots(2)$$

the expectation value of the energy for such hybrid is

$$\begin{aligned} \epsilon_h &= \cos^2\beta\epsilon_s + \sin^2\beta\epsilon_p \\ \epsilon_h &= \frac{\epsilon_s + 3\epsilon_p}{3} \quad \dots (3) \end{aligned}$$

for an Sp^3 hybrid with $\cos^2\beta = 1/4$, $\sin^2\beta = 3/4$. The formation of hybrids and σ -bond orbital are characterized by the bond orbital parameters V_1 , V_2 and V_3 which are in fact the metallic, covalent and polar energies respectively.

The metallic energy V_1 for sp^3 hybrids is given by [7,8]

$$V_1 = 1/4 (\epsilon_s - \epsilon_p) \quad \dots (4)$$

Where ϵ_s and ϵ_p are the free atom energies for S and P states, V_1 is the principal term which gives the valency bonds and conduction bonds their width, but it does not affect the total energy in the bond orbital approximation. For this case promotion energy, which is the energy required to promote every electron from its atomic orbital to hybrid orbital is given by [9]

$$E_{\text{pro}} = -2V_1 \quad \dots (5)$$

The covalent energy V_2 is given by [9]

$$V_2 = \frac{\eta\hbar^2}{md^2} \quad \dots (6)$$

Where d is the nearest neighbour distance and η remains constant over the entire range of interest -3.19, -3.26 and -3.22 respectively, for sp , sp^2 and sp^3 hybrids obtained using Harrison universal parameters [7]. According to Harrison [9], this variation is not important and we can take a approximate value -3.22 for tetrahedral semiconductors. Therefore equation [6] reduces to

$$V_2 = -\frac{3.22\hbar^2}{md^2} \quad \dots(7)$$

The coupled hybrids from bonding and anti-bonding states of energy $\epsilon_{h\pm}V_2$ and the gain in energy, called the σ -bonding energy and is given per bond by

$$E_{\text{sig}} = 2V_2 \quad \dots (8)$$

Since there are two electrons for each bond. In a polar bond the two hybrids forming the bond have different energy. The polar energy or hybrid ionic energy V_3 is defined to be the half the difference as follows:

$$V_3 = \frac{(\epsilon_h^c - \epsilon_h^a)}{2} \quad \dots (9)$$

Where ϵ_h^c and ϵ_h^a are cation and anion hybrid energy respectively.

The bond orbital parameters are based upon the tight binding theory, with universal parameters introduced by Harrison [10-13] for the systematic study of properties of semiconductors.

The bond energy E_b , containing promotion energy, σ -bonding energy, overlap interaction effect of metallicity and polarity can be expressed as follows:

$$E_b = V_2 (1 - \alpha_m) + 3 [(V_1^a)^2 + (V_1^c)^2] (1 - \alpha_p^2)^{3/2} / 4V_2 \quad \dots (10)$$

Where α_m is the metallicity defined as

$$\alpha_m = \frac{2V_1}{V_2} \quad \dots (11)$$

α_p is the polarity defined as

$$\alpha_p = \frac{V_3}{(V_2^2 + V_3^2)^{1/2}} \quad \dots (12)$$

V_1^a and V_1^c are the s-p splitting of the anion and cation respectively, we assumed that V_1^a and V_1^c can be taken equal to V_1^s which is the average s-p splitting i.e.

$$V_1^a = V_1^c = V_1^s \quad \dots (13)$$

The metallic energy V_1 is given as [7-9]

$$V_1 = \frac{(\epsilon_s - \epsilon_p)}{4} - \frac{\lambda_{sp\sigma} \hbar^2}{3md^2} \quad \dots (14)$$

Where ϵ_s and ϵ_p are the atomic term values. Their difference $(\epsilon_s - \epsilon_p)$ has been obtained by Harrison [7-9] by using tight binding theory with universal parameters given as

$$\epsilon_s - \epsilon_p = -\frac{5.55 \hbar^2}{md^2} \quad \dots (15)$$

and parameter $\lambda_{sp\sigma}$ is given as

$$\lambda_{sp\sigma} = -\frac{27 \pi^2}{256} \quad \dots (16)$$

using equations (14) to (16) the metallic energy V_1 can be written as

$$V_1 = -1.05 \frac{\hbar^2}{md^2} \quad \dots (17)$$

using equations (11) (13) and (17) with equation (10), the bond energy E_b can be written as

$$E_b = 0.347 V_2 + 3V_1^s (1 - \alpha_p^2)^{3/2} / 2V_2 \quad \dots (18)$$

We have calculated bond energy for III-V group of semiconductors by using equation (18). The input data is given in Table-1. The calculated values of bond energy are compared with the available experimental values [9] as well as with the values obtained by Harrison [9] in Table-2.

Table-1. The values of bond orbital parameters (V_2 , V_3) average s-p splitting (V_1^s) and polarity (α_p) of III-V group of semiconductors.

Compound	V_2 (ev)	V_3 (ev)	V_1^s (ev)	α_p
BN	-10.35	3.12	1.70	0.41
BP	-6.605	1.20	1.54	0.00
BA _s	-6.235	1.07	1.65	0.00
AlN	-7.215	4.09	1.54	0.59
AlP	-4.465	2.17	1.40	0.47
AlAs	-4.205	2.04	1.50	0.44
AlSb	-3.610	1.48	1.35	0.54
GaN	-7.005	3.92	1.65	0.62
GaP	-4.355	2.00	1.50	0.52
GaAs	-4.100	1.87	1.60	0.50
GaSb	-3.535	1.30	1.44	0.44
InN	-6.285	4.150	1.49	0.64
InP	-3.870	2.23	1.35	0.58

InAs	-3.645	2.10	1.44	0.53
InSb	-3.115	1.54	1.30	0.51

Table-2. The value of bond energy E_b (ev) for III-V group of semiconductors

Compound	E_b		
	Present work equation (18)	Expt. values	Harrison values
BN	-3.92	-3.34	-6.45
BP	-2.83	-	-
BAs	-2.82	-	-
AlN	-2.76	-	-
AlP	-2.00	-2.13	-2.04
AlAs	-2.04	-	-
AlSb	-1.70	-	-
GaN	-2.71	-	-
GaP	-1.99	-	-
GaAs	-2.03	-1.63	-1.61
GaSb	-1.86	-	-
InN	-2.42	-	-
InP	-1.72	-	-
InAs	-1.79	-	-
InSb	-1.60	-1.40	-1.14

Result and Discussion: We have studied the bond energy in III-V group of semiconductors. For this purpose we have B-series, Al-series, Ga-series and In-series from III-V group of semiconductors. We have calculated bond energy for III-V group of semiconductors by using equation (18). The input data is given in table-1. The calculated values of bond energy are compound with available experimental values [9] as well as with the values obtained by Harrison [9] in table-2. It is found from table-2 that the values of bond energy obtained by Harrison are far from the experimental values in most of semiconductors in comparison to our results. It shows improvement over the work of Harrison. We have also predicted the values of bond length of some semiconductors belonging III-V group of semiconductors, for which values of bond energy are not reported so, far in the literature.

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