



A Semi-Empirical Approach to Bulk Modulus of $A^N B^{8-N}$ Semiconductors and Their Alloys

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ABSTRACT

In this study, a semi-empirical relation has been developed for bulk modulus in terms of bond energy and bond length and applied to elemental and binary semiconductors. The basis of this formula originates from the very definition of bulk modulus. The universal parameter tight binding approach has been utilized with some modification in the overlap parameter to evaluate bond energy and bond length. The results are in reasonable agreement with those of experiments. The new formula has also been applied to ternary as well as quaternary alloys of II-VI and III-V semiconductors including some highly mismatched alloys. The trend of variation of bulk modulus with composition for both cationic and anionic substitution is explained in terms of ionic size effect.

Keywords: Bond energy; Bond length; Bulk modulus; Solar cell; Highly mismatched alloys; Universal parameter tight binding theory

INTRODUCTION

Semiconductors have long been used widely in electronic industry and today there is hardly any field left without the application of semiconductors. This is because each type of semiconductors has some specific characteristics for an application. The range and horizon of application of semiconductors is broadened further by allowing them to tailor the material properties like lattice parameters, band gaps, bond length, ionicity hardness, bulk modulus etc. required for the new and desired applications [1-13]. For example, the dilute nitride alloys $GaAs_{1-x}N_x$ and $Ga_{1-x}In_xAs_{1-y}Ny$; dilute oxide alloys $ZnS_{1-x}O_x$ and $Zn_{1-x}Cd_xTe_{1-y}O_y$ and some other such combinations $B_xGa_{1-x}N$, $ZnO_{1-x}Te_x$

have been identified as Highly Mismatched Alloys (HMAs) which are the potential candidates for high efficiency solar cell. However, the stability of solar cells is of concern for their application in space, where they have to withstand bombardment of high energy particles like electrons, protons cosmic rays etc. that can cause severe damage to solar cells. Also in domestic, industrial and commercial applications the electronic appliances have to face mechanical stresses and electrical jerks due to voltage fluctuations.

Therefore, study on mechanical properties of these semiconductors and their alloys are of prime importance. Among these properties, focus has been made on bulk modulus, which has in many cases been correlated with material strength and hardness, and it is commonly accepted

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that material with larger bulk modulus are accepted to be harder ones. Of course, this is not always true and recently it has been found that even the materials with very high bulk moduli have low hardness. For example, Rhenium was predicted to have high bulk modulus (405 GPa), but its (Vickers's) hardness was found to be 16.7 GPa, which is about five times lower than that of diamond [14]. Based on this common concept, C_3N_4 was initially proposed to be one of the hardest materials comparable with diamond as its bulk modulus was estimated to be 443 GP, but later on it was synthesized and its hardness was found to be even lower than diamond and BN [15]. Even then bulk modulus is considered as one of the important parameters to characterize physical properties, and for many applications it is used as indicator for materials strength and hardness. In the backdrop of the above scenario, a semi-empirical formula has been developed and presented in this study for bulk modulus of Group IV and IV-IV, II-VI and III-V semiconductors and their ternary and quaternary alloys.

MATERIALS AND METHODS

Theoretical Methods

Brief review of earlier researches: On the theoretical front empirical tight binding method [16], effective bond orbital method [17,18], empirical self-consistent pseudopotential method [19] and density functional theory [20] have emerged as powerful tools for precise calculation of ground state properties of materials. Although various software is, available for these methods, they require profound understanding of the nature of chemical bonding in materials and also advanced computational facilities. Empirical methods easy to work and they also produced results quite in agreement with experimental values and also with those obtained from the advanced computational schemes. Therefore, a number of empirical methods have been developed by researchers for computing bulk modulus of semiconductors. Cohen developed the following bond length (d in Å) dependent relation for bulk modulus of semiconductors.

$$B=1761d^{-3.5} \quad (1)$$

Where;

B=Bulk modulus.

Later on an empirical parameter, λ was introduced in this formula to incorporate the effect of ionicity which stands as follows,

$$B=(1971-220\lambda)/d^{3.5} \quad (2)$$

Where;

$\lambda=0,1$ and 2 for group-IV and IV-IV, III-V and II-Vi respectively.

This formula was quite successful in estimating bulk modulus of III-V semiconductors, but a deviation of estimated values from experimental ones resulted in the range 10.1%-17.3% in case of II-VI systems. This relation was further extended to

study non-octet semiconductors like Si_3N_4 for which following modified formula was suggested.

$$B=<N_c>(1971-220\lambda)/4d^{3.5} \quad (3)$$

Where;

$<N_c>$ =Stands for an average coordination number.

Lam, et al., however, deduced an analytical relation of bulk modulus to the lattice parameters within the local density approximation and the pseudopotential as [27]:

$$B=(1971/d^{3.5})-408(\Delta Z)^2/d^4 \quad (4)$$

Where;

$\Delta Z=0,1,2,3$ for group-IV, III-V, II-VI and I-VII semiconductors respectively. But this formula was applicable to III-V semiconductors only. For II-VI systems they suggested some modification in it. Al-Douri, et al., also suggested a formula similar to that of Cohen.

$$B=(3000-100\lambda)(a/2)^{-3.5} \quad (5)$$

Where;

a =Lattice parameter. This formula estimated the values of bulk modulus which are consistent with the experimental results.

Neumann proposed a formula of bulk modulus in terms of lattice parameter 'a' and spectroscopically defined bond ionicity, f_i figured as:

$$B=b_0a^{-m}(1-g_0f_i) \quad (6)$$

Where;

b_0 , m and g_0 are constants and have the same value for all compounds. Al-Douri further proposed two formulae as:

$$B=(60-\lambda 20) \cdot (E_{g\Gamma X}/\alpha_m) \quad (7)$$

$$B=(30+\lambda 10) [((P_t^{1/2}/E_{g\Gamma X})/3)] \quad (8)$$

Where;

α_m =Metallicity (in eV); $E_{g\Gamma X}$ =Energy gap (in eV) along $\Gamma-X$. $\lambda=0, 2$ and 2.65 for group IV, III-V and II-VI semiconductors respectively.

P_t =Transition pressure.

Kamran, et al., however, suggested and also attempted to give theoretical basis to the following formula of bulk modulus:

$$B=(1938.72-506.702 f_i)/d^{3.5} \quad (9)$$

Where;

f_i =Bond ionicity.

Results obtained using this formula, in general, fall within 19% of the experimental values. In the bond orbital method however, the bulk modulus was proposed as:

$$B=2^*3^{1/2}(V_2 \alpha_c^3 + 7.8/d^2)/3d^3 \quad (10)$$

Where;

V_2 =Covalent energy, is given by,

$$V_2 = -\eta \hbar^2 / 4\pi^2 m d^2 \quad (11)$$

Here;

η = Overlap parameter,

α_c = Covalence of the bond and m is the mass of the electron.

This formula could give somewhat better results. In the ionic charge approach of bond orbital model, Verma proposed a d -3 dependence formula of bulk modulus.

A new formula proposed: Various formulae noted in the above sub-section clearly demonstrated the bond length dependence of bulk modulus along with some other parameters like bond ionicity, band gap, covalency, transition pressure, metallicity, covalent energy, bond charge etc. But the values predicted with different formulae differ widely among themselves and from the experimental ones. Also, the d -dependence power varies like $d^{-3.5}$, d^{-4} and d^3 . This aspect, therefore, needs to be revisited. In this attempt, we begin with the basic definition of bulk modulus and proposed a semi empirical formula. From definition, bulk modulus, the property of a material showing its resistance to volume change on compression, is given by

$$B = -P / (dV/V) \quad (12)$$

Where;

dV/V = Volume strain is dimensionless and the stress

$$P = F/A = E/V \quad (13)$$

Here;

F = Force (restoring),

A = Area,

E = Energy

V = Volume.

The volume of the unit cell of a cubic crystal, $V \propto d^3$.

Where;

d = Bond length.

Therefore, bulk modulus should bear an inverse cubic dependence relation with bond length, *i.e.*

$$B \propto E/d^3 \quad (14)$$

Here, bond energy E_b is proposed to be used in place of E . This is because the bond energy of a stronger bond must be higher and for such a bond the resistance against any deformation (volume) should be higher giving rise to higher bulk modulus. Accordingly, B is expected to bear a linear relationship with E_b/d^3 . With this assumption, we have applied the Universal Parameter Tight Binding (UPTB) theory to evaluate E_b and d for group-IV, IV-IV, III-V and II-VI semiconductors and some ternary and quaternary alloys. Then graphs were plotted for B versus E_b/d^3 for group-IV and IV-IV, III-V and II-VI systems which were found to be linear, with the help of which the new relation has been proposed. But before arriving at the new relation, a brief introduction of UPTB theory appears plausible. In the UPTB formalism, the

bond energy is expressed in terms of four main contributing energy terms as:

$$E_b = E_p + E_\sigma + E_o + E_m \quad (15)$$

Where;

E_p = Promotional energy.

E_σ = Sigma bond formation energy.

E_o = Overlap energy.

E_m = Metallization energy.

These constituent energies are expressed in parameterized forms through the metallic, covalent, polar and hybrid energies, which are expressed in terms of atomic orbital energies. Actually, the metallic, covalent, polar and hybrid energies originate out of the non-zero matrix elements of the Hamiltonian between hybrids of the bond forming atoms.

The hybrid energy (expectation value) of a tetrahedral solid having sp^3 hybrids is given by

$$\epsilon_h = \frac{\epsilon_s + 3\epsilon_p}{4} \quad (16)$$

$$\text{Where } \epsilon_s = \langle s | H | s \rangle \quad (17)$$

$$\epsilon_p = \langle p_x | H | p_x \rangle = \langle p_y | H | p_y \rangle = \langle p_z | H | p_z \rangle \quad (18)$$

H = Hamiltonian of the system.

These energy values differ somewhat in the solids from the corresponding values for free atoms. However, following Harrison's prescription the free atom energy (Hartree-Fock term) values have been utilized in the present work. The metallic energy is given by

$$V_1 = -\langle h_i | H | h_j \rangle = \frac{1}{4}(\epsilon_p - \epsilon_s) \quad (19)$$

The hybrid covalent energy is expressed as

$$\begin{aligned} V_2 &= -\langle H^i | H | H^k \rangle \eta_{sp^3} \\ &= \frac{(-V_{ss\sigma} + 2\sqrt{3}V_{sp\sigma} + 3V_{pp\sigma})}{4} \\ &= -3.22 \frac{\hbar^2}{md^2} \end{aligned} \quad (20)$$

For tetrahedral solids, considering matrix elements between nearest neighbor atoms only, Froyen and Harrison proposed that;

$$V_{ilm} = \frac{\eta_{ilm} \hbar^2}{md^2} \quad (21)$$

Where;

where the subscript m is a quantum number, but m in the denominator represents the electron mass, d is the bond length (in Å) and η_{ilm} is a dimensionless coefficient with

$\eta_{ss\sigma}$, $\eta_{sp\sigma}$, $\eta_{pp\sigma}$, $\eta_{pp\pi}$ and $\eta_{sp\pi}$ having the following values:

$$\eta_{ss\sigma} = -1.30$$

$$\eta_{sp\sigma} = 1.42$$

$$\eta_{pp\sigma} = 2.22$$

$$\eta_{pp\pi} = 0.63$$

$$\text{and } \eta_{sp\pi} = -0.63$$

In case of polar covalent solids, the hybrid polar energy is represented as:

$$V_3 = \frac{1}{2}(\epsilon_h^c - \epsilon_h^a) \quad (22)$$

Where;

c(a)=Cation (anion).

Therefore, following Kraut and Harrison, a general expression of bond energy as given below was utilized.

$$E_b = 2V_2 + \frac{2\eta_o V_2^2}{|\epsilon_h^c + \epsilon_h^a|} \frac{1}{4} \frac{(V_{1c}^2 + V_{1a}^2 - V_{1IV(c)}^2 - V_{1IV(a)}^2)V_2^2}{(V_2^2 + V_3^2)^{3/2}} \quad (23)$$

Where;

$V_{1IV(c)}$ and $V_{1IV(a)}$ are the values of V_1 for the column-IV elements from the rows of the atoms corresponding to the cation and the anion respectively. In the equilibrium state, the bond energy is minimum. But among the various energy terms, only V_2 includes 'd'. So E_b was minimized with respect to V_2 . Then employing Newton-Raphson numerical technique, the self-consistent values of V_2 , d and E_b were obtained. For selection of the overlap parameter η_o , initially, Harrison's approach of using geometrical mean of η_o values corresponding to the respective homoploid semiconductor, i.e. for a compound A_iB_j with i and j denoting rows of elements A and B in the periodic table, the effective η_o is given by:

$$\eta_o = \sqrt{\eta_{oi}\eta_{oj}} \quad (24)$$

Where;

η_{oi} and η_{oj} =Values for η_o for the group-IV elements of the i^{th} and j^{th} rows respectively.

This mode of selection of η_o has earlier been used by Baranowski Talwar, et al. and Sasireka, et al., also, but in several cases the values of bond length deviated more from experimental values. In an attempt to improve the results, it is argued that elements exhibit periodic properties. So, each element of a period must have its own weightage in deciding the properties of a compound formed with the constituent elements. Therefore a weighted average of overlap parameters corresponding to the respective periods as given below was utilized in this study.

$$\eta_w = \frac{P_a\eta_a + P_c\eta_c}{P_a + P_c} \quad (25)$$

Where;

$P_a(P_c)$ =Period number considering c-row as P=1.

$\eta_o(\eta_c)$ =Overlap parameter of anion(cation).

This modification led to a two prong advantage first the results of bond length improved and second, the number of iterations reduced to get self-consistency.

RESULTS AND DISCUSSION

Using the method discussed, bond length and bond energy of group IV and IV-IV, III-V and II-VI semiconductors were calculated and are given in **Tables 1-3** respectively.

Table 1: Bond length, d (in Å) and bond energy, E_b (in eV) of semiconductors belonging to group IV and IV-IV semiconductors.

System		d (in Å)			E_b (in eV)	
		This Study	Exp.	Reported		
				Baranowski JM		Baranowski JM
IV	C	1.532	1.544	1.61	1.596	-30.877
and IV-IV	Si	2.326	2.352	2.35	2.346	-13.306
	Ge	2.428	2.449	2.45	2.455	-12.273
	Sn	2.703	2.81	2.8	2.734	-9.3222
	SiC	1.826	1.877	1.95	1.942	-21.506
	GeC	1.973				-19.215

SnC	2.143	-16.639
SiSn	2.58	-11.238
GeSn	2.64	-10.571
SiGe	2.398	-12.808

Table 2: Bond length, d (in Å) and bond energy, E_b (in eV) of Gr. III-V semiconductors.

Systems		d (in Å)				E_b (in eV)
		This study	Exp.	Reported		
	Baranowski JM			Baranowski JM	Talwar DN, et al.	
III-V	BN	1.538	1.565	1.57	1.561	-31.631
	BP	2.039	1.965	1.96	2.356	-19.88
	BAS	2.161	2.068	2.02	2.008	-17.888
	AlN	1.993	1.904	1.88	1.9	-23.763
	AIP	2.346	2.367	2.34	2.356	-15.207
	AlAs	2.42	2.442	2.42	2.435	-14.359
	AlSb	2.673	2.805	2.61	2.581	-10.632
	GaN	2.026	1.953	1.9	1.93	-22.712
	GaP	2.386	2.358	2.37	2.395	-15.445
	GaAs	2.451	2.448	2.11	2.474	-14.405
	GaSb	2.649	2.639	2.63	2.62	-12.203
	InN	2.225	2.163	2.04	2.043	-19.649
	InP	2.568	2.541	2.54	2.537	-13.814
	InAs	2.613	2.623	2.62	2.622	-13.028
InSb	2.812	2.805	2.82	2.768	-11.14	

Table 3: Bond length, d (in Å) and bond energy, E_b (in eV) of group II-VI semiconductors.

Systems		d (in Å)			E_b (in eV)	
		This study	Exp.	Reported		
	Baranowski JM			Baranowski JM	Talwar DN, et al.	
II-VI	BeO	1.521	1.65	1.46	1.256	-35.741
	BeS	2.18	2.1		1.898	-23.415
	BeSe	2.213	2.2		1.99	-21.528
	BeTe	2.342	2.4		2.15	-18.296
	ZnO	1.933	1.992	1.75	1.793	-28.812

ZnS	2.332	2.341	2.3	2.388	-21.247
ZnSe	2.428	2.445	2.3	2.509	-19.643
ZnTe	2.693	2.642	2.65	2.697	-16.954
CdO	2.101	2.03			-28.774
CdS	2.482	2.526	2.48	2.544	-19.623
CdSe	2.556	2.62	2.6	2.676	-18.318
CdTe	2.794	2.805	2.86	2.87	-16.005
HgS	2.342	2.513		2.556	-20.051
HgSe	2.783	2.635	2.59	2.69	-18.449
HgTe	2.902	2.797	2.85	2.886	-16.331

Graphs are plotted for bulk modulus (experimental) against E_b/d^3 for these systems for which linear graphs are obtained shown in **Figures 1-3** respectively. Regression analysis gives high correlation of 0.996, 0.991 and 0.979 respectively for these systems.

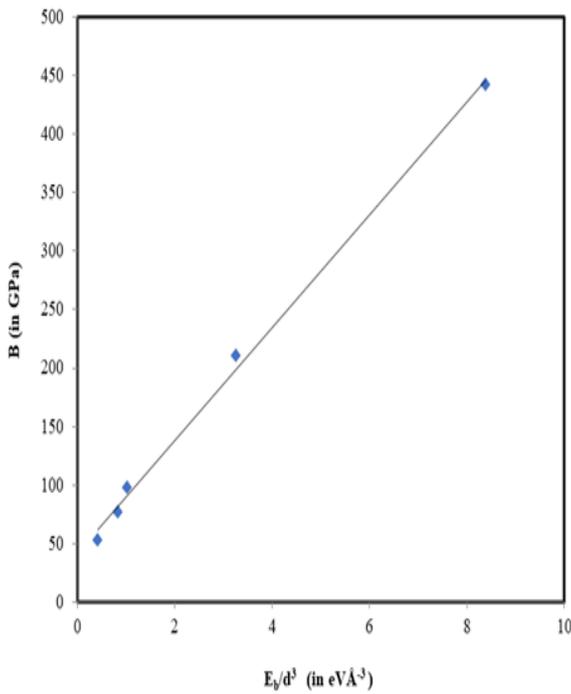


Figure 1: Plot of B versus E_b/d^3 for gr. IV and IV-IV semiconductors.

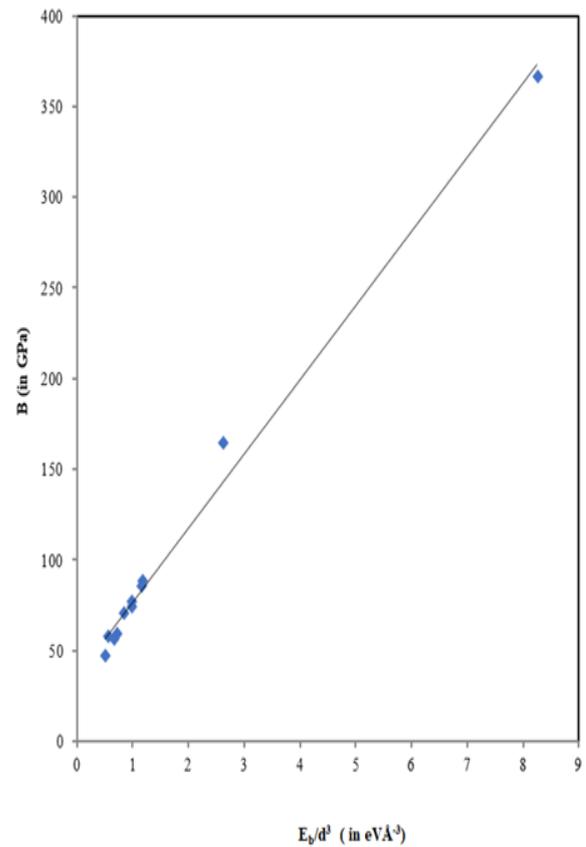


Figure 2: Plot of B versus E_b/d^3 for III-V semiconductors.

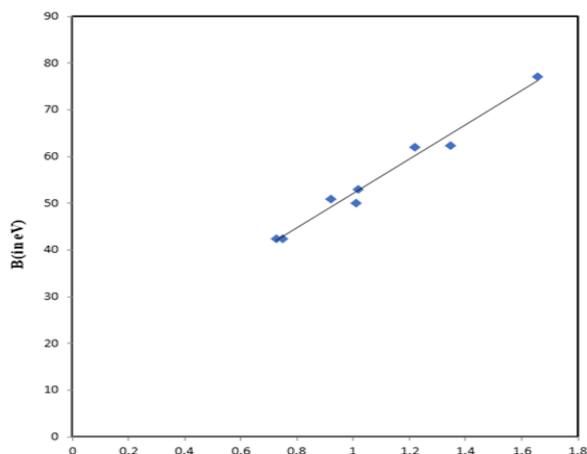


Figure 3: Plot of B versus E_b/d^3 for II-VI semiconductors.

With the help of these graphs, the following general relation is proposed for estimation of bulk modulus of the semiconductors

$$B = (48.23 - 7.39 \lambda^{0.63547}) E_b/d^3 + (41.97 - 5.80 \lambda^{2.19784}) \quad (26)$$

Where;

$\lambda = |G_B - G_A|/2$ with G_A and G_B being the group numbers of elements A and B respectively in the periodic table. The calculated values of bulk modulus along with the experimental and reported ones for group-IV and IV-IV, III-V and II-VI systems are shown in Tables 4-6 respectively.

Table 4: Bulk modulus B (in GPa) of gr. IV and IV-IV semiconductors.

Systems	Bulk modulus, B (in GPa)							
	This study		Exp.	Reported values				
	Using exp. d	Using cal. d	Lam PK, et al.	Kitamura M, et al.	Kamran S, et al.	Cohen ML	Misra G	Dutta MS
C	446.56	456.14	442	393	418.2	435	444.3	449.33
Si	91.29	92.97	98	87	97.4	99	100.1	92.06
Ge	82.27	83.32	77.2	76.3	84.2	85	87.4	84.26
Sn	62.23	64.74	53	46	52.1	57	55.8	67.62
SiC	198.82	212.23	211	185	202.9	213	212.7	187.87
GeC		162.63			181 ^a , 188 ^b			157.49
SnC		123.51			119 ^a , 133 ^b			120.72
SiSn		73.98			72.47 ^c , 68.55 ^c			77.23
GeSn		69.68			56 ^c , 53.8 ^c			73.67
SiGe		86.77			88.6 ^d , 87.6 ^c			88.13

Table 5: Bulk Modulus, B (in GPa) of III-V semiconductors.

Systems	Bulk modulus (B In GPa)						
	This work		Exp.	Reported values			
	Using exp. d	Using cal. d	Lam PK, et al.	Kitamura M, et al.	Kamran S, et al.	Misra G, et al.	Misra G, et al.
BN	373.9	391.25	367	346	373	367	351.2
BP	143.18	131.95	165	165	180.4	166	154.1

BA _s	118.77	108.56		138	151.8	138	
AlN	176.77	158.76			180.9		
AlP	83	84.27	86	80.5	88.3	86.7	86.3
AlAs	76.44	77.55	77	74	80.5	78.3	78.3
AlSb	55.84	58.9	58.2	54.1	56.1	57	59
GaN	160.69	147.71					
GaP	84.28	82.61	88.7	81.5	86.6	86.7	86.3
GaAs	76.27	76.12	74.8	72.4	77.4	76.1	76.1
GaSb	63.29	69.98	57	55.4	59.6	57.8	59.6
InN	115.47	169.02			111.1		
InP	70.56	69.48	71	60.8	66.1	67	68.7
InAs	65.65	65.99	60	56.3	61.2	61	62.8
InSb	56.78	56.63	47.4	44	47.7	47.1	49.4

Table 6: Bulk modulus, B (in GPa), of II-VI semiconductors.

Systems	Bulk modulus, B (in GPa)							
	This study		Exp. Lam PK, et al.	Reported values				
	Using exp. d	Using cal. d		Kitamura M, et al.	Kamran S, et al.	Misra G, et al.	Cohen ML, et al.	Kumar V, et al.
BeO	307.76	388.65						303.17
Bes	108.28	98.42		120	132.7			113.11
BeSe	89.66	88.36		105	113.2			96.55
BeTe	64	67.7		78	86.5			68.81
ZnO	149.32	161.96						146.19
ZnS	76.22	76.93	77.1	73.3	82.8	78.1	72	75.31
ZnSe	64.75	65.79	62.4	65.1	69.3	66.5	63.9	65.3
ZnTe	49.15	47.26	51	51.9	55.6	51.2	52.2	55.74
CdO	141.77	129.38						
CdS	60.1	62.52	62	53.2	62.6	60.3	59.5	56.79
CdSe	52.79	55.67	53		54.4	52.6	53.9	49.67
CdTe	42.01	42.33	42.4	40.2	42.9	41.2	44	43.32
HgS	61.79	72.72			60.1			56.52
HgSe	52.42	46.82	50		55.1	51.9	53	49.52
HgTe	42.79	39.92	42.3		46.1		45.7	41.87

In the above relation, λ takes care of the ionicity effect, because for $\lambda=0, 1, 2$ for group-IV and IV-IV, III-V and II-VI semiconductors for which the average bond ionicity increases along ((IV-IV) \rightarrow (III-V) \rightarrow (II-VI)). Hence the bulk modulus decreases in the sequence ((IV-IV) \rightarrow (III-V) \rightarrow (II-VI)). The calculated values of bulk modulus of the semiconductors studied are in reasonable agreement with the experimental and other reported values. It is interesting to note that the compounds involving elements from the carbon-row *i.e.* carbides, nitrides and oxides exhibit higher bulk moduli and their respective classes. This might be due to absence of core

p-electrons in atoms of elements from C-row which allows them in deeper overlapping of orbitals in bond formation. Encouraged with these results, the general formula was applied as an extension to the ternary systems $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and $\text{In}_{1-x}\text{Ga}_x\text{P}$ having cation substitution, and $\text{ZnS}_{1-x}\text{Se}_x$ and $\text{InP}_{1-x}\text{As}_x$ having anion substitution. Results are presented in **Tables 7 and 8**. The graphs showing variation of bulk modulus with composition are shown in **Figures 4 and 5**.

Table 7: Variation of Bulk Modulus (in GPa) with composition in ternary system $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and $\text{In}_{1-x}\text{Ga}_x\text{P}$.

System	Bulk modulus, B (in GPa)			
	$\text{Cd}_{1-x}\text{Zn}_x\text{S}$		$\text{In}_{1-x}\text{Ga}_x\text{P}$	
x	This work	Exp. (Lam PK, et al.)	This work	Exp. (Lam PK, et al.)
0	63.487	62	71.279	71
0.01	63.606		71.394	
0.025	63.787		71.572	
0.05	64.032		71.823	
0.075	64.337		72.121	
0.1	64.586		72.376	
0.2	65.777		73.555	
0.3	66.945		74.729	
0.4	68.211		75.943	
0.5	69.453		77.201	
0.75	72.871		80.587	
0.9	74.966		82.788	
1	76.498	77.1	84.281	88.7

Table 8: Variation of bulk modulus (in GPa) with composition in ternary systems $\text{ZnS}_{1-x}\text{Se}_x$ and $\text{InP}_{1-x}\text{As}_x$.

System	Bulk modulus, B (in GPa)			
	$\text{ZnS}_{1-x}\text{Se}_x$		$\text{InP}_{1-x}\text{As}_x$	
x	This work	Exp. (Lam PK, et al.)	This work	Exp. (Lam PK, et al.)
0	76.498	77.1	71.279	71
0.01	76.371		71.212	
0.025	76.143		71.131	
0.05	75.866		70.987	
0.075	75.515		70.841	
0.1	75.24		70.698	

0.2	73.933		70.123
0.3	72.728		69.52
0.4	71.475		68.966
0.5	70.319		68.42
0.75	67.462		67.053
0.9	65.793		66.278
1	64.749	62.4	65.773
			60

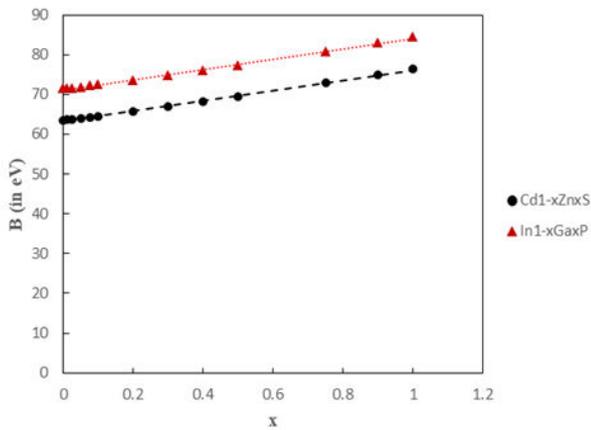


Figure 4: Plot showing the variation of bulk modulus (in GPa) with composition in ternary systems $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and $\text{In}_{1-x}\text{Ga}_x\text{P}$.

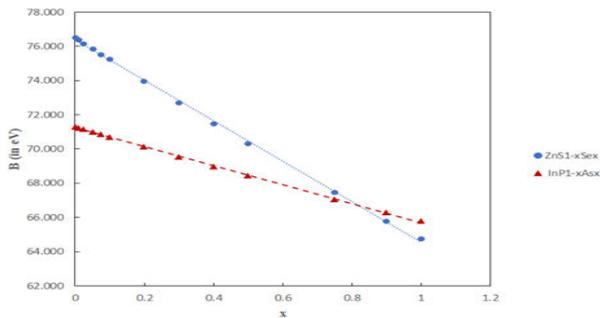


Figure 5: Plot showing the variation of bulk modulus (in GPa) with composition in ternary systems $\text{ZnS}_{1-x}\text{Se}_x$ and $\text{InP}_{1-x}\text{As}_x$.

Table 9: Variation of bond length, d (in Å), bond energy, E_b (in eV) and bulk modulus, B (in GPa) with composition in dilute oxide quaternary HMAAs $\text{Zn}_{1-x}\text{Cd}_x\text{Te}_{1-y}\text{O}_y$ and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}_{1-y}\text{O}_y$.

System →		$\text{Zn}_{1-x}\text{Cd}_x\text{Te}_{1-y}\text{O}_y$			$\text{Cd}_{1-x}\text{Zn}_x\text{Te}_{1-y}\text{O}_y$		
x	y	d (in Å)	E_b (in eV)	B (in GPa)	d (in Å)	E_b (in eV)	B (in GPa)
0.1	0	2.658	16.92	48.473	2.789	16.107	42.645
	0.02	2.645	17.181	49.482	2.773	16.393	43.613
	0.04	2.632	17.441	50.514	2.758	16.679	44.578
	0.1	2.592	18.221	53.813	2.712	17.538	47.672
	0.4	2.393	22.125	74.695	2.484	21.832	67.708

It can be seen that B increases with x in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and $\text{In}_{1-x}\text{Ga}_x\text{P}$ whereas it decreases with x in $\text{ZnS}_{1-x}\text{Se}_x$ and $\text{InP}_{1-x}\text{As}_x$. This is primarily because of ionic size effect. With decreasing ionic size in the former case ($\text{Cd}^{+2}=0.78$ Å; $\text{Zn}^{+2}=0.6$ Å; $\text{In}^{+3}=0.8$ Å, $\text{Ga}^{+3}=0.62$ Å) the bond length decreases, ionicity decreases and the bulk modulus increases, whereas in the latter case the increasing ionic size ($\text{S}^{-2}=1.84$ Å; $\text{Se}^{-2}=1.98$ Å; $\text{P}^{-3}=2.12$ Å; $\text{As}^{-3}=2.22$ Å) leads to opposite effect. The results also exhibit a small departure from the Vegard's law. Therefore, bond length and bond energy of these systems were calculated using Vegard's law. Such deviations from Vegard's law have also been reported in the lattice constants and bulk modulus in $\text{ZnS}_x\text{Se}_{1-x}$, lattice constants and band gaps in $\text{A}_x\text{Zn}_{1-x}\text{O}$ ($\text{A}=\text{Ca}, \text{Cd}, \text{Mg}$), $\text{BxGa}_{1-x}\text{N}$ and band gap in $\text{BxIn}_{1-x}\text{N}$ alloys.

The study is further extended to dilute oxide and diluted nitride quaternary HMAAs $\text{Zn}_{1-x}\text{Cd}_x\text{Te}_{1-y}\text{O}_y$, $\text{Cd}_{1-x}\text{Zn}_x\text{Te}_{1-y}\text{O}_y$ and $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{Ny}$, $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{Ny}$. Results are given in [Tables 9 and 10](#).

	0.8	2.128	27.33	119.588	2.179	27.557	113.246
	1	1.996	29.932	153.689	2.026	30.419	149.786
0.2	0	2.675	16.819	47.651	2.772	16.208	43.325
	0.02	2.661	17.082	48.677	2.757	16.491	44.28
	0.04	2.648	17.346	49.692	2.742	16.774	45.262
	0.1	2.607	18.136	52.976	2.697	17.623	48.374
	0.4	2.405	22.088	73.714	2.472	21.868	68.561
	0.8	2.135	27.358	118.672	2.172	27.528	114.091
	1	2	29.993	153.141	2.022	30.358	150.315
0.3	0	2.691	16.717	46.887	2.756	16.31	43.994
	0.02	2.677	16.984	47.895	2.741	16.59	44.966
	0.04	2.663	17.25	48.929	2.727	16.87	45.932
	0.1	2.622	18.051	52.161	2.682	17.709	49.095
	0.4	2.416	22.052	72.827	2.461	21.905	69.369
	0.8	2.141	27.386	117.91	2.166	27.5	114.812
	1	2.003	30.054	152.801	2.019	30.297	150.645
0.5	0	2.724	16.514	45.385	2.724	16.514	45.385
	0.02	2.709	16.787	46.392	2.709	16.787	46.392
	0.04	2.695	17.06	47.39	2.695	17.06	47.39
	0.1	2.652	17.88	50.589	2.652	17.88	50.589
	0.4	2.439	21.978	71.029	2.439	21.978	71.029
	0.8	2.154	27.443	116.274	2.154	27.443	116.274
	1	2.011	30.176	151.719	2.011	30.176	151.719

As expected the ionic-size (ionicity) effect is clearly reflected in these systems too. The results can be seen with γ ranging from 0 to 1 for a given value of x and similarly with x ranging from 0 to 0.5 for a given value of γ .

CONCLUSION

In consideration of the importance of bulk modulus of semiconductors for various applications including solar cells, a semi empirical formula for bulk modulus of semiconductors has been proposed involving bond energy and bond length. It has been applied to group IV and IV-IV, III-V and II-VI semiconductors and also to ternary and quaternary alloys. Trend of variation of bulk modulus with composition (alloy) is interesting to note. It is hoped that this study may shed light in better understanding of the trend of variation of various properties of semiconductor alloys especially in highly mismatched alloys.

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