VARIATION OF MICROHARDNESS WITH COMPOSITION IN $A^N B_{1-x}^{8-N} C_x^{8-N}$ AND $A_{1-x}^N C_x^N B^{8-N}$ TERNARY SEMICONDUCTORS

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Abstract-The composition effect on bond hardness and microhardness of semiconductors alloys, $InP_{1-x}As_x$, $In_{1-x}Ga_xP$, $ZnS_{1-x}Se_x$ and $Cd_{1-x}Zn_xS$ has been reported in this paper. The value of both bond hardness and microhardness tend to increase (decrease) with decrease (increase) in ionic size of the doped ion relative to the host ion. Based on this trend of variation a linear relation has been proposed between microhardness and bond hardness. The covalent and ionic contributions to bond hardness are separately computed and then the resultant value has been calculated for each of the systems studies with x ranging from o to 1. Results are in good agreement with the experimental and reported values.

Keywords: semiconductor alloys**,** atomic stiffness, bond hardness, microhardness, ionicity.

1. INTRODUCTION

During the last few decades the study of various properties of tetrahedral semiconductors and their alloys, and their variation with impurity content has drawn considerable attention of scientist and researchers due to their important practical and technological applications in the fields of, laser diode, light emitting diode, opto-electronic devices, solar cell, infrared detector, quantum dot, quantum well, quantum wire etc. [1-7]. Beside electronic properties of semiconducting materials, structural properties also need to be addressed in order to understand their mechanical behaviour. Microhardness plays an important role in understanding the mechanical behaviour of materials. But the experimental [8] and theoretical values [1, 9-12] of microhardness of quite a few of these materials vary in a wide range and experimental values of microhardness of several materials are not known. On theoretical front ab initio techniques require sophisticated computational facilities, detailed crystal structure and significant effort of time. So, empirical and semi empirical methods are widely used which also estimate/predict values in close agreement with experimental values and /or those of ab-initio calculations in addition to providing the general trend of variation of physical properties with other parameters.. Empirical relations for the estimation of microhardness have been reported by several researchers [1, 9, 10, 12]. In this paper, we have made an attempt to propose a correlation between microhardness and bond hardness of II-VI and III-V binary semiconductors and their alloys. Also, the composition dependence of these properties has been proposed through linear relations.

2. THEORETICAL APPROACH

It is argued that increased bond stiffness (hardness) of a material must raise its stress or resistance against volume strain, which in turn increase its microhardness.

Therefore, it is expected that bond stiffness must reflect its signature on microhardness. In other words microhardness should increase (decrease) with increase (decrease) of bond hardness. This aspect has been shown [13] using bond hardness. But in a molecule of a compound the atoms do not remain neutral. The bond between atoms of a compound is partially ionic and partially covalent. Covalency of bond contributes to increased hardness of materials, whereas ionicity softens the bond [14-19]. Therefore, covalency and ionicity must have independent contributions to bond hardness as well as microhardness. Here we intend to compute the bond hardness considering the covalent and the ionic contributions separately and then obtaining the resultant of them. In this attempt, we, following Li and Xue [20] define the electron holding energy of atoms with a covalent bond as

$E_c = Z / R^c$ (1)

Similarly the electron holding energy of an atom with an ionic bond is defined as

$E_i = Z / R^i$ (2)

where Z is the number of valence electrons and $R^{c(i)}$ is the covalent (ionic) radius of the i^{th} atom. Accordingly, the atomic stiffness is expressed as

$$S^{c(i)} = E_{c(i)} / (R^{c(i)})^3 \quad (3)$$

The hardness of the covalent (ionic) bond a-b of a compound 'ab' defined as the electron- holding energy of the bond per unit volume, is given by the geometric mean of atomic stiffness per bond of atoms, i.e

$$H_{ab}^{c(i)} = (S_a^{c(i)} S_b^{c(i)} / C_{Na} C_{Nb})^{0.5} = (Z_a Z_b / C_{Na} C_{Nb})^{0.5} / (R_a^{c(i)})^2 (R_b^{c(i)})^2 \quad (4)$$

where C_{Ni} (i = a, b) is the co-ordination number of the i^{th} atom. Bond hardness of II-VI and III-V semiconductors was calculated using Eq. (4). The resultant bond hardness is given by

$$H_{ab} = H_{ab}^{c} f_c + H_{ab}^{i} f_i \quad (5)$$

where H_{ab}^{c} is the covalent contribution to the bond hardness, H_{ab}^{i} is the ionic contribution to the bond hardness, f_c is the covalency and f_i is the ionicity. The value of ionicity (f_i) and covalency (f_c) has been obtained from our newly proposed model [21], and accordingly the resultant bond hardness has been calculated. The available experimental values of microhardness (H in GPa) of III-V and II-VI semiconductors were then plotted against the computed bond hardness, H_{ab} (in GPa) (Eq. 5). Plots are linear (Fig. 2.1 and 2.2) with correlations of 0.996 and 0.999 respectively for III-V and II-VI semiconductors indicating strong linear dependence of microhardness on bond hardness.

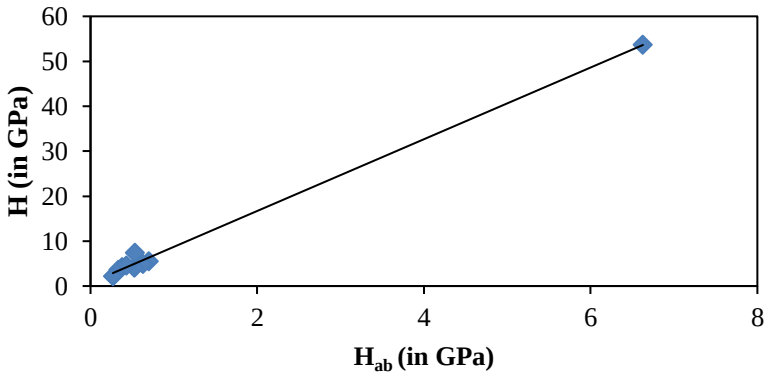

Fig. 2.1 Plot of microhardness, H versus bond hardness, H_{ab} of III-V semiconductors

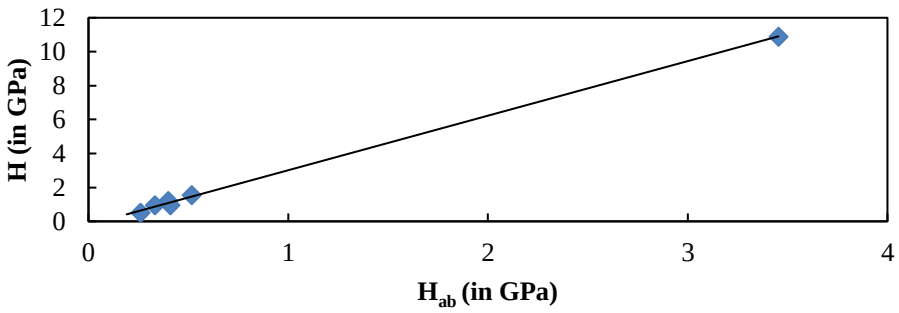

Fig. 2.2 Plot of microhardness, H versus bond hardness, H_{ab} of II-VI semiconductors

Accordingly, the following relation is proposed for microhardness in terms of bond hardness

$$H = a\, H_{ab} - b \quad (6)$$

W here a and b are the fitting parameters. The values of 'a' and 'b' are proposed as 7.9793, 0.7444 and 3.2154, 0.2006 for group III-V and II-VI semiconductors respectively. This relation has been utilised in computing microhardness of binary tetrahedral semiconductors and microhardness of other III-V and II-VI semiconductors for which experimental values, to the best of our knowledge, are not available. Thereafter, bond hardness and microhardness of ternary semiconductor alloys were computed by varying their composition (impurity content). For obtaining the bond Strength of $A_{1-x}^{N} C_x^{N} B^{8-N}$ semiconductor alloys, we have used the formula

$$H_{ab}(A_{1-x}^{N} C_x^{N} B^{8-N}) = (1-x) H_{ab}(AB) + x H_{ab}(CB) \quad (7)$$

Similarly, for $A^{N} B_{1-x}^{8-N} C_x^{8-N}$ alloys,

$$H_{ab}(A^{N} B_{1-x}^{8-N} C_x^{8-N}) = x H_{ab}(AC) + (1-x) H_{ab}(BC) \quad (8)$$

The corresponding microhardness of these ternary systems are computed as

$$H(A_{1-x}^{N} C_x^{N} B^{8-N}) = a H_{ab}(A_{1-x}^{N} C_x^{N} B^{8-N}) + b \quad (9)$$

$$H(A^{N} B_{1-x}^{8-N} C_x^{8-N}) = a H_{ab}(A^{N} B_{1-x}^{8-N} C_x^{8-N}) + b \quad (10)$$

Bond strength and microhardness of ternary semiconductors alloys have been computed for x=0 to1using Eqs. (7), (8), (9) and (10). Results are given in Table 3 and 4 along with available experimental and reported values for comparison. The computed values are in good agreement with the reported values

3. RESULTS AND DISCUSSION

Calculated values of bond strength (H_{ab} in Gpa) using Eq. (5), bond ionicity (f_i) [21] and bond covalency (f_v) [21] of group III-V and II-VI are presented in Table 3.1. Estimated values of microhardness (H in GPa) of group III-V and II-VI semiconductors using Eq. (6) are given in Table 3.2 along with experimental and the reported values. Results obtained are in reasonable agreement with the experimental and other reported values [1, 8, 9, 12, 13] which support the validity of the relation, Eq. (6).

DOI Number: https://doi.org/10.30780/specialissue-ICAASET021/025 pg. 161
Paper Id: IJTRS-ICAASET2021-025

Table-3.1 Calculated Bond Strength (H_{ab} in GPa) using Eq. (5), bond ionicity(f_i) and bond covalency (f_v) for group III-V and II-VI semiconductors

	Systems	f_i Ref. [21]	f_c Ref. [21]	H_{ab} (in GPa) (Eq.5)	Systems		f_i Ref. [21]	f_c Ref. [21]	H_{ab} (in GPa) (Eq.5)
					II-VI				
III-V	BN	0.158	0.842	6.627		BeO	0.453	0.547	3.454
	BP	0.227	0.773	4.898		BeS	0.573	0.427	2.288
	BAS	0.243	0.757	4.650		BeSe	0.596	0.404	2.003
	BSb	0.276	0.724	4.175		BeTe	0.637	0.363	1.674
	AlN	0.216	0.784	1.228		ZnO	0.547	0.453	1.081
	AlP	0.298	0.702	0.697		ZnS	0.626	0.374	0.615
	AlAs	0.312	0.688	0.628		ZnSe	0.647	0.353	0.517
	AlSb	0.348	0.652	0.527		ZnTe	0.679	0.321	0.411
	GaN	0.224	0.776	1.177		CdO	0.602	0.398	0.721
	GaP	0.297	0.703	0.598		CdS	0.660	0.340	0.399
	GaAs	0.314	0.686	0.532		CdSe	0.676	0.324	0.332
	GaSb	0.348	0.652	0.431		CdTe	0.705	0.295	0.261
	InN	0.262	0.738	0.749		HgS	0.661	0.339	0.305
	InP	0.329	0.671	0.377		HgSe	0.678	0.322	0.249
	InAs	0.343	0.657	0.334		HgTe	0.705	0.295	0.191
	InSb	0.375	0.625	0.268					

Table-3.2 Microhardness, H (in GPa) of Gr. III-V and II-VI semiconductors obtained from bond hardness [Eq. (6)] along with experimental and reported values

System		Microhardness, H (in GPa)					
		This study	Exp. (Ref. 8)	Reported			
				Ref.[1]	Ref. [9]	Ref.[12]	Ref. [13]
III-V	BN	53.62	34.3-73.0	39.70	30.02	45.8	54.49
	BP	39.8	31.4-40	25.91	16.89	32.3	20.12
	BAS	37.8	19	19.46	12.33	24.2	16.55
	BSb	34.05					11.67
	AlN	10.54			18		24.44
	AlP	6.31	5.5	8.71	9.816	10.9	7.91
	AlAs	5.76	4.8,5	6.67	6.914	6.3	6.18
	AlSb	4.95	4	3.18	4.351		3.89
	GaN	10.13		27.10	13.95		24.67
	GaP	5.51	9.45	8.55	7.41		8.00
	GaAs	4.98	7.5,7.21	5.86	5.172		6.27
	GaSb	4.18	4.48	2.75	3.091		3.95
	InN	6.72		14.90	9.816		17.94
	InP	3.75	4.10,4.30	4.78	4.813		5.26
	InAs	3.41	3.30,3.84	3.68	3.123		3.95
	InSb	2.88	2.20	2.05	1.464		2.18
II-VI	BeO	10.91	9.1-12.7	8.98	6.94		15.34
	BeS	7.16		3.12	3.72		4.56
	BeSe	6.24		2.54	2.59		3.63
	BeTe	5.18		1.50	1.74		2.39
	ZnO	3.27	3.9,4.8	4.22	3.39	4.6	9.18
	ZnS	1.78	1.7,2.8,3.5	1.75	1.78	3.3	2.33
	ZnSe	1.46	1.3-1.8	1.36	1.23	1.7	1.70
	ZnTe	1.12	0.8-1.1	0.96	0.75	1.0	0.95

	CdO	2.11					6.58
	CdS	1.08	1.1,1.22	1.00	1.19	1.1	1.40
	CdSe	0.87	0.7-1.2	0.68	0.78	0.8	0.95
	CdTe	0.64	0.4-0.64	0.37	0.41	0.5	0.35
	HgS	0.78		0.99	0.89		1.08
	HgSe	0.60		0.68	0.55		0.68
	HgTe	0.41		0.29	0.24		0.15

In some of theoretical studies [1, 12] nitride and oxide semiconductors have not been included for estimation of microhardness of group III-V and II-VI systems respectively. Also, BSb and CdO also do not figure in these studies. Further, the experimental values of microhardness of BSb, AlN, GaN, InN, BeS, BeSe, BeTe,CdO, HgS, HgSe and HgTe are to the best of our knowledge, not available and are being reported for the first time.
A notable difference in the calculated and experimental values of microhardness has been observed in BAs. It might be due to fact that the ionic radii of 'P' and 'As' in 4 coordination which they have in Zinc blende structure, are, to the best of our knowledge is not available and we have utilised their ionic radii in 6-coordination which may have sizable difference especially for As.
So, in the calculation the ionic radii of phosphide and arsenides in six coordination have been used. These results clearly indicate that the bond hardness has a prime role in deciding the microhardness of materials. Further the general agreement with the experimental and reported values support our model of inclusion of covalent and ionic contribution to the bond hardness.

Table-3.3 Bond hardness and microhardness of $InP_{1-x}As_x$ and $In_{1-x}Ga_xP$ along with experimental and reported values

Sytems	X	Bond hardness, H_{ab} (in GPa) This Work	Microhardness, H (inGPa) This Work	Exp.(Ref.[8])	Reported	bond ionicity (f_i) Ref.[21]
$InP_{1-x}As_x$	0	0.377	3.753	4.10,3.30	4.78[1],4.81[9],5.26[13]	0.329
	0.01	0.377	3.749			
	0.025	0.376	3.744			
	0.05	0.375	3.735			
	0.075	0.374	3.727			
	0.1	0.373	3.718			
	0.2	0.368	3.684			
	0.3	0.364	3.650			
	0.4	0.360	3.615			
	0.5	0.356	3.581			
	0.75	0.345	3.495			
	0.9	0.338	3.444			
	1	0.334	3.409	3.30,3.84	3.68[1],3.12[9],3.95[13]	0.343
$In_{1-x}Ga_xP$	0	0.377	3.753	4.10,4.30	4.78[1],4.81[9],5.26[13]	0.329
	0.01	0.379	3.770			
	0.025	0.383	3.797			
	0.05	0.388	3.841			
	0.075	0.394	3.885			
	0.1	0.399	3.929			
	0.2	0.421	4.105			
	0.3	0.443	4.282			
	0.4	0.465	4.458			
	0.5	0.488	4.634			
	0.75	0.543	5.075			
	0.9	0.576	5.340			
	1	0.598	5.516	9.45	8.55[1],7.41[9],8.00[13]	0.297

Table-3.4 Bond hardness, H_{ab} (in GPa) and microhardness, H (in GPa) of $ZnS_{1-x}Se_x$ and $Cd_{1-x}Zn_xS$ along with experimental and reported values

Sytems	X	Bond hardness, H_{ab} (in GPa)	Microhardness, M (inGPa)			Bond Ionicity (f_i)]
		This work	This work	Exp.(Ref. 8)	Reported	Ref.[21]
$ZnS_{1-x}Se_x$	0	0.615	1.777	1.7,2.8,3.5	1.75[1],1.78[9],3.3[12],2.33[13]	0.626
	0.01	0.614	1.774			
	0.025	0.613	1.769			
	0.05	0.610	1.761			
	0.075	0.608	1.753			
	0.1	0.605	1.745			
	0.2	0.595	1.714			
	0.3	0.586	1.682			
	0.4	0.576	1.651			
	0.5	0.566	1.619			
	0.75	0.542	1.541			
	0.9	0.527	1.493			
	1	0.517	1.462	1.3,1.8	1.36[1],1.23[9],1.7[12],1.70[13]	0.647
$Cd_{1-x}Zn_xS$	0	0.399	1.082	1.1,1.22	1.00[1],1.19[9],1.1[12],1.40[13]	0.660
	0.01	0.401	1.089			
	0.025	0.404	1.100			
	0.05	0.410	1.117			
	0.075	0.415	1.134			
	0.1	0.421	1.152			
	0.2	0.442	1.221			
	0.3	0.464	1.291			
	0.4	0.485	1.360			
	0.5	0.507	1.430			
	0.75	0.561	1.603			
	0.9	0.593	1.707			
	1	0.615	1.777	1.7,2.8,3.5	1.75[1],1.78[9],3.3[12],2.33[13]	0.626

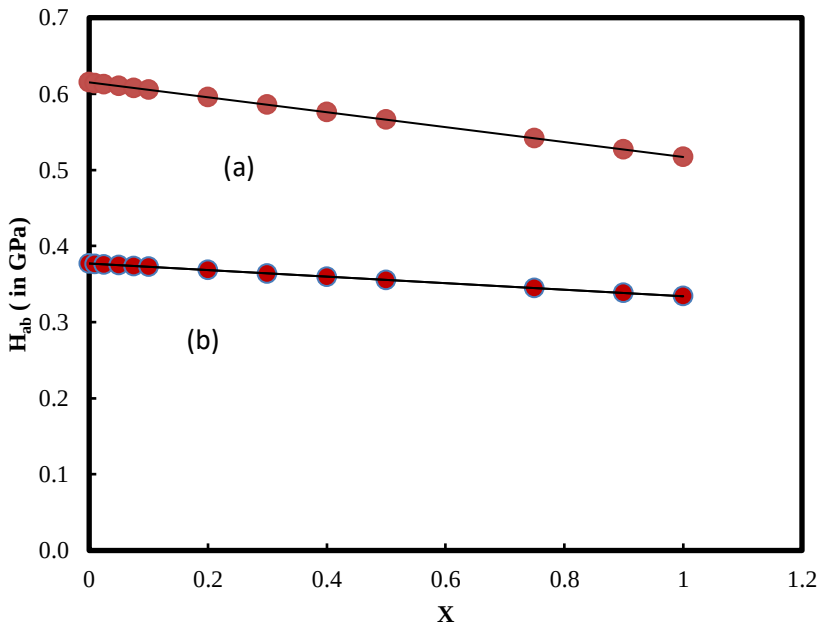

Fig. 3.1 Plot showing variation of Bond Hardness, H_{ab} with composition (x) in (a) $InP_{1-x}As_x$ and (b) $ZnS_{1-x}Se_x$

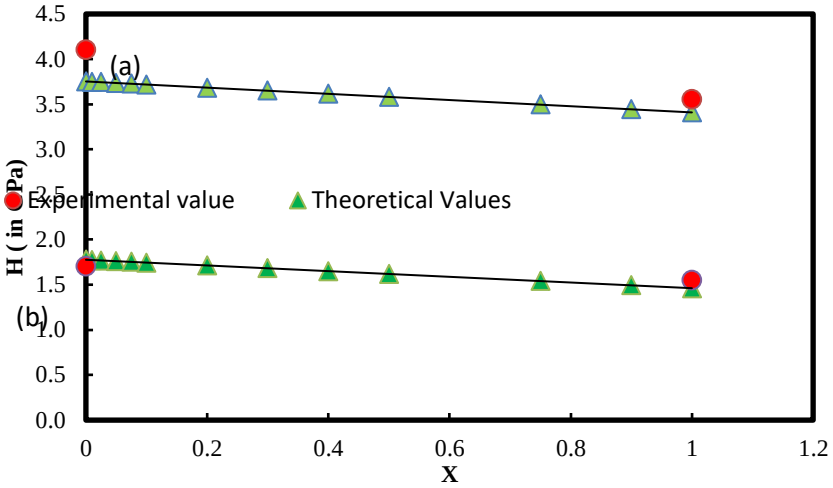

Fig. 3.2 Plot showing variation of microhardness, H with composition (x) in (a) $InP_{1-x}As_x$ and (b) $ZnS_{1-x}Se_x$

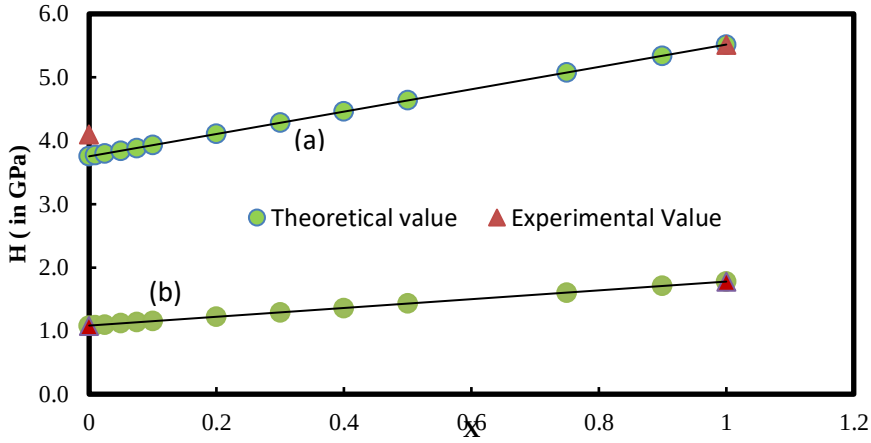

Fig. 3.3 Plot showing variation of Microhardness, H with composition (x) in (a) $In_{1-x}Ga_xP$ (b) $Cd_{1-x}Zn_xS$

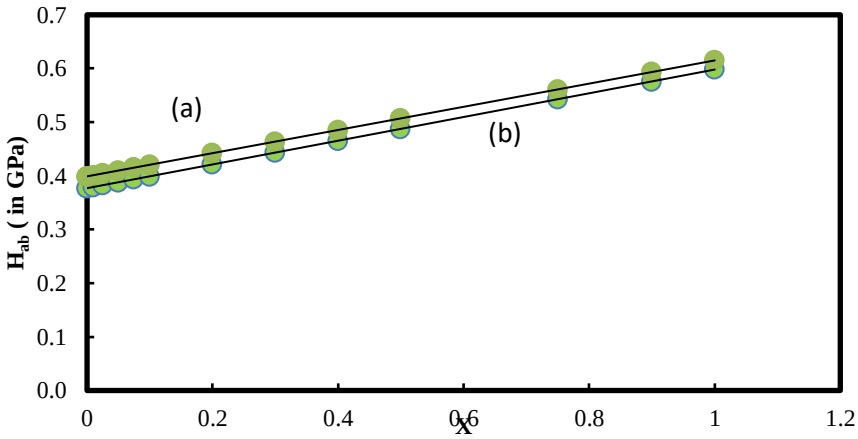

Fig. 3.4 Plot showing variation of bond hardness, H_{ab} with composition (x) in (a) $In_{1-x}Ga_xP$ (b) $Cd_{1-x}Zn_xS$

To understand the effect of composition on bond hardness and microhardness with anionic and cationic substitutions we have studies $InP_{1-x}As_x$, $In_{1-x}Ga_xP$, $ZnS_{1-x}Se_x$ and $Cd_{1-x}Zn_xS$ with x ranging from 0 to 1. Results are given in Table 1 and 2. The variations in microhardness with composition (x) are shown in Fig. 4 and 5 and the changes in bond hardness with x are shown in Fig. 3 and 6 in the systems. The effects of cationic and anionic substitutions in the alloys are clearly reflected. The increase in value of As-content in $InP_{1-x}As_x$ leads to decrease in bond hardness. On the other hand a gradual rise of bond hardness with x is observed in $In_{1-x}Ga_xP$. A similar trend is found for bond hardness in $ZnS_{1-x}Se_x$ and $Cd_{1-x}Zn_xS$. Similarly, the microhardness decreases with increasing As – content in $InP_{1-x}As_x$ and Se - content in $ZnS_{1-x}Se_x$. This may be assigned to the ionic - size effect, because the ionic size of As^{-3} (22.2 nm) is larger than that of P^{-3} (21.2 nm); and ionic Size of Se^{-2} (19.1 nm) is larger than S^{-2}(18.4 nm). In case the size of the impurity ion is smaller than the host ion, as in $In_{1-x}Ga_xP$ (In= 22.0 nm, Ga= 18.7nm) and $Cd_{1-x}Zn_xS$ (Cd= 15.8, Zn= 13.9)[22],the microhardness exhibit rising trend. This effect appears reasonable, because doping of a larger (smaller) ion will tend to increase (decrease) the bond length of the system which in turn, will weaken (strength) the bond and hence microhardness. In fact, the materials with shorter bonds have been identified as harder materials [23-25].

Plots of H_{ab} and H with x of the systems studies are linear with correlation coefficient $R^2 = 1$. To quantify these variations, the following relations are proposed:

$H_{ab}(InP_{1-x}As_x) = 0.377 – 0.043\ x$ (11)

$H(InP_{1-x}As_x) = 3.7526 – 0.3431\ x$ (12)
$H_{ab}\ (In_{1-x}Ga_xP) = 0.377 + 0.221\ x$ (13)
$H\ (In_{1-x}Ga_xP) = 3.7556 + 1.7634\ x$ (14)
$H_{ab}\ (ZnS_{1-x}Se_x) = 0.615 – 0.098\ x$ (15)
$H\ (ZnS_{1-x}Se_x) = 1.7769 – 0.3151\ x$ (16)
$H_{ab}\ (Cd_{1-x}Zn_xS) = 0.399 + 0.216\ x$ (17)
$H\ (Cd_{1-x}Zn_xS) = 1.0823 + 0.6945\ x$ (18)

Recent studies have clearly demonstrated that ionic materials always posses relatively lower hardness [14-19]. So, ionicity of chemical bond has been another factor, which affects the bond strength and the microhardness. With increasing size of doped ion the ionicity also increases which weakens the bond and lowers the microhardness. Such effects of ionicity on bond hardness and microhardness are clearly reflected in the systems studied. In case of cationic substitution in $In_{1-x}Ga_xP$ and $Cd_{1-x}Zn_xS$, the ionicity decreases giving rise to stronger bond and hence higher values of microhardness.

For bond hardness as well as microhardness perfect linearity is observed governed by the following relations

CONCLUSION

The effect of impurity content on bond hardness and microhardness of semiconductor alloys with isovalent cationic and anionic substitutions have been studied. The variations are interpreted in terms of ionic size and ionicity. The larger (smaller) ionic size of the doped atom tends to lower (raise) the bond hardness and microhardness. The study can be extended to other systems with both isovalent as well as heterovalent impurities to generalize the trend of variation with ionic size and /or ionicity, if any. The study may throw light in mechanical property- engineering which will be useful in designing materials for potential applications.

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