Cryst. Res. Technol.	36	2001	6	565–569

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Thermal Expansion Coefficient of Binary Semiconductors

The linear thermal expansion coefficient of tetrahedrally coordinated $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors has been calculated using plasmon energy data. A simple relation between the bond length and plasmon energy has been derived. The calculated values of thermal expansion coefficient and bond length have been compared with the experimental values and the values reported by different workers. An excellent experiment has been obtained between them.

Keywords: thermal expansion coefficient, bond length, $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors

(Received February 27, 2001; Accepted June 7, 2001)

1. Introduction

During last few years much attention has been given towards the study of A^{II} B^{VI} and $A^{III}B^{V}$ groups of semiconductors. This is because of their potential applications in a variety of optoelectronic devices such as nonlinear optics, light emitting diodes, photovoltaic cells, photo detectors, lasers, modulators, integrated circuits and filters. Different workers (REDDY et al.; NEUMANN 1987; GARBATO, RUCCI; LEVINE; WEMPLE, DOMENICO; PHILLIPS; VAN VECHTEN) have discussed various electronic, electrical and optical properties of these semiconductors. Recently, the first author (KUMAR 2000, KUMAR et al. 1996, 1994) has developed different models based on plasma oscillations theory of solids to describe the inter-atomic force constants, lattice energy, electronic polarizability, microhardness and bulk modulus of various binary and ternary semiconductors. In the present paper, the thermal expansion coefficient and the bond length of A^{II} B^{VI} and $A^{III}B^{V}$ semiconductors have been described from their plasmon energy. The knowledge of thermal expansion coefficient is very important in single crystal growth experiment (ISELER 1977; ISELER et al. 1978), in the choice of substrate materials suitable for epitaxial growth (BRUHLE) and in the understanding of the temperature dependence of the electronic properties (YAMAMOTO et al.). However, the bond length is important in the studies of dielectric constant, energy gaps and various structural properties of semiconductors.

The linear thermal expansion coefficient of tetrahedrally coordinated of A^{II} B^{VI} and $A^{III}B^{V}$ semiconductors and several other binary compounds has been studied by VAN UITERT et al. (1977, 1977-a, 1977-b), NEUMANN (1980, 1983, 1987), and several other workers (DEUS et al.; MAKOVETSKAYA et al.; BODNAR, KORZU; GLAZOV et al.; BRUHL et al.; KISTAIAH) have studied the thermal expansion coefficient of $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$ semiconductors having tetrahedral structure. Different approaches such as free energy consideration (NEUMANN 1980, 1983; NEUMANN et al.1984), dilatometry (MAKOVETSKAYA et al.; BODNAR, KORZU), measurement of change in density with temperature (GLAZOV et al.) and x-ray methods (DEUS et al.; BRUHL, NEUMANN; KISTAIAH et al.) have been used by these workers. In all

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these approaches experimental value of bond length is required in the calculation of thermal expansion coefficient. The experimental values of bond length are still unknown for some semiconductors. Therefore, I thought it would be of interest to develop a simple model for the calculation of bond length and thermal expansion coefficient of $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors, which do not require any experimental data except the plasmon energy. In this paper, the authors have proposed an empirical relation between linear thermal expansion coefficient (á$_L$) and plasmon energy (• ù$_p$) for these semiconductors. A simple relation between the bond length (d) and (• ù$_p$) has also been developed. Using these relations, the values of bond length and thermal expansion coefficient have been calculated. The calculated values of both the parameters, that is, the d and á$_L$ are compared with the experimental values and the values reported by different workers. An excellent agreement has been obtained between them.

2. Calculation

The free electron plasmon energy of binary semiconductors is given by

$$(\hbar w_p)^2 = \frac{4p\, N_e{}^2 e^2}{m}\,, \tag{1}$$

from which we have

$$N_e{}^2 = \frac{m}{4p\, e^2}(\hbar w_p)^2\,, \tag{2}$$

where N_e is the effective number of free electrons taking part in the plasma oscillations, e is the charge and m the mass of electron. N_e can be further written in terms of individual bond properties as (LEVINE)

$$N_e = \frac{\left[\ \frac{Z_A}{N_{CA}} + \frac{Z_B}{N_{CB}}\ \right]}{v_b}\,, \tag{3}$$

where Z_A and Z_B are the numbers of valance electrons of the atoms A and B, respectively, in a AB compound. N_{CA} and N_{CB} are the coordination numbers of the atoms A and B and v_b is the bond volume. For tetrahedral crystals $N_{CA} = N_{CB} = 4$, $Z_A + Z_B = 8$ and $v_b = 4d^3/3\sqrt{3}$. Substituting these values in equation (3), we get

$$N_e = \frac{3\sqrt{3}}{2d^3}\,. \tag{4}$$

For a compound, the plasmon energy shown in equation (1) can also be written as (MARTIN et al.)

$$\hbar w_p = 28.8\sqrt{\frac{Zs}{M}}\quad (eV)\,, \tag{5}$$

where Z is the effective number of valence electrons taking part in plasma oscillations, ó is the specific gravity and M is the molecular weight. Using equation (5), the plasmon energies of A^{II} B^{VI} and $A^{III}B^{V}$ semiconductors have been calculated taking Z=8, and ó and M from the data book (DAVID). The values of plasmon energies are listed in Table 1 for Wurtzite (W) or Zinc-blende (Zb) structure of these compounds.

From equations (2) and (4), we get following equation for the bond length of $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors

$$d = 15.30(\hbar w_p)^{-2/3} \text{ (d in Å and• } ù_p \text{ in eV) .} \tag{6}$$

VAN UITERT et al. (1977, 1977-a, 1977-b) have shown that the product of linear thermal expansion coefficient and melting temperature is a constant for materials with fixed ionicity and crystal structure, that is, $á_L T_m \cong 0.021$ for tetrahedral structure. In reality, the spatial extension of the orbital around the atoms involved may significantly affect anharmonicity and therefore, thermal expansion. This means that besides the bond ionicity the bond length must be taken into account in considering the average linear thermal expansion coefficient of binary semiconductors.

Based on above equation (6) and the theory proposed by NEUMANN (1980), we propose the following expression for linear thermal expansion coefficient in term of plasmon energy

$$a_L = \frac{A}{T_m} - B[15.30(\hbar w_p)^{-2/3} - d_0]^3 , \tag{7}$$

where A and B are the constants, T_m is the melting temperature and d_o the bond length of diamond, that is, d_o= 1.545 Å. The value of A = 0.021 for both, A^{II} $B^{VI}$and A^{III} B^{V}, compounds as estimated from a hard sphere model based on diamond. NEUMANN (1980) has obtained the values of B and $d_0$by extrapolating the available experimental data of $á_L$ and d (UITERT 1977; UITERT et al .1977-a, 1977-b). The values of B are equal to 3.3 and 10.0 ($10^{-6}K^{-1}$ $Å^{-3}$), respectively, for $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors and d_0 are, respectively, 1.382 and 1.561 Å (NEUMANN 1980).

3. Conclusion

The values of plasmon energy (• $ù_p$) and bond length (d) of $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors have been calculated using equations (5) and (6), respectively. The value of• $ù_p$ for BAs has been taken from our previous publication (KUMAR 2000) as the specific gravity of this compound is not known (WYCKOFF; DAVIS). However, from back calculation we can predict the value of ó, which comes out to be 5.23 for BAs. The values of linear expansion coefficient have been calculated using equation (7). The calculated values of all three parameters, that is,• $ù_p$, d and $á_L$ are listed in Table 1 along with the experimental values and the values reported by different workers for these semiconductors. An excellent agreement has been obtained between them. The main advantage of present model is the simplicity of the formulae, which do not require any experimental data except the plasmon energy of the $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors while the previous models require the experimental values of bond length of these semiconductors.

Hence, one can predict the values of thermal expansion coefficient for unknown semiconductors belonging to these groups from their plasmon energies.

Table 1: Bond length and linear thermal expansion coefficient of binary semiconductors.

Compd.	M	ó	• $ù_p$(eV)	Bond length 'd' (Å)		T_m(K)	$á_L$ ($10^{-6}K^{-1}$) at 300 K	
			Eq.(5)	Cal.Eq.(6)	Rep.* [28,29]	[10,29]	Cal.Eq.(7)	Reported
$A^{II}B^{VI}$								
BeO (W)	25.01	3.01	28.26	1.649	1.649	2800	7.437	6.2 [15]
BeS (Zb)	41.08	2.36	19.52	2.110	2.106	2293	7.885	
BeSe (Zb)	87.97	4.315	18.04	2.224	2.225	1964	8.723	
BeTe (Zb)	136.61	5.09	15.72	2.437	2.436	<1570	9.501	
MgTe (W)	151.9	3.85	12.97	2.771	2.777	>1300	7.310	
ZnO (W)	81.37	5.66	21.48	1.980	1.977	2250	8.627	7.2 [15]
ZnS (W)	97.43	4.1	16.71	2.341	2.342	2100	7.089	6.9 [17]
ZnSe (Zb)	144.34	5.42	15.78	2.432	2.454	1788	7.924	7.7 [17]
ZnTe (Zb)	192.99	6.34	14.76	2.543	2.636	1568	8.228	8.0 [17]
CdS (W)	144.46	4.82	14.88	2.529	2.530	1748	7.034	4.5 [17]
CdSe (W)	191.36	5.66	14.01	2.632	2.630	1512	7.434	7.3 [17]
CdTe Zb)	240.00	5.86	12.73	2.806	2.806	1365	5.856	5.1 [17]
HgS (Zb)	232.65	7.73	14.85	2.532	2.533	2023	5.356	
HgSe (Zb)	279.55	8.25	13.99	2.635	2.634	1070	13.13	
HgTe (Zb)	328.19	8.17	12.85	2.788	2.798	943	12.90	
$A^{III}B^{V}$								
BN (Zb)	24.82	3.49	30.55	1.566	1.565	3000	6.999	
BP (Zb)	41.78	2.9	21.46	1.966	1.965	2800	6.835	
BAs (Zb)	85.73	5.23+	20.12	2.068	2.068	2300	7.827	
AlN (W)	40.99	3.26	22.97	1.893	1.892	<2500	7.827	
AlP (Zb)	57.95	2.42	16.65	2.346	2.360	2100	5.161	
AlAs (Zb)	101.90	3.81	15.75	2.435	2.433	2013	3.756	3.5[29]
AlSb (Zb)	148.73	4.218	13.72	2.669	2.656	1300	2.551	4.5[17], 4.2[29]
GaN (W)	83.73	6.10	21.98	1.949	1.944	1500	13.412	
GaP (Zb)	100.69	4.13	16.50	2.360	2.360	1750	6.899	6.1[17], 5.3[29]
GaAs (Zb)	144.64	5.316	15.62	2.448	2.450	1510	6.928	7.2[17], 5.4[29]
GaSb (Zb)	191.47	5.619	13.95	2.640	2.649	980	8.866	6.5[17], 6.1[29]
InN (W)	128.83	6.88	18.82	2.162	2.154	1200		
InP (Zb)	145.79	4.787	14.76	2.542	2.541	1330	6.328	5.5[17], 4.6[29]
InAs (Zb)	189.74	5.66	14.07	2.625	2.614	1215	5.238	6.5[17], 4.7[29]
InSb (Zb)	236.57	5.775	12.73	2.806	2.805	798	7.017	5.6[17], 4.7[29]

*These values of bond length have been calculated from lattice parameters using relations d= 0.433 a_0 for Zinc-blende (Zb) and
d= 0.433 $(\sqrt{3}\, a_0^2\, c_0)^{1/3}$ for Wurtzite (W) crystals[17].

+Calculated from back calculation

Acknowledgement

The authors are grateful to Prof. B. B. Bhattacharya, Director and Prof. D. Chandra, Head, Department of Electronics and Instrumentation, Indian School of Mines, Dhanbad for their continuous inspiration and encouragement in conduction this part of work.

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