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RELATION BETWEEN THE ENERGY GAP AND ULTRASONIC WAVE PROPAGATION VELOCITIES IN SEMICONDUCTORS

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In this work the existence of the relation between the energy gap and ultrasonic wave velocities for semiconductors crystallizing into cubic and hexagonal systems has been shown. Data from the literature confirmed the validity of the relations obtained. Using the acoustical method the variation of the energy gap with the percentage composition of the solid solutions has also been obtained.

Introduction

Previously, paper [2], a relationship was established between the energy gap and the velocity of ultrasonic wave propagation for polycrystalline semiconductors of group $A^{II} B^{V}$. The validity of the derived expression was confirmed by experiment. In this paper similar dependencies for semiconductors of groups IV, III-V, and II-VI have been obtained. Semiconductors of groups IV, III-V, and some of group II-VI crystallize into a cubic system, while the remainder of II-VI crystallize into a hexagonal system. Thus the expressions derived in this work are valid for monocrystalline semiconductors crystallizing into both systems. The relation of these results to the question of chemical bonds in semiconductors was considered. As is well known, semiconductors of group IV have valent bonds and semiconductors of groups III-V, II-VI have valent-ionic bonds.

Theory

In our considerations we start with the well known thermodynamic relation

$$\left[\frac{\partial^2 U}{\partial^2 V}\right]_T = -\left(\frac{\partial p}{\partial V}\right)_T + T\left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)_T\right]_V, \tag{1}$$

where U is the internal crystal energy, T – the temperature, V – the volume and p – the pressure.

The bulk modulus $K = -V(\partial p/\partial V)_T$ may be expressed as a function of the propagation velocities of ultrasonic waves in the following manner:

$$-V\left(\frac{\partial p}{\partial V}\right)_T = \varrho\left(C^2_{l[111} - \frac{4}{3}C^2_{t[100]}\right) \tag{2}$$

for a cubic system; and

$$-V\left(\frac{\partial p}{\partial V}\right)_T = \varrho\,\frac{C^2_{l[001]}(C^2_{l[100]} - C^2_{t[100]}) - (2C^2_{l[101]} - C^2_{l[100]} - 2C^2_{t[001]})^2}{C^2_{l[001]} + C^2_{l[100]} - C^2_{t[100]} - 2(2C^2_{l[101]} - C^2_{l[100]} - 2^2_{t[001]})} \tag{3}$$

for a hexagonal system, where ϱ is the density of material, $c_{1[\ldots]}$ and $c_{t[\ldots]}$ are the velocities of longitudinal and transverse waves propagating in the given directions. The semiconductors of group IV are characteristically valent, and of the remaining groups valent-ionic. In general, the potential energy of atomic interaction may be written in the following form:

$$\Phi = Ae^{-R/a} - \frac{B}{R^n} - \frac{B_1}{R}. \tag{4}$$

In this formula the first part describes the forces of repulsion, the second, the forces of attraction, and the last, the ionic forces of attraction.

From formula (4) it may be derived that

$$\frac{\partial^2\Phi}{\partial R^2} = A_1\Phi + A_2\Phi_j, \tag{5}$$

where

$$A_1 = \frac{n[a(n+1) - R_0}{aR_0(an+R_0)}, \quad A_2 = \frac{[an^2 + R_0(n^2+n-2)}{R_0^2(an+R_0)},$$

where Φ is the potential energy of atomic interaction, and Φ_j is the ionic bond component.

Using the relation

$$\frac{\partial^2\Phi}{\partial V^2} = \frac{R_0^2}{9V^2}\,\frac{\partial^2\Phi}{\partial R^2}$$

and the fact that the kinetic energy does not directly depend on the volume, from equations (1), (2), (3), and (5) we obtain

$$\Phi = D_1 w^2 + D_2 \Phi_j, \tag{6}$$

where

$$w^2 = C^2_{l[111]} - \frac{4}{3} C^2_{t[100]} \tag{6a}$$

for a cubic system, and

$$w^2 = \frac{C^2_{l[001]}(C^2_{l[100]} - C^2_{t[100]}) - (2C^2_{l[101]} - C^2_{l[100]} - 2C^2_{t[001]})^2}{C^2_{l[001]} + C^2_{l[100]} - C^2_{t[100]} - 2(2C^2_{l[101]} - C^2_{l[100]} - 2C^2_{t[001]}} \tag{6b}$$

for a hexagonal system, with

$$D_1 = \frac{1}{9} a^2 R_0^2 A_1 \quad \text{and} \quad D_2 = -\frac{1}{9} A_2.$$

It is also known that the dependence of the energy gap on the potential energy of atomic interaction [1, 4] has a linear character:

$$E_g = a\Phi + b, \tag{7}$$

where a and b are constants for particular groups of semiconductors.

Associating the above dependence with the expression obtained above between the velocity of ultrasonic wave propagation and the energy gap (6) we obtain

$$E_g = a_1 w^2 + a_2 \Phi_j + b, \tag{8}$$

where w^2 is given by equations (6a) and (6b) for cubic and hexagonal systems respectively, a_1, a_2, b – constants characteristic for the particular semiconductor groups.

Expression (8) should be analysed with respect to the chemical bonds in the semiconductors. $\Phi_j = 0$ can be put equal to zero in formula (8) for semiconductors of group IV, which, as is well known, have pure valent bonding. Thus the dependence of the energy gap on the combination of ultrasonic wave velocities for this group is one straight line. For semiconductors of groups III-V and II-VI the share of the ionic component in the bond is different. In these compounds, the dependence of the energy gap on the ionic component has to be determined. If the coefficient of proportionality between E_g and Φ_j was equal for the whole group of semiconductors considered then in the dependence $E_g = f(w^2)$ all the compounds of types III-V and II-VI would lie on one straight line. However, because of the fact that the coefficient of proportionality between E_g and Φ_j is constant only for a given series of compounds, the dependence $E_g = f(w^2)$ will not be the same for the whole group of these compounds, but only for a given series. For the semiconductors having valent-ionic bonding, the relation between the energy gap and the velocities of ultrasonic wave propagation is

$$E_g = aw^2 + \beta, \tag{8a}$$

where a and β are constants, characteristic for a given series of semiconductors of groups III-V and II-VI.

For group III-V semiconductors three series have been distinguished:

MX_i-InSb, InAs, InP,
NX_i-GaSb, GaAs, GaP,
PX_i-AlSb, AlAs, AlP.

For these semiconductors three straight lines have been obtained for the dependence $E_g = f(w^2)$.

For group II-VI semiconductors two series have been distinguished:

RY_i-ZnSe, ZnTe, ZnS
TY_i-CdSe, CdTe, CdS.

Thus, for these semiconductors two straight lines have been obtained.

The dependence of the energy gap on the ionic component of the bond for semiconductors of groups III-V and II-VI is similar.

These relations for the solid solutions of particular groups of semiconductors may also be generalized. For this purpose the relationship between the velocity of ultrasonic wave propagation, the percentage composition, and the propagation velocities in the pure components [3] has been used. The following dependence has thus been obtained for solid solutions with cubic and hexagonal systems:

$$E_g = a\left[\frac{\mu M_1}{M} w_1^2 + \frac{(1-\mu)M_2}{M} w_2^2\right] + \beta, \tag{9}$$

where w_1, w_2 are the expressions given in formulae (6a, b) for the first and second components respectively, μ is the molecular fraction, M_1, M_2 are the masses of components, and $\bar{M}$ is the average mass, given by

$$\bar{M} = \frac{\mu_1 M_1 + \mu_2 M_2}{\mu_1 + \mu_2}.$$

Results

In Figs. 1 and 2 the dependence of the energy gap on the ultrasonic wave velocities, for semiconductors of groups IV, III-V, II-VI, respectively, are presented graphically. These dependences have been drawn on the basis of data from the literature. From these data the corresponding constants in equation (8) were determined to be:

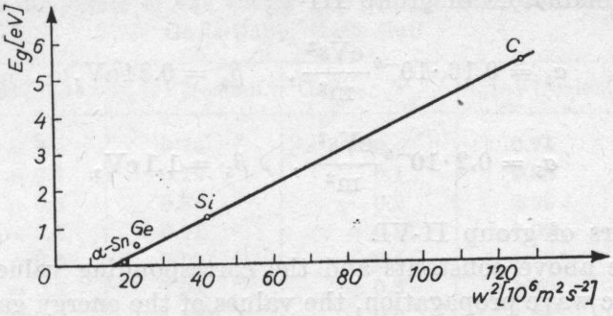

Fig. 1. Dependence of the energy gap on the combination of ultrasonic wave velocities for semiconductors of group IV

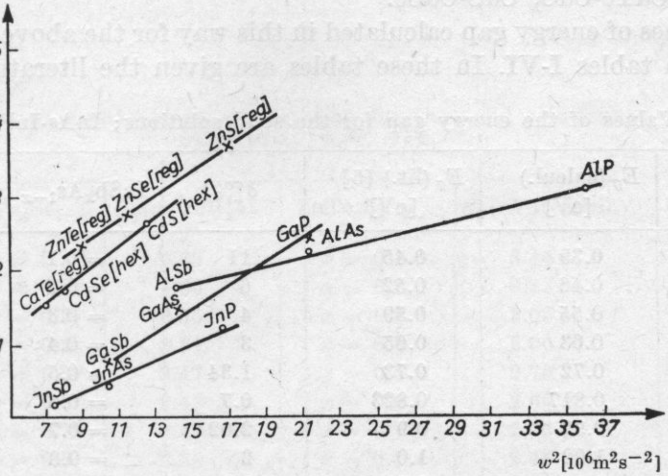

Fig. 2. Dependence of the energy gap on the combination of ultrasonic wave velocities for semiconductors of groups III-V and II-VI

$$a_1 = 0.0485\cdot 10^{-6}\,\frac{\mathrm{eVs^2}}{\mathrm{m^2}}, \quad b = -0.882\,\mathrm{eV},$$

for semiconductors of group IV;

$$a_1 = 0.115\cdot 10^{-6}\,\frac{\mathrm{eV\cdot s^2}}{\mathrm{m^2}}, \quad \beta_1 = -0.69\,\mathrm{eV},$$

$$a_2 = 0.14\cdot 10^{-6}\,\frac{\mathrm{eVs^2}}{\mathrm{m^2}}, \quad \beta_2 = -0.6\,\mathrm{eV},$$

$$a_3 = 0.062\cdot 10^{-6}\,\frac{\mathrm{eVs^2}}{\mathrm{m^2}}, \quad \beta_3 = 0.82\,\mathrm{eV},$$

— for semiconductors of group III-V;

$$\alpha_4 = 0.16 \cdot 10^{-6} \frac{\mathrm{eVs^2}}{\mathrm{m^2}}, \quad \beta_4 = 0.84\,\mathrm{eV},$$

$$\alpha_5 = 0.2 \cdot 10^{-6} \frac{\mathrm{eVs^2}}{\mathrm{m^2}}, \quad \beta_5 = 1.1\,\mathrm{eV},$$

for semiconductors of group II-VI.

Knowing the above constants and the corresponding values of the velocities of ultrasonic wave propagation, the values of the energy gap for the solid solutions were calculated according to equation (9). The following solid solutions were considered: InAs-InP, InAs-InSb, InSb-InP, GaAs-GaP, GaAs-GaSb, GaSb-GaP, AlAs-AlP, AlAs-AlSb, AlSb-AlP, ZnTe-ZnSe, ZnTe-ZnS, ZnS-ZnSe, CdTe-CdSe, CdTe-CdS, CdS-CdSe.

The values of energy gap calculated in this way for the above solid solutions are shown in tables I-VI. In these tables are given the literature values and

Table 1. Values of the energy gap for the solid solutions; InAs-InP, InAs-InSb

$InAs_{1-x}P_x$	E_g (calcul.) [eV]	E_g (lit.) [5] [eV]	δ [%]	$InSb_xAs_{1-x}$	E_g [eV] (calcul.)
$x = 0$	0.39	0.45	11	$= 0.1$	0.21
$x = 0.1$	0.46	0.52	6	$= 0.2$	0.23
$x = 0.2$	0.55	0.59	4	$= 0.3$	0.25
$x = 0.3$	0.63	0.65	3	$= 0.4$	0.28
$x = 0.4$	0.72	0.73	1.34	$= 0.5$	0.31
$x = 0.5$	0.817	0.823	0.7	$= 0.6$	0.35
$x = 0.6$	0.92	0.9	2.02	$= 0.7$	0.38
$x = 0.7$	1.02	1.0	2	$= 0.8$	0.40
$x = 0.8$	1.13	1.1	2.7	$= 0.9$	0.44
$x = 0.9$	1.25	1.2	3.9		
$x = 1.0$	1.37	1.31	4.5		

Table 2. Values of the energy gap for the solid solutions; InSb-InP, GaAs-GaP

$InSb_{1-x}P_x$	E_g [eV] (calcul.)	$GaAs_{1-x}P_x$	E_g (calcul.)	E_g (lit.) [5]	δ [%]
$= 0$	0.10	$x = 0.1$	2.47	2.59	4.6
$= 0.1$	0.17	$x = 0.2$	2.32	2.44	4.9
$= 0.2$	0.24	$x = 0.3$	2.17	2.31	6.0
$= 0.3$	0.34	$x = 0.4$	2.04	2.17	5.9
$= 0.4$	0.44	$x = 0.5$	1.92	2.04	5.8
$= 0.5$	0.55	$x = 0.6$	1.81	1.91	5.2
$= 0.6$	0.68	$x = 0.7$	1.71	1.79	5.0
$= 0.7$	0.80	$x = 0.8$	1.60	1.66	3.8
$= 0.8$	0.95	$x = 0.9$	1.51	1.55	2.5
$= 0.9$	1.12				
$= 1.0$	1.30				

Table 3. Values of the energy gap for the solid solutions: GaAs-GaSb, GaSb-GaP

$GaSb_{1-x}As_x$	E_g [eV] (calcul.)	$GaSb_{1-x}P_x$	E_g [eV] (calcul.)
$= 0$	**0.74**	$= 0$	**0.74**
$= 0.1$	**0.79**	$= 0.1$	**0.83**
$= 0.2$	**0.85**	$= 0.2$	**0.86**
$= 0.3$	**0.91**	$= 0.3$	**1.09**
$= 0.4$	**0.97**	$= 0.4$	**1.23**
$= 0.5$	**1.04**	$= 0.5$	**1.40**
$= 0.6$	**1.105**	$= 0.6$	**1.56**
$= 0.7$	**1.18**	$= 0.7$	**1.78**
$= 0.8$	**1.25**	$= 0.8$	**2.02**
$= 0.9$	**1.34**	$= 0.9$	**2.32**
		$= 1.0$	**2.63**

Table 4. Values of the energy gap for the solid solutions: ZnTe-ZnSe, ZnTe-ZnS

$ZnTe_xSe_{1-x}$	E_g (calcul) [eV]	$ZnTe_xS_{1-x}$	E_g [eV] (calcul.)
$x = 0.1$	2.65	$x = 0.1$	3.44
$x = 0.2$	2.60	$x = 0.2$	3.23
$x = 0.3$	2.55	$x = 0.3$	3.05
$x = 0.4$	2.51	$x = 0.4$	2.90
$x = 0.5$	2.47	$x = 0.5$	2.76
$x = 0.6$	2.43	$x = 0.6$	2.66
$x = 0.7$	2.40	$x = 0.7$	2.56
$x = 0.8$	2.36	$x = 0.8$	2.45
$x = 0.9$	2.33	$x = 0.9$	2.32

Table 5. Values of the energy gap for the solid solutions: ZnS-ZnSe, CdTe-SdSe

$ZnSe_xS_{1-x}$	E_g (calcul.) [eV]	$CdTe_xSe_{1-x}$	E_q [eV] (calcul.)
$x = 0.1$	3.55	$= 0.1$	1.52
$x = 0.2$	3.42	$= 0.2$	1.53
$x = 0.3$	3.30	$= 0.3$	1.55
$x = 0.4$	3.20	$= 0.4$	1.56
$x = 0.5$	3.10	$= 0.5$	1.58
$x = 0.6$	2.99	$= 0.6$	1.60
$x = 0.7$	2.92	$= 0.7$	1.62
$x = 0.8$	2.82	$= 0.8$	1.64
$x = 0.9$	2.76	$= 0.9$	1.66

Table 6. Values of the energy gap for the solid solutions: CdTe-CdS, CdS-CdSe

$CdTe_xS_{1-x}$	E_g [eV] (calcul.)	$CdSe_xS_{1-x}$	E_g [eV] (calcul.)
$x = 0.1$	1.56	$x = 0.1$	2.53
$x = 0.2$	1.64	$x = 0.2$	2.41
$x = 0.3$	1.72	$x = 0.3$	2.30
$x = 0.4$	1.81	$x = 0.4$	2.20
$x = 0.5$	1.90	$x = 0.5$	2.09
$x = 0.6$	2.01	$x = 0.6$	1.98
$x = 0.7$	2.13	$x = 0.7$	1.9
$x = 0.8$	2.26	$x = 0.8$	1.81
$x = 0.9$	2.41	$x = 0.9$	1.76

the percentage difference between these values, and those determined in this work by acoustic and other methods. On the basis of this data the dependence of the energy gap on the percentage composition of the above solid solutions has been made graphically and is shown in Figs. 3 and 4.

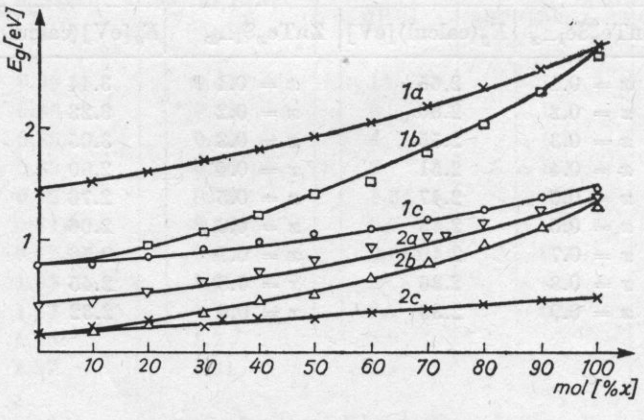

Fig. 3. Dependence of the energy gap on the percentage composition of solid solutions of group III-V

1a – GaAs-GaP, *1b* – GaSb-GaP, *1c* – GaSb-GaAs, *2a* – InAs-InP, *2b* – InSb-InP, *2c* – InSb-InAs

Conclusions

The relations obtained theoretically are in agreement with the experimental ones. This fact enables us to determine the energy gap indirectly with knowledge of the velocities of ultrasonic wave propagation for the pure semiconductors and their solid solutions. The results obtained by this method for some solid solutions have been compared to the data obtained by other methods i.e. (opti-

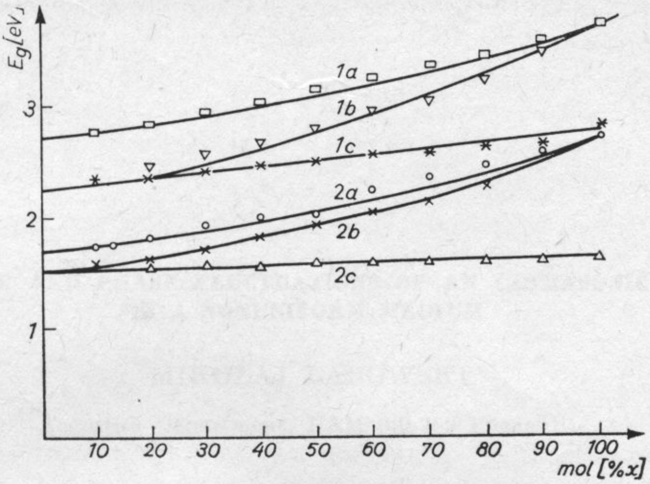

Fig. 4 Dependence of the energy gap on the percentage composition of solid solutions of group II-VI

1a – ZnTe-ZnS, *1b* – ZnSe-ZnS, *1c* – ZnSe-ZnTe, *2a* – CdSe-CdS, *2b* – CdTe-CdS, *2c* – CdTe-CdSe

cal and electrical). The maximum error between the values of the energy gap determined by the other methods and by the acoustic method is 11%. To determine the energy gap for semiconductors which have a cubic structure it is necessary to measure the velocity of longitudinal waves in the [111] direction and transverse waves in the [100] direction. For semiconductors with a hexagonal structure, it is necessary to measure the following velocities: of longitudinal waves in the directions [001], [100], [101] and of transverse waves in the directions [100], [001].

It is worth mentioning that the ultrasonic wave velocity is a parameter which may be easily measured. The accuracy of its determination is of the order of 0.2%.

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