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Abstract

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Thermodynamic Potential and the Band Gap of Semiconductor Compounds

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The forbidden band separates the valence band, filled with electrons, of the ground levels from the levels of excited states of electrons. The transition of electrons occurs by a jump upon absorption of energy equal to or exceeding the width of the forbidden band ([1]).

In describing the phenomenon of electron transfer in band theory, the physicochemical processes accompanying the activation of the intrinsic current carriers are not considered and are not taken into account. In reality, in the intrinsic light-absorption band a very considerable change in the physicochemical state of semiconductors is observed. Thus, for example, a decrease in the microhardness of germanium by up to 65%, cadmium sulfide by 45%, and antimony by 30% has been found. A change in the number of dislocations in germanium by 3 orders of magnitude did not affect the results. In metals, no such phenomena were observed ([2,3]). The reactive and reflective capacity of semiconductor compounds increases strongly in the intrinsic light-absorption band ([4,5]).

The chemical processes accompanying the activation of intrinsic current carriers are very significant. If it is assumed that chemical transformations constitute the greater part of the activation energy (it will be shown below that this is indeed the case), then from the magnitude of the experimentally obtained temperature coefficients of the band gaps one can conclude that a dissociation process is present. This conclusion is based on the observed changes in entropy, reaching 10–25 cal/g (the entropy is equal to the temperature coefficient with the opposite sign).

These circumstances prompted us to consider the process of activation of current carriers, representing it as dissociation of the semiconductor followed by activation of the current carriers, as in the doping of compounds with an excess of components.

In the simplest case, the process of activation of an electron and a hole in a semiconductor compound may be represented by the equation

$$\mathrm{AB_{tv}} \rightleftarrows \mathrm{A^{+}} + \mathrm{e} + \mathrm{B'} + \mathrm{d}, \qquad \Delta Z_1 = \Delta E; \tag{1}$$

A^+ is a cation, B' an anion, e an electron, d a hole, ΔZ_1 the change in the isobaric-isothermal potential, and ΔE the band gap.

Preserving the initial and final states, we divide reaction (1) into two stages

$$\mathrm{AB_{tv}} \rightleftarrows \mathrm{A} + \mathrm{B}, \qquad \Delta Z_2; \tag{2}$$

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{A}^+ + \mathrm{e} + \mathrm{B}' + \mathrm{d}, \qquad \Delta Z_3. \tag{3}$$

The sum of the energies of reactions (2) and (3) is equal to $\Delta Z_2 + \Delta Z_3 = \Delta Z_1 = \Delta E$. Reaction (2) represents the process of dissociation of AB into simple substances, for example under the influence of thermal fluctuations, obeying Boltzmann statistics. Reaction (3) describes the process of formation of ions, an electron, and a hole. The basis for considering the process of activation of current carriers as an equilibrium process is given in the works of Reiss, Bröbrik, and others ([6,7]).

To obtain the energy ΔZ_2 by thermodynamic means, information is required on the state of the dissociation products of AB. For this it is necessary to consider the equilibrium of the solid semiconductor with its vapor, for which $\Delta Z_{2\mathrm{tv}} = \Delta Z_{\mathrm{par}}$. Such an approach makes it possible to separate out the energy of the ionic-covalent bond (and, consequently, the dissociation energy) in the solid semiconductor between A and B, since all types of interaction associated with the crystalline state (van der Waals, metallic, etc.) are excluded when considering the chemical affinity in AB vapors.

In the general case, the calculation of $\Delta Z_{2\mathrm{par}}$ for AB presents no difficulty if, for any conditions, the change in the thermodynamic potential of formation of AB is known.

However, the standard isobaric-isothermal potential (Gibbs potential) is best suited to the conditions for measuring the band gap. Knowing the changes in the Gibbs potential for the conditions of equilibrium of the solid semiconductor with the vapor, one can obtain the energy for the dissociation of AB under any conditions. In addition, this procedure makes it possible to establish which dissociation products of AB, corresponding to the minimum dissociation energy, are formed in equilibrium with the solid semiconductor, and what work must be expended for the decomposition of AB at atmospheric pressure.

The decomposition products of semiconductor compounds may be different (As_4, Sb_2, Me_{tv}, Me_{gaz}, Se_2, P_4, etc.). Their state and composition depend on the magnitude of the Gibbs potential of formation and on the strength of the crystal lattice, which enters into the calculations through the saturated vapor pressure of the semiconductor. In very strong lattices, decomposition of the semiconductor in the region of intrinsic absorption into atoms is possible.

Considering the process of dissociation of a semiconductor compound at normal temperature, it should be noted that the probability of the appearance of a fluctuation capable of leading to dissociation of the AB bond is extremely small, and the number of “hot”simple substances is proportional to $e^{-\Delta Z_2/RT}$. Nevertheless, it is precisely the changes in the number of fluctuations with temperature that make it possible to determine the enthalpy of dissociation ($n_1/n_2 = Ae^{-\Delta H/RT}$) below the dissociation temperature. A dissociation probability equal to unity is reached at $RT = \Delta Z_2$. The change in the Gibbs potential ΔZ_2 then consists of the energy of rupture of the bond between A and B in the crystal and of the isothermal work of overcoming the pressure of the external medium (in our case 1 atm).

For illustration, let us consider the dissociation of solid aluminum antimonide; thermodynamically it can be shown that, in equilibrium with solid AlSb at p_{nas}AlSb, there are Al_{tv} and $\text{Sb}_{4\text{gaz}}$. These products correspond to the minimum dissociation energy (moreover, this agrees with mass-spectrometric data ([8])). The total change in the Gibbs dissociation potential of solid AlSb under normal conditions will be

$$\Delta Z_{\text{tv}}\text{AlSb} = -\Delta Z_{\text{par}}(p_{\text{nas}}\text{AlSb}) - \delta Z\text{AlSb}_{\text{tv}}(p_{\text{nas}}\text{AlSb} \to 1\ \text{atm}) +$$

$$+\delta Z\text{Al}_{\text{tv}}(p_{\text{nas}}\text{AlSb} \to 1\ \text{atm}) + \frac{1}{4}\delta Z\text{Sb}_4(p_{\text{nas}}\text{AlSb} \to p_{\text{nas}}\text{Sb}_4) +$$

$$+\frac{1}{4}\Delta Z\text{Sb}_4(p_{\text{nas}}\text{Sb}_4 \to 1\ \text{atm}) \qquad (4)$$

(p_{nas} is the saturated vapor pressure of the corresponding substances; the arrow indicates the limits of the isothermal work of transition).

The sum of the first and fourth terms on the right-hand side of equation (4) is equal to $-\Delta Z^0$AlSb (the second and third terms are equal to zero, since $\partial Z_{\text{tv}}/\partial p = 0$). Finally,

$$\Delta Z_{\text{tv}}\text{AlSb} = -\Delta Z^0\text{AlSb} + \frac{1}{4}\Delta Z\text{Sb}_4 \quad (p = 1\ \text{atm}). \qquad (5)$$

It should be noted that Sb_4 molecules, possessing the kinetic energy ΔZ_{tv}AlSb, are very “hot” and form vapors. Table 1 gives data on ΔZ_{tv} and $\Delta Z_{\text{tv}}/\Delta t$ for reaction (5), as well as similar quantities for other substances.

It follows from the table that the dissociation energies of semiconductors coincide with the band gaps, if the errors in determining the thermochemical quantities are taken into account. The temperature coefficients are also in good agreement. From chemical thermodynamics it is known that coincidence of energies and temperature coefficients is possible only for identical chemical processes with the same reaction equation and aggregate state of the reactants. From this one may conclude that the principal energy process associated with the formation of intrinsic current carriers is the dissociation of the semiconductor under the influence of external energy.

Table 1

Thermodynamic data for several semiconductor compounds, calculated Gibbs dissociation potentials, experimentally obtained band gaps, and corresponding temperature coefficients

Substance	Structure	Final dissociation products at 1 atm and 298° K	$-\Delta Z^0$, kcal/g-mol or kcal/g-atom	ΔZ_{tv} 298°, eV/g-mol or eV/g-atom	ΔE_{298°, eV, exp.	ΔS, cal/g	$-\frac{\partial Z_{298^\circ}}{\partial T}$, eV/g $\cdot 10^4$	$-\frac{\Delta E}{\Delta T}$, eV/g $\cdot 10^4$
BaO	NaCl	Ba_{tv}, O_2	123.5±2.5	5.3±0.15	5.1	23.5	10.3	9.0
ZnO	Wurtzite	Zn_{tv}, O_2	76.2±0.3	3.2	3.2	24.0	10.9	9.5 ($300 < T < 1400$° K)
AlSb	Sphalerite	Al_{tv}, Sb_4	21.7±2	1.4±0.15	1.5	11.2	4.8	4.1 ($100 < T < 290$° K)
GaP	Sphalerite	Ga_{tv}, P_2	29±4	1.9±0.2	2.0—2.2	18.6	8.1	5.4 ($373 < T < 500$° K)
ZnSb	Orthorhombic	Zn_{tv}, Sb_4	3.6±1.2	0.56	0.56	9.4	4.1	–
GdSb	Orthorhombic	Gd_{tv}, Sb_4	3.36	0.52	0.48	11.7	5.1	–

Substance	Structure	Final dissociation products at 1 atm and 298° K	$-\Delta Z^0$, kcal/g-mol or kcal/g-atom	ΔZ_{tv} 298°, eV/g-mol or eV/g-atom	ΔE_{298°, eV, exp.	ΔS, cal/g	$-\frac{\partial Z_{298^\circ}}{\partial T}$, eV/g $\cdot 10^4$	$-\frac{\Delta E}{\Delta T}$, eV/g $\cdot 10^4$
InAs	Sphalerite	In_{tv}, As_4	6.0±0.3	0.5±0.15	0.36	13.0	5.6	3.3–3.5 ($0 < T < 298$° K)
½ Bi_2Se_3	Rhombohedral	Bi_{tv}, Sb_{tv}	5.9±2	0.26±0.1	0.35	2.0	0.8	–
½ Bi_2Te_3	Rhombohedral	Bi_{tv}, Te_{tv}	3.7	0.16	0.15	2.5	1.0	2.5 ($20 < T < 200$° K)
Cd_3As_2	Tetragonal	Cd_{tv}, As_{tv}	2.8 (ΔH^0)	0.12	0.13	–	–	–

Note. Thermodynamic data are taken from (9-11), data on band gaps from (12, 13, 23).

Indeed, if we return to the expression $\Delta Z_1 = \Delta Z_2 + \Delta Z_3 = \Delta E$, then from the equality $\Delta Z_2 = \Delta E$ it follows that $\Delta Z_3 \simeq 0$, or the process of activation of an electron and a hole proceeds spontaneously. We add that the effect of hydrostatic compression on ΔE also agrees with the concept of semiconductor dissociation.

Taking into account the low accuracy with which thermochemical quantities and band gaps are determined, the data presented allow one at least to consider that the Gibbs dissociation potential basically determines the band gap of semiconductors.

The method described makes it possible to calculate the band gaps of substances that have not been studied. The Gibbs dissociation potentials of semiconductors make it possible to explain, on the basis of the Kapustinskii–Lotye rule known in chemical thermodynamics, the observed correlation between band gaps and various energetic and physical characteristics of the crystal lattice associated with chemical affinity, for example, lattice energy (14), atomization energy and specific surface energy (15), degree of ionicity (16), charge magnitudes and bond lengths (17), crystal-chemical elements (18–20), and interatomic distance (21).

A thermodynamic consideration of the process of activation of intrinsic current carriers removes the difficulties that arise when applying the band model theory to liquid semiconductors. Liquid systems, while not possessing strict lattice periodicity, in some cases retain semiconductor properties (some glasses, solutions, etc.) (22). The melting process is not directly connected with the Gibbs dissociation potential. At the melting point the forbidden band need not necessarily disappear (on melting, $\Delta Z_\ell = \Delta Z_{\mathrm{tv}}$, and consequently $\Delta E_\ell = \Delta E_{\mathrm{tv}}$).

The thermodynamic approach also opens up the possibility, in some cases, of using chemical thermodynamics to interpret changes in the concentrations of intrinsic current carriers, the influence of phase transitions, doping, etc.

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Note: Figure translations are in progress. See original paper for figures.

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