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A review of radiation enhanced diffusion in perspective materials

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Abstract

In this paper, lattice defects and vacancy diffusion coefficients for a variety of materials and temperatures have been calculated on the basis of a modified procedure in [V.A. Starostin, Phys. Chem. Mater. Treat. 5 (1999) 104 (in Russian)] of the model of Beloshitsky [V.V. Beloshitsky, Rad. Eff. 88 (1986) 249]. Arrhenius low enthalpies were defined as linear functions from the temperature for metals, insulators and semiconductors. The anomalous behavior of high temperature superconductors is discussed.

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Keywords: Unfolding nuclear reaction cross-section; Huge phase transition up to melting

1. Introduction

The depth profiling study of isotopes, created in solids by charged particle irradiation, is currently essential. A lot of experimental papers have been published on this topic in the past years (see the review in [3]). In this paper, the model [1,2,7], based on physical and chemical kinetics, is applied for the interpretation of the experimental results [4] for germanium together with previous data [5–8] on other semiconductors. This model is also applied for the interpretation of the experimental results [14,15,18–23] for PZT insulator, Zr metal and YBCO HTSC. As a result, important physical information is obtained.

2. Theoretical model

The modified Beloshitsky description [2] of process radiation enhanced diffusion of isotopes, created on sufficiently long and intensive irradiation of solids by charged particles, has been presented in my previous review paper [1]. Along with diffusion transfer, the capture of an active impurity (index a) by vacancies (v) in a condition (c) and its activation by defects (d) is assumed. The important issue of the model is that diffusion occurs in the presence of intensive creation and disappearance of (d–v) pairs. These processes are described by the following system of quasi-chemical reactions and the connected equations:

$$\mathrm{a}+\mathrm{v}=\mathrm{c}+\text{phonon},\quad \mathrm{d}+\mathrm{c}=\mathrm{a}+\text{phonon},$$
$$\mathrm{d}+\mathrm{v}=2\ \text{phonon},$$
$$\partial n_\mathrm{a}/\partial t = D_\mathrm{a}(\partial^2 n_\mathrm{a}/\partial x^2) - n_\mathrm{a}n_\mathrm{v}k_\mathrm{cap} + n_\mathrm{c}n_\mathrm{d}k_\mathrm{act} + jN_i\sigma_i(E_\mathrm{p}(x))\Theta(R_\mathrm{p}-x+x_0),$$
$$\partial n_\mathrm{c}/\partial t = n_\mathrm{a}n_\mathrm{v}k_\mathrm{cap} - n_\mathrm{c}n_\mathrm{d}k_\mathrm{act},$$
$$\partial n_\mathrm{d}/\partial t = D_\mathrm{dv}(\partial^2 n_\mathrm{d}/\partial x^2) - n_\mathrm{c}n_\mathrm{d}k_\mathrm{act} - n_\mathrm{v}n_\mathrm{d}k_\mathrm{ann} + jN_\mathrm{d}\Theta(R_\mathrm{p}-x+x_0),$$
$$\partial n_\mathrm{v}/\partial t = D_\mathrm{dv}(\partial^2 n_\mathrm{v}/\partial x^2) - n_\mathrm{a}n_\mathrm{v}k_\mathrm{cap} - n_\mathrm{v}n_\mathrm{d}k_\mathrm{ann} + jN_\mathrm{d}\Theta(R_\mathrm{p}-x+x_0),$$
$$x_0=-v_\mathrm{b}t,\quad E_\mathrm{p}(x)=E_0(1-x/R_\mathrm{p}),\quad \sigma_\mathrm{d}=3.52\times10^{-16}\ \mathrm{cm}^2,$$

where $\Theta(x)$ is a unit function; N and $N_i(t)$ are the density of nuclei of the substance and element, making an isotope, R_p the range of energy E_0 of ions from [9], j the current of ions, and D_a, D_dv, K_cap, K_act, K_ann are the free parameters of the model. For defects and vacancies, the condition was that the (d–v) flow would cause displacement of the border of a substance with speed V_b, determined using an irradiation

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dose. The initial conditions were assumed to be zero. The boundary conditions were chosen from the experimental data. The system of the equations under the above described initial and boundary conditions was solved numerically by the method of final differences. The values of model variables were selected by the method of least squares so that it would fit experimental ($N_a + N_c$) depth profile structures in the best way. The minimization was done by a simplex method.

3. Results of the calculations for semiconductors

The calculations of the experiment data [4] on activation definition of depth profile structures 71-As, 72-As, 74-As, 76-As and 67-Ga, arising in Ge on irradiation with 10 MeV proton current of 0.1 μA/cm^2 for 0.5 h, have been carried out. Depth profile structures 73-As, 73-Se and 75-Se, arising in Ge under the irradiation by α-particles of 20 MeV by a current of 0.1 μA/cm^2 for 0.5 h, were also processed. The published data on the reaction cross sections $\sigma_i(E_p)$ from a library of acknowledged EXFOR datas [11,12] were used in the model. For an isotope 71-As, the maximal cross section of the (p,γ) reaction of 14.31 mbarn is estimated as well. The rough unfolding of the cross section of the (α,p) reaction for an isotope 73-As is shown in Fig. 1. It should be noted that the resonance width is approximately twice less than that of the cross section of Zr^{92}(p,n)Nb^{92m} reaction for the rest sample [1], although the dipole sums are almost the same (see Table 1). The points at 10.8 and 24.2 MeV are extracted from EXFOR. The calculation results are given in Table 2. The enthalpy of defect migration in Ge $H_{dv} = 14\,896$ cal/mol ($T_{eff} = 528$ K) and $H_{dv} = 37\,756$ cal/mol ($T_{eff} = 621$ K) was estimated using the absolute values of self-diffusion coefficients. A comparison of these enthalpies with similar data for silicon [5] shows a good agreement at 621 K, but demonstrates a much smaller value at 528 K. However, the value at 528 K agrees well with our data [7] for GaAs and GaP. In our paper [10], the equation $H_{dv} = H_{dv0} + N * R * T_{eff}/2$, where $N = 45$ for semiconductors and $H_{dv0} = 5393$ cal/mol for silicon, $R = 1.98584$ cal/mol/K is obtained. The contradiction in enthalpy for Ge can be overcome by assuming a jump in N from 45 up to 9 somewhere between 621 and 528 K. In Table 3 the values of H_{dv0} for a set of semiconductors are given. The data in Table 3 can be described by the formula $H_{dv0} = k * (M)^{1/2}$, where $k = 1126.55$ cal/mol, which coincides with factor Z in the formula $H = H_0 - k * Z$ from [13]. However, our handling of results from [8] at low temperature (167–218 K) self-diffusion in MCT resulted in $N = 43$ and $H_{dv0} = 4801$ cal/mol. This shows existence of upper limit weight $M_0 = 288.8668$ of the period on molecular weight. Also, these results suggest the absence of a jump in enthalpy.

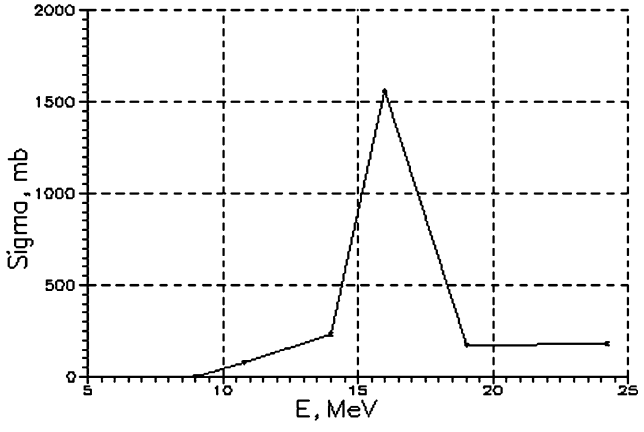

Fig. 1. Unfolding of Ge-70(α,p)As-73 nuclear reaction cross section.

Table 1
Dipole sums (MeV * barn)

Nuclear reaction	Rest sample	Shake sample	References
Zr-92(p,n)Nb-92m	5	2.5	[1]
Pb-206(p,n)Bi-206	–	0.47	[10]
Ge-70(α,p)As-73	5	–	This paper

Table 2
Calculated diffusion coefficients

Isotope	D_a, 10^{-11} cm^2/s	D_{dv}, 10^{-11} cm^2/s	Threshold, MeV	Reaction
Ga^{67b}	6395.147	6288.1	4.577	(p,α)
As^{71b}	9127.133[a]	6288.1	1.654	(p,γ)
As^{72}	9810.129	6288.1	5.133	(p,n)
As^{74}	10712.11	6288.1	3.345	(p,x)
As^{76b}	12620.77	6288.1	3.630	(p,n)
Se^{73}	2823.848	0.00046	7.567	(α,n)
As^{73b}	2823.848[b]	0.00046	9.0	(α,p)
Se^{75}	633.854	0.00046	6.309	(α,x)

[a] Is obtained by interpolation.
[b] The Coulomb barrier (is obtained by fit).

Table 3
H_{dv0} values for set of semiconductors

Semiconductor	H_{dv0}, cal/mol	Molecular weight	N	References
Si	5393	28.0855	45	[5]
SiC	6177	40.0965	45	[6]
Ge	10020	72.59	45 9	This paper
GaP	12677	100.6938	9	[7]
GaAs	13803	144.6416	9	[7]
$Hg_{0.76}Cd_{0.24}Te$	4801	307.0271	43	[8]

4. Results of the calculations for PZT insulator

The calculations of the experimental data [14] on activation definition of depth profile structures 51-Cr, 99-Mo and 93m-Mo, arising in a shaken sample $PbZr_{0.54}Ti_{0.46}O_3$ on irradiation by 20 MeV α-particle current of 0.4 μA/cm^2 have been carried out. Depth profile structures of 48-V,

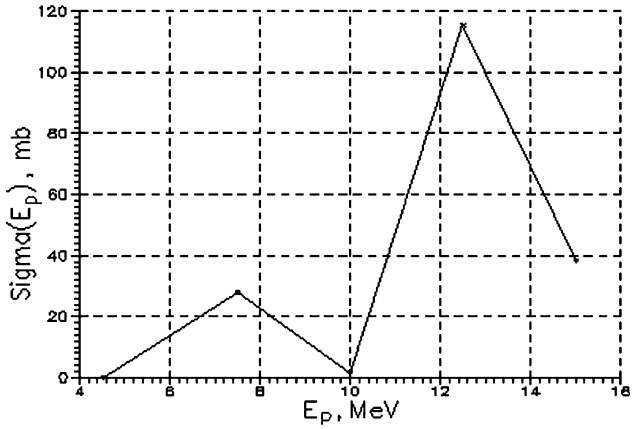

Fig. 2. Unfolding of Pb-206(p,n)Bi-206 nuclear reaction cross section.

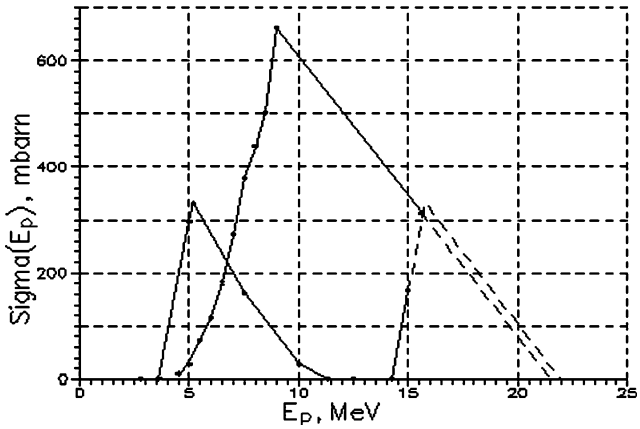

Fig. 3. Unfolding of Zr-92(p,n)Nb-92m nuclear reaction cross section (two peaks) comparison with [16,17] data (one peak).

Table 4
Calculated diffusion coefficients and rate constants for PZT quasi-chemical reactions

Isotope	D_a, $cm^2 \times 10^{-11}$ s	k_{act}, $cm^3 \times 10^{-23}$ s	T_{eff}, K
Cr^{51}	30.83936	171.2558	870
Mo^{99}	15.46319	21414.71	870
Mo^{93m}	21.14248	283.2381	870
V^{48}	91.27899	94176.47	580
Nb^{90}	496.0296	94219.17	580
Nb^{92m}	1824.119	52935.0	580
Bi^{206}	1033.513	8034.059	580

92m-Nb, 90-Nb and 206-Bi, arising in PZT under irradiation by protons of 15 MeV by a current of 0.1 μA/cm^2 were also processed. The published data on the reaction cross sections $\sigma_i(E_p)$ from the library of acknowledged EXFOR datas [11,12] was used in the model. The rough unfolding of the cross section of the (p,n) reaction for an isotope 206-Bi is shown in Fig. 2. The calculation results are given in Table 4. The enthalpy of defect migration in PZT $H_{dv} = 20332$ cal/mol ($T_{eff} = 870$ K) and $H_{dv} = 13747$ cal/mol ($T_{eff} = 580$ K) was estimated using the absolute values of self-diffusion coefficients (70934.61 and 60457.36 in units 10^{-11} cm^2/s).

5. Results of the calculations for Zr metal

According to the theoretical model [7] experimental data [15] on 15 MeV proton irradiation (0.1 μA/cm^2) transmutation of Nb isotopes into zirconium shaken samples was investigated (see Table 5). Self-diffusion enthalpy was calculated as $H_{dv} = 77080$ J/mol at a surface temperature of 572 K. Experimental data [15] on 92m-Nb isotope depth profile and experimental data on Zr^{92}(p,n)Nb^{92m} reaction cross-section [16,17] was conflicting. The deconvolution problem for cross-section of the Zr^{92}(p,n)Nb^{92m} reaction was solved (see Fig. 3) for the shaken zirconium sample.

Table 5
Calculated diffusion coefficients and rate constants for Zr quasi-chemical reactions

Isotope	D_a, $cm^2 \times 10^{-11}$ s	K_{act}, $cm^3 \times 10^{-23}$ s
Nb^{90}	14169.550	13480.470
Nb^{92m}	1721.945	3953.513
Nb^{95m}	12981.160	13469.250

6. Results of the calculations for YBCO HTSC

We investigated the self-diffusion in HTSC $YBa_2Cu_3O_{7-\delta}$ on the experimental data [18–21]. The results are shown in Table 6. As against self-diffusion in metals, insulators and semiconductors, the enthalpy temperature dependence for YBCO appears to be a huge phase transition covering the entire temperature range from absolute

Table 6
Calculated self-diffusion enthalpies for HTSC YBCO

T, K	H_{dv}, cal/mol	References
434	12386	[18]
621	22136	[19]
734	12217	[20]
870	20777	[21]

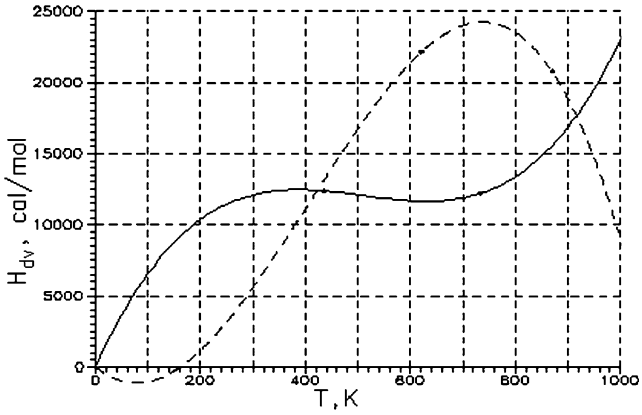

Fig. 4. Prospective temperature dependence for HTSC YBCO self-diffusion enthalpy.

Table 7
Calculated self-diffusion enthalpies for strongly ion implanted HTSC YBCO

Ion	T, K	H_{dv}, cal/mol	References
O^{18}	434	16271	[23]
D	306	17449	[23]
C	366	18107	[22]
C	375	18342	[22]
C	357	17718	[22]
C	347	17392	[22]

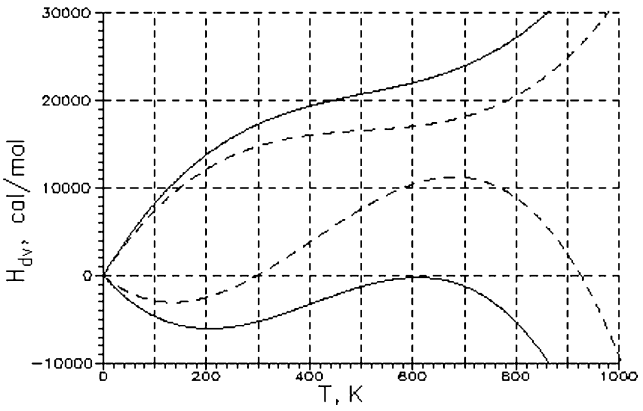

Fig. 5. Prospective temperature dependence for strongly implanted HTSC YBCO self-diffusion enthalpy.

zero up to a melting point of about 1308 K (see Fig. 4). In Fig. 4 two "conjugated" curves are given:

$$H_{dv}(T) = -a_1 * T^3 + b_1 * T^2 - S_1 * T,$$
$$H_{dv}(T) = a_2 * T^3 - b_2^* T^2 + S_2 * T,$$

where $a_1 = 0.000176530$, $a_2 = 0.000111890$ cal/mol/K^3; $b_1 = 0.21580$, $b_2 = 0.17033$ cal/mol/K^2. The parameters a and b are determined on the data of Table 6 by the method of least squares.

We investigated the self-diffusion in HTSC samples $YBa_2Cu_3O_{7-\delta}$, strongly implanted by an isotope of oxygen O-18, by carbon and by deutrium on the experimental data [22,23]. The results are shown in Table 7. In Fig. 5 the rough temperature dependence self-diffusion enthalpy in the assumption of invariancy of parameters a and b from the introduced dose and from the introduced ion is given.

7. Conclusion

On the basis of processing various experimental data [2–5,8,14,15,18–23] on the uniform radiation-enhanced diffusion model, put forward in our works [1,2,5–7,10], are constructed linear dependences of the kind

$$H_{dv}(T) = N * R * T/2 + H_{dv0}$$

on the method of least squares for metal, insulator and semiconductor self-diffusion enthalpies. Here $R = 1.98584$ cal/mol/K is the universal gas constant. The results are shown in Table 8. As against self-diffusion in metals, insulators and semiconductors, the enthalpy temperature dependence for HTSC appears to be a huge phase transition covering the entire temperature range from absolute zero up to the melting point (see Figs. 4 and 5).

Table 8
The appreciated parameters of linear regression

Material	N	H_{dv0}, cal/mol
Zr	61	−15704
PZT	23	490
Si	45	5393

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