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On diffusion of radiation defects during low and high temperature implantation near phase transitions

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Abstract

Since the last decade, radiation defects in solids during surface modification by ion beams have been extensively investigated. In this paper, defect diffusion coefficients for a variety of implantation energies and temperatures have been calculated on the basis of a modified model [V.A. Starostin, Phys. Chem. Mater. Treat. 5 (1999) 104–105] by Beloshitsky [P.A. Aleksandrov et al., Rad. Eff. 88 (1986) 249–255] with an emphasis given to relevant experiments [K.D. Demakov and V.A. Starostin, Tech. Phys. 46(4) (2001) 490–491]. For combinations of hydrogen in silicon (0.6 keV, 40 K), deuterium in diamond-like carbon (27 keV, 293 K) and arsenic in silicon (40 keV, 1123 K) this resulted in the equal value of the defect diffusion coefficient. A similar value is obtained for thermal diffusion of lead in zirconium. The advanced model enables quantitative estimates of self-diffusion coefficients as well as both defects and lattice vacancy profiles to be obtained. © 2002 Published by Elsevier Science B.V.

Keywords: Radiation defects; Self-diffusion coefficients; Lattice vacancy

1. Introduction

The behavior of implanted ions in any prospective materials according to ion current density and ion energy, temperature of the material, and chemical properties of interacting substances is of great theoretical and applied importance. In this paper, we review our calculations.

2. Theoretical model

In order to explain the impurity drift to a depth exceeding its range by an order of magnitude, a theoretical model for the process has been developed. Apart from diffusion transport, the impurity is assumed to be captured in some traps. It should be noted that a pure diffusion equation in the presence of a source does not yield a solution with a maximum located at a distance from the boundary exceeding the range of the ions (of the source). A transient process—post-irradiation cooling down—occurs rapidly and therefore is neglected. An important feature of the model is its no equilibrium—the diffusion occurs against the background of intense defect generation and annihilation. These processes are described by the following set of equations:

$$\partial n_a/\partial t = D_a \partial^2 n_a/\partial x^2 - n_a n_v k_{cap} + n_c n_d k_{act} + F(x) \quad (1)$$

$$\partial n_c/\partial t = n_a n_v k_{cap} - n_c n_d k_{act} \quad (2)$$

$$\partial n_d/\partial t = D_{dv} \partial^2 n_d/\partial x^2 - n_c n_d k_{act} - n_v n_d k_{ann} + j_0 N \sigma_d \Theta(R_p - x + x_0) \quad (3)$$

$$\partial n_v/\partial t = D_{dv} \partial^2 n_v/\partial x^2 - n_a n_v k_{cap} - n_v n_d k_{ann} + j_0 N \sigma_d \Theta(R_p - x + x_0) \quad (4)$$

$x_0 = -\upsilon_b t$, $E_p(x) = E_0(1 - x/R_p)$, $\sigma_d = 3.52\times 10^{-20}$ m^2, $F(x) = j_0 \exp(-(R_p - x + x_0)^2/2\Delta R_p^2)/\sqrt{2\pi}\Delta R_p$ for the ion implantation case and $F(x) = j_0 N_i \sigma_i(E_p(x))\Theta(R_p - x + x_0)$ for isotopes, created into solids by charge particles irradiation, where $\theta(x)$ is unit function, R_p is the defect creator range, ΔR_p is the straggling, j_0 is the implantation current density, N is the atom concentration in the target material, σ_d is the cross-section for defect formation. Eqs. (1) and (2) describe the impurity in mobile (n_a) and trapped (n_c) states, respectively. Eqs. (3) and (4) describe interstitial atoms (n_d) and vacancies (n_v), respectively. Based on the experimental data, the boundary conditions for an impurity have been chosen in the following form:

$$n_a(x_0,t) = n_c(x_0,t) = 0 \quad (5)$$

which can be interpreted as an impurity evaporation from the sample surface. For interstitials and vacancies

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Table 1
Calculated zirconium self-diffusion coefficients and enthalpy

T (K)	D_{dv} $m^2\times10^{-15}$ s	n[a]	ΔH_{dv} (J/mol)	H_{dv} (J/mol)
823	0.42526	1	4236	162 795
873	0.51414	3	12 749	171 308
893	4.8596	0	0	158 559
953	18.544	0	46	158 605
1003	4.8384	4.5[b]	19 571	178 131
1058	0.90909	10	44 040	202 599
1123	0.10101	18	76 996	235 556

[a] $(\Delta H_{dv}/n)=4278$ J/mol.
[b] Pb–Zr phase transition point (1003 K).

we have used the condition that the gradients are equal in absolute value, so that the interstitial flux would cause the substance boundary motion at the velocity of v_b:

$$-dn_d(x_0,t)/dx=dn_v(x_0,t)/dx=Nv_b/D_{dv} \qquad (6)$$

The initial conditions and the conditions at the opposite boundary have been taken in the following form:

$$n_a(x,0)=n_c(x,0)=n_d(x,0)=n_v(x,0)=0, \quad 0<x<l$$
$$n_a(l,t)=n_c(l,t)=n_d(l,t)=n_v(l,t)=0, \quad 0<t<t_{max} \qquad (7)$$

The set of Eqs. (1)–(4) with the initial and boundary conditions described by Eqs. (5)–(7) has been machine-computed according to a finite difference method. The parameters D_a, D_{dv}, k_{cap}, k_{act}, k_{ann} have been evaluated by a least-squares minimization routine so that they best fit the experimental data. To provide the parameter stability against small variations in the experimental data we have minimized to the level consistent with the experimental error and with no negative values condition.

3. Zirconium self-diffusion

3.1. Interstitials and vacancy migration into zirconium around the α–β phase transition temperature point

In Perez and Dyment [4] Pb thermo-diffusion into α–Zr from the temperature region 823 to 1123 K was investigated (Zr α–β phase transition temperature = 1135 K). From experimental data we can see that Pb ions current (defined from integral dose) follow Arrhenius low (enthalpy = 229 654 J/mol) in all points exclude 1003 K (where current = normal value/3.5). Our calculations was made according to the Beloshitsky model [2] modified in Starostin [1].

Table 2
Calculated diffusion coefficients

N	Isotope	D_a ($m^2\times10^{-15}$ s)	D_{dv} ($m^2\times10^{-15}$ s)
1	Nb^{90}	14169.550	837.7493
2	Nb^{92m}	1721.945	837.7493
3	Nb^{95m}	12981.160	837.7493

Table 3
Calculated rate constants for quasi-chemical reactions

N	K_{cap} ($m^3\times10^{-29}$ s)	K_{act} ($m^3\times10^{-29}$ s)	K_{ann} ($m^3\times10^{-29}$ s)
1	0.9751433	13480.470	352.4452
2	0.9751433	3953.513	352.4452
3	0.9751433	13469.250	352.4452

Self-diffusion coefficients and Arrhenius low enthalpies was defined (see Table 1). Quantum near 4278 J/mol from Table 1 (for VI period of Mendeleev table element) not equal to 4716 J/mol from [5] (for V period of Mendeleev table elements). Parity low for quantum numbers from Table 1 can be clearly seen.

3.2. Zirconium self-diffusion data from 15 MeV protons irradiation transmutation Nb isotopes radiation stimulated diffusion

According to the theoretical model [6] experimental data [7] on 15 MeV protons irradiation (0.001 A/m^2) transmutation Nb isotopes into zirconium rotate sample was investigated (see Tables 2 and 3).

Self-diffusion enthalpy was calculated H_{dv} = 77080 J/mol at a surface temperature of 572 K. This value and Table 1 data can be seen in Fig. 1.

Experimental data [7] on Nb^{92m} isotope depth profile and experimental data on $Zr^{92}(p,n)Nb^{92m}$ reaction cross-section [8,9] was conflicting. The deconvolution problem for cross-section $Zr^{92}(p,n)Nb^{92m}$ reaction was solved (see Fig. 2) for the rotated zirconium sample.

4. Silicon self-diffusion

Silicon self-diffusion was investigated according to the theoretical model Eqs. (1)–(4). Defects migration

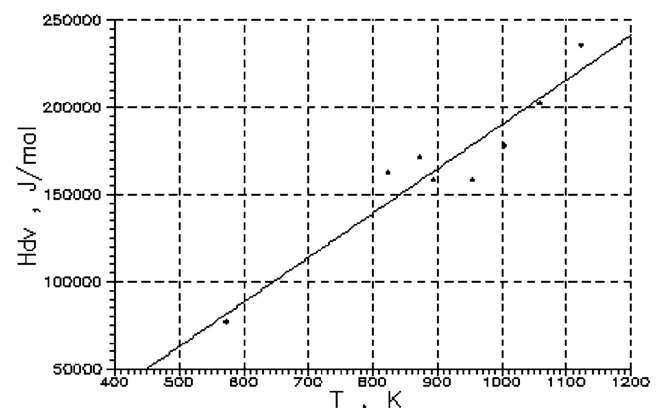

Fig. 1. Calculated zirconium self–diffusion enthalpy temperature dependence.

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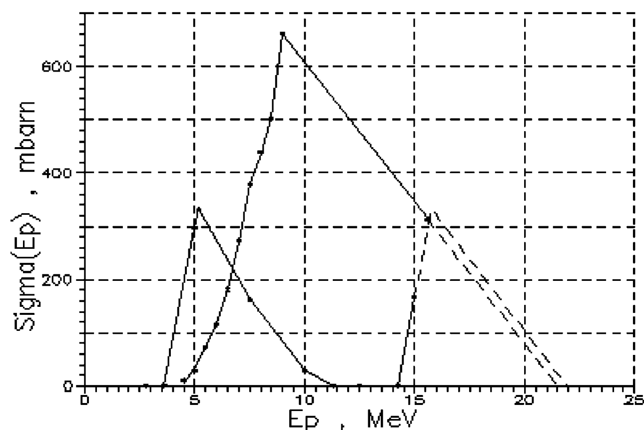

Fig. 2. Calculated $Zr^{92}(p,n)Nb^{92m}$ reaction cross-section (two peaks) comparison with [8,9] data (one peak).

enthalpies was calculated according to Arrhenius low from self-diffusion coefficients and effective surface temperatures.

Calculation results on As ions implantation (40 keV, 2×10^{21} m^{-2}) at high temperatures we can see in Table 4 [15].

Calculation results from depth profiles at different ions implantation into silicon and self-diffusion enthalpy concentration dependence for carbon and Yb ions can be seen in Table 5. Carbon and Yb ions into silicon

Table 4
Calculated silicon self-diffusion coefficients and enthalpy for As [15]

T_{sub} (K)	j_o (A m^2)	D_{dv} (m$^2\times10^{-15}$ s)	H_{dv} (J/mol)	T (K)
1323	0.1	0.204	270 425	1326
1323	0.4	0.0633	285 246	1335
873	0.4	0.0463	197 376	913
293	0.4	0.0127	133 672	589

Table 5
Calculated silicon self-diffusion enthalpy

Ion	T_{sub} (K)	j_o (A m^2)	E (keV)	T (K)	H_{dv} (J/mol)	Ref.
Yb	293	0.1	70	488	116 403[a]	[10]
					112 494	
					103 369	
Na	638	0.003	7	638	150 029	[11]
As	293	1.5	25	722	161 991	[12]
Tm	773	0.3	150	906	213 042	[13]
C	293	3.0	40	961	194 111[a]	[1]
					196 430	
					196 961	
As	1123	0.4	40	1143	239 260	[3]
Tl	1473	0.4	20	1478	295 459	[2]
As	1473	0.4	40	1482	310 372	[14]
Tl	1473	1.0	20	1484	293 253	[15]

[a] For pure silicon (and down-increase impurity concentration).

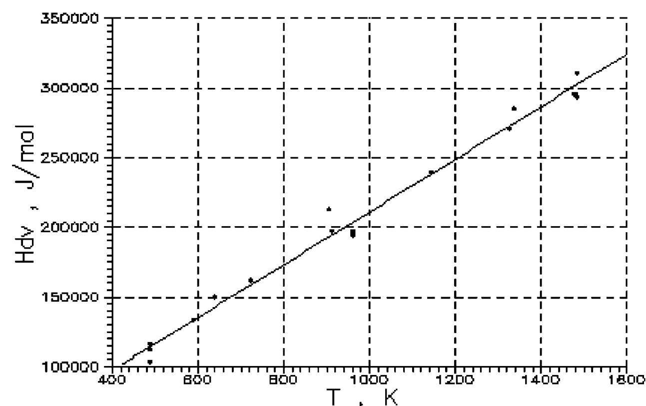

Fig. 3. Calculated silicon self–diffusion enthalpy temperature dependence.

migrate in different directions. Data from Tables 4 and 5 can be seen in Fig. 3.

4.1. Comparison with data on diffusion at 40 K

In [16], concentration profiles of molecular and atomic hydrogen implanted (0.6 keV, 0.025 A/m^2) at 40 K were studied using the $^1H(^{15}N,\alpha\gamma)^{12}C$ resonance reaction. We obtained similar self-diffusion coefficients (0.107×10^{-15} m^2/s). Noteworthy, however, is the much higher quasi-chemical activity of molecular hydrogen (compared with atomic hydrogen) in reactions of impurity capture, Frenkel pair annihilation, and impurity activation (by a factor of 76, 83387 and 12, respectively). We also determined the diffusion coefficients for molecular and free hydrogen in silicon (2.522×10^{-15} m^2/s, and 1.512×10^{-15} m^2/s, respectively).

The low- and high-temperature self-diffusion coefficients in silicon nearly coincide with [3] data. These values are close to 0.101×10^{-15} m^2/s, which was obtained by us from data [17] for deuterium implantation

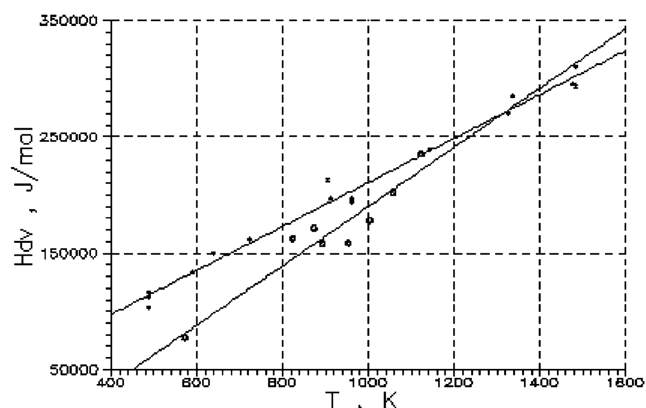

Fig. 4. Calculated zirconium and silicon self–diffusion enthalpy temperature dependence.

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(27 keV, 4 A/m^2) into diamond-like carbon films at room temperature. The diffusion coefficients of deuterium in C (2.612×10^{-15} m^2/s) and molecular hydrogen in Si are also close to each other. The similarity of C and Si properties was reported in [1].

5. Conclusion

In this paper silicon and zirconium self-diffusion enthalpy into wide temperature region was calculated (see Figs. 1, 3 and 4). Enthalpy at 1123 K in Table 1 is comparable with silicon into silicon value [3].

The deconvolution problem for the cross-section Zr^{92}(p,n)Nb^{92m} reaction was solved (see Fig. 2) for rotate zirconium sample. Comparison with the standard case data [8,9] was made.

It is shown that mechanisms behind low- and high-temperature migrations of interstitial-vacancy pairs during radiation-enhanced process are similar to each other (D_{dv} is approx. 10^{-16} m^2/s).

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