Thermodynamic calculations of self- and hetero-diffusion parameters in germanium

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V. Saltas[*], F. Vallianatos

School of Applied Sciences, Technological Educational Institute of Crete, Greece

HIGHLIGHTS

- Calculation of diffusivities of n- and p-type dopants in Ge from elastic properties.
- Calculation of point defect parameters according to the cBΩ thermodynamic model.
- Prediction of the pressure dependence of self-diffusion coefficients in Ge.

ARTICLE INFO

ABSTRACT

In the present work, the diffusion coefficients of n- and p-type dopants (P, As, Sb, Al) and self-diffusion in crystalline germanium are calculated from the bulk elastic properties of the host material based on the cBΩ thermodynamic model. The calculated diffusion coefficients as a function of temperature and the activation enthalpies prove to be in full agreement with the reported experimental results. Additional point defect parameters such as activation entropy, activation volume and activation Gibbs free energy are also calculated for each diffusing element. The pressure dependence of self-diffusion coefficients in germanium is also verified at high temperatures (876 K—1086 K), in agreement with reported results ranging from ambient pressure up to 600 MPa and is further calculated at pressures up to 3 GPa, where the phase transition to Ge II occurs.

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1. Introduction

Despite the main advantages of germanium as compared to silicon, i.e., lower band-gap, low activation temperatures of dopants and higher mobility of charge carriers, only very recently Ge has been incorporated in the development of n- and p-channel metal oxide semiconductor field effect transistors (MOSFET) by means of processes compatible with Si-based device fabrication [1—3]. In this direction, the accurate control of dopant diffusion in Ge-based nanoelectronic devices is essential and a lot of effort has been devoted to understanding the diffusion mechanisms both from a fundamental and an applied point of view [4—10]. It is now a well-documented fact that doping and self-diffusion in Ge takes place mainly through vacancies, while in Si the diffusion is quite more complicated through vacancies and self-interstitial sites [1,9,11,12]. From a thermodynamic point of view, the so-called cBΩ model

proposed by Varotsos and Alexopoulos [13—18] is able to calculate the diffusion coefficients based on the bulk elastic and thermal expansion properties of solids, giving an accurate estimation of point—defect parameters, such as activation enthalpy, activation volume and activation Gibbs free energy for one or more diffusion mechanisms in the solid. The validity of the cBΩ model has been confirmed on different kinds of solids such as noble gas solids, diamond, lead and alkali halides, metals and semiconductors, and superionic solids, as well as in various minerals with geophysical applications [19—38]. Very recently, the diffusion coefficients of In, Cu and Si in Ge have been calculated in terms of the cBΩ model, and appear to be in excellent agreement with the reported experimental data [28—30]. However and despite the technological interest of germanium, the diffusion of no other dopants in Ge has been investigated so far in the framework of this model.

Our intention in the present work is to examine the validity of the cBΩ model and calculate point defect parameters for various n- and p-type dopants (P, As, Sb and Al) diffused in germanium, for which the diffusion coefficients have been also determined experimentally as a function of temperature and are available in the

* Corresponding author.
  E-mail address: vsaltas@chania.teicrete.gr (V. Saltas).

literature [39,40]. Our study is further extended to self-diffusion in Ge, where we reproduce the pressure dependence of experimentally reported self-diffusion coefficients and we calculate them at higher pressures [11].

2. Diffusion in germanium in terms of the cBΩ model

According to the cBΩ thermodynamic model, the Gibbs free energy for an activation process such as the formation and migration of point defects is given by [14]:

$$g^{act} = c^{act} B \Omega \tag{1}$$

where B is the isothermal bulk modulus, Ω is the mean volume per atom and c^{act} stands for a dimensionless factor which at a first approximation is independent of temperature and pressure.

The self- or hetero-diffusion coefficient of a single mechanism which is expressed by the Arrhenius equation, $D = D_o exp(-g^{act}/k_b T)$, is then modified, according to Eq. (1) as:

$$D = \left(f\alpha^2 \nu\right) \exp\left(- c^{act} B \Omega / k_b T\right) \tag{2}$$

where in the pre-exponential term $D_o = f\alpha^2\nu$, f is the correlation factor that depends on the structure and the diffusion mechanism, α is the jump distance of the diffusant that is of the order of the lattice constant, and ν is the jump frequency which may be approximated to $\nu_D(m_m/m_d)^{1/2}$, with ν_D to be the Debye frequency and m_m, m_d to be the masses of the host material and the diffusant, respectively [17].

The significance of the cBΩ model lies on the estimation of the diffusion coefficients as a function of temperature and/or pressure, directly from the bulk properties of the host material (B, Ω), according to Eq. (2). In addition to the prerequisites for the known bulk properties, the factor c^{act} should be estimated correctly for the proper implementation of the model in the prediction of diffusion coefficients at extended temperature and pressure ranges. Different approaches have been proposed concerning the estimation of c^{act}, based on either a single experimental diffusion coefficient value in the case of no additional diffusion measurements at different temperatures, or the mean value from all the available experimental diffusion data [20,35]. A different approach to the estimation of c^{act}, according to the compensation effect, has been also reported [33]. In the first approach, c^{act} is estimated from Eq. (2) if the diffusion coefficient D_1 and the other parameters are known at a given temperature T_1, according to the following relation:

$$c^{act} = \ln\left(\frac{f\alpha^2 \nu_D}{D_1}\sqrt{\frac{m_m}{m_d}}\right)\frac{k_B T_1}{B_1 \Omega_1} \tag{3}$$

This estimation of c^{act} is inevitable when there is only a single measurement of the diffusion coefficient and may result in the calculation of the diffusion coefficients at other temperatures. However, if diffusion measurements have been carried out over a broad temperature range, the estimation of the mean value of c^{act} should be preferred. In this approach, the estimation rids of the uncertainties of the parameters which appear in the pre-exponential factor, such as the correlation factor and the jump frequency which are not always known, and is only subject to the experimental uncertainties of the measured diffusion coefficients [17,35].

The mean value of c^{act} is derived from Eq. (2) by taking the natural logarithm of both sides:

$$\ln D = \ln\left(f\alpha^2 \nu_D \sqrt{\frac{m_m}{m_d}}\right) - c^{act}\frac{B\Omega}{k_B T} \tag{4}$$

The validation of the cBΩ model results straightforward, if a linear correlation of the experimental lnD versus $B\Omega/k_B T$ is revealed, while c^{act} is estimated from the corresponding slope of the linear fitting. The value of c^{act} is necessary in order to proceed to the estimation of point defect parameters, as it is discussed in the following section.

The available data of $B(T)$ and $\Omega(T)$ for Ge−I phase [42] evinces a linear behavior at the temperature range (800 K−1200 K) of the reported diffusion measurements that are used in the present work [11,39−41], and can be approximated by the following relations:

$$B(T) = B_o + (T - T_o)(\partial B/\partial T)_P \tag{5}$$

and

$$\Omega(T) = \Omega_o[1 + \beta_o(T - T_o)]/Z \tag{6}$$

In the above relations, B_o is the bulk modulus at room temperature (RT) and $(\partial B/\partial T)_P$ is its temperature derivative, Ω_o is the volume of the unit cell at RT, β_o is the coefficient of volumetric thermal expansion at RT and Z is the number of atoms per unit cell. In the case of germanium, $\Omega_o = 2.264\cdot10^{-29}$ m³, $Z = 8$, $\beta_o = 1.82 \times 10^{-6}$ K⁻¹ and $(\partial B/\partial T)_P = -0.0126$ GPaK⁻¹ [43−45]. The value of B_o is estimated by linear extrapolation ($B_o = 80.1$ GPa) from the reported experimental data [42] according to Eq. (5), since its real value (74.9 GPa) is lower due to the non-linear behavior of bulk modulus at low temperatures.

By substituting the above values in Eqs (5) and (6), $B(T)$ and $\Omega(T)$ have been calculated as a function of temperature and thus the estimation of c^{act} is feasible according to Eq. (4). As it is depicted in Fig. 1, a linear correlation between experimental lnD and $B\Omega/k_B T$ holds for each of the n- (P, As, Sb) and p-type (Al) dopants diffused in Ge, as well as for self-diffusion in Ge (correlation factors, R > 0.98), suggesting clearly the validity of the cBΩ model. The values of c^{act} were estimated from the linear fittings in each case and are shown in Table 1. The applicability of the cBΩ model to describe n-type dopant diffusion in Ge has been reported very recently by Chroneos and Vork [46]. The validation of the cBΩ model for self-diffusion in Ge has been reported in the past by using indirect calculations based on diffusivity and solubility data of Cu diffusion in Ge [42]. A different experimental data set [11] with additional pressure-dependent diffusion coefficients has been used
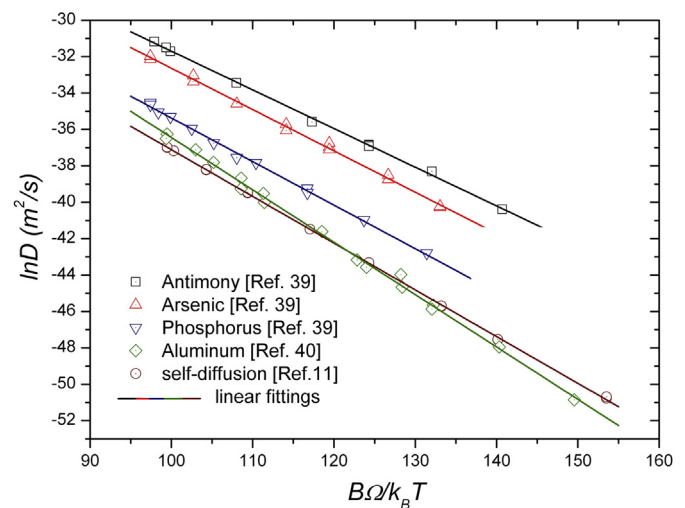

Fig. 1. Experimental diffusion coefficients of different dopant elements in Ge (P, As, Sb, Al and self-diffusion) with respect to the quantity $B\Omega/k_B T$. The linear behavior implies the validity of the cBΩ model, according to Eq. (4).