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Gold and silver diffusion in germanium: a thermodynamic approach

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Abstract Diffusion properties are technologically important in the understanding of semiconductors for the efficent formation of defined nanoelectronic devices. In the present study we employ experimental data to show that bulk materials properties (elastic and expansivity data) can be used to describe gold and silver diffusion in germanium for a wide temperature range (702–1177 K). Here we show that the so-called cBΩ model thermodynamic model, which assumes that the defect Gibbs energy is proportional to the isothermal bulk modulus and the mean volume per atom, adequately metallic diffusion in germanium.

1 Introduction

Germanium (Ge) was a material of traditional importance to the semiconductor industry, however, in the past decade it rivals silicon (Si) as it has superior materials properties (better carrier mobilities, low dopant activation temperatures and smaller band-gap) [1–5]. This is driven by the advent of high-k gate dielectric materials as these have eliminated the requirement of a good quality native oxide in advanced nanoelectronic devices [6, 7]. Additionally, the recent investigation of diffusion phenomena such as the discovery that boron diffuses slower in Ge than originally thought has also assisted the exploitation of Ge [8].

In Ge metals such as gold (Au) and silver (Ag) diffuse via the dissociative mechanism [9–11]. In the dissociative mechanism, proposed by Frank and Turnbull [11] there is a requirement for vacancies (V) that excange position with the dopant intersititials (D_i) to form a dopant substitutional to a Ge site (D_{Ge}) via the relation $D_i + V \leftrightarrow D_{Ge}$. The dissociative mechanism requires vacancies and this is compatible to Ge as this is the dominant intrinsic defect [5, 11].

The association of the defect Gibbs energy g^i (where i = defect formation f, diffusion activation act, or migration m) with bulk properties in solids is an issue that has led to different models for numerous decades [12–20]. A notable example is the model of Zener [12], which proposed that g^i is proportional to the shear modulus of the solid. The more recent model by Varotsos and Alexopoulos [13–19] (the so-called cBΩ model) postulated that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom Ω.

In previous studies [21–31] the cBΩ model was used to investigate the point defect processes in a wide range of crystalline materials, but was not employed to describe Au and Ag diffusion processes in Ge. In the present study we use the cBΩ to model Au and Ag diffusion in Ge by using isothermal bulk modulus and the mean volume per atom in a wide temperature range (827–1176 K).

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2 Methodology

2.1 Point defect parameters

Formally, the defect formation parameters in a system can be defined by comparing a real (i.e. defective) crystal to an isobaric ideal (non-defective) crystal [21, 24]. In this framework, the isobaric parameters are defined in terms of the corresponding Gibbs energy (g^f) as [21, 24]:

$$s^f = -\left.\frac{dg^f}{dT}\right|_P \tag{1}$$

$$h^f = g^f - T\left.\frac{dg^f}{dT}\right|_P = g^f + Ts^f \tag{2}$$

$$\upsilon^f = \left.\frac{dg^f}{dP}\right|_T \tag{3}$$

where P is the pressure, T is the temperature; s^f, h^f and υ^f represent the defect formation entropy, enthalpy and volume respectively.

Typically, in a monoatomic crystal with a single diffusion mechanism, the diffusion process can be described by the activation Gibbs energy (g^{act}). This is the sum of the Gibbs formation (g^f) and the Gibbs migration (g^m) processes. The activation entropy s^{act} and the activation enthalpy h^{act} can be defined by [21, 24]:

$$s^{act} = -\left.\frac{dg^{act}}{dT}\right|_P \tag{4}$$

$$h^{act} = g^{act} + Ts^{act} \tag{5}$$

The diffusivity D can be defined by [21, 24]:

$$D = fa_0^2 \nu e^{-\frac{g^{act}}{k_B T}} \tag{6}$$

where f depends upon the diffusion mechanism and structure, a_0 is the lattice parameter, ν is the attempt frequency and k_B is Boltzmann's constant.

2.2 The cBΩ model

The key of the cBΩ model is the description of the defect Gibbs energy g^i in terms of the bulk properties of the solid [21, 24]:

$$g^i = c^i B\Omega \tag{7}$$

where c^i is dimensionless.

$$s^i = c^i\Omega\left(\beta B + \left.\frac{dB}{dT}\right|_P\right) \tag{8}$$

$$h^i = c^i\Omega\left(B - T\beta B - T\left.\frac{dB}{dT}\right|_P\right) \tag{9}$$

$$\upsilon^i = -c^i\Omega\left(\left.\frac{dB}{dP}\right|_T - 1\right) \tag{10}$$

where β is the thermal (volume) expansion coefficient.

In principle, employing Eqs. (6) and (7) the diffusivity can be calculated in the framework of the cBΩ model at any temperature and pressure from a single experimental measurement using:

$$D = fa_0^2 \nu e^{-\frac{c^{act} B\Omega}{k_B T}} \tag{11}$$

Considering a single experimental measurement for a diffusivity D_1 value at a temperature T_1 the c^{act} can be calculated if we assume that the pre-exponential factor $fa_0^2\nu$ can be estimated. Then by using this c^{act} and Eq. 11 the diffusivity D_2 at any temperature T_2 can be calculated if we have the elastic data and expansivity data for T_2. In previous studies it was proposed that c^{act} is a constant that is independent of temperature and pressure to least to a first approximation [21, 24]. Finally, for constant temperature the D can be studied at any pressure (refer for example to [32–34]).

3 Results and discussion

3.1 Background

The intrinsic point defects are the main vehicles that facilitate self- and dopant diffusion in materials. The control of diffusion processes is necessary to achieve well defined regions in devices. Regarding self-diffusion in Ge it has been previously established that it is mediated by vacancies [35–38]. Consequent studies revealed that the diffusion of most dopants in Ge is mediated by vacancies [39–42]. Exceptions include copper (Cu), palladium (Pd), Au and Ag (refer to [43] and references therein). Au [10, 44–46] and Ag [47, 48] diffusion in Ge has been investigated for about six decades. Figure 1 represents the

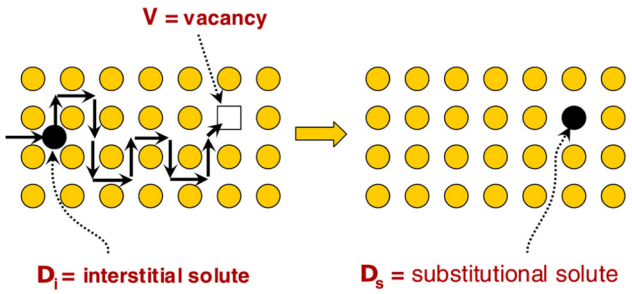


Fig. 1 A schematic representation of the dissociative diffusion mechanism

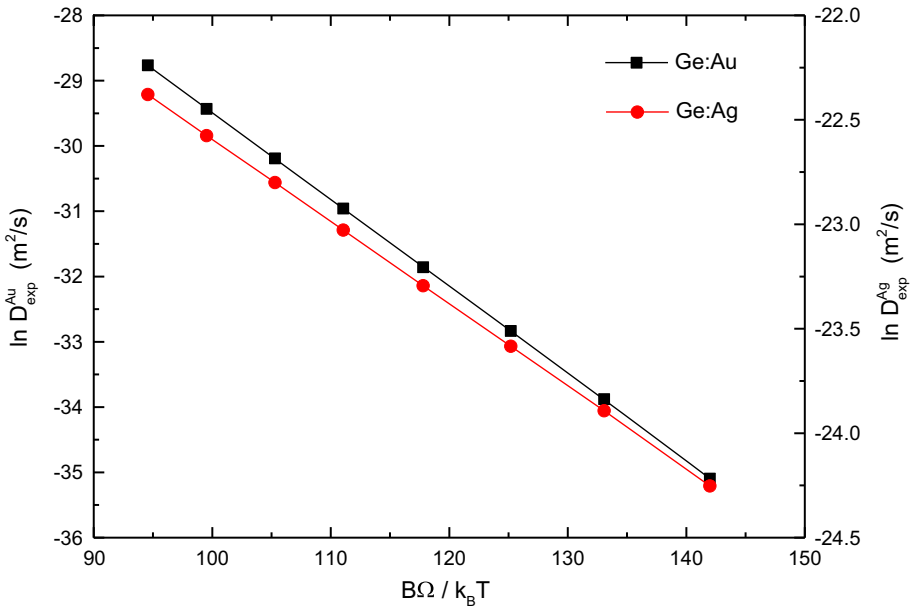


Fig. 2 The experimental [10] Au and Ag diffusion coefficients in Ge with respect to $\frac{B\Omega}{k_B T}$

dissociative mechanism (Frank and Turnbull mechanism [11]) that is the mechanism for Au and Ag transport in Ge [10]. In this the dopant interstitial migrates until it recombines with a vacancy to form a dopant substitutional (via $D_i + V \leftrightarrow D_{Ge}$).

The Au and Ag diffusion in the temperature range 873 K to 1193 K can be described through the Arrhenius following relations [10]:

$$D^{Au}_{exp} = 1.05e^{-\frac{1.52}{k_B T}} \cdot 10^{-6}\, m^2 s^{-1} \quad (12)$$

$$D^{Ag}_{exp} = 1.62e^{-\frac{0.45}{k_B T}} \cdot 10^{-8}\, m^2 s^{-1} \quad (13)$$

3.2 Au and Ag diffusion in Ge

In the present study we used the expansivity data of Kagaya et al. [49] and the isothermal bulk modulus data of Krishnan et al. [50]. As the single experimental measurement method may lead to errors other ways have been previously used to calculate c^{act} including the compensation law and the "mean value" method [21, 24, 26, 51, 52].

In the present study we used the mean value method because we wanted to limit the dependence of c^{act} on experimental uncertainties in the determination of a diffusivities [10], the expansivity [49] and isothermal bulk modulus [50]. In the mean value method a linear behavior of lnD with respect to $\frac{B\Omega}{k_B T}$ testifies the applicability of the cBΩ model, whereas from the slope c^{act} can be derived (refer to Eq. 11). Figure 2 reports the experimental [10] Au and Ag diffusion coefficients in Ge with respect to $\frac{B\Omega}{k_B T}$ verifying in essence that the relations are linear and can be represented by the following relations

$$D^{Au}_{cB\Omega} = 5.602e^{\frac{0.1332B\Omega}{k_B T}} \cdot 10^{-8}\, m^2 s^{-1} \quad (14)$$

$$D^{Ag}_{cB\Omega} = 7.953e^{\frac{0.0394B\Omega}{k_B T}} \cdot 10^{-9}\, m^2 s^{-1} \quad (15)$$

Relations 14 and 15 can be used to calculate the other Au and Ag diffusivity values with respect to temperature. The

Table 1 Characteristic calculated Au and Ag diffusion coefficients in Ge [10] alongside the elastic and expansivity data [49, 50] used here

T (K)	B (10^{11} Nm^{-2})	Ω (10^{-29} m^3)	D^{Au}_{exp} (10^{-14} m^2 s^{-1})	$D^{Au}_{cB\Omega}$ (10^{-14} m^2 s^{-1})	D^{Ag}_{exp} (10^{-11} m^2 s^{-1})	$D^{Ag}_{cB\Omega}$ (10^{-11} m^2 s^{-1})
827	0.709	2.289	0.05731	0.05821	2.93219	2.94378
877	0.703	2.292	0.19335	0.19119	4.20280	4.18625
925	0.697	2.294	0.54904	0.54528	5.72440	5.70943
975	0.690	2.298	1.45983	1.46085	7.64649	7.64385
1026	0.684	2.300	3.58797	3.58436	9.97896	9.97079
1074	0.678	2.303	7.73641	7.71866	12.5278	12.5131
1126	0.671	2.306	16.5171	16.6437	15.6817	15.7099
1176	0.665	2.309	32.1505	32.2189	19.0997	19.1033

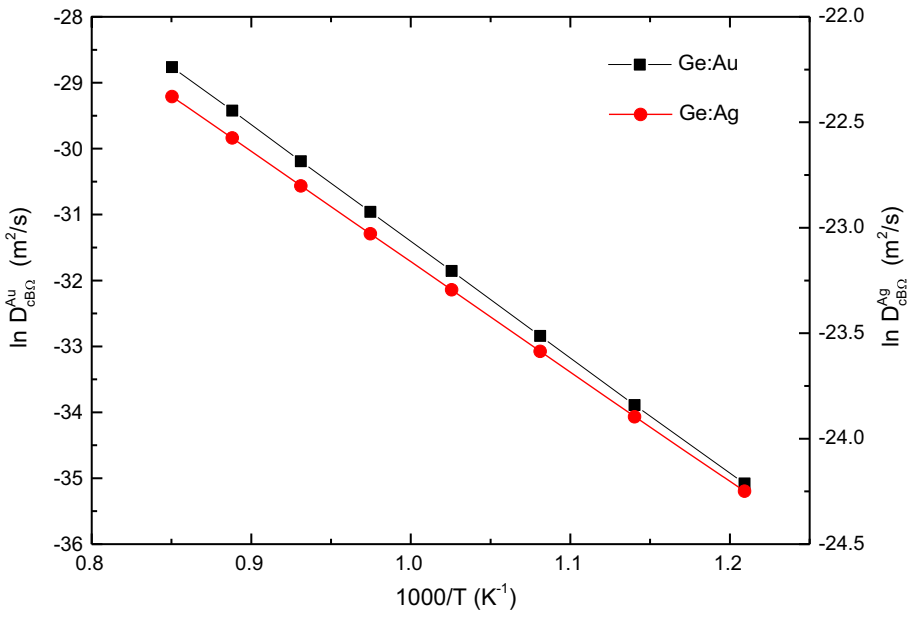


Fig. 3 The Arrhenius plot for Au and Ag diffusion coefficients calculated by the cBΩ model

only requirement is to have the corresponding elastic and expansivity data. As it can be observed from Table 1 the cBΩ model is in excellent agreement with experiment [10], as the experimental and calculated Au and Ag diffusion coefficients in Ge vary by less than 2 %. Figure 3 is the Arrhenius plot for Au and Ag diffusion coefficients obtained by calculated by the cBΩ model. Interestingly, the cBΩ model is in excellent agreement with experiment in a diffusion mechanism that is non-trivial. As it has been previously discussed [21, 24] the cBΩ model is appropriate when a single-diffusion mechanism is operating. Although Au and Ag diffusion in characterized by a single diffusion mechanism dissociative diffusion can be complicated as it requires both vacancies and interstitials, whereas the steps are not as well defined as in other mechanisms (for example the ring-mechanism for vacancy diffusion in Ge [43]).

4 Conclusions

Point defect processes in materials can be linked to the bulk properties through the cBΩ model. This in turn can be beneficial to numerous issues including novel nanoelectronic devices. In the present study, the efficacy of the cBΩ model has been tested to model diffusivity via the Frank and Turnbull mechanism. There is an excellent agreement between the calculated and experimental Au and Ag diffusivities in the temperature range considered. It is therefore evident that the Au and Ag dissociative mechanism in Ge can described with the cBΩ model. This in turn implies that the cBΩ model should be tested in systems with complicated diffusion mechanisms and defect processes [53–59].

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