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Copper diffusion in germanium: Connecting point defect parameters with bulk properties

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Abstract

Copper diffusion in germanium is fundamentally and technologically important as it has a very low activation energy and influences the precipitation and gettering of copper respectively. These constitute the understanding of copper's diffusion properties in germanium over a range of temperatures and pressures important. In the present study we use the cBΩ model in which the defect Gibbs energy is proportional to the isothermal bulk modulus (B) and the mean volume per atom (Ω). The elastic and expansivity data is used in the description of the cBΩ model to derive the copper interstitial diffusion coefficient in germanium in the temperature range 827 K to 1176 K. The calculated results are discussed in view of the available experimental data.

Keywords: Germanium; diffusion; Copper

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1. Introduction

Germanium (Ge) rivals silicon (Si) as it has superior carrier mobilities, low dopant activation temperatures and smaller band-gap [1-5]. In the early days of the semiconductor industry Ge was abandoned because of its poor quality native oxide [1]. Recently, the introduction of high-*k* gate dielectric materials has eliminated the requirement of a good quality native oxide in advanced nanoelectronic devices regenerating the interest on alternative materials such as Ge [6-8].

In Ge metals such as copper (Cu) have been used to increase the rate of crystallization and produce large grain crystals via the process of metal induced lateral crystallisation (MILC) [9]. Self-diffusion and most diffusion processes in Ge are governed by vacancies [10-16], whereas in Si self-interstitials also impact the defect processes [17,18]. Considering *n*-type dopant (P, As, and Sb) diffusion the most recent experimental and theoretical results are in agreement that it is vacancy-mediated [13,16]. From the *p*-type dopants indium diffuses with a vacancy-mechanism, whereas boron diffusion is interstitial but very slow [5,15]. Metal diffusion including Cu diffusion is an exception where interstitial-related mechanisms can be important [19-21]. In particular copper interstitials (Cu_i) can diffuse via direct interstitial or dissociative mechanisms and these are faster than vacancy-mediated mechanisms [19-21].

Interconnecting the defect Gibbs energy g^i (i = defect formation f, self diffusion activation act, or migration m) and bulk properties in solids has led to different models including the model by Zener [22] and the model by Varotsos and Alexopoulos [23-30]. In the model by Varotsos and Alexopoulos [23-29] (refered thereafter as the cBΩ model) it was proposed that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom Ω. The cBΩ model was employed to

study the point defect processes in numerous materials [31-41], but it has not been systematically used to describe to investigate the diffusion processes in group IV semiconductors.

In the present study we describe using the cBΩ model the Cu intersitial diffusion coefficients in Ge using the isothermal bulk modulus and the mean volume per atom.

2. Methodology

For a monoatomic crystal with a single diffusion mechanism diffusion process can be described by the activation Gibbs energy (g^{act}), which is the sum of the Gibbs formation (g^f) and the Gibbs migration (g^m). The activation entropy s^{act} and the activation enthalpy h^{act} are defined via [31, 34]:

$$s^{act} = -\frac{dg^{act}}{dT}\bigg|_P \tag{1}$$

$$h^{act} = g^{act} + Ts^{act} \tag{2}$$

The diffusion coefficient D is defined by:

$$D = fa_0^2 \nu e^{-\frac{g^{act}}{k_B T}} \tag{3}$$

Where f is the diffusion correlation factor depending on the diffusion mechanism and the structure, a_0 is the lattice constant, ν is the attempt frequency and k_B is Boltzmann's constant.

In the cBΩ model the defect Gibbs energy g^i is related to the bulk properties of the material via the relation [23-29]:

$$g^i = c^i B\Omega \tag{4}$$

Therefore, by Eqs. (3) and (4):

$$D = fa_0^2 \nu e^{-\frac{c^{act} B\Omega}{k_B T}} \tag{5}$$

This means that if there is an experimentally determined diffusivity D_1 value at T_1 the c^{act} can be calculated assuming that the pre-exponential factor $fa_0^2\nu$ can be determined. The calculation of the pre-exponential factor involves computing the diffusion correlation factor (which is dependent upon the diffusion mechanism and the crystal structure) and the attempt frequency. The attempt frequency is commonly approximated by the Debye frequency, which can lead to the introduction of errors. Thereafter, using c^{act} the diffusivity D_i at any temperature T_i can be calculated using Eq. 5 provided that the elastic data and expansivity are known for T_i. Importantly, c^{act} is to a first approximation a temperature and pressure independent constant [31, 34]. Finally, in the framework of the cBΩ model anharmonic effects can be described by the temperature decrease in B and by the thermal expansivity.

3. Results and discussion

The control of self-, dopant and impurity diffusion is very important during device fabrication. The diffusion of Cu in Ge impacts the electronic properties and influences other diffusion related phenomena including the precipitation and gettering of Cu [21]. The control and understanding of these processes are of technological importance to control the contamination levels of electronic devices during processing [21].

In previous work it was determined that Cu interstitial diffusion in Ge can be described via the Arrhenius relation [21]:

$$D_{exp}^{Cu} = 3.2e^{-\frac{0.18}{k_B T}} \cdot 10^{-7} m^2 s^{-1} \qquad (6)$$

In the present study, the expansivity data was taken from Kagaya *et al.* [42] and the isothermal bulk modulus data from Krishnan *et al.* [43]. These values [42-45] are

reported in Table 1 alongside the experimental Cu interstitial diffusion coefficients derived from Eq. 6. Typically, the method of the single experimental measurement can be employed to calculate the value of c^{act} in the cBΩ model but will depend upon the experimental error in the B, Ω parameters and the diffusivity value. Furthermore, there will be errors in the pre-exponential factor especially for materials were diffusion mechanisms are complicated. For these reasons here we employ the "mean value" method to calculate c^{act} [36, 39, 46, 47].

In the "mean value" method the linear behavior of lnD_{exp}^{Cu} with respect to $\frac{B\Omega}{k_B T}$ testifies the validity of the cBΩ model with the slope being c^{act} as it can be seen from Eq. 5. As it can be observed from Figure 1 there is a linear relation, which can be described by:

$$D_{cB\Omega}^{Cu} = 2.41e^{-\frac{0.0158B\Omega}{k_B T}} \cdot 10^{-5} m^2 s^{-1} \qquad (7)$$

Figure 2 is the Arrhenius plot for Cu interstitial diffusion coefficients in Ge determined by experiment [21] and calculated by the cBΩ model. Both this figure and Table 1 show that the cBΩ model is in excellent agreement with the experimental [21] Cu intersitial diffusion coefficients in Ge. Therefore, the cBΩ model describes Cu interstitial diffusion in Ge. Future studies will explore whether the cBΩ model can be employed to study other metals diffusing in Ge.

4. Conclusions

In the present study we employed the cBΩ model to describe metal diffusion in germanium. There is excellent agreement between the calculated and experimental diffusion coefficients of Cu interstitial diffusion in Ge in the temperature range considered. This extremely low activation energy diffusion process is a paradigm for related studies of metal diffusion in semiconductors and the present approach may be

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extended to these systems. Additionally, the cBΩ model can provide information concerning the formation, migration and defect volumes in these systems over a range of temperatures and pressures.
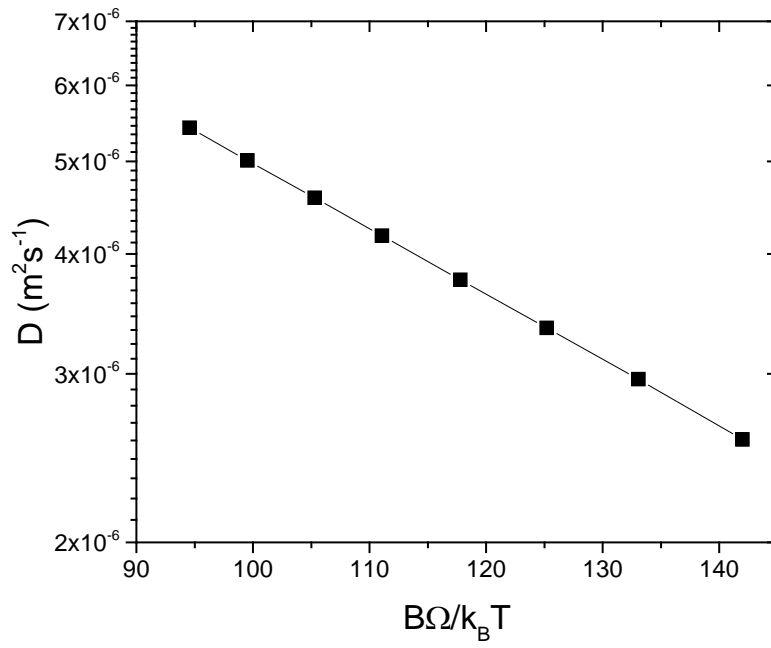
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Table 1. Characteristic calculated and experimental [21] Cu diffusion coefficients in Ge alongside the elastic and expansivity data [42-45] used in the cBΩ model.

T (K)	B (10^{11}Nm^{-2})	Ω (10^{-29}m^3)	D_{exp}^{Cu} (10^{-6}m^{2}s^{-1})	$D_{cB\Omega}^{Cu}$ (10^{-6}m^{2}s^{-1})	$\dfrac{D_{cB\Omega}^{Cu} - D_{exp}^{Cu}}{D_{exp}^{Cu}}$ (%)
827	0.709	2.289	2.56	2.56	0
877	0.703	2.292	2.96	2.96	0
925	0.697	2.294	3.35	3.33	-1
975	0.690	2.298	3.76	3.75	0
1026	0.684	2.300	4.18	4.17	0
1074	0.678	2.303	4.58	4.57	0
1126	0.671	2.306	5.01	5.01	0
1176	0.665	2.309	5.42	5.41	0

FIG. 1. The Cu diffusion coefficients in Ge with respect to $\frac{B\Omega}{k_B T}$.
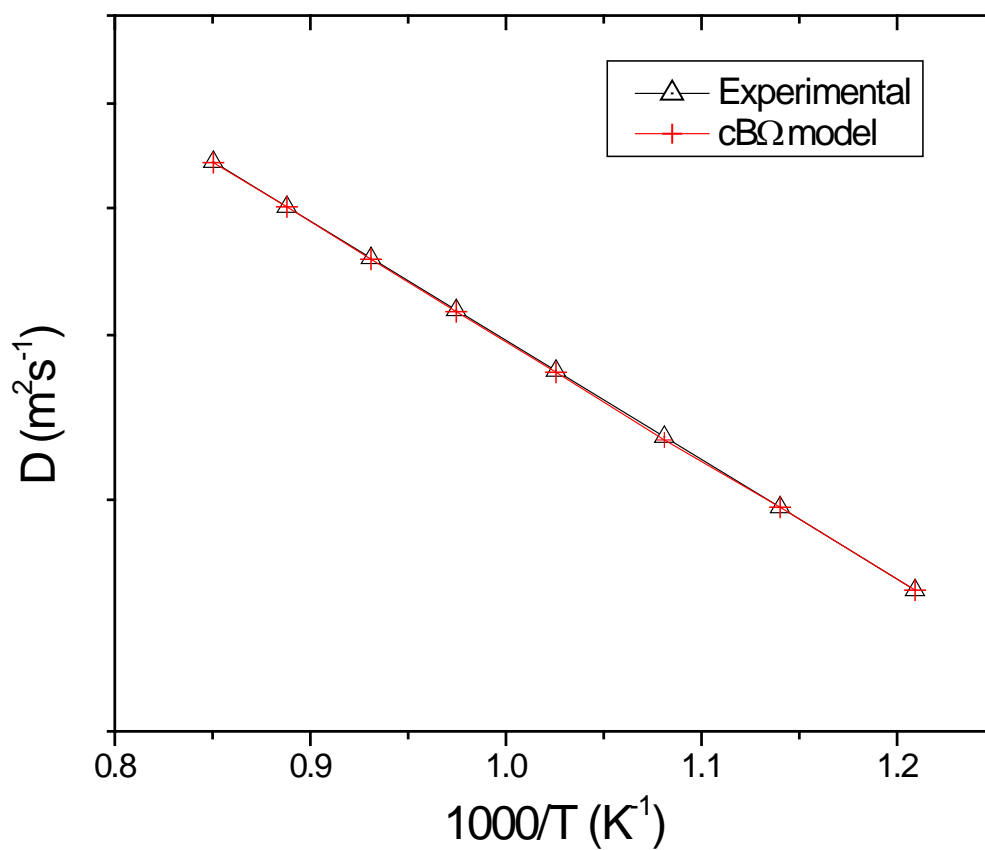
FIG. 2 The Arrhenius plot for Cu diffusion in Ge obtained by experiment [21] and calculated by the cBΩ model.