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Connecting bulk properties of germanium with the behavior of self- and dopant diffusion

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ABSTRACT

The understanding of self- and dopant diffusion properties over a range of temperatures and pressures can be technologically important for the formation of defined and efficient nanoelectronic devices. Phosporous, Arsenic and antimony are *n*-type dopants that can be considered for *n*-channel germanium metal oxide semiconductor field effect transistors. Using recent experimental data we show that elastic and expansivity data can reproduce the self-diffusion and *n*-type dopant diffusion coefficient of germanium in the temperature range 702–1177 K. This is achieved in the framework of the cBΩ model, which assumes that the defect Gibbs energy is proportinal to the isothermal bulk modulus and the mean volume per atom.

1. Introduction

The connection of the defect Gibbs energy g^i (i=defect formation f, self-diffusion activation act, or migration m) and bulk properties in solids is an important issue that has led to different models [1–10]. The model of Zener [1,2] proposes that g^i is proportional to the shear modulus of the solid. This is justified physically by the assumption that g^i accounts for the work to strain the lattice. A more recent model by Varotsos et al. [3–9] (refered to as the cBΩ model) proposed that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom Ω. The efficacy of the cBΩ model to describe defect processes in a range of systems including alkali and silver halides, PbF_2, AgI, diamond, olivine, ZnO, LiH, silicon (Si) and others has been established in previous studies [11–21]. The cBΩ model has not been systematically employed to investigate the diffusion processes in *n*-type doped germanium.

Si is the most studied group IV semiconductor with application in nanoelectronic, sensor and photovoltaic devices [22–26]. For many decades Si technology has benefited from the advantageous Si native oxide (i.e. SiO_2), which has superior materials properties as compared to other native oxides (for example GeO_2 in Ge technology). The scalability of Si and SiO_2 allowed for the efficient minaturization of Si-devices with the understanding of many defect processes at the atomistic scale becoming increasingly important [27–30]. The recent advent of high dielectric constant (high-k) dielectrics has allowed the use of alternative substrates such as $Si_{1-x}Ge_x$ and Ge [31–33]. The defect processes of these materials were relatively unknown compared to Si, with studies in the past few years aiming to bridge this gap in understanding [34–40].

Concerning the diffusion properties in group IV semiconductors recent advances in experimental (Time-of-Flight Secondary Ions Mass Spectrometry, TOF-SIMS) and theoretical (density functional theory) techniques have clarified most of the self- and dopant diffusion energetics and mechanisms [41–43]. Nevertheless, the interest in this

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family of materials will be continue as new members are considered with the addition of tin (Sn). Binary ($Sn_{1-x}Ge_x$ and $Sn_{1-x}Si_x$) and ternary ($Si_{1-x-y}Ge_xSn_y$) alloys are deemed to become important as they offer a large range of strain options enabling the lattice matching of Si or Ge with most III–V and II–VI alloys [44–46].

The cBΩ model is typically employed in materials with a single diffusion mechanism. In the present study we calculate the self-diffusion and *n*-type dopant diffusion coefficient in Ge using the cBΩ model.

2. Methodology

2.1. A. Point defect parameters

The defect formation parameters can be defined by comparing a real (i.e. defective) crystal to an isobaric ideal (no defects) crystal [11,14]. The isobaric parameters are defined in terms of the corresponding Gibbs energy (g^f) as [11,14]:

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

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

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

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.

For a monoatomic crystal with a single diffusion mechanism the self-diffusion process can be described by the activation Gibbs energy (g^{act}). g^{act} 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} are defined by [11,14]:

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

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

The diffusion coefficient or diffusivity D is defined by:

$$D = fa_0^2\nu e^{-g^{act}/k_BT} \tag{6}$$

where f is a numerical constant 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.

2.2. B. The cBΩ model

In the cBΩ model the defect Gibbs energy g^i is related to the bulk properties of the solid via [3–9]:

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

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.

The diffusion coefficient can be calculated using the cBΩ model at any temperature and pressure from a single experimental measurement. Combining Eqs. (6) and (7):

$$D = fa_0^2\nu e^{-c^{act}B\Omega/k_BT} \tag{11}$$

For an experimentally determined diffusivity D_1 value at T_1 the c^{act} can be calculated as the pre-exponential factor $fa_0^2\nu$ is roughly known or can be calculated. Then using c^{act} the diffusivity D_2 at any temperature T_2 can be calculated using Eq. 11, provided that the elastic data and expansivity are known for this temperature.c^{act} is a constant that can be assumed to be independent of temperature and pressure to a first approximation [11,14]. Using c^{act} in Eqs. (8)–(10) s^{act}, h^{act} and υ^{act} can be calculated at any T. For constant T the D can be studied at any pressure.

3. Results and discussion

3.1. A. Background

The intrinsic point defects in group IV semiconductors, *V* and *I*, are the main vehicles that facilitate self- and dopant diffusion. Understanding and controlling diffusion during device fabrication is important, with self-diffusion studies providing a direct route to intrinsic defect processes. The study of Werner et al. [47] provided evidence of the acceptor nature of the vacancy in Ge. The prevalence of the vacancy diffusion mechanism in Ge was verified by the agreement of Ge self-diffusion and the vacancy contribution to self-diffusion as deduced from copper (Cu) diffusion in dislocation-free Ge [48–50]. In recent work Hüger et al. [51] used isotopically modulated $^{70}Ge/^{nat}Ge$ multilayer structures to investigate the diffusional intermixing at the interface by neutron reflectometry. The Ge self-diffusion in the temperature range 702–1177 K can be described with a vacancy mechanism via an Arrhenius relation [51]:

$$D^V = 2.54e^{-3.13ev/k_BT}\cdot 10^{-3}\ m^2\ s^{-1} \tag{12}$$

In the present study the experimental self-diffusion coefficients of Hüger et al. [51] are used and reported in Table 1.

The main *n*-type dopants (A) in Ge are phosphorous (P), arsenic (As) and antimony (Sb). There is consensus between the experimental and theoretical studies that P, As and Sb diffuse in Ge via vacancy-mediated mechanisms [52–54]. Brotzmann et al. [36,52] determined that the diffusion of *n*-type dopants increases with the square of the free electron concentration. This dependence can be described by considering singly negatively charged dopant-vacancy pairs, $(AV)^-$, formed via the reaction $(AV)^- \leftrightarrow A_s^+ + V^{2-}$. Here A_s^+ represents the singly positively charged *n*-type dopant and V^{2-} the