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A thermodynamic approach of self- and hetero-diffusion in GaAs: Connecting point defect parameters with bulk properties

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The self- and hetero-diffusion in GaAs is investigated in terms of the cBΩ thermodynamic model, which connects point defect parameters with the bulk elastic and expansion properties. Point defect thermodynamic properties such as, activation enthalpy, activation volume, activation Gibbs free energy, activation entropy and isobaric specific heat of activation are calculated as a function of temperature for Ga, H and various n- and p-type dopants (Si, Be, Cr, Fe and Zn) diffused in GaAs. The present calculations are in good agreement with the reported experimental results. The pressure dependence of Ga self-diffusion is also investigated and the diffusivities and activation volumes are predicted at different temperatures from ambient pressure up to 10 GPa, above which GaAs is transformed into the orthorhombic structure. The activation volumes of dopants are also estimated at high temperature (1124 K), as a function of pressure.

1. Introduction

The drive to replace silicon (Si) with alternative materials such as III-V semiconductors is mainly due to their advantageous material properties that can include high electron mobility and lattice matching with ternary (and/or quaternary) III-V compounds.[1-5] III-V materials such as GaAs are technologically important for nanoelectronic devices, for lasers and radiation detectors and for high efficiency solar cells.[3,6] The scientific interest for GaAs is still undiminished, both from a practical and from a theoretical point of view.[7,8]

For the efficient miniaturization and optimization of electronic devices, it is necessary to understand defect processes formed during the growth processes.[9] Previous studies provided fundamental insights into the diffusion and other defect processes of III-V semiconductors.[10-25] Gallium diffusion dominates self-diffusion in GaAs.[16] The diffusion of various n- and p-type dopants in GaAs has been extensively investigated in the past.[13-25] Silicon is a commonly used n-type dopant,[6] that although is amphoteric (it can occupy both the Ga and As sites) in As-rich grown GaAs Si is an n-type dopant occupying the Ga site. Regarding acceptor doping, Beryllium and Zinc are significant p-type dopants in GaAs with high diffusion coefficients.[26]

Associating the defect Gibbs free energy g^i (i = defect formation f, self-diffusion activation act, or migration m) with bulk properties in solids is an issue that has been considered for more than six decades.[27-30] In the cBΩ model formulated by Varotsos et al. it was established that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom Ω.[31,32] The efficacy of the cBΩ model has been demonstrated in numerous and diverse systems including defect processes in Si, Ge, ZnO, olivine, diamond, PbF_2, UO_2, LiH, and AgI.[33-42]

In the present study we investigate the temperature and pressure dependence of self- and hetero-diffusion in GaAs in the frame of the cBΩ model. Based on elastic and expansion properties of GaAs, thermodynamic calculations of point defect parameters are carried out for the first time in a III-IV semiconducting system at high pressures, giving further insights to the diffusion mechanisms of various n- and p-type dopants. The structure of the present work is organized as follows. In section 2.1, we present briefly the cBΩ thermodynamic model providing all the necessary formulas for the estimation of the point defect thermodynamic properties as a function of temperature and/or pressure. In section 2.2 the necessary calculations for the determination of the bulk modulus and the mean atomic volume of GaAs are given and can be employed for any kind of dopant (n- or p-type). Subsequently, the application of the model to different dopants is presented and our predictions are discussed in comparison with the reported experimental results.

2. Methodology

2.1 Point defect parameters in terms of the cBΩ model

The self- or hetero-diffusion process of a single diffusion mechanism can be described by an Arrhenius equation of the diffusion coefficients D, according to the following relation

$$D = f g a_0^2 \nu e^{-g^{act}/k_B T} \quad (1)$$

where f is the correlation factor depending on the diffusion mechanism and the structure, g is a geometry factor, a_o is the lattice constant, ν is the attempt frequency and k_B is Boltzmann's constant.

In the frame of the cBΩ thermodynamic model,[31,32] the defect Gibbs free energy of activation g^{act} which is the sum of the formation (g^f) and migration (g^m) energy, is related to the bulk properties of the solid via

$$g^{act} = c^{act} B \Omega \quad (2)$$

where B is the isothermal bulk modulus, Ω is the mean volume per atom and c^{act} is a dimensionless factor that is considered to be independent of temperature and pressure under certain experimental conditions.

Based on Eq. (2), the thermodynamic properties of the point defects i.e., activation volume v^{act}, activation entropy s^{act} and activation enthalpy h^{act} of diffusion are expressed exclusively by the elastic and expansion properties of the bulk, at any temperature (or pressure), through the following relations

$$v^{act} = -\left(\frac{\partial g^{act}}{\partial P}\right)_T = c^{act}\Omega\left\{\frac{\partial B}{\partial P}\Big]_T - 1\right\} \quad (3)$$

$$s^{act} = -\left(\frac{\partial g^{act}}{\partial T}\right)_P = -c^{act}\Omega\left\{\frac{\partial B}{\partial T}\Big]_P + \beta B\right\} \quad (4)$$

$$h^{act} = g^{act} + Ts^{act} = c^{act}\Omega\left\{B - T\beta B - T\frac{\partial B}{\partial T}\Big]_P\right\} \quad (5)$$

where β is the coefficient of volume thermal expansion which is temperature and pressure dependent. In addition, the isobaric specific heat of activation c_P^{act} can be also derived from Eq. (5), according to

$$c_P^{act} = -\left(\frac{\partial h^{act}}{\partial T}\right)_P =$$

$$= -c^{act}\Omega T\left\{\beta^2 B + 2\beta\frac{\partial B}{\partial T}\Big]_P + B\frac{\partial \beta}{\partial T}\Big]_P + \frac{\partial^2 B}{\partial T^2}\Big]_P\right\} \quad (6)$$

In order to estimate the aforementioned point defect parameters using the cBΩ model (Eqs. (2)-(6)), the constant c^{act} should be determined. The latter may be derived from Eq. (2) where at T=0K the activation Gibbs energy becomes equal to the activation enthalpy and thus, $c^{act} = h_o^{act}/B_o\Omega_o$. Although the activation enthalpy at zero temperature may be calculated from first principles, the parameter c^{act} may also be determined from the available experimental diffusion data.[32] When only a single diffusion measurement D_1 at a given temperature T_1 (or pressure) is available, the parameter c^{act} can be calculated from Eq. (1), if the pre-exponential factor fga_0v is roughly known or can be calculated. Then, the diffusivity D can be calculated at any temperature (or pressure), provided that the elastic and expansion data are known for this temperature (or pressure). Alternatively, in the case where diffusion coefficients are experimentally known over a broad temperature (or pressure) range,[40,41] the mean value of c^{act} may be derived by substituting Eq. (3) in Eq. (1) and taking the natural logarithm of both sides

$$lnD = ln(fg\mathrm{a}_0^2v) - c^{act}\frac{B\Omega}{k_BT} \quad (7)$$

According to Eq. (7), a linear dependence of ln$D$ versus the quantity $B\Omega/k_BT$ indicates the validity of the cBΩ model regarding a single diffusion mechanism, while c^{act} arises directly from the slope of the line.

The previous considerations for the determination of the parameter c^{act} are subjected to the experimental uncertainties of the diffusion experimental data which in many cases might be considerable. However, by dividing Eq. (4) with Eq. (5) it arises that the ratio s^{act}/h^{act} depends only on the bulk properties of the crystal, according to the following relation[42]

$$\frac{s^{act}}{h^{act}} = -\frac{\frac{\partial B}{\partial T}\Big]_P + \beta B}{B - T\beta B - T\frac{\partial B}{\partial T}\Big]_P} \quad (8)$$

The quantities h^{act} and s^{act} can be usually determined experimentally from the slope and the intercept (i.e. the pre-exponential factor) of the corresponding Arrhenius plot of diffusion coefficients (see Eq. 1) and thus Eq. (8) may also serve to validate the cBΩ model.[42]

The aforementioned procedure may be used to calculate the temperature and/or pressure dependence of the thermodynamic properties of point defects, provided that the corresponding quantities (β, B, Ω) are known as a function of temperature and/or pressure. The pressure dependence of the diffusion coefficients may give us information about the diffusion mechanism in the host material, through the estimation of the activation volume. Indeed, if we differentiate Eq. (1) with respect to pressure, the following expression is derived for the activation volume[32]

$$v^{act}(P,T) = -k_BT\left(\frac{\partial lnD}{\partial P}\right)_T + k_BT\left(\frac{\partial ln(fg\mathrm{a}_0^2v)}{\partial P}\right)_T \quad (9)$$

In Eq. (9), the derivative of the second term in the right is equal to $\kappa(\gamma - 2/3)$ where γ is the Grüneisen constant. Recalling that the compressibility of the activation volume is defined as $\kappa^{act} = (-1/v^{act})(\partial v^{act}/\partial P)_T$, the activation volume which is temperature and pressure dependent, is then expressed as

$$v^{act}(P,T) = v^{act}(0,T)exp\left(-\int_0^P \kappa^{act}dP\right) \quad (10)$$

If we assume to a first approximation that κ^{act} is independent of pressure and that $\kappa\gamma \approx \kappa_o\gamma_o$ (the zero subscript refers to P=0), we may express the exponential of Eq. (10) in a series expansion of pressure, and by subsequent substitution in Eq. (9), we finally get

$$lnD(P,T) = lnD(0,T) - \left\{\frac{v^{act}(0,T)}{k_B T} - \kappa_o\left(\gamma_o - \frac{2}{3}\right)\right\}P +$$

$$+ \left\{\frac{\kappa^{act} v^{act}(0,T)}{2k_B T}\right\}P^2 - \left\{\frac{(\kappa^{act})^2 v^{act}(0,T)}{6k_B T}\right\}P^3 \quad (11)$$

Equation (11) describes the pressure dependence of the diffusion coefficients at a certain temperature, considering that the parameters κ_o, γ_o, κ^{act} and $v^{act}(0,T)$ are known at this temperature.

2.2 Determination of the bulk properties

Experimental data of the bulk modulus B and the mean atomic volume Ω are not always available as a function of temperature (and/or pressure), especially at high temperatures where the diffusion experiments are usually carried out. An extrapolation of the available data at high temperatures (or pressures) by assuming linear relations of B and Ω are not always sufficient, and may lead to misinterpretation or incorrect validation of the model.

In the case of GaAs, the temperature dependence of the mean atomic volume at ambient pressure ($\Omega(P = 0, T) = \Omega_o(T)$) may be calculated from the following relation

$$\Omega_o(T) = \Omega_o(T_R) exp\left(\int_{T_R}^{T} \beta(T)dT\right) \quad (12)$$

where T_R refers to room temperature, $\Omega_o(T_R) = 22.59 \times 10^{-29}$ m^3 is the mean volume per atom at ambient pressure[43] and β is the coefficient of volume thermal expansion. According to reported experimental results[44] of the linear thermal expansion coefficient a_l (see Fig. 1(a)), a linear relation holds for temperatures $T > T_\vartheta$ (T_ϑ = 360 K, is the Debye temperature of GaAs), with intercept $a_o = 5.67 \times 10^{-6}$ $^o C^{-1}$ and slope, $a_1 = 0.0015 \times 10^{-6}$ $^o C^{-2}$. For the isotropic GaAs, $\beta = 3\alpha_l$, and thus Eq. (12) leads to the following result

$$\Omega_o(T) = \Omega_o(T_o) exp\left\{3a_o(T - T_o) + \frac{3}{2}a_1(T^2 - T_o^2)\right\} \quad (13)$$

The calculated temperature dependence of the mean atomic volume, according to Eq. (13), is depicted in Fig. 1(b). Although a linear relation of $\Omega_o(T)$ is usually used in GaAs,[44] a small deviation from linearity is observed, especially at the temperature range of the reported diffusion data in GaAs (T > 500 K).

The Rose-Vinet universal equation of state (EoS)[45] is used to derive the temperature dependences of the bulk modulus $B(T)$ and its pressure derivative $(\partial B/\partial P)_T$, according to the following expressions:

$$B(T,X) =$$

$$= \frac{B_o(T_r)}{X^2}\{2 + [\eta_o(T_r) - 1]X - \eta_o(T_r)X^2\}e^{[\eta_o(T_r)(1-X)]} \quad (14)$$
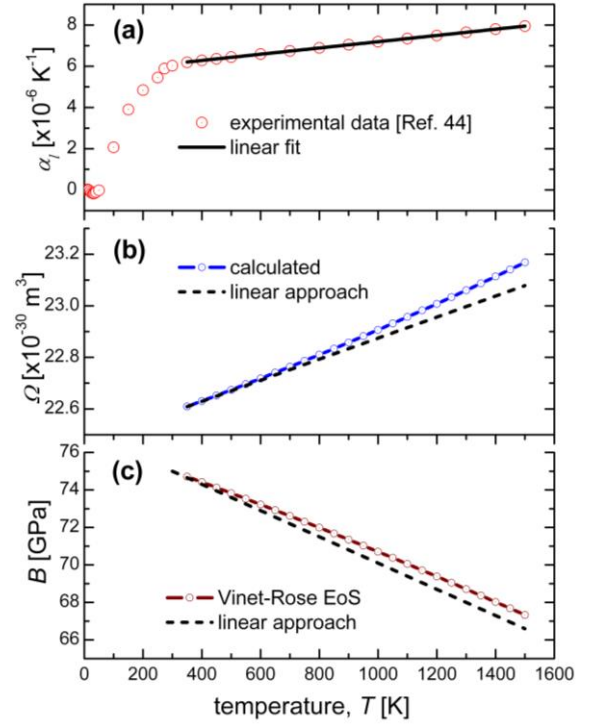
and

Fig. 1 (a) Experimental data of the linear thermal expansion coefficient (TEC) of GaAs and the linear fitting at T>350K. (b) The calculated mean atomic volume in the temperature range 350K – 1500K, according to the linear fitting of the TEC. (c) The calculated temperature dependence of the isothermal bulk modulus, according to the Rose-Vinet EoS. Linear approaches of $\Omega(T)$ and $B(T)$ are also included for comparison.

$$\left[\frac{\partial B}{\partial P}\right](T,X) =$$

$$= \frac{4 + [3\eta_o(T_r) - 1]X + \eta_o(T_r)[\eta_o(T_r) - 1]X^2 - \eta_o^2(T_r)X^3}{3\{2 + [\eta_o(T_r) - 1)X - \eta_o(T_r)X^2\}} \quad (15)$$

where B_o refers to zero (ambient) pressure, T_r is a reference temperature and the parameters X, $\eta_o(T)$ are defined as follows

$$X = \left[\frac{\Omega_o(T)}{\Omega_o(T_r)}\right]^{1/3} \quad (16)$$

and

$$\eta_o(T) = \frac{3}{2}\left[\left[\frac{\partial B}{\partial P}\right]_{P=0}(T) - 1\right] \quad (17)$$

In the case of GaAs, the bulk modulus B_o and its pressure derivative at room temperature are $B_o(300K) = (75.0 \pm 0.5)GPa$ and $(\partial B/\partial P)_{P=0}(300K) = 4.5 \pm 0.5$, respectively.[44] The temperature dependence of the calculated $B(T)$ is shown in Fig. 1(c). The above EoS should give more accurate results but it is not deviate considerably from the simplified linear approach of bulk modulus that is usually considered in the case of the GaAs semiconductor,[44] as it is seen in Fig. 1(c).

3. Results and discussion

In the following, we investigate the self-diffusion of Ga and the diffusion of H, n-type (Si) and p-type (Be, Fe, Cr, Zn) dopants in GaAs, in the frame of the cBΩ thermodynamic model. The reported experimental diffusion coefficients of the aforementioned elements in GaAs as a function of the quantity $B\Omega/k_BT$ are shown in Fig. 2.[13,16,20-22,24,25] The linear correlations between $\ln D$ and $B\Omega/k_BT$ (correlation factors, R>0.99) suggest the validity of the cBΩ model and thus enable the estimation of the parameter c^{act} in each case, according to Eq. (7). The calculated values of c^{act} for each element are listed in Table 1.

The various point defect parameters (activation volume, activation entropy, activation enthalpy, activation Gibbs free energy and activation isobaric specific heat) were calculated for all the aforementioned diffusants, according to Eq. (2) – (6) and the results are shown in Fig. 3, as a function of temperature. The ranges of these values along with their calculated uncertainties are summarized in Table 1. The corresponding reported experimental values of activation enthalpy, h_{exp}^{act} and activation entropy, s_{exp}^{act} are also included in Table 1 for comparison. The values of the experimental activation entropy were indirectly extracted from the experimentally determined pre-exponential factor D_o (except for the reported value of Ga), through the relation

$$s_{exp}^{act} = k_B ln\left(\frac{D_o}{gf\alpha^2\nu}\right) \quad (18)$$

where in the case of GaAs we have used the reported values: $g = 1$, $f = 1/2$, $\alpha = 5.653$ Å and $\nu = 7.17 \times 10^{12}$ Hz.[16,22,43]

As it is depicted in Fig. 3, the estimated values of activation Gibbs free energy slightly decrease with temperature while the corresponding term Ts^{act} increases, resulting to constant values of activation enthalpy ($h^{act} = g^{act} + Ts^{act}$). These values of activation enthalpy, calculated in the frame of the cBΩ model, are in very good agreement with the reported experimental activation energies, if the uncertainties are taking into consideration (see Table 1).[13,16,20-22,24,25] Our estimations of activation entropy deviate considerably from the corresponding reported values of most elements, except for the case of H, where accurate results are obtained. Notably, as indicated in
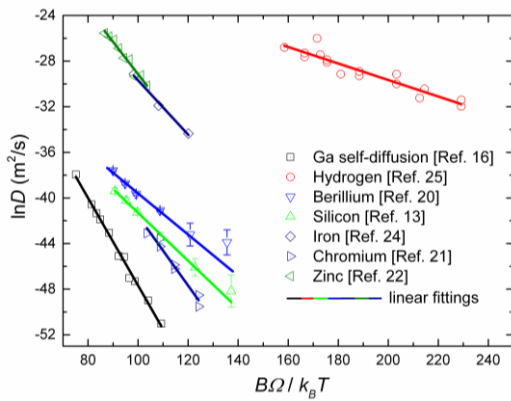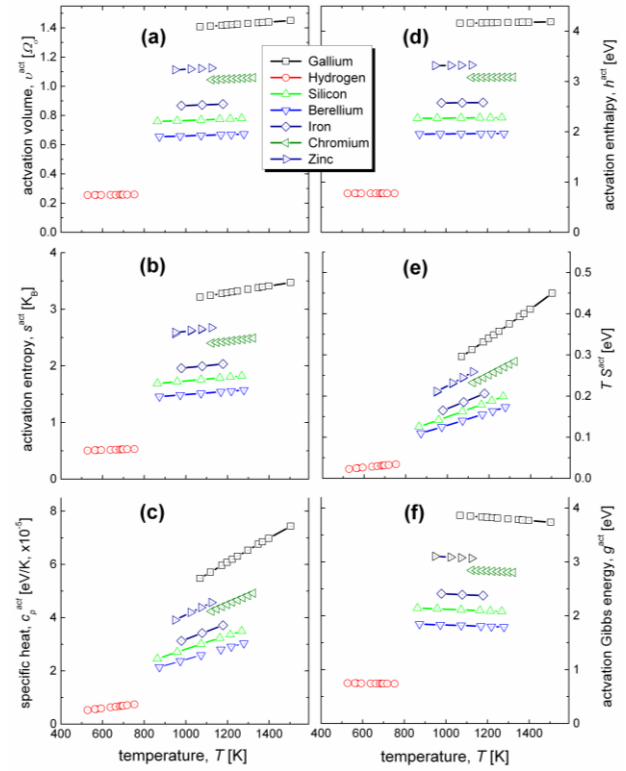
Fig. 3 Calculated point defect thermodynamic parameters of self- and dopant diffusion in GaAs as a function of temperature, according to the cBΩ model (Eqs. (2)-6). (a) Activation volume, υ^{act} (b) activation entropy, s^{act} (c) activation specific heat, c_P^{act} (d) activation enthalpy, h^{act} (e) the term Ts^{act}, ($h^{act} = g^{act} + Ts^{act}$) and (e) the activation Gibbs free energy, g^{act}.

Table 1, the reported values of activation entropy that were derived indirectly from Eq. (18), are either large (Fe, Cr) or have negative signs (Si, Be). However, the negative values of entropy suggest a process of concentration due to the action of additional forces opposing to diffusion process while, the large values (> 10 k_B) are not compatible with reported moderate values of activation enthalpies.[22] At this point, we have to note that the values of activation entropy are subjected to large uncertainties due to the experimental errors of the determination of activation enthalpy in diffusion measurements. Furthermore, this discrepancy is also due to the approach of the attempt frequency with the Debye frequency as well as the approximated values of the parameters f and g that were used in Eq. (18). Alternatively, we propose that reliable values of activation entropy may be derived according to Eq. (8), where the reported experimental values of activation enthalpy h_{exp}^{act} should be used. In this case, the 2nd term of Eq. (8) which depends only in the bulk properties of GaAs, increases smoothly from 5.79 to 7.15×10^{-5} K⁻¹ in the temperature range 350 K – 1500 K.

Finally, our calculated activation volumes range from 0.26 Ω_o in the case of the smallest diffusant atom (hydrogen) to 1.45 Ω_o for Ga self-diffusion, but practically all values are not affected by temperature, over the entire temperature range of the reported diffusion experiments.

Fig. 2 Experimental diffusion coefficients of self- and dopant-diffusion in GaAs as a function of the quantity $B\Omega/k_BT$. The linear fittings correspond to the implementation of the cBΩ model, according to Eq. (7).

Table 1. Calculated values with their uncertainties of the parameter c^{act}, activation enthalpy (h_{calc}^{act}), activation entropy (s_{calc}^{act}), activation Gibbs free energy (g^{act}), activation volume (v^{act}) and activation isobaric specific heat c_p^{act}, according to the cBΩ model for Ga self-diffusion and various dopants diffused in GaAs. The corresponding experimental values of activation enthalpy and activation entropy are also given for comparison. The experimental values of activation entropy (if not reported) were derived from the experimentally determined pre-exponential factor through $D_o = fga^2v_o exp(s/k_B)$.

Element [Ref.]	Temperature (K)	h_{exp}^{act} (eV)	s_{exp}^{act} (k_B units)	c^{act}	h_{calc}^{act} (eV)	s_{calc}^{act} (k_B units)	g^{act} (eV)	v^{act} (x10⁻²⁹ m³)	c_p^{act} (eV/K)
Ga[16]	1068 – 1503	4.24 ± 0.06	6.7 – 8.0	0.384 ± 0.010	(4.16 – 4.19) ± 0.17	(3.21 – 3.47) ± 0.14	(3.86 – 3.74) ± 0.15	(3.18 – 3.28) ± 0.13	(5.48 – 7.44) ± 0.26
H[25]	528 – 753	0.83	0.56	0.022 ± 0.002	0.77 ± 0.08	(0.50 – 0.53) ± 0.05	(0.74 – 0.75) ± 0.07	0.58 ± 0.06	(0.53 – 0.74) ± 0.06
Si[13]	863 – 1268	2.45	-3.4	0.210 ± 0.009	(2.27 – 2.28) ± 0.25	(1.69 – 1.82) ± 0.19	(2.08 – 2.14) ± 0.23	(1.72 – 1.76) ± 0.19	(2.46 – 3.50) ± 0.27
Be[20]	873 – 1278	1.95	-6.4	0.181 ± 0.012	(1.96 – 1.97) ± 0.23	(1.46 – 1.57) ± 0.18	(1.79 – 1.85) ± 0.22	(1.48 – 1.52) ± 0.18	(2.14 – 3.04) ± 0.31
Fe[24]	978 – 1178	2.7	11.4	0.238 ± 0.021	(2.57 – 2.58) ± 0.26	(1.96 – 2.03) ± 0.20	(2.37 – 2.41) ± 0.24	(1.96 – 1.99) ± 0.20	(3.13 – 3.71) ± 0.34
Cr[21]	1063 – 1263	3.2 ± 0.4	17.1	0.284 ± 0.018	(3.08 – 3.09) ± 0.22	(2.40 – 2.49) ± 0.17	(2.80 – 2.85) ± 0.20	(2.36 – 2.39) ± 0.17	(4.24 – 4.92) ± 0.32
Zn[22]	948 - 1123	3.21	3.97	0.306 ± 0.026	(3.31 – 3.33) ± 0.30	(2.57 – 2.68) ± 0.24	(3.07 – 3.11) ± 0.28	(2.51 – 2.54) ± 0.23	(3.91 – 4.57) ± 0.29

measurements in GaAs under pressure are not available in the literature. The pressure dependence of the diffusion coefficients for Ga self-diffusion was estimated according to Eq. (11), for pressures up to 10 GPa above which GaAs transforms from the zinc blende to the orthorhombic structure.[8,46] The values of the self-diffusion coefficients $D(0,T)$ at zero pressure that were used in Eq. (11), correspond to the reported experimental values of Fig. (3).[16] Based on Eq. (3), the compressibility of the activation volume may be deduced from the following relation

$$\kappa^{act} = \kappa_o - \frac{(\partial^2 B/\partial P^2)_T}{(\partial B/\partial P)_T - 1} \quad (19)$$

where $\kappa_o = 1/B_o$ is the bulk modulus at zero pressure which is temperature dependent (see Fig. 1c). Considering that $-B(\partial^2 B/\partial P^2)_T \approx (\partial B/\partial P)_T$,[47] the activation compressibility is finally simplified to

$$\kappa^{act} \approx \kappa_o \left(1 + \frac{(\partial B/\partial P)_T}{(\partial B/\partial P)_T - 1}\right) \quad (20)$$

We have to note that, in the quasi-harmonic approximation, the quantity $(\partial B/\partial P)_T$ has a constant value and does not depend on pressure or temperature, while it varies only slightly upon compression in a real (anharmonic) solid.[32] Thus, our previous assumption for pressure independent activation compressibility is a reasonable approximation in order to derive the analytical expression (see Eq. 11) for the calculation of diffusion coefficients as a function of pressure. The Grüneisen constant which is also temperature dependent, was estimated using the Dugdale-MacDonald equation,[48] $\gamma = [(\partial B/\partial P)_T - 1]/2$, which yields values from 1.80 to 1.84 in the temperature range (1068 K − 1503 K) of the reported Ga self-diffusion coefficients.

By substituting all the above parameters in Eq. (11), the pressure dependence of Ga self-diffusion coefficients in GaAs

depicted in Fig. 4a. Our estimations of activation volume (see Eq. 10) for Ga self-diffusion as a function of pressure are also shown in Fig. 4b. Our calculations are restricted to 1248 K, in order to avoid the change of GaAs to its liquid phase, in the high range of pressures.[46] We observe that, in all cases, the influence of pressure on the activation volume v^{act} is more pronounced than that of temperature, and all the values converge to around 1.0 Ω_o at high pressures. The pressure dependence of activation volumes of n- and p-type dopants
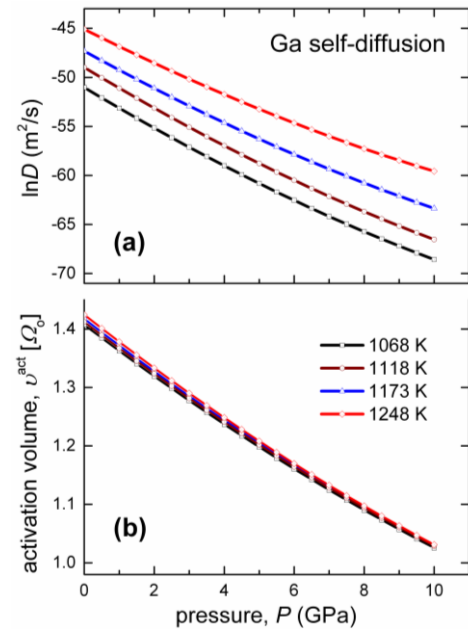

Fig. 4 Pressure dependence of Ga self-diffusion coefficients in GaAs, according to the cBΩ model in the temperature range, 1068K − 1248K. The corresponding variation of activation volumes is shown in (b). The pressure range is limited to 10 GPa, above which GaAs is transformed into the orthorhombic structure.

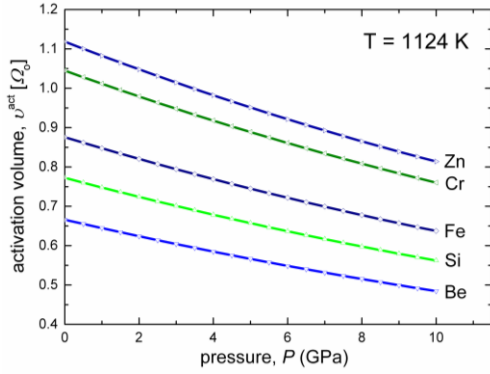(Si, Be, Fe, Cr and Zn) diffused in GaAs at constant temperature

Fig. 5 Pressure dependence of activation volumes of n-type (Si) and p-type (Be, Fe, Cr, Zn) dopants diffused in GaAs at constant temperature (1124 K).

for the other elements diffused in GaAs, in order to explain (or
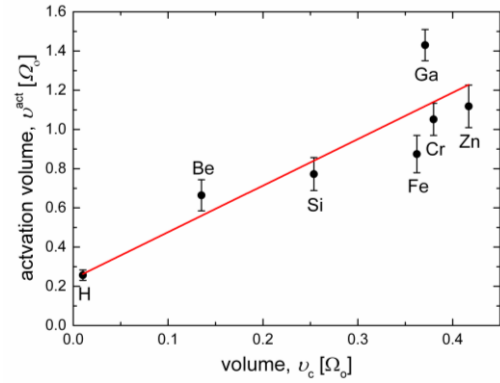

Fig. 6 Activation volume of each diffusing element with respect to the atomic volume calculated with the covalent radius of the elements. The (red) line represents the linear fit of the data.

(T=1124 K) is shown in Fig. 5.

Generally, the value and the sign of activation volume can provide information about the kind of the diffusion mechanism i.e., vacancies (V) or self-interstitials (I), through the relation $v_{V,I}^{act} = \pm \Omega_o + v_{V,I}^{r} + v_{V,I}^{m}$. The positive sign of the mean atomic volume Ω_o refers to vacancy and the minus to self-interstitial formation, while $v_{V,I}^{r}$ denotes the relaxation volume around a newly-created point defect (V or I) and $v_{V,I}^{m}$ is the corresponding migration volume. In the case of dopants diffused in interstitial sites, the activation volume equals to the migration volume of the interstitial diffusant, since no defect formation is required.[49] In a first approach, the positive estimated value of activation volume in Ga self-diffusion could be an evidence for vacancy-mediated diffusion with an outward (positive) or inward (negative) relaxation around the vacancies. Since the relaxation and the migration volumes are usually assumed to be smaller than Ω_o in magnitude, the sign of Ω_o actually determines the dominant diffusion mechanism.[50] Thus, in the case of Ga self-diffusion, an outward strong relaxation and/or a positive migration volume could result to an activation volume greater than Ω_o and comparable with our estimation ($\approx 1.4\ \Omega_o$). This value is consistent with vacancy self-diffusion by second-nearest-neighbor hopping, proposed by Wager[22] who performed atomistic thermodynamic calculations in order to study the energetics of Ga self-diffusion in GaAs.

In order to correlate the size of each diffusant atom to the corresponding activation volume and possible diffusion mechanisms, we have plotted in Fig. 6 the activation volume (at zero pressure) as a function of the atomic volume of the diffused elements using their covalent radii. Typically, the activation volume increases with the increase of the atomic volume of the diffusants, with noticeable deviation from linearity in the cases of Ga and Fe. Small atoms such as H preferentially reside in interstitials sites resulting in small value of activation volume, consistently with the present calculation ($v_H^{act} \approx 0.25\ \Omega_o$). In the case of Si atom which is much larger than H, its value of activation volume ($v_{Si}^{act} \approx 0.77\ \Omega_o$) indicates either an interstitial mechanism of diffusion where no defect formation is needed ($v_I^{f} = 0$) or a vacancy mechanism with a strong inward relaxation. Similar speculations could be made

predict) possible diffusion mechanisms. For example, in the cases of Zn and Be diffusion in GaAs, activation volume is higher in the case of the larger Zn atom ($v_{Zn}^{act} > v_{Be}^{act}$) implying that diffusion in interstitial sites is more preferable than in vacancies where the contribution to the formation volume should be significant. This is consistent with the interstitial-substitutional exchange mechanism (kick-out mechanism) which has been proposed by Yu et al. for Zn and Be diffusion in GaAs.[26]

4. Conclusions

The present work investigates the self- and dopants-diffusion in GaAs, in terms of the cBΩ thermodynamic model which connects the point defect parameters with the bulk elastic and expansion properties of the host material. Initiating from available experimental data of thermal expansion and the usage of the Rose-Vinet equation of state for GaAs, useful point defect parameters such as activation enthalpy, activation entropy, activation volume and activation isobaric specific heat were calculated as a function of temperature. Our results are in excellent agreement with the reported experimental activation enthalpies. Thus, we suggest that the activation entropies could be generally calculated from the experimentally determined activation enthalpies by using only the bulk properties of the material under investigation, in order to overcome the experimental uncertainties. The pressure dependence of Ga self-diffusion coefficients and activation volumes of Ga, H and other n- and p-type dopants were also estimated for the first time at elevated pressures and are discussed in the context of possible diffusion mechanisms reported in the literature. The potential of the model for the investigation of diffusion processes on a theoretical basis in previously studied unary semiconductors (Si and Ge) and binary semiconducting systems as in the present case may be also extended to other important III-IV semiconductors with limited diffusion experimental data and may suggest a possible universal application in different kind of solid compounds.

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