

Self diffusion in crystalline silicon and equation of state. Recent results

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Abstract— During the last few years detailed atomistic calculations have been reported within the local density approximation and the generalized gradient approximation in density functional theory to classify microscopic mechanisms and obtain the corresponding diffusion constant for self-diffusion in crystalline Si. Here, we discuss the interrelation of these results with those independently obtained from a thermodynamical model after considering equation of state that has just been suggested for silicon.

Index Terms— Activation energy, Defect volume, Diffusion, Equation of state, Elastic properties, Point defects, Thermodynamic parameters.

1 INTRODUCTION

Diffusion of a Si atom in Si crystal (self diffusion) is extremely important in technology and fundamental in science and it has been a subject of intensive research for more than half a century [1], [2]. The most direct experimental technique by means of which we determine the self-diffusion constant D is the detection of Si isotopes during diffusion processes in isotope-enriched samples [3], [4], [5]. In the vast majority of measurements, self-diffusion is studied in thermal equilibrium [5], [6], [7] and it is then dominated by the contribution of vacancies and interstitials (because in this case the concentration of the defect clusters – compared to that of vacancies and interstitials- is very small [8]). For example, using silicon isotope heterostructures the self-diffusion coefficient in thermal equilibrium was accurately determined over 7 orders of magnitude by Bracht *et al.*[5] They found that the temperature dependence of D can be well described by a single Arrhenius term with an activation energy of $4.75eV$.

Although it is experimentally possible to detect Si vacancies using EPR or positron-lifetime experiments, [9], [10] the situation is worse for Si self-interstitials which cannot be detected directly. The alternative is then to rely on numerical simulations to shed light on the efficient defects' mechanisms. Hence, a multitude of theoretical studies have been focused during the last decade on the investigation of

self-diffusion in bulk silicon which made use of either empirical potentials [8], [11], [12] or ab initio methods [13], [14], [15], [16], [17], [18], [19]. In particular, the last few years a number of studies appeared [11], [20], [21], [22] which were mainly addressed to the numerical estimation of the point defect parameters that are possibly involved in the self-diffusion processes in crystalline Si.

Among the latter studies, the most recent one by Kotzumi *et al.*[22] reported atomistic calculations within the local density approximation (LDA) [23], [24], [25], [26], [27] and the generalized gradient approximation (GGA) [26], [27] in density functional theory in order to obtain the corresponding diffusion constant for self-diffusion in crystalline Si. The formation free energies of intrinsic defects, which mediate the self-diffusion, were calculated and then diffusivity in each mechanism was computed from the mean-square displacements. They found that the interstitial mechanism constitutes the dominant contribution to the self-diffusion. In addition Kotzumi *et al.*[22] showed that GGA results in substantially improved values of the point defect parameters which provide diffusion constants in quantitative agreement with the experimental values over the whole temperature range investigated.

In view of the latter success of GGA results to describe the self-diffusion data, the following important question raises: A thermodynamical model, originally suggested in Refs [28], [29], [30], [31], [32], [33], and reviewed in Ref. [34] and more recently in Ref. [35], has been shown to reproduce the self-diffusion coefficients and the relevant point defect parameters in various categories of solids. For example, see the recent studies in diamond [36] and $\beta-PbF_2$ [37]. Furthermore, this model has been found to describe successfully [34] the thermodynamical parameters that de-

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scribe the (re)orientation process of electric dipoles (formed due to point defects) the relaxation time of which varies upon increasing the pressure, leading to emission of transient electric signals [38], [39], [40], [41] before the fracture. Therefore, it is of major interest to investigate whether the aforementioned GGA results, obtained in Ref. [22] in crystalline Si, are compatible with those predicted by this thermodynamical model, which interconnects, as it will be explained below, the thermodynamic parameters for the formation and/or migration of defects with bulk expansivity and elastic data in solids.

2 EQUATIONS OF STATE FOR SILICON AND THEIR CONNECTION WITH POINT DEFECTS PARAMETERS

In a very recent study, Pandya *et al* [42] made a comparative study of different equations of state for silicon in the pressure range 0-11 GPa. They compared the results of different equations of state (EOS) with available experimental data. In particular, Pandya *et al.* found that the EOS suggested in Ref. [43] for example does not give satisfactory agreement with the available experimental data, while the one by Kwon and Kim [44] does so. Thus, based on the latter EOS, Pandya *et al.* [42] published improved formulae for the temperature dependence of the thermal volume expansion coefficient β as well as for the variation of the isothermal bulk modulus B versus the temperature T (see their Equations (17) and (24), respectively). We shall use below those improved values of β and B to check the reliability of the thermodynamical model to which we now turn.

According to this model, the Gibbs energy g^f for the defect formation (f) is given by [29], [30], [31], [32], [33], [34] $g^f = cB\Omega$, where c is practically independent of temperature and pressure and Ω is the mean volume per atom. This equation finally leads [34] to the defect formation entropy s^f and the defect formation enthalpy h^f :

$$s^f = -c\Omega \left[\beta B + \left. \frac{dB}{dT} \right|_P \right] \quad (1)$$

$$\text{and } h^f = c\Omega \left[B - T\beta B - T \left. \frac{dB}{dT} \right|_P \right] \quad (2)$$

where of course those relations hold for constant pressure P .

3 COMPARISON OF THE GGA RESULTS WITH THOSE OBTAINED FROM THE RECENT EQUATION OF STATE

The aforementioned relations (1) and (2) given by the thermodynamical model suggest that the ratio s^f/h^f is given by:

$$\frac{s^f}{h^f} = - \frac{\beta B + (dB/dT)_P}{B - T\beta B - T(DB/dT)_P} \quad (3)$$

By inserting in Eq.(3) the values of β , B and $(dB/dT)_P$ reported by Pandya *et al.* [42] in their Figures 2 and 3 for the temperature range $T=1400$ K to $T=1500$ K, Eq.(3) leads to:

$$s^f/h^f \simeq 2 \times 10^{-4} K^{-1} \quad (4)$$

We now turn to the GGA results reported by Kotzumi *et al.* [22]. In their Table I, they report the formation enthalpy values: $h^f = 3.44eV$ and $h^f = 3.47eV$ for the split-110 (dumbbell) and hexagonal configuration of the self-interstitial mechanism, respectively. Further, in their Table II, the following formation entropy values: $s^f = 7.04k_B$ and $s^f = 6.50k_B$ (where k_B stands for Boltzmann's constant) are reported for those two configurations, respectively. These values of Kotzumi *et al.* [22] lead to the following ratios:

$$s^f/h^f \simeq 1.8 \times 10^{-4} K^{-1} \quad (5)$$

for the split-110 configuration and

$$s^f/h^f \simeq 1.6 \times 10^{-4} K^{-1} \quad (6)$$

for the hexagonal configuration.

Comparing the value of Eq. (4) found by the thermodynamical model with the GGA results of Eqs (5) and (6), we see a satisfactory agreement, which is closer for the split-110 configuration.

4 CONCLUSION

In conclusion, here we considered the formation enthalpy h^f and the formation entropy s^f deduced from the very recent [22] atomistic calculations by means of GGA, which reproduce successfully the experimental values of the self-diffusion coefficients. We find that the ratio s^f/h^f of these values is comparable to the one estimated from the thermodynamical model when taking into account the thermal expansion coefficient and the isothermal bulk modulus obtained from the most recent comparative analysis of the equations of state of Si as just published by Pandya *et al.* [42].

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