

# A Physics-Based Empirical Model for Ge Self Diffusion in Silicon Germanium Alloys

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## ABSTRACT

We propose a physics-based model for the Ge self diffusivity in SiGe alloys and empirically fit the model to previously reported experimental results [1-3]. The dominant mechanism for Ge self diffusion in SiGe is the vacancy exchange mechanism since the published data on Ge diffusivity are in most cases for experiments done at temperatures lower than 1050 °C. We added two new terms to modify the regular diffusivity equation to relate the diffusivity to the change in Ge concentration. The first term is a consequence of the change in the point defects disorder entropy [4] as a result of adding more Ge atoms to the SiGe system. The second term is to account for the change in formation and migration enthalpies of the point defects due to the change in Ge content in the alloy.

**Keywords:** SiGe, self-diffusion, modeling.

## 1 INTRODUCTION

SiGe alloys are gaining more attention in the industry due to their increased carrier mobility over Si and their compatibility with the cheap silicon process. However, there are some crucial differences between the SiGe and the Si process. One of those is the interdiffusion of Si and Ge in heterostructures and the fact that the self-diffusivity of Si and Ge will vary with the Ge content. In this paper we focus on the Ge self-diffusivity. Currently, there is no general equation to describe the self diffusivity of Ge in SiGe. Such an expression is required for the modeling of several process phenomena in SiGe, including SiGe interdiffusion [5] and SiGe oxidation [6].

The model presented here is able to predict the Ge self diffusivity in SiGe alloys for all various Ge concentrations and for all temperatures. The regular Arrhenius expression for self diffusivity is modified by adding a term to reflect the change in point defects disorder entropy as a result of the increase of Ge concentration in the SiGe alloy. The activation energy is also a function of Ge fraction to account for the change in the formation enthalpy of vacancies and migration enthalpy of the Ge by a vacancy mechanism.

## 2 THE MODEL

It has been established in the literature [4, 7] that the two main mechanisms for self diffusion in silicon and in germanium and consequently in silicon germanium are the interstitial-based and vacancy-based mechanisms. Therefore, the self diffusivity of Si or Ge in SiGe can be formulated in the same manner the self diffusivity of Si [4] is formulated:

$$\begin{aligned} D_{Xself} &= D_{XI} + D_{XV} \\ &= f_{XI} d_{XI} \frac{C_{XI}^*}{C_S} + f_{XV} d_{XV} \frac{C_{XV}^*}{C_S} \end{aligned} \quad (1)$$

where X stands for the diffusing species either Si or Ge,  $D_{XI}$  and  $D_{XV}$  are the diffusivities of X due to interstitial and vacancy based mechanisms respectively,  $f_{XI}$  and  $f_{XV}$  are correlation factors of diffusion for each mechanism,  $C_S$  is the number of lattice sites in the crystal,  $C_{XI}^*$  and  $C_{XV}^*$  are the equilibrium concentrations of interstitials and vacancies in the SiGe alloy respectively,  $d_{XI}$  and  $d_{XV}$  are the diffusivities of X species' interstitials and vacancies in the SiGe alloy. The equilibrium concentration of a point defect species can be expressed as [4]:

$$\frac{C_Y}{C_S} = \theta_Y \exp\left(\frac{S_Y^f}{k}\right) \exp\left(\frac{-H_Y^f}{kT}\right) \quad (2)$$

where  $H_Y^f$  is the enthalpy of formation of the point defect Y,  $S_Y^f$  is the disorder entropy not associated with configuration and is usually attributed to lattice vibrations, and  $\theta_Y$  is the number of degrees of internal freedom of the defect on a lattice site. The diffusivities of the point defects in the SiGe alloy can be expressed in terms of an Arrhenius expression.

Self-diffusion in pure Ge is mediated only by vacancies [8]. On the other hand, Ge diffuses in Si by a combination of vacancy and interstitial diffusion mechanisms [9]. However, it has been shown that Ge diffusion is dominated by a vacancy mechanism at low temperatures (below 1050°C) [9]. At high temperatures (above 1050°C), Ge diffusion in Si is dominated by interstitial assisted mechanism. This causes a break in the Arrhenius behavior of Ge diffusion around the 1050°C temperature. It has to be noted that 2 [1, 2] of the 3 studies used for empirical fitting in our work were done at

temperature lower than 1050°C. The only study [3] which swapped a wider temperature range (894-1263°C) did not observe a break in the Arrhenius behavior of the Ge diffusion in SiGe alloys. This can be partially attributed to the fact that Ge diffuses by vacancy mediated mechanisms in SiGe with  $x \geq 0.5$  [10]. It can also be attributed to the limited number of data points reported at high temperatures. The end result is that for the purpose of this study, Ge diffusion for temperatures lower than 1050°C is only considered. Consequently, the diffusion process is proposed to be dominated by vacancy mechanism for all Ge concentrations below 1050°C.

Laitinen et al. [1] claim that the dominant mechanism for the diffusion of Ge in SiGe with Ge content under 25% is the interstitialcy mechanism while the dominant mechanism above this concentration is the vacancy mechanism. The fact that Ge diffusion is dominated by vacancies in both Si and Ge at low temperatures leaves very little room for the validity of the argument used by Laitinen et al.

The above arguments will lead us to reduce the equation (1) to:

$$D_{xself} = D_{xv} = f_{xv} d_{xv} \frac{C_{xv}^*}{C_s} \quad (3)$$

Equation (3) is used instead of equation (1) in this paper to express self diffusivity in SiGe. This is mainly due to the experimental conditions of the reports in the literature. However, given the role of interstitials in the self diffusivity of Si and in the Ge diffusivity in Si, equation (3) is not valid for high temperatures (>1050°C for Ge and >900°C in Si-rich SiGe alloys). A more general expression based on equation (1) is required to explain the complete behavior of the self diffusivity of Ge and Si in SiGe alloys at a wider temperature range.

Using equations (2) and (3), a general expression for the self diffusion of Ge in SiGe can be obtained:

$$D_{Ge}^{SD} = D_{Ge0}' \exp\left(\frac{S_V^f(x)}{k}\right) \exp\left(-\frac{E_{Ge}'(x)}{kT}\right) \quad (4)$$

where  $D_{Ge0}'$  is the pre-exponential factor encompassing all the terms that are independent of temperature and Ge concentration in equations (2) and (3),  $x$  is the Ge fraction in the SiGe alloy,  $S_V^f(x)$  is the disorder entropy of formation of vacancies which is a function of the Ge concentration and  $E_{Ge}'(x)$  is the activation energy for the Ge self-diffusivity which is given by the sum of the enthalpy of formation and enthalpy of migration of the vacancies.

The vacancies in Si and in Ge can be viewed as two miscible gases which form a homogeneous mixture when mixed. The entropy of the mixture will be a linear function in the entropies of both gases with the constants proportional to their mole fraction [11]:

$$S_V^f(x) = S_{GeV}^f x + S_{SiV}^f (1-x) \quad (5)$$

where  $S_{GeV}^f$  and  $S_{SiV}^f$  are the disorder entropies of formation of vacancies in Ge and Si respectively. Similarly, the activation energy of mixing can be obtained from the thermodynamic theory of mixing two homogenous gases [11]:

$$E_{Ge}'(x) = E_{Ge} x + E_{Si} (1-x) \quad (6)$$

where  $E_{Ge}$  and  $E_{Si}$  are the activation energies for self diffusion in Ge and for Ge in Si respectively. Using equations (5) and (6), equation (4) can be rewritten as follows:

$$D_{Ge}^{SD} = D_{Ge0}' \exp(\Delta S_{Ge} x) \exp\left(-\frac{E_{Ge} + \Delta E_{Ge} x}{kT}\right) \quad (7)$$

where  $D_{Ge0}' = D_{Ge0} \exp(S_{SiV}^f)$ ,  $\Delta S_{Ge} = [S_{GeV}^f - S_{SiV}^f]/k$  and  $\Delta E_{Ge} = [E_{Ge} - E_{Si}]$ .

### 3 MODEL PARAMETERS

To obtain the actual values of  $D_{Ge}$ ,  $\Delta S_{Ge}$ ,  $E_{Ge}$  and  $\Delta E_{Ge}$ , the experimental results reported in the literature for Ge self diffusivity in SiGe alloys [1-3] were all plotted in one graph shown in figure 1. Ge self diffusivity at 43% Ge content as reported by Strohm et al. did not fit the trend shown in the graph for Ge self diffusivity and therefore was not included. Curve fitting was then done using a single equation (equation (7)) for all the data points. The result of the curve fitting is shown in figure 1. The best fit was obtained by using the following values for the model parameters:

$$D_{Ge}^{SD} = 310 \exp(-2.4x) \exp\left(-\frac{4.68 - 1.58x}{kT}\right) \quad (8)$$

Using equation (8), we can obtain expressions for the self diffusivity in pure Ge as well as the Ge diffusivity in pure Si. Those expressions can then be compared to the diffusivity equations reported in the literature. Ge diffusivity in pure Si can be easily obtained from equation (8) by setting  $x$  to zero:

$$D_{Ge} = 310 \exp\left(-\frac{4.68}{kT}\right) \quad (9)$$

Similarly, Ge self diffusivity in pure Ge can be obtained from equation (8) by setting  $x$  to 1:

$$D_{Ge}^{SD} = 28.12 \exp\left(-\frac{3.1}{kT}\right) \quad (10)$$

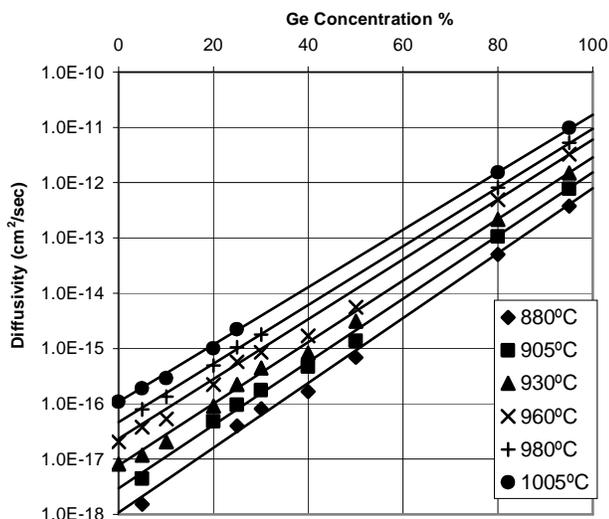


Figure 1: Ge diffusivity as predicted by our model (lines) compared to the experimental measurements done by Zangenberg et al. [2], Laitinen et al. for 80% Ge [1] and extrapolation from Strohm et al. measurements [3] for 5%, 25%, and 95% Ge content.

The prefactor and the activation energy for Ge diffusivity in Si are close to those reported by Zangenberg et al. [2] ( $D_0$  is the same  $310\text{cm}^2/\text{sec}$  and  $E_{\text{Ge}}$  was reported by Zangenberg et al. to be  $4.65\text{eV}$  compared to our reported value  $4.68\text{eV}$ ). It was indicated by Zangenberg et al. that the reported value lies within the range of previously reported values. This serves as the first check for our model.

Table 1 shows a comparison between our expectation for the Arrhenius expression for self diffusivity in pure Ge and the reported values in the literature for the same quantity. It is clear from the table that our model predicts a close value for the self diffusivity in pure Ge to those reported in the literature. This serves as another check for the validity for our model.

$D_0$ ( $\text{cm}^2/\text{sec}$ )	$E_{\text{Ge}}$ (eV)	Temperature Range (K)
7.8 (a)	2.97	1039-1201
32 (b)	3.1	1023-1156
44 (c)	3.14	1004-1189
10.8 (c)	3	1004-1189
24.8 (d)	3.14	822-1193
28.12 (e)	3.1	<1323

Table 1: Reported self diffusivities in Ge by (a) Letaw et al. [12], (b) Valenta and Ramasastry [13], (c) Widmer and GuntherMohr [14], (d) Vogel et al. [7] and (e) this work. After [7].

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