

Modeling Germanium-Silicon Interdiffusion in Silicon Germanium/Silicon Superlattice Structures

M. Hasanuzzaman*, Y. M. Haddara* and A. P. Knights**

*Department of Electrical and Computer Engineering
McMaster University, Hamilton, ON, Canada L8S 4K1

**Department of Engineering Physics
McMaster University, Hamilton, ON, Canada L8S 4L7

ABSTRACT

We present a model for the interdiffusion of silicon (Si) and germanium (Ge) in SiGe/Si superlattice structures. We considered both the vacancy exchange mechanism and the interstitial diffusion to fit the experimental data available in the temperature range 850-1125°C with Ge fraction up to 27% in SiGe. We considered the effect of Ge fraction on different material properties and we explicitly account for the lattice site conservation during the simulations. We were able to obtain excellent fits for all the cases. The same sets of fitting parameters can successfully describe the interdiffusion mechanism for both inert and oxidizing anneals for samples annealed below ~1075°C, where we find vacancy exchange mechanism dominates the interdiffusion process. For higher temperatures, Si interstitials dominate the interdiffusion mechanism.

Keywords: interdiffusion, SiGe, modeling, superlattice

1 INTRODUCTION

The incorporation of Silicon Germanium (SiGe) in device fabrication in recent years has facilitate increasing the device speed along with the continued device scaling and at the same time using the well matured low cost Si CMOS processing steps. SiGe/Si superlattice (SL) structures are used in applications such as photodiodes, waveguides and photodetectors [1]-[2]. Due to the high temperature fabrication process steps involved, the interdiffusion of Si and Ge in the structures is inevitable, which may lead to detrimental device performance. Thus getting an insight of the interdiffusion phenomena in SiGe/Si SL structures, accurate physically based atomistic models are needed. Few studies [3]-[4] have so far been reported to study the interdiffusion behaviour in Si_{1-x}Ge_x/Si SL structures. All these studies report effective diffusivity values for the interdiffusion process. In this work we have used the mathematical model for vacancy exchange mechanism and interstitial diffusion to describe the Si and Ge interdiffusion in Si_{1-x}Ge_x/Si SL structures annealed in the temperature range 850-1125°C in inert ambient and where experimental data are available in oxidizing ambient. While in the literature, experimental data are available with very high values of Ge fraction in Si_{1-x}Ge_x, we limit our

study for the Si_{1-x}Ge_x/Si SL structures containing Ge fraction up to 27%. While the vacancy exchange mechanism and interstitial diffusion mechanism have long been thought to play an important role in self and interdiffusion in semiconducting materials, it is very recently where we quantitatively showed that vacancy exchange mechanism alone is sufficient to describe the interdiffusion phenomena in Si/Si_{1-x}Ge_x/Si single quantum well structures at low anneal temperatures and interstitial diffusion mechanism can explain the interdiffusion phenomena at high anneal temperatures [5]. However, till to date, the vacancy exchange mechanism and the interstitial diffusion mechanism are not used quantitatively to describe the interdiffusion mechanism in Si_{1-x}Ge_x/Si SL structures.

2 MODELING INTERDIFFUSION FOR LOW TEMPERATURE ANNEALING

Vacancy exchange mechanism suggests that an atom and its adjacent vacant site interchange their position with each other for diffusion to occur. This concept was first proposed by Kirkendall *et al.* [6] in 1939 while describing the interdiffusion phenomena in metallic alloys. In 1942, Huntington and Seitz [7] proposed that the self-diffusion in metals occurs by vacancy exchange mechanism. Later, Smigelskas and Kirkendall [8] and Darken [9] reported further study on the vacancy exchange mechanism and provided a detailed mathematical model describing the phenomena. Though the standard process simulators [10]-[13] are capable to simulate diffusion phenomena, these are applicable for describing the diffusion of dilute dopants only. However, the interdiffusion of Si and Ge in Si_{1-x}Ge_x/Si SL structures involve the diffusion of the host atoms; the dilute dopant approximation no longer holds and the lattice site conservation constraint must be explicitly taken into account.

The equations those govern the interdiffusion of Si and Ge by vacancy exchange mechanism in Si_{1-x}Ge_x/Si SL structures are given by [5], [14],

$$\frac{\partial C_{Si}}{\partial t} = \frac{\partial}{\partial x} \left[D_{Si}^{int} \frac{C_V}{C_V^{*,int}} \frac{\partial C_{Si}}{\partial x} - D_{Si}^{int} C_{Si} \frac{\partial}{\partial x} \frac{C_V}{C_V^{*,int}} \right] \quad (1)$$

$$\frac{\partial C_{Ge}}{\partial t} = \frac{\partial}{\partial x} \left[D_{Ge}^{int} \frac{C_V}{C_V^{*,int}} \frac{\partial C_{Ge}}{\partial x} - D_{Ge}^{int} C_{Ge} \frac{\partial}{\partial x} \frac{C_V}{C_V^{*,int}} \right] \quad (2)$$

$$\frac{\partial C_V}{\partial t} = - \frac{\partial C_{Si}}{\partial t} - \frac{\partial C_{Ge}}{\partial t} \quad (3)$$

In these equations, C_{Si} , C_{Ge} , and C_V respectively are the concentrations of Si, Ge and vacancy. D_{Si}^{int} and D_{Ge}^{int} respectively are the Si and Ge self-diffusivities under inert intrinsic conditions. These parameters in general depend on the concentration of Ge and thus change as a function of time and position in the structure. Equations (1) and (2) respectively take into account the diffusion of Si and Ge under their own concentration gradient and the lattice motion to compensate for the difference in diffusivities. Equation (3) arises from the conservation of lattice site constraint. We also take into account the recombination between vacancies and interstitials by adding a bulk recombination term in (3). Considering that Ge has a catalytic effect on the equilibrium concentration of point defects [15]-[16], we implement these by [11],

$$C_X^{*,int}(SiGe) = C_X^{*,int}(Si) \exp\left(\frac{\Delta V_X}{kT}\right) \quad (4)$$

$$\Delta V_X = \Delta V_X^0 \cdot a_{SiGe} \cdot \frac{C_{Ge}}{5 \times 10^{22}} \quad (5)$$

where X refers to the point defect being considered, and for this case it is vacancy, V . $C_X^{*,int}(Si)$ is the equilibrium concentration in pure Si and we used the well-established default value given in [11]. The value of ΔV_X^0 is 25.6 for vacancy [11] and a_{SiGe} is calculated using Vegard's rule [17].

In this work we considered the experimental results reported by Griglione [3] and Holländer *et al.* [4]. Both these studies report SL structures grown on either Si or $Si_{1-y}Ge_y$ buffer layer. The studies reported the effective diffusivity values for Ge interdiffusion without regard to the atomistic mechanisms involved. Griglione used FLOOPS-ISE [12] process simulator to extract the effective diffusivity values of the Ge interdiffusion in $Si_{0.85}Ge_{0.15}/Si$ SL structures from the experimental SIMS profiles annealed at different temperatures for different anneal times both in inert and oxidizing ambients. On the other hand Holländer *et al.* reported effective diffusivity values for Ge interdiffusion extracted from experimental RBS profiles where the samples were annealed in inert ambient only.

In our work, we compare our simulated results with the reported experimental results. Where the experimental results are not available, we used the effective diffusivity values reported to extract the experimental profiles since the effective diffusivity values were reported to be extracted with reasonable fits with the experimental

profiles. We then compare our simulation result with these extracted experimental profiles.

We applied the model given in Eqs. 1-5 using the commercial process simulator FLOOPS-ISE [11]. While simulating the results reported by Griglione, we used the experimentally reported as-grown profile for Ge in the SL structures as the initial Ge profile. However for simulating the results reported by Holländer *et al.* we used a box type initial profile for Ge in the SL structures as the actual as-grown Ge profile was not available. The initial vacancy profile was set equal to the intrinsic equilibrium vacancy concentration at the structure. To calculate the initial profiles of Si we impose the conservation of lattice site constraint,

$$C_{Si} + C_{Ge} + C_V = 5 \times 10^{22} \quad (6)$$

In the simulations, the variations of D_{Si}^{int} and D_{Ge}^{int} as a function of Ge fraction in structures were taken into account. During the simulations we took the values of D_{Si}^{int} in pure Si from [18] and the values of D_{Si}^{int} for 80% Ge in $Si_{1-x}Ge_x$ from [19]. The values of D_{Ge}^{int} in Si for samples annealed below 1000°C were reported by Sharma [20] and the values of D_{Ge}^{int} in Si for higher temperatures and for Ge fractions of 10, 20 and 30% in $Si_{1-x}Ge_x$ were reported by Zangenberg *et al.* [21]. We allowed the values of D_{Ge}^{int} to vary and consider this as a fitting parameter during the simulations. We comment on the values used in the simulations later.

First, we applied the model for simulating anneals in inert ambient. Once we get good matches between the experimental and simulated Ge interdiffusion profiles, keeping the fitting parameters fixed for each anneal temperatures, the model was successful in simulating the Ge interdiffusion profiles for oxidizing ambient anneals without any need of additional fitting parameters.

Figures 1, 2 and 3 show typical fits for Ge interdiffusion in $Si_{0.85}Ge_{0.15}/Si$ SL structures grown on $Si_{1-y}Ge_y$ buffer. Figure 4 shows the actual value of D_{Ge}^{int} used in the simulations compared to the published values. For temperatures up to 1075°C, the values are close to the previously published values and for all the cases we were able to get reasonable fits of Ge interdiffusion profiles to the experimental profiles. However, for temperatures 1100 and 1125°C, the values of D_{Ge}^{int} close to the previously published values were not able to give good matches between the experimental and simulated Ge interdiffusion profiles, which indicates that the formulation presented so far is not sufficient to fully describe the diffusion mechanism at these temperatures and this necessitates to consider the contribution of interstitials in diffusion process.

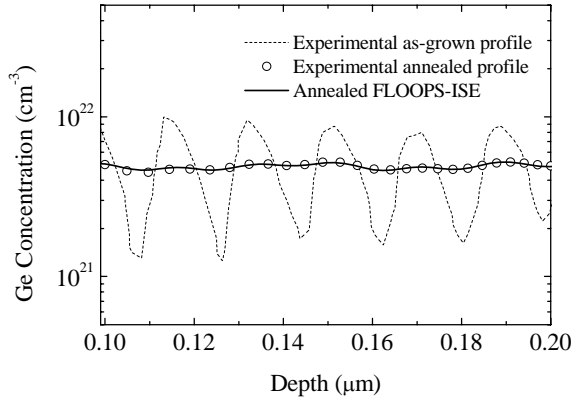


Figure 1: Ge interdiffusion in $\text{Si}_{0.85}\text{Ge}_{0.15}/\text{Si}$ SL grown on relaxed $\text{Si}_{0.85}\text{Ge}_{0.15}$ buffer after 3 min anneal in inert ambient at 950°C . Experimental data from [3].

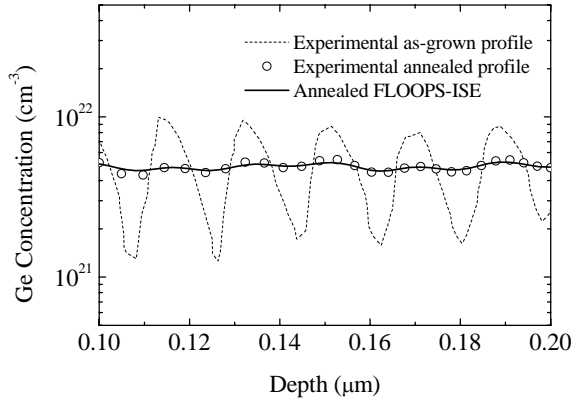


Figure 2: Ge interdiffusion in $\text{Si}_{0.85}\text{Ge}_{0.15}/\text{Si}$ SL grown on relaxed $\text{Si}_{0.85}\text{Ge}_{0.15}$ buffer after 3 min anneal in oxidizing ambient at 950°C . Experimental data from [3].

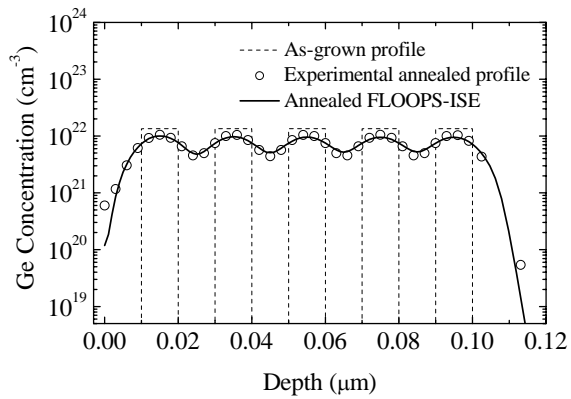


Figure 3: Ge interdiffusion in $\text{Si}_{0.73}\text{Ge}_{0.27}/\text{Si}$ SL grown on Si substrate after 100 sec anneal in inert ambient at 1025°C . Experimental data from [4].

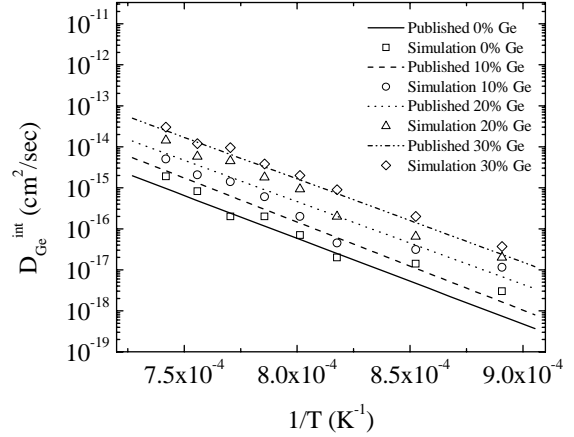


Figure 4: $D_{\text{Ge}}^{\text{int}}$ values used in the simulations compared with values from literature [20]-[21].

3 MODELING INTERDIFFUSION FOR HIGH TEMPERATURE ANNEALING

To take into account the contribution of interstitials in the interdiffusion mechanism, we have to consider the kick-out mechanism [22] and Frank-Turnbull mechanism [23]. The complete system of equations considering vacancy exchange mechanism, kick-out mechanism and Frank-Turnbull mechanism are given by [5],

$$\frac{\partial C_{\text{Si}}}{\partial t} = \frac{\partial}{\partial x} \left[D_{\text{Si}}^{\text{int}} \frac{C_{\text{V}}}{C_{\text{V}}^{\text{int}}} \frac{\partial C_{\text{Si}}}{\partial x} - D_{\text{Si}}^{\text{int}} C_{\text{Si}} \frac{\partial}{\partial x} \frac{C_{\text{V}}}{C_{\text{V}}^{\text{int}}} \right] + k_{f,\text{KO}} C_{\text{Si}} C_{\text{Ge}} - k_{r,\text{KO}} C_{\text{IGe}} C_{\text{Si}} + k_{f,\text{SiR}} (C_{\text{Si}} C_{\text{V}} - C_{\text{Si}}^* C_{\text{V}}^*) \quad (7)$$

$$\frac{\partial C_{\text{Ge}}}{\partial t} = \frac{\partial}{\partial x} \left[D_{\text{Ge}}^{\text{int}} \frac{C_{\text{V}}}{C_{\text{V}}^{\text{int}}} \frac{\partial C_{\text{Ge}}}{\partial x} - D_{\text{Ge}}^{\text{int}} C_{\text{Ge}} \frac{\partial}{\partial x} \frac{C_{\text{V}}}{C_{\text{V}}^{\text{int}}} \right] - k_{f,\text{KO}} C_{\text{Si}} C_{\text{Ge}} + k_{r,\text{KO}} C_{\text{IGe}} C_{\text{Si}} + k_{f,\text{GeR}} (C_{\text{IGe}} C_{\text{V}} - C_{\text{IGe}}^* C_{\text{V}}^*) \quad (8)$$

$$\frac{\partial C_{\text{Si}^*}}{\partial t} = \frac{\partial}{\partial x} \left[D_{\text{Si}} C_{\text{Si}}^* \frac{\partial C_{\text{Si}}}{\partial x} \right] - k_{f,\text{KO}} C_{\text{Si}} C_{\text{Ge}} + k_{r,\text{KO}} C_{\text{Si}} C_{\text{IGe}} - k_{f,\text{SiR}} (C_{\text{Si}} C_{\text{V}} - C_{\text{Si}}^* C_{\text{V}}^*) \quad (9)$$

$$\frac{\partial C_{\text{IGe}}}{\partial t} = \frac{\partial}{\partial x} \left[D_{\text{IGe}} C_{\text{IGe}}^* \frac{\partial C_{\text{IGe}}}{\partial x} \right] + k_{f,\text{KO}} C_{\text{Si}} C_{\text{Ge}} - k_{r,\text{KO}} C_{\text{Si}} C_{\text{IGe}} - k_{f,\text{GeR}} (C_{\text{IGe}} C_{\text{V}} - C_{\text{IGe}}^* C_{\text{V}}^*) \quad (10)$$

There is another equation to be considered that arises from the conservation of lattice site constraints and is given by Eq. 3. The reaction constants of the above equations are given by,

$$k_{f,\text{KO}} = 4\pi \cdot r_{\text{Si}} \cdot D_{\text{Si}} \quad (11)$$

$$k_{r,\text{KO}} = 4\pi \cdot r_{\text{Ge}} \cdot D_{\text{IGe}} \quad (12)$$

$$k_{f,SiR} = 4\pi r_{IVSi} (D_{ISi} + D_V) \quad (13)$$

$$k_{f,GeR} = 4\pi r_{IVGe} (D_{IGe} + D_V) \quad (14)$$

where the r 's are capture radii and we take this value equal to 0.5 nm following [24], D_{ISi} , D_{IGe} and D_V respectively are the diffusivities of the interstitial Si, interstitial Ge and vacancy. We assumed that each of these reactions is diffusion limited.

During the simulations, we used the published values [18]-[21] of D_{Si}^{int} and D_{Ge}^{int} . For D_{ISi} , we used the values given in FLOOPS-ISE [11], used the same value for D_{IGe} considering the similar atomic nature of Si and Ge. We used Eqs. 4-5 to calculate the values of C_V^* and C_{ISi}^* with $\Delta V_x^0 = 11.8$ for interstitials [11]. We found the simulations to be insensitive to the variations of C_{IGe}^* and thus we set arbitrarily $C_{IGe}^* = 0.01C_{ISi}^*$. With these comments, there is no other free parameter available.

Figure 5 shows typical fit for Ge interdiffusion profile at 1100°C inert ambient anneal. Excellent fits were obtained for all the cases at 1100 and 1125°C inert ambient anneals.

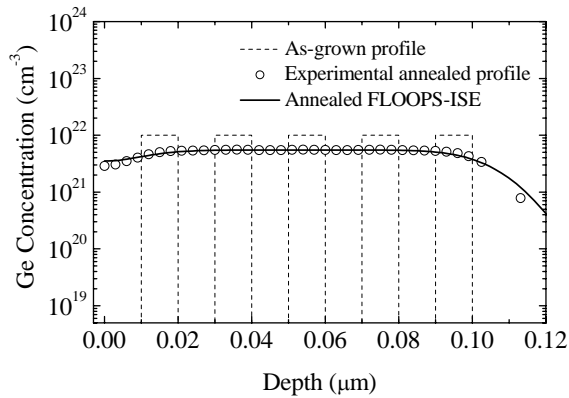


Figure 5: Ge interdiffusion in $\text{Si}_{0.80}\text{Ge}_{0.20}/\text{Si}$ SL grown on Si substrate after 1 min anneal in inert ambient at 1100°C. Experimental data from [4].

4 CONCLUSIONS

We have successfully modeled Si-Ge interdiffusion in $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ SL structures grown on relaxed $\text{Si}_{1-y}\text{Ge}_y$ buffer and Si substrate. During the simulations we considered the well established values of the intrinsic diffusivities of different species and the equilibrium point defect concentrations, including their dependences on the Ge fraction in the structures. We were able to successfully model experimental results on Si-Ge interdiffusion for a wide range of published data in the temperature range 850-1125°C with Ge fraction in $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ SL structures up to 27%. For temperatures up to 1075°C, interdiffusion of Si

and Ge mainly occurs by vacancy exchange mechanism. On the other hand for temperature at and above 1100°C, the interdiffusion of Si and Ge is controlled by diffusion of Si interstitials.

REFERENCES

- [1] C. Engel, P. Baumgartner, M. Holzmann, J. F. Nützel and G. Abstreiter, Thin Solid Films 294, 347, 1997.
- [2] O. Qasaimeh, P. Bhattacharya and E. T. Croke, IEEE Photonics Tech. Lett. 10, 807, 1998.
- [3] M. D. Griglione, PhD Thesis, University of Florida, 1999.
- [4] B. Holländer, R. Butz and S. Mantl, Phys. Rev. B 46, 4975, 1992.
- [5] M. Hasanuzzaman and Y. M. Haddara, J Mater Sci: Mater Electron, Published online, 2007, doi 10.1007/s10854-007-9391-5.
- [6] E. Kirkendall, L. Thomassen and C. Upthegrove, Trans. AIME 133, 186, 1939.
- [7] H. B. Huntington and F. Seitz, Phys. Rev. 61, 315, 1942.
- [8] A. D. Smigelskas and E. O. Kirkendall, Trans. AIME 171, 130, 1947.
- [9] L. S. Darken, Trans. AIME 175, 184, 1948.
- [10] SUPREM-IV.GS Manual, Stanford University, 1993.
- [11] FLOOPS-ISE Manual, Release 9.5, Integrated Systems Engineering.
- [12] FLOOPS-ISE Manual, University of Florida, Version 2002.
- [13] ATHENA User's Manual, SILVACO International, December 2002.
- [14] C. -Y. Tai, PhD Thesis, Stanford University, 1997.
- [15] A. Pakfar, Mat. Sci. Engg B 89, 225, 2002.
- [16] M. J. Aziz, Appl. Phys. Lett. 70, 2810, 1997.
- [17] A. R. Denton, N. W. Ashcroft, Phys. Rev. A 43, 3161, 1991.
- [18] R. J. Borg and G. J. Dienes, "An Introduction to Solid State Diffusion," Academic Press, 1998.
- [19] P. Laitinen, A. Strohm, J. Huikari, A. Nieminen, T. Voss, C. Grodon, I. Riihimäki, M. Kummer, J. Äystö, P. Dendooven, J. Räisänen, W. Frank and the ISODLE Collaboration, Phys. Rev. Lett. 89, 085902, 2002.
- [20] B. L. Sharma, Def. Diff. Forum 70-71, 1, 1990.
- [21] N. R. Zangenberg, J. Lundsgaard, J. Fage-Pedersen and A. N. Larsen, Phys. Rev. Lett. 87, 125901, 2001.
- [22] U. Gösele, W. Frank and A. Seegar, Appl. Phys. 23, 361, 1980.
- [23] F. C. Frank and D. Turnbull, Phys. Rev. 104, 617, 1956.
- [24] J. L. Ngau, P. B. Griffin and J. D. Plummer, J. Appl. Phys. 90, 1768, 2001.