Atomistic Modeling of Dopant Diffusion and Segregation in Strained SiGeC

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Abstract—In this work, density functional theory calculations are used to calculate the separate effects of stress/strain and chemical binding on diffusion, segregation and solubility of dopants in group IV alloy materials. Kinetic lattice Monte Carlo calculations are used to extract the effects of anisotropic stress and random alloy distributions. We find that segregation and solubility is dominated by stress effects, but that chemical interactions of Ge and C with point defects have a significant effect on diffusivity in SiGeC alloys.

I. INTRODUCTION

There is great interest in adding group IV impurities to Si for enhanced mobility, increased electrical activation, slower diffusion and reduced contact resistance of nanoscale MOSFETs. In order to control device structures at the nanoscale, a fundamental understanding of the effects of alloy concentration and associated strain is critical. In this work, we investigate activation and diffusion of dopants in SiGeC, considering both global strain compensation as well as local impurity configuration. Based on density functional theory (DFT) calculations, we developed simple models that can be used to predict the formation energy of a given configuration of dopants and alloy impurities in both stable and transition states. These models are then used in kinetic lattice Monte Carlo (KLMC) simulations to extract nanoscale response of dopant redistribution and activation. The calculations were done using the VASP software [1] using GGA functional [2], and diffusion paths were calculated using the nudged elastic band (NEB) method [3]. There are a range of interactions that need to be included when considering the effect of group IV impurities on dopant diffusion such as induced strain due size differences, impurity/dopant pairing, and impact of group IV impurities on the formation and migration

of dopant-defect complexes. In this work, we explore all of these interactions.

II. EFFECT OF STRAIN

The effect of strain on the formation energy of a defect/impurity in a solid can be taken from linear elasticity [4]:

$$E(\vec{\epsilon}) = E_{min} + \frac{\Omega}{2} \left(\vec{\epsilon} - \Delta\vec{\epsilon} \right) \mathbf{C} \left(\vec{\epsilon} - \Delta\vec{\epsilon} \right) , \qquad (1)$$

where $\mathbf{C}$ is the stiffness tensor of Si, strain $\vec{\epsilon}$ is defined relative to the equilibrium lattice vector of silicon, $\Delta\vec{\epsilon}$ is the induced strain tensor relative to reference lattice constant, and Ω is the volume of the system. Note that $\vec{\sigma} = \mathbf{C} \left(\vec{\epsilon} - \Delta\vec{\epsilon} \right)$ is the stress tensor. This expression can be used both to extract the induced strain from DFT calculations as well as to predict the change in solubility or diffusivity as a function of stress/strain state. The effect of stress/strain on a given process can be written as

$$F(\vec{\epsilon}) = F(0) \exp \left[\frac{E(\vec{\epsilon}) - E(0)}{kT} \right] , \qquad (2)$$

where $F(\vec{\epsilon})$ is the strain-dependent quantity of interest (e.g. diffusivity or solubility). We have found that the strain energy for systems with multiple impurities/dopants/defects can be accurately predicted based on simple linear superposition of induced strains of isolated components [4]. Table I lists induced strains for a range of impurities, defects and complexes.

III. SEGREGATION AND SOLUBILITY

Although, dopant/impurity binding has often been cited as basis for effect of alloy concentration on diffusion and segregation [5], we find that such direct binding effects between substitutional impurities are quite small (or repulsive) as listed in Table II. Thus, segregation and solubility of dopants in SiGeC alloys are driven by stress

C	Ge	Sn	Pb	V	I	
-0.42	0.05	0.21	0.26	-0.26	0.21	
B	Ga	In	P	As	Sb	Bi
-0.30	0.066	0.21	-0.084	0.013	0.16	0.23
B_3I	$B_{12}I_7$	As_4V	CV	GeV		
-0.30	-0.22	-0.08	-0.51	-0.21		

TABLE I

INDUCED STRAINS FOR IMPURITIES, DEFECTS AND COMPLEXES.

	E^{ij}_{1NN}	E^{ij}_{2NN}	E^{ij}_{3NN}	E^{ij}_{4NN}	E^{ij}_{5NN}
Ge-Ge	-0.0128	0.0022	-0.0048	-0.0028	0.0004
Ge-B	0.0170	-0.0164	0.0076	0.0019	-0.0074
Ge-V	-0.31				
C-As	0.17	-0.07			
C-P	0.29	-0.06			
C-B	0.56				
C-V	-0.48				

TABLE II

BINDING ENERGIES IN eV FOR n^{th} NEAREST NEIGHBOR (NNN) SUBSTITUTIONAL IMPURITY PAIRS.

Fig. 1. Comparison of prediction to experiment for segregation of B to biaxially strained SiGe alloys on unstrained Si at 850^oC. The contribution of the strain and binding terms to the segregation is shown, which illustrates that the effect of strain dominates the segregation. The change in solubility with strain follows the same behavior since induced strain for inactive clusters is negligibly small. Note that there is also a contribution of band-offsets (built-in voltage) to segregation (but not solubility), which is small for acceptors such as B, but dominates segregation of donors [6].

and to a lesser extent band offsets [6]. The models of binding and strain energies over possible configurations can be used to derive activation as a function of Ge or C content. The solubility increase which for B nearly corresponds to segregation ratio can be expressed as product of strain factor and binding factor at a given Ge content. Fig 1 shows the segregation of B to biaxially strained SiGe alloys on unstrained Si at 850^oC as a function of Ge content. The results show that boron preferentially segregates into SiGe alloys, as observed experimentally [5], [7], [8], with the segregation (and solubility) enhancement mainly due to global strain.

IV. DIFFUSIVITY

A major contributor to diffusivity in SiGeC alloy materials is the effect of stress. In general, compressive stress lowers the energy for vacancy complexes and thus increases the diffusion via vacancies, while the opposite behavior is seen for interstitial complexes and interstitial mediated diffusion. Figure 2 shows how biaxial strain effects the diffusion of common dopants. Note that the impact of stress on vacancy mediated diffusion is nearly the same for all impurities (and self-diffusion), as the transition state involves a vacancy separated between 2nd and 3rd nearest neghbor sites. In contrast, the impact of
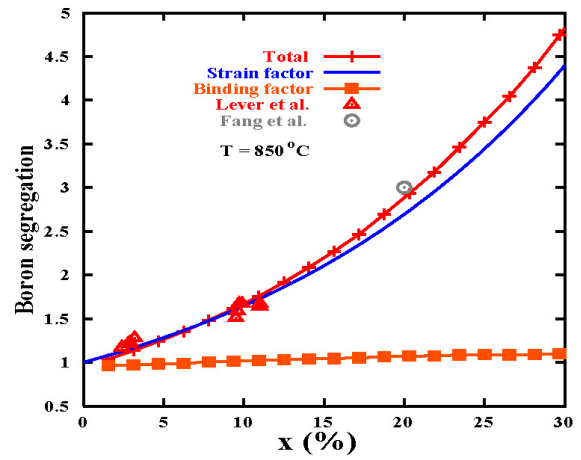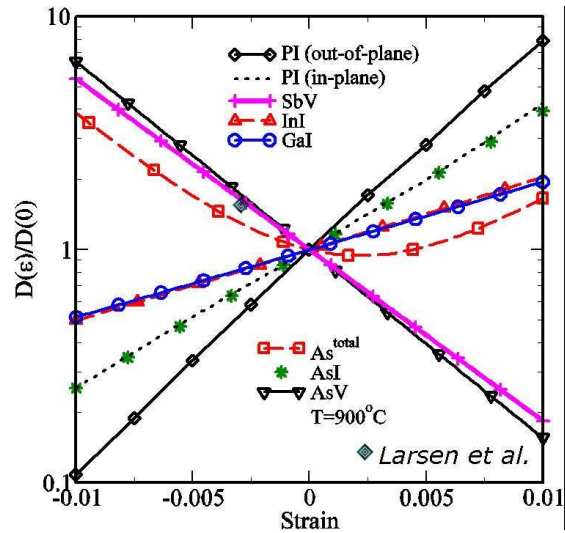

Fig. 2. Dopant diffusion as function of biaxial strain based on DFT calculations used in KLMC simulations. Experimental data for Sb diffusion from Larsen et al. [9] matches closely to predicted behavior.

stress on interstitial mediated diffusion varies strongly between dopants and is anisotropic for B, P and self-diffusion.

The second component influencing diffusion in SiGeC alloys is direct chemical interactions. In contrast to substitutional dopants, both Ge and (surprisingly) C have substantial binding energies with vacancies. For Ge, it is
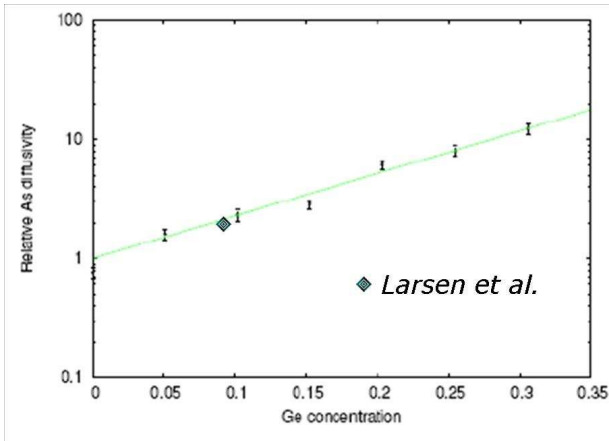
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Fig. 3. KLMC simulations of V-mediated As and Sb diffusion in SiGe using interactions from DFT. V-mediated As and Sb diffusion increase with Ge concentration. The model predictions are compared to experimental measurements on Sb from Larsen et al. [9]. Note that both the model and data include only the effects of alloy concentration. Compressive stress in SiGe on Si would lead to further increases in V-mediated diffusion.
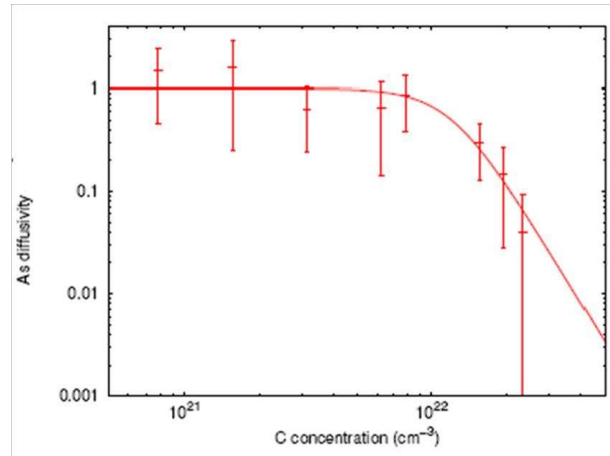

Fig. 4. Dependence of V-mediated As diffusion on substitutional C concentration based on KLMC simulations using binding and transition energies from DFT.

one Ge	1NN	2NN	3NN	-1NN	
BI	0.099	0.047	0.020	-0.027	
PI	0.11	0.05	-0.04		
two Ge	1-1	1-2	1-2 (GeGe)	1-3	2-2
BI	0.484	0.252	0.155	0.140	0.119

TABLE III
THE FORMATION ENERGY DIFFERENCE (IN eV RELATIVE TO PURE SI) OF THE TRANSITION STATE FOR I-MEDIATED DIFFUSION AS FUNCTION OF POSITION OF GROUP IV IMPURITIES IN SIX-MEMBERED RING.

associated with the lower formation energy (and thus higher equilibrium concentration) of vacancies in Ge and SiGe. This leads to enhanced diffusion via vacancy-mediated mechanisms in SiGe, as the compressive strain in SiGe on Si also reduces the vacancy formation energy. Figure 3 shows that increasing the Ge concentration leads to substantial increases in V-mediated diffusion of As (and Sb which shows nearly identical behavior).

The binding of V with C has a somewhat different effect. When 1NN to V, the C atom relaxes away from V, becoming almost co-planar with its 3 Si neighbors. The C/V exchange energy is very large (several eV), so that C effectively blocks V migration. Thinking that this might lead to reduced V-mediated diffusion, we explored the impact of C concentration on V diffusion and V-mediated As diffusion via KLMC. We found that C does indeed reduce V-mediated diffusion, but only for C concentrations of about 10^{22} (20% C) or more (see Fig. 4), much higher than is expected to be technologically feasible given the large Si-C size mismatch.

We find that Ge leads to increased energy of the transition state for dopant interstitial pairs and thus to reduced diffusivity. As seen in Table III, the effect is most pronounced for Ge atoms at substitutional site closest to the dopant in the transition state. Averaging over possible Ge configurations, we performed KLMC under anisotropic stress conditions. The diffusivity is statistically sampled by generating random Ge distributions

and averaging to obtain the ratio of diffusivity of B in SiGe to that in pure Si. We calculated $\overline{D}_{33}$ (out-of-plane) and $\overline{D}_{11}$ (in-plane) since biaxial stress produces anisotropic diffusion. Figure 5 shows comparison of KLMC results to experimental data by Moriya et al. [10]. KLMC results give an excellent prediction of change in diffusivities with Ge contents for strained SiGe. Both strain effects and chemical effects are important. However, the chemical effects appears somewhat weaker than suggested by data of Kuo et al. [11] who varied both composition and strain independently. This may be due to changes in dislocation structure of relaxed SiGe modifying the point defect concentrations in the experiments.

V. CLUSTERING

We find that BI can pair with a substitutional C atom. In the most stable BCI structure, B and C atoms share a substitutional site in a $\langle 100 \rangle$ split form. The
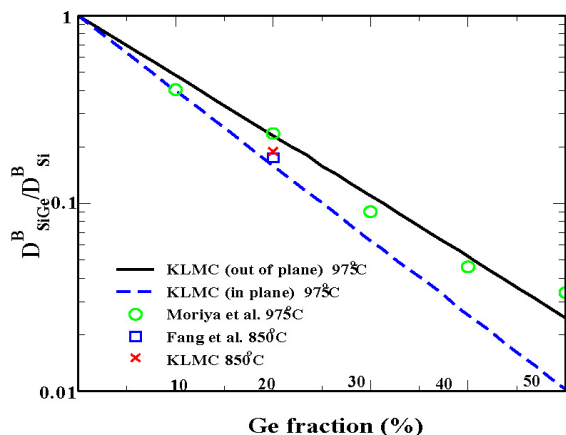
Fig. 5. B diffusivity in strained SiGe. Moriya's data was matched with out-of-plane KLMC result at 20% since it was reported in arbitrary units.

formation energies of stable C and B complexes are shown in Table V. Since the formation energies of mixed interstitial clusters involving both B and C are lower than for equivalent clusters with just B or C, high free carbon concentrations can be expected to lead to reduced B activation. This has been observed by de Souza and Boudinov [12]. B/C/I clustering is in competition with I reduction due to C/I clustering, which is usually the primary C effect. Optimum results are expected for C separated from B so that the C can reduce I concentrations without enhancing B/I clustering.

	BI (tet)	CI ⟨100⟩	BCI ⟨100⟩	B_2I
E_f (eV)	2.64	1.99	0.28	0.50

C_2I	B_3I	C_3I	$B_2CI(BBC)$	$BC_2I(CBC)$
0.68	-0.43	0.62	-1.13	-0.77

TABLE IV
FORMATION ENERGIES OF VARIOUS COMPLEXES RELATIVE TO SUBSTITUTIONAL C AND B, AND BULK SI. THE SYSTEM WAS RELAXED IN ORDER TO OBTAIN THE LOWEST ENERGY STATE.

VI. CONCLUSION

We have used DFT calculations combined with KLMC simulations to separately predict the effects of stress/strain and direct chemical interactions on the diffusion, segregation and solubility of substitutional dopants in SiGeC alloys. We find that there is little binding between group IV impurities and substitutional dopants, so that stress effects dominate segregation and solubility. However, significant interactions between Ge and C and point defects leads to significant impacts on dopant

diffusion beyond the effects of stress. In addition, we find clustering of mixed B/C/I complexes is favored over B/I and C/I complexes, with possible impacts on B activation if high C concentrations are used in heavily B-doped regions.

REFERENCES

[1] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, RC558 (1993); G. Kresse, and J. Furthmüller, **54**, 11169 (1996).
[2] J. Perdew *et al.*, *Phys. Rev. B* **46**, 6671 (1991).
[3] G. Henkelman, B. Uberuaga and H. Jónsson, *J. Chem. Phys.* **113**, 9901 (2000).
[4] M. Diebel, Ph.D. thesis (University of Washington) (2004).
[5] R. F. Lever, J. M. Bonar, and A. F. W. Willoughby, *J. Appl. Phys.* **83**, 1988 (1998).
[6] C. Ahn and S.T. Dunham, submitted to *Phys. Rev. B*.
[7] T. T. Fang, W. T. C. Fang, P. B. Griffin, and J. D. Plummer, *Appl. Phys. Lett.* **68**, 791 (1996).
[8] S. M. Hu, D. C. Ahlgren, P. A. Ronsheim, and J. O. Chu, *Phys. Rev. Lett.* **67**, 1450 (1991).
[9] A.N. Larsen, N. Zangenberg, and J. Fage-Pedersen, *Mat. Sci. Eng. B* **124-125**, 241 (2005).
[10] N. Moriya, L.C. Feldman, H.S. Luftman, C.A. King, J. Bevk and B. Freer, *Phys. Rev. Lett.* **71**, 883 (1993).
[11] P. Kuo, J. L. Hoyt, J. F. Gibbons, J. E. Turner, and D. Lefforge, *Appl. Phys. Lett.* **66** (5), 580-582 (1995).
[12] J.P. de Souza and H. Boudinov, *J. Appl. Phys.* **74**, 6599 (1993).