

Vacancy-mediated diffusion in biaxially strained Si

Damien Caliste,^{a)} Konstantin Z. Rushchanskii, and Pascal Pochet^{a)}

Laboratoire de Simulation Atomistique (L_Sim), SP2M, INAC, CEA-UJF, 38054 Grenoble Cedex 9, France

(Received 26 November 2010; accepted 6 January 2011; published online 21 January 2011)

We present an analysis of stress-enhanced vacancy-mediated diffusion in biaxially deformed Si (100) films as measured by the strain derivative (Q') of the activation energy. The strain dependence of Q' is demonstrated by means of a reanalysis of previously published experimental data, which both take into account the temperature dependence of and highlight the differences between tensile and compressive stress. Based on *ab initio* calculations, we predict that Q' in pure silicon is higher under compressive conditions due to a broken degeneracy of the split-vacancy configuration. © 2011 American Institute of Physics. [doi:10.1063/1.3548547]

Understanding the influence of stress on the diffusion of atomic species in Si-based alloys is a key challenge in modern semiconductor technology. In recent years, it has been shown that external strain can enhance or retard diffusion of impurities as well as self-diffusion of the alloy components.¹⁻⁷ For instance, in layered materials, such as the SiGe alloys used in electronics, the lattice mismatch between Si and Ge makes the connection between interdiffusion and stress of particular importance.¹

The physical parameter that describes the effect of strain on the diffusivity is denoted by Q' , the strain derivative of the activation energy Q . Experimentally, however, the two different ways of determining Q' used in literature^{2,5} provide scattered results.

In the present letter, we summarize these two approaches to experimentally obtain Q' and show their difference. By reanalyzing previously published experiments, we confirm that Q' is different between tensile and compressive environments. While current experimental values are scattered in proportion from 1 to 10, we show that our analysis makes all these results consistent. We then use *ab initio* calculations to study the strain dependency of Q' , reproducing both compressive and tensile behaviors and showing their relation to the strong nonlinear stress dependence of the vacancy barrier.

Let us begin by defining Q' ,

$$Q' = \frac{\partial Q}{\partial \varepsilon} = - \frac{\partial^2 \ln D}{\partial \varepsilon \partial \beta}, \quad (1)$$

where $\beta = 1/kT$, and assuming Q to be independent of T , we can write $D(T, \varepsilon) = D_0(\varepsilon) \exp^{-\beta Q(\varepsilon)}$; this assumption is standard for the present case since we do not consider interacting defects.⁸ Equation (1) is not useful to extract Q' from experimental data since it requires good activation energies from fits to the diffusivity values at different constraints. Cowern *et al.*² proposed to use a simplified version of Eq. (1)—called here q' —which is based on measurements of diffusivity at a fixed temperature, for a given deformation ($\varepsilon \neq 0$) and for relaxed conditions ($\varepsilon = 0$): $q'(T) = -(kT/\varepsilon) \ln[D/D(\varepsilon = 0)]$. In the limit of small variations of ε , this definition is equal to $q'(T) = -kT(\partial \ln D / \partial \varepsilon)$, which means that the value com-

puted by Cowern *et al.* is the strain derivative of diffusivity. One can show that

$$q'(T) = Q' - k \frac{\partial \ln D_0}{\partial \varepsilon} T. \quad (2)$$

Here, q' includes both the effects of stress on the diffusivity prefactor (D_0) and on the activation energy (through Q'). This expression shows a linear dependence of q' with the temperature, as it will be discussed later. The prefactor D_0 depends on several terms, namely, the lattice parameter, the vibrational entropy, and the configurational entropy.⁵

The results of Cowern *et al.* in their first paper of 1994 (Ref. 2) tend to show that the prefactor D_0 has no dependency on strain, thus having $q' = Q'$. However, the strain and the composition effects were not clearly decoupled in that work, as they reanalyzed later.⁴ More recent experiments confirm this dependency.⁵ Therefore, q' is different from Q' , as shown in Eq. (2).

Experimental values available from the literature in $\text{Si}_{1-x}\text{Ge}_x$ are listed in Table I together with the corresponding values of temperature, strain, and alloy concentration. Diffusion data have been obtained either with Ge tracer or Sb tracer. Most of the values have been derived using the formulation of Cowern *et al.*, i.e., using diffusivity ratios, thus obtaining q' , except for the values given by Refs. 5 and 6, which have been obtained by the ratio of activation energies, thus directly measuring Q' . We note that for the Ge tracer, the reported values of q' and Q' are highly scattered ranging from 10 to 160 eV per unit strain. The work of Zangenberg *et al.*⁶ is of special interest because it provides systematic studies of the diffusivity under a biaxial compressive and tensile strain of $\pm 0.2\%$ for films at the same composition $x = 0.1$ and for different temperatures. They reported two values for Q' : +160 eV per unit strain for the compressive and +115 eV per unit strain for the tensile strain. The discrepancy between these values and the previously reported ones comes from the improper comparison of Q' and $q'(T)$.

The values of $q'(T)$ for the experiments shown by Zangenberg *et al.* are obtained from $D(T, \varepsilon)$ in Fig. 4 of Ref. 6 and are shown in Fig. 1 as a function of temperature. Linear regression gives $q'(T) = 164 - 0.110T$ for compressive and $q'(T) = 75 - 0.049T$ for tensile strain, respectively, in eV per unit strain. Once a fit for q' has been obtained, Q' follows from Eq. (2). These Q' values ($Q'_{\text{comp}} = 164$ and $Q'_{\text{tens}} = 75$) are in good agreement with those obtained by Zangenberg *et al.*

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: damien.caliste@cea.fr and pascal.pochet@cea.fr.

TABLE I. Experimental values for the q' and Q' parameters in $\text{Si}_{1-x}\text{Ge}_x$ for Ge and Sb vacancy tracers at a given biaxial strain ε . The values in bold characters are reanalyses of the data from Eq. (2) of this letter.

Tracer	T (K)	ε (%)	x (%)	q' (eV ε^{-1})	Q' (eV ε^{-1})	Ref.
Ge	1070–1170	−0.71	17	19		1
Ge	1170–1320	−1.05	25	40 ± 5 ^a		2
Ge	1150	−1.26	30	17.8 ± 4.3 ^b		4
Ge	1200–1325	−0.21	10	26	164	6
Ge	1200–1325	+0.21	10	15	115	6
Ge	1040–1140	−0.21	7–20	10^c		9
Sb	1173–1300	−0.38	9	13 ± 3	25	3
Sb	1173–1300	+0.38	0	$17^d \pm 5$		3
Sb	1088–1198	−0.42	10		24/22 ^e	5
Sb	1013–1113	−0.84	20		24/25 ^e	5
Sb	860		0	13 ± 0.5 ^f		7

^aChemical effect was not distinguished.

^bStrain and composition effects were distinguished.

^cAn upper bound estimation. The reported effective value, which accounts for both vacancy and interstitial mediators, is $Q' = 0.25$ eV per unit strain.

^dThe result for tensile strain shows a highly scattered value, it has been obtained in pure silicon layers, where the interstitial contribution to the diffusion is of great importance (Ref. 3), with respect to the vacancy mechanism that is known to be the main mediator for Sb tracer. It is thus not comparable with the other results in this table.

^eWe have derived values for Q' at different strain using the data presented in Table II of Ref. 5, while only an average value of 24 ± 5 eV per unit strain has been reported in that paper.

^fValue for hydrostatic stress up to 3.0 GPa.

from Eq. (1). At around 1250 K, q' decreases to 26 and 15 for compressive and tensile deformation, respectively (see Fig. 1). These values now agree well with the other published values within the same temperature ranges. More interestingly, these results show that q' is also different between tensile and compressive strains.⁹

The temperature dependency of q' can also be applied for the Sb tracer measurements (see Table I). When reanalyzing the results of Kringhøj *et al.*³ for the vacancy-enhanced diffusion under compression of −0.38% in SiGe alloy, we found $q'(T) = 25 - 0.010T$ (see Fig. 1). The Q' value ($Q'_{\text{comp}} = 25$) is now consistent with the one obtained by Kuznetsov *et al.*⁵ for the same Ge concentration [22 eV per unit strain at −0.42%, see footnote (e) of Table I].

As can be seen in Table I, both Q' and q' are no longer scattered for a given tracer. Moreover, q' values are also

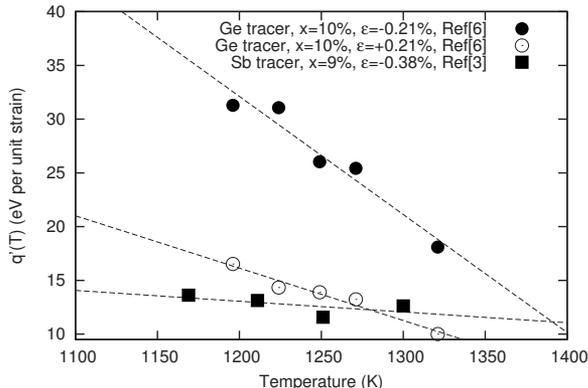


FIG. 1. Temperature dependencies of Q' parameter in biaxially strained $\text{Si}_{0.9}\text{Ge}_{0.1}$ for Ge and Sb tracers for compressive (filled symbols) and tensile (open symbols) strains. The experimental values have been extracted from the results of Zangenberg *et al.* (Ref. 6) (circles) and Kringhøj *et al.* (Ref. 3) (squares). The lines are linear regressions of the corresponding data.

consistent for both tracers, while this is not the case for the Q' values. We attribute this difference to an effect of the tracer itself on the migration path of silicon vacancy. Indeed, Sb is known to be positioned in a split-vacancy position,¹⁰ while the germanium traps the vacancy as first neighbor.¹¹ The activation energy Q as measured by a given tracer can be decomposed as a sum of the activation of silicon Q_{Si} and the tracer-vacancy binding energy Q_{b} . This expression shows that the way that Q_{b} is affected by the strain will influence the measured Q' for a given tracer. A study of Q_{b} can be challenging due to the nonlinear behavior of the activation energy in SiGe alloys¹² and is out of the scope of this letter.

We now propose an analysis based on the calculation results from a density functional theory (DFT) approach as implemented in the SIESTA code.¹³ The numerical results shown below have been obtained for pure silicon, thus focusing on Q_{Si} only and ignoring Q_{b} .

The effect of stress on the formation energies has already been calculated in DFT and it shows two quadratic behaviors for out-of-plane (JT_{\perp}) and in-plane Jahn–Teller (JT_{\parallel}) distortions, as shown in Ref. 14 where the activation energy was calculated under the approximation of linear elasticity for the activation point. In this letter, this assumption is revisited by calculating the transition states for a larger range of deformations (i.e., from −1% to +1%).

The DFT calculations were performed within the local density approximation. A double ζ polarized basis for Si was employed in a simple cubic supercell containing 216 atoms. Γ -point was used for Brillouin zone integration. These parameters are well suited for a single vacancy in pure Si, as reported in Ref. 15. The structures were relaxed using conjugate-gradient coordinate optimization until the force on each atom was less than 2 meV/Å. The lattice parameter perpendicular to the planar deformation is optimized for zero pressure. All equilibrium states of the vacancy were checked to present the JT distortion.

The activation barriers have been computed using the nudged elastic band method¹⁶ using between 21 and 41 replicas. Atoms in replicas are allowed to move along perpendicular forces until the highest value for all atoms in all replicas is below 50 meV/Å, and in some case, convergence was continued until perpendicular forces are less than 10 meV/Å. We have investigated the switch of a vacancy with one of its first neighbor, including switching between JT_{\parallel} and JT_{\perp} either on-site or during the vacancy jump.

We show that the so-called split vacancy¹⁷ is the lowest transition state in all cases. As a first approximation, its formation energy can be interpreted as the activation energy of the diffusion process. This approximation means that we neglect the thermal activations of the other paths. The formation energies of the split-vacancy, as obtained by *ab initio* calculations with respect to the biaxial stress, are shown in Fig. 2. The energy of the barrier grows with tension and decreases with compression, implying a negative formation volume as expected for vacancies. The evolution of the energy can be expanded to second order: $E(\varepsilon) = E(\varepsilon=0) + \alpha \cdot V^* \varepsilon + E'' \cdot \varepsilon^2$. The first order coefficient $\alpha \cdot V^*$ is directly related to the relaxation volume of the linear elasticity approximation. As shown in Fig. 2, the best fit is obtained when treating separately the compressive and the tensile branches (i.e., $E''_{\text{tensile}} \neq E''_{\text{compressive}}$). We obtain $\alpha \cdot V^* = 19.7$ eV per unit strain, which is in good agreement with

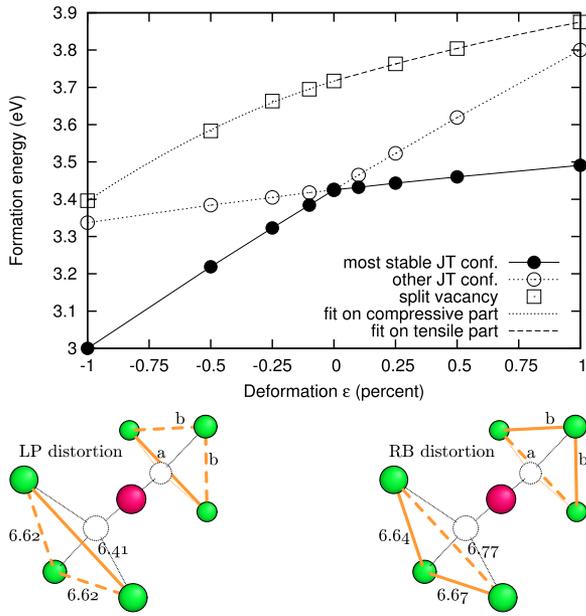


FIG. 2. (Color online) Formation energies obtained by *ab initio* calculations of the silicon vacancy in different JT rearrangements (Ref. 14) and of the split vacancy with respect to the biaxial deformation. The two schemes represent the local geometries around the moving atom in the split-vacancy configuration. Lengths are given in bohr with error bars of 0.02 bohr for a deformation of $\pm 1\%$. These positional errors are due to the fact that the given configurations are taken from NEB calculations and thus subject to the additional forces of the springs. The tensile region relaxes in RB distortion and the compressive region in LP one.

the value given in Ref. 18. Second order terms are evaluated as $E''_{\text{compressive}} = -1247$ and $E''_{\text{tensile}} = -397$ eV per squared unit strain. Allowing different values of V' for both tensile and compressive conditions changes the numerical values by less than 5%, confirming the linear elasticity approach for small deformations. For comparison, the E'' values for the JT_{\parallel} and JT_{\perp} vacancies are one order of magnitude smaller than the one of the split vacancy. Thus, the latter plays the key role in diffusion under strain, while the broken JT degeneracy¹⁴ has a minor effect. We attribute the strongly different E''_{tensile} and $E''_{\text{compressive}}$ values of the split vacancy to an electronic effect in the pairing between the first neighbors. This effect is highlighted by a different distortion in geometry either in compression or in tension. Indeed, the local environment of the split vacancy is closed to the one of a divacancy: with six pending silicon atoms.¹⁹ We observe for the split vacancy under strain the same kind of local rearrangement as for the divacancy. Under compressive strain, the system adopts a large pairing (LP) rearrangement, while it switches to resonant bond (RB) under tensile conditions. These modifications of local rearrangement are shown in Fig. 2. The short bond of the pairing case under compression is positioned in the biaxial strained plane, while under tension, it is the long bond that is located in this strained plane. Our results show that the degeneracy of the two distortions at equilibrium lattice parameter is broken by strain, as proposed by Makhov *et al.*¹⁹ for the divacancy.

Since Q' is approximated by the first derivative of $E_{\text{split}}(\epsilon)$, one can learn from Fig. 2 that Q' is first order dependent on ϵ in a non-negligible way. Indeed, our *ab initio* calculations show that purely vacancy-mediated diffusion at compressions of -0.25% (-0.38%) give a $Q' = 26(29)$ eV

per unit strain and for reciprocal tensile conditions it gives $Q' = 18(17)$ eV per unit strain. These values are in qualitative agreement with the experimental results, showing, as reported for SiGe,⁶ a different behavior depending on the sign of the strain. The numerical discrepancies are due not only to different binding effects between the experimental tracer and the vacancy but also partially due to interstitial-mediated diffusion. We attribute the fact that our results are closer to the Sb tracer data to the vacancy-tracer configuration. From an experimental point of view, the evaluation of Q' using Sb tracer under compressive conditions would be helpful to support our prediction, while the situation might be more complex for Ge tracer.

In conclusion, we have reanalyzed the existing experimental data on stress-enhanced diffusion in SiGe and shown that they are all consistent, per tracer experiments when using the proper definition for the strain derivative. In addition, we have reported theoretical values of the strain dependency of the Q' diffusivity derivatives for vacancy-mediated self-diffusion in biaxially strained Si. We predict that Q' is higher under compressive conditions due to the broken degeneracy of the split-vacancy configuration. This prediction can be tested using an Sb tracer under compressive and tensile strains.

This work was partially funded by the French National Research Agency (ANR) through OSiGe_Sim Project No. ANR-05-NANO-004. Calculation time was provided by the French GENCI Agency under Project No. t2010096107. We thank Dr. Hector Mera for valuable discussions.

- ¹D. B. Aubertine, M. A. Mander, N. Ozguven, A. F. Marshall, P. C. McIntyre, J. O. Chu, and P. M. Mooney, *J. Appl. Phys.* **92**, 5027 (2002).
- ²N. E. B. Cowern, P. C. Zalm, P. van der Sluis, D. J. Gravesteijn, and W. B. de Boer, *Phys. Rev. Lett.* **72**, 2585 (1994).
- ³P. Kringhøj, A. N. Larsen, and S. Y. Shirayev, *Phys. Rev. Lett.* **76**, 3372 (1996).
- ⁴N. E. B. Cowern, W. J. Kersten, R. C. M. de Kruij, J. G. M. van Berkum, W. B. de Boer, D. J. Gravesteijn, and C. W. T. Bulle-Liewma, in *Electrochemical Society Proceedings*, edited by G. R. Srinivasan, C. S. Murthy, and S. T. Dunham (Electrochemical Society, Pennington, NJ, 1999), Vol. 96-4, pp. 195–209.
- ⁵A. Y. Kuznetsov, J. Cardenas, D. C. Schmidt, B. G. Svensson, J. L. Hansen, and A. N. Larsen, *Phys. Rev. B* **59**, 7274 (1999).
- ⁶N. R. Zangenberg, J. Lundgaard Hansen, J. Fage-Pedersen, and A. Nylandsted Larsen, *Phys. Rev. Lett.* **87**, 125901 (2001).
- ⁷M. J. Aziz, Y. Zhao, H.-J. Gossmann, S. Mitha, S. P. Smith, and D. Schiferl, *Phys. Rev. B* **73**, 054101 (2006).
- ⁸D. Caliste and P. Pochet, *Phys. Rev. Lett.* **97**, 135901 (2006).
- ⁹D. B. Aubertine and P. C. McIntyre, *J. Appl. Phys.* **97**, 013531 (2005).
- ¹⁰H. Bracht and A. Chronos, *J. Appl. Phys.* **104**, 076108 (2008).
- ¹¹D. Caliste, P. Pochet, T. Deutsch, and F. Lançon, *Phys. Rev. B* **75**, 125203 (2007).
- ¹²R. Kube, H. Bracht, J. Lundgaard Hansen, A. Nylandsted Larsen, E. E. Haller, S. Paul, and W. Lerch, *J. Appl. Phys.* **107**, 073520 (2010).
- ¹³J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).
- ¹⁴K. Z. Rushchanskii, P. Pochet, and F. Lançon, *Appl. Phys. Lett.* **92**, 152110 (2008).
- ¹⁵F. El-Mellouhi, N. Mousseau, and P. Ordejón, *Phys. Rev. B* **70**, 205202 (2004).
- ¹⁶G. Henkelman and H. Jonsson, *J. Chem. Phys.* **113**, 9978 (2000).
- ¹⁷S. A. Centoni, B. Sadigh, G. H. Gilmer, T. J. Lenosky, T. Díaz de la Rubia, and C. B. Charles, *Phys. Rev. B* **72**, 195206 (2005).
- ¹⁸P. Ramanarayanan, K. Cho, and B. M. Clemens, *J. Appl. Phys.* **94**, 174 (2003).
- ¹⁹D. V. Makhov and L. J. Lewis, *Phys. Rev. B* **72**, 073306 (2005).