Stress enhanced self-diffusion in Si: Entropy effect in anisotropic elastic environment

Konstantin Z. Rushchanskii, Pascal Pochet,[a)] and Frédéric Lançon
Laboratoire de simulation atomistique (L_Sim), SP2M, INAC, CEA, 38054 Grenoble cedex 9, France

(Received 6 March 2008; accepted 1 April 2008; published online 17 April 2008)

We present a multiscale analysis on stress enhanced vacancy-mediated diffusion in strained Si that explicitly includes the Jahn–Teller structural distortion around vacancies. The resulting anisotropy combined with biaxial deformations applied to (100)-oriented films lead to an orientational dependency of the vacancy formation energy. At finite temperatures, it results in a strong entropy effect when thermal activation allows occupancy of high energy defect states. Kinetic Lattice Monte Carlo simulations reveal that the effective activation energy is a strongly nonlinear function of strain at small deformations. At larger deformations, it becomes linear where as the occupancy of the excited states becomes insignificant. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2912532]

Strained silicon (sSi) is an important material for modern semiconductor technology. Because it is achieved by using silicon germanium (SiGe) substrates, the sSi layer is mostly biaxially strained. Since the pioneering work of Cowern *et al.*,[1] it has been established that in Si and SiGe the strained state of the layer can enhance or retard chemical diffusion depending on the strain sign (compressive or tensile) and on the mediators involved in the diffusion (vacancy or interstitial). The vacancy mediated diffusion is enhanced by compressive strain and retarded by tensile strain [e.g., for Ge tracer in Ge (Ref. 2) or Sb tracer in Si (Ref. 3)], while the opposite phenomenon occurs for the interstitial mediated diffusion (e.g., for B tracer[1]). A widely used approach to the effect of stress on point defect diffusivity[4] is to apply a linear correction of the activation energy versus strain, described by the parameter $Q' = -kT(\partial \ln D/\partial \varepsilon)$, where D is the diffusivity, T is the temperature, k is the Boltzmann's constant, and ε is the strain. This approach is considered valid for small deformations, in the regime of Hook's law, even for an anisotropically stressed environment. In this letter, we show that defects involving a strongly anisotropic local lattice distortion can mediate diffusion in a *nonlinear* way already for *small* values of biaxial stress. We consider a neutral vacancy in Si with a tetragonal structure distortion due to the Jahn–Teller (JT) effect[5] as a simple prototype of the diffusion mediator with anisotropy in the strain response. Our calculations reveal that Q' cannot be assumed constant with respect to strain and that there is a nonlinear strain dependency of $Q'(\varepsilon, T)$ in sSi that cannot been neglected. We also show the importance of the temperature dependency of Q', which has not been previously taken into account. These conclusions are extended to charged vacancies as well as interstitials.

Our model for vacancy mediated diffusion in Si implies parameters (see Table I), obtained from *ab initio* calculations using SIESTA code[8] in a simple cubic (SC) box containing 216 atoms with Γ-point integration within the local-density approximation. The influence of external stress on formation energy E_f and activation energy E_a was taken into account in terms of the relaxation (V^r) and activation (V^a) volume tensors (see Ref. 4) within the harmonic approximation. The role of the temperature and stress on self-diffusion in Si has been investigated by using the time-resident algorithm[9] of kinetic lattice Monte Carlo (KLMC). The cell of the simulations contained 8×10^6 atoms. Averages were taken over up to 10^9 movements within a temperature range of 800–1500 K. All simulations contained one vacancy in the cell. Therefore to account for the temperature- and stress-variation of vacancy concentrations, the diffusivity obtained from KLMC runs was factored by $\exp(-\langle E_f \rangle / kT)$, where $\langle E_f \rangle$ is the average formation energy calculated for a given temperature.

We now present the KLMC results obtained for (100)-films under biaxial strain with stresses relaxed along the orthogonal axis.[1,2] Results are collected in Fig. 1. The E_a and E_f energies show nonlinear behavior in the range of ±2% strain; E_f shows asymptotic behavior with two different asymptotes depending on the sign of strain. This is related to the anisotropy of the V^r tensor and correspondingly to the anisotropic response to the external deformation field. For a neutral vacancy in Si, the JT elastic dipole can be treated as a three-state pseudospin, which reflects the three possible tetragonal JT distortions (see schemes in Fig. 1). In the undeformed structure, the three possible orientations lead to three degenerate states with the energy $E_f^{\sigma=0}$. Under biaxial stress σ_{biax}, these three states are splitted: the pseudospin, orthogonal to the deformation plane (see $J_\perp$ in Fig. 1) leads to one state with energy $E_\perp = E_f^{\sigma=0} + 2V_\perp^r \sigma_{\text{biax}}$, while the pseudospins in the plane of deformation (see $J_\parallel$ in Fig. 1) lead to two degenerate states with energy $E_\parallel = E_f^{\sigma=0} + (V_\perp^r + V_\parallel^r)\sigma_{\text{biax}}$. While $E_\perp$ is the ground state for compressive strain, for tensile strain the ground state corresponds to $E_\parallel$. Therefore, two

TABLE I. Parameters of the model of vacancy migration in Si. E_f and E_a are vacancy formation and activation energies (in eV) respectively, V^r and V^a are the relaxation and activation volume tensors, respectively, with componets (in Å^3) corresponding to principal directions. The principal axes $V_\parallel^r$ are parallel to the SC lattice vectors and $V_\parallel^a$ are oriented along the (111) SC lattice diagonals.

E_f	E_a	$V_\parallel^r$	$V_\perp^r$	$V_\parallel^a$	$V_\perp^a$	
3.42	3.71	11.43	−18.51	−20.03	−4.49	Our work
3.69	3.97	12.81	−16.88	−19.32	−3.66	Ref. 6
3.1	3.5					Ref. 7

[a)]Author to whom correspondence should be addressed. Electronic mail: pascal.pochet@cea.fr.

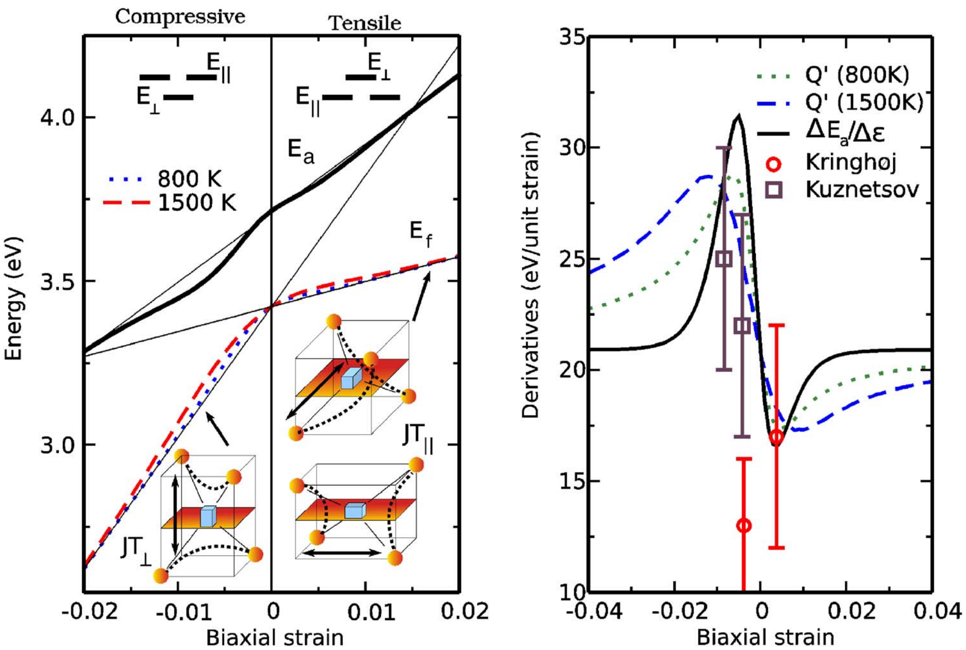

FIG. 1. (Color online) Left: the average values of activation (bold line) and formation (doted and dashed lines) energies calculated by KLMC for biaxially strained Si. The thin lines are $\langle E_a\rangle$ and $\langle E_f\rangle$ asymptotes. Schemes of the JT-dipole oriented orthogonal and parallel to the biaxial strain and its correspondence to the $\langle E_f\rangle$ asymptotes are also shown. Right: strain dependencies of the derivatives Q' and $\Delta E_a/\Delta\varepsilon$ for pure Si. Experimental values are results of Kringhøj *et al.* (Ref. 3) (circles), results extracted from Kuznetsov *et al.* (Ref. 10) as described in Ref. 19 of that article (squares).

different asymptotes are found in the strain dependency of E_f. For small deformations, the energy difference between ground and excited states is in the order of kT and excited state(s) can be thermally activated by reorientation processes. Thermal activation shows different behavior for compressive and tensile strains because the number of excited states are different in the two cases (Fig. 1, left panel). This leads to a significant entropy effect in the temperature dependence of the averaged value of $\langle E_f\rangle$ in the anisotropically deformed crystal and to its nonlinear strain dependence for small deformations.

In contrast to the V^r tensor, the V^a tensor is symmetrical with respect to uniaxial or biaxial strains applied to the (100)-lattice. Thus, the E_a energy for atomic migration does not depend on the initial state of the vacancy site,[11] i.e., the orientation of the pseudospin. For elementary movements by vacancy mediated mechanisms, the diffusivity rate is determined by the migration energy, which is the difference between E_a and E_f of the current state. Diffusivity mechanisms can involve the thermally activated step-by-step processes, where the initial state is first activated to the excited state before migration appears. For large strain values, the occupancy of the excited states is low and diffusivity occurs mainly by transition between vacancy ground states. Therefore, the strain dependency of the averaged $\langle E_a\rangle$ is linear, with a slope, which for biaxial stress is defined by the diagonal elements of the V^a tensor. For small values of strain, the average occupancy of the ground and excited states is of the same order, which enhances diffusivity through excited states. This leads to a nonlinear negative deviation of the averaged $\langle E_a\rangle$ from its asymptotic value (see Fig. 1).

As a result, the strain derivative Q' is not constant and shows a strong dependency on the applied deformation. In Fig. 1 (right panel), we present the calculated strain dependencies in silicon for the Q' parameter at two temperatures, as well as the strain derivative $\Delta E_a/\Delta\varepsilon$. The strain derivative was calculated as a finite difference with respect to the undeformed structure to allow comparison with the corresponding experimental values. The strain derivative of E_a has a simple relation with the Q' parameter, $\Delta E_a/\Delta\varepsilon = Q' - T(\partial Q'/\partial T)$. When we assume $\Delta E_a/\Delta\varepsilon$ to be temperature independent (i.e., Arrhenius law; only one diffusion mechanism is involved[12]) then $Q'(T)$ is a linear function and $\Delta E_a/\Delta\varepsilon$ is its value at 0 K. It is clearly seen that at low values of deformations $(\pm 0.5\%)$ Q' changes rapidly. For large strain $(> \pm 2\%)$ it asymptotically reaches a value of 21 eV per unit strain, which is very close to the value obtained by Ramanarayan *et al.*,[13] where the JT effect and thus the anisotropy of the defect were not taken into account.

Calculated values $\Delta E_a/\Delta\varepsilon$ versus strain cover the range of 16–32 eV per unit strain. Experimental values for Sb tracers, which are believed to be driven by pure vacancy mediator,[4] reproduce our theoretical range when presented as a function of the strain (see Fig. 1). Since Q' rapidly changes within the small ranges of biaxial stresses, we can conclude that uncertainty in different experimental values of Q' is mostly related with nonlinearity of the E_a strain dependency, which is observed for (100)-films.

In contrast, for (111)-oriented films, biaxial strain does not remove the degeneracy of neutral vacancy ground state. All orientations of the pseudospin remain equivalent in this geometry and only the E_a depends on the direction of migrations. Because the differences between splitted energies of barriers are small, E_a depends linearly on strain and Q' is constant.

Finally, our results for the neutral vacancy can be extended to other diffusion mediators in (100)-Si films. Indeed, the charged vacancy states[5] (except V^{2+} with isotropic T_d distortion) would lead to the same entropy effect in the E_a strain dependencies due to the anisotropic elastic response to external biaxial stress. V^{1+} has the same distortion symmetry D_{2d} as the neutral vacancy, therefore, its behavior should be qualitatively similar. V^{1-} is described by C_{2v} point group and its elastic response is characterized by a six-state pseudospin. Under biaxial strain these states lead to three energy levels, where each of them are doubly degenerate, thus entropy effects should also be significant. In the same way, the formation energy of the $\langle 110\rangle$ dumbbell interstitial[6] also splits in a biaxial strain environment allowing entropy effects, while elastic response of tetragonal as well as hexagonal interstitial[6] is isotropic and have no entropy contribution.

In conclusion, we have reported on the strain and temperature dependencies of vacancy mediated self-diffusion in Si. We have found a significant entropy effect for migration of vacancies in anisotropic strain conditions due to the JT distortion. For biaxially deformed (100) Si films, this effect leads to a linear temperature dependence and to a strong nonlinear strain dependence of the parameter Q'. This nonlinearity, being important for small strains, explains the scattering of Q' in published experimental results for these films. For (111) films the entropy effect is negligible and thus the strain dependence of the activation energy E_a is rather linear. This entropy effect should be significant for all materials where diffusion is mediated by defects with an anisotropic elastic response to the stressed environment.

Useful discussions with Dr. T. Deutsch and Dr. M.P. Persson are gratefully acknowledged. This work was partially founded by the French National Research Agency (ANR) through OSiGe_Sim Project No. ANR-05-NANO-004.

[1] N. E. B. Cowern, P. C. Zalm, P. van der Sluis, D. J. Gravesteijn, and W. B. de Boer, Phys. Rev. Lett. **72**, 2585 (1994).

[2] N. R. Zangenberg, J. Lundsgaard Hansen, J. Fage-Pedersen, and A. Nylandsted Larsen, Phys. Rev. Lett. **87**, 125901 (2001).

[3] P. Kringhøj, A. N. Larsen, and S. Y. Shirayev, Phys. Rev. Lett. **76**, 3372 (1996).

[4] M. J. Aziz, Y. Zhao, H.-J. Gossmann, S. Mitha, S. P. Smith, and D. Schiferl, Phys. Rev. B **73**, 054101 (2006).

[5] G. D. Watkins, Phys. Status Solidi A **186**, 176 (2001).

[6] S. A. Centoni, B. Sadigh, G. H. Gilmer, T. J. Lenosky, T. D. de la Rubia, and C. B. Musgrave, Phys. Rev. B **72**, 195206 (2005).

[7] F. El-Mellouhi, N. Mousseau, and P. Ordejon, Phys. Rev. B **70**, 205202 (2004).

[8] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).

[9] A. B. Bortz, M. H. Kalos, and J. L. Lebowitz, J. Comput. Phys. **17**, 10 (1975).

[10] A. Y. Kuznetsov, J. Cardenas, D. C. Schmidt, B. G. Svensson, J. L. Hansen, and A. N. Larsen, Phys. Rev. B **59**, 7274 (1999).

[11] M. S. Daw, W. Windl, N. N. Carlson, M. Laudon, and M. P. Masquelier, Phys. Rev. B **64**, 045205 (2001).

[12] D. Caliste and P. Pochet, Phys. Rev. Lett. **97**, 135901 (2006).

[13] P. Ramanarayanan, K. Cho, and B. M. Clemens, arXiv:cond-mat/0211072.