

Vacancy-mediated diffusion in disordered alloys: Ge self-diffusion in $\text{Si}_{1-x}\text{Ge}_x$

P. Venezuela, G. M. Dalpian, Antônio J. R. da Silva, and A. Fazzio

Instituto de Física, Universidade de São Paulo, CP 66318, CEP 05315-970, São Paulo SP, Brazil

(Received 22 February 2002; published 3 May 2002)

A model is proposed for vacancy mediated diffusion in disordered alloys, with particular application to Ge self-diffusion in $\text{Si}_{1-x}\text{Ge}_x$. We argue that if the vacancies formation energies (VFE) have a strong dependence on the configuration of nearest neighbor (NN) atoms, there will be preferential diffusion paths for some concentrations. For $\text{Si}_{1-x}\text{Ge}_x$ we show that the VFE vary linearly from 2 to 3 eV as the number of NN Ge atoms varies from 4 to 0. Thus, the equilibrium population of the various kinds of vacancies changes significantly with x , and the diffusion proceeds by paths that do not necessarily resemble the concentration of the alloy.

DOI: 10.1103/PhysRevB.65.193306

PACS number(s): 66.30.Fq, 61.72.Bb, 61.72.Ji

The possibility of assembling devices in the nanometer size scale has made the understanding of atomic diffusion a crucial issue.¹ Many of the structures that have been built or proposed rely in their specific atomic distribution profiles to function. Therefore, it is necessary to understand how these atoms diffuse at the relevant temperatures. As far as atomic diffusion in ordered materials is concerned, several theoretical² and experimental³⁻⁵ studies were done recently. But atomic diffusion in disordered materials, due to its complexity, has received much less attention. Nevertheless, the importance of atomic diffusion in a disordered host cannot be overestimated because many of the materials that are technologically important are disordered, for example, substitutionally disordered alloys (e.g., $\text{Si}_{1-x}\text{Ge}_x$), amorphous isolants (e.g., $\alpha\text{-SiO}_2$), and amorphous semiconductors (e.g., $\alpha\text{-Si:H}$).

The interest in studying the $\text{Si}_{1-x}\text{Ge}_x$ alloys stems from the fact that they are, currently, being used in a wide range of technological applications, mainly as heterostructure bipolar transistors. Moreover, many technological applications have been suggested recently, for example, transistors for quantum computing.⁶ Also, from a fundamental point of view, this material may be viewed as a model system to study the effects of disorder. In particular, atomic diffusion can be quite complex in $\text{Si}_{1-x}\text{Ge}_x$. For example, self-diffusion and impurity or dopant diffusion often proceeds via different mechanisms in the elemental components Si and Ge. Therefore, this poses the questions of what are the diffusion mechanisms in the $\text{Si}_{1-x}\text{Ge}_x$ alloy and how do they change with x .

Recently, Zangenber *et al.*⁷ have reported experimental results about the Ge self-diffusion in $\text{Si}_{1-x}\text{Ge}_x$ for $0 \leq x \leq 0.5$. They measured the Ge diffusion coefficients by means of secondary-ion-mass spectrometry, for both relaxed as well as strained alloys, during annealing with temperatures between 850 to 1050 °C. For the relaxed alloys they reported a decrease in the activation energies (E_a) with Ge composition (x). In particular, for $x=0$ and $x=0.5$ they have found $E_a(x=0)=4.65$ eV and $E_a(x=0.5)=3.23$ eV, respectively. Interestingly, the activation energy for $x=0.5$ is already very close to its known value⁴ in pure Ge ($E_a(x=1)=3.09$ eV). To explain this result, the authors speculated that for $x \approx 0.5$ the Ge atoms diffuse by paths that resemble pure Ge.

However, their results lack a firmer theoretical model, since at $x=0.5$ it is not obvious why the Ge atoms would prefer to diffuse always through Ge-like environments. In the present work we provide a microscopic model, based on results obtained by means of systematical *ab initio* calculations, that supports their speculations. We also discuss the diffusion of Ge for other concentrations of the alloy. Our main point is the following: if the diffusion is mediated by intrinsic defects, such as vacancies, for example, and the formation energies of these defects depend strongly on their immediate neighborhood, then, in a disordered alloy, there will be preferential paths for the diffusion (for some concentrations). It should be pointed out that, even though we discuss in detail the Ge self-diffusion in the $\text{Si}_{1-x}\text{Ge}_x$ alloy, this conclusion may be extended to other systems. The hopping ionic conductivity in Ce-doped SrF_2 (Ref. 8) is an example of a diffusion process in a quite different material, but with a mechanism that is similar to what we propose here.

It is believed that self-diffusion in pure Ge is mediated only by vacancies.⁴ On the other hand, in pure Si, Ge diffuses by a combination of vacancy and interstitial-related mechanisms.⁵ Consequently, it is reasonable to assume that vacancy-mediated Ge diffusion is present in $\text{Si}_{1-x}\text{Ge}_x$ for any x , and that interstitial-mediated Ge diffusion is relevant for Si-rich alloys becoming unimportant at some composition x^* , which is experimentally obtained to be around $x^* = 0.2$.⁷

Since $\text{Si}_{1-x}\text{Ge}_x$ is a substitutionally disordered alloy, the vicinity of a vacancy is not uniquely determined. As far as the nearest neighborhood (NN) is concerned, there are five different kinds of vacancies, and to understand the vacancy-mediated Ge diffusion in this alloy it is necessary to determine the relative population of each kind of vacancy for a given composition and temperature.

We have calculated the formation energies of vacancies in $\text{Si}_{0.5}\text{Ge}_{0.5}$ using first-principle methods. To our knowledge, this is the first *ab initio* study of defects properties in a substitutionally disordered material, where the disorder is considered explicitly. We used supercells with 128 atoms where the atoms were distributed as special quasirandom structures (SQS's).⁹ Details of the preparation of the supercell were given elsewhere¹⁰ and here we only mention two important points: (i) due to the SQS approach the disorder of the alloy

is taken into account in an explicit way and (ii) the negative bowing of the lattice parameter of $\text{Si}_{1-x}\text{Ge}_x$ was considered explicitly. Also, it is important to mention that in a 128 atoms supercell the distance between vacancies in neighboring cells is about 15.5 \AA .

The total energy calculations¹¹ are based on the density functional theory¹² with the local density approximation¹³ for the exchange-correlation potential. The electron-ion interactions are described using norm-conserving pseudo-potentials of Bachelet, Hamann, and Schlüter,¹⁴ in the Kleinman-Bylander¹⁵ form. A plane wave basis set with an energy cutoff (E_{cut}) of 12 Ry was used, but tests with $E_{\text{cut}} = 24$ Ry showed that none of our conclusions would be affected by using a larger E_{cut} . The Brillouin zone (BZ) was sampled using the Γ point.

In order to create the vacancy a chosen atom is removed from the 128 atoms cell. However, in a random alloy every site is unique, so we need to sample different possible vacancy sites. We did that by repeating the calculation for vacancies with different vicinities. After the removal of the chosen atom the system is relaxed until all force components are smaller than 25 meV/\AA .

The formation energy of a neutral vacancy sitting in a vicinity denoted by σ is given by

$$E_F^\sigma(i) = E_T^\sigma(i) - E_{\text{Si}_{1-x}\text{Ge}_x} + \mu_i. \quad (1)$$

Here i represents the element that was removed to create the vacancy (Si or Ge), $E_T^\sigma(i)$ is the total energy of the system with the vacancy, $E_{\text{Si}_{1-x}\text{Ge}_x}$ is the total energy of the alloy without any defects, and μ_i is the chemical potential for the element i .¹⁶

We have calculated the vacancies formation energies at the $x=0.5$ alloy for 12 different sites. Those sites were occupied by a Si atom before the vacancy was created.¹⁷ From our results we conclude the following. (i) The most important factor to determine the formation energy of the vacancy is the number of Si and Ge atoms in the NN. Starting with a configuration where there are only Ge atoms surrounding the vacancy, for which the formation energy is slightly above the vacancy formation energy in pure Ge, we observe that, as Si atoms are added to the NN of the vacancy, the formation energy increases until it reaches a value that is slightly below the formation energy of the vacancy in pure Si. This trend in the formation energies is due to the smaller dangling bond energy of a Ge atom when compared to a Si atom. (ii) When sites with the same NN are compared, the formation energies vary by about 0.1 eV for different second neighborhoods (SN's). (iii) For sites with the same first and second neighborhoods the difference in the formation energies is only 0.001 eV. This implies that the configuration of the third neighborhood and beyond is not relevant for the determination of a vacancy formation energy.

In Fig. 1 we plot the formation energies of the vacancies as a function of the number of Si in their NN's. In order to draw a general picture we display the formation energies for the same NN averaged over different SN. The error bars

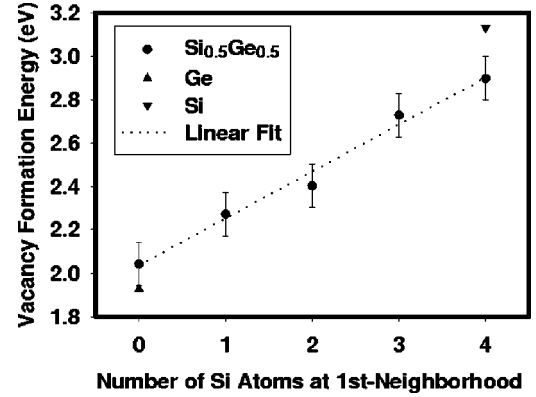


FIG. 1. Formation energies of the vacancies as a function of the number of Si in the nearest neighborhood. The error bars represent schematically the variations in the energies due to different second neighborhood configurations. The linear interpolation (dotted line) is just a guide to the eye. The triangles are the vacancies' formation energies for pure Si (down) and pure Ge (up), respectively.

represent schematically the variation in the energies due to the different SN configurations and the dotted line is a linear interpolation of the data. We see that the formation energies increase almost linearly. The triangles represent the vacancy formation energies in pure Si (Ref. 18) and pure Ge (Ref. 19).

At the thermodynamical equilibrium the population of a σ vacancy in $\text{Si}_{1-x}\text{Ge}_x$ is given by

$$N^\sigma = N_S P^\sigma(x) \exp(-G_F^\sigma/k_B T), \quad (2)$$

where N_S is the total number of sites in the lattice, $P^\sigma(x)$ is the configurational probability for the σ configuration to exist in the x concentration alloy, G_F^σ is the Gibbs free formation energy of the vacancy at configuration σ , and T is the temperature.

Assuming that, for a given temperature and composition, the vibrational entropy and the finite temperature correction of the internal energy of a vacancy is similar for all vicinities,²⁰ we can calculate the relative population of the σ vacancy as

TABLE I. Relative population of vacancies with N_{Ge} Ge atoms in the nearest neighborhood, in equilibrium at $T=950 \text{ }^\circ\text{C}$. (Values smaller than 0.001 are shown as 0.)

N_{Ge}	Ge concentration		
	5%	50%	95%
0	0.243	0	0
1	0.256	0.004	0
2	0.442	0.119	0
3	0.053	0.273	0.023
4	0.006	0.604	0.976

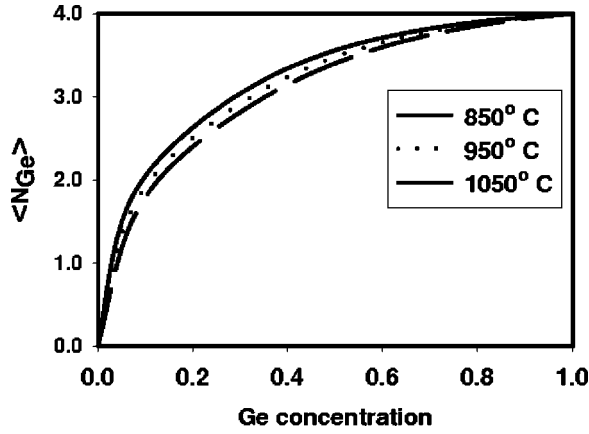


FIG. 2. Average number of Ge atoms in the nearest neighborhood of a vacancy as a function of the composition.

$$n^\sigma(x, T) = \frac{P^\sigma(x) \exp(-E_F^\sigma/k_B T)}{\sum_\sigma P^\sigma(x) \exp(-E_F^\sigma/k_B T)}. \quad (3)$$

In Table I we show the relative populations for each kind of vacancy calculated using Eq. (3). These populations were calculated assuming that the slope of the curve in Fig. 1 (formation energy versus number of Si in the NN), obtained for the $x=0.5$ alloy, does not change significantly for the other compositions. The populations are presented for one of the annealing temperatures of Ref. 7, $T=950^\circ\text{C}$. We can see the following. (i) In the $x=0.5$ alloy, most of the vacancies will have four or three Ge atoms in their NN's, because those are the vacancies with lowest formation energies. (ii) For Ge-rich alloys the relative population of vacancies surrounded only by Ge atoms is even larger due to the statistical predominance of these sites in the network. (iii) For Si-rich alloys there is a competition between two factors: lower formation energies, which favor vacancies with Ge-rich NN's, and the configurational probabilities $P^\sigma(x)$ which favor vacancies with Si-rich NN's. The vacancies with Si_2Ge_2 vicinities will predominate but the populations of all other kinds of vacancies are non-negligible.

In Fig. 2 we plot the average number of Ge atoms in the NN of a vacancy ($\langle N_{\text{Ge}} \rangle$), as a function of the composition x . The three curves correspond to typical annealing temperatures of Ref. 7: $T=850, 950, \text{ and } 1050^\circ\text{C}$. It is interesting to note that these curves are far from being linear, with $\langle N_{\text{Ge}} \rangle$ being already very close to 3.5 at the $x=0.5$ alloy. For $x < 0.5$, $\langle N_{\text{Ge}} \rangle$ decreases quickly to zero and for $x > 0.5$ it increases smoothly to four.

Based on the results presented here we can draw a picture of the vacancy-mediated Ge diffusion in $\text{Si}_{1-x}\text{Ge}_x$ that explains most of the results of Ref. 7. According to Fig. 2 it is clear that there are at least two distinct regimes for this diffusion. If x is about 0.5 or larger, the diffusion will be pure-Ge-like. In Fig. 3 we show a schematic picture of a likely configuration surrounding a vacancy in the alloy for this regime. A diffusion step happens when one of the four labeled Ge atoms in the figure jumps to the vacancy site.

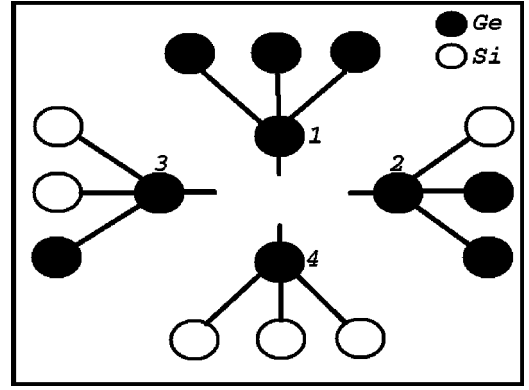


FIG. 3. Schematic picture for a likely vacancy vicinity in $\text{Si}_{1-x}\text{Ge}_x$, for x about 0.5 or larger.

When a given jump occurs, the vacancy changes from a configuration with formation energy E_F^i to a configuration with formation energy E_F^f . The energy barrier for such a jump may be approximately written as $E_m^* + \delta E_F$, where δE_F is either zero when the jump creates a vacancy with lower or equal formation energy, i.e., $E_F^f \leq E_F^i$, or it has the value $\delta E_F = E_F^f - E_F^i$ if the vacancy formation energy increases, i.e., $E_F^f > E_F^i$. The E_m^* term depends only weakly on which process occurs, or, using Fig. 3 as an example, of which of the four atoms is migrating.²¹ Thus, the preferential process to occur will always have the smallest possible δE_F , which in general will be $\delta E_F = 0$. In this case the final vacancy configuration will either be the same as the initial one, or will be such that it has a smaller formation energy. For example, in Fig. 3 the most likely atom to migrate is atom 1 because only this case will result in $\delta E_F = 0$ (the initial and final configurations are the same). This conclusion, together with the result from Fig. 2, implies that the Ge atoms, while migrating, will have predominantly as NN's other Ge atoms, and the diffusion will be similar to the self-diffusion in pure Ge. This explains why, even for $x=0.5$ where there are as many Si as Ge atoms, the experimentally measured activation energy for Ge self-diffusion is already very close to its value in pure Ge.

The other regime applies to the Si-rich alloy. In this case the average number of Ge atoms in the NN of a vacancy drops quickly because vacancies with Si-rich vicinities are progressively more likely to happen. In this regime the diffusion of Ge will be much more complex because the atom will find several kinds of environments while diffusing, and no preferential paths will necessarily exist. However, the activation energy should increase quickly to reach its value in pure Si. Moreover, for low Ge concentration alloys, the interstitial-mediated diffusion should become non-negligible, adding more complexity to the diffusion.

In conclusion, the formation energy of a vacancy in $\text{Si}_{1-x}\text{Ge}_x$ depends strongly in its NN. For a NN with four Ge atoms it is about 2 eV and for a NN with four Si atoms it is about 3 eV. It implies that, at equilibrium, vacancies with Ge rich NN will predominate for x about 0.5 or larger. For Si-rich alloys, the population of vacancies with all possible vi-

cinities will be significant. As a consequence, the vacancy mediated Ge self-diffusion can be analyzed in two main regimes. For x about 0.5 or larger, Ge atoms will diffuse in pure-Ge-like paths. On the other hand, for Si-rich alloys Ge will diffuse by more complex paths, because the exis-

tence of Si atoms that are NN to the vacancies will become unavoidable.

This research was supported by CNPq and FAPESP. We also would like to thank CENAPAD-SP for computer time.

-
- ¹H. Bracht, S. P. Nicols, W. Walukiewicz, J. P. Silveira, F. Briones, and E. E. Haller, *Nature* (London) **408**, 69 (2000).
- ²P. E. Blöchl, E. Smargiassi, R. Car, D. B. Laks, W. Andreoni, and S. T. Pantelides, *Phys. Rev. Lett.* **70**, 2435 (1993); B. Sadigh, T. J. Lenosky, S. K. Theiss, M.-J. Caturla, T. D. da la Rubia, and M. A. Foad, *ibid.* **83**, 4341 (1999); W. Windl, M. M. Bunea, R. Stumpf, S. T. Dunham, and M. P. Masquelier, *ibid.* **83**, 4345 (1999).
- ³A. Ural, P. B. Griffin, and J. D. Plummer, *Phys. Rev. Lett.* **83**, 3454 (1999).
- ⁴M. Werner, H. Mehrer, and H. D. Hochheimer, *Phys. Rev. B* **32**, 3930 (1985).
- ⁵P. Fahey, S. S. Iyer, and G. J. Scilla, *Appl. Phys. Lett.* **54**, 843 (1989).
- ⁶R. Vrijen, E. Yablonovitch, K. Wang, H. W. Jiang, A. Balandin, V. Roychowdhury, T. Mor, and D. DiVincenzo, *Phys. Rev. A* **62**, 012306 (2000).
- ⁷N. R. Zangenberg, J. Lundsgaard Hansen, J. Fage-Pedersen, and A. Nylandsted Larsen, *Phys. Rev. Lett.* **87**, 125901 (2001).
- ⁸P. Dorenbos, S. Vrind, J. Dolfing, and H. W. den Hartog, *Phys. Rev. B* **35**, 5766 (1987).
- ⁹S. H. Wei, L. G. Ferreira, J. E. Bernard, and A. Zunger, *Phys. Rev. B* **42**, 9622 (1990).
- ¹⁰P. Venezuela, G. M. Dalpian, A. J. R. da Silva, and A. Fazzio, *Phys. Rev. B* **64**, 193202 (2001).
- ¹¹M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, *Comput. Phys. Commun.* **107**, 187 (1997).
- ¹²P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964); W. Kohn and L. J. Sham, *Phys. Rev. A* **140**, 1133 (1965).
- ¹³D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹⁴G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- ¹⁵L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ¹⁶ μ_i depends on the growth conditions of the material. For element- i -rich growth conditions, μ_i equals $\mu_{i(\text{bulk})}$, the chemical potential of element i in the bulk, and the chemical potential of the other element equals $\mu_{\text{SiGe}(\text{bulk})} - \mu_{i(\text{bulk})}$. Here we consider only Si-rich conditions, but if Ge-rich conditions would be considered all the formation energies would increase by only 0.014 eV.
- ¹⁷It is unimportant whether a Si or a Ge atom is removed from the alloy to create the vacancy. We have checked this by calculating the formation energies of two vacancies with exactly the same configurations but in which either a Si or a Ge atom was removed. The difference in the formation energies in these two cases is smaller than 0.01 eV.
- ¹⁸M. J. Puska, S. Pöykkö, M. Pesola, and R. M. Nieminen, *Phys. Rev. B* **58**, 1318 (1998).
- ¹⁹A. Fazzio, A. Janotti, A. J. R. da Silva, and R. Mota, *Phys. Rev. B* **61**, 2401 (2000); A. Janotti, R. Baierle, A. J. R. da Silva, R. Mota, and A. Fazzio, *Physica B* **273-274**, 575 (1999).
- ²⁰A. F. Kohan, G. Ceder, D. Morgan, and C. G. Van de Walle, *Phys. Rev. B* **61**, 15 019 (2000).
- ²¹We have calculated the migration barrier for Ge diffusion in pure Si and pure Ge and obtained 0.15 and 0.25 eV, respectively. Therefore, it is likely that E_m^* will fall in this range for all possible migration paths in the alloy.