

## Activation volume for boron diffusion in silicon and implications for strained films

Yuechao Zhao and Michael J. Aziz<sup>a)</sup>

*Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138*

Hans-J. Gossmann

*Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974*

Salman Mitha

*Charles Evans and Associates, 301 Chesapeake Drive, Redwood City, California 94063*

David Schiferl

*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

(Received 2 September 1998; accepted for publication 28 October 1998)

The diffusivity of B in Si is enhanced by pressure, characterized by an activation volume of  $V^* = -0.17 \pm 0.01$  times the atomic volume;  $V^*$  is close to the formation volume of the self-interstitial determined by atomistic calculations. The results for hydrostatic pressure are used to make predictions for the effect of biaxial strain on diffusion. Assuming an interstitial-based mechanism and a range of values for the anisotropy in the migration volume, comparison is made between our results, the atomistic calculations, and the measured dependence of B diffusion on biaxial strain. We find a qualitative consistency for an interstitial-based mechanism with the measured strain effect on diffusion in Si-Ge alloys, but not with the measured strain effect in pure Si. Experiments and calculations to determine the origin of this discrepancy are discussed. © 1999 American Institute of Physics. [S0003-6951(99)03801-2]

Because understanding and controlling diffusion related phenomena become increasingly important as semiconductor device dimensions decrease, diffusion in Si has been heavily studied. Despite this emphasis there remains no consensus about the relative concentrations and mobilities of the point defects involved in the diffusion of many substitutional elements. A study of the dependence of the atomic diffusivity on pressure  $P$  and stress  $\sigma$  can provide valuable information to help elucidate atomistic diffusion mechanisms. Additionally, for band gap engineering purposes, biaxial stress is designed into certain epitaxial semiconductor devices, e.g., heterojunction bipolar transistors for high-power and high-speed applications such as wireless communications. The study of stress effects on diffusion is an important part of the study of the stability of such strained-layer epitaxial materials. Furthermore, although bulk wafers cannot sustain significant nonhydrostatic stresses at diffusion temperatures, such stresses are sustained near interfaces with patterned films and in the films themselves. These stresses in integrated circuit materials and other multilayer devices can be quite large due to growth stresses, interfacial stresses, thermal expansion mismatch, or dislocations.<sup>1</sup> The complexities associated with nonhydrostatic stress states in these materials (as well as in initially biaxially strained materials after the breakdown of a smooth, flat film morphology) make the interpretation of stress effects in terms of basic mechanisms and the prediction of stress effects from known mechanisms quite difficult. However, in certain cases, hydrostatic pres-

sure and simple nonhydrostatic stress states can provide sufficient information to permit the prediction of behavior under arbitrary stress states.<sup>2,3</sup>

Because diffusion of substitutional elements in Si occurs by the superposition of the contributions from vacancy (V)-

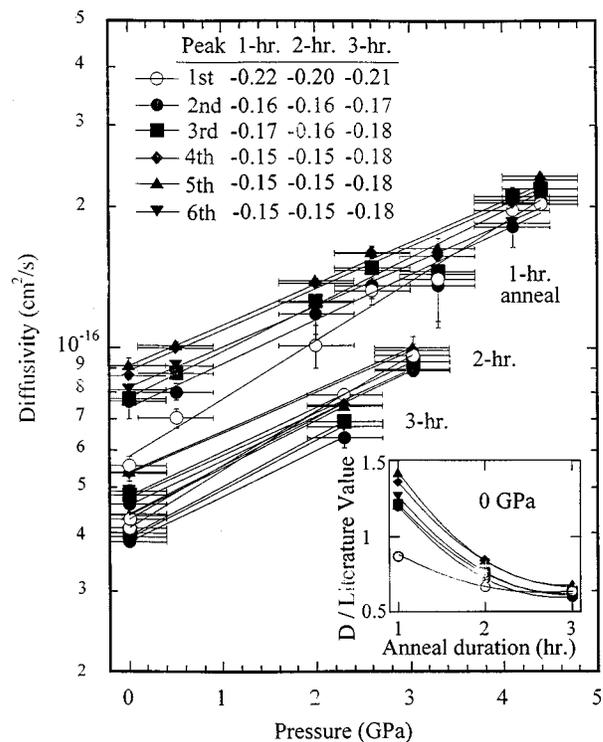


FIG. 1.  $D$  vs  $P$  at 810 °C. Inset: 0 GPa data replotted vs time with quadratic fits to data points; anomalous first spike is lowest curve. The rate of decay for spikes 2–6 appears to be the same at high  $P$  as at 0 GPa.

<sup>a)</sup>Electronic mail: maziz@harvard.edu

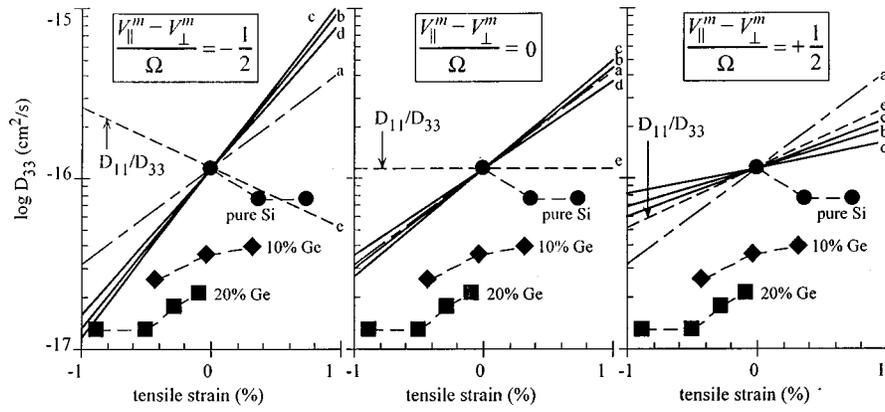


FIG. 2. Comparison of interstitial-based mechanisms in biaxially strained Si-Ge films for the indicated assumed values of migration strain anisotropy. Vertical offsets represent composition effect at constant strain; slopes represent strain effect at constant composition. Data points from Kuo *et al.* for B diffusion in 0%, 10%, and 20% Ge alloys. Curve (a):  $Q'$  reported for OED of Si/Ge multilayers by Cowern *et al.* Curve (b): B diffusion in Si from Eq. (1) and our measurement of  $V^*$ . Also shown is the strain dependence of the I-based contribution to Si self-diffusion, from Eq. (1) using: (c) the TBA calculation of Tang *et al.* for the  $\langle 110 \rangle$  dumbbell self-interstitial ground state and assuming  $V_I^m = 0$ ; (d) the *ab initio* calculation of Antonelli and Bernholc assuming a tetrahedral interstitial saddle point. Curve (e): ratio of  $D_B$  parallel ( $D_{11}$ ) and perpendicular ( $D_{33}$ ) to surface in Si. Straight lines chosen to go through unstrained pure Si data point; only slopes are significant except for curve (b).

and interstitial (I)-mediated mechanisms, the diffusivity responds to variations in I and V concentrations induced by temperature ( $T$ ),  $P$ , and nonequilibrium point defect injection. When a solid is subjected to changes in  $P$  and  $T$ , the mobilities of all point defects are altered immediately. Additionally, the point defect concentrations quickly re-equilibrate at the surfaces and other point defect sources, if they exist; a growing diffusional zone of point defect re-equilibration then sweeps through the specimen from these sources. When the region sampled by experiments equilibrates rapidly with the sources compared to the experimental time scale, the measured diffusivity is the equilibrium value. Under these circumstances, the  $P$  dependence of the diffusivity is commonly characterized by the activation volume,  $V^* = -kT \partial \ln D_A(T, P) / \partial P$ , where  $D_A$  is the equilibrium diffusivity under intrinsic doing conditions for element A in Si and  $kT$  has the usual meaning. There is growing evidence<sup>4</sup> that boron diffusion is almost solely I mediated, in which case it can be shown that  $V^* = V_{BI}^f + V_{BI}^m = V_I^f + V^{\text{asso}} + V_I^m + (V_{BI}^m - V_I^m)$ , where the formation volume  $V_{BI}^f$  is the volume change of the system upon formation of a B-I pair, the migration volume  $V_{BI}^m$  is the additional volume change when the B-I pair reaches the saddle point in its migration path,  $V_I^f$  and  $V_I^m$  are the formation and migration volumes, respectively, of a bare Si self-interstitial, and the pairing volume  $V^{\text{asso}}$  is the volume change upon association of a B-I pair from a widely separated B and I. Although the corresponding terms in the activation energy have been predicted by atomistic calculations and volume changes for V-based mechanisms have been calculated,<sup>5-8</sup> few volume changes have been calculated for I-based mechanisms.<sup>5,6</sup>

In the present study we used B delta-doped Si(001) superlattices (DSL) for high sensitivity  $D_B$  measurements. The DSL samples were fabricated by low  $T$  molecular beam epitaxy growth<sup>9</sup> on a float-zoned substrate. Samples contain six equally spaced  $\sim 10$ -nm-wide B-rich layers spaced 100 nm apart with peak concentrations of  $2 \times 10^{19}$  atoms/cm<sup>3</sup>. The first spike is at 70 nm depth. Diffusion in these samples in vacuum and in Ar at atmospheric  $P$  has been characterized

extensively.<sup>9</sup> The bulk, as-grown samples were thinned mechanically from the back side to  $\sim 35 \mu\text{m}$  thick. After thinning, the samples were cleaned using the standard RCA method, leaving a clean SiO<sub>2</sub> layer. To prevent oxidation-enhanced diffusion a 12-nm-thick Si<sub>3</sub>N<sub>4</sub> layer was immediately deposited on the freshly cleaned samples using argon-nitrogen dual-beam sputtering at low temperature.

High  $P$  anneals were performed in a high- $T$ , high- $P$  diamond anvil cell (DAC) using fluid argon as the inert, clean (0.99998 and passed through a Ti gettering furnace), hydrostatic  $P$  transmitting medium.  $P$  in the DAC was measured<sup>10</sup> using the  $P$ -induced wavelength shift of Sm:yttrium-aluminum-garnet (YAG) fluorescence. The B concentration-depth profiles were measured using secondary ion mass spectrometry (SIMS) with an 8 keV primary oxygen ion beam at 27° from normal incidence.<sup>11</sup>

Values for  $D_B$  were determined using the process simulator PROPHET by evolving the measured initial profile numerically and finding the best fit to the measured final profile. Under extrinsic doping conditions, which is the case for our samples, the extrinsic diffusivity  $D_B^{\text{EXT}}$  is expressed as  $D_B^{\text{EXT}} = [hD_B / (1 + \beta)](1 + \beta p / n_i)$ ,<sup>12-14</sup> where  $p$  is the hole concentration,  $n_i$  is the  $P$ -dependent<sup>15</sup> intrinsic carrier concentration,  $h$  is the electric field enhancement factor, and  $\beta$  is the ratio of the contributions to B diffusion from positively charged and neutral interstitials. Because these contributions have the same activation energy,<sup>13</sup> we have assumed<sup>16</sup> that they also have the same activation volume resulting in a  $P$ -independent  $\beta$ .

In Fig. 1 we show the time-averaged intrinsic diffusivity over 1-3 h anneals versus  $P$ . The activation volumes for the individual spikes are reported in units of  $\Omega$ , the atomic volume of Si at standard  $T$  and  $P$ . The decrease of  $D_B$  with time, shown explicitly in the inset, is consistent with the measured<sup>14</sup> effective self-interstitial diffusivity of  $D_I = 1.5 \times 10^{-12}$  cm<sup>2</sup>/s in these samples; this value yields a diffusion time of 40 min for penetration of the diffusional boundary layer from the surface to the bottom spike. We expect therefore that  $V^*$  measured on the longer anneals is truly charac-

teristic of equilibrium conditions. The nature of the uncharacteristic behavior of the first spike and the transient behavior for all spikes is not understood; the latter may be related to dissolved oxygen precipitation,<sup>17</sup> as our molecular beam epitaxy (MBE)-grown layers have an oxygen content of  $\sim 10^{18}/\text{cm}^3$ . However, with the exception of the first spike, all  $V^*$  values lie in the range  $(-0.17 \pm 0.02)\Omega$ . Therefore our measurement of  $V^*$  using spikes 2–6 is not subject to the nuances of the interpretation of the origin of the time dependence.<sup>18</sup>

Recently, an *ab initio* calculation was made of the energetics of B diffusion in Si;<sup>19</sup> however, there has not yet been a calculation of the corresponding volumetrics involving B. In the absence of dopants, a  $\langle 110 \rangle$  dumbbell self-interstitial ground state with  $V_1^f = -0.10 \Omega$  was predicted by a recent tight-binding approximation (TBA)-based calculation.<sup>6</sup> In combination with our measurements, this implies  $V_{\text{BI}}^{\text{asso}} + V_{\text{BI}}^m = -0.07 \Omega$ , a quite small value that is not inconsistent with the common assumption that each of these individual terms is negligible. The TBA calculation also predicts the tetrahedral interstitial configuration ( $I_T$ ) to be the saddle point of the migration path. If this is true, the formation volume of  $I_T$ , predicted to be  $-0.28 \Omega$  by an early *ab initio* calculation,<sup>5</sup> represents  $V_1^f + V_1^m$ . All three results would be mutually consistent if  $V_1^m = -0.18 \Omega$ .

We now compare our results and those of the atomistic calculations with the measured effect of biaxial stress on diffusion. Experimentally,<sup>20</sup> the influence of biaxial stress has been commonly characterized by  $Q'$ , the apparent change in activation energy  $E^*$  with biaxial (tensile) strain  $\epsilon$  at constant composition. There is a thermodynamic relationship<sup>2</sup> between hydrostatic and biaxial stress effects on the diffusivity:

$$\frac{V^*}{\Omega} + \frac{3}{2} \frac{Q'}{Y\Omega} = \pm 1 + (V_{\parallel}^m - V_{\perp}^m)/\Omega, \quad (1)$$

where the  $+$ ( $-$ ) sign is for a vacancy (interstitial)-based mechanism,  $Y$  is the biaxial modulus, and  $(V_{\parallel}^m - V_{\perp}^m)/\Omega$  is the anisotropy in the migration volume. Experimentally, Kuo *et al.*<sup>21</sup> isolated the effects of strain and composition on B diffusion normal to the surface in biaxially strained Si–Ge alloy films. Their results are the data points in Fig. 2. Also, Cowern *et al.*<sup>20</sup> reported a value of  $Q' = -12 \pm 6$  eV per unit strain for the interstitial contribution to oxidation-enhanced interdiffusion of Si–Ge. The long-short dashed curve (a) represents their inferred  $Q'$  value at 810 °C. The predicted biaxial strain dependence of B diffusion in pure Si, made from our experiment [curve (b)] using Eq. (1), is plotted assuming a reasonable range for the anisotropy in the migration volume, 0 or  $\pm 1/2$  as indicated. Also shown are predictions made from Eq. (1) and the atomistic calculations. The slopes of the data of Kuo *et al.* for B diffusion in the Si–Ge alloys fall within the range of the other values for  $(V_{\parallel}^m - V_{\perp}^m)/\Omega = 0$  or  $\pm 1/2$  whereas the slope of their data for B diffusion in pure Si under tensile strain is opposite in sign. The similarity of the slopes in curves (a)–(d) and in the alloy data of Kuo *et al.* indicate a qualitative consistency with an interstitial-based mechanism for these cases whereas their pure Si data do not follow this consistent pattern. Kuo *et al.* suggested that the difference between the pure Si and alloy data may be

due to B–Ge pairing in the alloys. Although this may be true, it does not explain the discrepancy between the predictions and the pure Si data. Direct measurements of the activation volume in the alloys would help solve this puzzle. Additionally, a direct theoretical or experimental determination of the migration volume anisotropy would be of great value.<sup>3</sup> Knowledge of this parameter would also permit the prediction of the effect of an arbitrary stress state on the diffusivity in an arbitrary direction, which would be of great value in process simulation. The anisotropy in  $D_B$  resulting from the various values of the migration strain anisotropy is shown by curve (e) in the figures.

Work at Harvard was supported by NSF-DMR-95-25907. Work at LANL was supported by the Division of Materials Sciences, DOE under Contract No. W-7405-ENG-36 with the University of California.

<sup>1</sup>H. Park, K. S. Jones, J. A. Slinkman, and M. E. Law, *J. Appl. Phys.* **78**, 3664 (1995).

<sup>2</sup>M. J. Aziz, *Appl. Phys. Lett.* **70**, 2810 (1997).

<sup>3</sup>M. J. Aziz, *Mater. Res. Soc. Symp. Proc.* **469**, 37 (1997).

<sup>4</sup>H.-J. Gossmann, T. E. Haynes, P. A. Stolk, D. C. Jacobson, G. H. Gilmer, J. M. Poate, H. S. Luftman, T. K. Mogi, and M. O. Thompson, *Appl. Phys. Lett.* **71**, 3862 (1997).

<sup>5</sup>A. Antonelli and J. Bernholc, *Phys. Rev. B* **40**, 10643 (1989). This early calculation did not consider a wide variety of possible defect relaxations.

<sup>6</sup>M. Tang, L. Colombo, J. Zhu, and T. Diaz de la Rubia, *Phys. Rev. B* **55**, 14279 (1997).

<sup>7</sup>O. Sugino and A. Oshiyama, *Phys. Rev. B* **42**, 11869 (1990).

<sup>8</sup>A. Antonelli, E. Kaxiras, and D. J. Chadi, *Phys. Rev. Lett.* **81**, 2088 (1998).

<sup>9</sup>H.-J. Gossmann, in *Delta Doping of Semiconductors*, edited by E. F. Schubert (Cambridge University Press, Cambridge, 1996), pp. 161 and 253.

<sup>10</sup>Y. C. Zhao, W. Barvosa-Carter, S. D. Theiss, S. Mitha, M. J. Aziz, and D. Schiferl, *J. Appl. Phys.* **84**, 4049 (1998).

<sup>11</sup>The run-to-run temperature reproducibility is responsible for a  $\pm 7\%$  uncertainty in  $D$ ; the run-to-run SIMS depth profiling reproducibility is typically responsible for another  $\pm 7\%$  uncertainty.

<sup>12</sup>P. M. Fahey, P. B. Griffin, and J. D. Plummer, *Rev. Mod. Phys.* **61**, 289 (1989).

<sup>13</sup>R. B. Fair, in *Impurity Doping Process in Silicon*, edited by F. F. Y. Wang (North-Holland, Amsterdam, 1981), p. 315.

<sup>14</sup>H.-J. Gossmann, G. H. Gilmer, C. S. Rafferty, F. C. Unterwald, T. Boone, J. M. Poate, H. S. Luftman, and W. Frank, *J. Appl. Phys.* **77**, 1948 (1995).

<sup>15</sup>Via the  $-24.5$  meV/GPa band gap narrowing; see S. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981), p. 16.

<sup>16</sup>This assumption could result in a small error that can be corrected when appropriate data become available.

<sup>17</sup>W. T. C. Fang, T. T. Fang, P. B. Griffin, and J. D. Plummer, *Appl. Phys. Lett.* **68**, 2085 (1996).

<sup>18</sup>An alternative interpretation, that the time scale for self-interstitials to reach spikes 2–6 from the surface is much longer than 3 h, seems implausible in light of the measured value of  $D_1$  quoted above.

<sup>19</sup>J. Zhu, T. Diaz de la Rubia, L. H. Yang, C. Mailhot, and G. H. Gilmer, *Phys. Rev. B* **54**, 4741 (1996).

<sup>20</sup>N. E. B. Cowern, W. J. Kersten, R. C. M. de Kruif, J. G. M. van Berkum, W. B. de Boer, D. J. Gravesteijn, and C. W. T. Bulle-Liewma, in *Proceedings of the 4th International Symposium on Process Physics and Modeling in Semiconductor Devices*; edited by G. R. Srinivasan, C. S. Murthy, and S. T. Dunham (Electrochemical Society, Pennington, NJ, 1996), Vol. 96-4.

<sup>21</sup>P. Kuo, J. L. Hoyt, J. F. Gibbons, J. E. Turner, and D. Lefforge, *Appl. Phys. Lett.* **66**, 580 (1995).