

Activation volume for phosphorus diffusion in silicon and $\text{Si}_{0.93}\text{Ge}_{0.07}$

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The hydrostatic pressure dependence of the diffusivity of P in compressively strained $\text{Si}_{0.93}\text{Ge}_{0.07}$ and unalloyed Si has been measured. In both cases the diffusivity is almost independent of pressure, characterized by an activation volume V^* of $(+0.09 \pm 0.11)$ times the atomic volume Ω for the unalloyed Si, and $(+0.01 \pm 0.06) \Omega$ for $\text{Si}_{0.93}\text{Ge}_{0.07}$. The results are used in conjunction with the reported effect of biaxial strain on diffusion normal to the surface to test the prediction for an interstitialcy-based mechanism of Aziz's phenomenological thermodynamic treatment of diffusion under uniform nonhydrostatic stress states. The prediction agrees well with measured behavior, lending additional credence to the interstitial-based mechanism and supporting the nonhydrostatic thermodynamic treatment. © 2005 American Institute of Physics. [DOI: 10.1063/1.1896445]

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 dopants. A study of the dependence of the atomic diffusivity on pressure P and stress σ can provide valuable information to help elucidate atomistic diffusion mechanisms. Additionally, biaxial strain is commonly designed into epitaxial semiconductor devices for enhanced carrier mobility or band gap engineering purposes. 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.¹ The complexities associated with spatially nonuniform 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 pressure and simple nonhydrostatic stress states can provide sufficient information to permit the prediction of behavior under arbitrary stress states.²

Because diffusion of substitutional elements in Si occurs by the superposition of the contributions from vacancy (V) and interstitial (I)-mediated mechanisms, the diffusivity responds to variations in I and V concentrations induced by temperature T , P , and 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

at 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, $V^* \equiv -kT\partial(\ln D_A)/\partial P$, where D_A is the equilibrium diffusivity under intrinsic doping conditions for element A in Si and k is Boltzmann's constant. It appears that at low and intermediate concentrations, phosphorus diffusion is almost solely I mediated,³ in which case it can be shown that $V^* = V_{PI}^f + V_{PI}^m = V_I^f + V^{\text{asso}} + V_I^m + (V_{PI}^m - V_I^m)$, where the formation volume V_{PI}^f is the volume change of the system upon formation of a PI pair, the migration volume V_{PI}^m is the additional volume change when the PI 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^{asso} is the volume change upon association of a PI pair from a widely separated P 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,⁴ few volume changes have been calculated for I -based mechanisms.⁵

The samples for the present investigation were grown on (001)-Czochralski Si wafers at the molecular beam epitaxy facility at University of Aarhus.⁶ Two compositions were used for the experiment. The structure of the unalloyed Si sample, denoted "0%," is Si(200 nm)/P-doped Si(25 nm)/Si(600 nm)/Si(001) substrate. The structure of the alloy sample, denoted "7%," is Si(100 nm)/compressively strained $\text{Si}_{0.93}\text{Ge}_{0.07}$ (60 nm)/P-doped, compressively strained $\text{Si}_{0.93}\text{Ge}_{0.07}$ (25 nm)/compressively strained $\text{Si}_{0.93}\text{Ge}_{0.07}$ (60 nm)/Si(500 nm)/Si(001) substrate. The peak concentration of P spike, located at a depth of ~ 200 nm, is $1 \times 10^{19} \text{ cm}^{-3}$, which is slightly higher than the intrinsic carrier concentration of $n_i = 3 \times 10^{18} \text{ cm}^{-3}$ at the anneal temperature 840°C .⁷ The samples contain $< 10^{18} \text{ cm}^{-3}$ of carbon and $< 10^{16} \text{ cm}^{-3}$ of oxygen.

To shield the surface from reacting with the atmosphere and thereby minimize the injection of point defects, the

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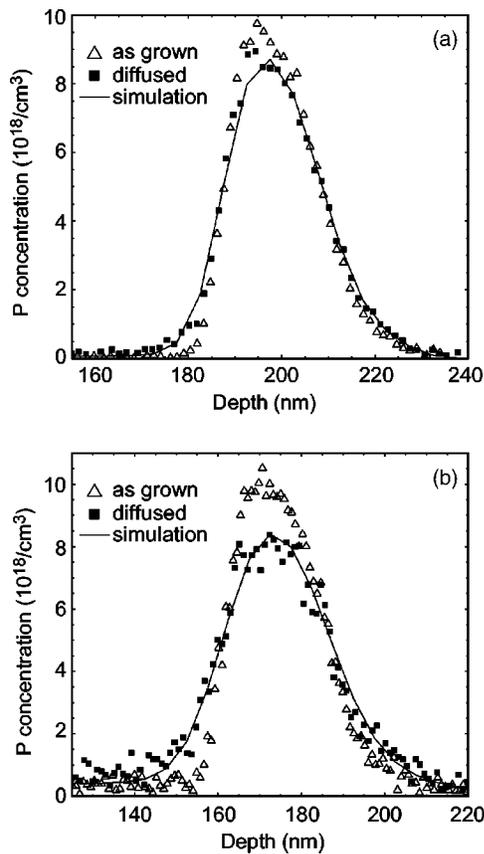


FIG. 1. SIMS concentration-depth profiles for (a) unstrained unalloyed Si sample and (b) 7% Ge sample under biaxial compressive strain. Triangles: as-grown samples. Squares: after annealing at 840 °C for 1 h at (a) 0 GPa; (b) 2.3 GPa. The solid line represents the result from the simulation using the linear diffusion equation with (a) $D=2.4 \times 10^{-17}$ cm²/s; (b) $D=7.6 \times 10^{-17}$ cm²/s.

samples were capped by radio frequency sputtered 100 nm SiO₂ followed by 100 nm Si₃N₄ layers. Uncertainties associated with the transient time to establish point defect equilibrium⁸ are believed to be significant; experiments on samples annealed in forming gas^{6,9} indicate a possible systematic error of 20% in D .

For pressure annealing, the bulk, as-grown samples were thinned mechanically from the backside to ~ 35 μ m thick in order to fit to the sample chamber. High P anneals were performed in a high- T , high- P diamond anvil cell (DAC) using fluid argon as the inert, clean, hydrostatic pressure transmitting medium. P in the DAC was measured¹⁰ using the P -induced wavelength shift of Sm: yttrium–aluminum–garnet fluorescence. The details are described elsewhere.¹¹

Phosphorus concentration-depth profiles were measured using secondary ion mass spectrometry (SIMS) using an Atomika 4000 apparatus with a 3.5 keV beam of O₂⁺ at an angle of 20° from normal. In Fig. 1 we show representative concentration-depth profiles measured by SIMS.

The values of D_P were determined by evolving the measured as-grown profiles numerically according to the diffusion equation and finding the value of the diffusivity for the best fit to the measured final profiles. Noise in the tails of the profiles introduced unnecessary levels of noise in the resulting activation volume and so the region over which the simulation was compared to the measured profile was restricted to 185–220 nm for 0% samples and 150–200 nm for 7% samples. Because the results of fitting the 0% profiles to the

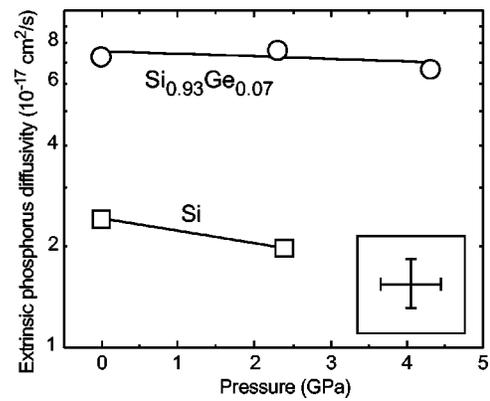


FIG. 2. Phosphorus diffusivity vs pressure at 840 °C. Circles: Si_{0.93}Ge_{0.07} samples under biaxial compressive strain; squares: unstrained unalloyed Si samples. The cross in the inset is a typical error bar.

nonlinear diffusion equation¹² were more sensitive to the locations of the boundaries of the comparison region than were the results of fitting to the linear diffusion equation, we chose to pursue fits to the linear diffusion equation only. The result is a report of the concentration-averaged actual (or extrinsic) diffusivity.¹³ For these samples the reported value of V^* is not affected by the choice of diffusion equation.

In Fig. 2 we show the best-fit diffusivity versus pressure.¹⁴ The best-fit activation volume is $V^* = (0.09 \pm 0.11)\Omega$ for Si, and $(0.01 \pm 0.06)\Omega$ for Si_{0.93}Ge_{0.07}, where Ω is the atomic volume at standard temperature and pressure. The small positive value indicates that pressure retards phosphorus diffusion very slightly, if at all.

The nonhydrostatic thermodynamic treatment of diffusion of Aziz² proposes a relationship between the activation volume V^* characterizing diffusion under hydrostatic pressure and the derivative Q' of the apparent activation energy with respect to biaxial strain at constant composition

$$\frac{V^*}{\Omega} + \frac{3}{2} \frac{Q'}{Y\Omega} = \pm 1 + A, \quad (1)$$

where the plus sign applies to a vacancy mechanism, the minus sign to an interstitial-based mechanism, Y is the biaxial modulus at elevated temperature and pressure, and A is the anisotropy of the migration volume (for $A=0$ diffusion remains isotropic under biaxial strain). Equation (1) is consistent with the diffusion results for Sb, a vacancy diffuser,^{11,15} but inconsistencies have been observed for the diffusion of boron, which diffuses by an interstitial-based mechanism.^{11,16}

Phosphorus diffusion in strained and strain-relaxed Si_{1-x}Ge_x has been measured by Christiansen *et al.*,¹⁷ who were able to estimate from their results an average value of $Q' = -13$ eV per unit strain for alloys spanning $x=0.1-0.2$. In obtaining this estimate they made the assumptions that (i) over the range $x=0-0.2$, Q' is independent of composition; (ii) for each composition, Q' is the same for strained and unstrained material; (iii) the pre-exponential factor varies in a specified way over this composition range; and (iv) the pre-exponential factor is independent of strain. The value of Q' for unalloyed Si is not measured directly but only presumed to be the same as for alloys of 10%–20% Ge. We use Eq. (1) to compare phosphorus diffusion under hydrostatic and biaxial stress using our measured values of V^* and Christiansen *et al.*'s value of Q' . In Table I we show the value of

TABLE I. Migration volume anisotropy, A , calculated from Eq. (1) using the activation volumes measured in this work and the biaxial strain effect reported by Christensen *et al.* The uncertainties in A exceed the uncertainties in V^*/Ω by the unreported uncertainties associated with the Q' measurement.

| Material | V^*/Ω | Q' (eV) | A for interstitial-based mech. | A for vacancy-based mech. |
|---|-----------------|-----------|----------------------------------|-----------------------------|
| Unstrained unalloyed Si | 0.09 ± 0.11 | -13 | $0.13 \pm$ at least 0.11 | $-1.86 \pm$ at least 0.11 |
| Biaxially strained $\text{Si}_{0.93}\text{Ge}_{0.07}$ | 0.01 ± 0.06 | -13 | $0.04 \pm$ at least 0.06 | $-1.96 \pm$ at least 0.06 |

the migration volume anisotropy required to reconcile the experimental results assuming both an interstitial-based mechanism and a vacancy-based mechanism in turn. The unreasonably large^{11,16} resulting value of the anisotropy for a vacancy-based mechanism is consistent with existing evidence that P diffusion occurs virtually entirely by an interstitial-based mechanism.³ The near-zero resulting value for the anisotropy for an interstitial-based mechanism is very reasonable. In fact, based solely on crystallography, $A=0$ has been predicted by Daw *et al.*¹⁸ for boron diffusion by an interstitialcy mechanism with a hexagonal saddle point and a ground state consisting of a substitutional boron bound to a silicon self-interstitial. *Ab initio* calculations¹⁹ indicate that phosphorus diffuses through a similar mechanism, in which case we might expect $A=0$ here as well. The uncertainty in Q' has not been reported but we expect that it is sufficiently large that the difference between zero and the resulting value for A in Table I is insignificant.

Equation (1) with $A=0$ has been shown^{11,15} to describe very well the behavior of Sb diffusion in Si and dilute Ge alloys. However, for boron diffusion large inconsistencies with Eq. (1) with $A=0$ have been observed^{11,16} between individual data sets for Q' and the V^* measurements.

Large inconsistencies among the data sets for Q' themselves have also been noted.¹¹ The reasons for the inconsistencies with the predicted value of $A=0$ are presently unknown, but it is natural to speculate that the phenomenological thermodynamic treatment may not be valid for the interstitialcy mechanism, possibly due to subtleties about the degeneracies and point symmetries of ground-state and saddle-point configurations.^{11,18} The present work shows the first success of the nonhydrostatic thermodynamic treatment for an interstitial-based mechanism. It is worth noting that for both Sb and P, the measured values of V^*/Ω are small and non-negative (lying between about 0.0 and 0.1) despite different point-defect mechanisms, and the power of the nonhydrostatic thermodynamic treatment is a successful “prediction” of very different Q' values for the two cases (+17 eV for Sb vs -13 eV for P) from a knowledge of the mechanism. The resolution for other cases must await future work.

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¹³That is, the ratio of the phosphorus flux to the phosphorus concentration gradient. The fitting results in an average value over the concentration regime over which our measurement is sensitive: from about $10^{18}/\text{cm}^3$ to $10^{19}/\text{cm}^3$; n_i falls near the middle of this range.

¹⁴The uncertainties in D relevant for reckoning the uncertainty in V^* arise from run-to-run temperature irreproducibility and sample-to-sample SIMS irreproducibility. We also account for variations in the fitted V^* resulting from varying the boundaries of the fitted region of all samples together. The run-to-run temperature reproducibility is responsible for a $\pm 7\%$ uncertainty in D . The uncertainty in the pressure measurement is ± 0.4 GPa over the range 0–5 GPa but is virtually zero for the 0 GPa samples. In the unalloyed Si (low diffusivity) samples we estimated the combined effects of $\pm 7\%$ uncertainty in D due to temperature measurement and $\pm 17\%$ uncertainty in nonzero P from a statistical simulation resulting in $V^* = (0.09 \pm 0.10) \Omega$. We separately evaluated the uncertainty in V^* due to the uncertainty in SIMS depth profiling as $\pm 0.04 \Omega$ by varying our treatment of the SIMS data (e.g., depth scale calibration) within bounds given by their uncertainties. These contributions were assumed to add in quadrature, resulting in an overall uncertainty of $\pm 0.11 \Omega$. In the Si-Ge alloy (high diffusivity) samples, the run-to-run SIMS depth profiling reproducibility is responsible for only a $\pm 7\%$ uncertainty in D , which we added in quadrature to the $\pm 7\%$ uncertainty due to temperature measurement to obtain a nominal uncertainty in D of $\pm 10\%$. We estimated the combined effects of these uncertainties in D and the uncertainty in P by a statistical simulation resulting in $V^* = (0.01 \pm 0.06) \Omega$. For the purpose of evaluating V^* we have ignored these systematic errors in D : the difference between extrinsic and intrinsic diffusivity (factor of 0.6) the transient time for point defect equilibration (possible 20% error) the sensitivity of the fitted D to the boundaries of the fitted region in each individual sample (possible 10% error) the uncertainty in depth scale for the as-grown concentration-depth profile (possible 5% error).

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