Activation volume for antimony diffusion in silicon and implications for strained films

Yuechao Zhao and Michael J. Aziz[a)]
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

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The diffusivity of Sb in Si is retarded by pressure, characterized at 860 °C by an activation volume of $V^* = +0.07 \pm 0.02$ times the Si atomic volume. V^* is close to values inferred from atomistic calculations for a vacancy mechanism. Our results for hydrostatic pressure are used to predict the effect of biaxial strain on Sb diffusion. The prediction matches measured behavior for Sb diffusion in biaxially strained Si and Si–Ge films. This work lends additional support to the predominance of the vacancy mechanism for Sb diffusion and demonstrates the first steps in the development of a capability for predicting the effect of nonhydrostatic stress on diffusion. © *1999 American Institute of Physics.* [S0003-6951(99)03233-7]

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 σ can provide valuable information to help elucidate atomistic diffusion mechanisms. Additionally, for band-gap engineering purposes, biaxial strain 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.[1] 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 pressure and simple nonhydrostatic stress states can provide sufficient information to permit the prediction of behavior under arbitrary stress states.[2–4]

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 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 reequilibrate at the surfaces and other point defect sources, if they exist; a growing diffusional zone of point defect reequilibration 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 doping conditions for element A in Si and kT has the usual meaning. There is a general consensus[5] that Sb diffusion is almost solely V mediated, in which case it can be shown that $V^* = V^f_{\mathrm{Sb}V} + V^m_{\mathrm{Sb}V} = V^f_V + V^{\mathrm{asso}} + V^m_{\mathrm{Sb}V} = (+\Omega + V^{\mathrm{rel}}_V) + V^{\mathrm{asso}} + V^m_{\mathrm{Sb}V}$, where the formation volume $V^f_{\mathrm{Sb}V}$ is the volume change of the system upon formation of a Sb-V pair by creating a vacancy at a kink site at the surface and bringing it next to a preexisting Sb; the migration volume $V^m_{\mathrm{Sb}V}$ is the additional volume change when the Sb-V pair reaches the saddle point in its migration path; V^f_V is the formation volume of an isolated vacancy, which is the sum of the Si atomic volume, Ω, and the relaxation volume V^{rel}_V; and the pairing volume V^{asso} is the volume change upon association of a Sb-V pair from a widely separated Sb and V. Several of these volume changes for V-based mechanisms have been predicted by *ab initio* and atomistic calculations.[6–9]

In the present study we used Sb delta-doped Si(001) superlattices (DSL) for high sensitivity D_{Sb} measurements. The DSL samples were fabricated by low T molecular beam ep-

[a)]Electronic mail: maziz@harvard.edu

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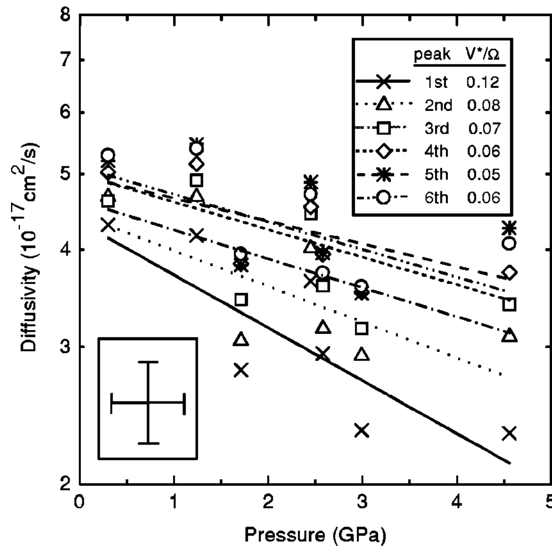

FIG. 1. Intrinsic Sb diffusivity vs P at 860 °C. Typical error bars for data points are shown in inset on the left-hand side. Activation volumes calculated from best-fit slopes are shown in inset at right-hand side.

itaxy growth[10] on a float-zone substrate. Samples contain six equally spaced ~10 nm wide Sb-rich layers spaced 100 nm apart with peak concentrations of 6×10^{19} atoms/cm^3. The first spike is at 50 nm depth. Diffusion in these samples in vacuum and in Ar at atmospheric P has been characterized extensively.[10] The bulk, as-grown samples were thinned mechanically from the backside to ~35 μm thick. After thinning, the samples were cleaned using the standard RCA method,[11] leaving a clean SiO_2 layer. To prevent ambient effects on diffusion, a Si_3N_4/SiO_2 passivation layer was produced by immediately depositing a 12 nm thick Si_3N_4 layer on the freshly cleaned samples using argon–nitrogen dual-beam sputtering below 180 °C.

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 hot Ti gettering furnace), hydrostatic P transmitting medium. P in the DAC was measured[12] using the P-induced wavelength shift of Sm:YAG fluorescence. The Sb concentration-depth profiles were measured using secondary ion mass spectrometry (SIMS) with an 8 keV primary oxygen ion beam at 26° from normal incidence.

Values for D_{Sb} 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 is expressed as $D_{Sb}^{ext}=hD_{Sb}(1+\beta n/n_i)/(1+\beta)$,[13–15] where n is the electron concentration, n_i is the P-dependent[16] intrinsic carrier concentration, h is the electric field enhancement factor, and β is the ratio of the contributions to Sb diffusion from negatively charged and neutral vacancies. We have assumed[17] that these contributions have the same activation volume resulting in a P-independent β.

In Fig. 1 we show the time-averaged intrinsic diffusivity[18] for 1 h anneals versus P. Our measured values, extrapolated to 1 atm, are consistent with the values of $4-5\times10^{-17}$ cm^2/s obtained from previous measurements with ~1 atm Ar as the annealing ambient.[19] The average of

TABLE I. Theoretical and measured volume changes (in units of Ω) associated with Sb diffusion in Si. Values for the right-hand side column are obtained by subtracting V_V^f from V^*; in the bottom three rows our experimental value of V^* is used.

Work	V^*	V_V^f	$V^{asso}+V_{SbV}^m$
Sugino and Oshiyama	+0.066	−0.468	+0.534
This work	+0.07		
Antonelli and Bernholc		+0.75	−0.68
Tang *et al.*		+0.03	+0.04
Antonelli, Kaxiras, and Chadi		−0.09	+0.16

the slopes of the fitted curves is $V^*=+0.07\,\Omega$ with a least-square error of ±0.02 Ω. The nature of the uncharacteristic behavior of the first spike, which had been observed previously for these samples[19] and B-delta doped samples[4] is not understood. The measured effective diffusivities of vacancies[19] and interstitials are, respectively, 5×10^{-11} and 1×10^{-11} cm^2/s in these samples;[20] these values yield diffusion time constants of 1.2 and 6.0 min, respectively, for vacancies and interstitials to traverse the top 600 nm region containing the Sb spikes. Therefore we expect that V^* measured on the 1 h anneals is truly characteristic of equilibrium conditions. This expectation is consistent with the lack of a time dependence observed by Mogi *et al.*[19] in samples simultaneously grown with ours.

There have been theoretical calculations of formation volumes for Si vacancy and the activation volume for Sb diffusion in Si. Antonelli and Bernholc in their *ab initio* calculations predicted $V_V^f=+0.75\,\Omega$ under hydrostatic pressure.[6] Tang *et al.*[8] permitted a greater degree of relaxation in a tight-binding calculation and predicted a formation volume of $V_V^f=+0.03\,\Omega$ for the Si vacancy. Most recently, an *ab initio* calculation by Antonelli, Kaxiras, and Chadi[9] (AKC) with extensive relaxations indicates that the formation volume for the predominant vacancy under pressure is −0.086 Ω. Sugino and Oshiyama[7] (SO) performed a first-principles calculation of Sb diffusion in Si by a vacancy mechanism, reporting a change in activation energy of −0.7 eV at 6 GPa pressure. This change does not include the $+p\Omega$ lattice site creation term in the work of vacancy formation and hence we interpret it to indicate $V^*-p\Omega=-0.934\,\Omega$, implying $V^*=+0.066\,\Omega$. Likewise, we interpret their calculations for the bare Si vacancy as indicating a formation volume of $V_V^f=-0.468\,\Omega$. Table I summarizes the experimental and theoretical values. It is evident that the calculation of SO for V^* is in good agreement with our results. However, the most recent calculations of Tang *et al.* and of AKC disagree with those of SO regarding V_V^f. Therefore we regard the theoretical values as unsettled; e.g., the sum $V^{asso}+V_{SbV}^m$ may yet be very small or quite substantial. The discrepancy between SO and AKC may be related to how the lattice parameter was varied and the pressure evaluated in the two studies. It may also be related[6] to the difference between the P dependence of the enthalpy of formation, which was essentially calculated by SO, and that of the Gibbs free energy of formation, which was essentially calculated by AKC.

We now compare our results with the measured effect of biaxial stress on diffusion. Experimentally,[21] the influence of biaxial stress has been commonly characterized by Q', the

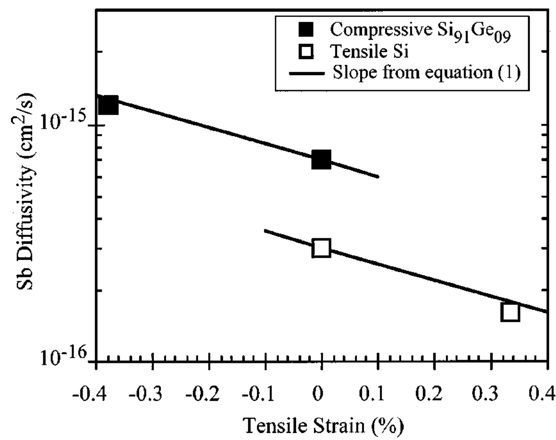

FIG. 2. Biaxial strain effect on Sb diffusion in Si–Ge at constant composition. Data points represent average values from Kringhoj *et al.* (Ref. 21) over range 900–1030 °C. Lines from Eq. (1) using V^* measured in this work and zero migration volume anisotropy.

apparent change in activation energy E^* with biaxial (tensile) strain ϵ at constant composition. There is a thermodynamic relationship[2] between hydrostatic and biaxial stress effects on the diffusivity:

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

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. In the simplest case of a vacancy mechanism in which the system in the saddle point has a symmetry axis along the direction of the elementary atomic jumps, ⟨111⟩, the migration volume anisotropy is zero. Whereas this condition should be satisfied for the vacancy contribution to self-diffusion, in some cases of dopant diffusion a saddle point has been identified in which the vacancy is at or near the third nearest-neighbor position[7,22,23] to the dopant atom. In these cases it remains to be seen whether the broken symmetry causes the continued use Eq. (1) plus the assumption of zero migration volume anisotropy to result in an error of any significance.

Experimentally, Kringhoj *et al.*[21] isolated the effects of strain and composition on Sb diffusion normal to the surface. They reported $Q'=13\pm 3$ eV per unit strain for compressively strained $Si_{91}Ge_9$ films and $Q'=17\pm 5$ eV for tensile Si films. According to Eq. (1) this value in and of itself requires V^* to be near zero, in conflict with the early results of Antonelli and Bernholc. Inserting our measured value of $V^*=+0.07\,\Omega$ and Kringhoj's values for Q' into Eq. (1) we find $V^*+(3/2)(Q'/Y)=(+0.93\pm 0.20)\,\Omega$ for the compressively strained $Si_{91}Ge_9$ alloy and $V^*+(3/2)(Q'/Y)=(+1.20\pm 0.33)\,\Omega$ for tensile Si. This is in excellent quantitative agreement with the prediction of $+1\,\Omega$ for a simple vacancy mechanism. Graphically this agreement is illustrated in Fig. 2. The data points are from Kringhoj *et al.* The slopes of the lines indicate the value of Q' expected from the vacancy mechanism for the biaxial experiment by inputting into Eq. (1) $V^*=+0.07\,\Omega$ and $Y=180.5$ GPa[24] with zero for the migration strain anisotropy. The offset between lines is a free parameter representing the effect of composition at constant strain; lines have been chosen to go through the data points at zero strain.

These results provide further evidence that Sb diffuses predominantly by a vacancy mechanism, and demonstrate that we are beginning to acquire predictive capability for the effect of stress on Sb diffusion. However, for diffusion in non-⟨001⟩ directions by a vacancy mechanism still more information is required, as the migration volume anisotropy is not necessarily zero even for self-diffusion. Its value needs to be determined by theoretical calculations and/or experimental measurements.

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[17] This assumption could result in a small error that can be corrected when appropriate data become available. The contributions are known to have different activation energies (see Ref. 14).
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