Nonequilibrium experiments on self-diffusion in silicon at low temperatures using isotopically enriched structures

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Abstract

Self-diffusion in silicon has been studied using epitaxially grown isotopically enriched structures under nonequilibrium concentrations of native point defects created by thermal oxidation and nitridation. Comparing identical anneals for phosphorus, antimony, and self-diffusion in Si, we obtain experimental evidence for a dual vacancy–interstitial mechanism of self-diffusion with the possibility of a small substitutional exchange component. We determine that in the temperature range 800–1100 °C, the interstitial-mediated fraction of self-diffusion is confined between 0.50 and 0.62. The corresponding activation enthalpies are 4.68 and 4.86 eV for the interstitial and vacancy mechanisms, respectively. Furthermore, both mechanisms exhibit large activation entropies. This constitutes direct experimental evidence of the remarkable similarity between the energetics of these native point defects in silicon. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Self-diffusion is the most fundamental diffusion process in silicon. Experimental study of atomic-scale mechanisms of Si self-diffusion reveals information about the thermodynamic properties of the native point defects in this material. In this respect, it provides direct quantitative comparison to ab initio and atomistic theoretical calculations. Moreover, it supplies key parameters for predictive modeling of dopant diffusion in Si device technology.

On the atomic-scale, diffusion in Si can be mediated by either native point defects, namely self-interstitials (I) and vacancies (V), or by a direct substitutional exchange mechanism (E) which occurs in their absence [1–6]. It is the competition between these three microscopic mechanisms that we study in this work.

2. Experiment

Experimentally, this study relies on two key components. The first is the use of isotopically enriched Si structures. The growth of these structures by chemical vapor deposition (CVD) has been possible only very recently [7–10]. Using these structures has advantages over metal-diffusion and radioactive tracer experiments, since direct measurement of the diffusion of Si atoms over a wide temperature and time range becomes possible. The isotope structures used in this experiment had a surface layer of approximately 170 nm containing the three stable isotopes of Si in their natural abundances, and a buried layer heavily depleted in $^{28}$Si and $^{30}$Si. For example, $^{30}$Si, the isotope used to monitor self-diffusion, was reduced from a natural abundance of 3.10% at the surface to 0.002% at the buried layer.

The second key component of this study is using nonequilibrium experiments, where native point defect concentrations are perturbed from their equilibrium values by well-studied surface reactions, to determine the fractional contributions of the three microscopic mechanisms to Si self-diffusion. Two such surface reactions are...
oxidation and nitridation. It has been well established that thermal oxidation of the surface injects I into the bulk, whereas nitridation results in V injection. Anneals in an inert ambient, on the other hand, give the equilibrium diffusion coefficient. Inert anneal data alone, however, cannot reveal which microscopic diffusion mechanisms are actually involved.

In order to obtain quantitative information about these microscopic mechanisms of self-diffusion, a comparison to dopants under identical oxidation and nitridation anneals is necessary. A well-suited set of dopants is P, which diffuses mainly by an I-mechanism, and Sb, which is a vacancy diffuser. Therefore, in addition to the isotope structure, P and Sb structures were also fabricated for this experiment, using ion implantation followed by a drive-in inert anneal, and epitaxial growth of intrinsic Si to from a surface layer.

After growth, these three structures were annealed in a furnace in an oxidizing (100% O₂) ambient at 800–1100°C for times between 1 and 100 h, and in a nitridizing (100% NH₃) ambient at 1000 and 1100°C for 1–5 h. In addition, all structures were annealed in an inert ambient (100% Ar) at temperatures ranging from 900°C to 1100°C for times between 1 and 72 h.

The diffusion profiles resulting from all anneals for ³⁰Si, P, and Sb were obtained by secondary ion mass spectrometry (SIMS). The details of the SIMS analysis has been given elsewhere [9,10].

3. Results and discussion

The P, Sb, and self-diffusion coefficients in Si under both inert and oxidizing ambient were extracted by taking the as-grown profile, and using TSUPREM-4, a simulation program, to numerically diffuse it by solving the appropriate form of Fick’s second law until a least-squares fit was achieved to the SIMS profile after annealing. Fig. 1 shows the SIMS profiles and the simulation fits of the 900°C anneals for ³⁰Si, P, and Sb under inert and oxidizing ambient. Nitridation experiments were only performed at 1000°C and 1100°C. SIMS plots at these higher temperatures, including nitridation, have already been given elsewhere [9,11,12]. The extracted equilibrium (inert anneal) coefficients show a good fit to Arrhenius behavior with a single activation enthalpy in all cases. For P and Sb, we find that

\[
D^\text{eq}_\text{P} = 1.37 \exp(-3.55/kT) \quad (1a)
\]

and

\[
D^\text{eq}_\text{Sb} = 49 \exp(-4.19/kT) \text{ cm}^2/\text{s}, \quad (1b)
\]

respectively. These values agree well with previously published data [13]. In addition, the equilibrium self-diffusion coefficients exhibit an excellent fit to the expression obtained in Refs. [7,8] using similar isotope layers,

\[
D^\text{eq}_{\text{Si}} = 560 \exp(-4.76/kT) \text{ cm}^2/\text{s}, \quad (1c)
\]

and lie well within the error bars reported in that work. In Eqs. (1), k is the Boltzmann’s constant and T denotes absolute temperature.

It is evident from Fig. 1 that self- and P diffusion are enhanced during oxidation at 900°C, whereas Sb diffusion is retarded. The same behavior is observed for oxidation in the whole temperature range 800–1100°C. During nitridation at 1000 and 1100°C, however, Sb and self-diffusion are enhanced, whereas P diffusion is
The I-mediated fraction of self-diffusion of atomic-scale defects under oxidation are related to the fractional contribution at temperatures of 800°C under inert annealing for each species is listed in Table 1. These values are plotted in Fig. 2 including the error bars shown in Fig. 2. These results qualitatively show that P diffusion mainly by an I-mechanism, whereas Sb diffusion is V mediated. The fact that Si self-diffusion is enhanced by both V and I injection gives a clear hint that it has non-negligible vacancy and interstitial components. Indeed, if either one of the point defect mechanisms were solely dominant, a retardation in diffusion would have been observed when the opposite type of defect is injected. On the other hand, if the exchange mechanism were dominant, perturbing the point defect concentrations as above would not have any effect on the self-diffusion coefficient.

The ratio of the diffusivity under oxidation to that under inert annealing for each species is listed in Table 1 at temperatures of 800–1100°C. These diffusivity ratios under oxidation are related to the fractional contributions of atomic-scale diffusion mechanisms by [2,11],

\[
\frac{D_X^{\text{ox}}}{D_X^{\text{eq}}} = f_{\text{eq}} \frac{C_X^{\text{eq}}}{C_Y^{\text{eq}}} + f_{\text{ox}} \frac{C_X^{\text{ox}}}{C_Y^{\text{ox}}} + f_{\text{AE}},
\]

where A represents the diffusing species (A = P, Sb, or in the case of self-diffusion, Si), and \(f_{\text{eq}}, f_{\text{ox}},\) and \(f_{\text{AE}}\) are the I, V, and E fractions, respectively, of A diffusion under equilibrium conditions. The ratios involving the I and V concentrations on the right-hand side are the perturbation levels of these defects under nonequilibrium conditions. The superscripts eq and ox denote equilibrium and oxidation, respectively. Diffusivity ratios and point defect perturbation levels measured at the end of the experiment are time averaged values. Furthermore, all results reported in this work represent an average over possible charge-states of the native point defects present under intrinsic conditions.

Assuming \(f_{\text{PI}} = 1, f_{\text{SM}} = 0,\) and \(f_{\text{ST}} = 0,\) we have solved Eq. (2) for \(f_{\text{SI}}\), and listed the values obtained in the temperature range 800–1100°C in the last column of Table 1. These values are plotted in Fig. 2 including the error bars. These error bars are due partly to relaxing the above assumptions on \(f_{\text{PI}}, f_{\text{SM}},\) and \(f_{\text{SI}},\) and partly to taking into account experimental uncertainty. The high-temperature experiments have shown that at 1000°C and 1100°C, \(f_{\text{PI}} \approx 0.96\) and \(f_{\text{ST}} \approx 0.14,\) and in conjunction with the low-temperature data, at 800–1100°C, \(f_{\text{ST}} \leq 0.03\) [9,11]. Solving the system of three equations (one equation each for P, Sb, and self-diffusion) having the form Eq. (2) with these upper and lower bounds, and taking into account our estimate of the experimental error, ±5%, in the measured diffusivity ratios listed in Table 1, we arrive at the error bars shown in Fig. 2.

In the same figure (Fig. 2), we have also plotted, represented by solid lines, \(f_{\text{SI}}\) extracted from experimental studies of substitutional–interstitial metal diffusers (e.g., Au, Zn, and Pt) in Si [1,14–16]. Results from other similar experiments (see the references in Refs. [1,14–16]), a combination of Zn and self-diffusion data [7,8], and tight-binding calculations [17] exhibit similar trends. In striking contrast to these results, \(f_{\text{SI}}\) obtained directly using isotopically enriched structures manifests a much weaker dependence on temperature. Furthermore, we observe an increase in \(f_{\text{SI}}\) with decreasing temperature, which is exactly the opposite of the trend extracted from metal diffusion experiments. Our findings show that within the temperature range 800–1100°C, \(f_{\text{SI}}\) is confined between 0.5 and 0.62.

The temperature dependence of the X component of self-diffusion \(D_{\text{SI}}\), is given by

\[
D_{\text{SI}}(T) = f_{\text{SI}}^{\text{ox}} D_{\text{SI}}^{\text{eq}} = d_{\text{ox}} \exp(-H_X/kT),
\]

with the temperature independent pre-factor

\[
d_{\text{ox}} = l_X g_X a_0^3 v_X \exp(S_X/k),
\]

where X = I, V, or E, \(l_X\) is the correlation factor (we do not use the traditional notation of \(f_{\text{SI}}\) for the correlation factor in order to distinguish it from \(f_{\text{SI}}^{\text{ox}}\)). \(g_X\) is the geometry factor, \(a_0\) is the lattice constant, and \(v_X\) is the attempt frequency. Furthermore, for the point defect

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<th>Temperature (°C)</th>
<th>Diffusivity ratios under oxidation</th>
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<tr>
<td></td>
<td>(^{30}\text{Si})</td>
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<tr>
<td>1100</td>
<td>1.53</td>
</tr>
<tr>
<td>1000</td>
<td>2.46</td>
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<tr>
<td>900</td>
<td>5.16</td>
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<td>800</td>
<td>14.57</td>
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mechanisms, the activation enthalpy $H_X$ equals the sum of the formation and migration enthalpies of the defect $X$, and similarly the activation entropy $S_X$ equals the sum of the respective entropies. Eqs. (3) show clearly that an Arrhenius fit of the product $f_{\text{SiX}}$ and $D_{\text{self}}^X$ yields $H_X$ and $S_X$. As a result, we find that the I and V components of Si self-diffusion exhibit excellent fit to $D_{\text{self}}^I = 149 \exp(-4.68/kT)$ and $D_{\text{self}}^V = 636 \exp(-4.86/kT) \text{cm}^2/\text{s}$, respectively, as plotted in Fig. 3. Using the same values for the constants in Eqs. (3) as in Ref. [7,8], and taking into account the error bars in our measured results, we get $H_I = 4.68^{+0.12}_{-0.15}$ eV and $H_V = 4.86^{+0.15}_{-0.19}$ eV, and $S_I = 10.2^{+1.2}_{-1.8} \text{k}$ and $S_V = 12.8^{+1.8}_{-1.5} \text{k}$. These results, on the other hand, strongly suggest the converse, with the difference between $H_I$ and $H_V$ is on the order of only a few tenths of an eV. The value of $H_I$ obtained in this work agrees, within error bars, with that extracted recently from the energetics of self-interstitial clusters in Si [18]. Focusing on the results for $S_I$ and $S_V$, we see that both entropies are large and comparable in magnitude. Our results agree with the theoretical findings of Ref. [19] that even simple native point defects can have large entropies of formation, and that they are similar in magnitude.

In conclusion, we have studied Si self-diffusion under nonequilibrium conditions using isotopically enriched structures in the temperature range 800–1100°C. We find that, on the atomic-scale, self-diffusion is mediated by a dual vacancy–interstitial mechanism with the possibility of a small exchange component. These results constitute direct experimental evidence of the strong competition between the I- and V-mechanisms of self-diffusion and of the remarkable similarity between the energetics of these native point defects in silicon.

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References