Accurate measurements of the intrinsic diffusivities of boron and phosphorus in silicon

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All activity in modeling transient diffusion behavior relies on knowledge of the inert intrinsic diffusivities of dopants in Si. The measurements upon which these values are based were conducted over 15 years ago. Since then, the quality of wafers used in industrial applications has significantly changed. This will affect the effective diffusivity through changes in trap concentrations. The reliability of measurement techniques has also changed dramatically from tracer and staining methods to secondary ion mass spectrometry (SIMS) measurements that are dominant today. Finally, our understanding of diffusion behavior has changed significantly. For example, we now understand that the extraction of diffusivities from implanted samples with no pre-anneal includes a significant transient effect. We have measured the inert intrinsic diffusivities of As, B, P, and Sb in different substrates in defect-free Czochralski and float zone wafers and epitaxially grown layers. All samples underwent a 30 min anneal at 1000 °C in dry oxygen in order to grow a cap oxide and eliminate transient enhanced diffusion. We performed SIMS analysis on an initial batch of samples to evaluate the different factors that may affect the diffusivity in a nonideal manner and concluded that there are no transient effects but that surface effects are important. Hence, for the fast moving dopants (B, P) we restrict our data extraction to the deep implants. Our data show that B and P diffusivities are different than the values commonly assumed in the literature at low temperatures. We compare our results to previously published data in light of the factors mentioned here.
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Modern diffusion models rely on expressions of the type

$$D^{\mathrm{eff}}=D^{*}f(C_I,C_V), \quad (1)$$

where D^{eff} is the effective diffusivity, D^* is the diffusivity under intrinsic inert conditions, C_I and C_V are the concentrations of interstitial and vacancies, respectively, and f is a function that captures the dependence of the effective diffusivity on point defect concentrations.[1] The form of the function f depends on the atomistic mechanisms that govern the diffusion process. A common assumption is that the diffusion process is governed by an interstitial-assisted mechanism and a vacancy-assisted mechanism acting simultaneously. In that case

$$f=f_I\frac{C_I}{C_I^*}+(1-f_I)\frac{C_V}{C_V^*}, \quad (2)$$

where C_I^* and C_V^* are the thermal equilibrium concentrations of interstitials and vacancies, respectively, and f_I is the fraction of dopant that diffuses according to the interstitial mechanism.[1] Even if one does not utilize the effective diffusivity approximation (1), the continuity equation for the diffusing species is still written in terms of D^*, the diffusivity under intrinsic inert conditions.

Much work has been done, and continues to be pursued, to model diffusion under nonequilibrium conditions in semiconductor processes. This includes, for example, the modeling of oxidation enhanced diffusion,[1,2] as well as damage-induced transient enhanced diffusion (TED).[3–9] This work necessarily presumes accurate knowledge of the value of D^* for common dopants. Deviations from D^* are characterized and models and model parameters deduced from these deviations and their variation as a function of experimental conditions. Additionally, recent work on *ab initio* modeling of dopant diffusion processes for the purpose of understanding which mechanisms should dominate the diffusion of a particular dopant as well as deducing the values of model parameters use published values of D^* to evaluate the accuracy of the theoretical computation.

The assumption that D^* is accurately known for common dopants is unjustified in light of the fact that most published data date back 15–20 years. During that time frame, there was considerable activity to characterize the baseline diffusivities (D^*) of common dopants in Si and numerous papers were published reporting varying results. The papers that will be cited here are ones that reported on work that was rigorous, thorough, and well documented. Our reasons for revisiting this subject are not any deficiency in the quality of the work or the reports, but rather due to the additional

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knowledge of diffusion processes that has accumulated during the past two decades. Specifically:

(1) The role of substrate defects has come to be recognized as a significant factor in affecting the measured diffusivity and substrate quality has certainly changed during the last 20 years;
(2) effects such as TED and dose loss after an implant have been discovered and should be taken into account when analyzing the data; and
(3) measurement techniques have improved considerably. Secondary ion mass spectrometry (SIMS) is now the method of choice as opposed to radio tracer and spreading resistance techniques.

This letter reports experiments and data analysis conducted to extract the baseline diffusivities of common dopants in Si. Our measurements are compared with previously published data and the differences are accounted for based on the experimental conditions reported.

We obtained implants of B, P, As, and Sb into Czochralski (CZ) and float zone (FZ) substrates. In all cases, the implant dose was $4\times10^{13}\,\mathrm{cm}^{-2}$, which yields a peak concentration lower than the intrinsic carrier concentration at temperatures of 850 °C and higher. For each substrate type, samples were obtained of each dopant implanted at 60 keV, placing the peak concentration near the surface. For the remaining samples, the implant energy was chosen to yield $R_p\approx0.4\,\mu$m.

The wafers were all annealed for 15 min at 1000 °C in dry oxygen. This step was performed to remove the damage from the implants. It also had the desired result of growing a cap oxide layer to prevent dopant loss during subsequent anneals. Dopant profiles after subsequent anneals were compared to profiles measured after this pre-annealing step. In other words, the ''initial'' state of the wafers is considered to be their state after this 1000 °C step, so that enhancement to dopant diffusion from implant damage would have no effect on the results. Samples from each wafer were then annealed at 850 °C for 1, 6, and 5 days; at 900 °C for 6 h, 2, and 3 days; and at 1000 °C for 1, 3, and 5 h.

We performed SIMS to obtain dopant profiles from our samples in two stages. In the first stage, a small number of samples was analyzed to screen for three basic issues that could confound the analysis of the data: substrate effects, the choice of implant energy (deep versus shallow), and transient enhanced diffusion. We were unable to obtain useful data from the FZ samples. Our first pass measurements on these wafers yielded an unexplained step in the background matrix signal which cast doubt on the validity of measurements performed on these wafers. No additional work was performed to investigate this anomaly and hence we will not discuss these samples further in this letter. A small number of epi samples was obtained and dopant diffusivities extracted from these were found to closely correspond to those seen in the CZ samples. Hence, only the results from CZ wafers are reported here. We found that for B-doped samples, simulation of diffusion behavior of shallow implants depended strongly on the assumptions made about the behavior at the surface. We are specifically concerned here with bulk diffusion. Hence, to avoid uncertainty in the analysis we restricted ourselves in the remainder of the work to samples that had received deep implants. We observed no time dependence to the diffusivity on P-doped and B-doped samples at 850 °C, confirming that the implant damage was completely annealed and TED completed during the pre-anneal step.

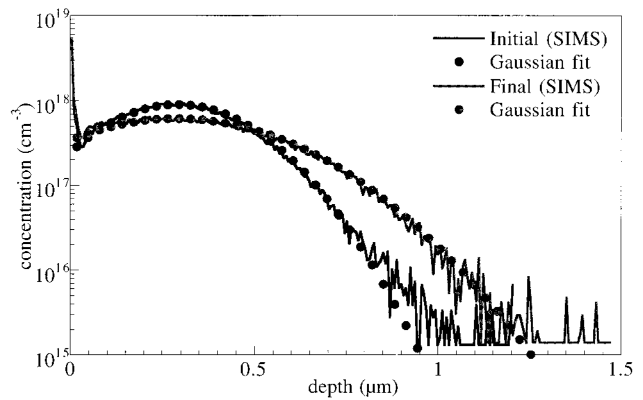

FIG. 1. Profile of P diffusion in CZ Si after a 1000 °C preanneal and after a further anneal at 850 °C for 5 days. Gaussian fits confirm the absence of transient effects.

In the second stage, SIMS was performed on samples that had received deep implants, and had undergone the longest anneal at each temperature (4 dopants $\times3$ temperatures$=12$ samples). Figure 1 shows a typical case and the resulting fits to the diffusion profile. Clearly, the profiles can be fit by simple Gaussian's. This further confirms that we are observing and measuring inert intrinsic diffuion in the absence of concentration-dependent or transient effects. It also makes it straightforward to extract dopant diffusivities from the profiles thus measured.

Figures 2 and 3 show, respectively, the resulting diffusivities for P and B compared with previously published data. The error bars shown on our data points represent our estimate of worst case extraction error due to SIMS depth and concentration errors. This estimate was obtained from analyzing the data for the lowest anneal temperature used ($T=850$ °C, lowest temperature yields lowest diffusivity and greatest uncertainty) using the Monte Carlo algorithm published by Gossman *et al.*[10] From the two figures, it is clear that our data matches models in current use at high temperatures (>1000 °C).

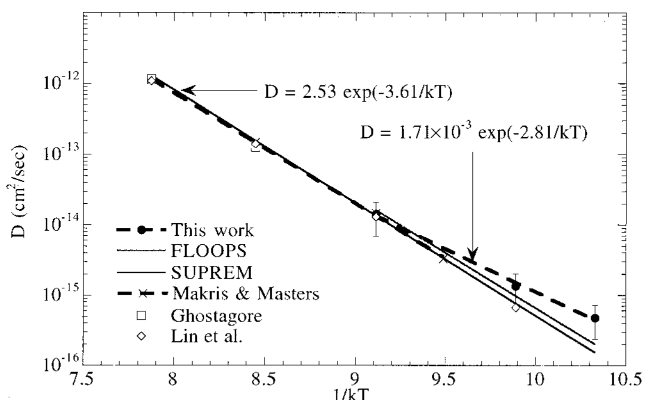

FIG. 2. Phosphorus diffusivity from this study compared with the results of Lim *et al.* (see Ref. 11), Makris and Masters (see Ref. 16), Ghostagore (see Ref. 17), as well as the expressions used in the popular process simulators SUPREM (see Ref. 14) and FLOOPS (see Ref. 15).

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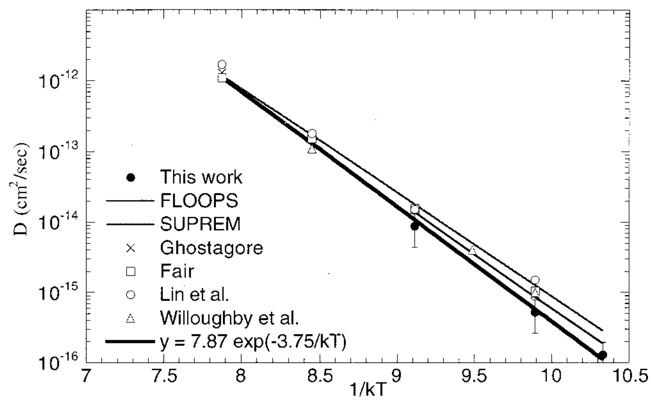

FIG. 3. Boron diffusivity from this study compared with the results of Fair (see Ref. 13), Lim *et al.* (see Ref. 11), Willoughby *et al.* (see Ref. 12), Ghostagore (see Ref. 18), as well as the expressions used in the popular process simulators SUPREM (see Ref. 14) and FLOOPS (see Ref. 15).

However, our measurements went down to a range of temperatures lower than any previously reported data (850–900 °C). In some cases, specifically for the P diffusivity, this yields an extrapolation error in fitting an Arrhenius relationship to the previously reported data that becomes the dominant error component in extracting an activation energy. The only study previously reporting P diffusion data below 1050 °C was that of Lim *et al.*[11] In their case, they used spreading resistance profiles to extract the diffusivity. Our data at 900 °C yields a diffusivity approximately twice that extracted from their data. The present measurements utilizing SIMS measurement of the P profile are more accurate and yield a more reliable value for the activation energy of P diffusion in Si. We obtain, for the P diffusivity at low temperature

$$D_{\mathrm{P}}=1.71\times 10^{-3}\exp\left(-\frac{2.81\ \mathrm{eV}}{kT}\right). \tag{3}$$

Our high temperature measurements fit well with the expressions in current use. The low temperature data has a significantly lower activation energy. Initially we considered a combination of defects with multiple charge states participating in the diffusion process to explain this. However, the difference in the activation energy between the two temperature ranges is too large to be thus explained. It is possible that a different defect altogether is responsible for the diffusion in the lower temperature range (e.g., an interstitial in a different configuration within the lattice resulting in a different energy of formation). These measurements and possible explanations of the results merit further work.

In the case of B diffusion, the difference between our data and previously reported data is more immediately obvious. In many cases (e.g., Willoughby *et al.*[12] and Lim *et al.*),[11] the samples used had not undergone a pre-anneal step. For the times and temperatures used this could lead to overestimating the diffusivity by as much as a factor of 4. Since these data, and similar ones, were used in obtaining average diffusivities by researchers such as Fair,[13] and the SUPREM,[14] and FLOOPS[15] developers, all of the expressions in current use are likely to overestimate the diffusivity of B at low temperatures. In our case, we specifically guard against this effect. We obtain

$$D_{\mathrm{B}}=7.87\exp\left(-\frac{3.75\ \mathrm{eV}}{kT}\right). \tag{4}$$

We tried to perform a similar analysis for the cases of As and Sb. Unfortunately, the decision we made based on B data to use only deep implants was probably not justified for these slower dopants and resulted instead in a very low resolution of dopant motion (≈500 Å). Hence, we do not have reliable data on As or Sb diffusion.

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