Abstract

In a series of experiments, Chantre et al. measured vacancy–phosphorus pairs after laser annealing of silicon samples. These experiments were reproduced by numerical simulations of the diffusion and recombination of vacancies and self–interstitials and the interaction of vacancies with phosphorus atoms. The simulations lead to a range of possible values for the equilibrium concentration of vacancies.

1. Introduction

Diffusion of dopants in silicon is generally accepted to result largely from their interactions with intrinsic point defects like vacancies and self–interstitials. Accordingly, a considerable number of experimental studies has been devoted to studying the basic properties of the intrinsic point defects like diffusion coefficients and equilibrium concentrations. However, agreement between the results remained rather limited.

A particular experimental method which gave excellent results in metals is quenching. In early quenching experiments, Elstner and Kamprath [1] found deep donors characterized by an ionization level at $E_v + 0.37$ eV and suggested them to be caused by clusters of about 4 to 6 vacancies. After the paradigm change from vacancy–dominated to self–interstitial–dominated diffusion in silicon, this defect was associated by Seeger and Frank [2] with the self–interstitial. Both interpretations are questionable since values around $E_v + 0.4$ eV are usually associated with interstitial iron [3–5]. In the work of Chantre et al. [6–9], however, phosphorus–vacancy pairs and aluminum–vacancy pairs were identified by DLTS after quenching from 1280 °C. These experiments provide strong evidence that the equilibrium concentration of vacancies exceeds that of self–interstitials at this temperature. However, apart from the approximate quantitative interpretation by the authors, no detailed analysis of the experiments was given until now.

The goal of this work was to investigate the introduction of vacancies during ramping–up and their kinetics during cooling–down by solving an appropriate set of continuity equations numerically. The resulting point–defect parameters obtained by fitting the depth profile of phosphorus–vacancy pairs measured by Chantre et al. are discussed with respect to previous estimates.

2. Experimental Details

The experimental details were described by Chantre et al. [6, 7] and are repeated here in an abbreviated form for the sake of convenience. The experiments were performed with a cw argon laser with a scanned beam diameter of 50 µm. The scan speed was varied between 1 and 50 cm/s. The temperature profile for a scan speed of 10 cm/s was taken directly from the original article [6] and is shown in Figure 1. The temperature distribution within the sample was assumed to be characterized by a temperature gradient of -120 K/µm from the surface into the bulk.

![Figure 1. Surface temperature induced by the laser annealing with a scan rate of 10 cm/s](image-url)
3. Model Details

The kinetics of the species involved was assumed to be governed by the reactions

\[ I + V \rightleftharpoons 0, \quad V + P \rightleftharpoons E, \quad I + E \rightleftharpoons P \quad (1) \]

between self–interstitials \( I \), vacancies \( V \), substitutional phosphorus atoms \( P \), and phosphorus–vacancy pairs \( E \).

The diffusion of self–interstitials and vacancies was simulated by solving the equations

\[
\frac{\partial C_I}{\partial t} = \text{div} \left( D_I \cdot C_I^{eq} \cdot \text{grad} \frac{C_I}{C_I^{eq}} \right) - k_B \cdot (C_I \cdot C_V - C_I^{eq} \cdot C_V^{eq}) - k_E \cdot (C_I \cdot C_E - C_I^{eq} \cdot C_E^{eq}) \cdot C_P \cdot \exp \left( \frac{E_B}{k \cdot T} \right), \quad (2)
\]

\[
\frac{\partial C_V}{\partial t} = \text{div} \left( D_V \cdot C_V^{eq} \cdot \text{grad} \frac{C_V}{C_V^{eq}} \right) - k_B \cdot (C_I \cdot C_V - C_I^{eq} \cdot C_V^{eq}) - k_P \cdot (C_V \cdot C_P - \frac{C_{Si}}{4}) \cdot \exp \left( -\frac{E_B}{k \cdot T} \right) \quad (3)
\]

Therein, the symbols \( D \), \( C \), and \( C^{eq} \) denote respectively diffusion coefficients, concentrations, and equilibrium concentrations of the species indicated by the subscript letter. The second term on the right–hand sides describes bulk recombination with the bulk–recombination constant \( k_B \), the third term in (2) describes the reaction between self–interstitials and phosphorus–vacancy terms with the reaction constant \( k_E \), and the third term in (3) the reaction between vacancies and substitutional phosphorus atoms with the reaction constant \( k_P \). \( E_B \) is the binding energy of phosphorus–vacancy pairs, \( C_{Si} = 5 \cdot 10^{22} \text{ cm}^{-3} \) the concentration of the silicon atoms. The reaction constants \( k_x \) were assumed according to Waite’s theory of diffusion–limited reactions [10] with a reaction radius of 5 Å.

The effects of the temperature gradient are included implicitly in (2) and (3) by evaluating the gradients of \( C_I^{eq}/C_I^{eq} \) and \( C_V^{eq}/C_V^{eq} \) instead of the gradients of \( C_I \) and \( C_V \) as conventionally. This method has been used for the simulations of crystal growth by Habu et al. [11]. However, it has to be noted that the correct formulation of the influence of temperature gradients on the diffusion of intrinsic point defects is still in debate and that it was argued in other investigations [12] that thermal gradients can be safely ignored. At the top surface, Dirichlet boundary conditions with the equilibrium concentrations were assumed for self–interstitials and vacancies. As initial conditions, the equilibrium concentrations at 200 °C were taken.

The substitutional phosphorus atoms and the phosphorus–vacancy pairs were assumed to be immobile within the time–frame of the experiment so that the change in their concentrations is described locally by

\[
\frac{dC_P}{dt} = -\frac{dC_E}{dt} = +k_E \cdot \left( C_I \cdot C_E - \frac{C_I^{eq} \cdot C_V^{eq}}{C_{Si}} \cdot 4 \cdot C_P \cdot \exp \left( \frac{E_B}{k \cdot T} \right) \right) - k_P \cdot (C_V \cdot C_P - \frac{C_{Si}}{4}) \cdot \exp \left( -\frac{E_B}{k \cdot T} \right). \quad (4)
\]

The initial conditions for the phosphorus atoms was a homogeneous doping with a concentration of 3·10^{15} \text{ cm}^{-3}, for the phosphorus–vacancy pairs, a negligibly low concentration was assumed.

For the diffusion coefficient and equilibrium concentration of self–interstitials, the parameters were taken from the work of Falster et al. [13]. However, as discussed later, these parameters are uncertain for the results of this work. The diffusion coefficient and equilibrium concentration of vacancies was used in the form

\[
X(T) = X(1550 K) \cdot \exp \left( \frac{E_X}{k \cdot 1550 K} - \frac{E_X}{k \cdot T} \right) \quad (5)
\]

with the \( X \) standing for \( D_V \) and \( C_V^{eq} \), and \( E \) either for the migration energy or the formation energy of the vacancies, respectively. Following the work of Falster et al. [13], an migration energy of 0.35 eV was assumed for the vacancies.

For the binding energy \( E_B \) various estimates were suggested in the literature. Most of them are not reliable since they were based on diffusion models with doubtful implicit assumptions. Therefore, suitable values were assumed to be within the range of 0.85 eV from the electron–paramagnetic–resonance investigation of Watkins and Corbett [14] to 2.2 eV from the ab–initio simulation of Car et al. [15] within which basically all other estimates can be found also.

4. Results and Discussion

Already the first simulations showed that interactions with self–interstitials are negligible. This was expected, at least for bulk recombination. An estimate of the time constant for bulk recombination

\[
\tau_B = \frac{1}{k_B \cdot (C_I^{eq} + C_V^{eq})} \quad (6)
\]

evaluated with the parameters of Falster et al. [13] gave a value of about 1.5 ms at the highest temperature of 1277 °C. This time constant exceeds the time at which the samples are at sufficiently high temperatures by far.
Although all simulations were performed with the full system, it is nevertheless remarkable that the experimental set-up is sensitive predominantly to vacancy parameters.

The goal of this investigation was to evaluate whether unambiguous vacancy parameters can be extracted from the experiments of Chantre et al. For given values of the binding energy $E_B$ of phosphorus–vacancy pairs and the formation energy $E_f^V$ of the vacancies, it was indeed found that both $C_{eq}^V(1550 \text{ K})$ and $D_V(1550 \text{ K})$ had to be optimized to reproduce the experimental profiles. This is in contrast to a number of experiments based on impurity or metal diffusion where only the product of the two is of primary importance. Figure 2 shows a typical simulation for $E_B = 1.8 \text{ eV}$ and $E_f^V = 3.8 \text{ eV}$. For these conditions, values of $C_{eq}^V(1550 \text{ K}) = 3.1 \times 10^{14} \text{ cm}^{-3}$ and $D_V(1550 \text{ K}) = 2.2 \times 10^{-5} \text{ cm}^2/\text{s}$ were obtained by the optimization. The time $t = 0$ corresponds, as in Figure 1 and in the original article of Chantre et al., to the time at which the local surface temperature has its maximum. For $t \to \infty$, all vacancies are finally bound in vacancy–phosphorus pairs. Also shown are simulations in which the effects of the temperature gradient on diffusion is ignored. It is apparent from the comparison that the temperature gradient causes a driving force in the direction opposite to the concentration gradient. Therefore, an overestimation of the final concentration of phosphorus–vacancy pairs results if the temperature gradient is not taken into considerations.

To estimate the influence of the binding energy of the phosphorus–vacancy pairs and of the formation energy of the vacancies, the former was varied from 1 to 1.8 eV, and the latter from 3.8 to 4.6 eV. Within these limits, after optimizing $C_{eq}^V(1550 \text{ K})$ and $D_V(1550 \text{ K})$, the experimental data was reproduced with basically the same accuracy. The values for $C_{eq}^V(1550 \text{ K})$ and $D_V(1550 \text{ K})$ so obtained are shown in Figures 3 and 4, respectively.

The equilibrium concentrations of vacancies obtained within this analysis ($3.1 \times 10^{14}$ to $8.3 \times 10^{14} \text{ cm}^{-3}$) are compared in Figure 5 with some literature values [12, 13, 16–22]. The values found here agree well with values obtained from simulations of crystal growth which are currently assumed to be the most reliable.

The only parameter related to intrinsic point defects which is known with sufficient precision is the tracer diffusion coefficient $D_T$. Taking the relation reported by
5. Conclusions

In this work, laser–annealing experiments of Chantre et al. [6,7] were reproduced by numerical simulations. It was found that the experiments are sensitive predominantly to vacancy–related parameters. The equilibrium concentration of vacancies at 1550 K and the fractional diffusivity of silicon via self–interstitials found by reverse engineering were found to give plausible values.

Figure 5. Equilibrium concentrations of vacancies

Bracht et al. [23] from studies of isotope–enriched structures, a value of $1.87 \times 10^{-13}$ cm$^{-3}$ is obtained at 1550 K. Ignoring direct mechanisms, this value corresponds to

$$D_T = f^V \cdot D_V \cdot \frac{C_{eq}^V}{C_{Si}^V} + f^I \cdot D_I \cdot \frac{C_{eq}^I}{C_{Si}^I},$$  \hspace{1cm} (7)

with $f^V = 0.5$ [24] and $f^I = 0.7273$ [25] standing for the tracer correlation coefficients via vacancies and self–interstitials, respectively. From solving (7) for $D_I \cdot C_{eq}^I$, the fractional diffusivity of silicon via self–interstitials

$$f_{Si}^I = \frac{D_I \cdot C_{eq}^I}{D_I \cdot C_{eq}^I + D_V \cdot C_{eq}^V}$$  \hspace{1cm} (8)

can be estimated. For the range of $D_I(1550 \text{ K}) \cdot C_{eq}^I (1550 \text{ K})$ obtained here ($6 \times 10^{-14}$ to $2.2 \times 10^{-13}$ cm$^2$/s), plausible values for $f_{Si}^I$ in the range from 0.324 to 0.782 result.