

Direct experimental evidence for diffusion of dopants via pairs with intrinsic point defects

P. Pichler, R. Schork, T. Klausner, and H. Rysse^{a)}

Fraunhofer-Arbeitsgruppe für Integrierte Schaltungen, Artilleriestrasse 12, 8520 Erlangen, Germany

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Boron was implanted into silicon at a wafer temperature of 950 °C. The resulting boron profile showed a marked uphill diffusion at the surface and a very high diffusion enhancement. Initially homogeneously distributed antimony atoms showed remarkable redistribution effects after the implantation. These experiments allow the validation of diffusion theories, including the effects of point defect gradients on the migration of dopants. It will be shown that the experimental results agree well with the predictions of pair diffusion theories.

Despite large efforts in recent years, the basic diffusion mechanisms are still under discussion.¹ Basically, there are two common formulations of the diffusion equations for dopants which include the effects of gradients of the point-defect concentrations. The first formulation arises generally from pair diffusion theories² and is identical to a diffusion equation derived from Master's equation.¹ For the sake of simplicity, we consider the equations for intrinsic concentrations only. The total flux of dopant atoms J_A is given by the sum of the fluxes of atoms diffusing via interstitials J_{AI} and vacancies J_{AV} as diffusion vehicles:

$$\begin{aligned} J_A &= J_{AI} + J_{AV} \\ &= -D_{0I} \cdot \text{grad}(C_A \cdot s_I) - D_{0V} \cdot \text{grad}(C_A \cdot s_V) \\ &= -D_{0I}(s_I \cdot \text{grad} C_A + C_A \cdot \text{grad} s_I) \\ &\quad - D_{0V}(s_V \cdot \text{grad} C_A + C_A \cdot \text{grad} s_V). \end{aligned} \quad (1)$$

In this formula, $s_I = C_I/C_I^{\text{eq}}$ and $s_V = C_V/C_V^{\text{eq}}$ represent the oversaturations of interstitials and vacancies, respectively. C and C^{eq} stand for concentrations and equilibrium concentrations. The subindices A , I , and V denote dopant atoms, interstitials, and vacancies, respectively. D_{0I} and D_{0V} are the intrinsic dopant diffusivities via interstitials and vacancies. Their sum gives the diffusion coefficient under intrinsic and inert conditions.

A second approach, based on atomistic theories and neglecting pair formation,³ leads to a formulation which is in its fundamental structure identical to a diffusion equation derived from the Fokker-Planck equation for stress-dependent diffusion.¹ It reads:

$$\begin{aligned} J_A &= J_{AI} + J_{AV} \\ &= -D_{0I}(s_I \cdot \text{grad} C_A - C_A \cdot \text{grad} s_I) \\ &\quad - D_{0V}(s_V \cdot \text{grad} C_A - C_A \cdot \text{grad} s_V). \end{aligned} \quad (2)$$

It should, however, be noted that the influence of the gradient of the self-interstitials on dopant diffusion in the work of Maser³ has been derived as a nonobvious analogy to vacancy diffusion. Other studies of atomistic diffusion of dopants via self-interstitials predict a different sign for the

effect of the gradient of the self-interstitials on dopant diffusion⁴ leading to the same self-interstitial contribution-like pair diffusion models:

$$\begin{aligned} J_A &= J_{AI} + J_{AV} \\ &= -D_{0I}(s_I \cdot \text{grad} C_A + C_A \cdot \text{grad} s_I) \\ &\quad - D_{0V}(s_V \cdot \text{grad} C_A - C_A \cdot \text{grad} s_V). \end{aligned} \quad (3)$$

To demonstrate the effects of the differences between the formulations, let us assume that a dopant atom diffuses primarily via vacancies, that the dopant concentration is initially constant, and that the concentration of vacancies increases with depth. According to the pair-diffusion theories leading to Eq. (1), mobile vacancy-atom pairs are formed proportionally to the vacancy concentration and diffuse due to their gradient. This leads to an effective flux of dopant atoms toward the surface. In the case of Eqs. (2) and (3), the dopant atoms jump proportionally to the probability that a vacancy is near. This probability increases with depth so that the dopant atoms migrate toward the bulk.

Under usual conditions, like prevailing in oxidation or nitridation experiments, the gradients of the point-defect concentrations are nearly constant in the vicinity of the surface because of their large diffusion coefficients. In experiments with high concentrations of, e.g., phosphorus, on the other hand, the effects of the point-defect gradients cannot be separated clearly from other effects. These experiments are, therefore, not suited to distinguish between the theories.

In our experiment,⁵ we generated Frenkel pairs continuously during high-temperature implantation of boron at 950 °C with 120 keV and a dose rate of $\sim 3 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ until a dose of 10^{15} cm^{-2} was reached. During the implantation process, Frenkel pairs are generated in large numbers close to the surface. They diffuse into the bulk and recombine or they migrate to the surface where they are annihilated leading to a very steep gradient at the surface.

In the absence of macroscopic defects, we assume that the generation and recombination of point defects in the bulk takes place only via the Frenkel-pair mechanism. The diffusion of the point defects can then be described by the following continuity equations:⁶

^{a)}Also: Lehrstuhl für Integrierte Schaltungen, Universität Erlangen-Nürnberg, Artilleriestrasse 12, 8520 Erlangen, Germany.

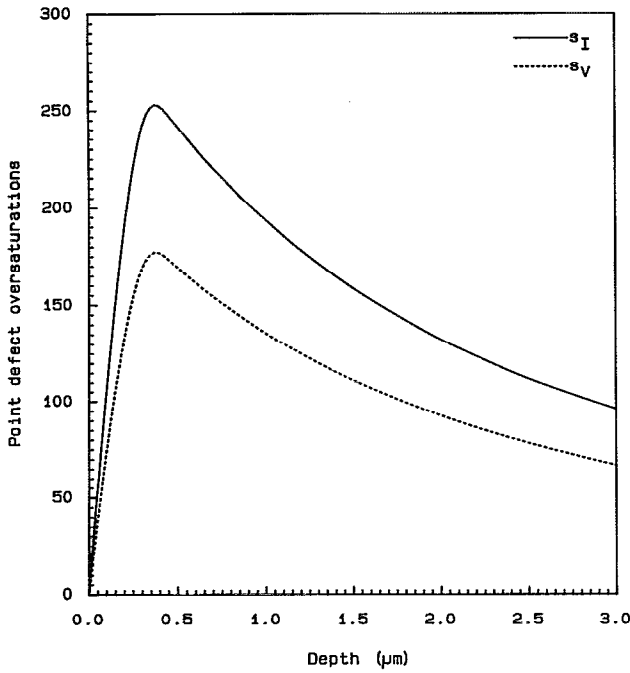


FIG. 1. Self-interstitial and vacancy oversaturation after the high-temperature implantation of boron.

$$C_I^{eq} \cdot \frac{\partial s_I}{\partial t} = \text{div } D_I \cdot C_I^{eq} \text{ grad } s_I - K_B \cdot C_I^{eq} \cdot C_V^{eq} \cdot (s_I \cdot s_V - 1) + G_I, \quad (4)$$

$$C_V^{eq} \cdot \frac{\partial s_V}{\partial t} = \text{div } D_V \cdot C_V^{eq} \text{ grad } s_V - K_B \cdot C_I^{eq} \cdot C_V^{eq} \cdot (s_I \cdot s_V - 1) + G_V, \quad (5)$$

with the boundary conditions

$$\frac{\partial s_I}{\partial n} = -\frac{K_I}{D_I} \cdot (s_I - 1); \quad \frac{\partial s_V}{\partial n} = -\frac{K_V}{D_V} \cdot (s_V - 1). \quad (6)$$

The generation terms G_I and G_V describe the generation of interstitials and vacancies due to the ion implantation. D_I and D_V stand for the diffusivities of silicon self-interstitials and vacancies. K_I , K_V , and K_B denote their surface recombination velocities and bulk recombination rate, respectively.

Figure 1 shows the simulated oversaturation of interstitials and vacancies as a function of depth at the end of the implantation process. Details of the simulations will be published elsewhere.⁷ These numerical simulations show that the changes in the point-defect oversaturations after about 100 s are small so that the point-defect oversaturations are in steady state for the most part of the process. The quotient of the oversaturations of interstitials and vacancies is approximately given by the quotient of the vacancy and interstitial self-diffusion coefficient $s_I/s_V \sim D_V C_V^{eq}/D_I C_I^{eq}$ which is about 1.5 at 950 °C.

Due to the gradients of the point-defect concentrations, the boron profile shows a marked uphill diffusion (Fig. 2). Since it is assumed that boron diffuses predomi-

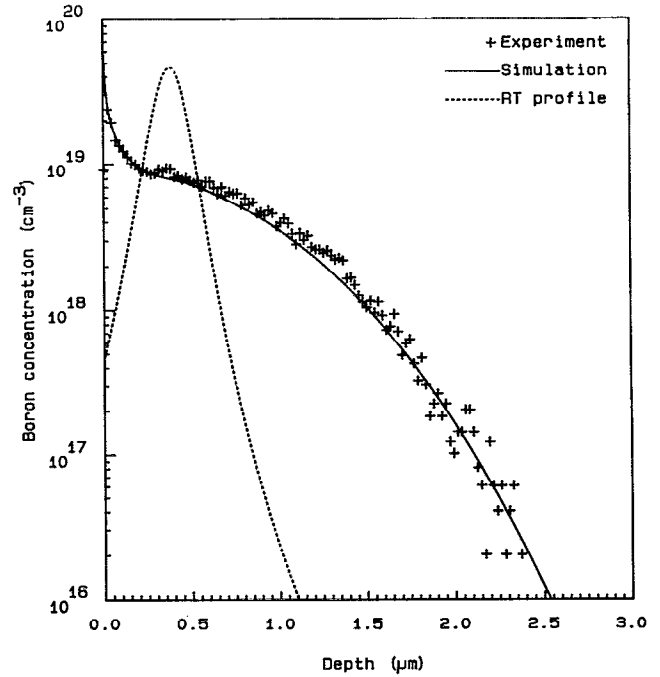


FIG. 2. Simulation of the boron distribution after the high-temperature implantation compared to the room-temperature implantation profile.

nantly via self-interstitials⁸ ($D_{0V} \ll D_{0I}$), the experimental results indicate the validity of Eqs. (1) or (3) rather than of Eq. (2) for dopant diffusion of boron via self-interstitials. This is in agreement with the findings of Loualiche *et al.*⁹, who used proton irradiation in the temperature range from 500 to 800 °C. However, Eqs. (2) or (3) could still be

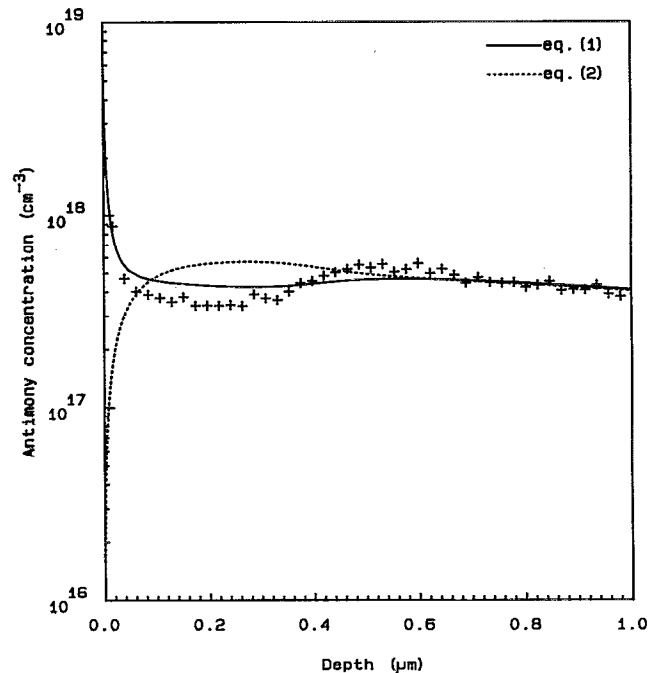


FIG. 3. Simulation of the effects of point-defect gradients on the diffusion of antimony.

valid for diffusion of dopants via vacancies. Therefore, prior to the implantation of boron at 950 °C, antimony, which is assumed to diffuse predominantly via vacancies⁸ ($D_{0I} \ll D_{0V}$), was implanted into the wafer and annealed to give a flat profile within the first micrometer. In Fig. 3, the antimony profile after high-temperature implantation is displayed together with numerical solutions according to Eqs. (1) and (2), the latter being identical to Eq. (3) for the set of parameters used. The experimental profile shows an uphill diffusion at the surface and less pronounced in a depth of about 500 nm. This uphill diffusion is caused mainly by the gradients of the point defects because the boron concentration is intrinsic for the most part of the process and nearly intrinsic toward the end of the process. Since the solution to Eq. (1) agrees well with the experiments in contrast to the solution to Eqs. (2) and (3), we conclude that antimony diffuses at 950 °C predominantly via a vacancy-pair diffusion mechanism.

In conclusion, it has been demonstrated that diffusion experiments can be explained well under the assumption that boron and antimony diffuse at 950 °C preferentially

via pairs with point defects. Other theories predicting a dopant flux in the direction opposite to the flux of point defects lead to results which are in contrast to the experimental evidence. The diffusion of boron can be explained alternatively by an atomistic-diffusion model predicting dopant diffusion in the direction of the flux of self-interstitials.

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