General model and segregation coefficient measurement for ultrashallow doping by excimer laser annealing

Jean-Numa Gillet, a Jean-Yves Degorce, and Michel Meunierb
Laser Processing Laboratory, Department of Engineering Physics, École Polytechnique de Montréal, C. P. 6079, succ. Centre-ville, Montréal, Québec H3C 3A7, Canada

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A general model of ultrashallow doping by excimer laser annealing is derived from only one diffusion-segregation equation. In our model, the relative dopant profile after some laser shots reaches a stationary distribution, which only depends on the segregation and liquid-phase diffusion coefficients of the dopant but not on the laser-process parameters. From this result, a one-point method is proposed to experimentally determine the out-of-equilibrium segregation coefficient $k$.

Ultrashallow doping is essential to continue the downsizing for fabrication of the sub-100 nm metal–oxide–semiconductor (MOS) devices. For instance, the depth of a PMOS junction needs to be as shallow as 15–25 nm in the 90 nm complementary MOS technology. The formation of ultrashallow junctions also requires rapid and high-temperature annealing to increase dopant electrical activation and remove implantation defects in the silicon. Currently, conventional rapid thermal annealing (RTA) and field annealing reach a maximum dopant concentration at the material surface has to be measured prior to determine the $k$ values. Experimental dopant profiles are compared to simulations generated with experimental $k$ values. © 2005 American Institute of Physics. [DOI: 10.1063/1.1927275]
tion of $\chi(\mathbf{r}, t)$ from 0 to 1 inside a thin region with a finite thickness (of $\sim 5$ nm in our model) around the liquid-solid interface, since this interface can be located by thermal modeling.\textsuperscript{23–25} On the other hand, noting that the diffusion coefficient in the liquid phase $D_L$ ($\sim 10^{-4}$ cm$^2$/s) is higher by several orders of magnitude than that in the solid phase ($\sim 10^{-12} - 10^{-8}$ cm$^2$/s),\textsuperscript{13} $D$ in Eq. (2) can be approximated by $D(\mathbf{r}, t, D_j) = D_L \chi(\mathbf{r}, t)$ for both liquid and solid subdomains, which leads to an invariant profile $C(\mathbf{r}, t) = C_0(\mathbf{r})$ (with $C_0$ being the initial as-implanted concentration) in the part of the material that is never melted.

Now, we assume an arbitrary laser annealing process with a number of identical laser shots and a melted domain that takes the same maximal volume $\Omega_{\text{max}}$ during each shot. This assumption is reasonable since the needed number $N$ of laser shots to reach the permanent diffusion regime is low enough to avoid a nonreversible modification of the bulk thermal and optical properties. In such a reversible laser process, the dopant concentration solution $C(\mathbf{r}, t)$ of Eq. (2) converges after a number of shots $N \approx 10$ to a stationary solution $C_\text{av}(\mathbf{r})$ in the quenched material with the volume $\Omega_{\text{max}}$, which only depends on $D_L$, $k$, $\Omega_{\text{max}}$, and the average concentration $C_\text{av}$ over $\Omega_{\text{max}}$, but not on the laser-process parameters and initial profile $C_0(\mathbf{r})$. Indeed, in Eq. (2), the terms $\nabla \cdot (D \nabla C)$—which tends to make uniform the dopant profile over $\Omega_{\text{max}}$—and $-\nabla \cdot (DCA)$—which tends to push the dopant to the bulk surface—respectively, depend on the parameters $D_L$ and $k$ as well as the distribution $\chi(\mathbf{r}, t)$ for both. These are not related to the laser-process parameters in our model, since $D_L$ only depends on the dopant species,\textsuperscript{13} while $k$ is experimentally measured with a one-point method, as explained in the following, and $\chi(\mathbf{r}, t)$ can be assigned, as shown by Eqs. (2) and (3), independently of the moving interface velocity $d\mathbf{r} / dt$. Therefore, after a sufficient number of openings and closings of the melted zone, only the same diffusion states $C(\mathbf{r}, t)$—the equilibrium solutions of Eq. (2)—can be achieved by the dopant-diffusion process during each laser shot. As a consequence, when the permanent regime has been reached, the unique state $C(\mathbf{r}, t) = C_\text{av}(\mathbf{r})$, which is only related to $D_L$, $k$, and $\Omega_{\text{max}}$ as well as $C_\text{av}$ owing to mass conservation, is sufficient to determine the dopant profile in the quenched material after a laser shot.

Owing to the large dimensions of even few mm$^2$ of the incident normal beam of the excimer laser,\textsuperscript{7} heating can be considered as uniform in ELA, so that the dopant is only redistributed in the $x$ direction, which is perpendicular to the bulk surface.\textsuperscript{7,12–14} Therefore, $\mathbf{r}$ and $\nabla$ are replaced by the depth coordinate $x$ with $x = 0$ at the material surface and partial derivative $\partial / \partial x$, respectively, in Eqs. (2) and (3); and the dopant concentration solution $C(x, t)$ of Eq. (2) is one-dimensional (1D), assuming a 1D initial as-implanted profile $C_0(x)$. In ELA modeling, the solution $C(x, t)$ of Eq. (2) converges after a number $N$ of identical laser shots to the stationary dopant profile $C_\text{av}(x)$ in the quenched material with an average concentration $C_\text{av}$ over the maximal melt depth $h$. However, after scaling of the space-and-time coordinates in Eq. (2) as $\xi = x / h$ (with $0 \leq \xi \leq 1$) and $\psi = t / h^2$, respectively, another PDE is obtained in the scaled space time $(\xi, \psi)$, but with the same formulation than that of Eq. (2). Hence, the solution $C'(\xi, \psi) = C[x(\xi), t(\psi)]$ of the other PDE converges again to the same profile $C'(\xi) = C_\text{av}(x(\xi))$, which is now independent of $h$ owing to the scaling. After division by $C_\text{av}$, we obtain the relative profile $c(\xi) = C'(\xi) / C_\text{av}$, which only depends on the parameters $D_L$ and $k$. Consequently, $c(\xi)$ is the relative stationary dopant profile of all ELA processes with the same $D_L$ and $k$.

During ELA, the dopant at the moving interface has insufficient time to segregate with the equilibrium segregation coefficient $k_c$, so that a $k > k_c$ must be used in Eq. (2).\textsuperscript{14,17,18} We propose a one-point experimental method to measure the out-of-equilibrium segregation coefficient $k$. Our method only requires the experimental measurement of the relative stationary dopant concentration $c(0)$ at the surface $x = 0$, assuming that $h$ and $C_\text{av}$ are known. First, we derived from simulations with Eq. (2) and a finite-element method, an analytical relationship between $c(0)$ and the parameters $D_L$ and $k$ for the dopant in the silicon. We considered the same pre-computed thermal process to obtain $\chi(x, t)$ in Eq. (3). After $N \approx 10$ laser shots, we obtain relative profiles $c(\xi)$ for four dopant species: Sb, B, As, and In with the values of $D_L$ given in Ref. 13. For each dopant species, we also computed profiles $c(\xi)$ for 13 values of $k$ between $10^{-5}$ and 1, so that we obtained a database of 52 characteristic profiles $c(\xi)$. From our database, we extracted 52 values of $c(0)$. For each dopant species, we observed the same nonlinear behavior of $\log c(0)$ as a function of the segregation indicator $p = -\log k$. When $p \approx 0$ (i.e., $k \approx 1$), segregation is low and $\log c(0)$ linearly increases with $p$. However, when $p \approx 1$ (i.e., $k \approx 0.1$), the curve of $\log c(0)$ becomes nonlinear and saturates to a constant plateau when $p \approx 3$ (i.e., $k \approx 0.001$). By curve fitting with a hyperbolic tangent, we can therefore derive the following approximate analytic relationship between $\log c(0)$ and $p$:

$$\log c(0) = \alpha(D') \tanh p,$$

where the factor $\alpha$ depends on the dimensionless diffusion coefficient $D' = D_L / D_{\text{ef}}$ with $D_{\text{ef}} = 6.9 \times 10^{-4}$ cm$^2$/s being a reference set to the liquid diffusion coefficient of In. $\alpha$ in Eq. (4) only depends on the dopant species and linearly increases with $\log D'$ for the considered $D_L$ range ($\sim 10^{-4}$ to $\sim 7 \times 10^{-4}$ cm$^2$/s). Hence, $\alpha$ can be derived from the approximate analytic relationship: $\alpha(D') = b_0 + b_1 \log D'$, where $b_0 = 0.840 \pm 0.001$ and $b_1 = 0.705 \pm 0.031$ are fitting constants. Then, by dividing both sides of Eq. (4) by $\alpha$, one obtains the general behavior of the dopant at $x = 0$ after ELA, as shown in Fig. 1, which does not depend on the dopant species. After $\alpha$ is determined, the measurement of the only quantity $c(0)$ enabled us to obtain the diffusion coefficient $D$.
able us to determine the experimental $k$ value from Eq. (4) or the curve of Fig. 1. Our one-point method avoids the inconvenience of the preceding measurement methods of $k$, which require one to simulate a large number of dopant profiles associated with several $k$-values with a full numerical model and then find the best fit with the experimental dopant profile from which the experimental $k$ value is approximately obtained. Consequently, those methods demand the use of sophisticated and computationally expensive software tools for the experimentalist to be capable of measuring $k$, in contrast to the one-point method.

Our model has been compared to experimental results. Initial Gaussian profiles of As and In with maximal concentrations of $5 \times 10^{19}$ cm$^{-3}$ were implanted over a depth of $\sim 100$ nm in bulk Si. We performed 100 laser shots on the samples with an excimer laser (wavelength $\lambda = 248$ nm, pulse width $\tau = 15$ ns, and fluence $\phi = 0.6$ J/cm$^2$) to reach the final dopant concentration profiles. Two experimental relative profiles as obtained by SIMS are shown in Fig. 2 by the dotted curves marked by full lines with no mark and diamonds for In and As, respectively.

Moreover ELA is well adapted to In doping, because high solubility and electrical activation of In can be obtained by ELA, but not by RTA. From Fig. 2, we find in our samples $c(0) = 1$ and $c(0) = 5.25$ for As and In at $x = 0$, respectively. Then, with our one-point method, we obtain $k_{\text{As}} = 1$ (i.e., $p = 0$) and $k_{\text{In}} = 0.053$ (i.e., $p = 1.276$) in the As- and In-doped samples, respectively. As expected, these $k$ values are several orders of magnitude higher than those at equilibrium of 0.11 and $4 \times 10^{-4}$ for As and In, respectively. To validate our one-point method, we computed from Eq. (2) the relative stationary profiles $c(x/h)$ for As and In with the experimental $k$ values. These profiles are rescaled between $x = 0$ and $x = h$, and denoted by full lines with no mark for In and diamonds for As. As shown in Fig. 2, both computed profiles fit very well with the experimental ones. In addition, by linear interpolation with a first-order Taylor development, we can obtain with a good approximation from our database a full numerical profile of a dopant related to an arbitrary $k$ value. Therefore, we can also reconstitute with rapidity the numerical profile related to a measured $k$ value without further numerical simulation.

In summary, a general diffusion-segregation model was derived from only one PDE and was applied to ultrashallow doping by ELA. The relative stationary dopant concentration, which only depends on $D_L$ and $k$ in our model, is obtained after some laser shots. From this result, we proposed a one-point method for the experimental determination of the out-of-equilibrium $k$ value, which requires only the prior measurement of $c(0)$ and knowledge of $h$ and $C_{\text{av}}$. Experimental profiles fit very well with simulations obtained with experimental $k$ values.

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