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J. D. Fehribach, R. Ghez, and G. S. Oehrlein

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Asymptotic estimates of diffusion times for rapid thermal annealing

J. D. Fehribach,[a] R. Ghez, and G. S. Oehrlein
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

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Temperature profiles for rapid thermal annealing of ion implanted material are analyzed using asymptotic methods. Although only rapid thermal annealing is discussed, these methods are also applicable to many other annealing processes. Formulas for effective diffusion distance and effective annealing time are given which correct for the deviations of actual annealing profiles from ideal annealing profiles. The three major deviations considered are (1) ramp terms, (2) rising plateaus, and (3) plateau overshoots. The analysis shows that even relatively small deviations can have sizable effects.

When ion-implanted material is annealed, the ideal time-temperature profile $T(t)$ is rectangular (i.e., it is a step function). In practice, however, this ideal is not achieved. One finds instead that the ramp-up and ramp-down sections of the profile are not vertical, that the plateau temperature may not be constant, and that the ramp-up may overshoot the temperature plateau (see Fig. 1). In long furnace anneals, these effects tend to have little influence on the diffusion of the implanted material since they can be "averaged out" over the entire anneal. In rapid thermal annealing (RTA), however, they are experimentally much harder to control, and generally they have not been taken into account in the analysis of these short time anneals. In this letter, asymptotic methods are used to show that substantially more diffusion occurs during RTA when these deviations are present, even if their relative size is only several tenths of one percent. Equations are presented which can be used to more accurately calculate such diffusion parameters as effective diffusivity. It should be kept in mind, however, that while these results are particularly significant for RTA, they are in fact applicable to any annealing process.

Throughout this letter, assume that the temperature dependence of the diffusivity D of the implanted ions is given by the Arrhenius expression

$$D(T) = D_0 e^{-E/kT}, \tag{1}$$

where E is the activation energy, k is Boltzmann's constant, and D_0 is also constant. To demonstrate the effects of small perturbations in the annealing profile, consider the experimentally measurable parameter[1]

$$\theta = \int_{-\infty}^{\infty} D(T(t))\, dt. \tag{2}$$

In this letter, θ will be referred to as the *effective diffusion distance* (even though it has units of distance squared), and θ should be viewed as a measure of the extent to which the implanted ions have diffused in the sample. In the ideal situation where the temperature profile is rectangular, one easily finds that

$$\theta_{\text{ideal}} = (D_0 e^{-E/kT_p}) t_p = D_p t_p, \tag{3}$$

where T_p is the plateau temperature and t_p is the duration of the plateau.

Expressions such as (2), the integral of a rate constant, represent the effect of driving forces (here, temperature schedules) on a kinetic process. Such expressions have often been discussed in conjunction with thermally driven processes, e.g., flash desorption[2] or thermally stimulated currents.[3] For furnace diffusion, Eq. (2) has long been used to estimate effective diffusion temperatures,[4] and its numerical evaluation is standard practice.[5]

The first nonideal effects to be considered are those caused by the temperature ramps. Using Laplace's method[6] (a form of the method of steepest descents), one finds that these effects depend on the order of contact at the ramp-plateau junctions, i.e., they depend on the number of derivatives which are zero at these junctions[7] (see Fig. 2). To see that this is the case, assume that the ramp-up and the ramp-down junctions with the plateau occur at $t = 0$ and $t = t_p$ respectively. Then let the temperature profile be given by

$$T(t) = T_p[1 - f(t)], \tag{4}$$

where

$$f(t) = \begin{cases} f_1(t) & t < 0 \\ 0 & 0 \leqslant t \leqslant t_p. \\ f_2(t) & t_p < t \end{cases} \tag{5}$$

As for the functions f_1 and f_2, assume that f_1 makes nth order contact with the zero function at $t = 0$ [i.e., $f_1^{(i)}(0) = 0$ for $i = 0, ..., n$, but $f_1^{(n+1)}(0) \neq 0$], while f_2 makes mth order contact at $t = t_p$. Finally let $\beta = E/kT_p$. Then

$$\theta = D_0 \int_{-\infty}^{0} e^{-\beta/[1-f_1(t)]} dt + D_p t_p + D_0 \int_{t_p}^{\infty} e^{-\beta/[1-f_2(t)]} dt. \tag{6}$$

Provided $\beta \gg 1$ (here $\beta \gtrsim 30$), Laplace's method can be applied

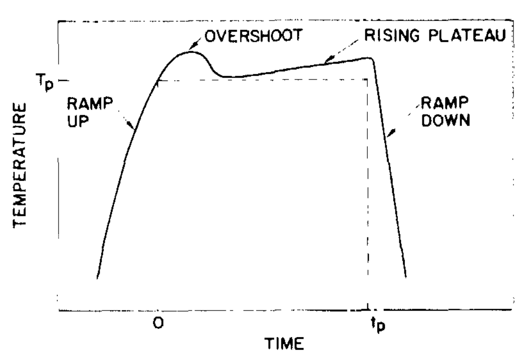

FIG. 1. Schematic of an ideal profile (represented by dashed lines) vs a "worst case" profile (represented by solid lines) for an anneal of time t_p at a plateau temperature T_p. The three profile deviations are indicated.

[a] On leave from Department of Mathematics, Duke University, Durham, North Carolina 27706.

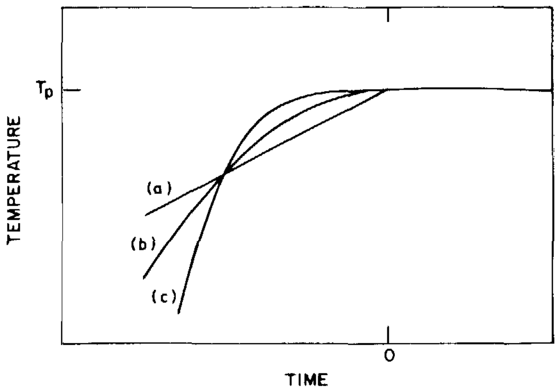

FIG. 2. Schematic of degrees of contact at the ramp-plateau junction: (a) zeroth order contact, (b) first order contact, and (c) third order contact. The plateau temperature is T_p and the junction occurs at time zero.

to the first and third integrals.[8] Assuming that $f_1(t)$ and $f_2(t)$ can be expanded in Taylor series near $t = 0$ and $t = t_p$ respectively, Laplace's method yields

$$\theta \sim D_p \left[\left(\frac{(n+1)!}{\beta |f_1^{(n+1)}(0)|} \right)^{1/(n+1)} \Gamma\left(\frac{n+2}{n+1} \right) + t_p + \left(\frac{(m+1)!}{\beta |f_2^{(m+1)}(t_p)|} \right)^{1/(m+1)} \Gamma\left(\frac{m+2}{m+1} \right) \right]. \quad (7)$$

The first and third terms in square brackets in Eq. (7) represent the additional time due to the ramp-up and the ramp-down [cf. Eq. (3)]. The entire bracketed term will be referred to in this letter as the *effective annealing time*.

To estimate the magnitude of these extra terms, consider an actual RTA profile for ion-implanted silicon[9] [see Fig. 3(a)]. Here data fitting indicates that the ramp-up and the ramp-down make respectively third and zeroth order contact with the plateau. Now assume an activation energy of 4 eV. Setting $n = 3$ and $m = 0$ in Eq. (7) and obtaining the values of $f_1^{(n+1)}(0)$ and $f_2^{(m+1)}(t^p)$ from the figure, one computes the first term in Eq. (7) to be 3.8 s and the third term to be 0.3 s. The ramp-up thus contributes a significant amount of extra time, while the ramp-down term is not as important. In general, one finds that the higher the order of contact at a ramp-plateau junction, the greater the amount of time contributed by that ramp. Since ramp-down contact is almost always of zeroth order, ramp-down times tend to be less significant. Ramp-up contact, on the other hand, is usually of higher order and thus is often significant.

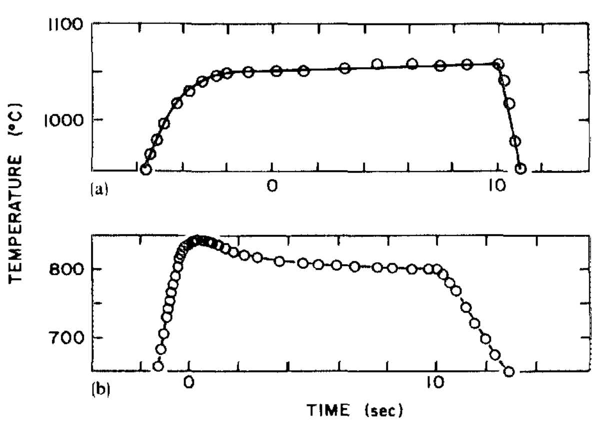

FIG. 3. Two nominal 10-s anneals: (a) For $t \leqslant 0$, the curve is $T(t) = 1050(1 - t^4/11000)$. For $t \geqslant 10$, the slope of the line is -109.1 °C/s. $T_p = 1050$ °C while $T_m = 1058$ °C. Because of the high degree of contact of the ramp-up and the rise in the plateau, $\theta/D_p = 15.2$ s. (b) This curve is formed by straight line segments connecting the data points. The 800 °C plateau is overshot by almost 50 °C. $\theta/D_p = 22.7$ s.

A second difficulty which one encounters in measuring the effective diffusion distance from a temperature profile is that the plateau is not always constant. Rather it may rise by as much as 10° in 10 s. To see what effects this rise has on θ, consider a linearly rising plateau:

$$T(t) = T_p + (T_m - T_p)\frac{t}{t_p}, \quad (8)$$

where T_p is the temperature at the beginning of the plateau (and would be the constant plateau temperature if no rise occurred) and T_m is the temperature at the end of the plateau. Let $\delta = (T_m - T_p)/T_p$ be the relative increase in temperature. Restricting to just the plateau section of the profile, define

$$\theta_p = \int_0^{t_p} D(T(t))\, dt. \quad (9)$$

The assumption that $\delta \ll 1$ then yields

$$\theta_p \sim D_p t_p \left(\frac{e^{\beta\delta} - 1}{\beta\delta} \right). \quad (10)$$

So θ_p is still linear in t_p, but now there is a weighting factor (in brackets)[10] which is independent of t_p and which goes to 1 as δ goes to 0.

Returning to the previous example, from Fig. 3(a) one sees that the plateau temperature rises 8° in 10 s. Thus $t_p = 10$ s and $\delta \cong 6.0 \times 10^{-3}$. Again assuming an activation energy of 4 eV, Eq. (10) yields that $\theta_p/D_p \cong 11.1$ s. The effective annealing time for this temperature profile is then found by replacing the plateau term in Eq. (7) by Eq. (10). Combining the previous calculations for the ramp-up, the plateau, and the ramp-down, one finds an effective annealing time of 15.2 s. Thus the effective diffusion distance for the anneal represented in Fig. 3(a) (having a nominal annealing time of ten seconds) is the same as the effective diffusion distance for an ideal rectangular anneal with a plateau temperature of 1050 °C and with a plateau time of 15.2 s. Samples annealed under this temperature profile would show significantly more diffusion (i.e., θ would increase by a factor of 1.52) than would be expected for an ideal profile with plateau at 1050 °C.

The methods discussed so far work well in analyzing the annealing profile in Fig. 3(a). But of course the temperature rise across a plateau is not always linear [indeed it is not entirely linear even in Fig. 3(a)]. In addition, data fitting a power of t at a ramp-plateau junction may be impossible, particularly if the ramp-up overshoots the plateau (cf. Fig. 1). To overcome these problems, one needs a method for calculating the effective diffusion distance which does not require curve fitting. Such a method is described next. First digitize the annealing profile into a set of discrete points (as in Fig. 3). Then write θ as the sum of integrals between each pair of successive points in the profile. Let Δt_i be the length of the ith time interval of the profile, let T_i be the temperature at the beginning of the ith interval, and let T_p be the nominal plateau temperature for the entire profile. Also define $\beta_i = E/kT_i$. Approximating the profile between such pairs by straight lines, one can then use the asymptotic approximation for linear profiles given by Eq. (10) to find the summation formula

$$\theta = \sum_i \int_{t_i}^{t_{i+1}} D_0 e^{-E/kT(t)}\, dt \qquad (11a)$$

$$\sim D_p \sum_i e^{\beta_i(T_i/T_p - 1)} \left(\frac{e^{\beta_i\delta_i} - 1}{\beta_i \delta_i} \right) \Delta t_i. \qquad (11b)$$

In the last equation, δ_i is the relative rise or fall in temperature across the ith time interval, i.e., $\delta_i = (T_{i+1} - T_i)/T_i$. Note that while the derivation of Eq. (10) assumed that the temperature was increasing across the interval, the equation is still valid when the temperature decreases. In the later case, however, δ is negative.

As an application of Eq. (11b), consider the annealing profile[9] in Fig. 3(b). This profile contains a significant overshoot of its 800 °C plateau. Such overshoots may occur for $T_p \lesssim 900$ °C. Again using an activation energy of 4 eV, Eq. (11b) yields an effective annealing time of 22.7 s for this nominal 10-s anneal. The effective diffusion length for this anneal is thus the same as that of an 22.7-s ideal anneal with a plateau temperature of 800 °C.

It should be emphasized that the diffusivity must be given by Eq. (1) for these results to be applicable, although similar analytic formulae could be developed for *any* given functional form $D(T)$. In particular, effects associated with defect removal in the RTA of silicon can cause a substantial change in activation energy across a small temperature range.[11] The results of this letter are not applicable to anneals whose plateaus are in the neighborhood of such a range. When Eq. (1) is satisfied, three points may be concluded from this work. Firstly, the order of contact at the ramp-plateau junctions is the key in determining the importance of the ramps to the annealing process. Secondly, even relatively small deviations from an ideal profile can significantly change the effective annealing time in RTA. This point is of particular importance when one is working with multiple-pulse anneals where the effects of ramps and overshoots are compounded. The last point is that Eqs. (7), (10), and/or (11b) can be used to accurately compute effective annealing times. Since θ values can be measured from ion-implant concentration profiles, these equations can be used to calculate effective diffusivities and activation energies.[12] Diffusion parameters calculated in this manner would be more accurate than those calculated by simply dividing the measured value of θ by the nominal annealing time. Diffusivities could be changed by roughly a factor of 2 in 10-s anneals and by perhaps a factor of 5 in 1- or 3-s anneals.

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[1] Because of the form of Eq. (3), Dt is often used instead of θ to denote this parameter. Since it is experimentally measurable, it is used to compute values for D_0 and E. Strictly speaking, the integral in Eq. (2) should be carried out over the time interval of the anneal. However, since $T(t)$ is essentially zero for values of t outside this interval, the limits of integration may be extended without changing the value of the integral. This parameter is also used to solve the diffusion equation when D_0 is independent of concentration and position; see R. Ghez, G. S. Oehrlein, T. O. Sedgwick, F. F. Morehead, and Y. H. Lee, Appl. Phys. Lett. **45**, 881 (1984).

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[5] S. J. Rothman, in *Diffusion in Crystalline Solids*, edited by G. E. Murch and A. S. Nowick (Academic, NY, 1984), pp. 1–61.

[6] See, for example, C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw–Hill, NY, 1978), pp. 261–263.

[7] In the laboratory the order of contact is determined by how fast the heat source brings the sample to the plateau temperature: the longer and slower the approach, the higher the order of contact (cf. Fig. 2).

[8] Only the sections of the ramps within roughly 20° of the plateau cause a significant amount of diffusion. Physically, this is the key in the use of Laplace's method.

[9] Experimental details of the measurement procedure have been described by T. O. Sedgwick, S. A. Cohen, G. S. Oehrlein, V. R. Deline, R. Kalish, and S. Shatas, in *VLSI Science and Technology/1984*, edited by K. E. Bean and G. A. Rozgonyi (The Electrochemical Society, Pennington, NJ, 1984), p. 192.

[10] Equation (10) is also interesting since it may be possible to calculate an activation energy from a single plateau temperature using this equation and several profiles with sufficiently small δ values.

[11] Such effects have been reported by G. S. Oehrlein, R. Ghez, J. D. Fehribach, E. F. Gorey, T. O. Sedgwick, S. A. Cohen, and V. R. Deline, in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors*, edited by J. M. Parsey (The Metallurgical Society of AIME, Cleveland, 1984).

[12] These calculations may have to be iterative since the correction terms contain β which in turn depends on the activation energy.