DEFECT ANNEALING IN IRRADIATED SEMICONDUCTORS

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INTRODUCTION

This report describes progress for the period April 1, 1965 to September 30, 1965 in the research program supported by NASA Research Grant NsG-602.

Research work in this period involved:

1. Further investigation of the possibility of obtaining exact analytic solutions of the general annealing equations with one secondary defect complex.
2. Development of approximate solutions of the annealing equations with one secondary defect complex.
3. Computer calculations to investigate the behavior of the approximate solutions.

ANNEALING MODEL WITH ONE SECONDARY DEFECT COMPLEX

The isothermal annealing equations consistent with this model have been given previously (1) as

$$\frac{di}{dt} = -K_1Vi \tag{1}$$

$$\frac{dv}{dt} = K_1Vi - K_2V(I_o - C) + K_3C \tag{2}$$

$$\frac{dc}{dt} = K_2V(I_o - C) - K_3C \tag{3}$$

$$i = V + C \tag{4}$$

where

i = interstitial concentration

V = vacancy concentration

C = secondary defect complex concentration

I = impurity concentration

o = subscript denoting initial value

K_1, K_2, K_3 = rate constants

For convenience, the fraction of defects not annealed defined by $p \equiv \frac{i}{i_o}$ can be introduced and equations (1), (2), (3), (4) rewritten as

$$\frac{dp}{dt} = -K_1 V p \tag{5}$$

$$\frac{dv}{dt} = K_1 V i_o P - K_2 V (I_o - C) + K_3 C \tag{6}$$

$$\frac{dc}{dt} = K_2 V (I_o - C) - K_3 C \tag{7}$$

$$i_o P = V + C \tag{8}$$

Numerical solutions of the set of equations (5) - (8) can be readily obtained (1). However, the equations contain a rather large number of constants whose values are uncertain. The rate constants K_1, K_2, K_3 are particularly uncertain. In view of this situation, a detailed comparison of the predictions of the annealing model with experimental isothermal annealing curves is difficult. In general, it is necessary to select empirical values for the model parameters. Attempts to fit annealing data in this manner, using numerical computer solutions of the annealing equation, have so far been unsuccessful. This result is attributed to the large number of empirical model parameters rather than to a failure of the model itself.

As a consequence of the difficulties with numerical solutions, further efforts were made to obtain exact analytic solutions of the annealing equations for the general case $K_1 \neq K_2$.

The set of equations (5), (6), (7) represents a set of coupled, non-linear, first order differential equations. Equation (8) is redundant. It is possible to replace the coupled set of first order equations by an uncoupled set of second order equations. Differentiation and substitution operations performed with (5), (6), (7) lead to

$$\frac{d^2p}{dt^2} - \left(1 + \frac{K_2}{K_1}\right) \frac{1}{p}\left(\frac{dp}{dt}\right)^2 + \left[(K_1 - K_2) i_o p + (K_2 I_o + K_3)\right] \frac{dp}{dt} + K_3 K_1 i_o p^2 = 0 \tag{9}$$

$$\frac{d^2V}{dt^2} - \frac{1}{V + \frac{K_3}{K_2-K_1}} \left(\frac{dv}{dt}\right)^2 + \left[\frac{V(K_2I_o + K_3+K_2V)}{V + \frac{K_3}{K_2 - K_1}} + K_2I_o+K_3+2K_2V+K_1V \right] \frac{dv}{dt} + $$

$$+ K_1V^2 (K_2I_o + K_3 + K_2V) = 0 \qquad (10)$$

$$(I_o-C)\frac{d^2C}{dt^2} + \left(1 + \frac{K_1}{K_2}\right)\left(\frac{dc}{dt}\right)^2 + \left[I_o(K_2I_o+ K_3) + \left(\frac{2K_1K_3}{K_2} + K_1I_o - 2K_2I_o\right) C + \right.$$

$$\left. + (K_2 - K_1)\, C^2 \right] \frac{dc}{dt} + \left(\frac{K_3{}^2K_1}{K_2} + K_3K_1I_o\right) C^2 - K_3K_1C^3 = 0 \qquad (11)$$

Equation (9) is of particular interest since p is the quantity measured in isothermal annealing experiments.

Equations (9), (10), (11) can be reduced to first order equations by introducing $X = \frac{dp}{dt}$, $y = \frac{dv}{dt}$, and $Z = \frac{dc}{dt}$. This procedure yields

$$X \frac{dx}{dp} - \frac{A}{p} X^2 + (Bp + C)\, X + Dp^2 = 0 \qquad (12)$$

$$y \frac{dy}{dv} - \frac{1}{v + L}\, y^2 + \left[\frac{v(M + Nv)}{v + L} + M + \theta v \right] y + Pv^3 + Qv^2 = 0 \qquad (13)$$

$$(I_o - C)\, Z\frac{dZ}{dc} + AZ^2 + (E + FC + GC^2)\, Z + HC^2 - JC^3 = 0 \qquad (14)$$

where

$A \equiv 1 + \frac{K_2}{K_1}$

$B \equiv (K_1 - K_2)\, i_o$

$C \equiv K_2I_o + K_3$

$D \equiv K_3K_1i_o$

$E \equiv I_o\, (K_2I_o + K_3)$

$F \equiv \frac{2K_1K_3}{K_2} + K_1I_o - 2K_2I_o$

$G \equiv K_2 - K_1$

$$H \equiv \frac{K_3^{\,2} K_1}{K_2} + K_3 K_1 I_o$$

$$J \equiv K_3 K_1$$

$$L \equiv \frac{K_3}{K_2 - K_1}$$

$$M \equiv K_2 I_o + K_3 = C$$

$$N \equiv K_2$$

$$\Theta \equiv 2K_2 + K_1$$

$$P \equiv K_1 K_2$$

$$Q \equiv K_1 (K_2 I_o + K_3)$$

By means of suitable substitutions, equations (12), (13), (14), can all be transformed to Abelian differential equations of the first kind. The standard Abelian form is

$$U^1 = f_o(s) + f_1(s)\, y + f_2(s)\, y^2 + f_3(s)\, y^3 \tag{15}$$

Unfortunately, no standard technique exists for solving Abelian equations. The substitutions

$$X = \frac{1}{U_1}\ , \ y = \frac{1}{U_2}, \text{ and } Z = \frac{1}{U_3}$$

transform (12), (13), (14) into

$$U_1{}' = - \frac{A}{p} U_1 + (Bp + C)\, U_1{}^2 + Dp^2 U_1{}^3 \tag{16}$$

$$U_2{}' = \frac{1}{V + L}\ U_2 - \left[\frac{V(M+NV)}{V+L} + M + \Theta V \right] U_2{}^2 + (PV^3 + QV^2) U_2{}^3 \tag{17}$$

$$U_3{}' = - \frac{A}{I_o - C}\ U_3 + \frac{E + FC + GC^2}{I_o - C}\ U_3{}^2 + \frac{HC^2 - JC^3}{I_o - C}\ U_3{}^3 \tag{18}$$

The problem of finding exact analytic solutions of the annealing equations is therefore equivalent to the problem of solving the Abelian equation (15). Attempts to find exact closed form solutions for (16), (17), and (18) have so far been unsuccessful.

APPROXIMATE SOLUTIONS FOR $K_1 \neq K_2$

As has already been indicated, the annealing equation of primary interest is the p equation

$$\frac{d^2p}{dt^2} - \left(1 + \frac{K_2}{K_1}\right)\frac{1}{p}\left(\frac{dp}{dt}\right)^2 + \left[(K_1 - K_2)\, i_o p + (K_2 I_o + K_3)\right]\frac{dp}{dt} + K_3 K_1 i_o p^2 = 0 \qquad (9)$$

An obvious approximation technique is to consider a partially linearized version of (9). Consider the equation

$$\frac{d^2p}{dt^2} + \alpha\left(\frac{dp}{dt}\right)^2 + \beta\frac{dp}{dt} + \gamma = 0 \qquad (19)$$

where

$$\alpha \doteq -\frac{1}{p}\left(1 + \frac{K_2}{K_1}\right)$$

$$\beta \doteq K_1 i_o\left(1 - \frac{K_2}{K_1}\right) p + (K_2 I_o + K_3)$$

$$\gamma \doteq K_1 i_o K_3 p^2$$

will be taken to be constants. The substitution

$X = \frac{dp}{dt}$ yields

$$\frac{dy}{dt} = -\left(\alpha y^2 + \beta y + \gamma\right)$$

Direct integration of this equation gives

$$\int \frac{dy}{\alpha y^2 + \beta y + \gamma} = -\int dt$$

$$\frac{1}{\delta}\,\mathrm{Ln}\left(\frac{2\alpha X + \beta - \delta}{2\alpha X + \beta + \delta}\right) = -t + c_1 \qquad (20)$$

where

$$\delta = \left(\beta^2 - 4\alpha\gamma\right)^{1/2}$$

and

$$\beta^2 - 4\alpha\gamma > 0$$

The initial condition $X = -K_1 i_o$ for $t = 0$ requres that

$$C_1 = \frac{1}{\delta} \mathrm{Ln}\left(\frac{\beta - \delta - 2\alpha K_1 i_o}{\beta + \delta - 2\alpha K_1 i_o} \right) \qquad (21)$$

Equation (20) can be solved for X to obtain

$$X = \frac{dp}{dt} = \frac{\exp\left[(C_1 - t)\delta\right] \quad (\beta + \delta) + \delta - \beta}{2\alpha\left[1 - \exp \delta \, C_1 - t)\right]} \qquad (22)$$

Direct integration of (22) leads to

$$p = \frac{\beta + \delta}{2\alpha\delta} \left\{ \delta(C_1 - t) + \mathrm{Ln}\left[1 - \exp \delta (t - C_1)\right] \right\} \qquad (23)$$

$$+ \frac{\beta - \delta}{2\alpha\delta} \left\{ \delta(C_1 - t) - \mathrm{Ln}\left[1 - \exp \delta (C_1 - t)\right] \right\} + C_2$$

The initial condition $p = 1$ at $t = 0$ requires that

$$C_2 = 1 - \frac{\beta + \delta}{2\alpha\delta} \left\{ \delta C_1 + \mathrm{Ln}\left[1 - \exp(-\delta C_1)\right] \right\} \qquad (24)$$

$$- \frac{\beta - \delta}{2\alpha\delta} \left\{ \delta C_1 - \mathrm{Ln}\left[1 - \exp(\delta C_1)\right] \right\}$$

Numerical calculations to compare the solution (23) with exact computer solutions have not yet been carried out in view of the fact that a more promising approximation was discovered. It was observed that for a high percentage of experimental isothermal annealing curves, p shows a very flat plateau region out to quite large time values. The interpretation of this behavior in terms of the kinetic annealing model is that the rate constant K_3, which governs the breakup rate of secondary defect complexes, must be very small. It would appear then, that if an approximate solution of equation (9) could be found for $K_3 = 0$, it would be a very useful solution.

For $K_3 = 0$, equation (9) becomes

$$\frac{d^2p}{dt^2} - \left(1 + \frac{K_2}{K_1}\right) \frac{1}{p} \left(\frac{dp}{dt}\right)^2 + \left[(K_1 - K_2)\, i_o p + K_2 I_o\right] \frac{dp}{dt} = 0$$

or

$$\frac{d^2p}{dt^2} - \frac{A}{p}\left(\frac{dp}{dt}\right)^2 + (Bp + C)\,\frac{dp}{dt} = 0 \qquad (25)$$

The substitution $X = \frac{dp}{dt}$ in (25) yields

$$\frac{dX}{dp} - \frac{A}{p}X + (Bp + C) = 0 \qquad (26)$$

The solution of (26) is

$$X = \frac{Bp^2}{A - 2} + \frac{Cp}{A - 1} + C_3p^A \qquad (27)$$

The constant C_3 can be determined from the condition $X = K_1i_o$ for $p = 1$ as

$$C_3 = -\left(K_1i_o + \frac{B}{A-2} + \frac{C}{A-1}\right) \qquad (28)$$

Equation (27) can then be expressed as

$$X = \frac{dp}{dt} = \frac{B}{A-2}p^2 + \frac{C}{A-1}p - p^A\left(K_1i_o + \frac{B}{A-2} + \frac{C}{A-1}\right)$$

so that, in terms of the original constants

$$\frac{dp}{dt} = -K_1i_o\,p\left[p + \frac{I_o}{i_o}\left(p^{K_2/K_1} - 1\right)\right] \qquad (29)$$

Equation (29) can be used to find the annealing plateau level for a particular set of model parameters. For $K_3 = 0$, the plateau criterion is $\frac{dp}{dt} = 0$. The plateau level, $p = P$, is then given by the equation

$$P + \frac{I_o}{i_o}\left(P^{K_2/K_1} - 1\right) = 0 \qquad (30)$$

In general, it is not possible to solve (30) explicitly for P. However, for $K_2 = K_1$ the solution is

$$P = \frac{1}{1 + \frac{i_o}{I_o}} \qquad (31)$$

This result was obtained previously (1) from the analytic solution of the annealing equation for the $K_1 = K_2$ case with K_3 small. For arbitrary

K_2/K_1 , equation (30) can be solved by interation to give plateau levels to any desired accuracy.

In order to obtain the fraction of defects not annealed, p(t), it is necessary to integrate equation (29). This leads to

$$\frac{1}{K_1 i_o} \int_p^1 \frac{dp}{p\left[p + \frac{I_o}{i_o}\left(p^{K_2/K_1} - 1\right)\right]} = t \qquad (32)$$

For arbitrary K_2/K_1, there is no analytic closed form expression for the integral

$$G(p) = \int_p^1 \frac{dp}{p\left[p + \frac{I_o}{i_o}\left(p^{K_2/K_1} - 1\right)\right]} = t$$

This integral can be readily integrated numerically, however, A computer program was written to perform the integration by Simpson's Rule. The solution of the annealing equation (25) can then be written as

$$\frac{1}{K_1 i_o} G(p) = t \qquad (33)$$

It might be noted that G(p) is dimensionless and depends on the ratios $\frac{I_o}{i_o}$ and $\frac{K_2}{K_1}$.

NUMERICAL CALCULATIONS

The possibility of using equation (33) to empirically fit isothermal annealing data was investigated. This curve fitting requires that values be selected for $\frac{I_o}{i_o}$, $\frac{K_2}{K_1}$, and $K_1 i_o$. The ratio $\frac{I_o}{i_o}$ can be established with fairly good accuracy. Then, since the plateau equation (30) involves only $\frac{K_2}{K_1}$ and $\frac{I_o}{i_o}$, a value of $\frac{K_2}{K_1}$ can be selected to give the proper plateau level. Solving (30) for $\frac{K_2}{K_1}$ yields

$$\frac{K_2}{K_1} = \frac{\mathrm{Ln}\,(1 - \frac{i_o}{I_o}\,P)}{\mathrm{Ln}\,P} \qquad (34)$$

The integral G(p) can now be evaluated and a value of $K_1 i_o$ chosen to give the best overall fit between the experimental annealing curve and the theoretical predictions of eq. (33).

This curve fitting procedure was employed for an experimental isothermal annealing curve obtained by Pigg (2) for n-type germanium at 455°C. In this case, $\frac{I_o}{i_o} = 2.81$ and the observed plateau level is $P = 0.22$. The required empirical value of $\frac{K_2}{K_1}$ is given by (34) as $\frac{K_2}{K_1} = 0.0539$. Figure (1) shows the experimental curve and the best theoretical fit. Further calculations of this type are in progress for other isothermal annealing curves reported in the literature.

REFERENCES

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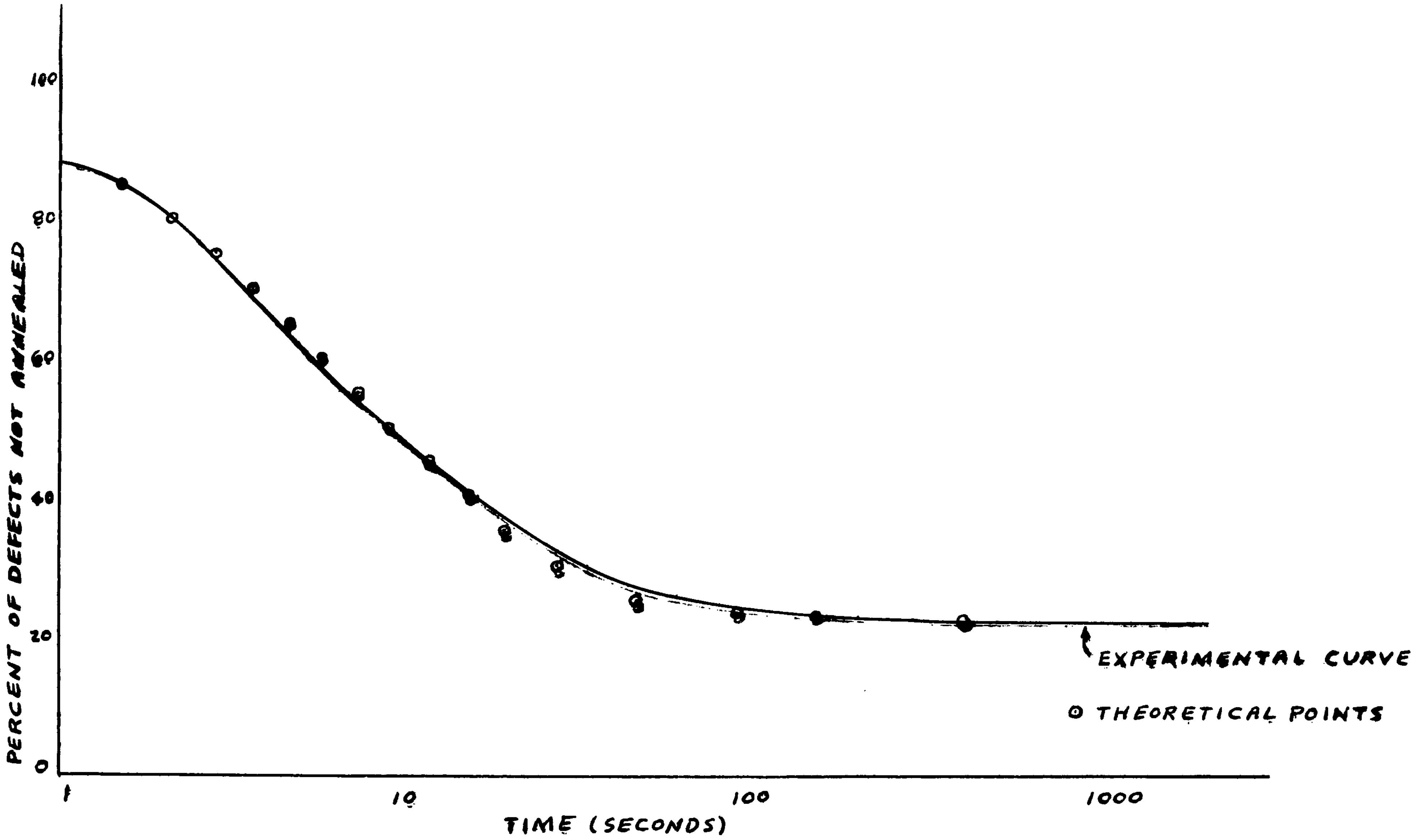

Figure 1. Theoretical Fit of Isothermal Annealing Data For n-Type Germanium at 455°C.