# DEFECT ANNEALING IN IRRADIATED SEMICONDUCTORS

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## INTRODUCTION

This report describes progress for the period October 1, 1964 to March 31, 1965 in the research program supported by NASA Research Grant NsG-602.

Research work in this period involved:

1. Extension of the annealing model to include an arbitrarily large number of secondary defect complexes.
2. Solution of the annealing equations with any number of secondary defect complexes.
3. Computer calculations and data analysis to evaluate the behavior of the kinetic annealing model with one secondary defect complex.

There was one publication during the report period:

"Model For Defect Annealing in Diamond Lattice Semiconductors" by W. Maurice Pritchard, Bulletin of the American Physical Society, Series II, Vol. 10, No. 3, 1965.

## EXTENSION OF THE ANNEALING MODEL TO INCLUDE MORE THAN ONE SECONDARY DEFECT COMPLEX

The kinetic annealing model can be readily extended to include two secondary defect complexes. The schematic representation of this extended model is

$$V + i \xrightarrow{K_A} \text{Annihilation}$$

$$V + I_1 \underset{K_{1B}}{\overset{K_{1F}}{\rightleftarrows}} C_1$$

$$V + I_2 \underset{K_{2B}}{\overset{K_{2F}}{\rightleftarrows}} C_2$$

where

$V$ = concentration of free vacancies

$i$ = concentration of interstitials

$I_1$ = concentration of type 1 impurity

$I_2$ = concentration of type 2 impurity

$C_1$ = concentration of type 1 defect complex

$C_2$ = concentration of type 2 defect complex

The K's are rate constants.

This schematic representation is based on the assumption that the two defect complexes involve different impurity elements. However, the same representation can be used if only one impurity element is involved. In this latter case, $I_2 = I_1$.

The annealing equations consistent with this model are

$$\frac{di}{dt} = -K_A Vi \tag{1}$$

$$\frac{dv}{dt} = -K_A Vi - K_{1F}V(I_{01} - C_1) - K_{2F}V(I_{02} - C_2) + K_{1B}C_1 + K_{2B}C_2 \tag{2}$$

$$\frac{dc_1}{dt} = K_{1F}V(I_{01} - C_1) - K_{1B}C_1 \tag{3}$$

$$\frac{dc_2}{dt} = K_{2F}(I_{02} - C_2) - K_{2B}C_2 \tag{4}$$

$$i = V + C_1 + C_2 \tag{5}$$

where $I_{01}$ and $I_{02}$ are impurity concentrations at $t = 0$. If $C_2$ is eliminated by using the conservation relation (5), the set of equations becomes

$$\frac{di}{dt} = K_A Vi \tag{6}$$

$$\frac{dv}{dt} = -(K_A - K_{1F})Vi + K_{2B}i - (K_{1F}I_{01} + K_{2F}I_{02} + K_{2B})V \tag{7}$$

$$- K_{2F}V^2 + (K_{1F} - K_{2F})VC_1 + (K_{1B} - K_{2B})C_1$$

$$\frac{dC_1}{dt} = K_{1F}I_{01}V - K_{1F}VC_1 - K_{1B}C_1 \tag{8}$$

This set of simultaneous equations can then be solved by a standard power series approach using the series expansions

$$i = \sum_{n=0}^{\infty} a_n t^n \tag{9}$$

$$V = \sum_{n=0}^{\infty} b_n t^n \tag{10}$$

$$C_1 = \sum_{n=0}^{\infty} d_n^1 t^n \tag{11}$$

Substituting the series representations (9), (10) and (11) into equations (6), (7) and (8) and equating coefficients of corresponding powers of t yields the following expressions for the expansion coefficients:

$$a_n = -\frac{K_A}{n} \sum_{i=0}^{n-1} a_i b_{n-1-i} \tag{12}$$

$$\begin{aligned} b_n = {} & \left(1 - \frac{K_{2F}}{K_A}\right) a_n + \frac{K_{2B}}{n} a_{n-1} - (K_{1F}I_{01} + K_{2F}I_{02} + K_{2B}) \frac{b_{n-1}}{n} \\ & - \frac{K_{2F}}{n} \sum_{i=0}^{n-1} b_i b_{n-1-i} + \frac{(K_{1B} - K_{2B})}{n} d_{n-1}^1 \\ & + (K_{1F} - K_{2F}) \sum_{i=0}^{n-1} d_i^1 b_{n-1-i} \end{aligned} \tag{13}$$

$$d_n^1 = \frac{K_{1F}I_{01}}{n} b_{n-1} - \frac{K_{1B}}{n} d_{n-1}^1 - \frac{K_{1F}}{n} \sum_{i=0}^{n-1} d_i^1 b_{n-1-i} \tag{14}$$

These expressions are valid for $n \geq 1$. For $n = 0$,

$$\begin{aligned} a_o &= i_o \\ b_o &= V_o \\ d_o^1 &= C_o = 0 \end{aligned} \tag{15}$$

If both secondary defect complexes are associated with the same impurity element, $I_1 = I_2 = I$ and $I = I_o - C_1 - C_2$. In this case, the annealing equations are:

$$\frac{di}{dt} = - K_A\, Vi \tag{16}$$

$$\frac{dv}{dt} = - K_A Vi - K_{1F}V(I_o - C_1 - C_2) - K_{2F}\, V\, (I_o - C_1 - C_2)$$
$$+ K_{1B}\, C_1 + K_{2B}C_2 \tag{17}$$

$$\frac{dc_1}{dt} = K_{1F}V(I_o - C_1 - C_2) - K_{1B}C_1 \tag{18}$$

$$\frac{dc_2}{dt} = K_{2F}V\,(I_o - C_1 - C_2) - K_{2B}C_2 \tag{19}$$

$$i = V + C_1 + C_2 \tag{20}$$

If $C_2$ is eliminated as before, the system of equations to be solved is:

$$\frac{di}{dt} = K_A Vi \tag{21}$$

$$\frac{dv}{dt} = - (K_A - K_{1F} - K_{2F})\, Vi + K_{2B}i - (K_{1F}I_o + K_{2F}\, I_o + K_{2B})\, V$$
$$- (K_{1F} + K_{2F})V^2 + (K_{1B} - K_{2B})\, C_1 \tag{22}$$

$$\frac{dc_1}{dt} = K_{2F}V(I_o + V - i) - K_{1B}\, C_1 \tag{23}$$

The series expansions (9), (10), and (11) can again be employed. Following the same procedure as before leads to these general expressions for the expansion coefficients for $n \geqslant 1$:

$$a_n = -\frac{K_A}{n} \sum_{i=0}^{n-1} a_i\, b_{n-1-i} \tag{24}$$

$$b_n = (1 - \frac{K_{1F} + K_{2F}}{K_A})\, a_n + \frac{K_{2B}}{n}\, a_{n-1} - (K_{1F}I_o + K_{2F}I_o + K_{2B})\, \frac{bn-1}{n}$$
$$- \frac{(K_{1F} + K_{2F})}{n} \sum_{i=0}^{n-1} b_i b_{n-1-i} + \frac{(K_{1B} - K_{2B})}{n}\, d^1_{n-1} \tag{25}$$

$$d^1_n = \frac{K_{2F}}{n} \left[ I_o b_{n-1} + \sum_{i=0}^{n-1} b_i b_{n-1-i} + \frac{n}{K_A}\, a_n \right] - \frac{K_{1B}}{n}\, d^1_{n-1} \tag{26}$$

The kinetic annealing model can be further extended to include an arbitrary number, J, of types of secondary defect complexes involving vacancies and impurity atoms. The schematic representation of the model in this case is:

$$V + i \xrightarrow{K_A} \text{Annihilation}$$

$$V + I_1 \underset{K_{1B}}{\overset{K_{1F}}{\rightleftarrows}} C_1$$

$$V + I_2 \underset{K_{2B}}{\overset{K_{2F}}{\rightleftarrows}} C_2$$

$$\vdots$$

$$V + I_j \underset{K_{jB}}{\overset{K_{jF}}{\rightleftarrows}} C_j$$

$$\vdots$$

$$V + I_J \underset{K_{JB}}{\overset{K_{JF}}{\rightleftarrows}} C_J$$

It will be assumed that each type of defect complex involves a different impurity element. The annealing equations for this general case are:

$$\frac{di}{dt} = K_A Vi \tag{27}$$

$$\frac{dv}{dt} = - K_A Vi - V \sum_{j=1}^{J} K_{jF} (I_{oj} - C_j) + \sum_{j=1}^{J} K_{jB} C_j \tag{28}$$

$$\frac{dc_j}{dt} = K_{jF} V (I_{oj} - C_j) - K_{jB} C_j \qquad j = 1,2,...J \tag{29}$$

$$i = V + \sum_{j=1}^{J} C_j \tag{30}$$

The conservation relation (30) can be used to eliminate one of the $C_j$ and thus reduce by one the number of differential equations to be solved. However, this is not necessary and is of marginal benefit if J is large. Therefore, in this case, the complete set of differential equations will be solved by the power series method. Equation (30) can then be used as a check on the series solutions.

The required series expansions are

$$i = \sum_{n=0}^{\infty} a_n t^n \tag{31}$$

$$V = \sum_{n=0}^{\infty} b_n t^n \tag{32}$$

$$C_j = \sum_{n=0}^{\infty} d_n^j t^n \tag{33}$$

Introducing the series expansions (31), (32), and (33) into the system of equations (27), (28), and (29) and yields the following expressions for the expansion coefficients when $n \geq 1$:

$$a_n = -\frac{K_A}{n} \sum_{i=0}^{n-1} a_i b_{n-1-i} \tag{34}$$

$$b_n = a_n - \frac{b_{n-1}}{n} \sum_{j=1}^{J} K_{jF} I_{oj} + \frac{1}{n} \sum_{j=1}^{J} \sum_{i=0}^{n-1} K_{jF} d_i^j b_{n-1-i} + \frac{1}{n} \sum_{j=1}^{J} K_{jB} d_{n-1}^j \tag{35}$$

$$d_n^j = \frac{K_{jF} I_{oj}}{n} b_{n-1} - \frac{K_{jB}}{n} d_{n-1}^j - \frac{K_{jF}}{n} \sum_{i=0}^{n-1} d_i^j b_{n-1-i} \tag{36}$$

The objective in extending the kinetic annealing model to include more than one type of secondary defect complex is to obtain a more realistic model. For example, Watkins and Corbett (1) have established the existence of approximately 20 types of secondary defect complexes in irradiated silicon. Isothermal defect annealing in silicon can be qualitatively described by considering only one defect complex; the Si - E center (vacancy trapped by a doping impurity atom) or the Si-A center (vacancy trapped by an oxygen atom) depending on the relative concentrations of the trapping agents. A complete quantitative description of the isothermal annealing process may require the consideration of at least these two defect complexes.

## ERROR ESTIMATES FOR SERIES SOLUTIONS OF ANNEALING EQUATIONS

Series solutions of the isothermal annealing equations have been obtained for several cases. The general procedure for carrying out numerical calculations using these solutions is to perform computer computations to evaluate a finite number of series expansion coefficients for each variable involved. The series expansions are thus truncated after a finite number of terms. The exact number of terms retained depends, of course, on the accuracy desired. This truncation process introduces errors in the annealing variables.

The truncation error was investigated for the simplest case of only one defect complex. There are three series expansions to be investigated in this case;

$$i = \sum_{n=0}^{\infty} a_n t^n$$

$$V = \sum_{n=0}^{\infty} b_n t^n$$

and $$C_1 = \sum_{n=0}^{\infty} d_n^1 t^n$$

The coefficients $a_n$, $b_n$ and $d_n^1$ are given by equations (34), (35), and (36) with $J = 1$ as

$$a_n = -\frac{K_A}{n} \sum_{i=0}^{n-1} a_i b_{n-1-i} \tag{37}$$

$$b_n = a_n - \frac{b_{n-1}}{n} K_{1F} I_{01} + \frac{K_{1F}}{n} \sum_{i=0}^{n-1} d_i^1 b_{n-1-i} + \frac{K_{1B}}{n} d_{n-1}^1 \tag{38}$$

$$d_n^1 = \frac{K_{1F} I_{01}}{n} b_{n-1} - \frac{K_{1B}}{n} d_{n-1}^1 - \frac{K_{1F}}{n} \sum_{i=0}^{n-1} d_i^1 b_{n-1-i} \tag{39}$$

For parameters characteristic of irradiated Si and Ge crystals, the term $a_n$ in equation (38) dominates the other terms. Therefore, the algebraic sign of $b_n$ is the same as $a_n$. If this is the case, by inspection of equation (37) the $a_n$ must have alternating signs. It then follows that the $b_n$ have alternating signs.

By inspection of equation (39), the $d_n$ must also have alternating signs.

For a series of terms with alternating signs, the error resulting from the truncation of the series (the sum of the remaining terms) is always smaller in absolute value than the last term retained. The truncation error in i, V, and $C_1$ can then be readily determined. The computer program for evaluating a set of series expansion coefficients can be designed to select a number of coefficients such that the truncation error is less than some predetermined value.

EVALUATION OF THE ANNEALING MODEL WITH ONE DEFECT COMPLEX AND $K_A \neq K_{1F}$.

This represents an extension of the study described in the previous progress report ("Defect Annealing in Irradiated Semiconductors", Progress Report No. 1, October 1, 1964). The previous study was restricted to the case $K_A = K_{1F}$.

The power series solutions of the annealing equations were employed. The computer generated isothermal annealing curves for $K_A \neq K_{1F}$ were found to be qualitatively correct. No detailed attempts to fit experimental annealing curves have been made as yet. Primary emphasis during this report period was placed on investigating the effect of varying the model parameters on the level of the plateau in the isothermal annealing curve. The objective here was to establish a procedure for determining a set of model parameters to give a particular plateau level. This is a necessary first step in attempting to fit experimental data with a theoretical annealing curve.

A systematic variation of model parameters in conjunction with computer calculations of plateau levels led to the conclusion that the plateau level depends only on the ratios $\frac{I_o}{i_o}$ and $\frac{K_A}{K_{1F}}$.

The fraction of defects not annealed at the plateau level must then have the functional form

$$f_p = f_p\left(\frac{I_o}{i_o}, \frac{K_A}{K_{1F}}\right) \tag{40}$$

Figure 1 is based on calculated plateau levels for a range of values of $I_o/i_o$ and $K_A/K_{1F}$. The exact mathematical form of the functional relationship indicated in equation (40) has not yet been determined. However, Figure 1 can be used as a guide in selecting a set of empirical model parameters to produce a particular plateau level.

It might be noted that additional flexibility is gained by removing the $K_A = K_{1F}$ restriction. In the evaluation of the $K_A = K_{1F}$ case ("Defect Annealing in Irradiated Semiconductors", Progress Report No. 1, October 1, 1964), it was found that the plateau level depended only on the ratio $\frac{I_o}{i_o}$.

## REFERENCES


1. Watkins, G. D. and J. W. Corbett, Phys. Rev. 121, 1001 (1961)

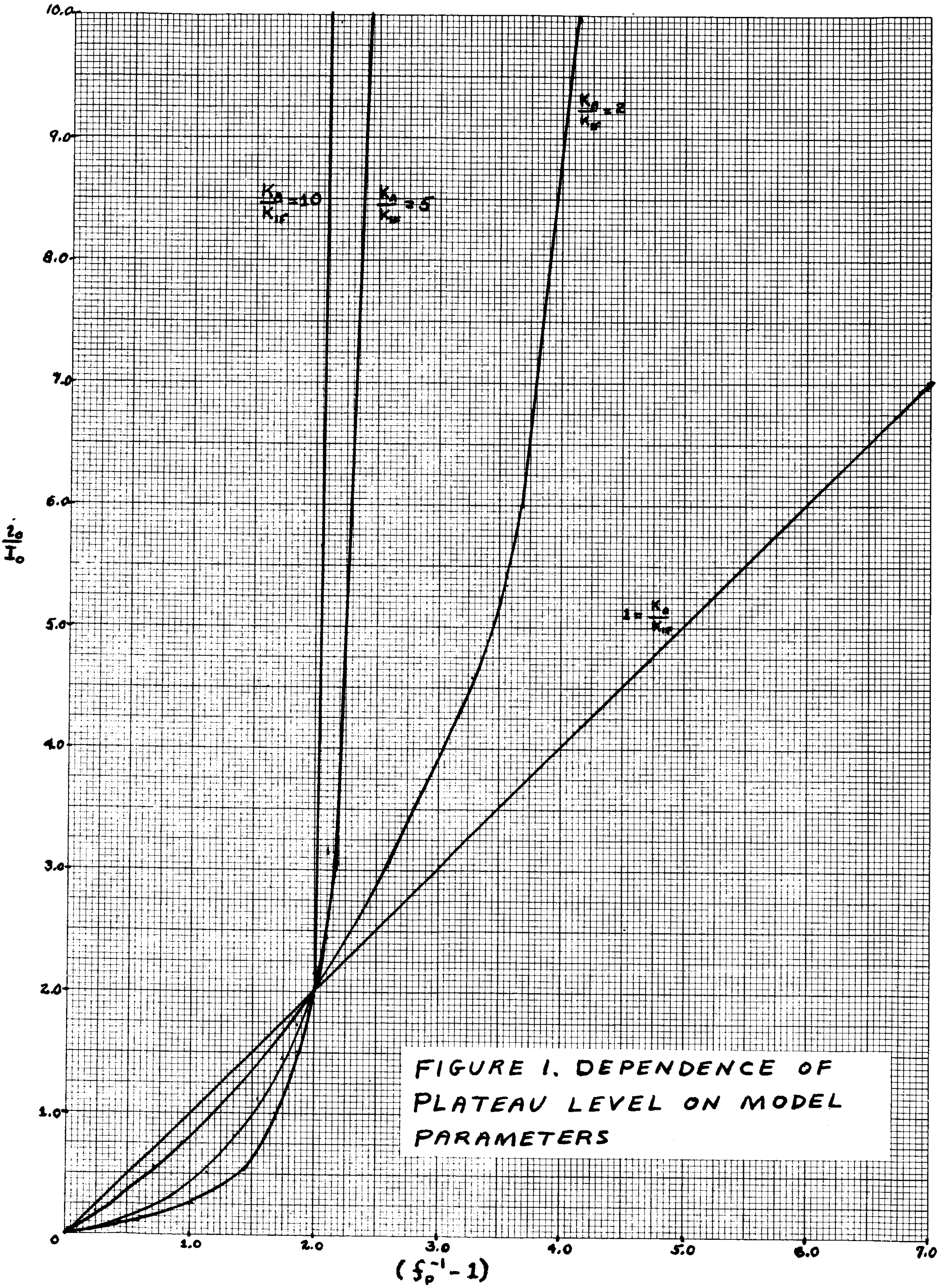


FIGURE 1. DEPENDENCE OF PLATEAU LEVEL ON MODEL PARAMETERS