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Theoretical Investigation of Radiation Damage and Transport Properties of Solar Cells

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Introduction

Theoretical investigation of the radiation damage in solar cells has been carried out from two different points of view. One is a phenomenological approach and the other is a quantum mechanical treatment. In this report research works carried out after January 1968 will be covered.

1. Interference Effect on Annealing Temperature of A-Centers and E-Centers in Silicon. (collaboration with P.H. Fang, NASA ERC).

The purpose of this work is to interpret the significance of two recent experimental observations on the annealing of defects in silicon:

1. The annealing temperature of the A-center (oxygen vacancy complex, V-O) is about 350°C[1]. In the case where substantial amounts of bismuth (donor impurity) are present, Corelli et al[2] observed the isochronal annealing temperature of the A-center absorption band (12 μ) appears to have two stages, near 140°C and 250°C, respectively.

2. Two annealing stages are observed associated with E-centers (vacancy-donor impurity complex, V-I) by Saito et al[3] at 150°C and 220°C, respectively, with anomalously high frequency factors associated with the low temperature annealing stages.

These two observed phenomena are related through the following reaction scheme:

$$V + \begin{cases} O \underset{K_{Ad}}{\overset{K_{Af}}{\rightleftharpoons}} A \\ I \underset{K_{Id}}{\overset{K_{If}}{\rightleftharpoons}} E \end{cases} \qquad (1)$$

where K's are reaction constants (therefore, positive). The subscripts are for defect species (A and E) and for the formation (f) and the dissociation (d).

The rate equations associated with Eq.(1) are:

$$-\frac{dA}{dt} = K_{Ad}\,A - K_{Af}\,V\,O$$

$$-\frac{dE}{dt} = K_{Ed}\,E - K_{Ef}\,V\,I \qquad (2)$$

Introducing the following initial conditions (subscript O denotes for t = 0).

$$V + E + A = V_o \ ,$$

$$O + A = O_o \ ,$$

$$I + E = I_o \ . \qquad (3)$$

Eq.(2) becomes,

$$-\frac{dA}{dt} = (K_{Ad} + K_{Af}O_o + K_{Af}V_o)A + K_{Af}O_o E - K_{Af}A(E+A) - K_{Af}V_o O_o \ ,$$

$$-\frac{dE}{dt} = (K_{Ed} + K_{Ef}I_o + K_{Ef}V_o)E + K_{Ef}I_o A - K_{Ef}E(E+A) - K_{Ef}V_o I_o \ . \qquad (4)$$

Eq.(4) are a cumbersome system of non-linear differential equations. However, this system is greatly simplified by two considerations: (1) the coefficient of the linear term is larger than that of the non-linear term, and (2) since we are interested in annealing, i.e., in the diminishing region of A and E, the higher order term of A and E can be neglected. We have a system of two linear equations, therefore, we have two rate constants of annealing:

$$(\tau_\pm)^{-1} = \left[K_{Ad} + K_{Ed} + K_{Af}(O_o+V_o) + K_{Ef}(I_o+V_o)\right] \pm \left\{\left[(K_{Ad} - K_{Ed}) + K_{Af}(O_o+V_o) - K_{Ef}(I_o+V_o)\right]^2 + 4K_{Af}K_{Ef}O_o I_o\right\}^{1/2} \qquad (5)$$

We note that the rate constants in our system depend on initial concentrations of various components which imply that the annealing temperature is concentration dependent. This is an interesting consequence of the interference effect. There is no information available for all K's, but the general form of K's is

$$K = K_o \, e^{-E/kT} \tag{6}$$

where E is the activation energy of the reaction process. Since the annealing stage of ordinary (no coupling) A-centers occurs near 350°C with an activation energy of 1.29 ev, and that of E-centers near 130°C with an activation energy of 0.94 ev[1], we conclude:

$$K_{Ad} + K_{Af} O_o + K_{Af} V_o > K_{Ed} + K_{Ef} I_o + K_{Ef} V_o \tag{7}$$

In this case, Eq.(5) implies,

$$(\tau_+)^{-1} > K_{Ad} + K_{Af}(O_o + V_o)$$

$$(\tau_-)^{-1} < K_{Ed} + K_{Ef}(I_o + V_o) \tag{8}$$

Therefore, the cross-terms of Eq.(4), which occur because of the simultaneous presence of A- and E-centers, have the effect that, first, there are two annealing stages. Second, the high temperature annealing stage occurs at higher temperatures than that of the E-centers. Both of these qualitative characteristics are confirmed by the experiment cited.

Numerical calculations cannot be made at present because of the large number of unknown parameters (K's) and because the oxygen vacancy and donor impurity contents of the silicon specimens of these two experiments are different.

In the work of Saito, et al[3], anomalously large values of jumping frequency (corresponding to K_o of Eq. (6)) were observed. A phenomenological explanation was made. The present model yields

two levels of activation energy corresponding to multiple K's in the linear approximation (Eq.(5)) and would lead to an infinite number of levels in the original non-linear equation.

References

1) G.D. Watkins and J.W. Corbett, Disc. Faraday Soc. 31, 86 (1961).

2) J.C. Corelli, J.W. Westhead, and R. Chiang, Bull. Am. Phys. Soc. 13, 359 (1968).

3) H. Saito, N. Fukuoka, H. Hattori, and J. H. Crawford, Jr., Radiation Effects in Semiconductors, (F.L. Vook, Ed. Plenum Press, N.Y. 1968).

2. Some Mathematical Analysis of Annealing Kinetics
(Collaboration with P.H. Fang, NASA, ERC, Reported at Conference on Radiation Damages in Solar Cells held at NASA GSFC, April 1968)

Various defects and centers are created in semiconductors by irradiation and these are thermally annealed. The mechanism of creation and annihilation of these defects is treated by means of very much simplified mathematical models, i.e. chemical reaction kinetics. Even with this simplification, basic equations often turn out to be coupled non-linear equations and therefore rigorous solutions have not been found.

We have resolved some of the characteristics of annealing kinetics and irradiation kinetics in which the non-linear effects are taken into account.

Another problem we have formulated is the isochronal annealing kinetics. In annealing kinetics equations there appear several reaction constants which are function of temperature. Therefore, each time temperature is changed, we will be dealing with a different set of kinetic equations. Hence the problem of isochronal annealing

is not to solve just a set of kinetic equations, but it amounts to solve as many sets of kinetic equations as the number of times the temperature is changed during measurements. This fact has never been emphasized in the literature. We have taken this fact explicitly into account and found a method of obtaining isochronal annealing curves.

3. First Principle Calculation of the Energy of Formation of a Defect in Metals and Semiconductors. (Collaboration with M. M. Sokoloski, Bull. Amer. Phys. Soc. Ser.II, 14, 613 (1969))

In the investigation of the annealing mechanism of radiation damage it is usually assumed that the numerical value of the activation energy of vacancy migration is known. In order to find relations between annealing mechanisms and the transport properties of semiconductors it is necessary to calculate this energy from more fundamental properties of semiconductors.

For this purpose we start with N nuclei of charge ze and zN electrons and construct a crystal, find the wave functions for all the electrons and calculate the ground state energy of this many-electron system. Using a proper set of Bloch basis functions we found the many-body crystal Hamiltonian which will enable us to calculate the band structure and the cohesive energy of the crystal. Activation energy of vacancy formation or impurity introduction will then be unambiguously defined because the vacancy or the impurity introduces a well-defined perturbation.

4a. Application of the Cluster Variation Method to the s-d Interaction Hamiltonian. (with J.Halow and T. Morita, Phys. Rev. 175, 680 (1968)).

4b. Ground-State Energy of the Anderson Model by the Cluster-Variation Method. (with S.M. Bose, Phys. Rev. 176, 600 (1968)).

The ground state energy of a system which contains an impurity is directly related to the energy of impurity introduction. It is, therefore, interesting to be able to calculate the ground state energy of such a system for which a usual perturbation theory does not apply. (This is a case in which the energy of impurity introduction is so small that a usual perturbation theory gives no answer). These examples are furnished by magnetic impurities introduced into normal metals. We have applied the cluster variation method for this purpose and found the energy lowering very accurately. This is very encouraging because we should be able to find energies of vacancy formation and impurity introduction as soon as the rigorous many-body Hamiltonian, which was discussed in the previous section, becomes very important.

Personnel

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