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Isochronous and isothermal annealing of defects

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The regularities of isothermal and isochronous discrete and continuous annealed material at a constant rate are considered on the example of monomolecular reaction and bimolecular recombination of Frenkel pairs. For isochronous annealing of radiation defects after neutron irradiation of GaP, process parameters were obtained.

Keywords: annealing, defects, bimolecular reaction, approximation, GaP.

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Introduction

The question of annealing of defects that arise in the technological process of growing or the process of irradiation of crystalline bodies is of important scientific and practical importance for establishing the nature of defects and processes of their transformation in order to obtain material with given parameters.

After a short-term annealing of close pairs, there is a long-term one (1 s - 1 hour). The difference between these annealings is not only in the relaxation time scale, but in the nature of ongoing processes. When the defects are Frenkel pairs, uniformly distributed over the volume, the effect of short-term annealing can be neglected [1].

Simulation of long-term annealing processes at the atomic level requires high speed and computer memory. Significant progress in the modeling of such processes has been achieved using a macroscopic approach, which allows describing the temporal evolution of the concentration of defects using a system of differential equations for various types of defects: interstitial atoms, vacancies, clusters, dislocation loops, pores, impurities, precipitates, grain boundaries, etc.

I. Isothermal annealing

The change in the concentrations of interstitial atoms I(t) and vacancies V(t) associated with mutual recombination is represented by equations [2]:

$$dV(t)/dt = -K(T)V(t)I(t),$$

$$dI(t)/dt = -K(T)V(t)I(t),$$

$$V(0) = V_0, I(0) = I_0,$$

here $K(T)$ is the recombination constant, $K(T) = 4\pi r D(T)$, $D(T) = D_0 \exp(-E/kT)$ - is the diffusion coefficient of the faster component, r is the radius of the defect recombination region [3].

The solution of these equations under the condition of constant temperature T = const describes the process of isothermal annealing:

$$I(t) = I_0(V_0 - I_0)/\left(\left(V_0 exp\left(K(T)\right)t(V_0 - I_0)\right) - I_0\right),$$

$$V(t) = I(t) + V_0 - I_0.$$

Let's consider two options.

1. Close concentrations of interacting defects. Let $I_0 = V_0$, then $I(t) = V(t)$,

$$dI(t)/dt = -K(T)I(t)^2,$$

$$I(0) = I_0.$$

The solution of the bimolecular reaction equation (second-order reaction) is

$$I(t) = I_0./(I_0\mathrm{K(T)t} + 1).$$

This solution can be obtained by the limit transition $I_0 \to V_0$ from the previous solution.

2. Concentrations of defects differ significantly. Let V(t) = V_0,

$$dI(t)/dt = -K(T)V_0 \cdot I(t),$$

$$I(0) = I_0.$$

The solution of the monomolecular reaction equation (first-order reaction) is

$$I = I_0 \exp(-KV_0 t),$$

which can be used to describe the flow of a defect on an unbounded trap.

This solution can also be obtained from the very first solution at another boundary transition $I_0 \ll V_0$.

Therefore, by changing the difference $V_0 - I_0$, it is possible to smoothly transition from a bimolecular reaction to a monomolecular reaction.

II. Isochronous discrete annealing

It is clear that each step of isochronous annealing is isothermal annealing. So, if we take as the initial value obtained in the previous step, and also explicitly introduce the temperature dependence of the recombination coefficient $K(T_i) = K_0 exp\left(-E/kT_j\right)$, where E is the activation energy of the diffusion process of the component and replace t with $\Delta t = const$ - duration of one step of annealing, then the value of the concentration at the i-th step will be written in the general form and in the two limiting cases by the expressions:

$$I_i = I_{i-1}(V_0 - I_0)/\left((I_{i-1} + V_0 - I_0)exp\left(K_0\Delta t(V_0 - I_0)\right)exp(-E/kT_i) - I_{i-1}\right),$$

$$I_i = I_{i-1}/(I_{i-1}K_0\Delta t\ exp(-E/kT_i) + 1),$$

$$I_i = I_{i-1}exp(-K_0V_0\Delta t \exp(-E/kT_i)),$$

Thus, the obtained expressions are recurrent dependences of the concentration of defects on temperature. It is convenient to use them in case when during isochronous annealing there is a different temperature step. But, if annealing is carried out with a constant step at the temperature ΔT, then instead of recurrent expressions for the analysis of experimental data, analytical ones can be used, in which the concentration I_j on j - therefore, the steps will be expressed through the initial concentration I_0, the initial temperature T_0, the size of the temperature step ΔT and the step number j.

Let's consider the step-by-step transition from a recurrent connection to dependence on the step number for a monomolecular reaction. Let's write the expressions for j steps starting from the first:

$$I_1 = I_0\ exp\left(-K_0\Delta t\ exp(-E/kT_1)\right),$$

$$I_2 = I_1\ exp\left(-K_0\Delta t\ exp(-E/kT_2)\right),$$

$$I_i = I_{i-1}\ exp\left(-K_0\Delta t\ exp(-E/kT_i)\right),$$

Expressing the next in terms of the previous one, we get:

$$I_j = I_0 exp\left(-K_0\Delta t\ \sum_{i=1}^{j} exp(-E/kT_i)\right).$$

For a bimolecular reaction:

$$1/I_1 = exp(E/kT_1)/K_0\Delta t + 1/I_0,$$

$$1/I_2 = exp(E/kT_2)/K_0\Delta t + 1/I_1,$$

$$1/I_j = exp\left(-E/kT_j\right)/K_0\Delta t + 1/I_{j-1}.$$

Expressing the next in terms of the previous one, we get:

$$1/I_j = \sum_{i=1}^{j} exp(E/kT_i)\ /K_0\Delta t + 1/I_0.$$

III. Isochronous continuous annealing at a constant rate

Consider the case of linear dependence of temperature on time $T = T_0 + at$, then time equations can be rewritten as temperature equations:

$$dV(T)/dT = -K_0 exp(-E/kT)V(T)I(T)/a,$$

$$dI(T)/dT = -K_0 exp(-E/kT)V(T)I(T)/a,$$

$$V(T_0) = V_0,\ \ V(T_0) = V_0\ .$$

For concentrations we have a relation

$$V(T) = I(T) + V(T_0) = V_0,$$

Let's divide the variables:

$$dI(T)/(I(T) + V_0 - I_0)I(T) = -K_0 \exp(-E/kT)dT/a$$

We integrate:

$$I(T) = I_0(V_0 - I_0)/\left((V_0 \exp\left(K_0(V_0 - I_0)\int_{T_0}^{T} exp(-E/kT)dT/a\right) - I_0\right)$$

The result was obtained through the integral, which is not taken analytically.

It is easier to obtain the result by numerical integration of the differential equation for dimensionless concentration and temperature, by entering a unit of concentration $N = V_0 - I_0$ and the unit of temperature $|\tau = a/K_0N$, then $i = I(T)/N,\ v = V(T)/N$. We obtain $i = i_0/\left(v_0 exp\left(\int_{T_0}^{T} exp(-E/kT)dT/\tau\right) - i_0\right)\Big)$.

IV. Application to experimental results

Isochronous annealing of radiation defects in GaP irradiated with reactor neutrons (F = 3 10^{16} n/cm^2) was carried out in the temperature range from room temperature to 600^0 C. The calculated concentration of damages that affect the fundamental absorption is an exponential function of the annealing temperature (Fig. 1.) [4].

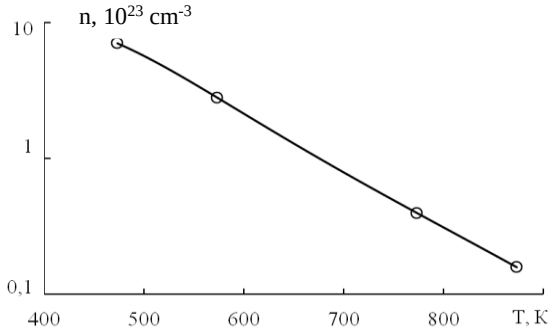

Fig. 1. Concentrations of radiation defects of the GaP sample, from the isochronous annealing temperature.

Smooth approximation dependence (Fig. 1.), obtained according to the model of the bimolecular reaction of the annealing of Frenkel pairs with initial concentrations of defects $I_0 = 7{,}1\ 10^{23}$ cm^{-3}, $V_0 = 7{,}3\ 10^{23}$ cm^{-3}, the activation energy E = 0,28 eV and the annealing constant $K_0/a = 9{,}4\ 10^{-24}$ cm^3/K.

Conclusions

Analytical time dependences of the concentration of defects in the case of isothermal annealing by the mechanism of recombination of a pair of defects using the example of a Frenkel pair are presented. Limiting cases represent 1st and 2nd order reactions.

Iterative temperature dependences of the concentration of recombining defects were obtained during isochronous annealing with a fixed exposure time at a constant temperature.

The solution in the integral representation of isochronous annealing with a fixed rate of temperature change is given. Approximation of the experimental data by the solution of differential equations obtained by the numerical method was carried out.

The possibility of explaining annealing by one mechanism is shown. The initial concentrations of pairwise recombining defects, the recombination constant, and the activation energy of the process are presented.

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Ізохронний та ізотермічний відпал дефектів

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Розглянуто закономірності ізотермічного та ізохронного дискретного та безперервного відпалу матеріалу з постійною швидкістю на прикладі мономолекулярної реакції та бімолекулярної рекомбінації пар Френкеля. Отримано параметри процесу для ізохронного відпалу радіаційних дефектів після нейтронного опромінення GaP.

Ключові слова: відпал, дефекти, бімолекулярна реакція, апроксимація, GaP.