Theory for diffusivity measurements when the temperature is ramped linearly

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Abstract. Nearly all measurements to determine diffusion coefficients in solids are performed using either isochronal or isothermal measurements. These are usually done using large discrete steps in the annealing temperature. In certain diffusion systems more than one diffusion mechanism may exist in different temperature regimes. The transition temperature between these can be missed when using large temperature steps for annealing. This paper derives the necessary equations for diffusivity measurements where the temperature is ramped linearly and a composition-depth profile is simultaneously performed *in situ*. This yields the diffusion coefficient at small temperature intervals over the whole temperature range.

1. Introduction

In general, nearly all measurements to determine diffusion coefficients in solids are performed using either isochronal or isothermal measurements [1, 2]. Usually, these are done with fairly large discrete steps in temperature, with 100 °C or 50 °C steps being the norm. The diffusion coefficient, at a particular temperature, depends primarily on the microstructure of the substrate, with the type of impurity (i.e. the diffusion species) being of secondary order. When a phase change occurs in the substrate material or when a chemical reaction occurs between the diffusion species and the substrate, the diffusion mechanism usually undergoes a discrete change with a corresponding change in the diffusion coefficient as a function of temperature. When either of these occurs, the large steps in temperature can result in one missing the transition from one diffusion mechanism to another. Consequently, it is often highly desirable to perform *in situ* diffusion measurements during the heating cycle.

Theron [3, 4] developed a method for dealing with the diffusion in the case of a linear increase in temperature and real time analysis. He set up a general rate equation and made the assumption that this rate variable had an Arrhenius temperature behaviour. This resulted in differential equations for standard diffusion limited kinetics and Nernst-Einstein diffusion limited kinetics. These differential equations are solvable in terms of the Exponential Integral for those two cases.

In this paper we also assume a temperature which is ramped linearly while doing simultaneously non-destructive depth profiling (typically with RBS) to determine the diffusion of a diluted species in a homogeneous substrate at small temperature intervals. Analytical equations for such diffusivity measurements are derived.

2. Theory

A key assumption in our theory is that the diffusion coefficient D has an Arrhenius behaviour with respect to the absolute temperature T, i.e.

$$D = D_0 \exp\left(-\frac{E}{k_B T}\right) \tag{1}$$

where E is the activation energy and k_B is the Boltzmann constant [1,2]. This form allows one to calculate the diffusivity D at any temperature; with good accuracy within the temperature range for which (1) was determined, and with reduced accuracy outside this temperature regime. The assumption (1) is also commonly assumed in diffusion studies.

The one-dimensional time-dependent Fick diffusion equation is given by

$$\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2} \tag{2}$$

In solutions to this equation, the diffusion coefficient D usually appears together with the time t as the factor Dt [2,5]. To illustrate this, consider an initial profile of a semi-infinite layer given by

$$N(x, 0) = N_0 \quad \text{for } x < x_0$$
$$N(x, 0) = 0 \quad \text{for } x > x_0 \tag{3}$$

The solution is given by [2]

$$N(x,t) = \frac{N_0}{2} \, erfc\left(\frac{x - x_0}{2\sqrt{Dt}}\right) \tag{4}$$

The Complementary Error Function in (4) is given by [6]

$$erfc \; z = 1 - erf \; z = 1 - \frac{2}{\sqrt{\pi}} \int_0^z \exp\left(-t^2\right) dt \tag{5}$$

The original profile (3) and the diffused profile (4) for model values for the depth scale x and diffusion coefficient D, are illustrated in Figure 1. In practice, the depth profile data of the diffused semi-infinite layer which is annealed for a known time t at a specific temperature T is fitted to equation (4) to give a value for D.

In the different (depending on the boundary values) solutions to (2), the D is taken as a constant value, i.e. it is then a solution of the Fick diffusion equation at a specific temperature T. In the case of a linear increase in temperature with time t there is also a corresponding increase in the D values – cf. equation (1). The cumulative effect of increasing the temperature on the factor Dt can be approximated by the limit of a Riemann integral of infinitesimal small increases in t. Thus, the factor Dt becomes $\int D(t)dt$.
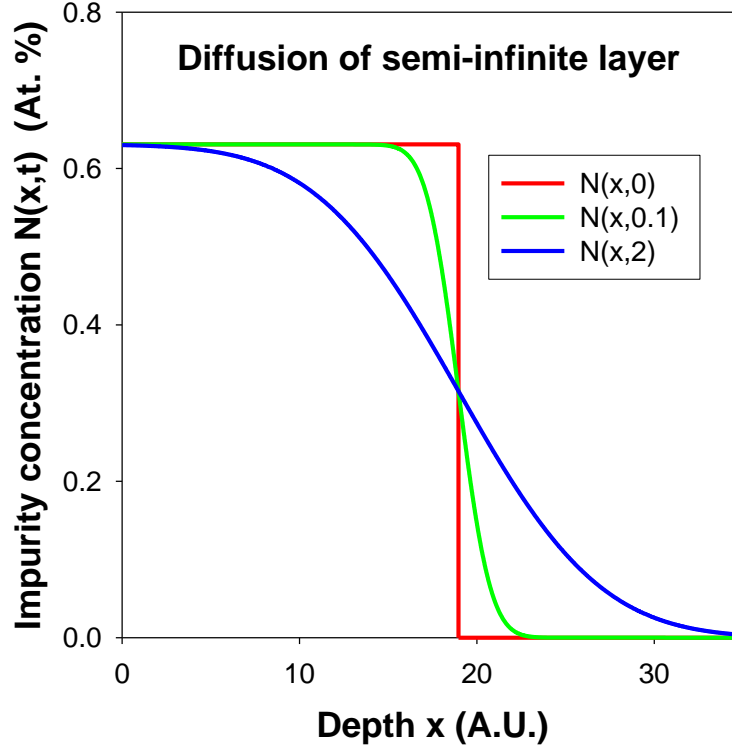
Figure 1. Diffusion of a semi-infinite layer with original profile given by (3) for two different times indicated in the figure.

Using assumption (1), i.e. that over this (limited) temperature range the diffusion coefficient has an Arrhenius behaviour, the integral becomes

$$\int_0^{t_a} D(t)dt = \int_0^{t_a} D_0 \exp\left(-\frac{E}{k_B(T_b + \alpha t)}\right)dt \tag{6}$$

where t_a in the two integral limits is the time at which a measurement is taken, and the absolute temperature is given by the linear function $T = T_b + \alpha t$, where T_b is the temperature at which the ramping started and α is the heating rate. Making two transformations, and integrating by parts give

$$\int_0^{t_a} D(t)dt = \frac{D_0}{\alpha}\left[T \exp\left(-\frac{E}{k_B T}\right) - T_b \exp\left(-\frac{E}{k_B T_b}\right)\right] + \frac{D_0}{\alpha}\frac{E}{k_B}\left[E_1\left(\frac{E}{k_B T_b}\right) - E_1\left(\frac{E}{k_B T_a}\right)\right] \tag{7}$$

where the Exponential Integral function $E_1(x)$ is defined as [6]

$$E_1(x) = \left[\int_x^{\infty} \frac{\exp(-t)}{t}dt\right] \quad \text{with } x > 0 \tag{8}$$

with an asymptotic expansion (i.e. $x \gg 1$) given by

$$E_1(x) = \frac{e^{-x}}{x}\left[1 - \frac{1}{x} + \frac{2}{x^2} - \frac{3}{x^3} + \ldots\right] \tag{9}$$

Using the first two terms in (9) and after some algebra, one finds that (7) reduces to

$$\int_0^{t_a} D(t)dt = \frac{k_B}{\alpha E}\left[T_a^2 D(T_a) - T_b^2 D(T_b)\right] \tag{10}$$

where $T_a = T_b + \alpha t_a$. Because the diffusion coefficient at the start of the ramping temperature (typically room temperature of 300 K) is extremely small, the last term is approximately zero. Thus

$$\int_0^{t_a} D(t)dt \approx \frac{k_B}{\alpha E} T_a^2 D(T) \tag{11}$$

With the notation

$$\int_0^{t_a} D(t)dt = \Delta \tag{12}$$

equation (11) can be written as

$$\frac{k_B}{E} D(T_a) = \alpha \frac{\Delta}{T_a^2} \tag{13}$$

Taking the logarithm and substituting the Arrhenius form of D

$$\ln\frac{k_B}{E} + \ln D_0 - \frac{E}{k_B T_a} = \ln\left(\alpha \frac{\Delta}{T_a^2}\right) \tag{13}$$

Thus from a plot of $\ln\left(\alpha \frac{\Delta}{T_a^2}\right)$ against $\frac{1}{T_a}$, the slope yields the activation energy E and from the intercept D_0 can be obtained, from which the diffusion coefficient D can be calculated via (1).

The increment between successive T_a values depends primarily on the time taken to perform a depth analysis of the diffusing impurity. In practice, for RBS analysis this may result in the increment being of the order of 1 or 2 K. This is small enough to pinpoint the temperature at which the activation energy changes. Since the activation energy E of diffusion represents the average energy needed by a diffusing atom to either pass over or tunnel through the potential barrier between the two semi-equilibrium positions of the atom, a change in the value of E represents two different diffusion mechanisms operating. Information on the exact temperature can provide valuable reference data for DFT (density functional theory) calculation on diffusion traps in a substrate [8, 9].

3. Conclusions

Equations are derived to extract diffusion coefficients at very small temperature intervals from *in situ* real-time non-destructive analysis of an impurity profile in a substrate heated to have a linear increase in temperature of the substrate as a function for time. A key assumption in this

derivation is that the diffusion coefficient over the whole temperature range has an Arrhenius dependence on temperature. The initial temperature must start at a temperature where the diffusion is negligibly low. The solution is given in terms of the Exponential Integral function. Taking the first two terms of the asymptotic power expansion of this function yields an analytical equation from which the diffusion coefficient D at small temperature intervals can be determined.

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