Part I : Preliminaries (Thermodynamics and Kinetics)

Module 5: Fick's laws of diusion and their solution

6.1 Motivation

Suppose it takes about an hour to dope silicon to a concentration of 10 boron atoms at a depth of 2 microns by diffusion. How long will it take to dope silicon to the same concentration of boron atoms at a depth of 4 microns?

6.2 Fick's rst law

Fick's first law states that the flux of atoms is in such a way as to reduce the concentration gradients; that is, the atoms move from regions of higher concentration to regions of lower concentration. The proportionality constant is known as diffusivity. Mathematically,

$$\mathbf{J} = -D\nabla c \tag{6}$$

where $\mathbf{J}$ is the atomic flux per unit area per unit time, ∇c is the concentration gradient, and D is the diffusivity. The negative sign indicates that the flux is in opposite direction to the concentration gradient.

6.3 Fick's second law

Consider a control volume as shown in Fig. 25. If there are no sources or sinks of atoms in the control volume, then, the rate of accumulation or depletion of atoms in the control volume is equation to the divergence of the flux. Mathematically,

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} \tag{7}$$

Using the Fick's first law expression for $\mathbf{J}$, one obtains the so called Fick's second law in its usual form, namely,

$$\frac{\partial c}{\partial t} = \nabla \cdot [D\nabla c] \tag{8}$$

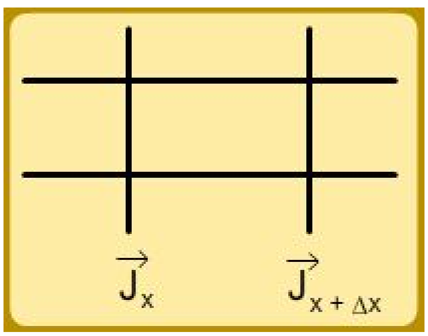

Figure 25: Control volume for the calculation of divergence of flux. The difference between the atomic flux at $x + \Delta x$ and x determines the rate of accumulation/depletion of atoms in the control volume.

6.4 Physical meaning of Fick's second law

Consider the one-dimensional form of the Fick's second law. Let us assume that D is not a function of concentration. Then,

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{9}$$

The second derivative on the right hand side of the equation represents curvature of the composition profile. Fick's second law indicates that if the curvature is positive, then the concentration increases with time; and, of the curvature is negatice, then the concentration decreases with time. Thus, any sinudoidal concentration profile as shown in Fig. 26, will change as shown in the figure and hence, as time proceeds, the concentration inhomogeneities will be evened out.

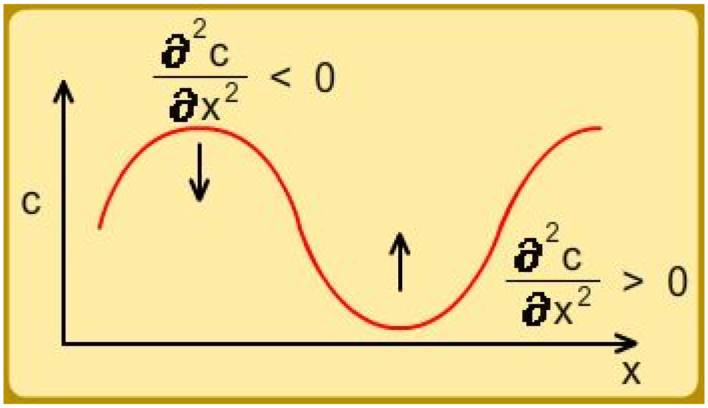

Figure 26: Physical meaning of Fick's second law.

6.5 Steady-state diusion

Consider the diffusion equation:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} \tag{10}$$

Suppose a steady state is established, then, the left hand side of the above equation is zero. Hence, $\mathbf{J}$ is a constant; that is, $D\nabla c$ is a constant. Hence, if the diffusivity is independent of concentration, the concentration gradient is a straight line; otherwise, the concentration profile is non-linear.

6.6 Solutions to the non-steady state diusion equation

The diffusion equation is a second order partial differential equation. Hence, its solution is determined by the initial and boundary conditions. Different initial and boundary conditions lead to different solutions. In these notes, we do not describe these solutions; however, some of these solutions (including the error function solution) are described in Porter, Easterling and Sherif [2].

One of the most important characteristics of the solutions to the diffusion equation is the diffusion distance x_D: it is defined as $\sqrt{Dt}$; in other words, the distance over which diffusion takes place is proportional to $\sqrt{t}$. Thus, to answer the question at the beginning of this module, a two fold increase in distance will correspond to a four-fold increase in time; hence it would take about four hours for the doping to reach the same levels at a depth of 4 microns.

6.7 Tutorial problems and questions

1. What are the units of $\mathbf{J}$, D and ∇c?

Answer

1. Units of flux, $\mathbf{J}$: m^{-2} s^{-1}

   Units of diffusivity, D: m^{2}s^{-1}

   Units of ∇c: m^{-1}

2. The diffusivity of atomic hydroen in steel is given as 10^{-9} m^{2}s^{-1}. If hydrogen with a concentration of 1 kg m^{-3} is stored in a steel container of thickness 5 mm, calculate the amount of hydrogen that escapes the cylinder (per unit area per second).

Answer

Given: $D = 10^{-9}$ m^{-2} s^{-1} . The concentration gradient across the wall of the container is 200 kg m^{-4}. Assuming that the steady state is attained after some time, using Fick's first law, we find that the flux is 2 x 10^{-7} kg m^{-2} s^{-1} .

Supplementary information

The Fick's first law is an empirical law. It is based on observations. It is not valid for all materials. It also introduces a material specific property called diffusivity. Such laws are in general known as constitutive laws.

Since Fick's first law connects concentration gradient (which is a vector) with atomic flux (which is another vector), the connecting parameter, namely diffusion, can only be a scalar, or second rank tensor. The diffusivity is in fact a second rank tensor. If we think in terms of matrices, this is equivalent to saying that the column matrix of concentration gradient is connected to the column matrix of atomic flux through a full matrix, namely, diffusivity.

The Fick's second law, even though called a law is just a combination of law of conservation of mass with the constitutive law, namely Fick's first law. Conservation of mass is valid for all materials. It does not introduce any material specific properties. Such laws are called conservation laws.

One usually finds the constitutive and conservation laws of this type in many physical situations. For example, Hooke's law and Fourier's law of heat conduction are constitutive laws. Combining conservation of energy with Fourier's law of heat conduction, one obtains the partial differential equation that describes non-steady state heat conduction. This equation, if normalised, has the same form as the diffusion equation that results from Fick's second law. Hence, their solutions are also identical.

There are only a few conservation laws. In these course notes, we only use conservation of mass and energy. Charge is also another conserved quantity, though, we will not have a chance to use charge conservation in this course.