

Chapter 10.00B

Physical Problem for Partial Differential Equations Chemical Engineering

Problem Statement

Diffusion refers to the process of molecule transport by molecular motion from a region of higher concentration to that of lower concentration and is utilized to model mass transport in a number of natural and industrial processes such as amino acid exchange in cell biology, polymers, drug delivery through membranes, water purification using membranes, and semiconductor doping to name a few. Semiconductor doping is the process of introducing dopants (such as boron and phosphorus) into a semiconductor such as silicon to enhance its electric properties for use in microchip fabrication.

Diffusion is mathematically described by Fick's second law given by [1]

$$\frac{\partial c}{\partial t} = D\nabla^2 c \quad (1)$$

where ∇ denotes the gradient (or del) operator given by

$$\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} \quad (2)$$

i, j, k are unit vectors along x, y and z directions.

Thus, Equation (1) can be expanded in rectangular coordinates to

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \quad (3)$$

where

c = concentration (mole/volume).

D = diffusion coefficient.

x, y, z denote instantaneous spatial positions in the three directions and t denotes time.

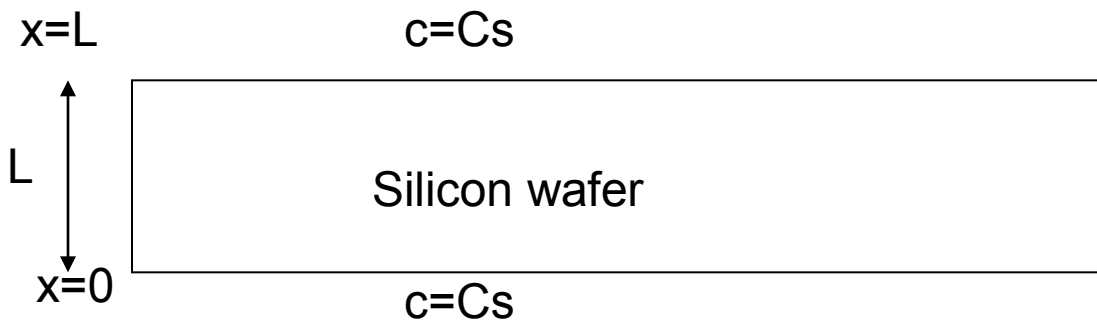
Equation (3) is a homogeneous parabolic partial differential equation which can be solved using numerical techniques such as forward difference method [2]. Since it is first order in time and second order in space, one initial condition (IC) in time and two boundary conditions (BC) in each of the spatial dimensions are required to obtain a solution. The equation can also be solved analytically by separation of variables to obtain the concentration c at any given time instant and spatial position. The analytical solution to Equation (3) is a

Fourier series. In case of equilibrium or steady state, the concentration is invariant in time and Equation (1) reduces to

$$D\nabla^2 c = 0 \quad (4)$$

Equation 4 is known as Laplace equation which can be readily solved with the use of two boundary conditions.

Consider the diffusion of a dopant (boron) into a silicon wafer, which is cylindrical in shape. It is assumed that the radius of the silicon wafer is sufficiently large compared to its thickness, hence it is modeled as a slab of thickness L (Fig 1). The surfaces in contact with the dopant are assumed to be fully saturated with it, so that $c = C_s$ at the surfaces. The solubility (C_s) and diffusivity (D) of boron in silicon, at an operating temperature of 1100°C , are 2.15×10^{20} (*atoms/cm³*) and 2×10^{-16} (*cm²/s*) (in N2 medium), respectively [3, 4]. In addition, it is assumed that initially at $t = 0$, there is no dopant in the wafer, that is $c = 0$.



Assuming that the wafer radius is significantly larger than the wafer thickness and that the dopant concentration does not vary along the radius and the circumference but varies only along the wafer thickness, Equation (1) reduces to a one-dimensional problem

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (5)$$

with the following boundary and initial conditions

$$x = 0, c = C_s,$$

$$x = L, c = C_s,$$

and

$$t = 0, c = 0.$$

Equation 5 is normalized such that

$$T = \frac{t}{\tau},$$

$$X = \frac{x}{L}.$$

Thus, the normalized equation gets the form

$$\frac{\partial c}{\partial t} = \frac{\tau D}{L^2} \left(\frac{\partial^2 c}{\partial X^2} \right)$$

Substituting

$$\tau = \frac{L^2}{D}$$

The normalized equation reduces to

$$\frac{\partial c}{\partial T} = \left(\frac{\partial^2 c}{\partial X^2} \right), \quad 0 < X < 1 \quad (6)$$

with the following boundary conditions

$$X = 0, c = Cs$$

$$X = 1, c = Cs$$

and

$$T = 0, c = 0$$

To obtain a numerical solution, the equation is discretized in time and space, using the forward finite difference method [2].

$$\frac{c_X^{T+1} - c_X^T}{\Delta T} = \frac{(c_{X+1}^T - 2c_X^T + c_{X-1}^T)}{(\Delta X)^2} \quad (7)$$

Subscripts denote spatial position and superscripts denote time, ΔX and ΔT denote grid size and time step, respectively. The boundary and initial conditions can be written as

$$c_X^0 = 0,$$

$$c_0^T = Cs, \quad (8)$$

$$c_1^T = Cs,$$

$$r = \frac{\Delta T}{(\Delta X)^2},$$

$$c_X^{T+1} = c_X^T(1 - 2r) + r(c_{X+1}^T + c_{X-1}^T). \quad (9)$$

For convergence $r \leq \frac{1}{2}$

The following grid and time step sizes were used

$$\Delta X = 0.01, \Delta T = 5e-5, \text{ therefore } r = 0.5$$

The numerical solution, obtained by sequentially solving Equation (9) and applying the boundary conditions in Equation (8), is shown in Figs 1 and 2 for two different time instants.

To obtain the analytical solution, substitute $y = Cs - c$, Equation (6) reduces to

$$\frac{\partial y}{\partial T} = \left(\frac{\partial^2 y}{\partial X^2} \right) \quad (10)$$

with the following boundary and initial conditions

$$X = 0, y = 0$$

$$X = 1, y = 0$$

$$T = 0, y = Cs$$

Equation (10) is solved using separation of variables

$$y = T_1(T)X_1(X) \quad (11)$$

Substituting Equation (11) into Equation (10), we get

$$T_1'(T)X_1(X) = X_1''(X)T_1(T) \quad (12)$$

$$\frac{X_1''(X)}{X_1(X)} = \frac{T_1'(T)}{T_1(T)} = -\lambda \quad (13)$$

Thus, we have the following two equations

$$\frac{T_1'(T)}{T_1(T)} = -\lambda \quad (14)$$

$$\frac{X_1''(X)}{X_1(X)} = -\lambda \quad (15)$$

Solving Equations (14) and (15),

$$T_1(T) = Ae^{-\lambda T} \quad (16)$$

$$X_1(X) = B \cos(\sqrt{\lambda}X) + C \sin(\sqrt{\lambda}X) \quad (17)$$

Substituting boundary conditions in Equation (17),

$$0 = B * 1 + 0$$

$$B = 0$$

$$0 = C \sin(\sqrt{\lambda})$$

$$\sqrt{\lambda} = n\pi$$

Substituting Equations (16), (17) into (11), we get a solution for all possible values of n

$$y = \sum_{n=0}^{\infty} A_n e^{-(n\pi)^2 T} \sin(n\pi X) \quad (18)$$

Using the initial condition, we get

$$Cs = \sum_{n=0}^{\infty} A_n \sin(n\pi X) \quad (19)$$

To obtain A_n , we use the following identity

$$\int_0^1 \sin^2(n\pi x) dx = \frac{1}{2}$$

$$\int_0^1 \sin(n\pi x) \sin(m\pi x) dx = 0; n \neq m$$

Multiplying both sides of Equation (19) by $\sin(n\pi X)$, we get

$$\int_0^1 Cs \sin(n\pi X) dX = \frac{A_n}{2}$$

$$A_n = \frac{2Cs}{n\pi} (-\cos(n\pi) + 1)$$

When n is even, $A_n = 0$

When n is odd,

$$A_n = \frac{4Cs}{n\pi}; n = 2k + 1; k = 0, 1, 2, \dots$$

Thus, we get the following solution

$$y = Cs - C = \sum_{n=0}^{\infty} \frac{4Cs}{n\pi} e^{-(n\pi)^2 T} \sin(n\pi X)$$

$$C = C_S - \sum_{n=0}^{\infty} \frac{4C_S}{n\pi} e^{-(n\pi)^2 T} \sin(n\pi X); \quad n = 2k + 1; k = 0, 1, 2, \dots$$

The terms for $k = 1, 2, \dots$ decay much faster than those for $k = 0$. The effect of increasing time compounds the decay of the exponential term. Therefore, after some time, only terms with $k = 0$ (that is, $n = 1$) remain in the equation. Thus, we have the following analytical solution for the diffusion equation

$$C = C_S - \frac{4C_S}{\pi} e^{-\pi^2 T} \sin(\pi X) \quad (19)$$

where

C_S is the solubility as defined above.

The numerical solution obtained from Equations (8) and (9) is compared with the analytical solution from Equation (20). The spatial variation of the dopant concentration along the wafer thickness at two different time instants, obtained using the numerical and analytical techniques, is compared in Figures 1 and 2. This demonstrates an excellent agreement between the numerical and analytical solutions.

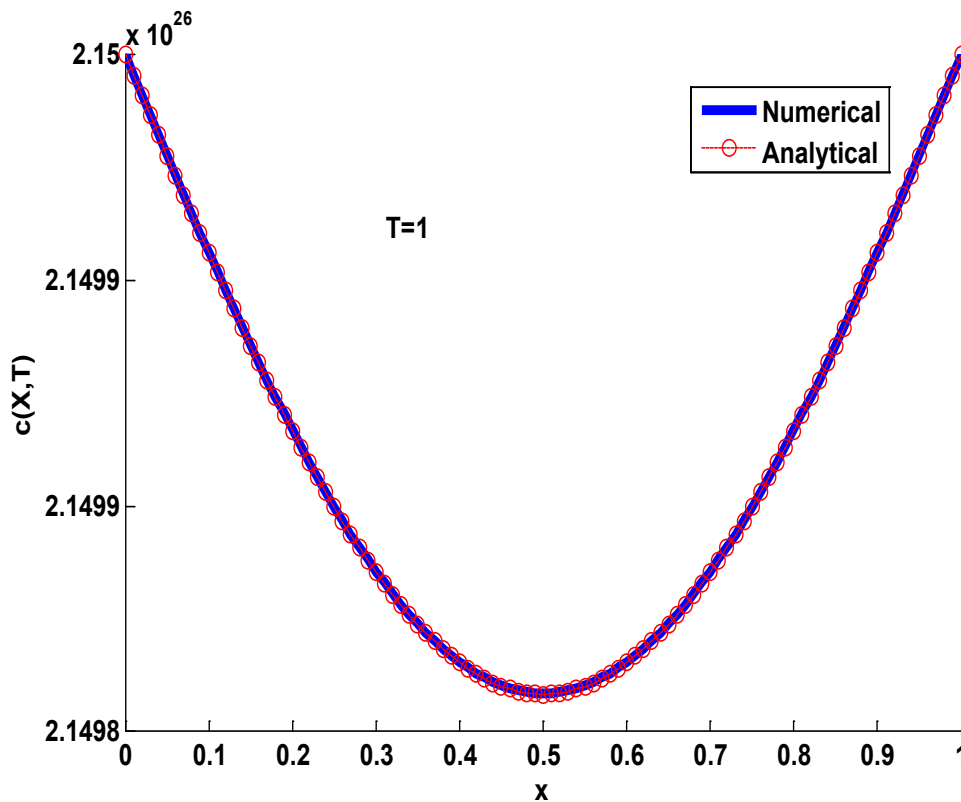


Figure 1: Comparison of the spatial variation of dopant concentration at $T = 1$, that is, $t = \tau$ from numerical and analytical technique.

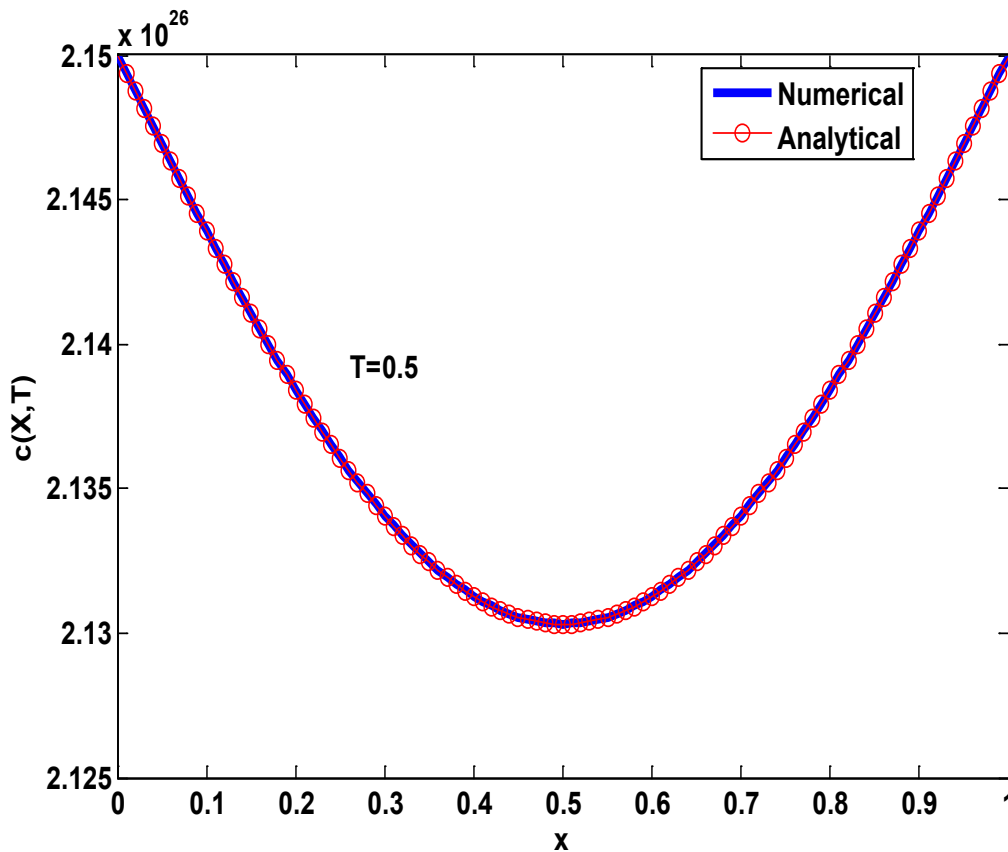


Figure 2: Comparison of the spatial variation of dopant concentration at $T = 0.5$, that is, $t = 0.5\tau$ from numerical and analytical technique

References

1. Bird R.B., Stewart W.E., Lightfoot E.N. Transport Phenomenon, John Wiley & Sons; 2007.
2. Gupta, SK. Numerical Methods for engineers. New Age International, 1995, pp 339-340.
3. Boron and Phosphorus Diffusion through an SiO₂ layer from a Doped Polycrystalline Si Source under Various Drive-in Ambients", K. Shimakura, T. Suzuki, and Y. Yadoiwa [NEC], Solid State Electronics 18 991 (1975)
4. G. L. Vick and K. M. Whittle. Solid Solubility and Diffusion Coefficients of Boron in Silicon. . Electrochem. Soc., Volume 116, Issue 8, pp. 1142-1144 (1969)

PARTIAL DIFFERENTIAL EQUATIONS

Topic	Physical problem for partial differential equations for chemical engineering
Summary	A physical problem of dopant diffusion
Major	Chemical Engineering
Authors	Reetu Singh, Venkat R. Bhethanabotla
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Web Site	http://numericalmethods.eng.usf.edu
