

Diffusion-Key Role in Solid State Crystalline Material - A Review

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ABSTRACT

Solid-state diffusion is a process which is responsible for the transport of atoms or ions of the solid reactant and product during the reaction and crystal growth of the solid product. The overall kinetics is usually significantly influenced by the relatively slow and highly activated solid-state diffusion. Due to the involvement of nucleation and crystal growth of the solid product, crystallographic properties of the solid reactant and product have a large influence on the overall kinetics as well since those properties determine how nucleation and crystal growth proceed. Diffusion is the net movement of molecules or atoms from a region of high concentration (or high chemical potential) to a region of low concentration (or low chemical potential) as a result of random motion of the molecules or atoms. The main advantage of diffusion methods is that one can grow crystals of insoluble substances under normal conditions without special apparatus. It is sufficient to cause two substances to diffuse in opposite directions, whereupon the product is formed by reaction.

Keywords: Diffusion, Nucleation, Lattice, Solid-State Diffusion, Crystal Growth, Diffusivity.

I. INTRODUCTION

Diffusion describes the process by which atoms move in a crystal lattice. Although this includes self-diffusion phenomena, our interest is in the diffusion of impurity atoms that are introduced into the silicon lattice for the purpose of alternating its electronic properties. In addition to concentration gradient and temperature. Geometrical feature of the crystal lattice (such as crystal structure and defect concentration) play a key role in this process. Diffusion can be defined as the mass flow process in which atoms change their positions relative to neighbors in a given phase under the influence of thermal and a gradient. The gradient can be a compositional gradient, an electric or magnetic gradient, or stress gradient. Solid state diffusion is believed to be responsible for the transport of ions and atoms which are necessary for the reaction and crystal growth of the solid product.

However, in kinetic modeling of gas-solid reactions, crystal growth and solid-state diffusion are either not considered or not considered properly. In this article, the important roles of solid-state diffusion and crystal growth of the solid are discussed mainly.

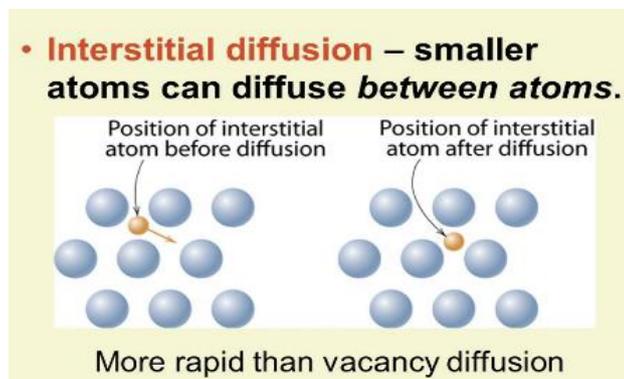
1.0. Diffusion mechanisms, Steady-state and Non-steady-state diffusion

In pure metals self-diffusion occurs where there is no net mass transport, but atoms migrate in a random manner throughout the crystal. In alloys inter-diffusion takes place where the mass transport almost always occurs so as to minimize compositional differences. Various atomic mechanisms for self-diffusion and inter-diffusion have been proposed. The most energetically favorable process involves an interchange of places by an atom and a neighboring vacancy. Vacancy Diffusion: This process demands not only the motion of vacancies, but also the

presence of vacancies. The unit step in vacancy diffusion is an atom breaks its bonds and jumps into neighboring vacant site.

1.1 Interstitial diffusion:

Here impurity atoms move through the crystal lattice by jumping from one interstitial site to the next. They may start at either lattice or interstitial sites and may finally end up in either type of site. However, interstitial site to another adjacent interstitial site. Hydrogen, Carbon, Nitrogen and Oxygen diffuse interstitially in most metals, and the activation energy for diffusion is only that associated with motion since the number of occupied, adjacent interstitial sites usually is large.



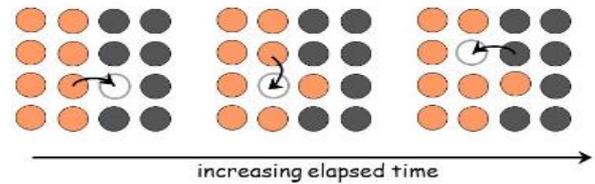
1.2. Substitutional Diffusion:

Here impurity atoms wander through the crystal by jumping from one lattice site to the next. Thus substituting for the original host atom. However, it is necessary that the adjacent site be vacant; that is, vacancies must be present to allow substitutional diffusion to occur. These vacancies are provided by thermal fluctuations in the lattice. Since equilibrium concentration of vacancies is quite low, it is reasonable to expect substitutional diffusion to occur at a much slower rate than interstitial diffusion. However, the equilibrium number of self-interstitial atoms present at any temperature is negligible in comparison to the number of vacancies. This is because the energy to form a self-interstitial is extremely large.

Substitution-diffusion

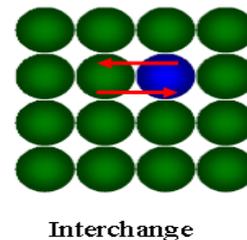
Vacancy Diffusion:

- applies to substitutional impurities
- atoms exchange with vacancies
- rate depends on (1) number of vacancies;
(2) activation energy to exchange.



1.3. Interchange Diffusion:

This occurs when two or more atoms diffuse by an interchange process. Such a process is known as a cooperative interchange when a large number is involved. The probability of interchange diffusion effects is relatively low.



Interchange

There is a difference between diffusion and net diffusion. In a homogeneous material, atoms also diffuse but this motion is hard to detect. This is because atoms move randomly and there will be an equal number of atoms moving in one direction than in another. In inhomogeneous materials, the effect of diffusion is readily seen by a change in concentration with time. In this case there is a net diffusion. Net diffusion occurs because, although all atoms are moving randomly, there are more atoms moving away from regions where their concentration is higher.

II. STEADY-STATE DIFFUSION

Diffusional processes can be either steady-state or non-steady-state. These two types of diffusion processes are distinguished by use of a parameter called flux. It is defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time. For steady-state diffusion, flux is constant with time, whereas for non-steady-state

diffusion, flux varies with time. A schematic view of concentration gradient with distance for both steady-state and non-steady-state diffusion processes are shown in figure.

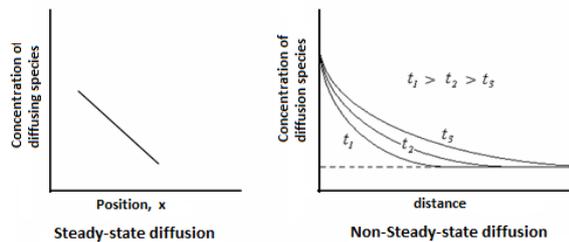


Figure 1. Steady-state and Non-steady-state diffusion processes.

Steady-state diffusion is described by Fick's first law which states that the diffusion flux(J) along x is proportional to the concentration gradient. The constant of proportionality is called diffusion coefficient (diffusivity), D (cm^2/sec). Diffusivity is characteristic of the system and depends on the nature of the diffusing species, the matrix in which it is diffusing, and the temperature at which diffusion occurs. Thus under steady-state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction. For the one-dimensional case, Fick's first law is given by

$$J_x = -D \frac{dc}{dx} = \frac{1}{A} \frac{dn}{dt}$$

and $J_x \neq f(x, t)$

where D is the diffusion constant, dc/dx is the gradient of the concentration c , dn/dt is the number of atoms crossing per unit time a cross-sectional plane of area A . The minus sign in the equation means that diffusion occurs down the concentration gradient. Although, the concentration gradient is often called the driving force for diffusion (but it is not a force in the mechanistic sense), it is more correct to consider the reduction in total free energy as the driving force.

2.1. Non Steady-state diffusion:

Most interesting cases of diffusion are non-steady-state processes since the concentration at a given position changes with time, and thus the flux changes with time. This is the case when the diffusion flux depends on time, which means that a type of atoms accumulates in a region or is depleted from a region

(which may cause them to accumulate in another region). Fick's second law characterizes these processes, which is expressed as: $\frac{dc}{dt} = -\frac{dJ}{dx} = \frac{d}{dx} \left(D \frac{dc}{dx} \right)$

where dc/dt is the time rate of change of concentration at a particular position, x . If D is assumed to be a constant, then $\frac{dc}{dt} = D \frac{d^2c}{dx^2}$

Solution to the above expression is possible when meaningful boundary conditions are specified. One common set of boundary conditions can be written as

$$\text{For } t = 0, \quad C = C_0 \quad \text{at } 0 \leq x \leq \alpha$$

$$\text{For } t > 0, \quad C = C_s \quad \text{at } x = 0$$

$$C = C_0 \quad \text{at } x = \alpha$$

And the solution is

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$$

Where C_x represents the concentration at depth x after time t . The term **erf** stands for Gaussian error function. Corresponding error function values for a variable are usually found from standard mathematical tables. The above equation demonstrates the relationship between concentration, position, and time. Thus the equation can be used to explain many practical industrial problems like corrosion resistance of duralumin, carburization and de-carburization of steel, doping of semi-conductors, etc.

Factors that influence diffusion:

Ease of a diffusion process is characterized by the parameter D , diffusivity. The value of diffusivity for a particular system depends on many factors as many mechanisms could be operative.

Diffusing species: If the diffusing species is able to occupy interstitial sites, then it can easily diffuse through the parent matrix. On the other hand if the size of substitutional species is almost equal to that of parent atomic size, substitutional diffusion would be easier. Thus size of diffusing species will have great influence on diffusivity of the system.

Temperature: Temperature has a most profound influence on the diffusivity and diffusion rates. It is known that there is a barrier to diffusion created by neighboring atoms those need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion. Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature.

$$D = D_0 \exp \left(-\frac{Q}{RT} \right)$$

Where D_0 is a pre-exponential constant, Q is the activation energy for diffusion, R is gas constant (Boltzmann's constant) and T is absolute temperature. From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient. It can also be observed that there exists a linear proportional relation between $(\ln D)$ and $(1/T)$. Thus by plotting and considering the intercepts, values of Q and D_0 can be found experimentally.

Lattice structure: Diffusion is faster in open lattices or in open directions than in closed directions.

Presence of defects: As mentioned in earlier section, defects like dislocations, grain boundaries act as short-circuit paths for diffusing species, where the activation energy is less. Thus the presence of defects enhances the diffusivity of diffusing species.

III. CONCLUSION

Fick's law for the diffusion of adatoms in surface reconstruction was derived systematically via the homogenization of a Burton-Cabrera-Frank (BCF) type model. The effective surface diffusivity and adatoms mobility involve discrete averages of microscale material parameters. The mathematical procedure applied here, based on multiscale expansions under singular perturbation, differs from the direct coarse graining of kinetic boundary

conditions for steps applied previously to constant microscale parameters.

IV. REFERENCES

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