CHAPTER 6

GROWTH OF AN A-B CRYSTAL
6.1 Introduction

When a crystal is growing from the solution, molecules, atoms or ions are attached to its surface in a regular way [1]. The theory of the formation of growth sites on perfect planes was established by Stranski [2] and others but it was recognized that the nucleation rate was too low to account for the observed growth rate at low supersaturation in certain cases [3]. To overcome this, the brilliant ideas of Burton, Cabrera and Frank [4] were introduced and these set the stage for surface kinetic models employed today. Less attention has been paid to the growth of A-B crystals. Bennema and Gilmer [5] applied the BCF theory to A-B crystals in terms of the 'growth units'. Using the work of BCF, Takata and Ookawa [6, 7] have shown that the equilibrium structure of the step in the case of stoichiometric A-B crystal depends on the ratio of partial pressures of the components in the binary systems and discussed the rate of advance of a straight step.

In the present chapter, the author has evaluated the velocity of step in the case of curved step and also in the case of straight step using the simple model for surface diffusion. The BCF surface diffusion equations for two-components are considered in section 6.2 and these are solved under appropriate boundary conditions for the case of
curved step in section 6.3 and in case of straight step in section 6.4. In each case, the rate of advance of step is evaluated as a function of supersaturation.

6.2 Surface Diffusion Equation

One of the most attractive and logical theories of crystal growth assumes that the rate limiting step occurs on the surface and considerations must be given to surface adsorption, surface diffusion, step incorporation etc, of each component when a mixed crystal grows from solution. Diffusion of adsorbed molecules across the surface is a two-dimensional problem. As an example, the author has first considered the simplest case of one-dimensional diffusion across a unit width of one component (say A). The distance from the kink-site or step which acts as a sink for molecules (as they are incorporated into the lattice) can be defined as \( y \). A typical \( C_s^A - y \) plot is shown in fig. 6.1, where \( C_s^A \) is the concentration of the component A at \( y \) [8,9]. In any element \( 6y \) the molecular flux per unit width entering at \( y \) is

\[
J_s^A_y = -D_s^A \frac{dC_s^A(y)}{dy} \tag{6.1}
\]

and the flux of molecules leaving out at \( y + \delta y \) is

\[
J_{s,y+\delta y}^A = J_s^A_y + \left(-\frac{dJ_s^A_y}{dy}\right)\delta y \tag{6.2}
\]
FIG. 6.1. A TYPICAL PLOT OF $C_S^A - y$.
where $D_s^A$ is the surface diffusion coefficient of the component $A$. The molecular flux from the bulk to the surface

$$\text{Flux}_{BS} = k_{BS} C_B^A$$ (6.3)

where $C_B^A$ is the bulk concentration and $k_{BS}$ is a constant reflects the molecular impingement on the surface. Similarly, the flux from surface to bulk is

$$\text{Flux}_{SB} = k_{SB} C_s^A$$ (6.4)

At steady state, the total flux of molecules entering should be equal to the flux leaving i.e., from eqs. (6.1) to (6.4),

$$- \left( \frac{dJ_s^A}{dy} \right) \delta y + k_{BS} C_B^A \delta y - k_{SB} C_s^A(y) \delta y = 0.$$. (6.5)

The ratio of the constants is given by [8]

$$k_{SB}/k_{BS} = C_B^A/C_{s\infty}^A.$$ (6.6)

Using the eq. (6.6) to eliminate $k_{BS} C_B^A$ in eq. (6.5)

$$- \frac{d}{dy} \left( J_s^A \right) + k_{SB} \left[ C_{s\infty}^A - C_s^A(y) \right] = 0.$$ (6.7)

or

$$- \frac{d}{dy} \left[ - D_s \frac{dC_s^A(y)}{dy} \right] + k_{SB} C_s^A \psi^A = 0.$$ (6.8)

Simplifying

$$- D_s \frac{d^2\psi^A}{dy^2} + k_{SB} \psi^A = 0.$$ (6.9)
where \( \psi^A = S^A_B - S^A_s \), \( S^A_B \) and \( S^A_s \) are the supersaturations of the components A in bulk and surface respectively. These values become

\[
S^A_s = \frac{(C^A_s - C^A_{SE})}{C^A_{SE}} \quad \text{and} \quad S^A_B = \frac{(C^B_A - C^B_{BE})}{C^B_{BE}}. \tag{6.10}
\]

Since \( k_{SB} \approx 1/T^S \), \( T^S \) is the relaxation period, then eq. (6.9) can be written as

\[
\frac{d^2 \psi^A}{dy^2} = \frac{\psi^A}{(D^A_s T^A_s) (x^A_s)^2} = \frac{\psi^A}{(x^A_s)^2}. \tag{6.11}
\]

The same derivation would be applicable for other component, also for two-dimensional diffusion in either Cartesian or polar co-ordinates. The general equations are

\[
\nabla^2 \psi^A = \psi^A/(x^A_s)^2 \quad \text{and} \quad \nabla^2 \psi^B = \psi^B/(x^B_s)^2, \tag{6.12}
\]

where \( x^A_s \) and \( x^B_s \) are the mean displacements before reevaporation of A and B adatoms.

6.3 Curved Step

6.3.1 Equations and Boundary Conditions

The step is considered to be a line sink for the surface adsorbed atoms or molecules. A given atom or molecules arriving on the surface would diffuse toward the step but, in most cases, it would desorb before it travels any
significant distance. There then exists some mean distance $x_s^A$ and $x_s^B$ for A and B adatoms. With many atoms adsorbing and diffusing on the surface, the surface diffusion equation for A and B atoms in polar coordinates can be written. In polar coordinates, with no angle dependence the equations (6.12) may be rewritten as [10]

$$\frac{d^2 \psi^A}{dr^2} + \frac{1}{r} \frac{d \psi^A}{dr} = -\frac{\psi^A}{(x_s^A)^2} \text{ and } \frac{d^2 \psi^B}{dr^2} + \frac{1}{r} \frac{d \psi^B}{dr} = \frac{\psi^B}{(x_s^B)^2}.$$  

(6.13)

Eqs. (6.13) are the differential equations which describe the rate of surface diffusion. To solve these equations, it is assumed that there is a circular island on the surface. Atoms or molecules from the bulk solution are adsorbed and incorporated into the sides of the island so that it grows radially. Setting the origin at $r = 0$, the following boundary conditions are used.

1. When the equilibrium exists between the bulk solution and surface, $\psi^A$ and $\psi^B \to 0$ as $r \to 0$.

2. Let $\psi^A \to \psi^A(\rho)$, $\psi^B \to \psi^B(\rho)$, where $\rho$ is the radius of the island at the time it is studied.

Finally, one should not neglect the fact that molecules reach the sides of the island from both sides, that is both when $r < \rho$ and when $r > \rho$, where $\rho$ is the radius of the island. The solutions of the eqs. (6.13) are
\[ \psi^A = C_1^A I_0(r/x_s^A) + C_2^A K_0(r/x_s^A) \]
\[ \psi^B = C_1^B I_0(r/x_s^B) + C_2^B K_0(r/x_s^B), \]  
(6.14)

where \( C_1^A, C_2^A, C_1^B \) and \( C_2^B \) are the constants which can be determined using the boundary conditions. The terms \( I_0 \) and \( K_0 \) are Bessel functions which behave schematically as shown in fig. 6.2.

The first case of \( r > p \), where \( p \) is the radius of island, is considered. Using the first boundary conditions of \( \psi^A \rightarrow 0 \) and \( \psi^B \rightarrow 0 \) as \( r \rightarrow 0 \) in eqs. (6.14),
\[ C_1^A = 0 \; \text{and} \; C_1^B = 0. \]  
(6.15)

From the second boundary conditions
\[ C_2^A = \frac{\psi^A(p)}{K_0(p/x_s^A)} \; \text{and} \; C_2^B = \frac{\psi^B(p)}{K_0(p/x_s^B)}. \]  
(6.16)

Substituting the values of \( C_1^A, C_2^A, C_1^B \) and \( C_2^B \) in eqs. (6.14), one can find
\[ \psi^A = \frac{\psi^A(p) K_0(r/x_s^A)}{K_0(p/x_s^A)} \; \text{and} \; \psi^B = \frac{\psi^B(p) K_0(r/x_s^B)}{K_0(p/x_s^B)}. \]  
(6.17)

These are the solutions of the differential equations for the surface diffusion when the curved step is considered of
FIG. 6.2. BEHAVIOUR OF BESSEL FUNCTIONS $K_0(\tau)$ AND $I_0(\tau)$.
radius \( \rho \) and \( \rho < r \). Similarly the calculations are carried out for the second case of \( r \) is less than the radius of the island. The corresponding values are

\[
\psi^A = \psi^A(\rho) \frac{I_0(\rho/x_s^A)}{I_0(\rho/x_s^A)} \quad \text{and} \quad \psi^B = \psi^B(\rho) \frac{I_0(\rho/x_s^B)}{I_0(\rho/x_s^B)}. \tag{6.18}
\]

Eqs. (6.17) and (6.18) give the solutions for the eqs. (6.13) for the case of circular steps.

6.3.2 Step Velocity

From the solutions of the surface diffusion equation, the fluxes of A and B atoms or molecules on the surface going to the curved step are calculated on either side of the step and hence the velocity of the step is calculated. Once the step velocity is known, the growth rate of solid solutions can be found. The flux of A and B atoms on the surface going to the curved step is

\[
j^A = 2\pi \rho D_s^A C_sE^A \frac{\delta \psi^A}{\delta r} \bigg|_{r=\rho} \quad \text{and} \quad j^B = 2\pi \rho D_s^B C_sE^B \frac{\delta \psi^B}{\delta r} \bigg|_{r=\rho},
\tag{6.19}
\]

where \( D_s^A \) and \( D_s^B \) are the surface diffusion coefficient of A and B adatoms. In the case of \( r > \rho \), from eqs. (6.17) and (6.19)

\[
j_1^A = \frac{2\pi \rho D_s^A C_sE^A \psi^A(\rho)}{x_s^A} \frac{K_1(\rho/x_s^A)}{K_0(\rho/x_s^A)},
\]
Similarly the flux of molecules, for the second case \( r < \rho \), going to the step

\[
j_2 = \frac{2\pi \rho D_s^A C_{SE}^A \psi^A(\rho)}{x_s^A} \frac{I_1(\rho/x_s^A)}{I_0(\rho/x_s^A)}.
\]

(6.21)

The total flux on either side of the island is the sum of \( j_1 \) and \( j_2 \). From eqs. (6.20) and (6.21) on simplifying, one can get

\[
j^A = 4\pi \rho D_s^A C_{SE}^A \psi^A(\rho)/x_s^A \quad \text{and}
\]

\[
j^B = 4\pi \rho D_s^B C_{SE}^B \psi^B(\rho)/x_s^B.
\]

(6.22)

If the step height is \( h \) units, the velocity of advance of the step is given by

\[
\frac{dr}{dt} = v_\rho = \text{molecular flux at } \frac{\text{molecular volume}}{\text{unit length-time}} \times \frac{\text{molecular volume}}{h}. \quad (6.23)
\]

Using eqs. (6.22, 6.23), the rate of advance of the step is [10, 11]

\[
v_\rho = \frac{2}{h} \left[ D_s^A D_s^B C_{SE}^A C_{SE}^B \psi^A(\rho) \psi^B(\rho)/x_s^A x_s^B \right]^{1/2}.
\]

(6.24)
This equation may also be applied to a straight step, \( \rho \rightarrow \infty \), and for this case we define \( \psi = \psi_{\infty} \) as \( \rho \rightarrow \infty \).

Thus

\[
\nu_{\infty} = \frac{2}{R} \left[ D_s A D_s B C_s E C_s E B \nu_A \nu_B^{\psi} A B / x_S A B \right]^{1/2} \tag{6.25}
\]

From these eqs. (6.24) and (6.25) one can calculate the growth rate of crystals.

6.4 Straight Step

6.4.1 The Model

Many crystal growth theories, that is, two-dimensional growth theories [12], surface diffusion and dislocation theories, mass transfer limited growth [9], probabilistic models etc. are available but some only in an abbreviated form. Part of the reason for this lack of a critical evaluation lies in the fact that many theories are quite complicated in either a mathematical or logical sense. The most important reason may be that none of the theories has yielded results which can be easily used to describe or predict the growth rate of crystals as convenient functions of the important independent system variables. Of all the growth theories mentioned above, the BCF surface diffusion and dislocation model and the mass transfer limiting model appears to be most reasonable [8].
Generally in the BCF model, the molecules are transferred from the bulk to the surface, surface diffusion to the step, step diffusion on the kink and incorporated in the kink site. The kink distribution in the step is a function of super-saturation, temperature and molecular interaction energies. The simplest model to be considered for surface diffusion would be an evenly spaced kink distribution on a single straight step as shown in fig. 6.3. In contrast to mono-atomic crystals, the step of an A-B crystal has two kinds of kinks, i.e., A type kink and B type kink. Usually the equilibrium structure of a straight step is determined by minimizing the free energy of the total system consisting of steps, surface and bulk liquid. The kink spacing is chosen as $x_0$ and the coordinates of each A type kink are given by $2nx_0$, $y = 0$ and B type kink are $(2n + 1)x_0$, $y = C$, $n = 0, \pm 1, \pm 2, \ldots \ldots$ so that the distance between the two successive A type kink is $2x_0$ as shown in fig. 6.3.

6.4.2 Solutions of the Differential Equations

As already defined for the potential functions

$$\psi^A(x, y) = S^A_B - S^A_s$$ and $$\psi^B(x, y) = S^B_B - S^B_s,$$ (6.26)

where $S$ is the supersaturation, the sufices $B$ and $s$ denote for the bulk and surface respectively, superscripts $A$ and $B$ refer to the components. In our model, $\psi^A$ and $\psi^B$ are
FIG. 6.3. KINK DISTRIBUTION ON A STRAIGHT STEP.
periodic in $x$. The surface diffusion equations in two-
dimensional cartesian coordinates

$$
\nabla^2 \psi^A = \frac{\partial^2 \psi^A}{\partial x^2} + \frac{\partial^2 \psi^A}{\partial y^2} = \frac{\psi^A}{(x_s^A)^2} \quad \text{and} \quad \nabla^2 \psi^B = \frac{\partial^2 \psi^B}{\partial x^2} + \frac{\partial^2 \psi^B}{\partial y^2} = \frac{\psi^B}{(x_s^B)^2}
$$

(6.27)

where $x_s^A$ and $x_s^B$ are the mean displacements before re-
evaporation of $A$ and $B$ adatoms. To solve these equations,
one may try with $[13, 14]$

$$
\psi^A = \chi^A(x) \chi^A(y) \quad \text{and} \quad \psi^B = \chi^B(x) \chi^B(y) \quad \text{(6.28)}
$$

then, for the component $A$

$$
\frac{(x_s^A)^2}{x^A(x)} \frac{d^2 x^A(x)}{dx^2} = 1 - \frac{(x_s^A)^2}{y^A(y)} \frac{d^2 y^A(y)}{dy^2}. \quad \text{(6.29)}
$$

As the left hand side of eq. (6.29) is a function of $x$
and the right hand side a function of $y$, for the equality
to hold for all $x$ and $y$, both sides should equal to a
constant ($-k^A$).

$$
d^2 x^A(x) \frac{dx^A(x)}{dx^2} = -(x_s^A)^2 \frac{d^2 y^A(y)}{dy^2} = -(1 - k^A) \frac{y^A(y)}{(x_s^A)^2}. \quad \text{(6.30)}
$$

The solution of the eq. (6.30) may be written as

$$
\chi^A(x) = a_1 \sin(\gamma x / x_s^A) x + b_1 \cos(\gamma x / x_s^A) x. \quad \text{(6.31)}
$$

Using the first boundary condition

$$
\psi^A(x, y) = \psi^A(2nx_0 + x, y), \quad \text{(6.32)}
$$
where $n$ is any integer, the author has

$$X^A(x) = X^A(2n\pi_0 + x),$$  \hspace{1cm} (6.33)

$$\frac{dX^A(x)}{dx} = \frac{d}{dx} X^A(2n\pi_0 + x),$$  \hspace{1cm} (6.34)

$$\frac{d^2X^A(x)}{dx^2} = \frac{d^2}{dx^2} X^A(2n\pi_0 + x)$$

Using these boundary conditions, the solution of the eq. (6.30) can be written as

$$X^A(x) = a_1 \sin(2\pi N x/2\pi_0) + b_1 \cos(2\pi N x/2\pi_0)$$  \hspace{1cm} (6.35)

where $N$ is an integer and $a_1$ and $b_1$ are constants. On comparing the eqs. (6.31) and (6.35),

$$K^A = (2\pi N/2\pi_0)^2 (x_s^A)^2.$$  \hspace{1cm} (6.36)

The differential equation for $y$ becomes [13]

$$\frac{d^2y^A}{dy^2} = \left[ - \frac{1}{(x_s^A)^2} + (\frac{2\pi N}{2\pi_0})^2 \right] y^A(y) = (M_N^A)^2 y^A(y).$$  \hspace{1cm} (6.37)

The solution of the above equation is

$$y^A(y) = c_1 \exp(M_N^A y)$$  \hspace{1cm} (6.38)

where $c_1$ is a constant.

The second boundary condition is

$$\frac{\partial y^A}{\partial x} = 0 \text{ at } x = \pi_0 + 2n\pi_0$$

or

$$y^A(y) \frac{dx^A}{dy} = 0 \text{ at } x = \pi_0 + 2n\pi_0.$$  \hspace{1cm} (6.39)
From the identities (6.33) and (6.34)

\[
\frac{d}{dx} x^A(x_0 + 2nx_0) = \frac{d}{dx} x^A(x_0) = 0
\]

\[
= \left(\frac{2\pi N}{x_0}\right)[a_1(+1) - b_1(0)] = 0. \quad (6.40)
\]

Therefore \(a_1 = 0\) and \(x^A(x) = b_1 \cos(2\pi N x / 2x_0)\).

(6.41)

Using equations (6.28), (6.38) and (6.41)

\[
\psi^A(x, y) = b_1 C_1 \cos(2\pi N x / 2x_0) \exp(M_N^A \gamma). \quad (6.42)
\]

The general solution to equation (6.42) is therefore [13]

\[
\psi^A(x, y) = \beta^A \sigma^A \sum_{i=0}^{\infty} \gamma_i \cos(k_i^A x) \exp(M_i^A \gamma) \quad (6.43)
\]

where \(\beta^A = (\sigma^A - \sigma_{\text{step}}^A) / \sigma^A\), the retardation factor, \(\sigma\) is the relative supersaturation given by the supersaturation minus one. \(\sigma_{\text{step}}^A\) is the relative supersaturation of \(A\) at step. Similarly,

\[
\psi^B(x, y) = \beta^B \sigma^B \sum_{i=0}^{\infty} \gamma_i \cos(k_i^B x) \exp(M_i^B \gamma). \quad (6.44)
\]

where \(k_i = 2\pi i / 2x_0\) and \(M_i = [k_i^2 - \frac{1}{(x_s^A)^2}]^{1/2}\).

(6.45)

Eqs. (6.43) and (6.44) are the solutions to the eqs. (6.27).
6.4.3 The Rate of Advance of a Straight Step

The flux of A atoms going from a distance $x_0$ from the A type kink, at steady state, in the direction of positive y is

$$j_+^A = \int_{-x_0}^{x_0} D_s^A C_s E^A \frac{\partial j^A}{\partial y} \, dx,$$

(6.46)

where $D_s^A$ is the surface diffusion coefficient of A adatoms or adsorbed molecules. The total flux of A atoms is

$$j^A = j_+^A + j_-^A = 4 \int_{0}^{x_0} - D_s^A n_{so}^A \frac{\partial \theta}{\partial y} \, dx.$$  

(6.47)

From eq. (6.43)

$$\frac{\partial \theta}{\partial y} = \beta^A \sigma^A \left[ \gamma_0 M_0^A + \sum_{i=0}^{\infty} \gamma_i M_i^A \cos k_i^A x \right]$$

(6.48)

where $M_0^A = -1/x_s^A$. Substituting eq. (6.48) in eq. (6.47) and integrating, the author gets the flux [13, 14]

$$j^A = -4 D_s^A C_s E^A \beta^A \sigma^A \left[ -\frac{\gamma_0^A}{x_s^A} + \sum_{i=0}^{\infty} \frac{\gamma_i M_i^A}{k_i^A} \sin k_i^A x \right]_0^{x_0}$$

$$= 4 D_s^A C_s E^A \beta^A \sigma^A \gamma_0^A x_0/x_s^A.$$

(6.49)

Similarly, the flux of B atoms can be shown that

$$j^B = 4 D_s^B C_s E^B \beta^B \sigma^B \gamma_0^B x_0/x_s^B.$$

(6.50)

where $D_s^B$ is the surface diffusion coefficient of B atoms.
or molecules. If the step height is \( h \) units, the velocity of advance of the step is

\[
v_\infty = \text{the flux of molecules} \times (v_m/hx_0) \tag{6.51}
\]


where \( v_m \) is the molecular volume which is assumed to be equal for \( A \) and \( B \) type molecules. From eqs. (6.49), (6.50) and (6.51)

\[
v_\infty = 2v_m \gamma_0 \left[ D_s A D_s B C_{SE} A C_{SE} B \beta^A \beta^B \sigma^A \sigma^B / x_s A x_s B \right]^{1/2}.
\]

Eq. (6.52) gives the velocity of a straight step with the inclusion of the new factor \( \gamma_0 \), the kink retardation factor, which is independent of the components.

6.5 Conclusion
The kink retardation factor originated when it was postulated that the crystal growth process would occur only at kink sites. It is a dimensional quantity with maximum value of unity. The BCF differential equations for the surface diffusion have been set up and solved for two different cases. Atoms or molecules from the bulk adsorb on the surface on both sides of the step. In the case of curved step treated in section 6.3, the current of atoms on either side of the step is separately calculated and net flux of atoms to the growing island is found. The rate of advance of the curved step is determined and hence the velocity of the straight step for the case of binary system
is calculated. The arguments and discussions given in section 6.3 pertain to a single island of curved step on the surface. A similar treatment may be used to determine the step velocities when they are multiple, annular islands separated by some step spacings.

In order to calculate the velocity of a straight step of a stoichiometric A-B crystal, the author has chosen a simple model of an evenly spaced kink distribution on a single straight step for the surface diffusion of A and B type of molecules. The BCF differential equations for the distribution of A and B components are considered and they are solved. The potential functions of the A and B components are determined. The flux of molecules going to the kink is separately calculated and the velocity of advance of the straight step in the case of an ideally stoichiometric A-B crystal is determined. There have been a number of ways to estimate the growth rate of crystal by determining the velocity of step.
References

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