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# Transient surface supersaturation after crystal submersion ( II )

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## ABSTRACT

In our earlier papers [ M. Rak, Proc. SPIE 3178 (1997) 108 and M. Rak et al., J. Cryst. Growth 197 (1999) 944 ], we solved the time-dependent equation of Burton, Cabrera and Frank (BCF) for transient state conditions occurring immediately after submersion of a crystal surface in supersaturated solution. As a result, the expression for the transient surface supersaturation was found and discussed. In this paper we present an approximation of that expression. The approximation enables a simple estimation of the time required to attain the steady-state value of the surface supersaturation.

**Keywords:** time-dependent BCF equation, surface supersaturation, surface diffusion theory of crystal growth, solution growth.

## 1. INTRODUCTION

In our previous papers [1, 2] we studied, using the surface diffusion theory [3, 4] of Burton, Cabrera and Frank (BCF), the transient surface supersaturation $\sigma_S$ occurring immediately after submersion of crystal face in supersaturated solution. For this purpose, we solved [1, 2] the BCF time-dependent equation:

$$\frac{\partial^2 n}{\partial x^2} + \frac{n_e}{\lambda^2}(1+\sigma) - \frac{n}{\lambda^2} = \frac{\tau}{\lambda^2}\frac{\partial n}{\partial t} \qquad (1)$$

where $n \equiv n(x,t)$ is the local concentration of growth units at the surface; $n_e$ is the equilibrium concentration of growth units at the surface; $\sigma$ is the relative supersaturation just above the surface and very far from a step, so it is the same as the bulk supersaturation; $\lambda$ is the mean diffusion distance of the growth unit adsorbed on the surface and $\tau$ denotes the relaxation time for leaving the surface adsorption layer. The relaxation time $\tau$ is related to the activation free energy $\Delta G$ for desorption by Eyrings' formalism [3]:

$$\tau = \frac{h}{k_B T}\exp\left(\frac{\Delta G}{k_B T}\right), \qquad (2)$$

where h is Planck's constant, $k_B$ is the Boltzmann constant and T denotes temperature.

To formulate the initial condition, we assumed [1, 2] that, as soon as the crystal face is submerged in the supersaturated solution, the surface supersaturation $\sigma_S$ is equal to the bulk supersaturation $\sigma$:

$$\sigma_S(x,0) = \sigma\ , \qquad (3)$$

where the surface supersaturation $\sigma_S \equiv \sigma_S(x, t)$ is defined as:

$$\sigma_S = \frac{n - n_e}{n_e}\ . \qquad (4)$$

Eq. (1) was solved [1, 2] for a parallel sequence of equidistant steps and the origin of the coordinate system chosen in the centre of the step terrace. The positions $x = \pm x_0/2$ (where $x_0$ denotes the interstep distance) corresponding to the step edges were assumed [1, 2] to remain unchanged during the transient state. Furthermore, the boundary conditions assumed [1, 2] symmetrical diffusion fields around steps and equilibrium concentration n of growth units at the step edges. Taking into account Eq. (4), the solution for Eq. (1) with initial condition (3) was found [1, 2] in the following form:

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$$\sigma_S(x,t) = \sigma\left\{1 - \frac{\cosh(x/2\lambda)}{\cosh(x_0/2\lambda)} + \right. \qquad (5)$$

$$\left. - 4\pi\sum_{k=1}^{\infty}(-1)^k \frac{(2k-1)\cos\left[\pi(2k-1)x/x_0\right]}{\pi^2(2k-1)^2 + (x_0/\lambda)^2}\exp\left[-\frac{\pi^2(\lambda/x_0)^2(2k-1)^2+1}{\tau}t\right]\right\},$$

The analysis of the transient surface supersaturation, expressed by Eq. (5), revealed [1, 2] that the time $t_S$ required to attain the steady-state value of $\sigma_S$ does not depends on the bulk supersaturation $\sigma$, but it increases with increasing relative interstep distance $x_0/\lambda$. Furthermore, the longest period of time $t_{S0}$ is necessary to reach the steady-state value of $\sigma_S$ at the centre of the step terrace ($x = 0$) and therefore this point is of particular interest.

The aim of this paper is to present an approximation of Eq. (5) which enables a simple estimation of the time $t_S$ required to attain the steady-state value of surface supersaturation after submersion of crystal face in the supersaturated solution.

## 2. APPROXIMATION OF EQ. ( 5 )

In order to find an approximation of Eq. (5) we follow in the way similar to that presented in one of our earlier papers [5]. Therefore, we use the effective time $t_{eff}$ defined [5] as:

$$t_{eff} = \tau\left[1 - \frac{\cosh(x/\lambda)}{\cosh(x_0/2\lambda)}\right] . \qquad (6)$$

In the summation term of Eq. (5), we now replace the power $[\pi^2(\lambda/x_0)^2(2k-1)^2+1]t/\tau$ by $t_{eff}/\tau$, which leads to an approximation:

$$4\pi\sum_{k=1}^{\infty}(-1)^k \frac{(2k-1)\cos\left[\pi(2k-1)x/x_0\right]}{\pi^2(2k-1)^2 + (x_0/\lambda)^2}\exp\left[-\frac{\pi^2(\lambda/x_0)^2(2k-1)^2+1}{\tau}t\right] \approx$$

$$\approx 4\pi \exp\left(-\frac{t}{t_{eff}}\right)\sum_{k=1}^{\infty}(-1)^k \frac{(2k-1)\cos\left[\pi(2k-1)x/x_0\right]}{\pi^2(2k-1)^2 + (x_0/\lambda)^2} . \qquad (7)$$

Taking into account that the solution given by Eq. (5) fulfils the initial condition [Eq. (3)], we find:

$$-4\pi\sum_{k=1}^{\infty}(-1)^k \frac{(2k-1)\cos\left[\pi(2k-1)x/x_0\right]}{\pi^2(2k-1)^2 + (x_0/\lambda)^2} = \frac{\cosh(x/\lambda)}{\cosh(x_0/2\lambda)} \qquad (8)$$

This result is also obtainable using the Fourier expansion corresponding to the function $\cosh(x/\lambda)/\cosh(x_0/2\lambda)$ in the interval $(-x_0/2 , x_0/2)$. Upon substituting Eq. (8) into Eq. (7), we have an approximation of Eq. (5) in the following form:

$$\sigma_S^A(x,t) = \sigma\left[\frac{t_{eff}}{\tau} + \left(1 - \frac{t_{eff}}{\tau}\right)\exp\left(-\frac{t}{t_{eff}}\right)\right] , \qquad (9)$$

where $t_{eff}$ is expressed by Eq. (6). The approximation given by Eq. (9) and the solution found previously [ Eq. (5) ] take the same initial and steady-state values. In addition to this, Eq. (9) fulfils the boundary conditions assumed for solving the BCF time-dependent equation.

## 3. DISCUSSION

In order to illustrate the solution given by Eq.(5) and its approximation [Eq. (9)], we perform calculations for bulk supersaturations sufficiently low to predict the BCF spiral growth mechanism. The relative interstep distance $x_0/\lambda$ present in Eqs. (5) and (6) can be found using one of the known approximations of the interstep distance (see e.g. Ref [6] ). However, since this distance depends not only on supersaturation but also on the edge free energy and the number of cooperating spirals, we assume several values of $x_0/\lambda$ ($x_0/\lambda$ = 2, 3, 4, 5) to show the influence of $x_0/\lambda$ on behaviour of the surface supersaturation. In Fig. 1 the surface supersaturation $\sigma_{S0}$ at the centre of step terrace (x = 0) is shown as a function of the relative time $t/\tau$.

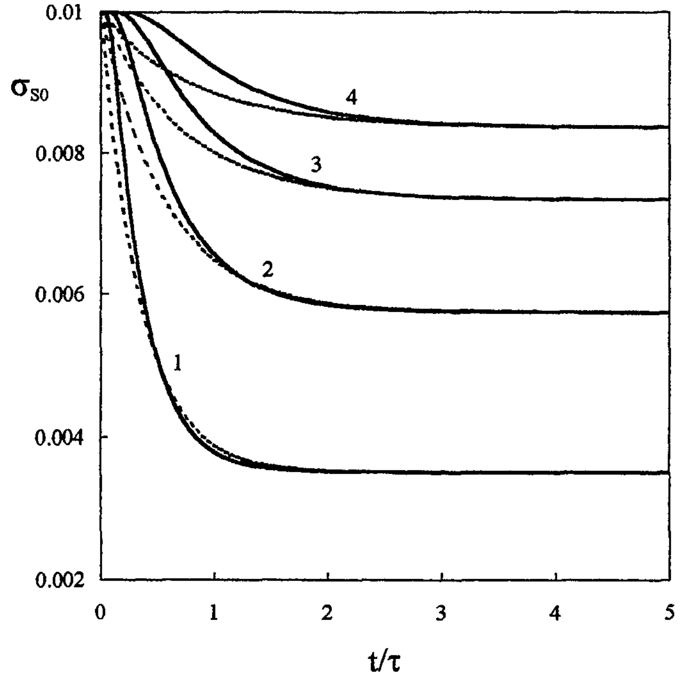

Fig. 1. Surface supersaturation $\sigma_{S0}$ at the centre of the step terrace (x = 0) versus relative time $t/\tau$ for bulk supersaturation $\sigma$ = 0.01. Curves 1, 2, 3 and 4 correspond to the relative interstep distance $x_0/\lambda$ = 2, 3, 4 and 5, respectively. Full and dashed lines correspond to Eq. (5) and (9), respectively.

The full and dashed lines correspond to $\sigma_{S0}$ calculated from Eq. (5) and $\sigma_{S0}^{A}$ calculated from Eq. (9), respectively. It can be seen in Fig. 1 that, at small values of $t/\tau$, the function $\sigma_{S0}(t)$ differs from the exponential function $\sigma_{S0}^{A}(t)$. The difference is more considerable for greater values of the relative distance $x_0/\lambda$. The slope $(\partial\sigma_S/\partial t)_{t=0}$ of the curve $\sigma_S(t)$ at t = 0 is equal to zero, which means that at t = 0, the surface supersaturation $\sigma_S$ remains constant (cf. full lines in Fig. 1). This result is obvious from physical point of view. At t = 0, the behaviour of the surface supersaturation is determined by the exchange of growth units between the crystal surface and the solution bulk. The net flux $j_V$ of growth units exchanged with the bulk of the solution is equal[3, 4] to:

$$j_V = \frac{n_e(\sigma - \sigma_S)}{\tau} \qquad (10)$$

However, just after submersion of the crystal face in supersaturated solution, the surface supersaturation $\sigma_S$ is equal to bulk supersaturation $\sigma$ [cf. Eq. (3)]. In consequence, at t = 0, the net flux $j_V$ is equal to zero and $\sigma_S$ remains constant at t = 0. At t > 0, the surface supersaturation is reduced by the surface flux of growth units going to the step edges.

In Fig. 2 the surface supersaturations $\sigma_S$ and $\sigma_S^A$ are shown, for $x_0/\lambda$ = 3 and various values of $t/\tau$, as a function of the relative distance $x/x_0$ from the step centre. It can be noticed that with increasing distance $x/x_0$ from the step centre, the difference between $\sigma_S$ and $\sigma_S^A$ diminishes and for $x = (0.2 \div 0.3)x_0$ reaches zero. Then it changes its sign and with increasing x, the absolute value of the difference increases. Consequently, for $x = (0.2 \div 0.3)x_0$, values of $\sigma_S$ and $\sigma_S^A$ are very close to each other.

Although the behaviour of the functions $\sigma_S(t)$ and $\sigma_S^A(t)$ is different at the beginning of the transient state, these both

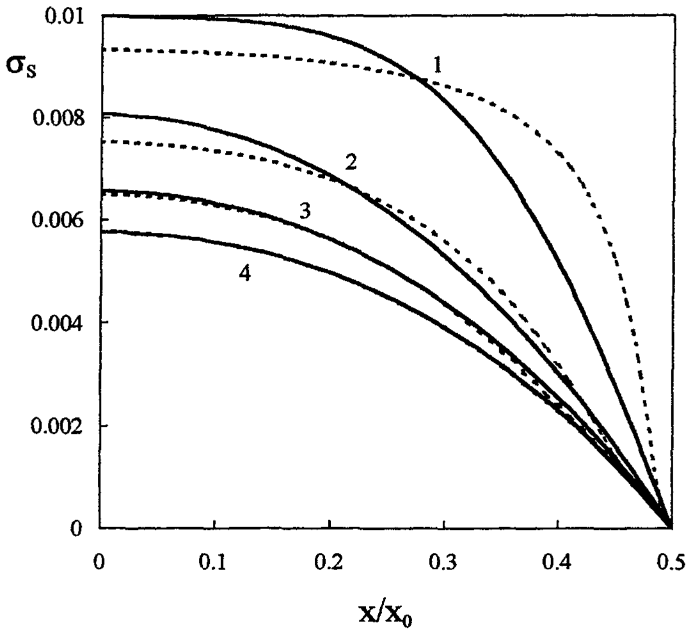

Fig. 2. Surface supersaturation $\sigma_S$ versus relative distance $x/x_0$ from the terrace centre, plotted for $x_0/\lambda = 3$, $\sigma = 0.01$ and various values of the relative time $t/\tau$. Curves 1, 2, 3 and 4 correspond to $t/\tau = 0.1, 0.5, 1$ and 3, respectively. Full and dashed lines correspond to Eq. (5) and (9), respectively.

functions attain their steady-state value at the same time (cf. Fig. 1). Therefore, the time $t_S$ required to attain the steady-state value of the surface supersaturation can be estimated with the use of Eq. (9). In transient state analysis, it is usually assumed that the steady-state is attained when the transient part of the equation is not greater than 0.01 of its initial value. Consequently, the exponential term in Eq. (9) can be neglected when it is not greater than 0.01 of its value at $t = 0$. This means that the time $t_S$ necessary to attain the steady-state value of the surface supersaturation can be estimated as:

$$t_S \approx 4.6\, t_{eff} \ , \qquad (11)$$

where $t_{eff}$ is given by Eq. (6). Values of the characteristic time $t_{S0}$ (for $x = 0$) and the time $t_S$ for $x = 0.25x_0$, obtained using Eq. (11), are presented in Table 1.

Table 1. Values of the relative time $t_S/\tau$ obtained using Eq. (11) and those following from Eq. (5), for various values of $x_0/\lambda$. Results for $x/x_0 = 0$ and $x/x_0 = 0.25$.

$x/x_0 = 0$

| $x_0/\lambda$ | $t_{eff}/\tau$ Eq.(6) | $t_S/\tau$ Eq.(11) | $t_S/\tau$ |
|---|---|---|---|
| 2 | 0.35 | 1.62 | 1.43 |
| 3 | 0.57 | 2.64 | 2.41 |
| 4 | 0.73 | 3.38 | 3.22 |
| 5 | 0.84 | 3.85 | 3.87 |
| 6 | 0.90 | 4.14 | 4.41 |
| 7 | 0.94 | 4.32 | 4.89 |
| 8 | 0.96 | 4.43 | 5.32 |

$x/x_0 = 0.25$

| $x_0/\lambda$ | $t_{eff}/\tau$ Eq.(6) | $t_S/\tau$ Eq.(11) | $t_S/\tau$ |
|---|---|---|---|
| 2 | 0.27 | 1.24 | 1.29 |
| 3 | 0.45 | 2.07 | 2.12 |
| 4 | 0.59 | 2.71 | 2.74 |
| 5 | 0.69 | 3.18 | 3.17 |
| 6 | 0.77 | 3.53 | 3.47 |
| 7 | 0.82 | 3.78 | 3.70 |
| 8 | 0.86 | 3.97 | 3.88 |

In this table, we also show values of the characteristic time $t_{S0}$ and the time $t_S$ calculated from Eq. (5). To calculate the times $t_{S0}$ and $t_S$ from Eq. (5) we also assumed that the transient part (summation term) in Eq. (5) can be neglected when it is not greater than 0.01 of its initial value. It follows from the results presented in Table 1 that, in the centre of step terrace ($x = 0$), the simple expression (11) may be used for estimation of the characteristic time $t_{S0}$ only at not too large values of the interstep distance ($x_0/\lambda \leq 7$). At large $x_0/\lambda$, values of $t_{S0}$ estimated using Eq. (11) are too low in comparison with those following from Eq. (5). It can also be noted that at the point $x=0.25x_0$, where the difference between $\sigma_S$ and $\sigma_S^A$ is negligible (cf. Fig. 2), the difference between values of $t_S$ estimated using Eq. (11) and those following from Eq.(5) is also negligible.

## 4. CONCLUSIONS

The present study shows that for not too large interstep distances $x_0/\lambda$, the time $t_S$ necessary to attain the steady-state value of the surface supersaturation $\sigma_S$ is approximately equal to 4.6 $t_{eff}$, where $t_{eff}$ is expressed by Eq. (6). This simple estimation demonstrates that the time $t_S$ does not depends on value of bulk supersaturation but it increases with increasing interstep distance $x_0/\lambda$ and with increasing distance from the step edge. It should also be pointed out that the time $t_S$ is directly proportional to the relaxation time $\tau$ for leaving the surface adsorption layer. This means that the time $t_S$, required to attain the steady-state value of $\sigma_S$, is related to the activation free energy $\Delta G$ for desorption, and temperature of the solution [cf. Eq. (2)].

## 5. LIST OF SYMBOLS

| | |
|---|---|
| $\Delta G$ | Activation free energy for desorption. |
| $j_V$ | Net flux of growth units exchanged with the solution bulk. |
| $h$ | Planck's constant. |
| $k_B$ | Boltzmann constant. |
| $n$ | [$\equiv n(x,t)$] Local concentration of growth units at the surface. |
| $n_e$ | Equilibrium concentration of growth units at the surface. |
| $T$ | Temperature. |
| $t$ | Time. |
| $t_{eff}$ | Effective time defined by Eq. (6). |
| $t_S$ | Time required to attain the steady-state value of $\sigma_S$. |
| $t_{S0}$ | Characteristic time, required to attain the steady-state value of the surface supersaturation $\sigma_{S0}$. |
| $x$ | Distance from the step centre. |
| $x_0$ | Interstep distance. |
| $\lambda$ | Mean diffusion distance of the growth unit adsorbed on the surface. |
| $\sigma$ | Relative supersaturation just above the surface and very far from a step, so it is the same as the bulk supersaturation. |
| $\sigma_S$ | [$\equiv \sigma_S(x,t)$] Surface supersaturation expressed by Eq. (5) |
| $\sigma_S^A$ | [$\equiv \sigma_S^A(x,t)$] Surface supersaturation $\sigma_S$ approximated by Eq. (9). |
| $\sigma_{S0}$ | Surface supersaturation $\sigma_S$ at the centre of the step terrace ($x=0$). |
| $\sigma_{S0}^A$ | Surface supersaturation $\sigma_{S0}$ approximated by Eq. (9). |
| $\tau$ | Relaxation time for leaving the surface adsorption layer. |

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