

Estimation of surface supersaturation in Monte Carlo simulations of single crystal growth

M. Rak ^{a,*}, A. Brozi ^a, J. Żmija ^b

^a Institute of Physics, Technical University of Lodz,
ul. Wólczajska 219, 90-924 Łódź, Poland

^b Institute of Applied Physics, Military University of Technology,
ul. Kaliskiego 2, 00-908 Warszawa, Poland

* Corresponding author: E-mail address: mirarak@p.lodz.pl

Received 25.04.2010; published in revised form 01.07.2010

Methodology of research

ABSTRACT

Purpose: The aim of this study is to propose a new calculation method using Monte Carlo simulations making it possible to estimate surface supersaturation and its transient behavior.

Design/methodology/approach: Monte Carlo simulation method is used for investigations of crystal growth from microscopic point of view. It is assumed that the surface supersaturation may be represented by the number of growth units adsorbed on the crystal surface at any given moment.

Findings: The presented method allows us to analyze the surface configuration of a growing crystal face and the mechanism of single crystal growth in various assumed growth conditions (supersaturation, temperature).

Research limitations/implications: The results of the performed simulations show the influence of changes in bulk supersaturation on the behavior of surface supersaturation, which is very difficult to experimentally measure. In this way, some analytical results calculated previously and concerning transient behavior of surface supersaturation can also be verified.

Originality/value: For the first time, Surface Roughening Coefficient (SRC) is defined and the method of its calculation is shown. The SRC coefficient allows us to estimate surface supersaturation determining growth mechanism and, in consequence, determining the quality of grown crystals. The results are useful for control of growth process to obtain good quality single crystals.

Keywords: Analysis and modelling; Computer assistance in the engineering tasks and scientific research; Crystal growth; Material science; Monte Carlo simulation

Reference to this paper should be given in the following way:

M. Rak, A. Brozi, J. Żmija, Estimation of surface supersaturation in Monte Carlo simulations of single crystal growth, Journal of Achievements in Materials and Manufacturing Engineering 41/1-2 (2010) 91-95.

1. Introduction

Surface concentration of growth units and hence, surface supersaturation depending on crystal growth conditions determine crystal growth mechanism and crystal growth rate. Therefore, the quality of obtained single crystals depends on surface supersaturation.

If, during crystal growth, bulk supersaturation is changed, either intentionally or accidentally, then the concentration of growth units on the crystal surface, and hence, surface supersaturation, change with time so as to adjust to new growth conditions. For that reason, the changes in bulk supersaturation during crystal growth process are very harmful for quality of obtained single crystals. In order to decrease the effect of the changes in bulk supersaturation on surface supersaturation, appropriate control systems should be used during growth process.

However, during short duration of the transient state of surface supersaturation, experimental observations in situ would disturb surface processes (surface diffusion, adsorption, desorption) of growth units (e.g. molecules). In consequence, the obtained results of such experiments would be incorrect and not useful to study transient surface supersaturation. Therefore, at present, theoretical research is the only source of information about the transient surface supersaturation which, despite its short duration, may strongly affect morphology and quality of crystals. Results of such investigations are very important and helpful in designing and choice of control systems appropriate for growth process of a given single crystal.

Previously, the transient surface supersaturation caused by an abrupt (stepped) change in value of bulk supersaturation was studied theoretically [1,2] with the use of time dependent model of Burton, Cabrera and Frank (BCF) [1-3].

The aim of this study is to verify the theoretical results [1,2] concerning transient state of surface supersaturation. The verification is performed with the use of computer experiments - the Monte Carlo (MC) simulation of crystal growth. In order to perform such a verification, it is necessary to create a method for estimation of surface supersaturation during the Monte Carlo simulations, and in this study such a method is proposed.

2. Model

Monte Carlo simulations methods are very helpful tool for investigations of crystal growth process of bulk crystals (e.g. Refs [4-10]) as well as crystal thin films (e.g. Refs [11-17]). In the presented study, the used algorithm of the performed Monte Carlo simulations is similar to both the original algorithm proposed by Gilmer and Bennema [4,5] and its modification presented in Ref. [6]. We simulate growth of the (001) face of a simple cubic crystal. A two-dimensional (2D) array represents a crystal surface containing a step. Growth units in the crystal-solution interface are represented by solid tetragonal blocks. Three kinds of elementary events are taken into account: creation, annihilation and surface diffusion. For relative bulk supersaturation β , the frequencies of creation (k_i^+), annihilation (k_i^-) are given by the following formulae [6]:

$$k_i^- = \frac{k_B T}{h} \exp \left[+\alpha \frac{\beta}{4} (2-i) - \frac{\beta}{2} \right] \tag{1}$$

where i and j are the numbers of solid lateral neighbours at a given location as needed to determine probabilities of creations and annihilations respectively, k_B - Boltzmann's constant, h - Planck's constant, T - temperature. The above presented equations fulfil the reversibility principle, which states that in equilibrium ($\beta=0$) and at $i=2$ the probabilities $k_2^- = k_2^+$.

The parameter α describes thermal roughening of the crystal surface and is defined [6,18-20] as:

$$\alpha = \frac{2(\varphi_{ss} + \varphi_{ff}) - 4\varphi_{sf}}{k_B T} \tag{2}$$

where φ_{ss} is the bond energy of a solid-solid nearest neighbour pair, φ_{sf} is the energy of solid-fluid pair, φ_{ff} is the corresponding interaction energy between the average contents of the neighbouring blocks of fluid. It was proved theoretically (e.g. Refs. [3,6,18-20]) and demonstrated experimentally many times (e.g. Refs. [18,20]) that for $\alpha < 3.5$ the growing surface is rough and grows according to continuous model of growth. On the other hand, for $\alpha > 4.0$ and low values of β , the surface becomes flat and grows according to 2D nucleation mechanism or, if there are steps on the surface, it grows according to BCF surface diffusion model (e.g. Refs. [3,6,18-20]).

Surface diffusion is interpreted as two events: annihilation and creation, occurring immediately one after the other, its frequency k_{ij} is given by:

$$k_{ij} = \frac{k_B T}{h} \exp \left[\alpha \left(\frac{j-i}{4} - \beta \right) \right] \tag{3}$$

where i and j are the numbers of solid lateral neighbours in the starting and target positions, respectively, and (X_s/a) is the relative surface diffusion distance (a - lattice constant). The microscopic reversibility principle still holds.

Figure 1 presents the algorithm as applied to a single location on the crystal surface.

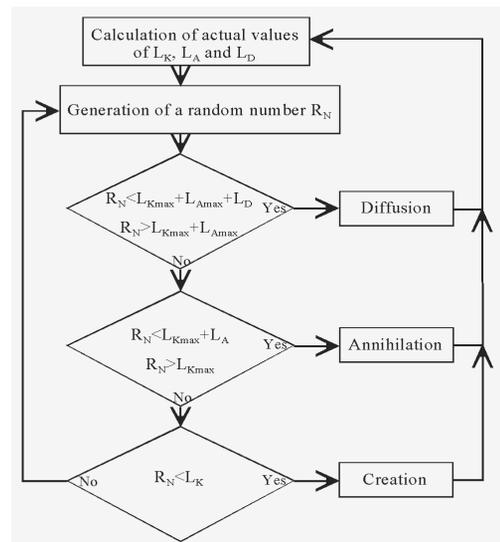


Fig. 1. Flow chart of the Monte Carlo model as applied to a single location on the crystal surface

In the Monte Carlo method, the selection of the event to perform in any given location and the decision whether to perform or abandon the event chosen are realized by comparison of random integral number with some number intervals denoted as L_{Kmax} , L_{Amax} and L_{Dmax} (representing the greatest possible values of creation, annihilation and diffusion frequencies, respectively) and L_K , L_A and L_D (representing the actual frequencies in the chosen location) [4-6].

The periodic boundaries of the array representing crystal surface make the single step equivalent to the train of parallel equidistant steps with interstep distance equal to the length of the side of the array.

Figure 2 presents example of crystal surface containing steps growing at $\alpha = 5.0$, $\beta = 0.03$, and $X_s/a = 1$ for the array dimensions 50×100 . The parameter values used correspond to the growth conditions assumed earlier [1,2] for theoretical analysis of transient surface supersaturation.

The Monte Carlo method presented above does not allow direct calculation of the surface concentration of growth units and hence, surface supersaturation. Therefore we propose a novel method to estimate supersaturation during MC simulations. Such an estimation has never been performed previously. The presented method assumes that in any given moment, the surface supersaturation may be represented by the number of growth units adsorbed on the crystal surface. For this purpose, we define and calculate Surface Roughening Coefficient (SRC) being an average number of vertical walls adjacent to a location. We calculate it as

an average (over whole array representing crystal surface) of the following values calculated for every location:

$$SRC = \sum_{\text{whole array}} \frac{W_{m,n}}{M \times N} \quad (4)$$

where:

and M and N are the array dimensions, m and n are location indices and $w_{m,n}$ is the crystal height at a given location m, n .

Our calculations show that the SRC value is a linear function of bulk supersaturation β for a given interstep distance X_0 (equal to the length of the surface array side). On the other hand, the surface supersaturation σ_s is expressed as (e.g. Refs. [1,2,18,20]):

$$\sigma_s = \frac{n - n_e}{n_e} \quad (5)$$

where:

n and n_e denote local concentration of growth units at the surface and the equilibrium value of n , respectively.

It is known (e.g. Refs. [3-5,18]) that the surface supersaturation σ_s is also a linear function of β for interstep distance X_0 assumed to be independent of β . Therefore, we can study the transient state of SRC instead of the transient state of σ_s caused by an abrupt (stepped) change in bulk supersaturation β and qualitatively compare both results.

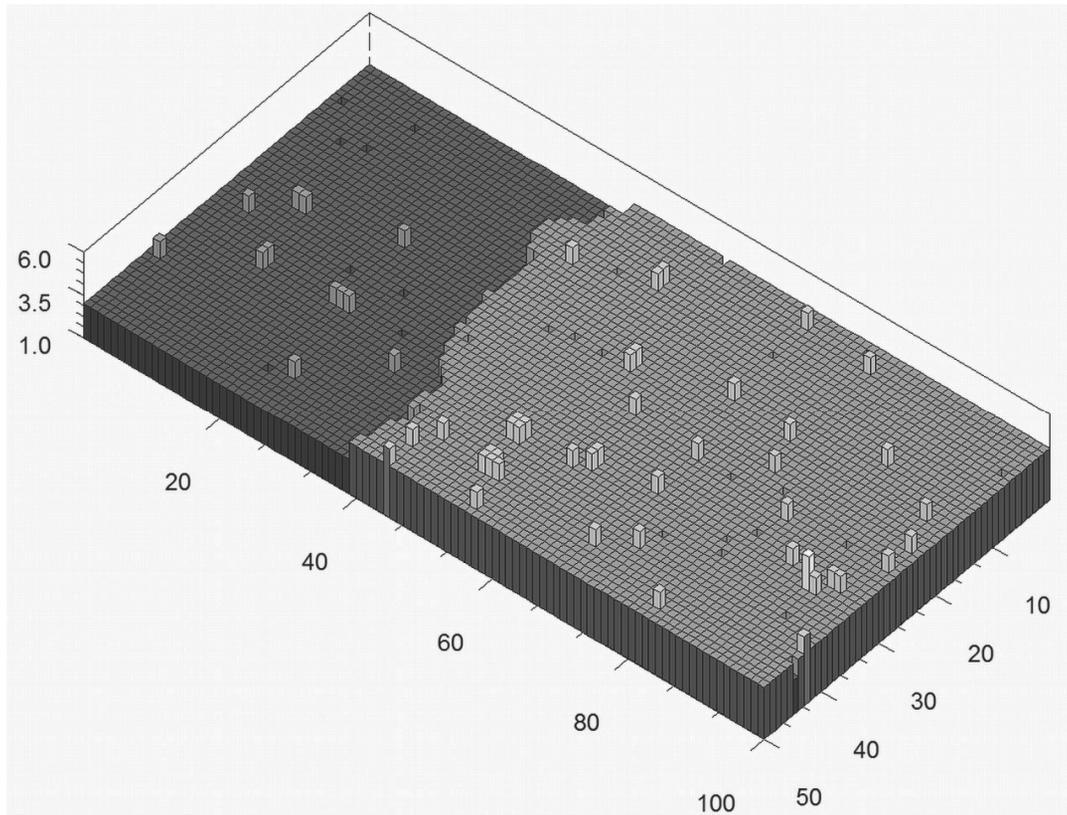


Fig. 2. Example of crystal surface containing steps growing at $\alpha = 5.0$, $\beta = 0.03$, $X_s/a = 1$ for the array dimensions 50×100

An abrupt change in value of bulk supersaturation causes that surface supersaturation σ_s and the coefficient SRC tend to new constant values corresponding to the new value of β . It is obvious that the steady-state values of σ_s and SRC are theoretically attained after infinite time. However, it is possible to find a characteristic time t_s , after which the change in value of σ_s (or SRC) in its time dependence is sufficiently small to be neglected and therefore, the new steady-state value of σ_s (or SRC) is attained. We assume that the steady-state is attained when the slope of the line approximating dependence of SRC on time falls below 10^{-5} . The unit of time t_u is defined as a sum of reciprocals of frequencies of all elementary events. In the case of the abandoned events, the reciprocal of the sum of the least probable possible events (corresponding to probabilities k_0^+ , k_4^- and k_{40}) is used in the summation:

$$t_u = \sum_{\text{creations}} \frac{1}{k_1^+} + \sum_{\text{annihilations}} \frac{1}{k_1^-} + \sum_{\text{diffusions}} \frac{1}{k_{1j}} + \sum_{\text{abandoned}} \frac{1}{k_0^+ + k_4^- + k_{40}} \quad (6)$$

As the length of the time unit t_u varies for each step time, time t

$$t = \sum_{n=1}^{N_t} t_{u,n} \quad (7)$$

should be expressed as . This means that the number of cycles N_t can be treated as a measure of time.

For our investigations of transient behaviour of SRC caused by abrupt (stepped) increase or decrease in value of bulk supersaturation β , the initial value of β denoted as β_0 was assumed and calculations of SCR were performed during growth of several layers. When roughness of the array representing growing crystal surface did not change and hence, SCR reached a constant value corresponding to the assumed growth conditions, the simulations were stopped, new value of β denoted as β_1 was introduced and simulations were continued.

3. Results and conclusions

In order to compare the obtained results of MC simulations with our previous theoretical results [1,2] for transient surface supersaturation, the MC simulations were performed for very low values of β and high values of α to avoid formation of 2D nuclei and hence, a change in the growth mechanism during growth process [6,18-20].

In our study, values of the abrupt change in bulk supersaturation are small enough to preserve the observed growth mechanism. The calculations results confirm that for a given interstep distance X_0 , value of SRC, similarly as σ_s , is proportional to bulk supersaturation β , which means that in MC simulations, SRC can be used for analysis of surface supersaturation behavior. The obtained results of simulations show that the calculated parameter SRC increases after abrupt (stepped) increase in value of β (Figure 3) and decreases when β is reduced (Figure 4).

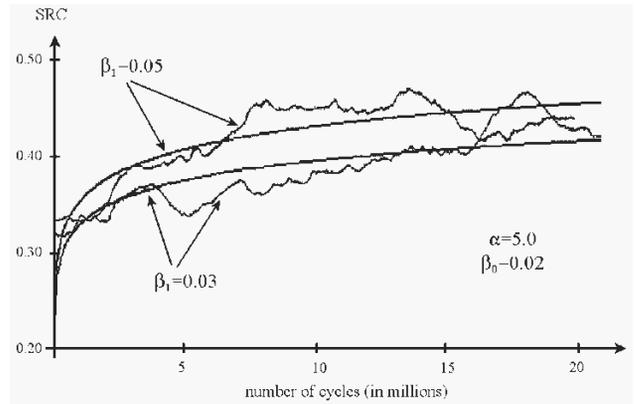


Fig. 3. Coefficient SRC versus number N of cycles after abrupt increase in bulk supersaturation β , at $\alpha = 5.0$, $X_s/a = 1$ and array dimensions 50×100 . At $N = 0$, bulk supersaturation $\beta_0 = 0.02$ is abruptly increased to $\beta_1 = 0.03$ or to $\beta_1 = 0.05$

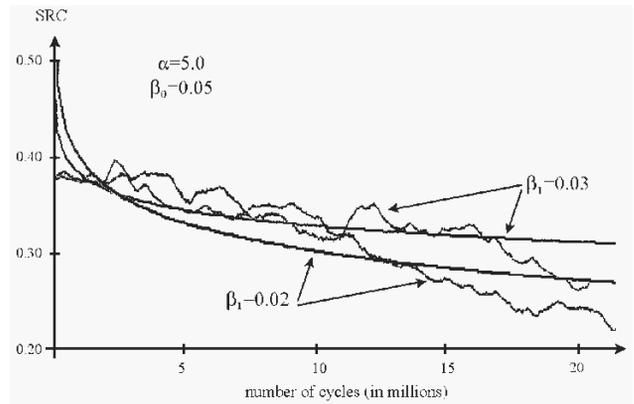


Fig. 4. Coefficient SRC versus number N of cycles after abrupt decrease in bulk supersaturation β , at $\alpha = 5.0$, $X_s/a = 1$ and array dimensions 50×100 . At $N = 0$, bulk supersaturation $\beta_0 = 0.05$ is abruptly decreased to $\beta_1 = 0.03$ or to $\beta_1 = 0.02$

The calculations performed also show that the characteristic time necessary to attain the new steady state value of SRC does not depend on the difference between values β_0 and β_1 (where β_0 and β_1 mean the initial at $t=0^-$ and final at $t=0^+$ values of β , respectively). In other words, the characteristic time does not depend on the value of increment or decrement in β . This is the first confirmation of our previous results [1,2] that the characteristic time t_s necessary to attain the new steady state value of σ_s does not depend on the value of abrupt (stepped) increment or decrement in bulk supersaturation.

We also analysed the simulation results for various interstep distances X_0 (represented in the model by the array side length) equal to 100, 150 and 200 units. It should be noticed that the characteristic time t_s increases with increasing interstep distance X_0 . These results are in accordance with our earlier theoretical analysis [1,2].

The comparison of our earlier results [1,2] for transient behaviour of surface supersaturation with the presented above results obtained for transient behaviour of SRC is qualitative only because quantitative comparison of such MC results with theoretical or experimental ones is impossible. However, to date, the presented above results are the only verification of the earlier results [1,2] for transient supersaturation. Therefore the obtained good qualitative accordance of the results compared is an important result, because it implies that the previous theoretical considerations [1,2] are correct and useful for choice of control systems in practice of single crystal growth.

It should be also pointed out that the presented in this paper definition and calculation method of SRC should be useful for Monte Carlo simulations performed for other investigations of crystal growth (for example, researches devoted to effect of additives on crystal growth process).

References

- [1] M. Rak, Transient Behaviour of Surface Supersaturation Caused by Variation in Bulk Supersaturation, *Surface Science* 442 (1999) 149-160.
- [2] M. Rak, Transient Behaviour of Surface Supersaturation Caused by an Abrupt Change in Bulk Supersaturation, *Surface Science* 494 (2001) 60-74.
- [3] J.P. Van der Eerden, Crystal Growth Mechanisms, *Handbook of Crystal Growth*, 1a. Fundamentals, Editor D.T.J. Hurle, North-Holland, Amsterdam, 1993, 307-476.
- [4] G.H. Gilmer, P. Bennema, Simulation of Crystal Growth with Surface Diffusion, *Journal of Applied Physics* 43 (1972) 1347-1360.
- [5] G.H. Gilmer, P. Bennema, Computer simulation of crystal surface structure and growth kinetics, *Journal of Crystal Growth* 13/14 (1972) 148-153.
- [6] M. Rak, M. Izdebski, A. Brozi, Kinetic Monte Carlo Study of Crystal Growth from Solution, *Computer Physics Communications* 138 (2001) 250-263.
- [7] J.-W. Lee, N.M. Hwang, D.-Y. Kim, Growth morphology of perfect and twinned face-centered-cubic crystals by Monte Carlo simulation, *Journal of Crystal Growth* 250 (2003) 538-545.
- [8] W.J.P. Van Enkevort, J.H. Los, Tailor-made inhibitors in crystal growth: A Monte Carlo simulation study, *Journal of Physical Chemistry C* 112/16 (2008) 6380-6389.
- [9] J. Kundin C. Yürüdü, J. Ulrich and H. Emmerich, A phase-field/Monte-Carlo model describing organic crystal growth from solution, *The European Physical Journal B - Condensed Matter and Complex System* 70 (2009) 403-412.
- [10] Ch. Misbah, O. Pierre-Louis, Y. Saito, Crystal surfaces in and out of equilibrium: A modern view, *Review of Modern Physics* 82 (2010) 981-1040.
- [11] T.P. Schulze and P. Smereka, An Energy Localization Principle and its Application to Fast Kinetic Monte Carlo Simulation of Heteroepitaxial Growth, *Journal of the Mechanics and Physics of Solids* 57 (2009) 521-538.
- [12] M. Saum, T.P. Schulze and C. Ratsch, Inverted List Kinetic Monte Carlo with Rejection Applied to Directed Self-Assembly During Epitaxial Growth, *Communications in Computational Physics* 6 (2009) 553-564.
- [13] M. Saum and T.P. Schulze, The Role of Processing Speed in Determining Step Patterns during Directional Epitaxy, *Discrete and Continuous Dynamical Systems B* 11 (2009) 443-457.
- [14] A. Ali Messaoud1, A. Chikouche, A. Estèv, G. Landa, M. Djafari Rouhani, Atomic Scale Simulation of Thin Film Growth by Kinetic Monte Carlo Method, *International Journal of Recent Trends in Engineering* 2 (2009) 85-88.
- [15] T.P. Schulze, P. Smereka, An Energy Localization Principle and its Application to Fast Kinetic Monte Carlo Simulation of Heteroepitaxial Growth, *Journal of the Mechanics and Physics of Solids* 57 (2009) 521-538.
- [16] M. Saum, T.P. Schulze and C. Ratsch, Inverted List Kinetic Monte Carlo with Rejection Applied to Directed Self-Assembly During Epitaxial Growth, *Communications in Computational Physics* 6 (2009) 553-564.
- [17] M. Saum, T.P. Schulze, The Role of Processing Speed in Determining Step Patterns during Directional Epitaxy, *Discrete and Continuous Dynamical Systems B* 11 (2009) 443-457.
- [18] P. Bennema, G.H. Gilmer, Kinetics of crystal growth, in: *Crystal Growth: An Introduction*, ed. P. Hartman, North-Holland Publishing Company 263-327 (1973).
- [19] P. Bennema, Growth Forms of Crystals, Possible Implications for Powder Technology, *KONA Powder and Particle Journal* 10 (1992) 25-40.
- [20] P. Bennema, Growth and Morphology of Crystals Integration of Theories of Roughening and Hartman-Perdok Theory, *Handbook of Crystal Growth*, 1a. Fundamentals, Editor D.T.J. Hurle, North-Holland, Amsterdam, 1993, 477-581.