HETEROGENEOUS NUCLEATION AND DEPLETION EFFECT IN NANOWIRE GROWTH

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ABSTRACT

Recent experiments of Ross, Kodambaka et al. proved possibility of mononuclear regime with heterogeneous nucleation as well as jerky growth in VLS process for silicon nanowires. In this work, theoretical model is presented which incorporates the effects of (i) mononuclear regime with layer by layer growth, (i) heterogeneous nucleation of each new layer at the edge of Au-Si droplet, (iii) drop of supersaturation after each successful nucleation and respective fast layer growth, (iv) time-dependent nucleation barrier during each new waiting period and (v) correlation between subsequent waiting periods (non-markovian sequence of waiting periods).

Key words: nucleation, nanowires, modeling, thermodynamics, growth, step-flow kinetics

INTRODUCTION

Development of nanotechnologies provides new problems to the theory of phase transformations – nucleation, growth and coarsening in open nanosystems.

Step-flow kinetics is one of the newest experimentally investigated features of nanowire's growth [1-3] by VLS method. Nanowires grow by rapid increasing (few milliseconds) of the nanowire's height by the value of height of one monoatomic layer with great incubation time (several seconds) between these increasing. It is shown for the II-VI or III-V compounds where solubility of one component in the liquid alloy is very low that nucleation statistics is self-regulated and corresponds to sub – Poissonian distribution of waiting times between nucleation events [3]. In contrast, the solubility of Si in Au is very high and one would expect that self-regulation mechanism will not work in such systems. Yet, nature may not meet these expectations (see below).

Growth of sufficiently thin nanowires takes place in the mononuclear regime: for the growth of one atomic layer of the nanowire it is necessary for one nucleus to appear [4]. So, here we will limit ourselves with nanosystems in which the nucleation events proceed one by one and probability of simultaneous nucleation and of coexistence of several nuclei is negligible. Experimental results show that nucleus appears on the edge of the nanowire, on the junction

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of three phases: liquid, solid and vapor [2]. For the Si nanowires grown in atmosphere of low pressure of disilane it is shown that growth rate is diameter independent [5]. In this case, adsorbtion processes on the surface of the liquid droplet make the main contribution to the growth rate.

MODEL

We consider the possibility of stoichometric 2d island nucleation (*Fig.1*) (with concentration $c_i = 1$ for the case of pure Si nanowire growth) from the supersaturated liquid solution with average Si concentration c.

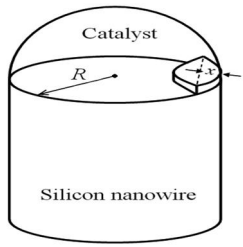

Fig. 1 – Model system for nanowire

For this we calculate the Gibbs free energy of the system $G(x)$ at different fixed number N_{Si} of Si atoms in the droplet with N_{Au} gold atoms (or fixed average concentration $c=N_{Si}/(N_{Au}+N_{Si})$) and look for minimum of this dependence. There x is one parameter that characterizes shape and size of the nuclei.

The shape of the nucleus corresponds to the contour TMPK, which is determined by the mechanical equilibrium (some of forces in x and y directions):

$$\begin{cases} \gamma_{i\alpha}\cos\theta_1 - \gamma_i \sin\theta_2 = 0 \\ \gamma_\alpha + \gamma_{i\alpha}\sin\theta_1 - \gamma_i \cos\theta_2 = 0 \end{cases}. \quad (1)$$

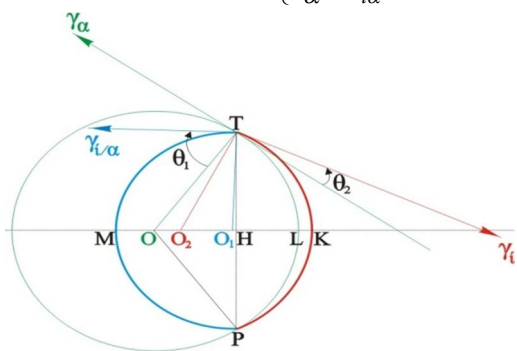

Fig. 2 – Shape of the nucleus and the directions of the surface tensions

There γ_i, γ_α are the surface tensions of silicon (i) and Au-Si liquid phase (α) and $\gamma_{i\alpha}$ is the interfacial tension between silicon and liquid phase.

In the following we will use constant values of interfacial tensions at $T = 823$K: $\gamma_\alpha = 0{,}9$ J.m^{-2} , $\gamma_i = 1{,}08$ J.m^{-2} , and $\gamma_{i\alpha} = 0{,}4$ J.m^{-2}.

RESULTS AND DISCUSSION

We cannot pretend on the prediction of mean waiting time in steady-state regime: evidently, this average time is just an inverse total flux J. Yet, one can suggest other characteristics. Typical time dependence of nucleation probability and of silicon content in gold droplet are presented on *Fig.3*. In particular,

Fig.3b demonstrates that system possesses elements of self organization – the concentration of silicon in the droplet soon "forgets" about its initial value and fluctuates around some steady-state asymptotic value determined by the magnitude of incoming flux: the larger is flux, the higher is average supersaturation.

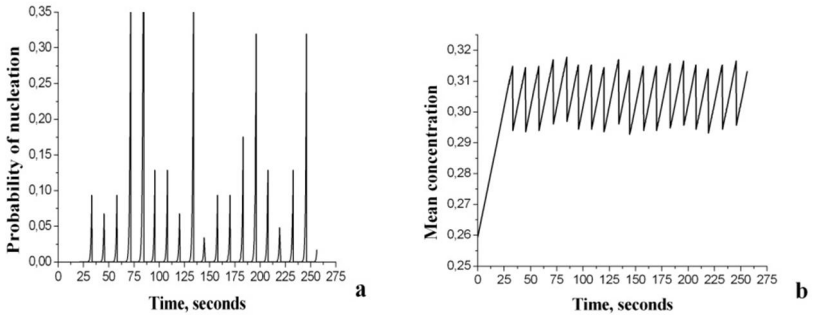

Fig. 3 – Typical nucleation probability dependence on time (a) and typical silicon concentration dependence on time (b) for Si nanowires with $R = 22$ nm grown at $T = 823$ K and disilane pressure $4 \cdot 10^{-7}$ Torr

Dependence of asymptotic average value of composition on incoming flux is described in *Fig.4a*.

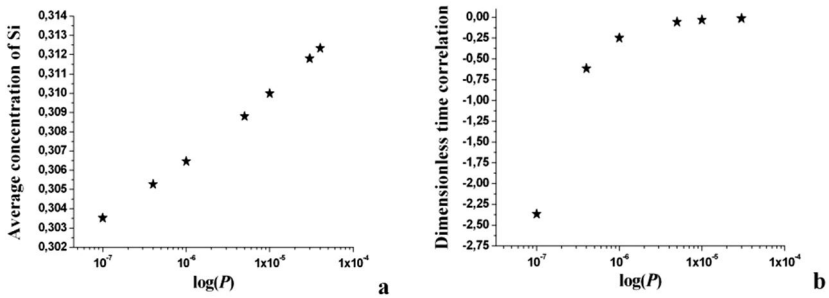

Fig. 4 – Dependence of average concentration (a) and dimensionless time correlation (b) on the logarithm of disilane pressure (in Torr) for Si nanowires with $R = 22$ nm grown at $T = 823$ K.

Distributions for the disilane pressure $P = 4 \cdot 10^{-7}$, $5 \cdot 10^{-6}$ and $3 \cdot 10^{-5}$ Torr are presented on the *Fig.5*. They are rather well fitted by Weibull distribution. Parameters of Weibull distribution function ($y = f(x \mid a,b) = ba^{-b}x^{b-1}e^{-\left(\frac{x}{a}\right)^b} I_{(0,\infty)}(x)$) are estimated. The larger is b, the narrower is distribution.

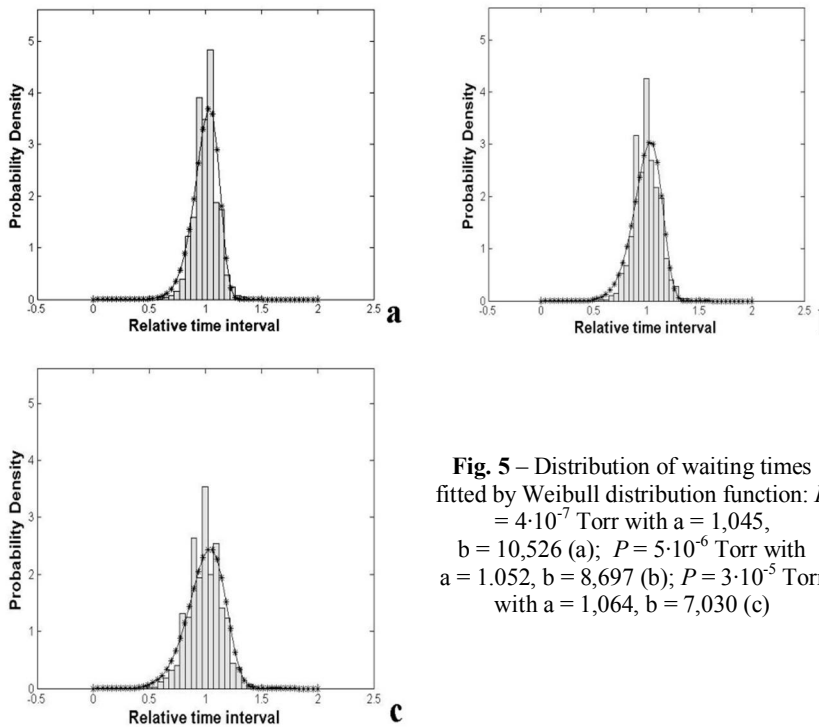

Fig. 5 – Distribution of waiting times fitted by Weibull distribution function: $P = 4 \cdot 10^{-7}$ Torr with a = 1,045, b = 10,526 (a); $P = 5 \cdot 10^{-6}$ Torr with a = 1.052, b = 8,697 (b); $P = 3 \cdot 10^{-5}$ Torr with a = 1,064, b = 7,030 (c)

CONCLUSIONS

1. Possibility of jerky motion is confirmed in the model using assumptions of heterogeneous nucleation, mononuclear mechanism and diameter independent growth rate.

2. Zeldovich nucleation theory (including determination of diffusivity in the size space) is adapted for the case of: a) heterogenous nucleation; b) complex geometry; c) time-dependent driving force.

3. Asymptotic supersaturation of liquid Au with Si increases with increasing incoming flux. Inverse supersaturation is a linear descending function of the flux density logarithm.

4. Standard deviation of reduced waiting times distribution increases with increasing deposition flux. It correlates with time correlation for subsequent monolayers. Stronger time correlation corresponds to narrower waiting time distribution. This result obtained for silicon repeats conclusion of [3] for VLS growth of GaAs nanowhiskers.

5. Waiting time correlation for subsequent events is negative and it increases by absolute value with decreasing incoming flux. Namely, the absolute value of the dimensionless time correlation is approximately inversely proportional to the flux density. Waiting time distribution is well fitted by Weibull plots with standard deviation decreasing with decreasing flux density.

Acknowledgements

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