

Theory of Repeating Nucleation in Point Contact Reactions between Nanowires

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ABSTRACT Modification of the classical Zeldovich nucleation theory for nonstationary conditions is presented. It is applied to the recently discovered repeating nucleation events in point contact reactions between metal and silicon nanowires to form epitaxial silicides; the nucleation provides the reproducible quasi-stationary conditions satisfying the fundamental suppositions of the modified theory. The modified theory enables us to predict the rate of repeating nucleation at nanoscale level by developing a theory of the incubation time. The understanding is extremely important for the design and applications of nanoheterostructures.

KEYWORDS Nanowires, homogeneous nucleation, point contact reactions, classical nucleation theory, nucleation rate, epitaxial growth

Recently the point contact reactions between silicon nanowires (covered by natural oxide) and nanowires or nanodots of metals (nickel, cobalt, platinum) were studied,^{1–3} and the nucleation and growth of epitaxial silicide in nanowire of Si were observed by high resolution transmission electron microscopy, as schematically depicted in Figure 1. These reactions have at least three remarkable features: (1) the product phase is quite different from that in thin film or bulk reactions (for example, in Ni–Si point contact reactions, the silicide phase is NiSi or NiSi₂, depending on the orientation of Si, instead of the Ni₂Si phase in thin film reactions); (2) the product phase is formed not in the point contact zone but instead near the nanowire tip or between two point contacts; and (3) the epitaxial growth of silicide inside the silicon nanowire is a “stop-and-go” process, consisting of a long incubation time of forming the critical disk of each new atomic layer of silicide and followed by a rapid stepwise epitaxial growth of this new layer, as shown in Figure 2.

From practical point of view, such reactions are very promising in providing, among other applications, the possibility of nanoheterostructure and nanogap production. From fundamental point of view, point contact reactions represent a new class of chemical actions between solids, in addition to the standard bulk diffusion couples and layered thin films. Actually, point contact reactions had been considered in binary powder mixtures (at the early stages of sintering),⁴ where authors modeled the diffusional interactions between powders via surface diffusion or/and vapor diffusion with phase formation at both sides of the contact. Contrary to this, in metal–Si nanowire point contact reac-

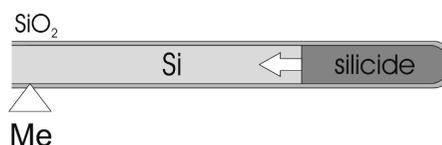


FIGURE 1. Schematic image of point contact reaction between metal and silicon nanowires, covered with thin ($\sim 1\text{--}2$ nm) film of silicon oxide with formation of Me–Si compound. The metal penetrates into the bulk of silicon via broken oxide film at the place of point contact, and the silicide grows from the tip of the nanowire toward the middle of it.

tions all reactant phases proceed inside the silicon nanowire, due to penetration (through the oxide film) of metal atoms into Si and their ensuing diffusion in Si.

The analysis of first two peculiarities is given elsewhere.⁵ Here we concentrate on the stop-and-go mode of reaction, treating it as a repeating nucleation in an open system under incoming flux of metal atoms. We modify Zeldovich classical model of nucleation according to the constraints of time-dependent driving force and try to avoid any arbitrary assumptions. We aim at verifying the validity of classical nucleation theory in nanoscale open systems.

Classical nucleation theory assumes a close system of metastable phase. Typically, an alloy is kept at a high

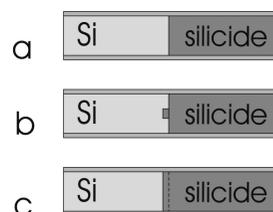


FIGURE 2. Stages of Me–Si reaction. Coherent surface between pure silicon and silicide is formed (a) and some incubation time is required before critical nucleus formation (b). It is supposed to be a disklike cylinder with atomic height and is formed in the middle of interphase surface, that is, homogeneously. After this, the next atomic layer is formed very fast (c) in comparison with incubation time.

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temperature in a single phase region to reach equilibrium, and subsequently annealed at a low temperature in a two-phase region to achieve instability due to supersaturation. Nucleation of a new phase occurs under a given supersaturation. In the early stage of the phase change, a steady state can be assumed, so that supersaturation can be taken constant. In the kinetics of nucleation or composition fluctuation, it is assumed that a continuous spectrum of embryos exists in the metastable phase. There is microreversibility in the size space between neighboring sizes of embryos. When an atom is added to the critical embryo, it becomes stable and its growth to macroscopic size is warranted, so it is removed from the spectrum of embryo distribution. This leads to an abrupt drop in the distribution and it is kinetically unreasonable, so Zeldovitch has introduced a steady state factor to make a smooth transition near the critical state.

In the stop-and-go behavior of epitaxial growth of silicide in nanowire of Si, the “stop” is because of the incubation time needed to nucleate a new disk of silicide on the epitaxial interface between the silicide and the Si. Since the silicide/Si interface is nearly perfect, no heterogeneity was found, so the growth of each new atomic layer of silicide requires the nucleation of a two-dimensional circular disk (Figure 2b) and the incubation time. The “go” is due to the rapid growth of a new epitaxial atomic layer after nucleation (Figure 2c). During the growth it depletes almost all the Ni atoms in the Si (as it follows from our analysis), and so the supersaturation drops. Hence Ni must be replenished and reach the supersaturation level needed for the nucleation of a new silicide layer. Since this is an open system, Ni will be supplied continuously via the point contact from the Ni nanowire which is in contact with the Si nanowire. The driving force of Ni supply into silicon is the difference between the solubilities of Ni in silicon at the point contact and at the Si/silicide interface. During the supply, the supersaturation of Ni in silicon is increasing constantly, making the probability of new 2D disk nucleation higher and higher. We imagine that the supersaturation of Ni in Si has a ratchet-type of time-dependent behavior; the period is the measured average incubation time, since the time of fulfilling the new plane is much less than the first one. The solubility of Ni in the Si increases to reach a high supersaturation for nucleation. After nucleation, the rapid growth of a new layer of silicide will deplete almost all the supersaturated Ni. For this rapid growth, a few thousands of Ni atoms are used up. Since the total number of Ni atoms in the length of several micrometers of silicon nanowire is of the same order, it means a sharp drop of supersaturation after the growth of each new layer. Thus, the supersaturation vanishes and must be rebuilt in the next incubation period. We have a ratchet-type behavior and, in turn, a repeating nucleation. Since the nucleation event proceeds in time-dependent conditions, the standard Zeldovich scheme of steady state should be modified to include the rate of supersaturation increase.

The incubation time includes the time of supersaturation increase to the level sufficient for a reasonable probability of nucleation. In this open system, the incubation period may consist of two parts; the first part is the time needed to build-up the supersaturation and the second part is the time needed for a subcritical embryo to become a stable critical nucleus. Since the supersaturation may increase slowly due to the rate limit of the point contact, the first part is much larger than the second one. The latter is defined as the period of no nucleation, and its distribution will be given later. For comparison, in a close system, the steady state nucleation assumes a constant supersaturation that is a given parameter in the beginning of nucleation, so the incubation time has no build-up of the supersaturation.

In this paper, our major effort is to construct a self-consistent scheme to provide the correct incubation time distribution. Knowing the mean incubation time and the cross-section of the Si nanowire, we obtain the theoretical nucleation rate of the repeating events of nucleation, and it can be checked with the experimentally measured nucleation rate. A very good agreement is shown.

Here we briefly review the main points in Zeldovich kinetic theory of nucleation. A slightly supersaturated system is considered in which compositional fluctuation leads to the formation of clusters of the precipitating phase. The size distribution function of clusters $f(a,t)$ is to be found, where $f(a,t)da$ is the number of clusters in the system with radius between a and $a + da$ per unit volume (if nucleation takes place at an atomic plane, the “volume” changes into “area”). In the original approach,⁶ a macroscopic size of a metastable phase was considered, but in principle it is possible to extrapolate this method onto analyzing an ensemble of nanoparticles undergoing phase transition⁷ with one nucleus per one nanoparticle. The main equation governing the process is⁸

$$\frac{\partial f}{\partial t} = -\frac{\partial s}{\partial a} \quad (1)$$

where s is the flux of clusters in “size space”, which can be expressed as

$$s = -B\frac{\partial f}{\partial a} + Af \quad (2)$$

The first term at the right-hand side of eq 2 represents a stochastic or “diffusive” part of a flux, and the second term is so-called regular or “drift” term. Parameter B plays the role of the “diffusivity of clusters in size space”. Parameter A presents drift velocity.

Thermodynamical equilibrium distribution function has the following form

$$f_0(a) = \text{const.} \exp\left(-\frac{\Delta G(a)}{kT}\right) \quad (3)$$

where $\Delta G(a)$ is the excess of Gibbs free energy of the system due to formation of nucleus with size a .⁹ ΔG has a maximum at some radius a_{cr} , corresponding to a critical nucleus.

The relation between coefficients A and B in eq 2 is found from the condition of zero flux at equilibrium

$$A = -\frac{B}{kT} \frac{\partial[\Delta G(a)]}{\partial a} \quad (4)$$

The value of A can be found from the limiting case at large overcritical nuclei $a \gg a_{cr}$. Detailed consideration¹⁰ gives us $A = (da/dt)_{\text{macro}}$, where $(da/dt)_{\text{macro}}$ is the rate of macroscopic growth of overcritical nuclei, which should be found from phenomenological equations based on deterministic laws (dependent on the model). Then B , as a function of a , can be written as

$$B(a) = -kT \left(\frac{\partial[\Delta G(a)]}{\partial a} \right)^{-1} \left(\frac{da}{dt} \right)_{\text{macro}} \quad (5)$$

Finally, using eq 1 and zero boundary conditions for the ratio $f^{\text{stationary}}(a)/f_0(a)$ at $a = 0$, $a \rightarrow \infty$, respectively,¹⁰ Zeldovich obtained an expression for stationary flux as

$$s_0 = \sqrt{-\frac{1}{\pi kT} \frac{\partial^2(\Delta G)}{\partial a^2} \Big|_{a_{cr}}} \cdot B(a_{cr}) f_0(a_{cr}) \quad (6)$$

This steady state flux is reached after a certain time. The time dependence of the nucleation flux is usually well approximated as

$$s(t) = \exp\left(-\frac{\tau_{\text{lag}}}{t}\right) \cdot s_0$$

where τ_{lag} is time lag of nucleation, which is approximately just a time of reaching the critical size by random walk in the size space. If the nucleation barrier is high enough, then τ_{crit} should be significantly less than the incubation time τ_{inc} , since the nucleation barrier makes most of attempting clusters be unsuccessful, so the τ_{inc} will be long.

The eq 6 is the main subject of our theoretical considerations in this work. We will find its explicit form for the nucleation of 2D islands at the interface of epitaxial silicide in the Si nanowire. This nucleation flux, eq 6, gives us a frequency (per unit area in our case) of the formation of such nucleus, which has overcome the critical size and grown

further, transforming into a macroscopic particle of the new phase. Therefore, the absolute rate of nucleation of viable nuclei, such nuclei which will not dissolve and have overcome thermodynamic barrier, will be s_0 multiplied by the total volume (area of surface) of the system.

To predict the distribution and the mean incubation time, τ_{inc} , which can be compared with experimental data, the rate of formation of overcritical nuclei should be found and will be given below. For the determinacy, we will use all the data for Ni–Si system in our further analysis, but the main qualitative features, of course, remain valid in general cases.

Compared to the classical nucleation theory, describing a continuous process of phase transition under constant external conditions (unchanged during steady state), in case of repeating nucleation in nanowire we have a significantly more complicated conditions owing to the self-regulated external flux of solute metal atoms into a silicon nanowire through the point contact. The nucleation and lateral growth of each new atomic layer of epitaxial silicide will deplete the Ni atoms in the Si nanowire, causing the change of nucleation conditions (supersaturation) and requiring the replenishment of additional flux for the next cycle of nucleation and growth. The problem becomes nonstationary. It is clear that the initial condition (and boundary condition at the point contact) must be specified for the rigorous solution of this problem. Unfortunately, they cannot be determined precisely because of unknown point contact area. Therefore, we should make a certain approximations that will enable us to build a solvable set of equations. For this we need to determine, first of all, the hierarchy of characteristic times. We will consider the following set of characteristic times:

τ_{inc} , the incubation time for nucleation of 2D island at the ideally flat silicide/Si interface;

τ_{plane} , time of lateral growth of 2D island until construction of new full lattice plane;

τ_{diff} , time of diffusive homogenization, or simply diffusion time (the time of equalization of metal concentration along the wire);

τ_{crit} , time of reaching the critical size by random walk in the size space; and

τ_{satur} , time of saturation of silicon with metal in each cycle of repeating nucleation.

First, the times τ_{inc} and τ_{plane} are known directly from the experiment.^{1–3} By order of magnitude they are about $\tau_{\text{inc}} \sim 10^{0-1}$ s and $\tau_{\text{plane}} \sim 10^{-(1-2)}$ s, so we can set up the inequality as $\tau_{\text{inc}} \gg \tau_{\text{plane}}$. Then we estimate the diffusion time. Since we assume that penetration of metal takes place only near the point contact, the diffusion process is determined by the bulk diffusivity. For interstitial diffusion of nickel in silicon, the diffusivity has been given as¹¹

$$D_{\text{Ni}} = 6.3 \times 10^{-8} \exp\left(\frac{-0.76eV}{kT}\right) \left(\frac{\text{m}^2}{\text{s}}\right) \quad (7)$$

For the typical experimental temperature¹⁻³ of about 1000 K, it gives $D_{\text{Ni}} \cong 9.387 \times 10^{-12} [\text{m}^2/\text{s}] \sim 10^{-11} [\text{m}^2/\text{s}]$. We estimate the diffusion time as $\tau_{\text{diff}} \sim l^2/D_{\text{Ni}}$, where l is the characteristic diffusion length, which is about a micrometer along the nanowire, $l \sim 10^{-6}$ m. Then we have $\tau_{\text{diff}} \sim 10^{-1}$ s, which is close to the τ_{plane} by order of magnitude, so $\tau_{\text{inc}} \gg \tau_{\text{diff}} \sim \tau_{\text{plane}}$.

Now we consider the relation between τ_{plane} and τ_{crit} . As it will be calculated below, a critical cluster in the epitaxial silicide growth contains only several atoms. So, if we assume microreversibility at nucleation scale,¹² τ_{crit} amounts to a negligible part of the time of building the whole of one silicide plane, containing several thousands of atoms. Thus, we can write $\tau_{\text{diff}} \sim \tau_{\text{plane}} \gg \tau_{\text{crit}}$ (actually, we will use only strong inequality in further theoretical treatments, $\tau_{\text{diff}} \gg \tau_{\text{crit}}$, but the relations of $\tau_{\text{plane}} \gg \tau_{\text{crit}}$ and $\tau_{\text{diff}} \sim \tau_{\text{plane}}$ help us realize the inequality).

The last characteristic time to be estimated is τ_{sat} . This time includes not only the diffusion of Ni inside nanowire but also the time to penetrate the point contact area barrier. We will see later that overcoming of a barrier takes more time than diffusion, so that $\tau_{\text{sat}} \gg \tau_{\text{diff}}$. We have an even stronger inequality of $\tau_{\text{sat}} \gg \tau_{\text{inc}}$.

So, the full hierarchy of characteristic times looks like this

$$\tau_{\text{sat}} \gg \tau_{\text{inc}} \gg \tau_{\text{diff}} \sim \tau_{\text{plane}} \gg \tau_{\text{crit}} \quad (8)$$

Now we consider the conditions at which nucleation of each new silicide plane takes place. We are interested in calculation of nucleation probability of a viable nucleus per unit time (or the frequency) ν , which is variable in time. By taking into account the inequality of $\tau_{\text{inc}} \gg \tau_{\text{diff}}$ in the chain in eq 8, we may conclude that during the period of expectation for a new overcritical cluster, the distribution of nickel atoms in the silicide can be assumed almost homogeneous (uniform) but varying with time. Indeed, as it was pointed out at the end of the previous section

$$\nu = s(t)\pi R^2 = \exp(-\tau_{\text{crit}}/t)s_0\pi R^2$$

Since incubation time is much larger than the τ_{crit} , we can safely use the steady-state approximation

$$\nu = s_0\pi R^2 \quad (9)$$

where R is a radius of the nanowire. According to eq 6, the steady state flux in space of sizes s_0 is the function of only the critical radius, which, at uniform quasi-stationary conditions, is the function of supersaturation of Ni solution in Si.

Since the last one is a function of time, the function $\nu(t)$, in principle, can be built.

In such a case, the distribution of incubation times for overcritical clusters nucleation has a following form (see Supporting Information Appendix A)

$$\rho(t) = \nu(t)e^{-\int_0^t \nu(t)dt} \quad (10)$$

that gives us the mean incubation time as follows (see ibidem):

$$\tau_{\text{inc}} = \int_0^\infty t\nu(t)e^{-\int_0^t \nu(t)dt} dt \quad (11)$$

In order to find the time distribution (eq 10), and then calculate the incubation time (eq 11), we should build Gibbs free energy excess ΔG as a function of nucleus' radius as to find a critical radius a_{cr} , and substitute it into the eq 6. We will assume a nucleus of new atomic plane to be a disk of atomic height h and radius a , which is formed in the middle of smooth silicon-silicide boundary. It can be easily shown (see Supporting Information Appendix B) that

$$\Delta G = \pi\gamma h \left(\frac{2a - a^2}{a_{\text{cr}}} \right) \quad (12)$$

where γ is an interfacial free energy between Si and NiSi. The critical radius is determined by the condition $\partial(\Delta G)/\partial a = 0$ and can be expressed as

$$a_{\text{cr}} = -\frac{\Omega}{RT} \cdot \frac{\gamma}{\Delta\bar{g}} \quad (13)$$

Here Ω is atomic volume, which we assume to be almost the same in the silicide and the silicon, at that in the silicon phase it is attributed to the couple of Ni and Si atoms

$$\Delta\bar{g} \approx g_0 - \frac{\partial g}{\partial x} x_0 \quad (14)$$

where g_0 and $g(x)$ are the Gibbs free energy per mole for NiSi phase (at stoichiometry) and Ni solution in Si (as a function of Ni molar fraction x), correspondingly, in units of RT , $x_0 = 1/2$ is a stoichiometric molar fraction of Ni in NiSi phase.

Using the model of regular solution (at small molar fractions)

$$\frac{g(x)}{RT} = \varepsilon x + (x \ln x + (1 - x) \ln(1 - x)) \quad (15)$$

with taking into account thermodynamic data^{13,14} (see Supporting Information Appendix C) we can estimate solubility of Ni in Si x^{\max} (for direct contact without present silicide), molar fraction x^e of Ni in Si at the equilibrium with NiSi, g_0 and parameter ε in eq 15, which are as follows: $x^{\max} \sim 10^{-2}$, $x^e \sim 10^{-6}$, $g_0 \approx (-43000 \text{ J/mol})/(R \cdot 1000 \text{ K}) \cong -5.17$, $\varepsilon \approx 2.96$ (found by fitting x^e).

In such a way one can calculate ΔG by using eq 12 at each $x^e < x < x^{\max}$ by substituting eqs 13 and 14, taking into account eq 15, which gives us in explicit form

$$\frac{\partial g(x)/RT}{\partial x} = \varepsilon + \ln \frac{x}{1 - x} \quad (16)$$

For the description of penetration of Ni-atoms into the bulk of Si-nanowire let us make at first some qualitative assumptions about the character of diffusion contact between Ni and Si. Taking into account the presence of oxide films on both wires, we exclude free transport of the components via the surface. At that, the only place of possible atoms' penetration is the "point" of mechanic contact of Ni- and Si-nanowires, where some kind of a gap in oxide is supposed. This defect place is, at the same time, both the gate for the diffusing Ni-atoms and the barrier on their way to the bulk of silicon. Saturated solution of nickel in silicon (at the absence of silicides) has the concentration x^{\max} . We will assume (as commonly accepted for interface kinetics), that the total atoms' flux I through the contact (number of Ni-atoms penetrating into the Si nanowire per time unit) is proportional to the deviation of local concentration of nickel at the contact zone (at Si side) from that equilibrium value, $I \sim (x^{\max} - x^{\text{contact}})$. Taking into account the mentioned assumption about practically uniform redistribution of nickel interstitials at each time moment, $x \approx x^{\text{contact}}$ (see section about time hierarchy), one gets the following equation for saturation rate

$$\frac{\partial x}{\partial t} = K(x^{\max} - x) \quad (17)$$

where kinetic coefficient K is a characteristic of the barrier height at the contact. This value is a major adjusting parameter of our model. The solution of eq 17 is trivial

$$x(t) = x^{\max} + (x_0 - x^{\max}) \exp(-Kt) \quad (18)$$

where x_0 is the mole fraction of Ni in silicon wire at some moment $t = 0$, just after formation of a new whole atomic

layer of silicide. Actually, x_0 for each new step of stop-and-go growth is determined by the waiting time at the previous step; the longer is this waiting time, the more metal atoms will come (the larger will be supersaturation just before new layer formation, the larger amount of extra atoms will remain after layer filling) so, the larger will be x_0 . In this paper, we will neglect the time correlation between subsequent steps and will treat x_0 as some average value, common for all steps. This average value is unknown, and it will be our main fitting parameter.

To calculate the absolute nucleation rate ν (probability per unit time, or just frequency), as it is determined by eq 9, we should implement a series of substitutions, bringing together the set of eqs 7, 3, 6, 14, and 15, taking into account an explicit form of ΔG (eq 12). Notice, that time dependence of ν includes account of changing supersaturation (according to eq 18) via dependence of critical radius a_{cr} on nickel fraction x , changing with time. The only elements undetermined yet are the expressions for macroscopic velocity $(da)/dt$ _{macro} in eq 6 and a pre-exponential factor "const" in eq 3. The last one can be qualitatively estimated as¹⁰ $\text{const} \sim a_{\text{cr}}/(s_{\text{at}})^2$, where $s_{\text{at}} \sim \Omega^{2/3} \sim h^2$ is interface surface per atom. In Supporting Information Appendix D the derivation of macroscopic growth rate near the critical value is given. With accuracy within the factor of the order of unity one has

$$\frac{da}{dt} a_{\text{cr}} \cong \frac{D(\pi R^2)^2 (x^e)^2 \Omega^2 \gamma^2}{(2\pi)^2 h^2 (kT)^2 a_{\text{cr}}^6} (a - a_{\text{cr}}) \quad (19)$$

Finally, let us summarize our results

$$\tau_{\text{inc}} = \int_0^\infty \nu(t) e^{-\int_0^t \nu(t) dt} dt \quad (11)$$

$$\rho(t) = \nu(t) e^{-\int_0^t \nu(t) dt} \quad (10)$$

$$\nu(t) = \pi R^2 s_0 (a_{\text{cr}}(x(t))) \quad (20)$$

(taking into account eq 9)

$$s_0 = \sqrt{\frac{\gamma h}{a_{\text{cr}} kT}} B(a_{\text{cr}}) f_0(a_{\text{cr}}) \quad (21)$$

(taking into account eqs 6 and 12)

TABLE 1. Full Set of Parameters, Used in Calculations, Which Are Not Fitted

caption	notation (equation, containing indicated parameter)	value [dimension]	origin/substantiation
temperature	T	1000 [K]	experimental conditions ¹⁻³ (see text)
diffusivity of Ni interstitials in Si at the given temperature	D	10^{-11} [m ² /s]	see text ¹¹
thermodynamic stimulus of NiSi-phase formation from pure Ni and Si per mole divided by RT	g_0 (14)	-5.17	see text ¹⁴
Ni mole fraction in Si at the equilibrium with NiSi-phase	x_e	1.67×10^{-6}	by order of magnitude ¹³
	ε (15)	2.69	estimated from data on equilibrium solubility x_e
volume per Si atom (assumed to be the same both for pure silicon and NiSi-phase)	Ω	2×10^{-29} [m ⁻³]	estimation
height of NiSi atomic plane	h	$3\sqrt{\Omega}$	estimation
radius of nanowire	R	10^{-8} [m]	as prepared ¹⁻³ (by order of magnitude)
length of nanowire from the point contact to silicide surface	L	10^{-6} [m]	as prepared ¹⁻³ (by order of magnitude)

$$f_0(a) \cong \frac{a_{cr}}{(s_{at})^2} \exp\left(-\frac{\pi\gamma ha_{cr}}{kT}\right) \quad (22)$$

(taking into account eqs 3, 4, and 12)

$$B(a_{cr}) \cong \frac{D(\pi R^2)^2 (x_e^e)^2 \Omega^2 \gamma}{(2\pi h)^3 k T a_{cr}^5} \quad (23)$$

(taking into account eqs 6 and 12).

We will use the equations listed above to plot the waiting time distribution (eq 10) and calculate the incubation time (eq 11) in order to compare our theoretical results with experimental data. As it was mentioned earlier, we chose Ni-Si system for our treatments. Let us specify all the parameters, necessary for the numerical calculation. The summary of all the initial quantities, which are considered as fixed values, is given in Table 1.

To start with, let us consider the experimental distribution of waiting times; see Figure 3. We used two types of distribution to fit the experimental data: log-normal and Weibull distributions which can be expressed correspondingly in a following way¹⁵

$$\rho_{L-N}(t) = \frac{1}{\sqrt{2\pi\sigma t}} \exp\left[-\frac{(\ln t - \mu)}{2\sigma^2}\right] \quad (24)$$

$$\rho_W(t) = \frac{\chi}{\lambda} \left(\frac{t}{\lambda}\right)^{\chi-1} \exp\left[-\left(\frac{t}{\lambda}\right)^\chi\right] \quad (25)$$

As it may be seen from Figure 3, log-normal is better fit for data points, instead, the better fit of theoretical curve is given by Weibull distribution. The mean experimental waiting time, that is, incubation time, is $\tau_{inc} \approx 2.86$ [s].

To plot a theoretical curve, we should also specify Si/NiSi interfacial free energy γ , the unknown kinetic parameter K (eqs 18 and 19) and initial Ni mole fraction x_0 . Although γ for the considered system is known ($\gamma \cong 0.8$ [J/m²]³), it should be noted, that in our case we have atomic height band (sidewall) between silicon and silicide island, so that effective interfacial free energy can be changed. Anyway, we will assume it not to be very different from this tabular value; we tried $\gamma = (0.60-0.80)$ [J/m²]. For each set of parameters we found a value of x_0 from the condition of self-reproducing regime; the total number of Ni atoms penetrating into the bulk of silicon during mean waiting time should be equal to the number of Ni atoms in the newly built silicide plane, see Figure 6. The parameter K was fitted at each γ to provide experimental value of incubation time (Figure 5).

In Figure 4, several theoretical time distributions are shown at different γ with corresponding values of K and x_0 , found as just described. It is well seen that the shape of distribution (the shape parameter χ in Weibull distribution) is strongly dependent on the value of γ and the best fitting

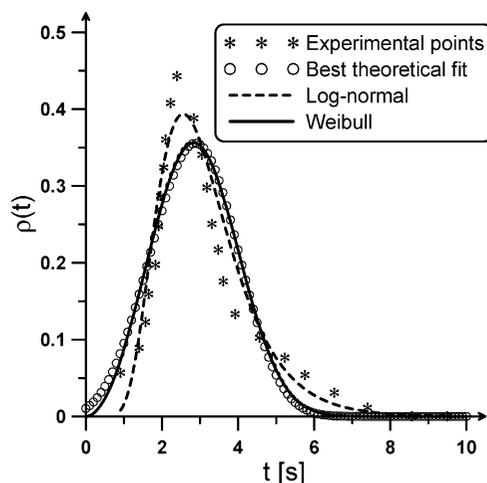


FIGURE 3. Distribution of waiting times for planes formation (critical nuclei forming), obtained both experimentally (stars) and theoretically (circles) and fitting with log-normal (dashed line) and Weibull (solid line) distributions; see text.

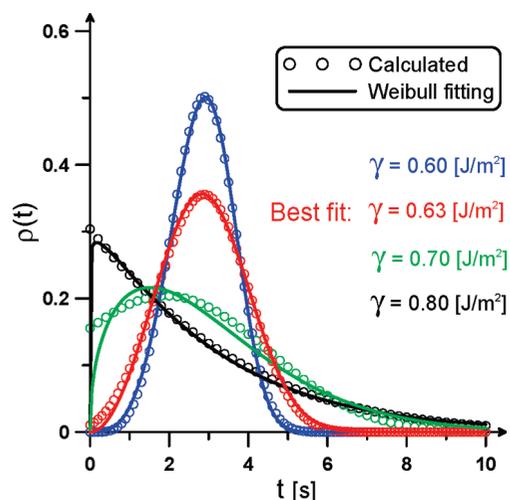


FIGURE 4. Several distributions of waiting times, which give the same mean incubation time, obtained theoretically (circled point) at different Si/silicide interfacial free energy. Solid lines are the corresponding Weibull fitting. The best fit satisfies experimental distribution, shown in Figure 3.

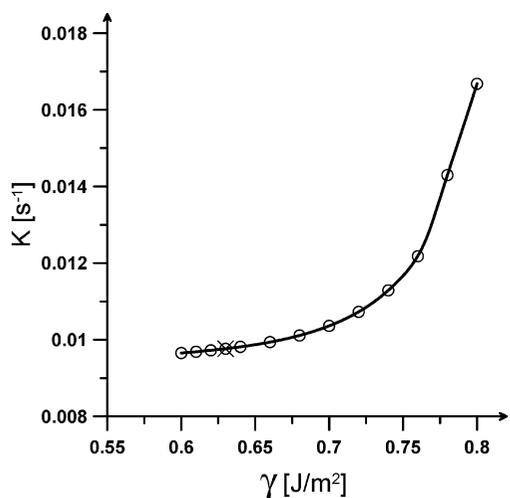


FIGURE 5. K - γ diagram (K is the rate constant of penetration into Metal via the point contact (see eq 17), and γ is Si/silicide interfacial free energy), reflecting the line providing the same value of mean incubation time, obtained in experiment. The upper left region of the diagram corresponds to lower incubation times; the lower right region corresponds to higher ones. The crossed point corresponds to the parameters providing the best experimental fit of incubation time distribution (Figure 3).

is provided with $\gamma \cong 0.63$ [J/m²]. It was also found that variation of K has slight influence on the shape of distribution, but significantly changes the incubation time. The line of constant incubation time (coinciding with experimental value) is plotted at K - γ diagram (Figure 5). The upper left region in this diagram corresponds to the less incubation times and the lower right region corresponds to the larger ones. Indeed, K is inversely proportional to the time of saturation, so the larger is γ , the larger is critical nucleus (at the same supersaturation); consequently, the larger saturation rate is needed for the same incubation.

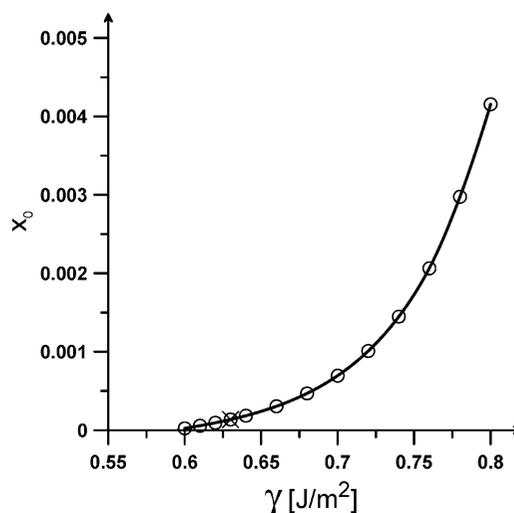


FIGURE 6. Dependence of “initial” (just after fulfilling the silicide’s new atomic plane - see Figure 2c) mole fraction of Ni solution in silicon, providing self-consistent repeating regime of “stop-and-go” silicide growth, on Si/silicide interfacial free energy. K - γ constraint (see Figure 5) is provided. The crossed point corresponds to the parameters providing the best experimental fit of incubation time distribution (Figure 3).

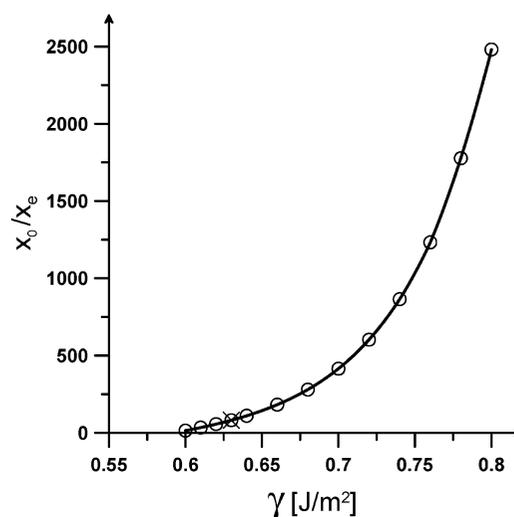


FIGURE 7. Dependence of relative “initial” mole fraction of Ni solution in silicon (see Figure 6) over its equilibrium value corresponding to pure silicon on Si/silicide interfacial free energy. K - γ constraint (see Figure 5) is provided. The crossed point corresponds to the parameters providing the best experimental fit of incubation time distribution (Figure 3).

The dependence of “initial” Ni mole fraction x_0 (at the beginning of the repeating cycles of nucleation) in absolute values and in units of supersaturation rate is shown in Figures 6 and 7, respectively. It is clear that at larger γ (large “surface energy”) high supersaturation should be achieved (larger “bulk” thermodynamic stimulus) to provide the same incubation time (note, that the maximal mole fraction $x^{\max} = 0.01$, the Ni solubility in pure Si prior to silicide formation, is still significantly higher in all the regimes). In Figure 8, the average ratio of the mole fraction at the end of incubation period to the initial one is shown. The larger ratio at smaller

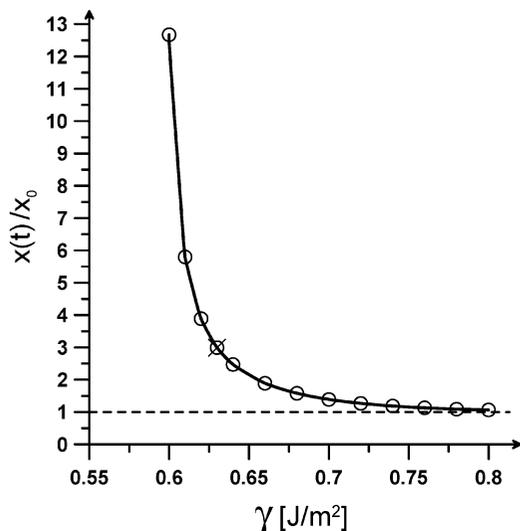


FIGURE 8. Dependence of the “final” mole fraction (just before formation of silicide’s new atomic plane) of Ni solution in silicon over its “initial” value, providing self-consistent repeating regime of “stop-and-go” silicide growth, on Si/silicide interfacial free energy. This ratio, obviously, reflects the increase of supersaturation achieved during incubation time. K - γ constraint (see Figure 5) is provided. The crossed point corresponds to the parameters providing the best experimental fit of incubation time distribution (Figure 3).

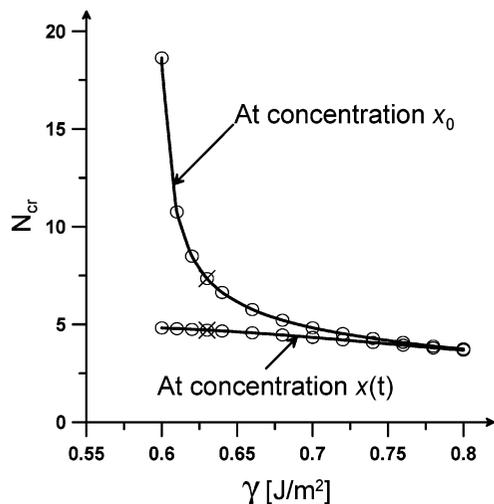


FIGURE 9. The number of atoms in critical nucleus at the “initial” and “final” mole fractions of Ni solution in silicon, connected by the condition of self-consistent repeating regime of “stop-and-go” silicide growth, on Si/silicide interfacial free energy. K - γ constraint (see Figure 5) is provided. The crossed points correspond to the parameters providing the best experimental fit of incubation time distribution (Figure 3).

γ can be explained by the small x_0 (compare with Figures 6 and 7). It correlates with the sizes of critical nuclei at the beginning and at the end of a nucleation cycle; see Figure

9. It is clearly seen that the critical size at the end of incubation period is almost the same for all γ (at all the regimes) and amounts to about four structural units of silicide (eight atoms in total). Conversely, the initial critical sizes vary in a broad range, which explains the shapes of curves in Figures 6–8.

In conclusion, the direct verification of classical Zeldovich nucleation theory is made. The model takes into account the depletion of nickel solution in silicon after each silicide layer filling. Distribution of waiting times in the stop-and-go silicide growth inside silicon nanowire satisfactorily fits experimental data at the minimal number of “hidden” parameters.

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Supporting Information Available. Modified Poisson distribution and mean waiting time, derivation of ΔG , estimation of thermodynamic parameters of the system, and derivation of the expression for macroscopic growth rate of an island of a new silicide plane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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