

# Supporting Information

## Theory of repeating nucleation in point contact reactions between nanowires

*Andriy O. Kovalchuk<sup>1\*</sup>, Andriy M. Gusak<sup>1</sup>, and King N. Tu<sup>2</sup>*

<sup>1</sup> Department of Theoretical Physics, Cherkasy National University, Cherkasy, Ukraine

<sup>2</sup> Department of Materials Science and Engineering, UCLA, Los Angeles, CA 90095,  
USA

## Appendix A

### Modified Poisson distribution and mean waiting time

If probability of nucleation  $dp_{dt}$  per short time interval  $dt$  is proportional to the interval:  $dp_{dt} = \nu \cdot dt$ , – this leads, as is well-known, to Poisson distribution, i.e. density of probability for nucleation time is given by the expression

$$\rho_\nu(t) = \nu \cdot e^{-\nu t}, \quad (\text{A01})$$

where  $\nu$  is a constant, having the meaning of nucleation probability per unit time or the frequency of nucleation. At that,  $e^{-\nu t}$  is the probability that during time  $t$  the nucleus hasn't appeared. If the frequency  $\nu$  depends on time, i.e.  $\nu = \nu(t)$ , the equation (A01) is no longer correct since we cannot simply substitute  $\nu$  by the corresponding time function in it. However, it is easy to find the correct distribution for such a more complicated case as well. Indeed, let's divide the time interval  $t$  into small  $\Delta t_i$  ones, during which the frequency  $\nu_i$  can be considered almost constant. Then, probability of “non-nucleation” during time  $t$  is equal, obviously, to the product of “non-nucleation” probabilities over all intervals entering it, i.e.  $\prod_i 1 - \nu_i \Delta t_i \cong \prod_i e^{-\nu_i \Delta t_i}$  which gives  $e^{-\sum_i \nu_i \Delta t_i}$ , and in the limit of  $\Delta t_i \rightarrow 0$ , apparently,  $e^{-\int_0^t \nu(t) dt}$ . Then, generalized density of probability becomes:

$$\rho(t) = \nu(t) \cdot e^{-\int_0^t \nu(t) dt}. \quad (\text{A02})$$

The incubation period is found from the common expression for mathematical expectation of nucleation time:

$$\tau_{inc} = \int_0^{\infty} t \cdot v(t) \cdot e^{-\int_0^t v(t) dt} dt. \quad (A03)$$

## Appendix B

### Derivation of $\Delta G$

Let us derive an expression for the total Gibbs free energy excess  $\Delta G$  of the quasi-infinite system, caused by appearance of the cylindric disk-like cluster of silicide with radius  $a$  and height  $h$  at the Si/silicide interface. It consists of two terms: the surface one,  $E^s$ , arising due to increasing total interphase surface (side face of a cylinder), and the bulk one, which includes the change of Gibbs energy inside the cylinder due to phase transformation inside it, and also the change of Gibbs energy in the whole volume of nickel solution due to its depletion caused by cluster formation. In spite of the fact that depletion is negligibly small, the last contribution does not vanish on account of infinitely large volume in which depletion takes place. Taking everything mentioned above into account, one can write:

$$\Delta G = E^s + N \cdot RT \cdot g_0 - N_0 \cdot RT \cdot g(x) + (N_0 - N) \cdot RT \cdot g(x'), \quad (B01)$$

where  $N_0$  is the total number of atoms in the system,  $N$  is the number of nickel atoms in the cluster,  $g_0$  and  $g(x)$  are Gibbs free energy per mole (with respect to nickel) for

stoichiometric silicide and for Ni solution in Si (as a function of Ni molar fraction  $x$ ) in units of  $RT$ , respectively,  $x$  is the initial mole fraction of nickel in solution and  $x'$  is that after disc formation (taking depletion into account). The latter value one can be found from the conservation law:  $N_0x = (N_0 - N)x' + Nx_0$ . Taking into account  $N \ll N_0$ , one obtains:

$$x' \cong x - \frac{N}{N_0} x_0. \quad (\text{B02})$$

Expanding  $g$  into the power series to the first order and substituting (B02), one can write:

$$g(x') \cong g(x) - \frac{\partial g}{\partial x} \frac{N}{N_0} x_0. \quad (\text{B03})$$

Substitution of (B03) into (B01) gives:

$$\Delta G = E^s + N \cdot RT \cdot \left( g_0 - g(x) - \frac{\partial g}{\partial x} x_0 \right). \quad (\text{B04})$$

Choosing the reference point of  $g$  at  $g(x=0)$  and taking supersaturation to be small (that is the case), one can use the value (14)  $\Delta \tilde{g} \approx g_0 - \frac{\partial g}{\partial x} \cdot x_0$  instead of the brackets in (B04), which yields:

$$\Delta G = E^s + N \cdot RT \cdot \Delta \tilde{g}. \quad (\text{B05})$$

Let us now assume the atomic volumes  $\Omega$ , referred to Ni atoms, to be the same in the solution and in the silicide, then  $N = \frac{\pi a^2 h}{\Omega}$ . And, finally, taking into account

$E^s = 2\pi ah \cdot \gamma$  (side face of a cylinder multiplied by interfacial free energy),

substitution into (B06) gives us:

$$\Delta G = 2\pi ah \cdot \gamma + \frac{\pi a^2 h}{\Omega} \cdot RT \cdot \Delta \tilde{g}. \quad (\text{B06})$$

Now, using the condition  $\frac{\partial(\Delta G)}{\partial a} = 0$  for critical radius  $a_{cr}$ , one can easily obtain:

$$a_{cr} = -\frac{\Omega}{RT} \cdot \frac{\gamma}{\Delta \tilde{g}}, \quad (\text{B07})$$

which coincides with (13). Inserting this expression into (B06) gives us (E13):

$$\Delta G = \pi \gamma h \left( a - a^2 / a_{cr} \right). \quad (\text{B08})$$

## Appendix C

### Estimation of thermodynamic parameters of the system

The data on solubility of Ni in Si for high temperatures in equilibrium with NiSi<sub>2</sub>-phase can be taken from the literature<sup>13</sup>. This phase is thermodynamically stable at high temperatures. Depending on temperature, the solubility varies from 10<sup>-6</sup> to 10<sup>-5</sup> in molar fraction. It is easy to estimate the solubility of Ni in Si in “meta-quasi-equilibrium” with NiSi and with Ni. For diluted solution of Ni in Si we can write dependence of Gibbs potential per mole as a function of molar fraction as follows:

$$g^m(x) = h \cdot x + RT \cdot \left[ -\ln x + (1-x) \ln(1-x) \right]. \quad (\text{C01})$$

Then, the derivative over molar fraction is

$$\frac{\partial g^m}{\partial x} = h + RT \cdot \ln \frac{x}{1-x}. \quad (\text{C02})$$

Construction of common tangent for equilibrium of this diluted solution with NiSi<sub>2</sub> (“12”-phase), NiSi (“11”-phase) and almost pure Ni (“10”-phase) gives:

$$h + RT \cdot \ln x_{12} = \frac{\Delta g_{12}^m}{1/3 - x_{12}} \approx \frac{\Delta g_{12}^m}{1/3}, \quad (\text{C03 a})$$

$$h + RT \cdot \ln x^e = \frac{\Delta g_{11}^m}{1/2 - x^e} \approx \frac{\Delta g_{11}^m}{1/2}, \quad (\text{C03 b})$$

$$h + RT \cdot \ln x^{\max} = \frac{0}{1 - x^{\max}} = 0. \quad (\text{C03 c})$$

Here  $\Delta g_{12}^m$  and  $\Delta g_{11}^m$  are estimated as the formation enthalpies (negative), since entropy terms are not known experimentally. They are as follows<sup>14</sup>:  $\Delta g_{12}^m \approx -30 \frac{kJ}{mol}$ ,

$\Delta g_{11}^m \approx -43 \frac{kJ}{mol}$ . For numerical estimations let us take  $T \cong 1000K$  (rather typical one for

the mentioned experiments). Combining equations (C03), we obtain:

$$x^e = x_{12} \cdot \exp \left\{ \frac{2\Delta g_{11}^m - 3\Delta g_{12}^m}{RT} \right\} \approx 1.6 \cdot x_{12} \sim 10^{-6}, \quad (\text{C04 a})$$

$$x^{\max} = x_{12} \cdot \exp \left\{ \frac{0 - 3\Delta g_{12}^m}{RT} \right\} \approx e^{10} \cdot x_{12} \sim 10^4 \cdot x_{12} \sim 10^{-2}. \quad (\text{C04 b})$$

## Appendix D

Derivation of the expression for macroscopic growth rate of an island of a new silicide plane

Let a critical (i.e. equilibrium for a given composition) new layer island appear at certain concentration in the whole silicon bulk phase. We shall treat the further growth of the nucleus so fast (in case of “survival”) that substance supply through a point contact is negligible during this time  $\tau_{crit}$ . This will allow using the law of conservation of matter. It is clear that deterministic equations of cluster growth are valid only at sizes which are above-critical (at that concentration gradient of nickel near the growing layer is positive, which provides substance flux towards the nucleus, as equilibrium concentration at the boundary of overcritical cluster is lower than for that of critical).

For a certain time point after spontaneous formation of a critical cluster (this moment is taken at zero), the law of matter conservation can be written in the following form (zero of  $z$  coordinate is chosen at the boundary between pure silicon and the silicide):

$$\int_0^{\infty} \frac{\pi R^2}{\Omega} \cdot [x_{\infty} - x(z)] dz = \Delta N, \quad (D01)$$

where  $x_{\infty}$  is mole fraction of nickel in the whole bulk (far from the silicide),  $x(z)$  – its concentration profile,  $\pi R^2$  – cross-section of a needle,  $\Delta N$  – number of excess nickel atoms in the growing island if compared to a critical value. On the other hand

$$\int_0^t \pi R^2 \cdot I dt = \Delta N, \quad (D02)$$

where

$$I = \frac{D}{\Omega} \frac{\partial x}{\partial z} \Big|_{z=0} \quad (\text{D03})$$

– diffusion flux of nickel towards the island. Substituting (D03) into (D02), one gets:

$$\frac{D}{\Omega} \int_0^t \frac{\partial x}{\partial z} \Big|_{z=0} dt = \frac{\Delta N}{\pi R^2} . \quad (\text{D04})$$

Differentiating (D04) over time, one finds the growth rate for the number of particles in the island:

$$\frac{1}{\pi R^2} \cdot \frac{d(\Delta N)}{dt} = \frac{D}{\Omega} \frac{\partial x}{\partial z} \Big|_{z=0} . \quad (\text{D05})$$

To find  $\frac{\partial x}{\partial z} \Big|_{z=0}$  at each time point one should, strictly speaking, solve a non-steady-state diffusion problem, which could extremely complicate the search for analytical (approximate, though) expression for macroscopic growth rate. Instead, let's take a more or less plausible approximation for diffusion profile at each current time point. It is evident that the function  $x(z)$  must be monotonically increasing, asymptotically tend to  $x_\infty$  at infinity, and the difference  $x_\infty - x(z)$  must be integrable within  $(0, \infty)$ . These requirements are easily satisfied if one chooses a quite convenient exponential form of the dependence:

$$x(z) = x_0 e^{-\alpha z} + x_\infty (1 - e^{-\alpha z}) , \quad (\text{D06})$$



where  $x_0$  and  $\alpha$  are time dependent parameters, which maintain the law of conservation and boundary condition in zero, which will be considered equilibrium, i.e. satisfying Gibbs-Thomson equation (for a two-dimensional case):

$$x(a) = x^e \left( 1 + \frac{\Omega}{kT} \frac{\gamma}{a} \right), \quad (\text{D07})$$

where  $a$  is cluster's radius,  $x^e$  is equilibrium mole fraction of nickel at the plane silicide boundary.

The choice of profile (D06) gives:

$$\left. \frac{\partial x}{\partial z} \right|_{z=0} = -\alpha(x_0 - x_\infty), \quad (\text{D08})$$

And substituting into (D01):

$$\frac{\pi R^2}{\Omega} \cdot \frac{x_\infty - x_0}{\alpha} = \Delta N. \quad (\text{D09})$$

Substituting (D09) into (D08), one has:

$$\left. \frac{\partial x}{\partial z} \right|_{z=0} = \frac{\pi R^2}{\Delta N} \cdot (x_\infty - x_0)^2, \quad (\text{D10})$$

and, finally, combining the last equation and (D05), one arrives at:

$$\frac{d(\Delta N)}{dt} = \frac{D \pi R^2}{\Omega \Delta N} \cdot (x_\infty - x_0)^2. \quad (\text{D11})$$

To obtain the ultimate equation for the growth rate we should only express both sides of (D11) in terms of  $a$ . For this let's put down:

$$\Delta N = \frac{\pi h}{\Omega} \cdot (a^2 - a_{cr}^2), \quad (D12)$$

where  $a_{cr}$  is the nucleus's critical radius, which gives for the derivative

$$\frac{d(\Delta N)}{dt} = \frac{2\pi h}{\Omega} \cdot a \frac{da}{dt}. \quad (D13)$$

Next, let's take into account that  $x_\infty - x_0 = x(a_{cr}) - x(a)$ , and using (D07) we find:

$$x_\infty - x_0 = \frac{x^e \Omega \gamma}{kT} \cdot \frac{a - a_{cr}}{a_{cr} a}. \quad (D14)$$

Substituting (D12 – D14) into (DA11), after some reductions we obtain:

$$\frac{da}{dt} = \frac{D \frac{4\pi}{3} R^2 (x^e)^2 \Omega^2 \gamma^2}{2\pi^2 h^2 (kT)^2 a^3 a_{cr}^2 (a + a_{cr})} \cdot (a - a_{cr}), \quad (D15)$$

and, finally, for the growth rate of the cluster in the vicinity of critical radius we have:

$$\left. \frac{da}{dt} \right|_{a_{cr}} = \frac{D \frac{4\pi}{3} R^2 (x^e)^2 \Omega^2 \gamma^2}{4\pi^2 h^2 (kT)^2 a_{cr}^6} \cdot (a - a_{cr}). \quad (D16)$$