Chemical tension and global equilibrium in VLS nanostructure growth process: from nanohillocks to nanowires

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1 Introduction

Semiconductor nanowires are of major interest for future applications in nanoelectronics, nanophotonics, and nanosensors [1–8]. Of the various ways of growing these structures, the vapor–liquid–solid (VLS) method is a most important one. In growing Si nanowires or whiskers using the VLS process, one may find no growth at all, the growth of hillocks, or the growth of nanowires. These results should have been caused by variations of experimental conditions. However, until recently, no systematic effort has been expended to identify the conditions and the associated mechanisms for the different results.

In recent experiments involving one of the present authors (Schmidt et al. [9]) using Au as the liquid droplet catalytic metal, the growth of Si nanowires (SiNWs) was found in lightly n- or p-doped Si, whereas no nanowire growth was observed under otherwise the same experimental conditions for highly p-doped Si. For highly p-doped Si, short and tapered nanostructures, sometimes resembling nanohillocks, were observed. Schmidt et al. [9] assumed that heavy p-doping affected the energies of the liquid-droplet and Si surfaces, which led to the difference in results. A quantitative model, yielding satisfactory fits to part of the experimental data, was thus proposed for the growth of Si nanohillocks and for diameter variations of Si nanowires [9].

The diameter of a Si nanowire changes as a function of its height: the further away from the substrate the smaller it becomes, until reaching a stable constant value. It is noted that for Si whiskers in the size range of μm, the whisker size variation and termination phenomena were already noticed in early times [10].

The model of Schmidt et al. [9] uses a stress-balance scheme to account for the roles of a line tension and three surface tensions, σ_{LS}, σ_{VL}, and σ_{VS}, respectively, those of the liquid–solid, the vapor–liquid, and the vapor–solid interfaces. These tensions are energy quantities, which may also be viewed as force quantities, as can be shown by the virtual work principle. The line, formed by the three interfaces, surrounds the wire growth front. With a line tension included, a quasi-static description of the Si nanowire as well as the nanohillock growth process is obtained. The line-tension value used was \( \sim 10^{-3} \text{ J/m} \), which has been suggested to be too large for the Au–Si system: by as much as two orders of magnitude [11]. Line tension with values ranging from slightly positive to negative have to be used to describe the growth of nanowires. Unlike surface tension which must be positive, the line tension can be either positive or negative [12, 13]. A negative line tension means that the line is more stable than the surfaces forming it, which is a highly controversial subject [13]. Instead of the line tension, in the present paper we use a concept based on the chemical driving force itself to formulate a chemical or chemical-tension model, which is a global equilibrium model, to describe the VLS process.

2 Formulation of the chemical model

To formulate the chemical model, we first use the system’s Gibbs free energy to show that the chemical driving force contributes two factors: an effective surface energy or tension factor and an effective line energy or tension factor. These factors are obtained in two ways: via the virtual work principle and via the minimization of the system’s Gibbs free energy change. On the one hand, the chemical-tension factors are readily identified using the virtual work principle. On the other hand, the system’s Gibbs free energy minimization method yields simultaneously the precise manner in which
these factors contribute in a configurational equation, Young’s equation, and in fact Young’s equation is itself the thermodynamic condition for yielding the minimum Gibbs free energy state of the system. The usual way of deriving Young’s equation is via a mechanical force balance analogue.

We now use the virtual work principle to identify the chemical-tension factors. Consider a nanowire at any stage during its growth, from onset to steady state. For the wire to grow a layer of an elementary thickness $l_o$, the system’s Gibbs free energy changes by [14, 15]

$$
\delta g = -\pi r^2 l_o \frac{k_B T}{\Omega} \ln \eta + 2\pi r l_o \sigma_{VS},
$$

where $r$ is the wire radius, $\Omega$ is the volume of a Si atom in the solid wire, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, and $\eta$, which is equal to $P_{Si}/P_{Si}^{eq}$, is the Si vapor pressure supersaturation ratio. Here $P_{Si}$ and $P_{Si}^{eq}$ are respectively the actual and thermal equilibrium Si vapor phase pressures in the ambient, with $P_{Si}^{eq}$ defined to be that for the equilibrium coexistence of the vapor and the solid separated by a flat interface. Since in VLS Si nanowire growth compound gaseous species such as SiH$_4$ are used, the Si pressures are effective ones. On the right-hand side of (1), the first term is due to the Gibbs free energy reduction caused by the crystal bulk formation, while the second is due to the increase in surface energy caused by the increase in surface area. The elementary thickness $l_o$ is defined to be one with an appreciable energy change for ensuring an equilibrium change to occur, which is of the magnitude of the atomic layer distance in the wire growth direction. Assuming the existence of an effective surface tension $\sigma_{LS}$ and an effective line tension $\tau^c$, which swept out on the nanowire growth front the area $\pi r^2$ and the circumference length $2\pi r$, respectively, and this changed the nanowire system’s energy by the same amount $\delta g$ expressed by (1), then we can write

$$
\delta g = \pi r^2 \sigma_{LS}^c + 2\pi r \tau^c = -\pi r^2 l_o \frac{k_B T}{\Omega} \ln \eta + 2\pi r l_o \sigma_{VS}.
$$

Clearly,

$$
\sigma_{LS}^c = -l_o \frac{k_B T}{\Omega} \ln \eta,
$$

(3)

$$
\tau^c = l_o \sigma_{VS}.
$$

(4)

Equation (3) defines the effective surface tension component of the chemical tension, $\sigma_{LS}^c$. It acts in the liquid–solid interface as an in-plane vector quantity just as the static liquid–solid interface tension $\sigma_{LS}$ does. Equation (4) defines the effective line-tension component of the chemical tension, $\tau^c$. It acts on the circumference of the liquid–solid interface as an in-plane vector quantity just as the static line tension at this circumference does. Here we have regarded $\sigma_{LS}^c$ and $\tau^c$ as tensions acting in the nanowire growth plane. However, because the growing Si layer is volumic, there is another degree of freedom in defining the chemical-tension quantities: normal to the growth plane, which is of no relevance to the present problem. For convenience, we shall now define the overall effective chemical tension as

$$
\sigma^c = \sigma_{LS}^c + \frac{\tau^c}{r} = -l_o \frac{k_B T}{\Omega} \ln \eta + l_o \sigma_{VS} r,
$$

(5)

where the use of the factor $1/r$ to multiply the term $\tau^c$ will be made clear in the next paragraph.

We now use the system’s Gibbs free energy minimization method to determine the rudimentary form of the system’s configurational equation (Young’s equation) and the precise manner of the chemical-tension contribution. This is most conveniently done by considering the formation of a first Si nanowire layer of an elementary thickness $l_o$ and a liquid Au–Si island simultaneously on the substrate from the vapor species, Fig. 1. The same result is obtained by separating the Au–Si island formation and the first Si layer growth steps. Assuming homo-epitaxial growth of the first Si layer on the substrate and that the liquid droplet is in dynamical equilibrium with the vapor [14, 15], this procedure yielded the system configurational condition for attaining the minimum Gibbs free energy as

$$
\sigma_{VL} \cos \beta_o = \sigma_{VS} - \sigma_{LS} - \sigma_{LS}^c - \frac{\tau^c}{r_o},
$$

(6)

In (6), $\beta_o$ is the initial contact angle between the liquid droplet outer surface and the liquid–Si interface, Fig. 1, and the terms $\sigma_{LS}^c$ and $\tau^c$ are given by (3) and (4). The mathematics involved in deriving (6) is somewhat complicated. The necessary details of the derivation are given in the appendix. Resulting from the energy increase at the outer cylindrical surface of the Si layer, the term $\tau^c$ given by (4) defines the effective line tension of the magnitude $l_o \sigma_{VS}$, as is seen via its $-1/r_o$ dependence in (6), which is the same dependence of the physical line tension $\tau$ [9, 16]. Note that both $\sigma_{LS}^c$ and $\tau^c$ are reduced quantities, as is seen from the presence of $l_o$ as a multiplier in the terms. Without the chemical driving force, $l_o = 0$ holds, and (6) reduces to $\sigma_{VL} \cos \beta_o = \sigma_{VS} - \sigma_{LS}$, which is the condition for attaining the minimum Gibbs free energy for the system of wetting a flat surface by a droplet. It is usually referred to as Young’s equation with the surface energy densities interpreted as surface tensions, which is a mechanical force balance or equilibrium analogue.

With the roles of the chemical driving force identified, we now follow Schmidt et al. [9] by writing the generalized Young’s equation for a Si nanowire grown already to some length as

$$
\sigma_{VL} \cos \beta_o = \sigma_{VS} \cos \alpha - \sigma_{LS} - \sigma_{LS}^c,
$$

(7)

to account for the wire body diameter change, where the angle $\alpha$ is the one between the SiNW growth front and the slope of the growing wire body in Fig. 2. Equation (7) is the chemical-model global equilibrium condition of the VLS process. It expresses the balance among the various system static factors, the surface energies, and the dynamic factor due to the growth

![Image](image-url)
of a crystal layer, the chemical tension. The derivation of (7) with the physical line tension $r$ in place of the present $\sigma^c$ term has been carried out by Chen et al. [16]. Their work resulted in a Neumann quadrilateral construction scheme, which has been adopted by Schmidt et al. [9] for the line-tension model. Actually, with the definitions of $\sigma_{LS}$ and $\tau^c$ known from (3) and (4), we have derived (7) using the formal procedure of Chen et al. [16], but no new physical insights are further obtained. The rest of our formulation follows closely that of Schmidt et al. First, without the SiNW growing, i.e. without driving force, and hence $l_o = 0$ holding, the initial condition reduces to

$$\sigma_{VL} \cos \beta_o = \sigma_{VS} - \sigma_{LS},$$  

subject to the constraint

$$\frac{\sigma_{VS}}{r_o} = \frac{kT}{\Omega} \ln \eta_{\min},$$

where $\eta_{\min} = P_{Si}^{eq}/P_{Si}$ with $P_{Si}^{eq}$ taking the minimum $P_{Si}$ value which maintains the initial stable droplet configuration. Second, in the line-tension model the liquid-droplet volume is a constant given by $V = V_o$, with

$$V_o = \frac{\pi}{3} \left( \frac{r_o}{\sin \beta_o} \right)^3 (1 - \cos \beta_o)^2 (2 + \cos \beta_o).$$

In the present model the expression for $V_o$ still holds but $V = V_o$ is no longer holding. In a given experiment $\eta$ is constant, but as the radius $R$ of the liquid droplet changes the Si concentration in the liquid also changes. This means that the Au content in the liquid is not changing but that of Si is changing and hence is the droplet volume. This volume is obtained as

$$V = V_o \frac{1 - \eta C_{Si}^{eq} \exp(-2\Omega \sigma_{VL} \sin \beta_o/r_o k_B T)}{1 - \eta C_{Si}^{eq} \exp(-2\Omega \sigma_{VL} \sin \beta/r_k B T)},$$

where $C_{Si}^{eq}$ is the thermal equilibrium concentration of Si in the liquid defined for the coexistence of the liquid and the Si vapor phases separated by a flat interface. For numerical calculations, further needed expressions are those of Schmidt et al. [9]. Specifically, their equations (5), (6), and (7), which are previously obtained the minimum attainable nanowire size as $14, 15$

$$r_{\min} = \frac{\Omega \sigma_{VS}}{k_B T \ln \eta}.$$  

Under steady state growth conditions $\alpha = 90^\circ$ holds, and this $r_{\min}$ expression is obtained by setting (5) to zero, which is valid if in (7) the relation

$$\sigma_{VL} \cos \beta = -\sigma_{LS},$$

is satisfied, which is the surface energy balance or equilibrium condition for realizing $r_{\min}$. It is required that the values of the energy densities or tensions in (16) satisfy the condition $\sigma_{VL} \geq \sigma_{LS} \geq 0$, for which the correspondingly allowed values of the angle $\beta$ range from $180^\circ$ for $\sigma_{VL} = \sigma_{LS}$ holding, down to $90^\circ$ for $\sigma_{LS} = 0$ holding.

Second, by providing metallic predeposits of different sizes and thus starting with liquid droplets of different sizes, Si nanowires with different radii can grow in the same experiment. Stable growth of a wire requires $r \geq r_{\min}$ and $\alpha = 90^\circ$ to hold, for which (7) reduces to

$$\sigma_{VL} \cos \beta = -\sigma_{LS} - \sigma^c.$$  

With wires of different $r$ values growing in the same experiment under a given $\eta$ value, we see from (5) that the values of $\sigma^c$ will also be different. Stable growth of these wires is attained because the values of $\beta$ will be self-adjusted according to (17) to satisfy the $\alpha = 90^\circ$ condition. For these cases $\sigma^c \leq 0$ must hold, where the equal sign applies to the $r_{\min}$ case.

Third, for such cases $\sigma^c < 0$ holds, and in the very large $r$ limit $\sigma^c$ reaches the limiting value $-(l/k_B T/\Omega) \ln \eta$. This reduces the effective magnitude of $\sigma_{LS}$ with a corresponding decrease of $\beta$ toward $90^\circ$ with $R = r$ holding, i.e. $R/r$ becomes smaller for larger-diameter wires ($R$ and $r$ are related by $r = R \sin \beta$); see Fig. 3 for a schematic illustration. Data of this phenomenon appear to be scattered in a large amount of available literature, but a systematic study is still lacking.

\[
\tan \alpha = -\frac{dh(r)}{dr}.
\]

\[
h = -\int_{r_o}^{r} \tan \alpha \, dr.
\]
3.2 Nanowires or nanohillocks?

The whisker/wire/hillock shape as a function of growth height has been calculated using the chemical model. The surface energy values used are those of Schmidt et al. [9]. A calculated Si nanowire shape curve is shown in Fig. 4a, and is compared to the fitting curve of the line-tension model [9]. Their calculated curve was satisfactorily fitted to a high-resolution transmission electron microscopy (TEM) image of a \( r \sim 10 \text{ nm} \) Si nanowire, shown in their Fig. 4, and also here as Fig. 4b. It is seen from Fig. 4a that the line-tension and chemical-tension model curves are nearly identical, i.e. the fits are equally satisfactory. The corresponding parameters for obtaining Fig. 4 are listed in Table 1, which will also be used in subsequent discussions, unless otherwise mentioned.

As expected, changes in \( \eta \) will result in different shapes of nanowire bases, leading to the growth of either Si nanowires or nanohillocks; see Fig. 5 and the corresponding \( \eta \) and other variable values shown in the legend that differ from those listed in Table 1. For a given \( \eta \) value, we have also calculated the Si nanowire or nanohillock growth dependency on the initial \( r_0 \) value, from nm to \( \mu \text{m} \), of the droplet, Fig. 6. In general, larger ones grow into wires or whiskers and smaller ones into hillocks.

From Figs. 4 to 6 it is concluded that the chemical model yields satisfactory quantitative fits to the experimental results, and the reasons for the fits and the predictions of the model warrant some discussion. In this model, via the chemical-tension term \( \sigma^c \), whether a wire or a hillock will grow is determined by two factors: the Si atom supersaturation, \( \eta \), and the wire/hillock radius \( r \) via the droplet radius \( R \). Since \( \sigma^c \) is a function of \( r \), it is not a constant during growth. For wire growth to occur \( \sigma^c(r) < 0 \) must hold throughout the growth process, for only then is the Gibbs free energy released by the growing bulk sufficient to compensate the associated increase in the wire surface energy. For the Si wire labeled as case 1 in Fig. 5, we show in Fig. 7a the values of \( \sigma^c(r) \) and in Fig. 7b the contact angles \( \alpha(r) \) and \( \beta(r) \). It is seen that \( \sigma^c(r) < 0 \) holds for all \( r \) values, and \( \alpha(r) \) and \( \beta(r) \) attain their final stable values of \( 90^\circ \) and \( \sim 130^\circ \), respectively. If \( \sigma^c(r_0) \geq 0 \) holds instead, then wire/hillock growth will never start, for reasons opposite to those of the \( \sigma^c(r) < 0 \) case. If \( \sigma^c(r_0) < 0 \) holds initially and for some time into growth but subsequently \( \sigma^c(r) > 0 \) occurs, then only a hillock can be grown. When \( \sigma^c(r) > 0 \) occurs, the growth must either stop or, alternatively, go into a mode with an ever-decreasing diameter via the mutual-adjustment among \( \alpha, \beta, \) and \( r \) in accordance with (5) and (7). To illustrate

<table>
<thead>
<tr>
<th>( \sigma_{VS} ) (N/m)</th>
<th>( \sigma'_{VS} )</th>
<th>( \sigma_S ) (N/m)</th>
<th>( \sigma'_S )</th>
<th>( \sigma_{VL} ) (N/m)</th>
<th>( T ) (°C)</th>
<th>( r_0 ) (nm)</th>
<th>( \ell ) (nm)</th>
<th>( \eta )</th>
<th>( \sigma' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.24</td>
<td>1.46</td>
<td>0.62</td>
<td>0.73</td>
<td>0.85</td>
<td>400</td>
<td>10</td>
<td>0.47</td>
<td>2.5</td>
<td>-0.17 to</td>
</tr>
<tr>
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<td></td>
<td>-0.05</td>
</tr>
</tbody>
</table>

TABLE 1 Values of the physical parameters used for obtaining the calculated Si nanowire-shape fitting curve shown in Fig. 4a. Legends: \( \sigma_{VS} = \sigma_{VS}/\sigma_{VL} \). \( \sigma'_S = \sigma'_S/\sigma_{VL} \). \( \sigma' = \sigma^c/\sigma_{VL} \).
this situation, for the hillock growth case 4 in Fig. 5, we show in Fig. 8a the corresponding values of $\sigma(r)$ and in Fig. 8b the contact angles $\alpha(r)$ and $\beta(r)$. It is seen that $\sigma(r)$ changed from initially negative values to positive values when $r/r_o$ reached the value of $\sim 0.68$. $\alpha(r)$ will approach but not really reach $90^\circ$, i.e. the growth was never stabilized. At some still smaller $r/r_o$ values, $\alpha(r)$ decreased monotonically and finally reached $0^\circ$, and $\beta(r)$ continued to increase and finally reached $180^\circ$. The final $\alpha(r)$ and $\beta(r)$ values are simultaneously reached at a small but non-zero $r/r_o$ value. In both Figs. 7b and 8b there is the initial sudden jump of the $\alpha(r)$ value. This is caused by the model set-up based on the physical assumption that the onset of the growth process is an abrupt one, via the implicit use of an $\eta_{\min}$ value for maintaining the Au–Si liquid cap stability for time $t \leq 0$, while, for $t > 0$, $\eta > \eta_{\min}$ is applied in a step-function manner. We believe that this should not have incurred large errors. The physical process of the growth onset should be a more gradual one and could be modeled accordingly.

From our simulation results it is seen that a larger supersaturation and/or a larger $r_o$ can lead to the stable growth of wires while the converse conditions can only lead to hillock growth or no growth at all. Si nanohillocks grow only in a limited range of $\eta_{\min}^h < \eta < \eta_{\max}^h$ values for a given $r_o$ or, alternatively, a small $r_o$ range for a given $\eta$ value. The condition $\eta_{\min}^h = \eta_{\min} > 1$ holds, where $\eta_{\min}$ is the needed $\eta$ value for the released $G$ from growing the bulk to compensate the energy increase due to the nanowire surface energy increase. The value of $\eta_{\min}^h$ can be directly computed from (9). We have done so for the Schmidt et al. case of $r_o = 10$ nm and obtained $\eta_{\min}^h = 1.31$, which is also the value noticed from our calculations in obtaining the results shown in Fig. 4. There is no easy way to obtain $\eta_{\max}^h$ except to perform calculations such as those shown in Fig. 4, from which we obtained for the same case that $\eta_{\max}^h$ is approximately 1.63.

In obtaining the fitting wire shape curve shown in Fig. 3 using the chemical model, the $l_0$ value used is 0.47 nm, which is two times the Si interatomic distance of $\lambda = 0.235$ nm, i.e. $l_0 = 2\lambda$, which seems to be of the right magnitude, i.e. of atomic dimension. There is a small range of the $l_0$ values for obtaining satisfactory fits.

The chemical-tension model gives clear-cut predictions which may be verified or refuted experimentally. For a given preformed Au–Si liquid droplet seed size, the model predicts the growth of Si nanohillocks in a small range of $P_{Si}$, and Si nanowires grow with still higher $P_{Si}$. Or, equivalently, for a given $P_{Si}$, no growth at all should occur for seed sizes below a critical size, growth of Si nanohillocks should occur for a narrow range of seed sizes larger than this critical size, and Si nanowires will grow for still larger seeds. Thus, the model can be experimentally proved or disproved in a straightforward manner.

4 Conclusions

In conclusion, a global equilibrium model describing the development of one-dimensional nanostructures in the
FIGURE 7  For case 1 of Fig. 5: (a) the corresponding $\sigma^c(\sigma_{\text{VL}})$ value as a function of $r(r_o)$ values. The steady state is indicated by the dotted vertical line. Note that $\sigma^c(\sigma_{\text{VL}}) < 0$ holds throughout the growth process, earlier transition and later steady-state stages all included; (b) the corresponding values of the contact angles $\alpha$ and $\beta$ as functions of $r(r_o)$ values. Reaching steady state, $\alpha = 90^\circ$ is attained, with a corresponding $\beta$ value of $\sim 130^\circ$ for this case. These values stay constant in steady state.

VLS process has been formulated by employing also the contribution of the chemical tension in addition to that of the physical tensions, i.e. surface energies. The chemical tension derives from the Gibbs free energy change due to the growth of a crystal layer of an elementary thickness. The system’s global equilibrium is arrived at via the balance of the static physical tensions and the dynamic chemical tension. The model gives very specific predictions concerning pressure and radius ranges in which Si nanohillocks should grow, which could and should be checked to verify or refute the model. Furthermore, our model is clearly applicable to explain the nanowire growth instability problem: there are experimental results showing nanowire diameter oscillations and they were not satisfactorily explained before. Invoking our present model and assuming an instability in the wire growth driving force, we believe that we can calculate this phenomenon. What distinguishes this approach from previous attempts is that this one will be with a firm basis of physics behind it. However, it appears that by far the most significant aspect of our present work is the mere fact of integrating together the system growth dynamic factor and the static system configurational factors, via a fairly straightforward method involving the system’s Gibbs free energy. This was definitely not done before. This approach may prove to be generally applicable to reacting systems. Should this be the case, the potential of this method will be beyond what can be currently speculated upon.

Appendix

We discuss two topics in this appendix: (A1) a justification of using the Gibbs free energy change minimization method; and (A2) derivation of (6) in the text.
The Gibbs free energy change minimization method as a valid approach to our problem is justified using the maximum Gibbs free energy degradation rate principle. This principle, proposed by Oswald in as early as 1920 for material science studies [1], states that a process will proceed via a path (among several possible or parallel ones) at a given instant or locality for which the decrease or release of the Gibbs free energy of the system is maximum. This is a powerful principle, for its equivalent forms make predictions that agree well in many natural phenomena, such as that a river never flows in a straight path and that lightning always follows a zigzag path, etc. In materials science, this principle has been used to qualitatively explain the phenomenon that one reaction may precede another even though the other will give rise to more total Gibbs free energy release upon completion. This is because the said reaction can release Gibbs free energy at a faster rate, though with a smaller total amount when completed (in relation to the other reaction possibilities). However, quantitative applications of this principle appear to be case specific and we are not aware of the existence of general roles governing such quantitative applications.

Here we quantitatively show that the method of minimization of the system’s Gibbs free energy, used to formulate our problem, derives from the maximum Gibbs free energy degradation rate principle. The formulation of our problem is based on the assumption that it may be treated as a quasi-equilibrium problem (more precisely, a quasi-static or quasi-steady state, as the case may be).

The maximum Gibbs free energy degradation rate principle states that a process will proceed via the path for which the decrease or release of the Gibbs free energy of the system is maximum. According to the convention that the energy change value is positive if it increases the system energy, mathematically this principle means that \(-\partial(\Delta G)/\partial t\) is maximum or \(\partial(\Delta G)/\partial t\) is minimum. For \(\partial(\Delta G)/\partial t\) to be minimum, the condition
\[
\frac{\partial}{\partial \xi} \frac{\partial(\Delta G)}{\partial t} = 0 \tag{A.1}
\]
must hold. In (A.1), \(\xi\) represents the system’s internal variable(s) or coordinate(s) that influences the system’s energy. There are two kinds of such variables: (1) the system’s composition which affects the system’s chemical energy; and/or (2) the system’s geometry/configuration which affects the system’s surface energies. In our case, we used \(\xi\), which is the height of the spherical cap of the liquid droplet, as the composition of the liquid is assumed to be a constant. Changing the differentiation order in (A.1), which is permitted for a single-valued function with continuous derivatives, as the thermodynamic functions are, we obtain
\[
\frac{\partial}{\partial t} \frac{\partial(\Delta G)}{\partial \xi} = 0 . \tag{A.2}
\]
Integration of (A.2) with respect to \(t\) yields
\[
\frac{\partial(\Delta G)}{\partial \xi} = a(t) , \tag{A.3}
\]
where \(a(t)\) is a function of \(t\). In the quasi-equilibrium approach, \(a(t)\) is regarded as so small that it vanishes. Thus, we obtain
\[
\frac{\partial(\Delta G)}{\partial \xi} = 0 , \tag{A.4}
\]
which shows that the Gibbs free energy change is minimum.

### A2

In this section we use the method of minimization of the system’s Gibbs free energy to arrive at the definitions of the chemical-tension terms, (3) and (4), of the text. In this approach, these terms will directly appear in the mechanical equilibrium expression allowing the system to attain its minimum Gibbs free energy state. To this end, we consider the onset stage of the nanowire growth process. That is, the system consists of the liquid droplet on a flat (Si) substrate upon which the first Si nanowire layer is grown epitaxially; see Fig. 2 of the text. This problem may be formulated by considering the formation steps of the droplet and the growth of the first nanowire layer simultaneously or separately, which will yield the same result. Hence, in the following we only discuss the simultaneous formation of the droplet and the first Si layer case. For this case, the Gibbs free energy change of the system is
\[
\Delta G_0 = \sigma_{VL} 2\pi R_{o} h_{o} + n_{o} \delta g_{\tau} + (\sigma_{LS} - \sigma_{VS}) \pi r_{o}^{2} \left[ \frac{k_{B} T}{\Omega} \ln \eta \right] , \tag{A.5}
\]
where \(R_{o}\) and \(h_{o}\) are the radius and height of the spherical-cap-shaped liquid droplet, respectively, \(\delta g_{\tau}\) is the Gibbs free energy difference of a Si atom in the liquid and in the vapor when the two materials are separated by a flat interface, \(n_{o}\) is the number of Si atoms in the liquid droplet, and \(r_{o}\) is the radius of the cylindrical SiNW layer. The liquid droplet is assumed to be in dynamical equilibrium with the vapor, and both \(n_{o}\) and \(\delta g_{\tau}\) are assumed to be constants. The last two terms on the right-hand side of (A.5) are due to the chemical energy change associated with the Si layer growth. The first of these two terms results from the energy increase at the outer rim surface of the Si layer, and the second from the volume energy change of the layer growth. For convenience of handling the mathematics, let us use the symbols given in (3) of the text to represent the appropriate terms (but not yet specifically asking for their physical meanings); then (A.5) becomes
\[
\Delta G_0 = \sigma_{VL} 2\pi R_{o} h_{o} + n_{o} \delta g_{\tau} + (\sigma_{LS} - \sigma_{VS}) \pi r_{o}^{2} \left[ -2\pi r_{o} \tau^{c} + \pi r_{o}^{2} \sigma_{LS}^{c} \right] . \tag{A.6}
\]
For \(\Delta G_0\) to be minimum, it requires \(\partial(\Delta G_0)/\partial h_{o} = 0\) to hold, that is,
\[
\sigma_{VL} \left( \frac{dR_{o}}{dh_{o}} h_{o} + R_{o} \right) + (\sigma_{LS} - \sigma_{VS} + \sigma_{LS}^{c}) \pi r_{o} \frac{dr_{o}}{dh_{o}} + \tau^{c} \frac{d\tau}{dh_{o}} = 0 . \tag{A.7}
\]
The geometry of the droplet shows that
\[ r_o = \sqrt{R_o^2 - (R_o - h_o)^2}, \]  
and hence
\[ \frac{d R_o}{d h_o} = \frac{R_o}{\sqrt{R_o^2 - (R_o - h_o)^2}}. \]

Using (A.9), (A.7) becomes
\[ \left( \sigma_{VL} + \sigma_{LS} - \sigma_{VS} + \sigma_{LS}^c + \frac{\tau^c}{r_o} \right) \left( \frac{d R_o}{d h_o} \right) h_o + R_o = \left( \sigma_{LS} - \sigma_{VS} + \sigma_{LS}^c + \frac{\tau^c}{r_o} \right) h_o, \]  
or, equivalently,
\[ \frac{(d R_o / d h_o) h_o + R_o}{h_o} = \frac{\sigma_{LS} - \sigma_{VS} + \sigma_{LS}^c + \tau^c / r_o}{\sigma_{VL} + \sigma_{LS} - \sigma_{VS} + \sigma_{LS}^c + \tau^c / r_o}. \]

Assuming that the liquid droplet takes a spherical shape that has the same volume as the spherical cap but with a different radius \( R_o \). Volume conservation implies that \( \frac{4}{3} \pi R_3^3 = \frac{1}{3} \pi h_o^2 (3 R_o - h_o) \), from which we obtain \( R_o = (4 R_3^3 + h_o^2) / (3 h_o^2) \) and \( d R_o / d h_o = (h_o^3 - 8 R_3^3) / 3 h_o^2 \). Substituting these into (A.11), we obtain
\[ \frac{(2 h_o^3 - 4 R_3^3) / h_o^2}{h_o} = 1 - \frac{R_o}{h_o} = \frac{\sigma_{LS} - \sigma_{VS} + \sigma_{LS}^c + \tau^c / r_o}{\sigma_{VL} + \sigma_{LS} - \sigma_{VS} + \sigma_{LS}^c + \tau^c / r_o}. \]  

Equation (A.12) simplifies into
\[ \cos \beta_o = 1 - \frac{h_o}{R_o} = \frac{\sigma_{LS} - \sigma_{VS} + \sigma_{LS}^c + \tau^c / r_o}{\sigma_{VL}}. \]

or, in a more familiar form,
\[ \sigma_{VL} \cos \beta_o = \sigma_{VS} - \sigma_{LS} - \sigma_{LS}^c - \tau^c / r_o, \]  
which is (6) in the text of the paper. Moreover, it is seen from (A.14) that the role of the term \( \sigma_{LS}^c \) is equivalent to that of the term \( \delta_{LS} \), and the role of the term \( \tau^c \) is that of a line tension. The fact that \( \tau^c \) behaves as a line tension is evidenced by the \( 1 / r_o \) dependence in (6) or (A.14), which is the same as that of a static line tension [1, 7].

REFERENCES
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