Is there a thermodynamic size limit of nanowires grown by the vapor-liquid-solid process?

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For nanowires grown by the vapor-liquid-solid (VLS) process, expressions of the thermodynamically allowed minimum sizes of the wire and the liquid droplet are derived using Si nanowires (SiNW) grown from metal–silicon (M–Si) liquid as the model case. The liquid droplet minimum size is determined by a unique set of external M and Si vapor phase pressure values. The SiNW minimum size expression contains two contributions, one depending on composition of the liquid and one depending on the droplet size. These expressions do not predict a limit on the attainable VLS SiNW minimum size, implying ever smaller SiNW can be grown until reaching some growth kinetic limit which is presently unknown. © 2003 American Institute of Physics.

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Semiconductor nanowires (SNW) have the potential for continuing the solid state electronic circuitry miniaturization process beyond the size limit the Si integrated circuit (IC) technology will soon face at the field effect transistor channel length of ~10 nm. Device actions have already been demonstrated for some SNW.¹,² Presently the SNW are also in the ~10 nm diameter range. Hence, to be competitive with Si ICs, their size needs to be further reduced. To this end, the question whether a SNW size limit exists needs to be addressed. Answers to this question will depend on the used SNW growth methods for which an important one is the vapor-liquid-solid (VLS) growth process. In this letter we examine the size limit of the VLS SNW, on the basis of thermodynamics and using Si nanowire (SiNW) as the model case.

Figure 1 shows the schematics of the VLS SiNW growth process, which involves four phases of materials of a metal–Si (M–Si) binary system: the Si₁ and M₁ vapors, the M–Si liquid, and the solid SiNW. In 1965 Wagner and Ellis³ discussed two points of the basic mechanisms governing the VLS process, which were applicable to growth of whiskers of diameters in the micron range then, and are applicable to nanowire growth today. One point is on the unidirectional growth of the crystal and another on its size. Unidirectional growth of the VLS SiNW results from the difference of the sticking coefficients of the impinging vapor phase Si₁ atoms on liquid and on solid Si surfaces. Being an ideal rough surface with a sticking coefficient of nearly 1, the liquid surface captures practically all the impinging Si₁ atoms, while the solid Si surfaces reject almost all of these atoms because the sticking coefficients are orders of magnitude smaller. Thus, axial growth of the Si crystal fed by the liquid will be at a rate exceeds its lateral growth rate by orders of magnitude, leading to the apparent unidirectional growth. Their second point is that the liquid droplet must be stable: the stability of a liquid droplet of radius r in its own vapor depends on the degree of supersaturation S, as given by

\[ r_{\text{min}} = \frac{2\Omega_{\text{v}} \sigma_{\text{ev}}}{k_B T \ln(P_{\text{Si}}/P_M)} = \frac{2\Omega_{\text{v}} \sigma_{\text{ev}}}{k_B T \ln(P_{\text{Si}}/P_M)} \]

by equating the Si and M chemical potentials in the liquid, respectively, to that in the vapor phases. In Eq. (1) \( P_{\text{Si}} \) and \( P_M \) are, respectively, the Si and M vapor phase pressures in thermal equilibrium coexistence with the liquid of composi-

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FIG. 1. A schematic diagram showing the VLS SiNW growth processes. Together with the radii of the liquid droplet and the SiNW, four phases of materials are indicated.
tion (Si concentration) $\bar{C}$ in large quantity and having a flat surface. Here the trivial difference between $\sigma_{i\ell}$ and the SiNW-liquid interfacial energy density $\sigma_{s\ell}$ is ignored. The liquid composition $\bar{C}$ is determined by

$$\bar{C} = \frac{1}{\gamma_{Si}(\bar{C})B_{Si}} \bar{P}_{Si}, \quad 1 - \bar{C} = \frac{1}{\gamma_{M}(\bar{C})B_{M}} \bar{P}_{M},$$

(2)

and the ratio

$$\frac{\bar{C}}{1 - \bar{C}} = \frac{\gamma_{M}C_{M}B_{M}}{\gamma_{Si}C_{Si}B_{Si}} \frac{\bar{P}_{Si}}{\bar{P}_{M}}.$$  

(3)

In Eqs. (2) and (3) $\gamma_{Si}(\bar{C})$ and $\gamma_{M}(\bar{C})$ are, respectively, the extended (chemical) activity coefficients of Si and M in the liquid which are themselves functions of $\bar{C}$, and $B_X$ is the pressure constant of the appropriate vapor species given by $B_X = (2 m_X h^2)/(k_B T)$, where $m_X$ is the mass of an atom of the X species, Si or M, and $h$ is Planck’s constant.

The minimum SiNW size $r_{\ell}^{min}$ is equal to the critical radius of a cylindrical Si crystal nucleated from the liquid droplet of radius $r_{\ell}^{max}$ and of composition $\bar{C}$, which reads

$$r_{\ell}^{min} = \frac{\Omega_{i} \sigma_{sv}}{k_B T \ln(P_{Si}/\bar{P}_{Si}^{eq})} = \frac{\Omega_{i} \sigma_{sv}}{k_B T \ln(P_{Si}/\bar{P}_{Si}^{eq}) + k_B T \ln(P_{Si}/\bar{P}_{Si})},$$

(4)

where $\Omega_{i}$ is the volume of a Si atom in the SiNW and $\sigma_{sv}$ is the SiNW-vapor surface energy density. Equation (4) is obtained by equating the chemical potential of a Si atom in the SiNW to: either (i) that in the Si$_1$ vapor; or (ii) that in the liquid droplet. In Eq. (4) $\bar{P}_{Si}^{eq}$ is the Si vapor pressure over the equilibrium liquid with a flat surface and of composition $\bar{C}^{eq}$, to be discussed shortly. Using the Si whisker size as a parameter, method (i) has been employed by Givargizov$^5$ to numerically calculate the chemical potential difference of a Si atom in the vapor and in the Si crystal.

Equations (1) or (4) does not impose an absolute limit on $r_{\ell}^{min}$ or $r_{\ell}^{max}$, i.e., there is no thermodynamic (energetic) reason preventing VLS SiNWs from reaching an even smaller size. However, such limits may exist due to kinetic reasons for which the details are not yet known.

Conditions for VLS SiNW growth are revealed by Eqs. (1)–(3). Equation (3) shows that $\bar{C}$ is determined by the ratio of $\bar{P}_{Si}$ and $\bar{P}_{M}$, and Eq. (2) shows that for a given $\bar{C}$ the values of $\bar{P}_{Si}$ and $\bar{P}_{M}$ are unique. Equation (1) shows that for the liquid to exist as a droplet both the Si$_1$ and M$_1$ vapor phases must be supersaturated or overpressured to the same extent relative to those in equilibrium coexistence with the liquid of the same $\bar{C}$ with flat surfaces via $P_{Si}/P_{M} = \bar{P}_{Si}/\bar{P}_{M}$. However, Eq. (1) is not sufficient for determining whether a SiNW can grow from the liquid droplet. The allowed value range of $\bar{C}$ as given by Eq. (3) is between 0 and 1. Refer to Fig. 2, a typical eutectic type M–Si phase diagram with the two primary solid phase regions greatly exaggerated. SiNW can grow from the liquid droplet of composition $\bar{C}$ only in region IV wherein $\bar{C}^{eq} < C < \bar{C}^{max}$ holds, with $\bar{C}^{eq}$ and $\bar{C}^{max}$ lie, respectively, on the liquidus and solidus lines of the Si side of Fig. 2. In region II a metal wire can grow instead, while no wire can grow in regions I, III, and V.

SiNW forms by dissociation of the nonequilibrium liquid with $\bar{C} > \bar{C}^{eq}$, which is itself assumed to be able to form. This assumption is reasonable, as it is assured by the large sticking coefficient (~1) of the liquid surface for impinging vapor phase Si$_1$ atoms. For $P_{Si} > \bar{P}_{Si}^{eq}$ holding, if the liquid droplet composition ever dropped to $\bar{C}^{eq}$ it will be restored rapidly to approach $\bar{C}$ by capturing the impinging Si$_1$ atoms while rejection of these atoms occurs at the solid Si surfaces.

Via the two terms in its denominator, the most right-hand side of Eq. (4) shows that $r_{\ell}^{min}$ is due to two contributions. The term $k_B T \ln(P_{Si}/\bar{P}_{Si}^{eq})$ is from the liquid composition $\bar{C}$ coexisting with Si$_1$ of pressure $\bar{P}_{Si}$, which is supersaturated relative to the equilibrium liquid composition $\bar{C}^{eq}$ coexisting with Si$_1$ of pressure $\bar{P}_{Si}^{eq}$. This is seen by the use of Eq. (2) to obtain $k_B T \ln(P_{Si}/\bar{P}_{Si}^{eq}) = k_B T \ln(\gamma_{Si} C_{Si}^{eq}/\gamma_{Si} C_{Si} \bar{C}^{eq})$. The term $k_B T \ln(P_{Si}/\bar{P}_{Si})$ is due to vapor phase overpressure for restricting the liquid composition of $\bar{C}$ to a droplet of size $r_{\ell}^{max}$, as is seen by comparing it to Eq. (1). During SiNW growth, $r_{\ell}^{min}$ is changing but it still affects $r_{\ell}^{max}$ because the constancy of $r_{\ell}^{min}$ is maintained by transporting into the liquid a vapor phase Si atom of pressure $P_{Si}$ to replace the liquid phase Si atom consumed to grow the SiNW. That consumed Si atom has a chemical potential value including effects of both the liquid composition $\bar{C}$ and the droplet radius $r_{\ell}^{min}$.

Experimentally, VLS SiNWs are grown by decomposing SiH$_4$ over metal nanoparticles predeposited on substrates$^{6–10}$ by evaporating$^{8,11–13}$ or by laser ablating$^{6,14,15}$ M–Si alloy in gaseous ambients. In some cases it has been noticed that the SiNW size is smaller than the liquid droplet size$^{6,10}$ except when overcompensated by post-SiNW-growth oxidation due to exposure in air.$^7$ The fact that the SiNW size should be smaller than the liquid droplet size is seen by a comparison of Eqs. (1) and (4):

$$\frac{r_{\ell}^{min}}{r_{\ell}^{max}} = \frac{\Omega_{i} \sigma_{sv}}{2 \Omega_{i} \sigma_{e\ell}} \ln(P_{Si}/\bar{P}_{Si}) \frac{\bar{P}_{Si}}{\bar{P}_{Si}^{eq}}.$$  

(5)
lated curves are obtained using C¯ diagrams and the value 5 involved M–Si systems, using the appropriate phase
Eq.

In Fig. 3 the experimental data are within a faction of the
data of the activity coefficient values of the M–Si systems.
This needs the careful control of the pressures of both M1 and Si1 to a desired oversaturation level. Simply increase the Si1 pressure can drive the liquid droplet composition into the range \( C > C_{\text{max}} \) in Fig. 2 wherein only solid Si can exist, which will lead to direct nucleation of Si particles instead of VLS SiNW growth.

In conclusion, the thermodynamically allowed minimum sizes of nanowires grown by the VLS process have been examined, using SiNW grown from M–Si systems as the model case. There are two such sizes, one for the M–Si liquid droplet and the other for the SiNW. The liquid droplet minimum size is determined by a unique set of Si and M vapor phase pressure values. The SiNW minimum size contains two contributions, one depending on the liquid droplet composition and one depending on the droplet size. These expressions do not impose a limit on the minimum droplet and SiNW sizes. Thus, the SiNW can be grown to ever smaller sizes until reaching a kinetic limit that is presently not known. The sizes of a few smallest SiNWs appear to have approach some effective limits set by the liquid composition.

\( \Omega_f = \Omega_s \) and \( \ln(P_{Si}/\bar{P}_{Si}) < \ln(P_{Si}/\bar{P}_{\text{eq}}) \) hold, and \( \sigma_{sv} < 2\sigma_{\ell v} \) should hold, it is seen from Eq. (5) that \( r_s^\text{min} < r_{\ell}^\text{min} \) should also hold.

In experiments, SiNW of various sizes are found, because any liquid with \( r > r_s^\text{min} \) can grow. Clearly, those obtained using predeposited M nanoparticles will be strongly affected by the particle sizes.6–10 Presently, since the involved Si vapor phase pressure values are not known, Eq. (4) cannot be used for an accurate evaluation of the results. Here we use Eq. (4) to estimate the extent the SiNW sizes have reached by neglecting the effect of the finite size of the liquid droplet. Now, Eq. (4) is reduced to

\[
 r_s^\text{min} = \frac{\Omega_s \sigma_{sv}}{k_B T \ln(\bar{P}/\bar{P}_{\text{eq}})} = \frac{\Omega_s \sigma_{sv}}{k_B T \ln\left[ \gamma_{\text{Si}(C)/\gamma_{\text{Si}C_{\text{eq}}}C_{\text{eq}} \right]}
\]

The Si side of Fig. 2 shows that the maximum attainable Si concentration in the liquid droplet is \( C_{\text{max}} \), corresponding to the absolute attainable minimum wire size (due to the composition effect alone) at the maximum vapor phase Si pressure \( \bar{P}_{\text{max}} \). In Fig. 3 we compared some smallest SiNWs6–8,12,13 to the calculated minimum wire size for the involved M–Si systems, using the appropriate phase diagrams and the value \( \sigma_{sv} = 1610 \text{ ergs cm}^{-2} \). The calculated curves are obtained using \( \bar{C}_{\text{max}} \sim 1 \) and \( \gamma_{\text{Si}} \sim \gamma_{\text{SiC}} \) in Eq. (6). The latter condition means that the liquid is assumed to be an ideal solution, which is prompted by the lack of data of the activity coefficient values of the M–Si systems. In Fig. 3 the experimental data are within a faction of the calculated curves. These data include those stated by the authors,6,8,12,13 or measured by us from the authors’ results (e.g., from a micrograph);7 corrected (when possible),6,7 or uncorrected8,12,13 for oxidation effect after SiNW growth.

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