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

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(Received 8 April 2003; accepted 17 June 2003)

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.* [DOI: 10.1063/1.1599984]

Semiconductor nanowires (SNW) have the potential for continuing the solid state electronic circuitry miniaturization process beyond the 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 Si_1 and M_1 vapors, the M–Si liquid, and the solid SiNW. In 1965 Wagner and Ellis[3] 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 Si_1 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 Si_1 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[3] 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 $r^{\min}=(2\Omega_\ell\sigma_{\ell v})/(k_BT\ln S)$. Here Ω_ℓ is the volume of an average atom in the liquid, $\sigma_{\ell v}$ the liquid-vapor surface energy density, k_B is Boltzmann's constant, and T is the absolute temperature. We note that, however, this expression alone is not sufficient since a binary system is involved.

Due to the binary nature of the M–Si system, two minimum sizes are defined in the VLS process on the basis of thermodynamics: the minimum liquid droplet radius $r_\ell^{\min}$ and the minimum wire radius $r_s^{\min}$. Presently, a detailed expression for $r_s^{\min}$ is not available. Moreover, to ensure VLS SiNW growth, a set of conditions imposed by the binary nature of the system must be satisfied.

The minimum liquid droplet size $r_\ell^{\min}$ is equal to the critical radius of the M–Si liquid droplet nucleated by the two vapor phases M_1 and Si_1. Regarding the vapor phases as ideal gases with partial pressures P_{Si} and P_M, we obtain

$$r_\ell^{\min}=\frac{2\Omega_\ell\sigma_{\ell v}}{k_BT\ln(P_{Si}/\overline{P}_{Si})}=\frac{2\Omega_\ell\sigma_{\ell v}}{k_BT\ln(P_M/\overline{P}_M)}, \quad (1)$$

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

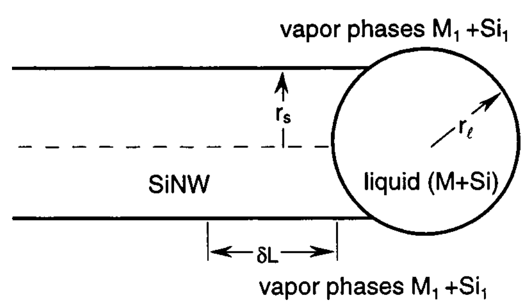

FIG. 1. A schematic diagram showing the VLS SiNW growth processes. Together with the radii of the liquid droplet and the SiNW, four phases of materials are indicated.

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tion (Si concentration) $\overline{C}$ in large quantity and having a *flat* surface. Here the trivial difference between $\sigma_{\ell v}$ and the SiNW-liquid interfacial energy density $\sigma_{s\ell}$ is ignored. The liquid composition $\overline{C}$ is determined by

$$\overline{C}=\frac{1}{\gamma_{\mathrm{Si}(\overline{C})}}\frac{\overline{P}_{\mathrm{Si}}}{B_{\mathrm{Si}}},\quad 1-\overline{C}=\frac{1}{\gamma_{\mathrm{M}(\overline{C})}}\frac{\overline{P}_{\mathrm{M}}}{B_{\mathrm{M}}}, \tag{2}$$

and the ratio

$$\frac{\overline{C}}{1-\overline{C}}=\frac{\gamma_{\mathrm{M}(\overline{C})}B_{\mathrm{M}}}{\gamma_{\mathrm{Si}(\overline{C})}B_{\mathrm{Si}}}\frac{\overline{P}_{\mathrm{Si}}}{\overline{P}_{\mathrm{M}}}. \tag{3}$$

In Eqs. (2) and (3) $\gamma_{\mathrm{Si}(\overline{C})}$ and $\gamma_{\mathrm{M}(\overline{C})}$ are, respectively, the extended (chemical) activity coefficients of Si and M in the liquid which are themselves functions of $\overline{C}$, and B_{X} is the pressure constant of the appropriate vapor species given by[4] $B_{\mathrm{X}}=(2\pi m_{\mathrm{X}}/h^2)^{3/2}(k_BT)^{5/2}$, 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 $r_s^{\min}$ is equal to the critical radius of a cylindrical Si crystal nucleated from the liquid droplet of radius $r_\ell^{\min}$ and of composition $\overline{C}$, which reads

$$\begin{aligned} r_s^{\min}&=\frac{\Omega_s\sigma_{\mathrm{sv}}}{k_BT\ln(P_{\mathrm{Si}}/\overline{P}_{\mathrm{Si}}^{\mathrm{eq}})}\\ &=\frac{\Omega_s\sigma_{\mathrm{sv}}}{k_BT\ln(\overline{P}_{\mathrm{Si}}/\overline{P}_{\mathrm{Si}}^{\mathrm{eq}})+k_BT\ln(P_{\mathrm{Si}}/\overline{P}_{\mathrm{Si}})}, \end{aligned} \tag{4}$$

where Ω_s is the volume of a Si atom in the SiNW and σ_{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) $\overline{P}_{\mathrm{Si}}^{\mathrm{eq}}$ is the Si vapor pressure over the equilibrium liquid with a flat surface and of composition $\overline{C}^{\mathrm{eq}}$, to be discussed shortly. Using the Si whisker size as a parameter, method (i) had 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 $r_s^{\min}$, i.e., there is no thermodynamic (energetic) reason preventing VLS SiNWs from reaching an ever 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 $\overline{C}$ is determined by the ratio of $\overline{P}_{\mathrm{Si}}$ and $\overline{P}_{\mathrm{M}}$, and Eq. (2) shows that for a given $\overline{C}$ the values of $\overline{P}_{\mathrm{Si}}$ and $\overline{P}_{\mathrm{M}}$ 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 $\overline{C}$ with flat surfaces via $P_{\mathrm{Si}}/P_{\mathrm{M}}=\overline{P}_{\mathrm{Si}}/\overline{P}_{\mathrm{M}}$. However, Eq. (1) is not sufficient for determining whether a SiNW can grow from the liquid droplet. The allowed value range of $\overline{C}$ 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 $\overline{C}$ only in region IV wherein $\overline{C}^{\mathrm{eq}}<\overline{C}<\overline{C}^{\max}$ holds, with $\overline{C}^{\mathrm{eq}}$ and $\overline{C}^{\max}$ 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 $\overline{C}>\overline{C}^{\mathrm{eq}}$, 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 $P_{\mathrm{Si}}>\overline{P}_{\mathrm{Si}}^{\mathrm{eq}}$ holding, if the liquid droplet composition ever dropped to $\overline{C}^{\mathrm{eq}}$ it will be restored rapidly to approach $\overline{C}$ by capturing the impinging Si_1 atoms while rejection of these atoms occurs at the solid Si surfaces.

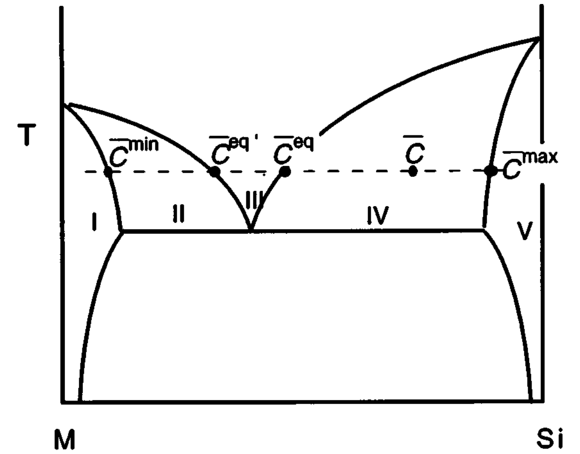

FIG. 2. A schematic phase diagram of a typical eutectic M–Si system. Note that the two primary solid phase regions are greatly exaggerated, particularly for the Si-rich phase which can actually not be discerned in an actual M–Si phase diagram, e.g., Au–Si. Also note the various (Si) concentrations indicated for the VLS SiNW growth process.

Via the two terms in its denominator, the most right-hand side of Eq. (4) shows that $r_s^{\min}$ is due to two contributions. The term $k_BT\ln(\overline{P}_{\mathrm{Si}}/\overline{P}_{\mathrm{Si}}^{\mathrm{eq}})$ is from the liquid composition $\overline{C}$ coexisting with Si_1 of pressure $\overline{P}_{\mathrm{Si}}$, which is supersaturated relative to the equilibrium liquid composition $\overline{C}^{\mathrm{eq}}$ coexisting with Si_1 of pressure $\overline{P}_{\mathrm{Si}}^{\mathrm{eq}}$. This is seen by the use of Eq. (2) to obtain $k_BT\ln(\overline{P}_{\mathrm{Si}}/\overline{P}_{\mathrm{Si}}^{\mathrm{eq}})=k_BT\ln[\gamma_{\mathrm{Si}(\overline{C})}\overline{C}/\gamma_{\mathrm{Si}(\overline{C}^{\mathrm{eq}})}\overline{C}^{\mathrm{eq}}]$. The term $k_BT\ln(P_{\mathrm{Si}}/\overline{P}_{\mathrm{Si}})$ is due to vapor phase overpressure for restricting the liquid of composition $\overline{C}$ to a droplet of size $r_\ell^{\min}$, as is seen by comparing it to Eq. (1). During SiNW growth, $r_\ell^{\min}$ is unchanging but it still affects $r_s^{\min}$ because the constancy of $r_\ell^{\min}$ is maintained by transporting into the liquid a vapor phase Si atom of 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 $\overline{C}$ 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):

$$\frac{r_s^{\min}}{r_\ell^{\min}}=\frac{\Omega_s\sigma_{\mathrm{sv}}}{2\Omega_\ell\sigma_{\ell v}}\frac{\ln(P_{\mathrm{Si}}/\overline{P}_{\mathrm{Si}})}{\ln(P_{\mathrm{Si}}/\overline{P}_{\mathrm{Si}}^{\mathrm{eq}})}. \tag{5}$$

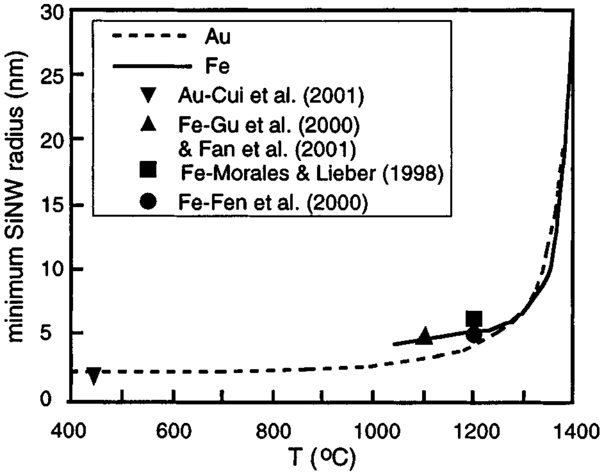

FIG. 3. Experimental data of some available smallest SiNWs compared to calculated curves using Eq. (6) for the appropriate M–Si system. The used Si surface energy density value is $\sigma_{sv} = 1610\ \mathrm{ergs\,cm^{-2}}$, from Ref. 5, and the used Au–Si and Fe–Si phase diagrams are from Ref. 16.

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

In experiments, SiNW of various sizes are found, because any SiNW with $r > r_s^{\min}$ 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

$$r_s^{\min} = \frac{\Omega_s \sigma_{sv}}{k_B T \ln(\bar{P}/\bar{P}^{\mathrm{eq}})} = \frac{\Omega_s \sigma_{sv}}{k_B T \ln[\gamma_{\mathrm{Si}(\bar{C})}\bar{C}/\gamma_{\mathrm{Si}(\bar{C}^{\mathrm{eq}})}\bar{C}^{\mathrm{eq}}]}. \quad (6)$$

The Si side of Fig. 2 shows that the maximum attainable Si concentration in the liquid droplet is $\bar{C}^{\max}$, corresponding to the absolute attainable minimum wire size (due to the composition effect alone) at the maximum vapor phase Si_1 pressure $\bar{P}^{\max}$. In Fig. 3 we compared some smallest SiNWs[6–8,12,13] to the calculated minimum wire size for the involved M–Si systems, using the appropriate phase diagrams[16] and the value[5] $\sigma_{sv} = 1610\ \mathrm{ergs\,cm^{-2}}$. The calculated curves are obtained using $\bar{C}^{\max} \sim 1$ and $\gamma_{\mathrm{Si}} - \sim \gamma^{\mathrm{eq}}_{\mathrm{Si}}$ 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 uncorrected[8,12,13] for oxidation effect after SiNW growth. Since in Fig. 3 the calculated curves do not include the effect of the finite size of the liquid droplet, they are those using an effective liquid composition to represent effects of the actual liquid composition and the droplet size. Thus, there is still room for further reducing the SiNW sizes. This needs the careful control of the pressures of both M_1 and Si_1 to a desired oversaturation level. Simply increase the Si_1 pressure can drive the liquid droplet composition into the range $\bar{C} > \bar{C}^{\max}$ 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.

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