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Critical condition for growth of silicon nanowires

Florian Dhalluin[a)]
Laboratoire des Technologies de la Microélectronique, CNRS, Université Joseph Fourier, UMR 5129, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France and Laboratoire Photonique sur Silicium, CEA/LETI, MINATEC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Pierre J. Desré
Laboratoire Photonique sur Silicium, CEA/LETI, MINATEC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Martien I. den Hertog
Laboratoire d'Étude des Matériaux par Microscopie Avancée, CEA/DRFMC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Jean-Luc Rouvière
Laboratoire d'Étude des Matériaux par Microscopie Avancée, CEA/DRFMC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Pierre Ferret
Laboratoire Photonique sur Silicium, CEA/LETI, MINATEC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Pascal Gentile
Laboratoire Silicium Nanoélectronique Photonique et Structure, CEA/DRFMC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Thierry Baron[b)]
Laboratoire des Technologies de la Microélectronique, CNRS, Université Joseph Fourier, UMR 5129, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

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The existence of a critical radius on the growth of Si nanowires by the vapor-liquid-solid mechanism is examined. By varying the experimental growth parameters, we have shown a dependence of the minimum nanowires radius with the Si reactive species partial pressure, demonstrating that the critical radius is not a limited one. A thermodynamical model giving a quantitative aspect of the dependence of a critical nanowire diameter on Si supersaturation in a Au-Si droplet is proposed. These results open up a way to grow many kinds of nanowires with nanometric diameter. The size control has important implications for electronic and optical properties of nanowires based devices.
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I. INTRODUCTION

Semiconductor nanowires (NWs) have been drawing more and more interest for some time, due to their numerous potential applications in nanoelectronics devices,[1] including interconnects,[2] transistor channels,[3] nanoelectrodes, or in the emerging application areas of photonics,[4] chemical sensors,[5] and solar cells. One of the most common ways to grow such nano-objects is the vapor-liquid-solid process (VLS).[6,7] In this process, material from vapor is incorporated in a binary liquid alloy droplet, which acts as a transient phase leading to the material growth. In the silicon nanowires case, the liquid alloy may be composed of a mixture of gold and silicon. Gas, such as silane or disilane, can be used as a vapor reactant. VLS can be decomposed in several steps: (1) the dissociative adsorption of silicon containing gaseous molecules at the droplet surface; (2) the silicon dissolution in the droplet, (3) its migration to the liquid-solid interface, and (4) the silicon atoms accretion to the wire.[8]

The physical properties of the NWs and so those of devices based on these structures strongly depend on the NWs size, and particularly for diameter under 10 nm where quantum confinement becomes important.[9–11] A key point is to control this size precisely and it requires understanding of the growth mechanism for small diameter. Some thermodynamic aspects of VLS have been mainly studied by Givargizov,[8] Tan,[12,13] and Ross.[14] On the basis of the Gibbs–Thomson relation and silicon vapor supersaturation, Givargizov has shown the existence of a critical radius under which no growth happens.[8] More recently, Tan *et al.* give a thermodynamic approach and conclude that there is no critical wire diameter.[12,13] In another topic, Ross *et al.* have explained Si NWs sawtooth faceting on the basis of a surface energy balance.[14] However, the thermodynamic aspect concerning the critical conditions of driving force for NW growth seems not to have been expressed at this time.

[a)]Electronic mail: florian.dhalluin@cea.fr
[b)]Electronic mail: thierry.baron@cea.fr

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Here we present an experimental study coupled with a thermodynamical approach to understand the critical parameters which prevent the growth of small diameter nanowires. We focus on a classical system, i.e., Si NWs obtained by the VLS process with gold as a catalyst. To obtain very small diameter and efficient catalyst (<10 nm), we use a two step process. First, we grow large diameter NWs which are covered by nanometric Au particles at the sidewalls. Second, we change the experimental parameters (Si reactive species partial pressure, growth temperature) to grow the nanometric diameter NWs from the nanometric particles at the sidewalls. In other words, we grow Si nanotrees (SiNTrs) with nanometric branches, without redeposing metallic seeds between growths. We show the existence of a silane partial pressure dependent critical radius, under which no branches grow. Then we identify the critical condition about driving force for small Si NWs diameter growth. Finally, we estimate the concentration of Si in the Au/Si droplet corresponding to each experimental critical radius.

II. EXPERIMENTAL PROCEDURE

SiNTrs were elaborated by chemical vapor deposition in a two steps growth process via the VLS mechanism on a (111) Si substrate in a low pressure chemical vapor deposition reactor at a base pressure held constant at 20 mbar. Gold was used as the catalyst, silane (SiH_4) as the Si source, and hydrogen (H_2) as a carrier gas. Small pieces of 10 mm $\times 10$ mm substrates were first deoxidized in a HF solution. 2 nm of gold were then deposited on these surfaces in a vacuum pressure of 10^{-6} Pa. The substrates were then loaded in the reactor and annealed under a H_2 flow, in order to form nanocatalysts by the dewetting of the Au layer. After cooling down the substrate to the growth temperature, SiH_4 was introduced. It is known for Si NWs grown by VLS that gold remains on the NWs sidewalls.[15–18] Energy dispersive x-ray (EDX) and scanning transmission electron microscope (STEM) analysis performed after the first growth step show bright spots identified as gold rich clusters of 3–4 nm diameter and 2 nm thickness (Fig. 1). These gold clusters were used as a reproducible way to obtain highly chemically reactive nanoseeds with a small and rather controlled diameter for branches growth. Then a second growth is carried out at 500 °C to obtain silicon nanobranches (SiNBs) from the gold particles present on the trunks. This second growth has been processed at different silane pressure: $P_{SiH_4} = 1.023, 0.267, 0.134, 0.054$ mbar.

III. RESULTS AND DISCUSSION

Figure 2 shows scanning electron microscopy (SEM) pictures of SiNTrs. We focus our attention only on SiNBs obtained by varying P_{SiH_4} and we show that their density decreases with P_{SiH_4}. The thinnest branches are obtained for the highest P_{SiH_4}, which means there is a dependence of the minimum branch radius with P_{SiH_4}. For $P_{SIH_4} = 0.054$ mbar and $P_{SIH_4} = 1.023$ mbar, the minimum radius measured decreases from 25 to 5 nm, respectively.

The minimum radius for each silane pressure is reported on Fig. 3. One can define two areas: one where SiNBs growth is possible and the other one where the presence of branches is not observed. It must be underlined that this critical radius is not an absolute one as it is silane pressure dependent. We will show that thermodynamics could give an explanation about this phenomenon, assuming that an increase of P_{SiH_4} leads to an increase of the supersaturation in silicon of the Au-Si droplet.

Our thermodynamic analysis is focused on the definition of initial conditions in the liquid Au/Si droplet to be fulfilled in order that branches and more generally speaking small diameter NWs growth proceeds via VLS. Recently, Kodambaka *et al.*[19] have proved from *in situ* measurements that the silicon nanowires VLS growth is controlled by the decomposition kinetics of the gaseous precursor at the surface of the Au/Si droplet, provided that this decomposition is irreversible or does not imply silicon removal after decomposition.

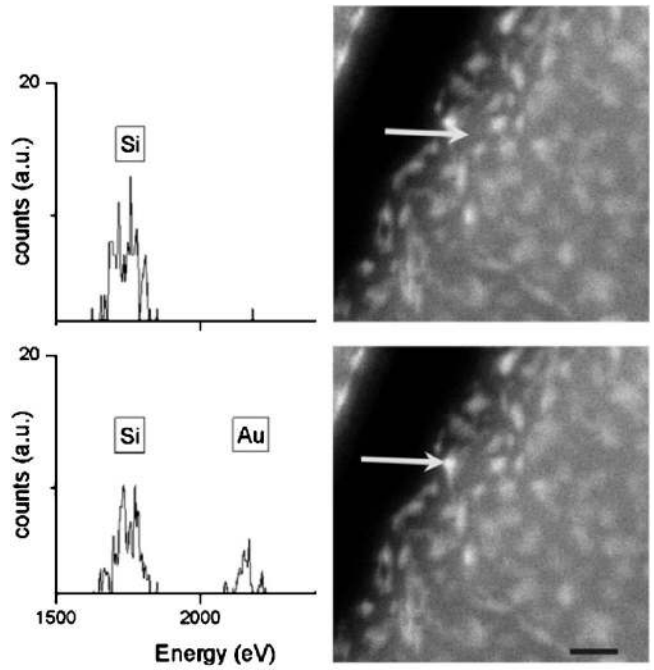

FIG. 1. EDX spectra and STEM images of a silicon nanowire. An arrow indicates where the EDX spectrum has been taken. The brighter particles are unambiguously gold rich clusters, as three typical gold lines appear in the EDX spectrum around 2200 eV. The scale bar is 10 nm.

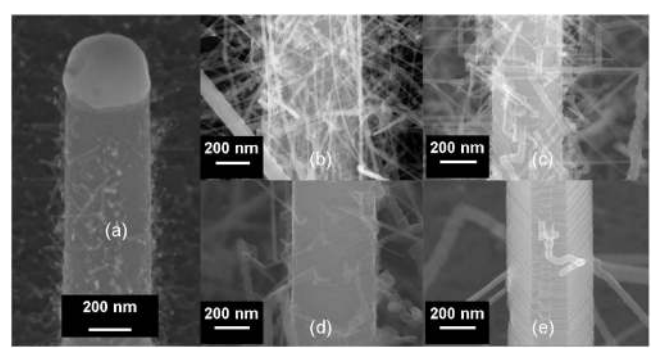

FIG. 2. SEM view of a silicon nanotree (a) and nanobranches grown at different silane partial pressures: (b) under 1.023, (c) 0.267, (d) 0.134, and (e) 0.054 mbar. Temperature was held at 500 °C during the branches growth. While silane partial pressure decreases, branch density decreases, and minimum branch radius increases.

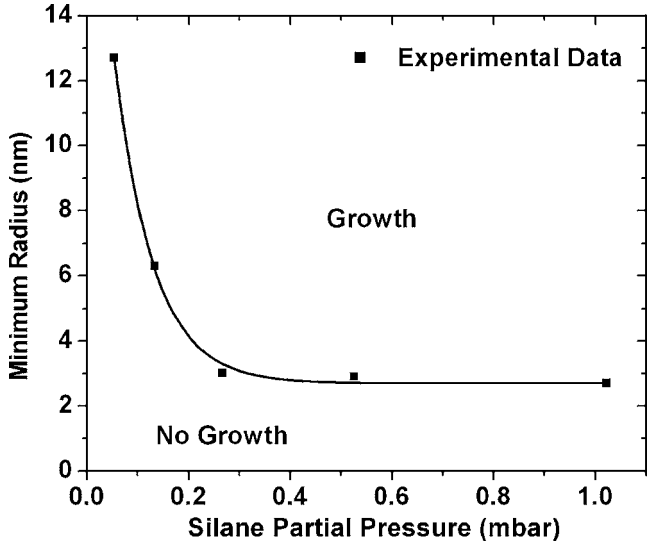

FIG. 3. Minimum branch radius vs partial silane pressure. Two areas exist: one where SiNBs growth is possible and the other one where the presence of branches is not observed, which means a silane pressure dependent critical radius exists, under which the nanobranches do not grow.

Arguing from the fact that the process is controlled by the kinetics of adsorption and decomposition of precursor gas at the droplet surface and that silane and disilane have the same behavior on the VLS mechanism, we consider that the initial state for the thermodynamic description is when Au/Si droplets are already supplied with silicon (which means that the initial thermochemical aspect concerning the decomposition reaction is not taken into account). Furthermore, as diffusion of Si in the droplet is not the rate limiting step,[19] a very small silicon concentration gradient is expected in the liquid and the silicon molar fraction x_{Si}^*, can be taken as being uniform through the droplet.

At first, our thermodynamic approach consists in expressing, from a general point of view, the molar Gibbs energy of crystallization of Si from a AuSi liquid alloy—$\Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P)$—under pressure P and at temperature T versus $\Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P_0)$, where $P_0=1$ bar. The molar Gibbs energy of crystallization of Si, from a Au/Si binary alloy, with Si molar fraction x_{Si}^*, is classically expressed versus chemical potentials of Si as

$$\Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P,x_{\mathrm{Si}}^*) = \mu_{\langle\mathrm{Si}\rangle}(T,P) - \mu_{[(\mathrm{Si})]}(T,P,x_{\mathrm{Si}}^*), \tag{1}$$

where $\mu_{\langle\mathrm{Si}\rangle}(T,P)$ is the chemical potential of crystal Si and $\mu_{[(\mathrm{Si})]}(T,P,x_{\mathrm{Si}}^*)$ is the chemical potential of Si in the liquid alloy of concentration x_{Si}^*, which measures the supersaturation of the droplet in Si.

Introducing the chemical potential of pure liquid Si as a reference $\mu_{(\mathrm{Si})}^0(T,P)$ in Eq. (1) it follows:

$$\begin{aligned}\Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P,x_{\mathrm{Si}}^*) &= (\mu_{\langle\mathrm{Si}\rangle}(T,P) - \mu_{(\mathrm{Si})}^0(T,P)) \\ &\quad - (\mu_{[(\mathrm{Si})]}(T,P,x_{\mathrm{Si}}^*) - \mu_{(Si)}^0(T,P)) \\ &= -\Delta G_{m,\mathrm{Si}}^{\mathrm{melt}}(T,P) - RT\ln a_{[(\mathrm{Si})]}^*(T,P,x_{\mathrm{Si}}^*),\end{aligned} \tag{2}$$

where $\Delta G_{m,\mathrm{Si}}^{\mathrm{melt}}(T,P)$ is the silicon molar Gibbs energy of melting. $a_{[(\mathrm{Si})]}^*$ is the activity of Si in liquid Au, Si at T and P corresponding to silicon molar fraction x_{Si}^*; (note that classically, for a component i in a solution, a_i and x_i are linked by the relation $a_i=\gamma_i.x_i$, where γ_i is the activity coefficient of component i; and γ_i is a function of T, P, and x_i).

Note that no crystallization driving force is available when $\Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P)=0$. Under such an equilibrium condition, one has from Eq. (2),

$$RT\ln a_{[(\mathrm{Si})]}^{\mathrm{eq}}[T,P,x_{\mathrm{Si}}^{\mathrm{eq}}(T,P)] = -\Delta G_{m,\mathrm{Si}}^{\mathrm{melt}}[T,P,x_{\mathrm{Si}}^{\mathrm{eq}}(T,P)], \tag{3}$$

where $a_{[(\mathrm{Si})]}^{\mathrm{eq}}[T,P,x_{\mathrm{Si}}^{\mathrm{eq}}(T,P)]$ is the activity of Si for concentration $x_{\mathrm{Si}}^{\mathrm{eq}}(T,P)$, at temperature T under pressure P, when equilibrium between liquid and silicon crystal is attained.

Returning to the general case where $\Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P,x_{\mathrm{Si}}^*) \neq 0$ and differentiating relation (2) versus pressure P at constant T and given concentration x_{Si}^* one obtains

$$\begin{aligned}&\left[\frac{\partial \Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P,x_{\mathrm{Si}}^*)}{\partial P}\right]_{T,x_{\mathrm{Si}}^*} \\ &= -\left[\frac{\partial \Delta G_{m,\mathrm{Si}}^{\mathrm{melt}}(T,P,x_{\mathrm{Si}}^*)}{\partial P}\right]_{T,x_{\mathrm{Si}}^*} \\ &\quad - \left[\frac{\partial RT\ln a_{\mathrm{Si}}^*(T,P,x_{\mathrm{Si}}^*)}{\partial P}\right]_{T,x_{\mathrm{Si}}^*} \\ &= -\Delta V_{m,\mathrm{Si}}^{\mathrm{melt}}(T,P) - \Delta \bar{V}_{m,\mathrm{Si}}(T,P,x_{\mathrm{Si}}^*),\end{aligned} \tag{4}$$

where $\Delta V_{m,\mathrm{Si}}^{\mathrm{melt}}(T,P)=V_{m,(\mathrm{Si})}^0 - V_{m,\mathrm{Si}}^{\mathrm{cryst}}$ is the molar variation of volume on melting which is a negative quantity for silicon.[20] $V_{m,(\mathrm{Si})}^0$ is the molar volume of pure liquid Si and $V_{m,\langle\mathrm{Si}\rangle}$ is the molar volume of crystal Si. $\Delta \bar{V}_{m,\mathrm{Si}}=\bar{V}_{m,[(\mathrm{Si})]}-V_{m,(\mathrm{Si})}^0$ is the "partial volume of mixing" of Si in the undercooled Au/Si liquid alloy. $\bar{V}_{m,[(\mathrm{Si})]}$ is the partial molar volume of Si in the alloy liquid droplet.

Integrating relation (4) at constant T and x_{Si}^* between pressure P_0 and P and considering that the Au, Si liquid alloy and solid silicon are uncompressible, in a first approximation, it follows:

$$\begin{aligned}\Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P,x_{\mathrm{Si}}^*) &= \Delta G_{m,\mathrm{Si}}^{\mathrm{cryst}}(T,P_0,x_{\mathrm{Si}}^*) - [\Delta V_{m,\mathrm{Si}}^{\mathrm{melt}}(T) \\ &\quad + \Delta \bar{V}_{m,\mathrm{Si}}(T,x_{\mathrm{Si}}^*)][P-P_0].\end{aligned} \tag{5}$$

Let us return to the actual VLS process configuration where an ensemble of Au/Si droplets is initially in contact with the silicon substrate. Owing to their nanometric size, the internal pressure within them is high and may attain several kilobars when radius is only of few nanometers. This pressure P is given by the classical Laplace relation, which, applied to spherical droplet of radius r_d, is written: $P-P_0 = 2\sigma_{\mathrm{Au,Si}}(T,x_{\mathrm{Si}}^*)/r_d$, where P_0 is taken equal to 1 bar. $\sigma_{\mathrm{Au,Si}}(T,x_{\mathrm{Si}}^*)$ is the surface energy of the droplet of radius r_d, with composition x_{Si}^*, at temperature T.

The real system, corresponding to a Au/Si droplet laying on a Si substrate, is modeled by a thermodynamics equivalence in which the system is represented by a thin Au/Si alloy liquid layer in contact with the Si substrate, with the

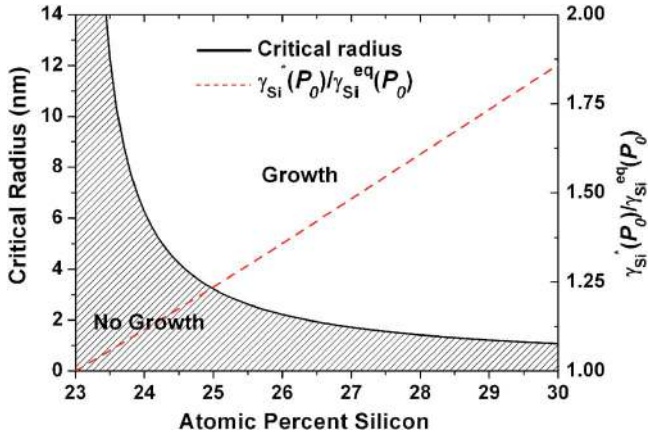

FIG. 4. (Color online) Critical radius droplet (solid line) and $\gamma_{Si}^{*}(P_0)/\gamma_{Si}^{eq}(P_0)$ (dashed line) vs the concentration of silicon in the Au/Si droplet. The critical radius droplet is the radius for which the driving force of Si crystallization in the Au-Si droplet on Si substrate gets cancelled.

same composition x_{Si}^{*} than that of the Au/Si droplet, and under an external pressure P equal to that in the droplet.

Reminding one that crystallization is not thermodynamically possible when $\Delta G_{m,Si}^{cryst}(T,P,x_{Si}^{*}) \geq 0$, the condition $\Delta G_{m,Si}^{cryst}(T,P,x_{Si}^{*})=0$ and the Laplace relation introduced in Eq. (5), allows one to formally define a critical droplet radius $r_{d,c}$ for wire growth, which is supersaturation dependent

$$r_{d,c} = \frac{2[\Delta V_{m,Si}^{melt}(T) + \Delta \bar{V}_{m,Si}(T,x_{Si}^{*})]\sigma_{AuSi}(T,x_{Si}^{*})}{\Delta G_{m,Si}^{cryst}(T,P_0,x_{Si}^{*})}, \quad (6)$$

where $r_{d,c}$ is only significant when the numerator and denominator of the fraction appearing in Eq. (6) have the same sign. Yet, as mentioned before, $\Delta V_{m,Si}^{melt}(T,P)$ is negative for silicon and can be evaluated. On the contrary, the partial molar volume of mixing $\Delta \bar{V}_{m,Si}$ which appears in Eq. (6) is unknown, but it is expected to be negative owing to the relatively strong heteroatomic interactions between Au and Si in the liquid state (as reflected by the negative enthalpy of formation of liquid AuSi—$\Delta H_f \approx -10$ kj/mole—and the existence of a particularly deep eutectic). Hence, the critical droplet radius for Si NWs growth, $r_{d,c}$, only exists when the Gibbs energy of crystallization of Si $P_0=1$ bar, $\Delta G_{m,Si}^{cryst}(T,P_0,x_{Si}^{*})$, is negative.

$\Delta G_{m,Si}^{cryst}(T,P_0,x_{Si}^{*})$ can be classically expressed as a function of the activities by the relation

$$\Delta G_{m,Si}^{cryst}(T,P_0,x_{Si}^{*}) = -RT \ln \frac{a_{Si}^{*}(T,P_0,x_{Si}^{*})}{a_{Si}^{eq}[T,P_0,x_{Si}^{eq}(T,P_0)]}$$
$$= -RT \ln \frac{\gamma_{Si}^{*}(T,P_0,x_{Si}^{*})x_{Si}^{*}}{\gamma_{Si}^{eq}(T,P_0)x_{Si}^{eq}(T,P_0)}, \quad (7)$$

where $x_{Si}^{eq}(T,P_0)$ is the molar fraction of silicon in the liquid at equilibrium with solid silicon under $P_0=1$ bar at temperature T. This is the concentration given by the classical phase diagram at T and P_0. $\gamma_{Si}^{*}(T,P_0,x_{Si}^{*})$ and $\gamma_{Si}^{eq}(T,P_0)$ are, respectively, the activity coefficients corresponding to concentration x_{Si}^{*} and $x_{Si}^{eq}(T,P_0)$. The ratio $\gamma_{Si}^{*}(T,P_0,x_{Si}^{*})/\gamma_{Si}^{eq}(T,P_0)$ is superior to one and increases with Si concentration in the droplet, as depicted in Fig. 4 (dashed line).[21] The term $\ln[\gamma_{Si}^{*}(T,P_0,x_{Si}^{*})x_{Si}^{*}/\gamma_{Si}^{eq}(T,P_0)x_{Si}^{eq}(T,P_0)]$ on the right hand side of Eq. (7) is designated as the supersaturation term $[x_{Si}^{*} > x_{Si}^{eq}(T,P_0)]$.

Therefore, $r_{d,c}$ can be rewritten

$$r_{d,c} = \frac{-2[\Delta V_{m,Si}^{melt}(T) + \Delta \bar{V}_{m,Si}(T,x_{Si}^{*})]\sigma_{Au,Si}(T,x_{Si}^{*})}{RT \ln\left[\frac{\gamma_{Si}^{*}(T,P_0,x_{Si}^{*})}{\gamma_{Si}^{eq}(T,P_0)} \frac{x_{Si}^{*}}{x_{Si}^{eq}(T,P_0)}\right]}. \quad (8)$$

It results from Eq. (8) that the greater supersaturation is the smaller critical radius $r_{d,c}$. It must be emphasized that the existence of such a critical droplet radius, which is primary due to the high internal pressure in the nanometer size droplet, becomes effective owing to the specific physical property of silicon of being more compact in the liquid state than in the solid state ($\Delta V_{m,Si}^{melt} < 0$). Hence, the same conclusions could be drawn for any kind of NWs, provided this later condition is fulfilled, as it is for Ge,[20] Ga,[22] Bi,[20] Ce,[23] La,[24] and Pr.[24] It must also be noted that the as defined critical droplet radius must be distinguish from that which would derive from the classical thermodynamic treatment nucleation. In other words, the critical radius given by Eq. (6) is a necessary condition for nanowires growth but could not be a sufficient one owing to possible nucleation phenomena.

In order to compare the value of $r_{d,c}$ with the ones of the experimental critical radii, relation (8) has been applied for $T=500$ °C (773 K). $\Delta V_{m,Si}^{melt}$ has been evaluated from the data given by the literature at the silicon melting point[26] $\Delta V_{m,Si}^{melt}(T_{Si}^{melt}) = -0.117 \times 10^{-5}$ m^3/mole and after temperature corrections using the thermal expansion[25] of solid Si:[26] $\alpha_{Si}^{s} = (1/V_{Si}^{s})(\partial V_{Si}^{s}/\partial T)_P = 9 \times 10^{-6}$ and liquid Si:[26] $\alpha_{Si}^{l} = (1/V_{Si}^{l}) \times (\partial V_{Si}^{l}/\partial T)_P = 1.4 \times 10^{-4}$, taken as a constant in the undercooled range up to $T=773$ K. This leads to $\Delta V_{m,Si}^{melt}(T=773\ \text{K}) = -0.245 \times 10^{-5}$ m^3/mole. Note that, as the thermal expansion is higher in liquid phase than in Si crystal and as undercooling is important, this leads to a significant temperature correction for $\Delta V_{m,Si}^{melt}$. However, the absolute value of $\Delta V_{m,Si}^{melt}$ at 773 K is possibly overestimated due to the supposed constancy of the liquid expansion coefficient in the large undercooled range considered in this application. As mentioned before, the partial molar volume of mixing of Si in Au, Si liquid alloy $\Delta \bar{V}_{m,Si}$ at $T=773$ K is expected to be negative. If so, the effect of the partial volume is added to the one resulting from the negative variation of molar volume on melting. Because of the lack of data for the expected additive effect due to the partial volume of mixing, $\Delta \bar{V}_{m,Si}$ has not been taken into account in the following application.

Again, owing to the relatively strong atomic interactions in the Au-Si liquid alloy, it has been proved[26] that the surface energy of liquid Au-Si does not vary significantly with Si concentration in the Si concentration range $0 < x_{Si} < 0.3$. So the value of the surface energy for the alloy Au-Si has been taken equal to that of pure Au (Ref. 27) ($\sigma_{Au} = 1.145$ J m^{-2}) but after temperature correction from the silicon melting temperature to $T=773$ K and with a temperature coefficient $d\sigma/dT = -0.19 \times 10^{-5}$ J m^{-2} K^{-1},[28] this leads to $\sigma_{Au,Si} = 1.25$ J m^{-2}. On the basis of the previous data, the variation of $r_{d,c}$ versus x_{Si}^{*} is represented in Fig. 4, $x_{Si}^{eq}(T,P_0)$ equal to 23% at 773 K.[29]

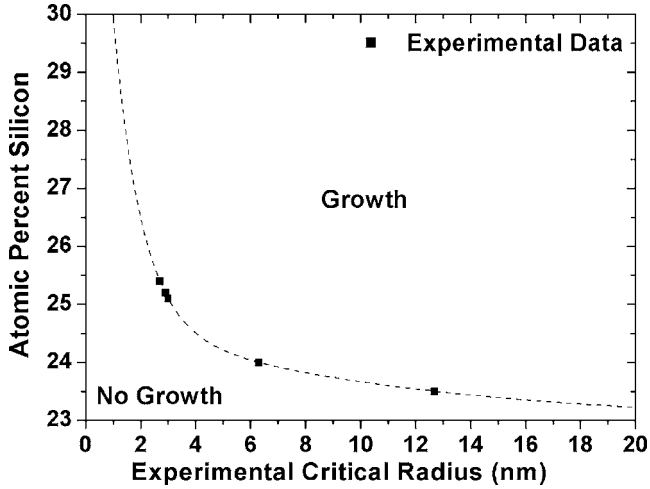

FIG. 5. Amount of silicon in Au/Si droplet vs experimental critical radius.

The critical condition about driving force for SiNBs and more generally small diameter NWs growth given by the present thermodynamic analysis appears to be in fairly good agreement with the experimental results where it has been revealed that possible wire growth depends on the precursor partial pressure. The supersaturation being certainly an increasing function of the partial pressure of the precursor gas, the previous experimental and theoretical results confirm that the relevant parameter for possible growth is the amount of supersaturation in the Au/Si droplet, represented in the present approach by the previously defined supersaturation term.

An experimental critical droplet radius could be associated to each branch minimum radius, $r_{b,\min} \approx r_{d,c}$, in order to estimate the silicon amount in the Au/Si droplet necessary for the SiNBs growth (at $T=500$ °C). Figure 5 depicts the amount of Si in Au/Si (at $T=773$ K) versus the experimental droplet radius. We find for radii inferior to 3 nm, a concentration of silicon in the Au/Si droplet setting between 25.1% and 25.4% though it is 23% for bulk at equilibrium, which is the limit of the curve when extrapolated for infinite radius. By extrapolating the curve for small radius, we can predict how much high the amount of silicon in the Au/Si droplet should be to grow branch of diameter under 1 nm: $x_{\mathrm{Si}}^{*} > 30\%$.

IV. CONCLUSIONS

In conclusion, we have experimentally demonstrated a dependence of the critical Si NWs diameter with the Si reactive species partial pressure during VLS growth and we have proposed a thermodynamic origin which gives a quantitative aspect of the dependence of the critical diameter versus the droplet supersaturation with Si. Our results provide insight into the physical processes controlling the growth of small diameter (<10 nm) NWs in the Si/Au system and this can be extended to materials for which atomic density is higher in the liquid state than in the crystalline state.

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