DETERMINATION OF STABLE AND METASTABLE DIAGRAMS INVOLVED IN THE DEVELOPMENT OF SEMICONDUCTOR NANOWHISKERS[1]

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Abstracts

Semiconductor nanowires are developed by many synthetic routes using gas, condensed phases and nanosized liquid metals such as gold droplets deposited on a silicon wafer. The supersaturation put forward to describe the process, needs the presence of a driving force allowing the evolution of the system between two metastable states. When the silicon is brought by a precursor such as silane or chlorosilane, the presence of a driving force is obvious and a coherent mechanism may be developed. When nanowires are grown without gaseous precursor, it is not clear whether or not the process implies the existence of metastable states and the mechanisms presented in the literature often contradicts the laws of phase diagrams. A coherent model is presented, using elementary thermodynamics by taking into account surface phenomena. Such a model having shown with silicon its predictive capacity, for instance the relationship between bulk and surface compositions or the existence of a minimum diameter for the silicon nanowire, it enlightens strongly the understanding of observed phenomena. The model has been successfully applied to the synthesis of germanium nanowires without precursor gas and the growth conditions for III-V semiconductors such as gallium arsenide has also been devised.

Keywords: Nanowires; Phase diagrams; Thermodynamics.

DETERMINAÇÃO DOS DIAGRAMAS ESTÁVEIS E METAESTÁVEIS EM RELAÇÃO AO DESENVOLVIMENTO DE NANOFIOS SEMICONDUTORES

Resumo

Os nanofios semicondutores são sintetizados por diferentes métodos usando um gás, fases condensadas e nano-gotas metálicas como, por exemplo, gotas de ouro depositadas sobre uma bolacha de silício. A supersaturação, necessária para descrever o processo de síntese, carece duma força motriz que permita a evolução do sistema entre dois estados metaestáveis. Se silício é fornecido por um precursor, tal como silano ou clorosilano, a presença da força motriz é óbvia e um mecanismo coerente pode ser desenvolvido. O problema torna-se mais complexo quando nanofios crescem sem precursor gasoso. Ainda não é claro se o processo implica a existência de estados meta-estáveis, até porque os mecanismos frequentemente apresentados na literatura contradizem as regras dos diagramas de fases. O objetivo deste trabalho é de mostrar como os argumentos de natureza termodinâmica e os dados experimentais fornecem um modelo geral e mais adequado para descrever o mecanismo SLS, envolvido no crescimento de nanofios cristalinos à base de silício. Este modelo já foi aplicado com sucesso para o crescimento de nanofios de germânio, assim como de semicondutores III-V.

**Palavras-chave:** Nanofios; Diagramas de fases; Termodinâmica.

INTRODUCTION

Semiconductor nanowires are one-dimensional structures, with unique electrical and optical properties, that are used as building blocks in nanoscale devices. Their low dimensionality means that they exhibit new properties such as quantum confinement effects, an increase of band gap compared to the bulk material.

Researchers have examined various ways of growing semiconductor nanowires, including laser ablation, chemical vapour deposition (CVD), template-assisted growth, and evaporation of condensed phases. All these approaches provide bulk quantities of semiconductor nanowires but they do not provide much control over the composition, size or crystallographic direction of the nanowire.

The growth of nanowires is commonly described either by the vapor-liquid-solid (VLS) or solid-liquid-solid (SLS) process.

A typical VLS mechanism starts with the dissolution of gaseous precursors (SiH_4, or GeH_4) into a nanosized liquid alloy droplet (metal-semiconductor) considered as a catalytic site. Once the liquid droplet is supersaturated with semiconductor component, the precipitation of solid semiconductor nanowire occurs. The process was named the VLS after the three phases involved (Figure 1).
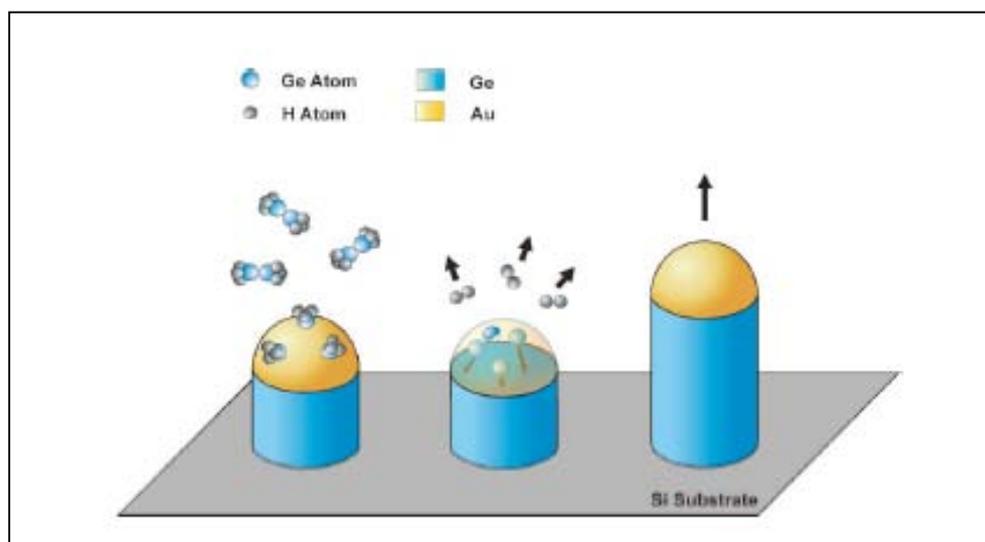
Figure 1: Scheme of semiconductor nanowires growth by the VLS mechanism

In the SLS process, silicon-based nanowires, such as those shown in Figure 2 are formed when metal (Au)-coated silicon substrate (wafer) are heated at high temperature in a stream of argon containing less than 10% of hydrogen. In that process, no gaseous precursor of silicon is used. The SLS process has been tentatively explained [1-4] by the silicon diffusion from the substrate to the gold-silicon melt formed on the surface at high temperature. With time, more silicon, from the substrate, diffuses into the droplet, making it supersaturated with silicon and then the coexisting pure silicon phase precipitates and crystallizes as nanowires. Because, during this process, the only source of silicon available is the one issued from the wafer, the process was termed SLS. It must be pointed out that, to our knowledge, no clear-cut evidence has been demonstrated in the literature to prove the unlimited dissolution of silicon from solid substrate into the droplet. It may be worthwhile to remind at this point some of the basic ideas on the solubility of a solute in a solvent. A solution said saturated with a solute is incapable of dissolving greater quantities of

that particular solute under equilibrium conditions. Supersaturation needs the presence of a driving force.
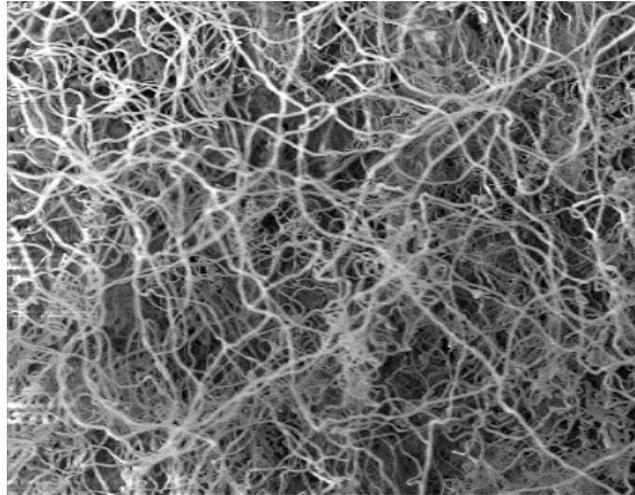
Figure 2: Nanowires grown by the SLS process

From a thermodynamic point of view, it is easy to accept the saturation of gold with silicon from the substrate. However, once the saturation is obtained, the chemical potential of silicon in solid, liquid alloy (metal-Si) and gaseous phases is the same, and there is no energetic reason for the silicon of the wafer to supersaturate the binary liquid phase.
The problem in these processes is to know how to reach supersaturation.

THE VLS PROCESS

In the VLS process, conditions are created where the vapor phase (SiH_4) is thermodynamically unstable relative to formation of the solid material to be prepared in condensed nanowires form. This includes usual situation of supersaturated vapor. Continuous vapor delivery provides the driving force for diffusion of the semiconductor from the liquid-catalyst particle surface to the growth interface. The driving force is easily obtained from the reaction:

$$SiH_4 \rightarrow Si + 2\,H_2 \qquad [1]$$
$$\Delta_{r1}G° = -40\,804 - 32.2835\,T \ln T + 127.2426\,T + 0.01443\,T^2$$
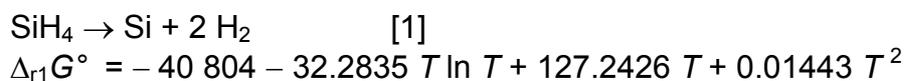
The above expression may be used with a maximum precision between 600 and 1200 K. The standard state are the silicon wafer (diamond structure) and the gases under the standard pressure $P° = 0.1$ MPa.
The temperature, partial pressure of H_2 and SiH_4 are imposed. Classical values are 650°C (923 K), 20 Pa and 1180 Pa of H_2 and SiH_4 pressure, respectively.
The driving force is $\Delta_{r1}G$, expressed by:

$$\Delta_{r1}G = \Delta_{r1}G° + RT \ln [(P_{H2}/P°)^2 / (P_{SiH4}/P°)] = \quad -117\,300\ \text{J in the experimental}$$
conditions.
The driving force may also be expressed by the difference between the values of the silicon chemical potential in the gaseous phase (equal to that in the liquid alloy) and that of the wafer:

$\Delta_{r1}G = \mu_{Si}$ (wafer) $- \mu_{Si}$ (gas) $= R\,T\,\ln\,[a_{Si}$ (wafer) $/ a_{Si}$ (gas)) $= -117\,300$ J.mol^{-1}
a_{Si} (wafer) $= 1$ because the silicon of the wafer is taken as standard state, it is easy to calculate a_{Si} (gas) $= 4.34 \times 10^6$.
The silicon activity in the SiH$_4$ of the gaseous phase is ~4.34 millions times higher than the activity of the silicon in the wafer or in the gold droplet, providing thus an easy way for the nanowire growth.
This result contrasts with the SLS process which is carried out in inert or reducing atmospheres.

THE SLS PROCESS

The only source of silicon in the SLS process is "apparently" the solid substrate (wafer). No driving force exists to explain the supersaturation without accounting for a metastable equilibrium. Sources of metastable state are either the nanometric liquid phase (Au-Si) or the gaseous phase based on silicon and both sources should be analyzed.
Thus, the purpose of the present work is to discuss from a thermodynamic point of view the growth of nanowires by the SLS process and to point out the conditions in which nanowires can be obtained. Our attention will be focused on the phase diagram which is reproduced in many articles from which we note that many aspects of the growth mechanism are poorly understood. Although several investigators have reported on the Au-Si diagram phase, no attention has been given to the system on which they deal with. They principally focused on the phase diagram corresponding to the bulk system, i.e. macroscopic solid in equilibrium with macroscopic liquid. This system, the only one diagram of Au-Si available in the literature, is far from those of interest for processing and growing nanowires. For the growth of nanowires, the starting system is macrometric solid (wafer) in equilibrium with nanometric liquid and hence the precipitation of silicon into nanowire occurs, the new system to be considered is the nanometric solid (nanowire) in equilibrium with nanometric liquid. Unfortunatlly, all these diagrams have not been constructed yet.


The Gibbs Energy of a Liquid Droplet

For the calculation of phase equilibria in multicomponent systems it is necessary to minimize the total Gibbs energy, G, of all the phases that take part in this equilibrium

$$G = \sum_i n_i G_i^{\varphi} = minimum,$$

Where n_i, the number of moles and G_i^{φ} the partial Gibbs energy of element i in the phase φ. A thermodynamic description of a system requires the assignment of thermodynamic functions of each phase.
Let us consider the following transformation:

$(1 - x)$ <Au, fcc> $+ x$ <Si, dia> $\rightarrow$ (Solution, liquid)   [2]
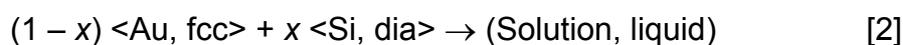
The molar Gibbs energy of the transformation is given by:

$\Delta_{tr}G = G_L - x\,G_{Si}^{o,liq} - (1 - x)\,G_{Au}^{o,liq}$ [3]

where x represents the mole fraction of Si in the liquid alloy.

By choosing as a standard state for the elements <Si, dia> and <Au, fcc>:

$G_{Si}^{o,dia}$ = $G_{Au}^{o,fcc}$ = 0, thus $\Delta_{tr}G = G_L$

G_L, the molar Gibbs energy of the liquid droplets is the sum of two contributions:[5] a volume contribution G_L^{vol}, the only one taken into account with a macroscopic liquid alloy, and a surface contribution G_L^{surf} which becomes noticeable when the size of the liquid droplet goes down below 100 nm:

$G_L = G_L^{vol} + G_L^{surf}$ [4]

The volume contribution is given by :

$G_L^{vol} = x\ G_{Si}^{o,liq} + (1 - x)\ G_{Au}^{o,liq} + R\,T\,[\,x \ln x + (\,1 - x\,) \ln (\,1 - x\,)\,] + G_L^{xs}$ [5]

Since $G_{Si}^{o,dia}$ = $G_{Au}^{o,fcc}$ = 0, $G_{Si}^{o,liq}$ and $G_{Au}^{o,liq}$ represent respectively the Gibbs energy of fusion of <Si, dia> and <Au, fcc>. G_L^{xs} represents the excess Gibbs energy of mixture given by the Redlich-Kister polynomial expansion:

$G_L^{xs} = x\,(\,1 - x\,) \sum_i\ L_i\,(\,1 - 2\,x\,)^i$ [6]

where L_i are the interaction parameters, which are temperature dependent.

The surface contribution is given, for a spherical droplet whose radius is r, by:

$G_L^{surf} = 2\,\sigma_{(L)}\ V_{(L)}\,/\,r$ [7]

$\sigma_{(L)}$ and $V_{(L)}$ are the surface tension and the molar volume of the liquid droplet, respectively ; r is the main curvature radii of the particle. If the semiconductor is under the formed a nanowire, the factor 2 disappears.

$G_{nano}^{surf} = \sigma_{(S)}\ V_{(S)}\,/\,r$ [8]

The molar volume $V_{(L)}$ and surface tension $\sigma_{(L)}$ were taken from the literature in which the Butler's[6,7] approach has been used for the calculation. The surface energies of alloys depend on their composition. There is a large uncertainty in the values of surface energies of solid-liquid interfaces of pure elements and therefore, of their alloys. For the sake of simplicity a linear dependence was assumed between $\sigma_{(L)}$ of pure Au and of pure Si. Application of such an approximation shows that it has a small effect on the equilibrium states. The Gibbs energy of the solid and liquid phases being known, it is possible to calculate the solid-liquid equilibria and to build up as much equilibrium diagrams as different values for the radius of the nanoparticle

Stable and Metastable Diagrams

The rule of common tangents, which is the geometrical interpretation of the Gibbs energy minimizing, is shown in Figure 3.
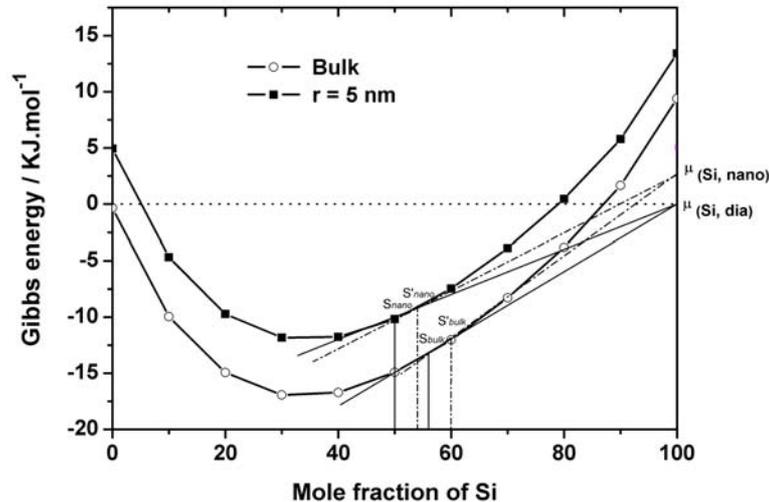
Figure 3: Comparison of the solubilities of a given particle (nano or macroscopic) in a given liquid (nano or macroscopic)

Two curves have been drawn: the lower one represents the molar Gibbs energy of a macroscopic liquid ($r = \infty$) whereas the upper one represents the molar Gibbs energy of droplets whose mean radius is $r = 5$ nm. On the same diagram, two points have been represented on the silicon axis. $G = 0$ states for the wafer, whereas $G > 0$ states for a nanoparticle. For each point, one tangent may be drawn to each curve. So, we can draw 4 tangents and define 4 solubilities. Such a construction gives access to one well-known result and another one more paradoxical:

• If the liquid alloy is nanometric, the solubility of a nanoparticle of Si is higher than that of bulk Si ($S'_{nano} > S_{nano}$). The conclusion is the same if the liquid alloy is macroscopic ($S'_{bulk} > S_{bulk}$). This conclusion agrees with the accepted statement that the solubility of small particules in a given solvent is higher than the solubility of large particles.

• However, if the solid Si is nanometric, its solubility is higher in a macroscopic liquid than in a nanometric liquid ($S'_{bulk} > S'_{nano}$). The conclusion is the same if the solid Si is macroscopic ($S_{bulk} > S_{nano}$). This phenomenon, which deserves attention means that the solubility of a given particle is always higher in a macroscopic solvent than in a nanometric solvent.

Calculations show that, at 1100°C, the solubility of bulk Si in a droplet ($r = 5$ nm) is $S_{nano} = 50$ mol % Si compared with $S_{bulk} = 56$ mol % Si; the solubility of a nanowire in the same droplet depends on the radius of the nanowire, but it is always observed that ($S'_{bulk} > S'_{nano}$). The calculated phase diagrams are shown in Figure 4
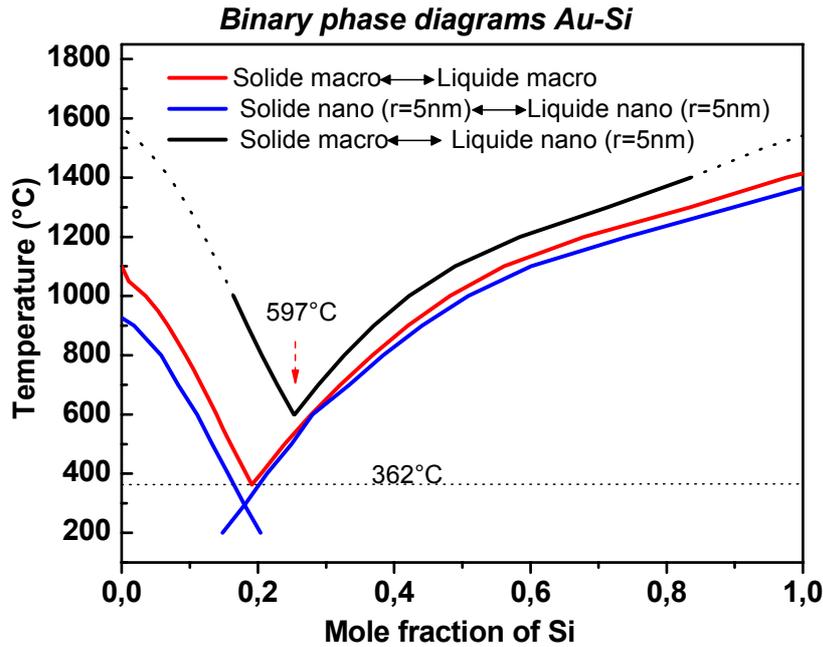
Figure 4 : The Au-Si phase diagrams according to the sizes of the particles

The conclusion to be drawn from the build up of nanodiagrams is that a gold droplet in equilibrium with the silicon of the wafer is saturated in silicon. Nanowires may be grown from the Au-Si liquid droplets only if the concentration of Si in the liquid is greater (supersaturation) than that in equilibrium with stable crystals of the same solid (saturation). A first examination of the condensed phases present in the system shows that there is no driving force coming from the wafer to justify any supersaturation of the gold droplet with silicon. It is thus necessary to look towards Si present in the gaseous phase.

Chemical Potentials of Gaseous Species

In the SLS mechanism, Au, Si and Ar (with or without H_2) are the main elements introduced in the synthesis chamber. Another element to be considered is oxygen which arises either from leakage, from degassing of Al_2O_3 tube or simply from SiO_2 which may be native or even intentionally grown by thermal deposition on the substrate. Hence, the silicon species present in the gaseous phase may be either Si, Si_2 and Si_3 in equilibrium with the solid silicon of the wafer, or SiO in equilibrium with the Si-SiO_2 mixture. A rapid analysis of the thermodynamic data shows that the predominating species in the temperature range of interest (800-1400°C) is SiO. The main equilibrium to be considered is thus the following one:

$$<Si> + <SiO_2> \rightarrow 2\,SiO \qquad\qquad [9]$$
$$R\,T \ln (P_{SiO} / P°)^2 = -\Delta_{r9}G° + R\,T \ln (a_{Si}\,a_{SiO2}) \qquad\qquad [10]$$

$\Delta_{r9}G°$ is calculated from Schnurre.[8] The partial pressure of SiO is strongly dependent on the imposed potential oxygen. The highest pressure of SiO is obtained when the oxygen potential is as close as possible to the oxygen pressure at Si-SiO_2 equilibrium. The standard state for SiO_2, Si and gaseous species are the solid

cristobalite, the pure solid silicon <Si, dia> and the gaseous species under a pressure $P° = 0.1$ MPa.

If the wafer ($a_{Si} = 1$) is in equilibrium with the solid cristobalite ($a_{SiO2} = 1$), the calculated partial pressure of SiO is 4.05 Pa at 1100°C. When the equilibrium is reached, the chemical potential of silicon is the same in every phase and no more driving force exists to justify the nanowire growth experimentally observed. The explanation of this process has to be researched in the presence of metastable equilibria developed in the system.

The only source of metastability comes from the fact that SiO$_2$ on the wafer is amorphous silica rather than crystallized under the form of stable cristobalite, as it can be easily shown by X-ray diffraction on the silica layers. Actually, all deposited and thermally grown oxides in semiconductor process are amorphous. The partial pressure of SiO developed by the equilibrium [9] would be higher above the Si/SiO$_2$ (amorphous) couple than above the Si/SiO$_2$ (cristobalite) couple:

$$P_{SiO} = K_9 \sqrt{a_{Si} \, a_{SiO_2}} \qquad [11]$$

$a_{SiO2, \, am}$ is calculated from the transformation:

$$<SiO_2>_{crist} \rightarrow <SiO_2>_{am} \qquad [12]$$
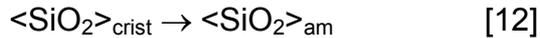
$$\Delta_{r12}G° = \mu°_{SiO2, \, am} - \mu°_{SiO2, \, crist} = - R \, T \ln a_{SiO2, \, am}$$

$\mu°_{SiO2, \, am}$ is obtained by extrapolation of $\mu°_{SiO2, \, L}$ towards low temperatures. At 1100°C:

$a_{SiO2, \, am} = 1.267$ and $(P_{SiO})_{Si \, dia/SiO2 \, am} = 4.562$ Pa $> (P_{SiO})_{Si \, dia/SiO2 \, crist} = 4.05$ Pa

This difference brings the driving force needed to supersaturate the gold droplets with Si. Gaseous SiO above the wafer, stable with respect to the Si/SiO$_2$ (amorphous) mixture, is thus metastable with respect to the Si/SiO$_2$ (cristobalite) mixture, and the reaction [9] will naturally proceed towards the decomposition of SiO. Without gold droplets, Si and SiO$_2$, resulting from the disproportion reaction

2 SiO $\rightarrow$ SiO$_2$ + Si, will germinate on the wafer. The gold droplets acting as a catalyst, SiO will decompose on the surface of the droplet and silicon will dissolve until the liquid-gas equilibrium is reached. When the liquid is in equilibrium with the gaseous phase but supersaturated in silicon with respect to the wafer, the precipitation of silicon nanowires will be observed. Amorphous SiO$_2$ synthesized by the disproportion reaction will deposit on the nanowire and on the wafer. Thus, the driving force of the silicon nanowire growth $\Delta_d G$ is the difference between the chemical potential of the silicon in the droplet in equilibrium with the gaseous phase and that of the silicon wafer:

$$\Delta_d G = \mu_{Si,supersaturation} - \mu°_{Si,saturation} = \mu_{Si,G} - \mu°_{Si,dia}$$
$$\Delta_d G = R \, T \ln a_{Si,G} = R \, T \ln [P_{Si,G}/P°_{Si}] \qquad [13]$$

The ratio $P_{Si,G}/P°_{Si}$ is calculated from the equilibrium Si + ½ O$_2$ $\rightarrow$ SiO by taking into account the fact that oxygen pressure, imposed by the system, is constant throughout the whole experiment:

$$\Delta G = \mu_{Si,G} - \mu°_{Si,dia} = R \, T \ln (P_{SiO \, Si \, dia/SiO2 \, am} \, / \, P_{SiO \, dia/SiO2crist}) \quad [14]$$

CONCLUSION

The thermodynamics of Au-Si has been considered with regard to the important gas-solid-liquid reactions which may occur in processing of Si-based nanowires. A data set was established to calculate and construct the phase equilibria in all systems Au-Si (macroscopic and/or nanoscopic range).

It is pointed out that care must be exercised to distinguish between the binary nature of the system (macroscopic or nanometric), and which phases are in equilibrium (solid, liquid and gaseous). For the first time, the driving force needed for supersaturation of nanodroplet liquid alloy has been clearly identified. The strength of a model lies in its predictive character. The model can also been applied to forecast with success the conditions needed to the growth of other semiconductor nanowires by the SLS process.

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