

## Research Article

# Thermodynamics of Silicon Nanowire Growth under Unintended Oxidation of Catalytic Particles

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In this paper, we focus on the thermodynamics of redox reactions occurring during the vapor-liquid-solid (VLS) growth of silicon nanowires (NWs) with the participation of liquid solutions of metal catalysts. The growth of NWs is difficult with the participation of Ti, Al, and Mg particles; this is because in this case, the drops of the metal catalyst are strongly oxidized and crystals either do not form at all or are characterized by instability in the direction of growth. However, the particles of Cu, Ni, and Fe give a much more stable growth of NWs. We have also established that if the oxide film of catalytic particles is formed by the basic metal oxides, then the silicon-NWs' growth slows down. In this work, we have concluded that only metals with a lower chemical affinity for O<sub>2</sub> than Si are applicable as catalysts for the NWs' growth.

## 1. Introduction

Current progress in the synthesis and characterization of the properties of the nanowires (NWs) depends on an understanding of the principles of their controlled growth and finding the possibilities of manipulating the super miniature objects of nature [1–6]. To control the NWs' growth via the vapor-liquid-solid (VLS) method, first, we must exclude the factors resulting in the crystal growth destabilization. For example, the presence of the residual oxygen in the gas phase during the NWs' growth process can lead to the unintentional oxidation of the catalytic particle, growth instability, or even blockage of the NWs' growth completely [7]. Therefore, to ensure controlled NW growth, it is crucial to study the thermodynamic conditions of the catalyst particles' oxidation process in the presence of a residual amount of O<sub>2</sub> in the gas phase as well as establish the factors affecting this process.

This work is a continuation of works [8] of this group, and it aims to consider the thermodynamics of redox reactions that accompany the growth of Si NWs according to the VLS scheme and occur with the participation of liquid-phase solutions of metal (Me) catalysts under the conditions of unintentional oxidation of catalytic particles. The NWs were grown by chemical vapor deposition and molecular beam epitaxy involving the particles Cu, Ti, Ni, Al, Fe, and Mg as growth catalysts. The NW growth was carried out by adding O<sub>2</sub> to the growth atmosphere. In this paper, we show that when growing Si NWs in a growth atmosphere, which has not undergone additional purification from O<sub>2</sub> residues, the Me-Si catalyst droplets are unintentionally coated by a Me<sub>n</sub>O<sub>m</sub> oxide film and deactivate the growth process. We have also observed that the particles of Cu, Ni, and Fe give a much more stable growth to NWs. However, the formation of a basic oxide (NiO, Cu<sub>2</sub>O, FeO, etc.) during the oxidation of the Me catalyst at the top of the NWs not only facilitates

the transition of Si from a liquid drop to an acidic oxide  $\text{SiO}_2$ , i.e., oxidation of the silicon atoms, but it also makes a reverse transition, a recovery, difficult. Hence, the growth of Si NWs in the presence of oxygen in the gas phase is substantially impeded. We have concluded that only metals with a lower affinity for  $\text{O}_2$  than for Si are applicable as catalysts for the growth of NWs. In this paper, we have also established that the transition of Si from a drop of Me-solution to the oxide layer is accompanied by the generation of heat. Therefore, with an increase of the growth temperature, the completeness of the oxidation of Si decreases and the completeness of its reduction increases. In the case of pure Me and Si, there is no mutual influence between them at the initial stage on the substrate. Therefore, as the growth temperature increases, the oxidation reaction of the Me-catalyst shifts towards the dissociation of  $\text{Me}_n\text{O}_m$  and the growth of Si NWs is facilitated.

## 2. Experimental Procedure

Si NWs were grown by chemical vapor deposition in the  $\text{SiCl}_4 + \text{H}_2$  system (NW growth experiments at a temperature of  $T = 1250\text{--}1650\text{ K}$ ) at the isoprin-type facility (NIIPM, Russia) and molecular beam epitaxy (growth experiments at  $T = 850\text{--}1100\text{ K}$ ) at the BAK-501 facility (Evatec, Switzerland) [1–3]. The vacuum level in the working chamber of BAK-501 was  $1 \times 10^{-8}$  Pa. Si wafers with the crystallographic orientation {111} served as growth substrates. NWs' growth was conducted with the participation of catalytic particles, which represent a supersaturated solution of a crystallizable substance in liquid drops of Cu, Ni, Fe, Ti, Al, and Mg of a limited volume. The particular metals were chosen as catalysts in this study because for them, the equilibrium partial  $\text{O}_2$  pressure,  $P_{\text{O}_2(\text{Me}_n\text{O}_m)}$ , in the reaction of oxide formation or dissociation at the growth temperature of the silicon-NW is either greater (Cu, Ni, and Fe) or less (Al, Ti, and Mg) than the equilibrium partial pressure  $\text{O}_2P_{\text{O}_2(\text{SiO}_2)}$  in the oxidation reaction for Si or  $\text{SiO}_2$  for the dissociation reaction. The diameters of the nanoparticles ranged from 50 to 200 nm. The fusion of catalyst particles with the Si substrate was conducted at  $1373\text{--}1673\text{ K}$  in the  $\text{H}_2$  atmosphere. The temperature of the growth process was chosen in the ranges of  $1250\text{--}1650\text{ K}$  and  $850\text{--}1100\text{ K}$  and was higher than the eutectic for each selected Me-Si system. The following temperatures were used for the growth of Si NWs for each catalyst metal:  $1643\text{ K}$  for Ti,  $1273\text{ K}$  for Mg,  $1073\text{--}1273\text{ K}$  for Al,  $1173\text{--}1273\text{ K}$  for Cu,  $1323\text{--}1473\text{ K}$  for Ni, and  $1543\text{ K}$  for Fe. The concentration of Si in droplets composed of catalyst metals for NW growth at the growth temperatures is 30% (atomic) ~for the Al-Si system, ~35% (atomic) for the Cu-Si system, ~57% (atomic) for the Mg-Si system, ~65% (atomic) for the Ni-Si system, ~67% (atomic) for the Fe-Si system, and ~90% (atomic) for the Ti-Si system.

The application of Me particles on the surface of the Si plate was carried out by sputtering a thin film with subsequent heating and breaking it up into separate drops. The Me film was divided into separate drops by annealing for 5–20 min at a temperature in the range of  $850\text{--}1650\text{ K}$  in

a high-temperature Nabertherm furnace (Germany) in an atmosphere of purified  $\text{H}_2$ . NWs were grown by varying the  $\text{O}_2$  content in the composition of the growth atmosphere from  $1\text{--}10^{-5}$  to  $5\text{--}10^{-3}\%$  (volume).

The composition of molecular beams and the residual gaseous medium was monitored by a quadrupole mass spectrometer. The crystal growth rate was measured using a laser ellipsometer. Morphological studies of the grown crystals were carried out by scanning electron microscopy, and the elemental and phase composition of the catalyst particles was determined by x-ray spectroscopy. The elemental composition of the catalyst particles was determined by an energy-dispersive X-ray spectral microanalysis (JSM-6380LV, JEOL, Japan). The phase composition of the particles was investigated by the method of diffraction of fast electrons "for reflection" on the electronograph EG-100M ("Electron," Ukraine) at an accelerating voltage of 80 kV. The elemental composition in this paper means the qualitative detection of the content of the elements that form the composition of the catalyst droplets without their quantitative calculation. Phase composition means a list of phases that are in this growth drop alloy, including the oxide shell.

## 3. Results and Discussion

*3.1. Influence of Catalyst Type, Oxygen Concentration, and Temperature on the NW's Growth: Experimental Data.* From experimental observations, we have observed that during the growth of Si NWs in a growth atmosphere which has not undergone additional purification from  $\text{O}_2$  residues, the drops of Me-Si catalyst unintentionally got coated by  $\text{Me}_n\text{O}_m$  oxide film. The presence of oxygen in the gas phase negatively affects the growth of the NWs with all types of catalyst metal particles.

Due to the presence of an oxide surface layer in liquid-phase droplets, the growth of NWs slows down with the participation of particles of Cu, Ni, and Fe and short and randomly oriented crystals are synthesized in some places of the substrate (Figures 1(a) and 1(b)). The observed growth rate of Si NWs in the presence of  $\text{O}_2$  in the gas phase can be several times slower than the growth rate of crystals growing under sterile conditions (Figure 1(c)).

In case of the other Me particle participation, such as Al, Ti, and Mg, the Si NWs' growth is either absent altogether or is characterized by strong morphological instability as a result of the presence of the oxide layer on the catalyst droplets (Figures 1(d)–1(f)). There are multiple types of bends on the crystals, and the angle of inclination during bending takes different values regardless of the radius of the NWs or the type of Me catalyst. Difficulties with the growth of Si NWs are due to strong oxidation caused by such metal particles as Al and Mg. Often, Al or Mg drops simply do not rise from the substrate. It was practically impossible to carry out a stable growth of Si NWs with the participation of these particles under ordinary conditions. In comparison, the metal particles Cu, Ni, and Fe give significantly more stable crystal growth, as shown in Figures 1(a)–1(c).

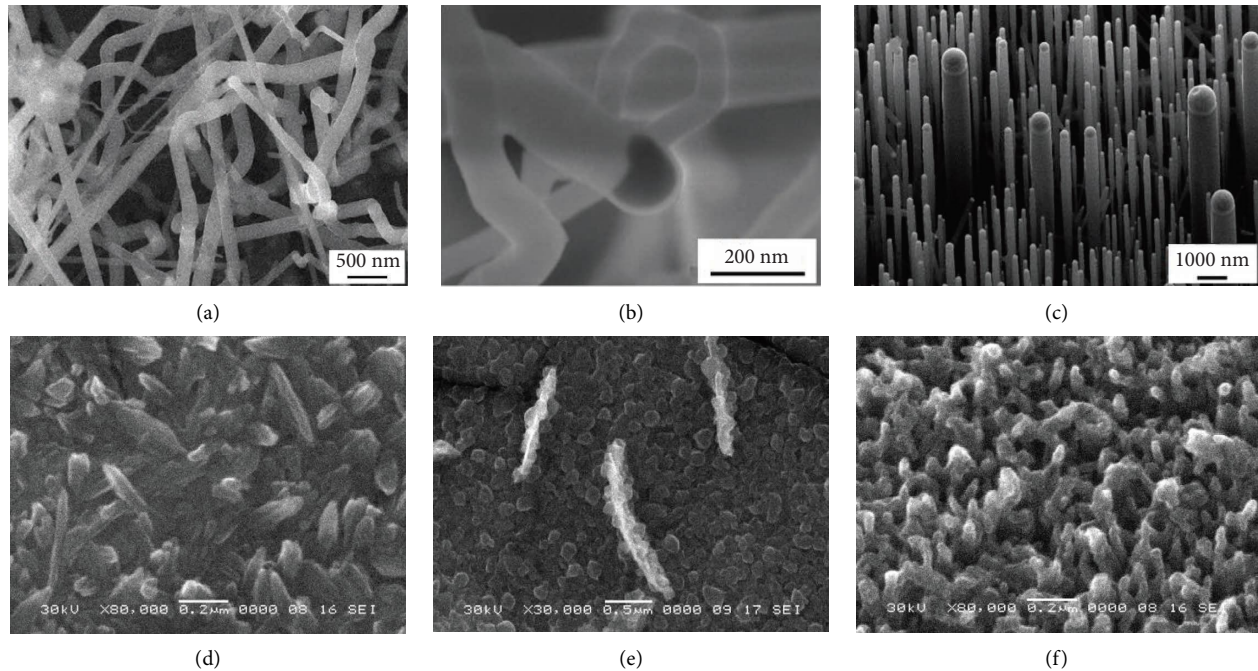


FIGURE 1: (a) and (b) are SEM images of Si NWs grown with the participation of catalytic Ni particles on a {111} Si substrate in a growth atmosphere that has not undergone additional purification from the presence of  $O_2$  at the temperature of 1473 K at various magnifications; (c) stable NW growth in the Ni-Si system at the same temperature of 1473 K (purification from the presence of  $O_2$  was performed to achieve stable nanowire growth). SEM images of the top view of {111} Si substrate samples with Ti (d), Mg (e), and Al (f) particles after 10 min of NW growth. These three samples (d, e) illustrate inhibition of NW growth due to surface oxide layer formation.

Figure 2(a) shows a SEM image of Si nanocrystals grown with the participation of catalytic particles of Cu on {111} Si substrate at  $T=1273K$  in two stages (Figure 2(a)):

- (1) First, in a molecular stream, purified from the presence of oxygen to a concentration of  $10^{-5}\%$  (volume) and less, and
- (2) Then, in a flux containing more than  $5 \times 10^{-3}\%$  (volume)  $O_2$

It can be seen that, at a low concentration of  $O_2$ , the NWs exhibit a stable growth, oriented perpendicular to the substrate (Figure 2(a) left), to a certain crystal height, and after increasing the oxygen supply to the gas phase to  $5 \times 10^{-3}\%$  (volume) and more, the crystal growth is characterized by extreme instability: the NWs have a random variable growth direction and cross section (Figure 2(a), right).

Figure 2(b) shows the electron-diffraction pattern of a portion of the oxide surface layer of a Ti-droplet. One can see a diffused halo indicating the presence of the amorphous  $TiO_2$  phase.

Figure 2(c) shows an image of nanowires that are obtained only at the first stage, i.e., in a molecular stream purified from the presence of oxygen. For the NW from Figure 2(c), the second stage was not used and oxygen was not added. In Figure 2(c), we can see a stable growth of NWs in the Cu-Si system upon resumption of the growth process after dry etching in a gaseous HCl stream. The NWs formed in two stages have cylindrical {111} Si monocrystals with

a blunt polycrystalline tip with a variable diameter, as shown in Figure 2(a).

To confirm that  $Me_nO_m$  oxide film is formed during NW growth when oxygen is supplied to the growth zone, and not after the catalyst particles are kept in the air before growth, we performed an energy-dispersive microanalysis of the elemental composition of Ti-Si particles before and after the growth of Si NWs (Figures 3(a) and 3(b)).

From Figure 3(a) it can be seen that after the fusion of catalytic Ti particles with the Si substrate and the formation of the Ti-Si alloy, oxygen was not identified in the system. Whereas, after growing Si NWs with the participation of the same particles in a stream containing more than  $5 \times 10^{-3}\%$  (volume)  $O_2$ , oxygen is present in the elemental composition of Ti-Si droplets (Figure 3(b)). The results indicate that the oxidation of catalyst particles occurs during the growth process, not at the stage of postgrowth cooling of NWS or aging of particles in  $H_2$  before growth. A large number of other metal elements (V, Al, Ge, Na, etc.) found in the EDS spectrum in the composition of the catalyst particles can be explained by their residual presence in the reaction zone of these elements after experiments with these metals.

To confirm the facts that (i) the NW's growth rate slows down due to the presence of  $Me_nO_m$  oxide film and not due to a change in the growth dynamics without the oxide participation, and that (ii) oxidation of the catalyst metal droplet occurs during the growth process, and not during cooling, we conducted the following experiments. After the formation of the  $Me_nO_m$  oxide film on the catalyst drop, the

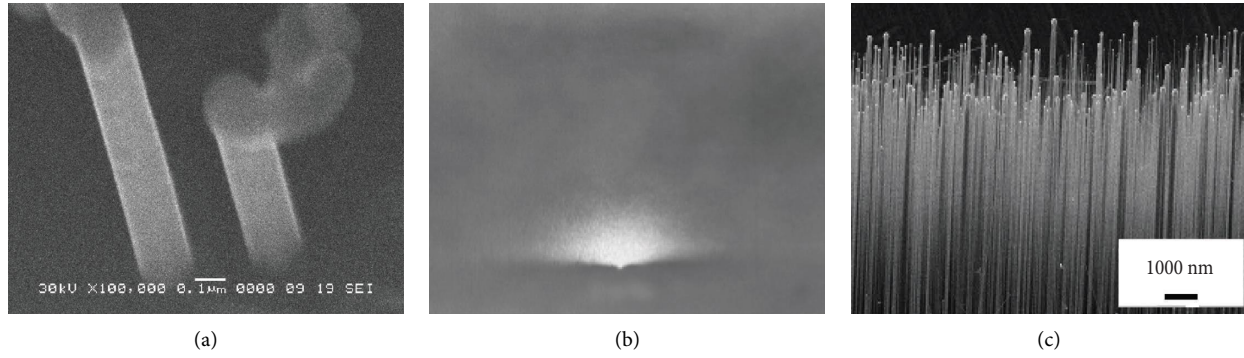


FIGURE 2: (a) SEM image of Si NWs grown with the participation of catalytic particles of Cu on a {111} silicon substrate in two stages: first, in a stream purified from the presence of oxygen to a concentration of  $10^{-5}\%$  (volume) and then in a stream containing  $5 \times 10^{-3}\%$  (volume)  $O_2$ ; (b) an electron-diffraction pattern characterizing the amorphous state of the oxide surface layer of a Ti-droplet; (c) stable growth of NWs in the Cu-Si system upon resumption of the growth process after dry etching in a gaseous HCl stream in a molecular stream purified from the presence of oxygen to a concentration of  $10^{-5}\%$  (volume).

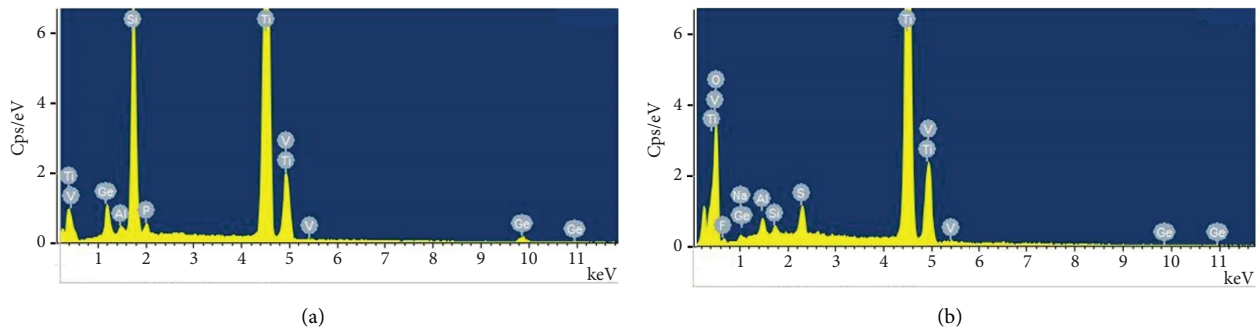


FIGURE 3: Energy-dispersive spectroscopy (EDX) spectrum of the Ti-Si catalytic particles before (a) and after (b) Si NW's growth in a stream containing more than  $5 \times 10^{-3}\%$  (volume)  $O_2$ .

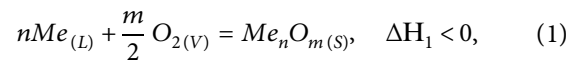
$O_2$  flow was shut off but without stopping the  $H_2$  flow, and an excess concentration of gaseous HCl was supplied to the gas phase. This promotes the removal of  $Me_nO_m$  layers at a high temperature by the dry etching reaction, for example,  $6HCl + Al_2O_3 = 2AlCl_3 + 3H_2O$  or  $4HCl + TiO_2 = TiCl_4 + 2H_2O$ . The resulting metal chlorides are easily removed by the gas flow. As a result of treatment of the surface of droplets and NWs with an etching atmosphere and subsequent renewal of the growth process, it was found that NWs grow stably after the oxide removal (Figure 2(c)) at the usual growth rate. No stable NW's growth was observed when the  $O_2$  supply was stopped but without preliminary etching, i.e., in the presence of an oxide film. The described observations could confirm that the oxidation of metal is taking place rather than the change of the dynamics of the growth process due to the  $O_2$  reaction with the components of the gas phases. The experiments conducted also explain that metal oxides are formed during growth and not at the cooling stage. It is obvious that the oxide layer is formed during the growth of the nanowire in the  $H_2$  stream containing a high concentration of  $O_2$   $5 \times 10^{-3}\%$  (volume).

Stable catalyst drops are required for the nucleation of Si monocrystal. However, in the presence of high oxygen concentrations, the metal catalyst oxidized. And unstable growth conditions are the main reason for the

polycrystalline Si formation and the random changes in the direction of growth. Polycrystalline segments at the ends of the crystals are shown in Figure 2(a).

With increasing temperature from eutectic to higher, the stability of the NWS' growth increases in the presence of any type of catalysts. As a rule, when a certain temperature is exceeded, the oxide film on the catalyst droplets is not detected, even if it was present at lower temperatures, and NWs have a stable growth at the higher temperatures. Most likely, at the higher temperatures, the process of hydrogen reduction of metals from their oxides ( $mH_2 + Me_nO_m = nMe + mH_2O$ ) [9] occurs. And the oxide film is destroyed.

**3.2. Total Oxidation Reaction of a Metal Catalyst and the Equilibrium Partial Oxygen Pressure.** To explain the obtained experimental results, we consider the total oxidation reaction of the Me catalyst in general form as follows:



where  $n$  and  $(m/2)$  are stoichiometric coefficients ( $n$  and  $m$  are indices in the oxide formula), and  $\Delta H_1$  is the thermal effect of the reaction. Subscripts in the brackets (L), (V), and (S) indicate the liquid, vapor, and solid phases, respectively.

Let us consider the simplest case of the absence of solutions between solids, i.e., when Me and its oxide are independent pure phases, the total number of which, including vapor, is three. In accordance with the Gibbs phase rule, the number of degrees of freedom  $F = C - P + 2$ , where  $C$  is the number of chemical components,  $P$  is the number of phases, and 2 is the number of externally controllable variables, i.e., temperature and pressure. In our case  $C = 2$  and  $P = 3$  as (1) demonstrates, since the degree of freedom  $F = 2 - 3 + 2 = 1$ , the system is univariate. Univariance of the system means that the equilibrium pressure of  $O_2$  depends only on temperature  $T$ , i.e.,  $p_{O_2} = f(T)$ .

This function can be obtained from the following expression for the equilibrium constant of reaction, expressed by (1):

$$K = \frac{a_{Me_nO_m}}{a_{Me}^n \cdot p_{O_2}^{m/2}}, \quad (2)$$

where  $a_{Me_nO_m}$  and  $a_{Me}$  are the activities of  $Me_nO_m$  and  $Me$ , respectively.

Since the activity of pure solids is practically equal to unity, from (2) we get

$$K = \frac{1}{p_{O_2}^{m/2}} = f'(T). \quad (3)$$

From (3), denoting  $p_{O_2}$  as  $p_{O_2(Me_nO_m)}$ , we find

$$p_{O_2(Me_nO_m)} = \left(\frac{1}{K^2}\right)^{(1/m)} = (f'(T))^{-(2/m)}. \quad (4)$$

Equation (4) characterizes the equilibrium partial oxygen pressure (dissociation pressure)  $p_{O_2(Me_nO_m)}$  in the reaction of the formation or dissociation of the  $Me_nO_m$  metal oxide.

If the actual partial pressure of oxygen in the gas medium is greater than the equilibrium partial pressure of oxygen, then the oxidation reaction (1) should proceed irreversibly in the forward direction [9]. In other words, in such a gaseous atmosphere during NW growth, the catalytic particles will be thermodynamically unstable and should completely oxidize over time. The resulting  $Me_nO_m$  oxides, for the most part, do not dissolve in the liquid droplet and must stand out from it, forming an oxide film on the surface. From this film, oxygen can pass into the solution of an Me-Si catalyst drop until the system reaches an equilibrium. Despite the oxidative nature of the entire process of Me oxidation, a reverse transition and reduction of metals can also be observed. This is possible if a chemical equilibrium does not limit the process and develops faster than others, for example, diffusion, stages. Then, the behavior of Me and Si atoms in the liquid-phase catalyst particles can be estimated based on the thermodynamic analysis of the oxidation reactions.

**3.3. Thermodynamic Analysis of Oxidation Reactions.** The oxidizing ability of the  $Me_nO_m$  layer is the ability of the oxide film to transfer a certain amount of oxygen to the liquid solution of the catalyst drop. Let us denote the oxidizing ability of the  $Me_nO_m$  layer as its equilibrium concentration

in the solution in contact with the film, namely,  $[O]_{Me_nO_m}$ . The oxidizing ability of the  $Me_nO_m$  layer can be found from the expression for the oxygen distribution constant  $K_O$  between the oxide film and the drop solution, as the ratio of the activities of the oxide and metal phases at the equilibrium:

$$K_O = \frac{a_{Me_nO_m}}{a_{O(Me)}}. \quad (5)$$

By definition, the constant  $K_O$  is a function of temperature only and does not depend on the concentration of oxygen distributed between the phases. The oxygen content in the Me-Si liquid drop is small, and as a comparison solution, we can take a solution that obeys Henry's law, i.e.,  $a_{O(Me)} = f_0[O]$ , where  $[O]$  is the oxygen concentration expressed in weight percent and proportional to the molar fraction for dilute solutions,  $f_0$  is the Henry's law constant. Since in our case  $f_0 \approx 1$ , then  $a_{O(Me)} \approx [O]$ . At equilibrium between the droplet solution and the oxide film, the concentration  $[O]$  corresponds to the oxidizing ability of the oxide layer, i.e.,  $a_{O(Me)} = [O] = [O]_{Me_nO_m}$ .

Since other components may be present in the oxide layer of the droplet, for example,  $SiO_2$ , then the activity of the metal oxide can be expressed as  $a_{Me_nO_m} = \gamma_{Me_nO_m} \cdot (Me_nO_m)$ , where  $\gamma_{Me_nO_m}$  is the activity coefficient, if the ideal solution is the reference solution and  $(Me_nO_m)$  is the concentration of  $Me_nO_m$  in the oxide layer. Hence, (5) can be written as follows:

$$K_O = \frac{\gamma_{Me_nO_m} \cdot (Me_nO_m)}{[O]_{Me_nO_m}}. \quad (6)$$

The  $K_O$  value can be found from the temperature dependence of the solubility of oxygen in molten Me-catalyst particles. When the oxide layer is in equilibrium with the liquid metal  $a_{Me_nO_m} = 1$ , and the oxidizing ability  $[O]_{Me_nO_m}$  is the highest and corresponds to the maximum concentration of oxygen (its solubility) in a drop of a catalyst at a given temperature  $[O]_{\max}$ . Thus, the distribution constant  $K_O$  can be represented as follows:

$$K_O = \frac{1}{[O]_{\max}}. \quad (7)$$

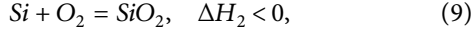
Consequently, the oxygen distribution constant  $K_O$  is equal to the reciprocal of the solubility of oxygen in the metal phase of the catalyst drop. Then, from equations (5)–(7) we obtain

$$[O]_{Me_nO_m} = [O]_{\max} \gamma_{Me_nO_m} \cdot (Me_nO_m). \quad (8)$$

Thus, at a given NWs growth temperature ( $[O]_{\max} = \text{const}$ ), the oxidizing ability of the oxide layer is proportional to the activity of the metal oxide in it.

With most Me-catalysts, oxygen forms basic oxides (NiO, CuO, FeO, etc.). Oxygen also interacts with Si contained in the solution, which has the second (and often the first) largest concentration in the drop after Me, according to the following reaction:

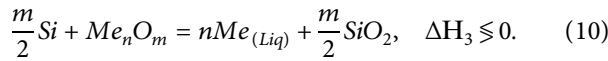




where silicon dissolved in a drop of liquid is indicated by square brackets. This results in the formation of acid oxide  $\text{SiO}_2$ , which passes into the oxide film.

Therefore, the values of activity  $a_{\text{Me}_n\text{O}_m}$  and oxidizing ability of the oxide layer  $[\text{O}]_{\text{Me}_n\text{O}_m}$ , should depend on the composition of the formed oxide film of the drop, in particular, on its basicity, i.e., from relationship  $((\% \text{Me}_n\text{O}_m)/(\% \text{SiO}_2))$ .

The total interaction of dissolved  $[\text{Si}]$  with solid metal oxide can be expressed by the following equation of a heterogeneous reaction:



In (10)  $\Delta H_3$  is negative (Cu, Ni, and Fe) and positive (Ti, Al, and Mg).

Consequently, reaction (10) will go to the right, i.e., Si will be oxidized and metal oxide will be reduced if, under the considered conditions, the dissolved Si has a greater affinity for oxygen than Me.

**3.4. Effect of Affinity of the Me Catalyst for  $\text{O}_2$  and Valency of Me to Their Oxidation Level.** According to Hess's law, the thermal effect of the redox reaction (10) will be determined by the difference in the heats of formation of the silicon and metal oxides, namely,  $\text{SiO}_2$  in equation (9) and  $\text{Me}_n\text{O}_m$  in equation (1). In the process of NW growth by the method of molecular beam epitaxy, gases are at low pressures and high temperatures. Under such conditions, their properties can be satisfactorily described by the laws of ideal gases, and instead of fugacity, it is possible to use partial pressures. The activity of pure solids is practically equal to unity. The equilibrium constant  $K_{\text{eq}}$  of reaction (10) does not depend on whether the substances are in the solution of the catalyst drop or in pure form. Then, according to the second law of thermodynamics and considering changes in the system of isobaric-isothermal potentials as well as going from the ratio of the logarithms of the reaction constants (1), (9), and (10) to the  $\text{O}_2$  partial pressures, we write  $K_{\text{eq}}$  as follows:

$$K_{\text{eq}} \approx \left( \frac{p_{\text{O}_2(\text{Me}_n\text{O}_m)}}{p_{\text{O}_2(\text{SiO}_2)}} \right)^{(m/2)}, \quad (11)$$

where  $p_{\text{O}_2(\text{Me}_n\text{O}_m)}$  and  $p_{\text{O}_2(\text{SiO}_2)}$  are the equilibrium  $\text{O}_2$  partial pressures of reactions of the formation or dissociation of metal and silicon oxides in the absence of solutions, characterizing the normal affinity of elements to  $\text{O}_2$ .

From (11), we can make several deductions:

- (1) If  $p_{\text{O}_2(\text{Me}_n\text{O}_m)} < p_{\text{O}_2(\text{SiO}_2)}$ , then  $K_{\text{eq}} < 1$ . In this case, the higher the normal affinity of the Me catalyst for  $\text{O}_2$  (i.e., the lower the equilibrium partial pressure of  $\text{O}_2$  in the reaction of formation or dissociation of its oxide  $p_{\text{O}_2(\text{Me}_n\text{O}_m)}$ ), the lower the equilibrium constant

$K_{\text{eq}}$  and the lower the possible oxidation state of Si. We can assume that metals whose normal affinity for  $\text{O}_2$  is higher than that of Si will be oxidized. From a comparison of the equilibrium partial pressures of  $\text{O}_2$  in the reactions of formation or dissociation of oxides for the considered Me catalysts (Table 1), it follows that, for example, the above inequalities are satisfied for Al, Ti, and Mg, and these Me can be almost completely oxidized.

- (2) On the other hand, such metal catalysts as Cu, Ni, and Fe are hardly oxidized during the growth of NWs, since for them  $p_{\text{O}_2(\text{Me}_n\text{O}_m)} > p_{\text{O}_2(\text{SiO}_2)}$ , i.e.,  $K_{\text{eq}} > 1$ , and the level of predominant oxidation of Si is high.

The effect of the valency of the Me catalyst on the level of its oxidation is considered via  $(m/2)$ , the exponent in the numerator of the right-hand side of (11). The higher the valency of Me, the greater the equilibrium constant  $K_{\text{eq}}$  and the higher its oxidation state. Therefore, for example, catalytic particles of metals such as Al, Sn, or Ti [10] having valences of 3 and 4, respectively, in comparison to particles of Cu, Ni, or Au [11] with valences 1 and 2, often do not give a stable growth of Si NWs because of their active unintentional oxidation. To be more precise, the index in the metal oxide formula  $m$  is related to the valence  $\nu$  as  $m = (\nu \times n/2)$ . So, the expression (11) can be written as  $K_{\text{eq}} \approx (p_{\text{O}_2(\text{Me}_n\text{O}_m)}/p_{\text{O}_2(\text{SiO}_2)})^{(\nu \times n/2)}$ . From this expression it can be seen that the equilibrium constant  $K_{\text{eq}}$  actually depends on the product of the metal valence  $\nu$  and the index of the metal in the formula of its oxide  $n$ . Therefore, for example, for CuO and  $\text{Cu}_2\text{O}$ ,  $m = 1$  in both cases,  $n = 1$  and  $\nu = 2$  for CuO and  $n = 2$  and  $\nu = 1$  for  $\text{Cu}_2\text{O}$ . Therefore, for these systems, due to differences in the index  $n$ , the dependence of the equilibrium constant on the valence of the metal will not manifest itself.

Thus, since the metal oxides of Ti, Al, and Mg have a low dissociation pressure, it is sufficient to have even very little oxygen content in the growth atmosphere to cause oxidation and stop the growth of NWs. Therefore, nonoxidative crystal growth involving Ti, Al, and Mg is possible either at extremely low, almost unattainable, partial pressure of oxygen or at a high vacuum.

**3.5. How Much Si Do We Need to Introduce into the Catalyst Drop in Order to Ensure Complete Reduction of the Metal Oxide at a Given Temperature?** For the liquid-phase solution at the top of the NWs, it is necessary to introduce adjustments taking into account the activities (concentrations) of the components. To do this, we write Van't Hoff isotherm equation for the chemical reaction (10) [12] as follows:

$$\Delta G = RT \left( \ln \frac{a_{\text{SiO}_2(\text{real})}^{(m/2)} \cdot a_{\text{Me}(\text{Liq})}^n}{a_{\text{Si}(\text{real})}^{(m/2)} \cdot a_{\text{Me}_n\text{O}_m(\text{real})}} - \ln K_{\text{eq}} \right). \quad (12)$$

For calculating the change of the isobaric-isothermal potential  $\Delta G$ , under the logarithm in (12), in the first term we have the product of the actual activities of the components of the reaction (10), and in the second term we have a similar product of equilibrium activities.

TABLE 1: Values of the logarithm of the equilibrium partial pressure of O<sub>2</sub> (dissociation pressure) for some synthesis reactions of the oxides of the metal catalysts for Si NW growth (per 1 mol of O<sub>2</sub>) [8].

Metal catalyst and Si NWs	Oxide synthesis reaction	$\lg p_{O_2} (Me_n O_m)$ at $T = 1000$ K
Cu	$4Cu + O_2 = 2Cu_2O$	-9.94
Ni	$2Ni + O_2 = 2NiO$	-16.02
Fe	$2Fe + O_2 = 2FeO$	-20.84
Si	$Si + O_2 = SiO_2$	-36.10
Ti	$Ti + O_2 = TiO_2$	-37.60
Al	$\frac{4}{3}Al + O_2 = \frac{2}{3}Al_2O_3$	-46.70
Mg	$2Mg + O_2 = 2MgO$	-53.20

Metals with  $K_{eq} > 1$ , see equation (11), are shown above of the shadowed Si row, while metals with  $K_{eq} < 1$  are shown below of the shadowed Si row.

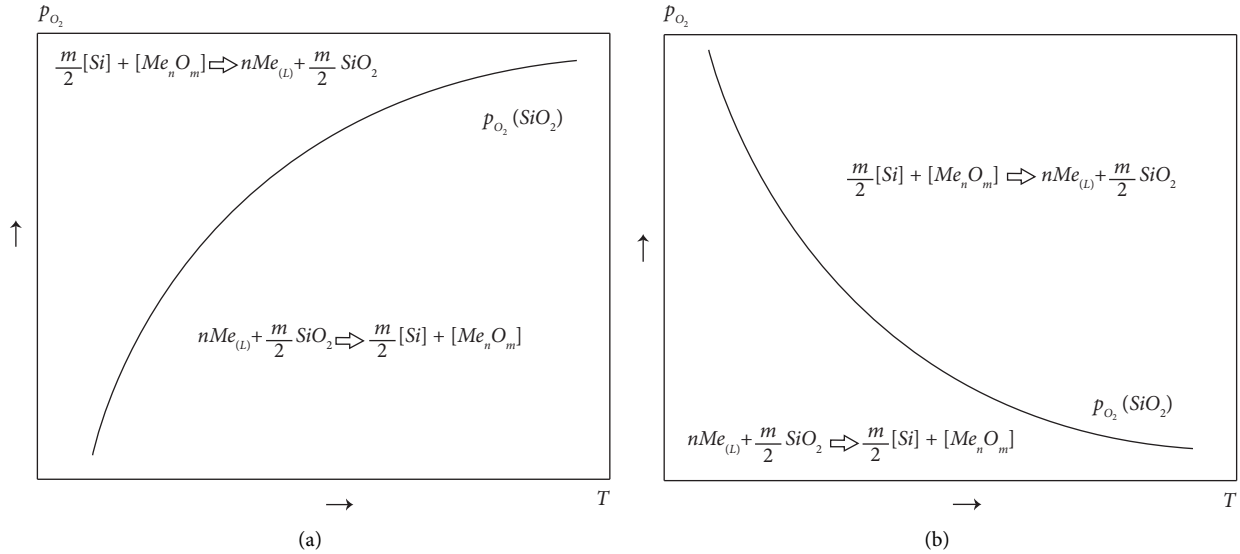


FIGURE 4: Graph for the direction determination of the reaction of formation or dissociation of  $Me_n O_m$  and  $SiO_2$  for metals with lower (a) and higher (b) affinity for oxygen than for silicon.

In order for reaction (10) to proceed in the direction of Si oxidation, the actual concentrations of components with  $\Delta G < 0$  are required, i.e.,

$$\frac{a_{SiO_2}^{(m/2)} \cdot a_{Me}^n}{a_{Si}^{(m/2)} \cdot a_{Me_n O_m}} < K_{eq} \quad (13)$$

In order for inequality (13) to work for any chosen Me catalyst at a certain given temperature ( $K_{eq} = const$ ), we can increase the Si concentration in Me ( $a_{Si}^{(m/2)}$ ) and the oxidizing ability of  $Me_n O_m$  ( $a_{Me_n O_m}$ ) as well as decrease the activity of  $SiO_2$  ( $a_{SiO_2}^{(m/2)}$ ). For metals with a high affinity for

oxygen, such as Ti, Al, Mg [13] than for Si ( $K_{eq} \ll 1$ ), inequality (11) is almost impossible to hold.

The lowest residual concentration of Si in a drop of catalyst after oxidation is determined by the conditions of reaction (10). A measure of the possible completeness of oxidation can be the silicon distribution coefficient between the metal and the oxide. For reaction (10), we write the distribution coefficient as follows:

$$K_{Si} = \frac{[SiO_2]}{[Si]}, \quad (14)$$

where  $[SiO_2]$  is the concentration of  $SiO_2$  in the oxide layer.

It follows from (14) that with an increase in the ability of Si to oxidize, its fraction in the oxide increases, while the residual concentration in the liquid Me-catalyst decreases and the distribution coefficient  $K_{Si}$  increases. Thus, an increase in  $K_{Si}$  means an increase in the oxidation possibility of crystallized Si and vice versa.

**3.6. Dependence of the Si Distribution Coefficient on the Temperature and Type of Oxide.** In this section, we determine the dependence of the distribution coefficient [14] on the composition of the catalyst drop and temperature. As mentioned above,  $SiO_2$  is an acid oxide. Therefore, during the oxidation of metal catalysts not only the bond strength of  $SiO_2$  with basic metal oxides (NiO, CuO, FeO, etc.) increases, but also their oxidizing ability or activity  $a_{Me_nO_m}$  increases as well. Thus, an increase in the basicity of the oxide layer on the droplet surface leads to an increase of  $K_{Si}$ . Indeed, the numerator in equation (14) increases, while the denominator decreases. Therefore, under the conditions of the presence of basic (or amphoteric) Me oxides, dissolved Si is oxidized much more completely.

According to Le Chatelier's principle, for metals with lower affinity for oxygen than silicon, e.g., Cu, Ni, and Fe, both the equilibrium constant  $K_{eq}$  and distribution coefficient  $K_{Si}$  decrease with increasing temperature. Indeed, both reactions (9) and (10) are exothermic and at constant pressure with increasing temperature, the equilibrium shifts to the left. If the system would be in equilibrium, then an increase in temperature should lead to a reverse transition of Si from oxide to liquid Me, as shown in Figure 4(a) for details.

For metals with a higher affinity for oxygen than for silicon, such as Ti, Al, and Mg, the equilibrium constant of reaction (10)  $K_{eq}$  increases with increasing temperature. In this case, reaction (10) is endothermic and with increase in the temperature, the equilibrium shifts to the right; hence, Si concentration in the solution decreases with the temperature increase.

The direction of the reaction and the affinity of  $Me_nO_m$  for Si will depend on the ratio of their actual and equilibrium concentrations. At a given temperature  $T$  and a constant value  $p_{O_2}$  ( $p_{O_2(ideal)}$ ) above the equilibrium value  $p_{O_2}$  ( $p_{O_2(SiO_2)}$ ), the reaction (10) shifts to the right. This case corresponds to points in the region above the curve in Figure 4(a). Below the curve, there are points belonging to

the reactions that are oxidizing with respect to this metal. In this case, the process goes in the direction of the dissociation of  $SiO_2$ . Thus, the upper field above the curve is a region of temperatures  $T$  and pressures  $p_{O_2}$  in which the metal is stable, while in the lower region the oxide is stable  $Me_nO_m$ . For an endothermic process involving Ti, Al, and Mg metals, the opposite relationship  $p_{O_2} = f(T)$  is obtained, as demonstrated by Figure 4(b).

This is probably why, at high temperatures, the formation of a surface oxide film on Me-Si droplets is not observed experimentally, and a stable growth of NWs is observed, which is absent at lower temperatures of the NW growing process [2, 15].

## 4. Conclusion

In the process of growing Si NWs in the presence of residual  $O_2$  impurities in the gas phase, the following qualitative conclusions can be drawn:

With the participation of catalytic particles of Ti, Al, and Mg, the growth of Si NWs is difficult, drops of the metal catalyst are strongly oxidized, and crystals either do not form at all or are characterized by instability in the direction of growth. At the same time, particles of Cu, Ni, and Fe give a much more stable growth of NWs.

The formation of a basic oxide (NiO, Cu<sub>2</sub>O, FeO, etc.) during metal oxidation facilitates the transition of Si from a solution of a catalyst drop to an oxide (oxidation of the semiconductor) while making a reverse transition, i.e., recovery, difficult. Therefore, the growth of silicon-NWs in the presence of oxygen in the gas phase is significantly slowed.

Only metals with a lower chemical affinity for  $O_2$  than for Si are applicable as catalysts for the growth of NWs. The transition of Si from a solution of a drop of Me catalyst to the oxide layer is accompanied by heat generation. Therefore, as the growth temperature increases the completeness of Si oxidation decreases and the completeness of its reduction increases. In the case of pure Me and Si, there is no mutual influence between them at the initial stage on the substrate. Therefore, as the growth temperature increases, the oxidation reaction of the Me-catalyst shifts toward the dissociation of  $Me_nO_m$  and the growth of Si NWs is facilitated. In this case, temperature increase would generally decrease the amount of oxides in the system since their individual equilibrium  $O_2$  partial pressure increases with temperature.

## Abbreviations

VLS: Vapor-liquid-solid

NWs: Nanowires.

## Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.



## Authors' Contributions

VAN and NS performed the experiment. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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