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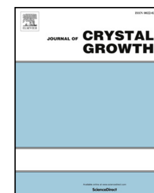
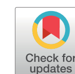


Thermodynamics of oxidation and reduction during the growth of metal catalyzed silicon nanowires



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ABSTRACT

We have studied the thermodynamics of oxide formation, and the recovery of silicon and the metal catalysts from the dissociation of their respective oxides during the growth process of Si nanowires (NWs) under the Vapor → Liquid Droplet → Solid (VLS) mechanism. It is demonstrated that Si NWs under growth temperatures are thermodynamically unstable in any gas phase containing even a small concentration of O_2, and under favorable kinetic conditions Si NWs should entirely convert into dioxide (SiO_2). Thermal dissociation of SiO_2 in the growth conditions for NWs is practically impossible as it would require either lowering the pressure of O_2 to an unachievable, critically low value or raising the temperature to a point which is impossible to reach in ordinary conditions. Decreasing the diameter, i.e., increasing the Si NW dispersity, leads to an increase in the interaction with O_2 and this O_2 will be held more tightly by Si. Thus, thinner NWs should oxidize stronger than thicker ones. The main metal catalysts for NW growth, as well as Si, are characterized by significant affinity with O_2 and inconvertible oxide formation reactions. The most stable Si NW growth is observed with metals (Au, Pt, Cu, Ni, etc.) whose oxides are less stable than SiO_2. Only metals with a lower affinity to O_2 than to H_2 or any other reducing agent are applicable to guarantee the recovery process when used as a catalyst for the growth of NWs.

1. Introduction

During nanowire (NW) growth under the Vapor → Liquid Droplet → Solid (VLS) mechanism clean growth should be created. When there is residual O_2 in the gas phase during epitaxial NW growth from molecular and chemical beams (for example SiH_4), vapor phase epitaxy, chemical vapor deposition or other stages, it leads to (i) unintended SiO_2 formation at the wire sidewalls and at the growing Si-substrate, (ii) accidental oxidation of catalyst particles and (iii) growth instability and in certain cases it can block NW growth [1–10]. In Ref. [1] the effect of oxide overlayer formation on the nucleation of nanowires and its effect on the reproducibility and yield of epitaxially grown nanowires were investigated. Gold-assisted low-temperature oxidation of silicon has already been reported by Hiraki et al. in 1971 [3,5]. Besides, in thermally grown SiO_2 a connected positive charge is always present and can lead to a change in the potential of Si NWs and unfavorable formation of coaxial p-n junctions. On the other hand, the presence of O_2 in the gas-phase atmosphere permits formation of coaxial Si/SiO_2 structures and growth of SiO_2 NWs which have excellent photoluminescent and dielectric properties and outstanding biocomparability, a fact that has attracted great attention from researchers [11–15]. Si/SiO_2 structures differ in the perfection of the semiconductor–dielectric boundary and the minimum charge density at this boundary ($\sim 10^{10}\,cm^{-2}$), which is especially important in the usage of SiO_2 as a gate dielectric in MOS and NMOS transistors based on NWs. Alloyed SiO_2 layers are a perfect source for Si diffusion alloying. SiO_2 can be used on the substrates as a masking material in the formation of regular NW systems and as an isolating and protecting cover at the surface of Si crystals [16].

In studies devoted to the growth of SiO_2 NWs, the applicability of the VLS mechanism has been suggested in order to explain local nucleation and growth of oxide wires [4,16,17–19]. However, such views are contrary to the modern understanding of NW growth by the VLS mechanism as a growth mechanism of exclusively crystalline, anisotropic materials [20], as SiO_2 can be easily formed in amorphous, isotropic conditions and is not crystallized at extremely high temperatures (1473–1573 K) [1,10,15].

Therefore, control and management of the formation process of SiO_2 layers requires a deep understanding of the thermodynamic conditions under which Si oxidation occurs during NW growth in the presence of

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O_2 as particles of metal catalysts are oxidized and also requires an understanding of how the crystal size affects SiO_2 oxidation and decomposition. That is why the aim of this work is to analyze the thermodynamics of the formation and dissociation processes of SiO_2 and oxides of metal catalysts during Si NW growth.

2. Effect of oxide overlayer formation on the growth silicon nanowires

The presence of a surface oxide layer on the growth substrate disturbs the fusion of the catalyst droplet with Si and the formation of a stable droplet of the Me-Si (metal-Si) solution [1,4]. The SiO_2 interlayer between the metal and the Si-substrate doesn't permit the formation of an equilibrium Me/Si boundary, and while the precursor gas (for example SiH_4) is fed into the growth zone the droplet either stays on the substrate or splits into smaller droplets giving rise to multiple NWs with different spatial orientations [1–4].

During growth of Si NWs in H_2 flow which has not undergone continuous purification of residual O_2 and which has minor residues of water vapor, a SiO_2 layer with a thickness of 0.5–1.5 nm is formed on the surface of the NWs and on the growth substrate. According to the results of a spectrum analysis of samples, the elemental composition of the NW surface oxide film can be expressed as SiO_x (where x is in the range of 1–2) [4]. Apparently, SiO_2 surface layers of Si NWs under temperatures below 1473 K can be formed only by a two-stage scheme: first axial growth of Si NWs, then radial growth of the oxide layer by means of Si oxidation.

Due to the presence of the oxide surface layer, the growth of Si NWs is slowed down and the crystals are characterized by high morphological instability with multiple bends of single- and multiple-bend character and different inclination angles that do not depend on the NW radius or type of metal catalyst [1,4].

3. Thermodynamics of formation, dissociation and recovery of SiO_2 and main metal catalysts

Si NWs grown with the participation of Au, Cu, Pt, Pd and some other metals are more resistant to oxidation and show more stable growth. However, the growth of Si NWs with the participation of Al, Mg, Zn or some other metals in the presence of even small concentrations of O_2 is difficult [2,4]. Due to oxidation of the NW sidewalls (at a low degree of hydrogen cleaning and in the presence of oxygen-containing components and water vapor), wires keep their cylindrical form and there is no facet formation under the Vapor → Solid mechanism, which is common for the two-stage growth process of Si NWs in conditions with no oxygen and water in the gas phase [4].

Directly after growth in a dry atmosphere, SiO_2 layers formed on Si NW sidewalls consisting of chain silicates Si—O—Si—O (Fig. 1a). The SiO_2 surface can also contain silanol groups Si—OH (Fig. 1b).

However, under temperatures more than 383–423 K a reversible process starts transforming silanol into siloxane with water separation. This reduces the length of the Si—O connection and significantly strengthens it. This process continues up to the moment when all trapped hydrogen is removed from the interface.

During Si NW growth with residual O_2 concentration in the growth atmosphere, SiO_2 is formed by an exothermic reaction

$$Si_{(S)} + O_{2(V)} \leftrightarrow SiO_{2(S)};\ \Delta H_1 < 0, \quad (1)$$

where ΔH_1 is the thermal effect of the reaction.

The reverse process of dioxide thermal dissociation comes with heat absorption. We shall consider the simplest case of the absence of solutions between solid materials, i.e., when Si and its oxide present pure independent phases and the total number of phases including the gas phase is three. In this case, the observed chemical system is a two-component–three substances system with one response equation. In accordance with Gibb's phase rule the system is monovariant (C = 2 + 2 − 3 = 1). This means that the equilibrium pressure of O_2 depends only on temperature $p_{O_2} = f(T)$.

This function can be derived from the expression for the reaction equilibrium constant K, see Eq. (1) [21]

$$K = \frac{a_{SiO_2}}{a_{Si}\cdot p_{O_2}}, \quad (2)$$

where a_{SiO_2} and a_{Si} are the activities of SiO_2 and Si, accordingly.

As the activities of pure solid materials are practically equal to 1, then from (2) we obtain

$$K = \frac{1}{p_{O_2}} = f(T). \quad (3)$$

From (3), specifyingp_{O_2} as $p_{O_2(SiO_2)}$, we obtain

$$p_{O_2(SiO_2)} = \frac{1}{K} = f^{-1}(T). \quad (4)$$

From (4) it is clear that the oxygen partial pressure$p_{O_2(SiO_2)}$ in the formation and dissociation reaction of silicone dioxide can be called the dissociation pressure of SiO_2.

Taking into account (4) we can write an equation for the standard change of Gibbs free enthalpy ($-\Delta G^0 = RT\ln K$)

$$-\Delta G^0 = -RT\ln p_{O_2(SiO_2)}. \quad (5)$$

In accordance with (5), the greater the ($-\Delta G^0$), the less the $p_{O_2(SiO_2)}$, the greater the affinity of Si to O_2 and the stronger and more stable the oxide. In the process of stability reduction, SiO_2 is able to dissociate at a given temperature and the partial pressure of O_2 increases upon reaching equilibrium. As temperature increases, the equilibrium constant K of the observed exothermic reaction decreases and the dissociation pressure under Eq. (4) grows, i.e., oxide stability lowers.

In order to evaluate the flow direction of the process we shall use the isotherm of Van't Hoff's chemical reaction [22], which in respect to our considered system will have the following form

$$\Delta G = RT\left(\ln\frac{1}{p_{O_2(\text{real})}} - \ln\frac{1}{p_{O_2(SiO_2)}}\right) = \ln p_{O_2(SiO_2)} - \ln p_{O_2(\text{real})}. \quad (6)$$

In this case, the equilibrium constant K in Eq. (3) is expressed through the dissociation pressure of SiO_2 as $p_{O_2(SiO_2)}$ with $p_{O_2(\text{real})}$ meaning the actual partial pressure of O_2 in the gas environment surrounding SiO_2 and Si.

Thus, the sign of ΔG, and hence the possible process direction at a given temperature, is defined by the ratio of the values of $p_{O_2(SiO_2)}$ and $p_{O_2(\text{real})}$. Between these values the following relationships are possible:

1. 1. $p_{O_2(\text{real})} > p_{O_2(SiO_2)}$, i.e., there is an excess of O_2 in comparison with the equilibrium concentration. In this case $\Delta G < 0$ and the reaction can proceed towards SiO_2 formation.
2. 2. $p_{O_2(\text{real})} < p_{O_2(SiO_2)}$, i.e., the actual O_2 pressure is less than the equilibrium pressure. In this case $\Delta G > 0$ and the process can go towards SiO_2 dissociation.
3. At $p_{O_2(\text{real})} = p_{O_2(SiO_2)}$, $\Delta G = 0$ and the system is in equilibrium.

This is illustrated in Fig. 2 in which the plot is constructed according to the equation

$$\ln p_{O_2} = \frac{\Delta H_T^0}{4,576\,T} - \frac{\Delta S_T^0}{4,576}, \quad (7)$$

where $\Delta H_T{}^0$ and $\Delta S_T{}^0$ are the changes in enthalpy and entropy at a given temperature, respectively, 4.576 is a numerical coefficient that is set using experimental data for a given temperature range and T is absolute temperature. Eq. (7) shows that the partial pressure $p_{O_2(\text{real})}$ is an exponential function of increasing temperature. Points located on the curve in Fig. 2a correspond to equilibrium systems and characterize the SiO_2 dissociation pressure, which increases with temperature

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