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Thermodynamic Theory of Phase Separation in Nonstoichiometric Si Oxide Films Induced by High-Temperature Anneals

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Abstract: High-temperature anneals of nonstoichiometric Si oxide (SiO_x , $x < 2$) films induce phase separation in them, with the formation of composite structures containing amorphous or crystalline Si nanoinclusions embedded in the Si oxide matrix. In this paper, a thermodynamic theory of the phase separation process in SiO_x films is proposed. The theory is based on the thermodynamic models addressing various aspects of this process which we previously developed. A review of these models is provided, including: (i) the derivation of the expressions for the Gibbs free energy of Si oxides and Si/Si oxide systems, (ii) the identification of the phase separation driving forces and counteracting mechanisms, and (iii) the crystallization behavior of amorphous Si nanoinclusions in the Si oxide matrix. A general description of the phase separation process is presented. A number of characteristic features of the nano-Si/Si oxide composites formed by SiO_x decomposition, such as the local separation of Si nanoinclusions surrounded by the Si oxide matrix; the dependence of the amount of separated Si and the equilibrium matrix composition on the initial Si oxide stoichiometry and annealing temperature; and the correlation of the presence of amorphous and crystalline Si nanoinclusions with the presence of SiO_x ($x < 2$) and SiO_2 phase, respectively, in the Si oxide matrix, are explained.

Keywords: thermodynamic theory; phase separation; nonstoichiometric Si oxide; Gibbs free energy; Si nanoparticles; penalty energy; stress; crystallization; thermodynamic equilibrium



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1. Introduction

The high-temperature phase separation of nonstoichiometric Si oxide (SiO_x , $x < 2$) films is a key method for producing composite structures consisting of nanosized Si (nano-Si) inclusions embedded in a Si oxide matrix, for Si-based nanoelectronic device applications. In particular, nano-Si/Si oxide composites are proposed for use in light emitting devices [1,2], flash memory floating gates [3,4], photodiodes [5,6], electron field emission cathodes [7,8], and solar cells [9,10]. The possibilities of extending the optical, luminescence, and electrical properties of such composites are sought by modifying them with such metals as Er [11], Sn [12], Sm [13], Fe [14], and Al [15].

Various methods, such as Si ion implantation in SiO_2 [16], sputtering [17] and electron beam evaporation [18,19] of Si and SiO, plasma-enhanced chemical vapor deposition [20,21], magnetron sputtering [22], and the thermal vacuum or reactive evaporation of SiO [23,24] are used in fabricating SiO_x films. The average size of the Si nanoparticles formed as a result of phase separation can be controlled by varying the annealing temperature, or by tuning the initial Si oxide composition. A reduction in oxygen content in the SiO_x films leads to an increase in the nano-Si size and density, and the standard deviation of their distribution [25,26]. Raising the annealing temperature also results in an increase in the average nano-Si size [27,28]. A higher level of flexibility is provided by the superlattice approach proposed by Zacharias et al. [29], in which thin SiO_x layers alternate with stoichiometric SiO_2 layers not undergoing separation, thus enabling an independent control of

the location, size (corresponding to the SiO_x layer thickness), and concentration of the Si nanoinclusions in the Si oxide matrix.

During high-temperature annealing, the partial or complete decomposition of nonstoichiometric Si oxide takes place, according to the following reaction:



where x_0 and x are the initial and the current stoichiometry indexes of the Si oxide phase, respectively. The reaction (1) leads to the separation of Si nanoparticles, and an increase in oxygen concentration in the surrounding Si oxide matrix.

The degree of phase separation in SiO_x films is often characterized by the equilibrium stoichiometry index of the Si oxide matrix, x_{eq} , which also indicates the amount of separated Si and, hence, the concentration and the average size of formed Si nanoinclusions. Experimental data show that $x_{eq} < 2$ (incomplete separation) for annealing temperatures below about 950 °C, and increases with the increase in both x_0 and T [30–32]. The degree of phase separation correlates with the amorphous or crystalline state of Si nanoinclusions. For annealing temperatures not exceeding approximately 950 °C, mainly amorphous Si (a-Si) nanoparticles form, while at higher temperatures, the formation of Si nanocrystallites takes place, as revealed by Raman scattering, infrared (IR) absorption, x-ray photoelectron spectroscopy (XPS), and high-resolution electron microscopy investigations [24,33,34].

Understanding the phase separation phenomenon in SiO_x films in terms of thermodynamics would enable the unveiling of its mechanisms, as well as laying the foundation for the macroscopic description of its kinetics. A thermodynamic approach requires knowledge about transformations of the Gibbs free energy in Si/Si oxide systems during high-temperature anneals. The minimum values of the Gibbs free energy determine the equilibrium between the separated Si and Si oxide phases, as well as the equilibrium Si oxide composition.

A literature review demonstrates that studies aimed at the thermodynamic description of phase separation in nonstoichiometric Si oxide films are practically absent. A limited number of papers [35,36] present thermodynamic analyses of Si–O systems, with emphasis on particular compositions such as Si₂O₃, SiO, and Si₂O, as well as different SiO₂ phases. To our best knowledge, the only recent attempt to phenomenologically introduce the Gibbs free energy of a nonstoichiometric Si oxide was undertaken by La Magna et al. [37], to describe the mechanism of the incomplete separation of the SiO_x phase, and its dependence on the initial Si oxide stoichiometry. The thermodynamically derived expression for the Gibbs free energy of Si oxide and Si/Si oxide systems was first presented in our publication [38]. By analyzing transformations of the Gibbs free energy with the annealing temperature and the amount of separated Si, the formation of equilibrium between bulk amorphous or crystalline Si and Si oxide was studied in detail. The thermodynamic model of equilibrium states in Si/Si oxide systems was later modified, to take into account other aspects of the phase separation process, such as the influence of stress [39,40] and nano-Si/Si oxide interfaces [41,42], and the crystallization behavior of amorphous Si nanoinclusions embedded in a Si oxide matrix [43].

In this paper, we review the theoretical models that we developed earlier, which constitute the general thermodynamic theory of phase separation in nonstoichiometric Si oxide films. The formation of nano-Si/Si oxide composites by high-temperature SiO_x decomposition is discussed in the framework of this theory, simultaneously taking into account various aspects of the phase separation process. A number of the characteristic features of this process, and the formed nano-Si/Si oxide composites, are explained, including: (i) the mechanism of the local separation of the Si phase, accompanied by a homogeneous increase in the stoichiometry index of the Si oxide matrix, (ii) the dependence of the amount of separated Si and the equilibrium matrix composition on the initial Si oxide stoichiometry and annealing temperature, and (iii) the correlation of the presence of amorphous Si nanoinclusions with the SiO_x ($x < 2$) phase, and crystalline Si inclusions with the SiO₂ phase, in the Si oxide matrix. The proposed general thermodynamic theory may be further used as a

basis for developing kinetic models, which will enable the optimization of technologies in the formation of nano-Si/Si oxide composites for a broad range of applications.

2. Theory and Results

As already mentioned in the Introduction section, the thermodynamic theory of phase separation in nonstoichiometric Si oxide films, induced by high-temperature anneals, integrates a number of theoretical models considered in our previous publications [38–43]. The subjects of these models are listed in the left-hand side of the diagram shown in Figure 1. Such integration will provide a deeper understanding of the SiO_x phase separation phenomenon in terms of thermodynamics, as is schematically shown in the central part of the diagram in Figure 1. The unified theory will enable us to predict the state of nano-Si/Si oxide composites (the quantity of separated Si, the equilibrium stoichiometry of the Si oxide matrix, the amorphous or crystalline state of Si nano-inclusions, etc.) as a function of the initial Si oxide composition and annealing conditions. Its different components have already been successfully applied to reveal the kinetic mechanisms of phase separation [44]; understand the annealing-induced transformations in Si oxide, oxynitride and nitride-based superlattices with nanometer thick layers [45–49]; and describe the structural properties of Si oxynitrides grown at different temperatures [50], as depicted in the right-hand side of the diagram presented in Figure 1. All the theoretical models composing the unified thermodynamic theory are reviewed below, followed by a general discussion of the phase separation process in SiO_x films, in the Discussion section.

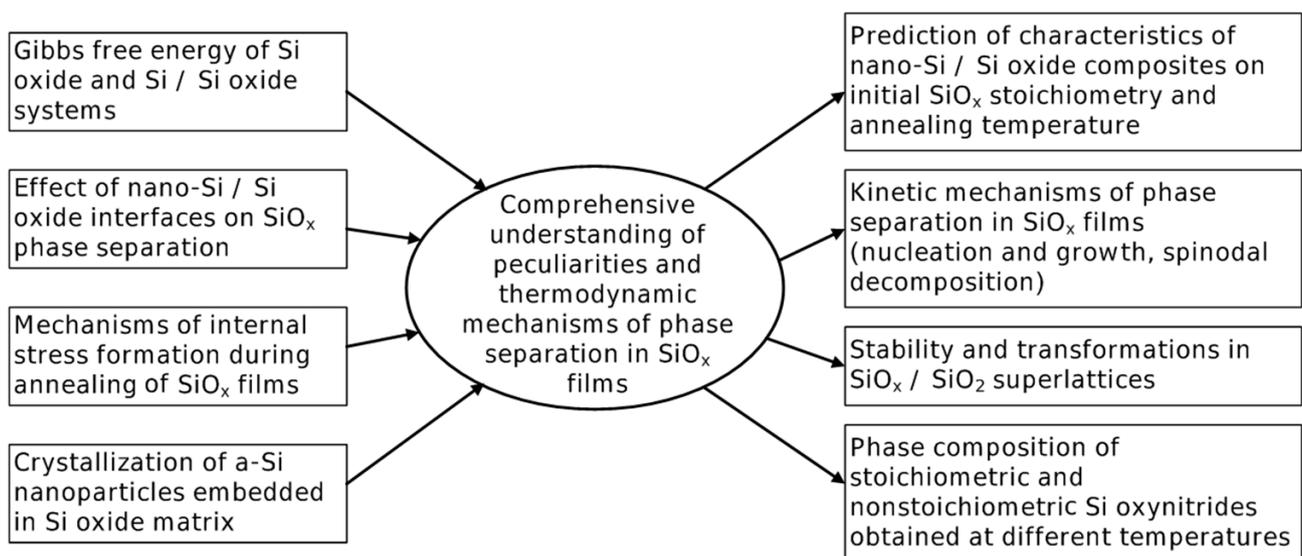


Figure 1. Diagram of the components and application areas of the thermodynamic theory of phase separation in SiO_x films.

2.1. Gibbs Free Energy of Si/Si Oxide Systems

The key issue in the thermodynamic theory of phase separation in SiO_x films is obtaining the Gibbs free energy of the Si oxides and Si/Si oxide systems. The method of deriving the Gibbs free energy of the mentioned systems, as well as the results of the study of equilibrium between the contacting Si and Si oxide phases, was described in detail in our previous publication [38]. According to the method used there, the temperature-induced separation of excess Si atoms from Si oxide with the initial stoichiometry x_0 is considered according to the reaction (1) until the equilibrium stoichiometry $x = x_{eq}$, corresponding to the minimum Gibbs free energy of the resulting Si/Si oxide system, is achieved. As a first approximation, contacting planar Si and SiO_x layers shown schematically in Figure 2 are assumed to form by SiO_{x0} decomposition, instead of experimentally observed nano-Si inclusions distributed within the Si oxide matrix. Such approximation enables us to ignore

the contribution to the Gibbs free energy from the interfaces between the nano-Si inclusions and the surrounding matrix. Moreover, the separation of Si in the amorphous state is considered in the most general case, Si oxide and crystalline Si (c-Si)/Si oxide systems being the partial cases.

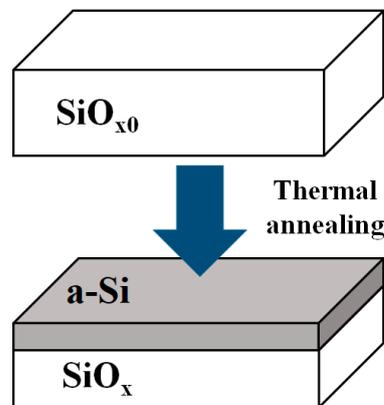


Figure 2. Geometry of the initial SiO_{x_0} phase, and phase separated a-Si/Si oxide system.

The following provisions establish the background for deriving the expression for the Gibbs free energy of Si oxides and Si/Si oxide systems [38]:

1. The Gibbs free energy of the a-Si phase is expressed in terms of the Gibbs free energy of c-Si plus the excess energy equal to $\Delta g_{ac} = \frac{h_E - s_E T}{N_A}$ per one Si atom [51]. Here, $h_E = 13,400$ J/mole is the molar crystallization enthalpy [52], $s_E = 3.97$ J/mole \times K is the molar excess entropy of amorphous-to-crystalline transition [53], and $N_A = 6.022 \times 10^{23}$ mole $^{-1}$ is the Avogadro constant, respectively.
2. The nonstoichiometric Si oxide phase is considered in the binary solution approximation [54], in which the SiO_x solution is formed by mixing elemental Si and oxygen atoms obtained by the decomposition of O_2 molecules.
3. The structure of Si oxide is made up of interconnected $\text{Si-O}_y\text{Si}_{4-y}$ tetrahedral units ($0 \leq y \leq 4$) with different oxidation degrees y of a central Si atom. In addition to the Si-Si and Si-O bond energies, each tetrahedral unit is characterized by the penalty energy Δ_y as the measure of the energy nonequivalence of the units with different values of y ($\Delta_0 = \Delta_4 = 0$ eV, $\Delta_1 = 0.5$ eV, $\Delta_2 = 0.51$ eV, and $\Delta_3 = 0.22$ eV) [55]. The probability of finding a tetrahedral unit with either value of y obeys the random bonding model proposed by Phillip [56].
4. The entropy of mixing is considered to be the configuration entropy of the Si oxide phase, associated with the number of arrangements of oxygen atoms between the pairs of Si atoms.

As demonstrated in [38], the Gibbs free energy of an a-Si/Si oxide system is conveniently expressed per one atom in this system, which naturally provides its dependence on the initial and current stoichiometry indexes of the Si oxide phase, x_0 and x , respectively, and the annealing temperature, as the variables:

$$g(x_0, x, T) = \frac{x_0}{1+x_0} \left\{ \frac{1}{x} \sum_{y=0}^4 \frac{4!}{(4-y)!y!} \left(\frac{x}{2}\right)^y \left[\frac{2-x}{2}\right]^{4-y} \Delta_y - kT \left(\frac{2}{x} \ln \frac{2}{2-x} - \ln \frac{x}{2-x} \right) - \frac{1}{x} \frac{h_E - s_E T}{N_A} \right\} \quad (2)$$

where $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann's constant. In deriving the expression (2), all the contributions which are not the functions of (x_0, x, T) were omitted, as they have no influence on determining the equilibrium states in Si/Si oxide systems. The first term between the braces is the part of the mixing enthalpy corresponding to the total penalty

energy of all the Si–O_ySi_{4–y} tetrahedral units composing the Si oxide matrix. The second term is the configuration entropy contribution, and the only one that is temperature-dependent. The third term expresses the excess Gibbs free energy of a-Si, as compared to that of c-Si. The expression (2) can be modified to provide the Gibbs free energy of other considered systems. In particular, the truncation of the term proportional to the $\frac{h_E - s_E T}{N_A}$ results in the Gibbs free energy per one atom of a c-Si/Si oxide system, while setting additionally $x = x_0$, turns it into the Gibbs free energy of the Si oxide phase.

Each term between the braces in the expression (2) corresponds to a single mechanism, which drives or counteracts the separation of the initial nonstoichiometric Si oxide into Si and SiO_x phases, depending on whether it is a descending or ascending function of x . The mathematical analysis shows that the only driving force for demixing is the tendency to decrease the total penalty energy of all the Si–O_ySi_{4–y} tetrahedral units, which has zero value for the coexisting stoichiometric Si and SiO₂ phases (only Si–Si₄ and Si–O₄ tetrahedra with $\Delta_0 = \Delta_4 = 0$). The phase separation is counteracted by the formation of the amorphous Si phase (in the case of a-Si/Si oxide systems), as well as by the decrease in the configuration entropy, with the increase in x leading to the increase in the respective Gibbs free energy contribution. As a result, the equilibrium between the Si and Si oxide phases is predicted at some value $x_{eq} < 2$, which may be interpreted in terms of the solubility limit of Si in SiO₂ [38].

The application of the expression (2) provides a description of equilibrium states in bulk Si/Si oxide systems. The calculated dependences of the Gibbs free energy on x for different temperatures and values of x_0 are shown in Figure 3a,b, respectively. The minima of the curves correspond to the equilibrium between the Si and Si oxide phases. It can be seen from Figure 3a,c that x_{eq} is predicted not to depend on the initial Si excess (value of x_0), which is also supported by the mathematical analysis of the expression (2) [38]. Moreover, x_{eq} in the described model decreases with annealing temperature (see Figure 3b,d), which corresponds to the increase in the concentration of the Si dissolved in SiO₂, in full consistency with the Si solubility concept. However, such findings contradict the experimental observations of phase separation in SiO_x films, with the formation of nanosized Si inclusions in the Si oxide matrix. According to these observations, the equilibrium Si oxide stoichiometry increases with both x_0 and annealing temperature [30–32]. Hence, the expression (2) should be modified, by taking into account additional mechanisms, to describe the experimental dependences of x_{eq} . These mechanisms and their effects on the equilibrium in nano-Si/Si oxide systems are discussed in the next sections.

2.2. Effect of Nano-Si/Si Oxide Matrix Interfaces on Phase Equilibria in Si/Si Oxide Systems

One of the mechanisms that might have an influence on phase separation in SiO_x films is the formation of interfaces of nano-Si inclusions with the surrounding Si oxide matrix. The total relative area of such interfaces is high enough in view of the small nano-Si sizes and their high concentrations. The interface-related contribution to the Gibbs free energy (2) is positive. Therefore, there is a need to verify the effect of the interface free energy on the value of x_{eq} and its dependence on the annealing temperature.

The effect of the interfaces between the nano-Si inclusions and the Si oxide matrix is described in [41,42]. For simplicity, Si nano-inclusions with equal radii R are considered. The radius R is calculated as follows:

$$R = \sqrt[3]{\frac{3\Omega}{4\pi} i} = \sqrt[3]{\frac{3\Omega}{4\pi} \frac{x - x_0}{x(1 + x_0)} \frac{C_0}{C_{incl}}} \quad (3)$$

where $\Omega \approx 2.29 \times 10^{-29} \text{ m}^3$ is the atomic volume of Si [57], i is the quantity of Si atoms in a single nano-inclusion, $C_0 = 7 \times 10^{22} \text{ cm}^{-3}$ is accepted to be the total atomic concentration of the SiO_x phase [37], and $C_{incl} \sim 10^{18} - 10^{19} \text{ cm}^{-3}$ is the typical concentration of Si nano-inclusions formed as a result of phase separation [58,59], respectively. R is directly related to the concentration of separated Si, which is expressed as $\frac{x - x_0}{x(1 + x_0)} C_0$.

The interface contribution to the Gibbs free energy per one atom for a nano-Si inclusion embedded in Si oxide looks as follows:

$$g_{interface} = 4\pi\gamma_{oa}R^2\frac{C_{incl}}{C_0} \quad (4)$$

where γ_{oa} is the specific interface energy of nano-Si/Si oxide interface. Since the analysis is carried out for the temperature range of incomplete phase separation, which implies the predominant formation of a-Si nanoinclusions [24,33,34], $\gamma_{oa} = 0.01 \text{ J/m}^2$ is set corresponding to the a-Si/SiO₂ interface [43].

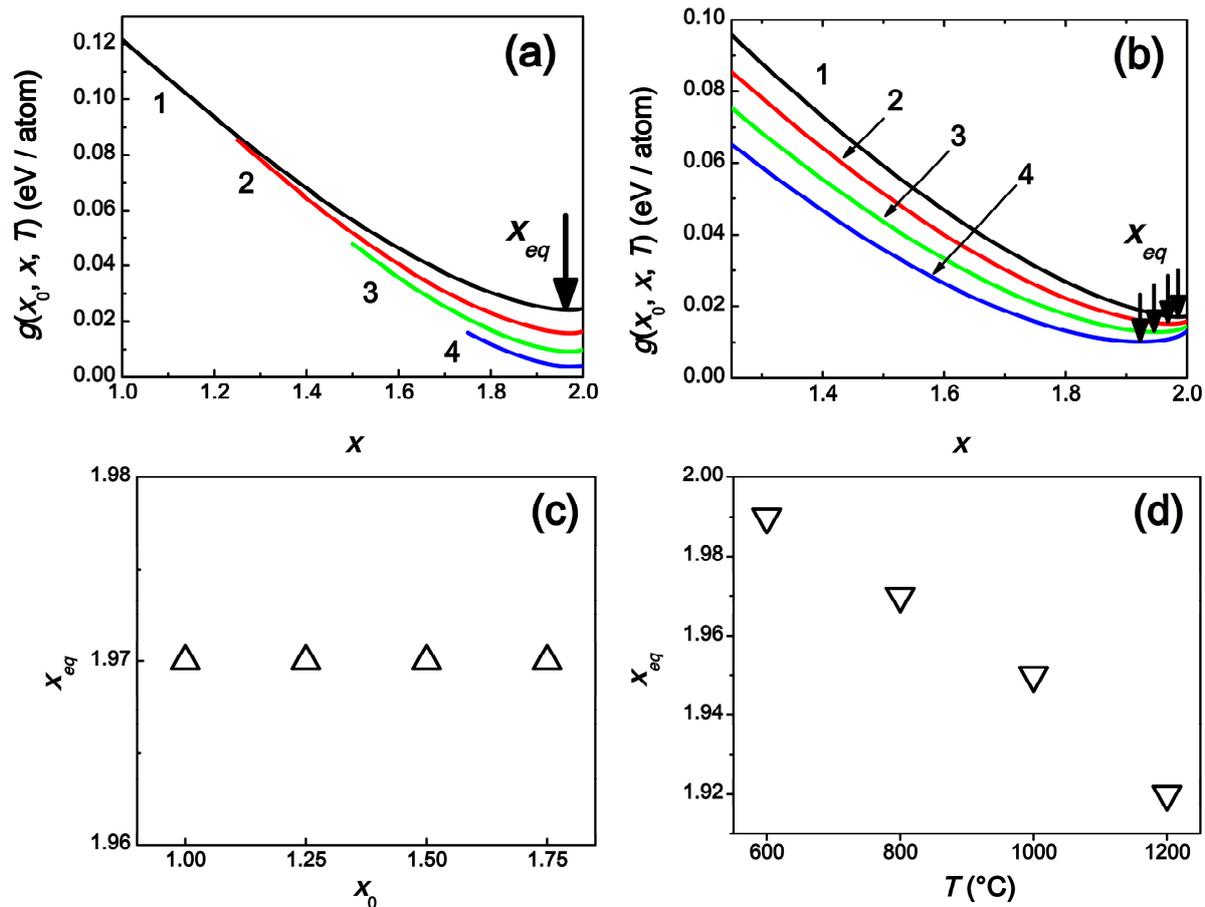


Figure 3. The dependence of the Gibbs free energy per one atom on the stoichiometry index of Si oxide in the a-Si/Si oxide systems, calculated by the expression (2). (a) For different initial Si oxide stoichiometry indexes, x_0 : 1—1, 2—1.25, 3—1.5, and 4—1.75. The annealing temperature $T = 800 \text{ }^\circ\text{C}$. (b) For different annealing temperatures, T : 1—600, 2—800, 3—1000, and 4—1200 $^\circ\text{C}$. The initial Si oxide stoichiometry $x_0 = 1.25$. The arrows in the panels indicate equilibrium stoichiometry indexes of the Si oxide phase. All the curves are shifted by $\frac{1}{1+x_0} \frac{hF - sET}{N_A}$ for better visualization. Panels (c) and (d) show the equilibrium stoichiometry index of Si oxide versus its initial stoichiometry and annealing temperature, recalculated using the data presented in panels (a) and (b), respectively.

Figure 4 shows the dependences of $g_{interface}$ calculated by the expression (4) on the stoichiometry index of the SiO_x matrix for different initial Si oxide stoichiometries x_0 and nano-Si concentrations. It can be seen from this figure that the contributions of a-Si/Si oxide interfaces to the Gibbs free energy do not exceed approximately $5 \times 10^{-4} \text{ eV/atom}$ for reasonable C_{incl} values, which is at least two orders of magnitude smaller than the data presented in Figure 3a,b. The partial crystallization of amorphous Si nanoinclusions may lead to the modification of γ_{oa} by about one order of magnitude (the specific energy of

the bulk c-Si/SiO₂ interface ranges from 0.1 to 0.6 J/m² [60,61]), which will result in the proportional change in the interface contribution to the Gibbs free energy. However, no significant modification in the Gibbs free energy expressed as the sum of (2) and (4) will be achieved. Moreover, multiple studies have demonstrated that the interface free energy of nanoparticles decreases upon reducing their sizes [62,63], which leads to an even smaller contribution to the Gibbs free energy from the nano-Si/Si oxide interfaces. Therefore, the role of the mentioned interfaces on equilibrium states in Si/Si oxide systems during phase separation in SiO_x films may be considered insignificant, and therefore ignored in further analysis.

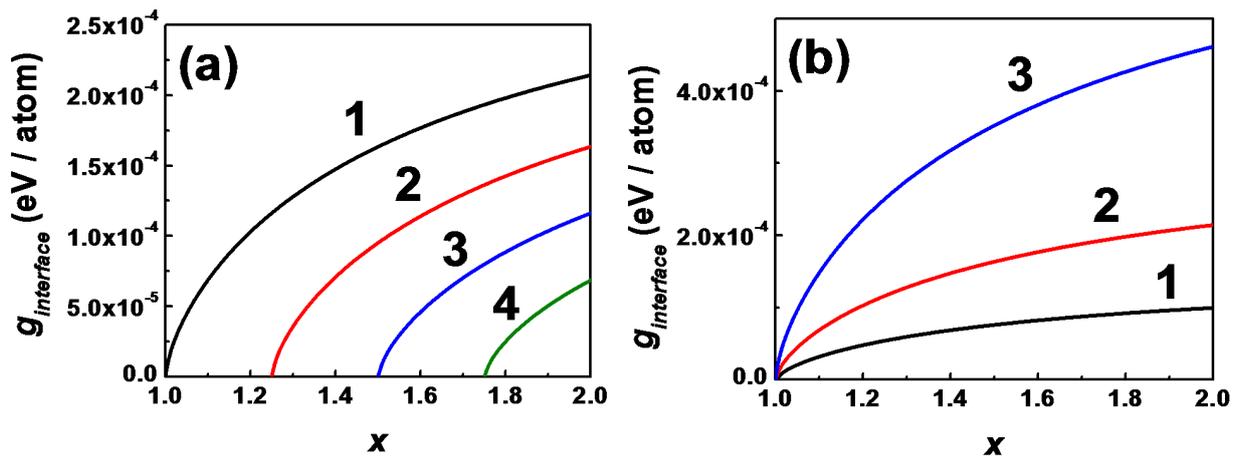


Figure 4. The dependence of the interface contribution to the Gibbs free energy of a-Si/SiO_x system on the stoichiometry index of the Si oxide phase. (a) For different initial Si oxide stoichiometries, x_0 : 1—1, 2—1.25, 3—1.5, and 4—1.75. The concentration of the Si nano-inclusions $C_{incl} = 10^{18} \text{ cm}^{-3}$. (b) For different concentrations of Si nano-inclusions, C_{incl} : 1— 10^{17} , 2— 10^{18} , and 3— 10^{19} cm^{-3} . The initial Si oxide stoichiometry $x_0 = 1$.

2.3. Influence of Internal Stress on Phase Separation in SiO_x Films

The formation of internal stress during the phase decomposition of SiO_x films was found to be key to define the equilibrium between the separated Si and Si oxide phases. The mathematical form of the stress-related contribution to the Gibbs free energy of Si/Si oxide systems was proposed in our earlier publication [39], and its parameters were determined by comparing the theoretical predictions with the experimental dependences of x_{eq} on the annealing temperature. Here, we briefly review the main results obtained in [39], as required for the further general analysis of the phase separation process in nonstoichiometric Si oxides. The possible mechanisms of the formation of internal stress are discussed in the Discussion section.

The formation of equilibrium states during the phase separation of SiO_x films under the action of internal stress was studied using the extended expression (2) for the Gibbs free energy per one atom:

$$g(x_0, x, T) = \frac{x_0}{1+x_0} \left\{ \frac{1}{x} \sum_{y=0}^4 \frac{4!}{(4-y)!y!} \left(\frac{x}{2}\right)^y \left[\frac{2-x}{2}\right]^{4-y} \Delta_y - kT \left(\frac{2}{x} \ln \frac{2}{2-x} - \ln \frac{x}{2-x} \right) - \frac{1}{x} \frac{h_{E-S} T}{N_A} \right\} + \chi(T)(x - x_0)^2 \quad (5)$$

where the last term is the stress-related Gibbs free energy contribution obtained by modifying the respective expression proposed in [37] with the temperature-dependent function $\chi(T)$. The mathematical form of this term fully complies with the requirements set up in [39], to enable the agreement of the theoretical and experimental dependences of the equilibrium stoichiometry of Si oxides on their initial composition and annealing temperature, namely:

1. the superlinear dependence on the difference between the current and the initial Si oxide stoichiometry indexes, to be able to reproduce the increase in the value of x_{eq} with the increase in x_0 ;
2. the descending dependence on the annealing temperature, to enable the minimum Gibbs free energy of a Si/Si oxide system shift toward smaller x , upon raising the temperature.

The values of the function $\chi(T)$ were found by comparing the values of x_{eq} calculated from the minimum condition of the expression (5), with the corresponding experimental saturation stoichiometry indexes of the Si oxide matrix obtained after anneals of SiO_x films at different temperatures. We present here only the results obtained for the thermal vacuum sputtered $\text{SiO}_{1.25}$ films [31]. The experimental dependence of the equilibrium stoichiometry index on the annealing temperature for these films is shown in Figure 5a, while Figure 5b provides, by symbols, the corresponding values of $\chi(T)$. The dependence $\chi(T)$ is reasonably fitted by the following exponential function [39]:

$$\chi(T) = \chi_0 + \chi_1 \times \exp\left(\frac{\varepsilon}{kT}\right) \quad (6)$$

where $\chi_0 = -0.52$ eV/atom, $\chi_1 = 0.18$ eV/atom and $\varepsilon = 0.11$ eV, respectively, for the considered $\text{SiO}_{1.25}$ case. The analysis of $\chi(T)$ for the other Si oxide compositions can be found in [39]. It should be noted that all the values of $\chi(T)$ are comparable, and agree with the respective parameter value obtained in the framework of the phenomenological approach [37].

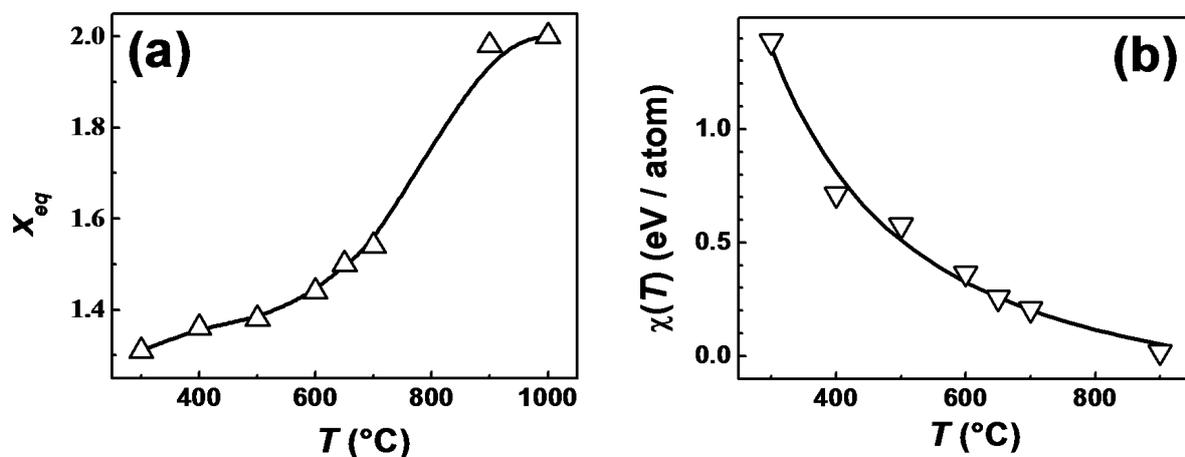


Figure 5. (a) The experimental temperature dependence of the equilibrium stoichiometry index of thermal vacuum sputtered $\text{SiO}_{1.25}$ films [31] (symbols). The line is a guide for eyes. (b) The values of $\chi(T)$ calculated using the data from panel (a) (symbols) and the approximation by the function (6) (line).

The dependences of $g(x_0, x, T)$ on x calculated by the expressions (5) and (6), using the fitted parameters χ_0 , χ_1 , and ε , are presented in Figure 6a,b for different initial SiO_x compositions and temperatures, respectively. The respective dependences of x_{eq} on the initial Si oxide stoichiometry and annealing temperature are shown in Figure 6c,d, respectively. As may be seen from this figure, the stress contribution to the Gibbs free energy of nano-Si/Si oxide systems enables us to reproduce the experimentally observed behavior of the equilibrium stoichiometry index of the Si oxide phase, with both its initial stoichiometry, and annealing temperature. The decrease in $\chi(T)$ with temperature points to the temperature-induced stress relaxation in phase-separated systems. The parameter ε characterizes the activation energy of such relaxation. As can be further seen from Figure 5b, the internal stress is fully relaxed ($\chi(T) = 0$) at temperatures above approximately 900 °C, which corresponds to complete SiO_x separation, and the formation of nearly stoichiometric

SiO₂ matrix composition. The appearance of internal stress has the most significant counter-acting effect on the phase separation process. Therefore, together with the transformation of the penalty energy of Si-O_ySi_{4-y} tetrahedral units, as described in Section 2.1, this must be regarded as the main mechanism that defines the formation of equilibrium states in nano-Si/Si oxide systems.

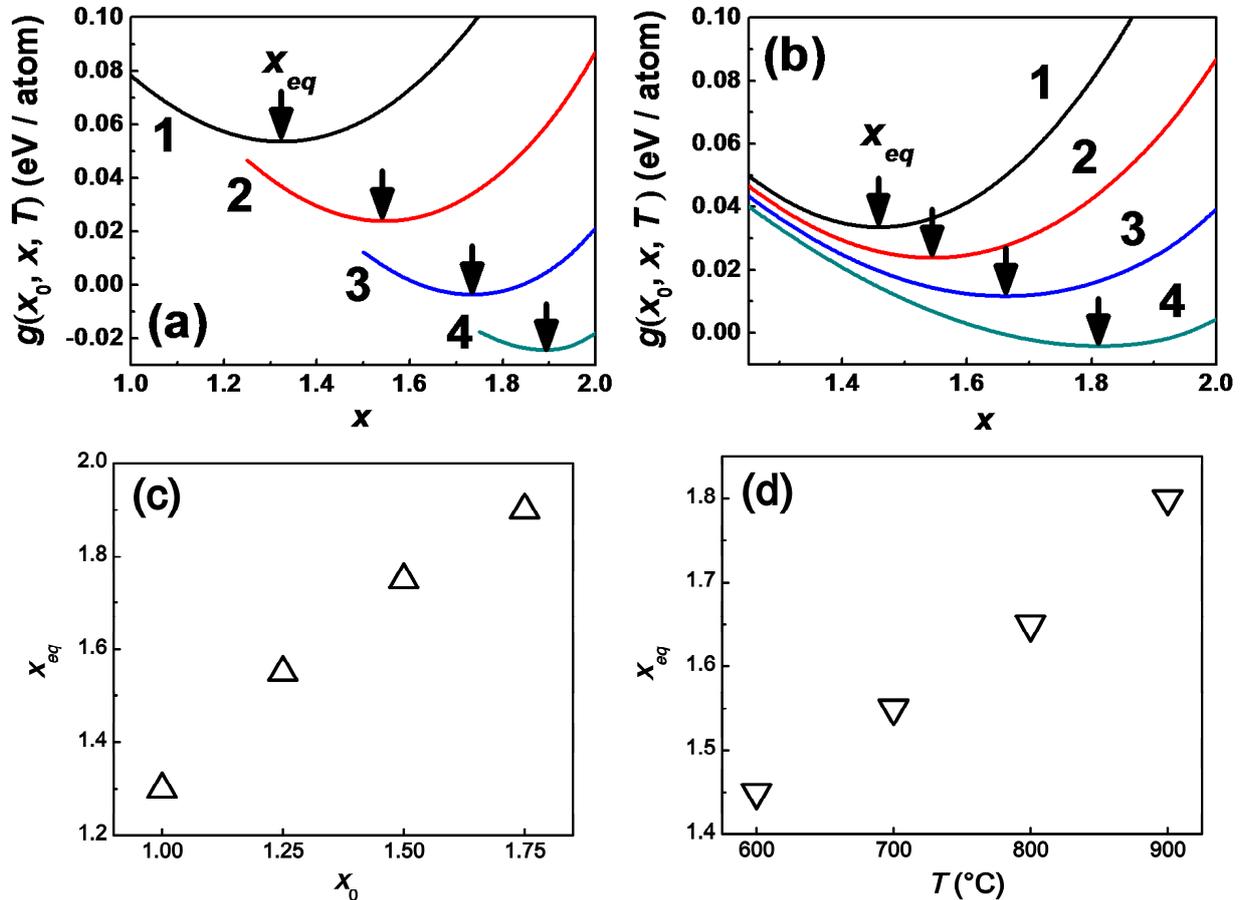


Figure 6. The dependence of the Gibbs free energy per one atom on the stoichiometry index of Si oxide in the a-Si/Si oxide systems, calculated by the expressions (5) and (6). (a) For different initial Si oxide stoichiometry indexes, x_0 : 1—1, 2—1.25, 3—1.5, and 4—1.75. The annealing temperature $T = 700\text{ }^\circ\text{C}$. (b) For different annealing temperatures, T : 1—600, 2—700, 3—800, and 4—900 $^\circ\text{C}$. The initial Si oxide stoichiometry $x_0 = 1.25$. The arrows in the panels indicate the equilibrium stoichiometry indexes of the Si oxide phase. All the curves are shifted by $\frac{1}{1+x_0} \frac{h_E - s_E T}{N_A}$ for better visualization. Panels (c) and (d) show the equilibrium stoichiometry index of Si oxide versus its initial stoichiometry and annealing temperature, recalculated using the data presented in panels (a) and (b), respectively.

2.4. Crystallization Model of Amorphous Si Nanoinclusions Embedded in the Si Oxide Matrix

This section presents a crystallization model of Si nanoinclusions in Si oxide matrix formed as a result of SiO_x phase separation [43]. The model considers the change in the Gibbs free energy of an a-Si particle with the radius R upon crystallization of its central part, as shown schematically in Figure 7. In this process, the Gibbs free energy decreases by $\frac{4\pi r^3}{3\Omega} \Delta g_{ac}$ due to the crystallization of a sphere with the radius r , and increases by $4\pi r^2(\gamma_{ac}^{eff} - \gamma_{oa}^{eff})$, where γ_{oa}^{eff} and γ_{ac}^{eff} are the interface energies of the amorphous and crystalline Si spheres of radius r , inherently taking into account the interaction with the surrounding Si oxide matrix, according to the effective interface concept [43,64,65]:

$$\gamma_{oa}^{eff} = \gamma_{oa} \exp\left(-\frac{R-r}{l_0}\right), \quad \gamma_{ac}^{eff} = \gamma_{ac} + (\gamma_{oc} - \gamma_{ac}) \exp\left(-\frac{R-r}{l_0}\right) \tag{7}$$

Here, $\gamma_{ac} = 0.231 \text{ J/m}^2$ [64], $\gamma_{oc} = 0.41 \text{ J/m}^2$ [61], and $\gamma_{oa} = \gamma_{oc} - 1.73 \times \gamma_{ac} = 0.01 \text{ J/m}^2$ [64] (see also Section 2.2) are the specific energies of a-Si/c-Si, c-Si/Si oxide, and a-Si/Si oxide interfaces, respectively, and $l_0 = 2.532 \text{ \AA}$, corresponding to the interatomic distance in crystalline Si, is regarded as the effective screening or bonding length related to the interatomic force range in Si and Si oxide materials [65].

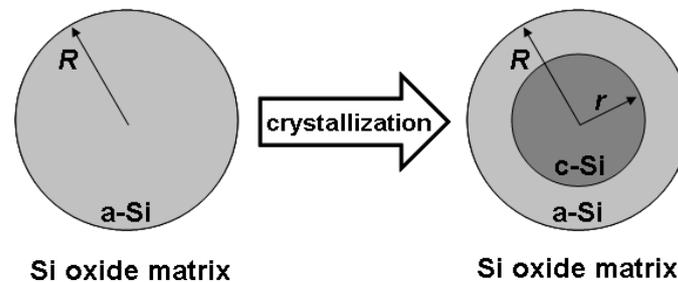


Figure 7. The geometry of amorphous (left) and partly crystallized (right) Si nanoinclusion in Si oxide matrix.

Hence, the crystallization of a central Si sphere with the radius r leads to the following change in the Gibbs free energy expressed per one atom in the initial a-Si nanoinclusion:

$$\Delta g_{cryst} = -\xi^3 \frac{h_E - s_E T}{N_A} + \frac{3\Omega\xi^2}{R} \left[\gamma_{ac} + (\gamma_{oc} - \gamma_{ac} - \gamma_{oa}) \exp\left(-\frac{R(1-\xi)}{l_0}\right) \right] \quad (8)$$

where the relative radius of the internal crystallized part of the nanoinclusion $\xi = \frac{r}{R}$ is introduced. The minimum values of the expression (8) define the equilibrium states of the Si nanoinclusion, while its maximum values set nucleation barriers for the amorphous-to-crystalline transition.

The calculations by the expression (8) enabled us to obtain the following main results concerning crystallization of a-Si nanoinclusions in Si oxide matrix, which are important for the further general analysis of the phase separation process in SiO_x films [43]:

1. The crystallization of an amorphous Si nanoinclusion is incomplete, and an amorphous shell between the crystalline core and the Si oxide matrix always remains. This result is illustrated by the exemplary dependences of Δg_{cryst} on ξ , for different initial radii R at $900 \text{ }^\circ\text{C}$ presented in Figure 8a, in which ξ_{min} corresponds to the equilibrium states.
2. A minimum radius of amorphous Si nanoinclusions exists, below which crystallization becomes energetically unfavorable. The value of this radius increases with the increase in annealing temperature. The dependence of the Gibbs free energy change on ξ for a Si nanoinclusion, with the radius below the crystallization threshold, is illustrated by the curve (1) in Figure 8.
3. The crystallized Si fraction (value of ξ_{min}) increases, and the nucleation barrier for crystallization decreases, with the increase in a-Si nanoinclusion size, due to the weakening of the influence of the Si oxide matrix on the crystallization process. The saturation of the nucleation barrier at $R \approx 2 \text{ nm}$ points to an almost complete loss of this influence. This result is illustrated by the dependences presented in Figure 9a,b for the crystallization temperature of $900 \text{ }^\circ\text{C}$ (see also Figure 8a,b).

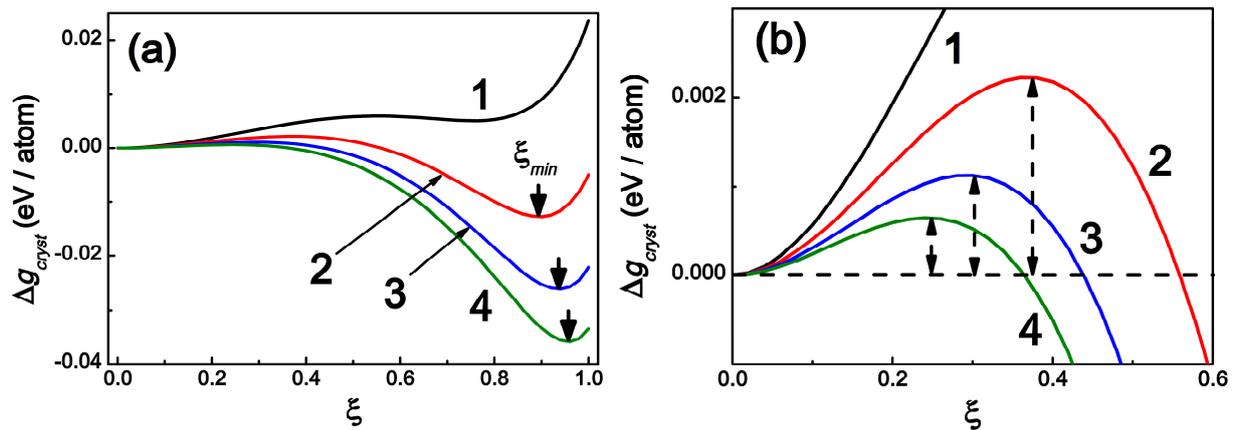


Figure 8. Dependence of the Gibbs free energy per atom of a spherical Si inclusion in the Si oxide matrix upon the relative radius of its internal crystallized part at $T = 900$ °C for different Si radii R : 1—1.5, 2—2, 3—2.5, and 4—3 nm. The arrows in panel (a) indicate the equilibrium values of the relative radius of the internal crystallized part of the nanoinclusions. The double arrows in panel (b) show the nucleation barriers for crystallization.

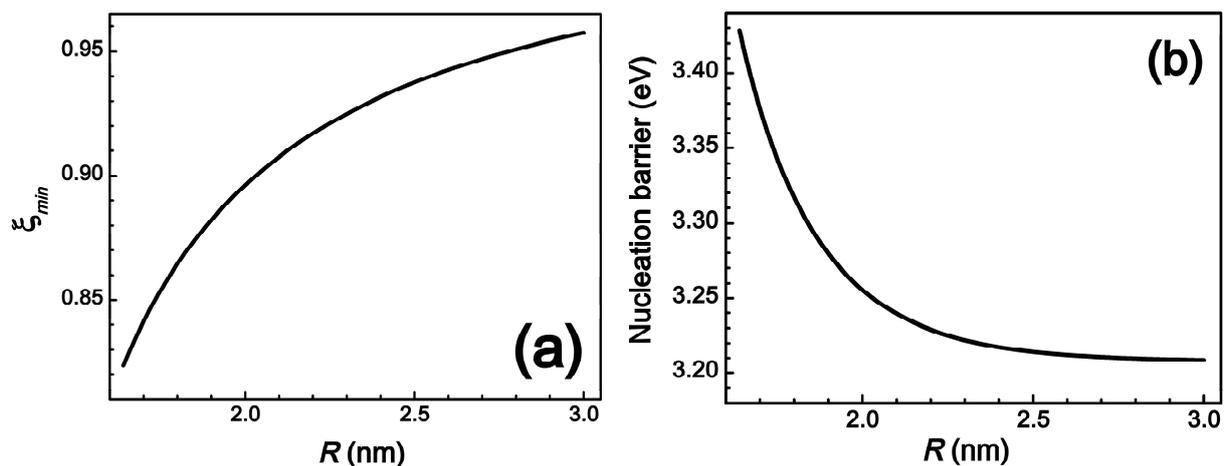


Figure 9. The dependence of the relative radius of the internal crystallized part corresponding to the minimum Gibbs free energy (a) and nucleation barrier (b), on the radius of the initially amorphous Si nanoinclusion in the Si oxide matrix at $T = 900$ °C.

It should be noted, as well, that both the nucleation barrier increases, and ξ_{min} decreases, with temperature. This has an effect on the Si crystallization kinetics, and the distribution function of Si nanocrystals in the Si oxide matrix [43].

3. Discussion

In this section, a general analysis of the phase separation process, during the annealing of nonstoichiometric Si oxides, is provided. We discuss the elementary stages of this process, the mechanisms governing the system's evolution, and the dependence of the characteristics of formed nano-Si/Si oxide composites on the initial Si oxide parameters and annealing temperature.

As was already mentioned in Section 2.1, all the mechanisms that act during the phase separation of SiO_x films are characterized by their contributions to the Gibbs free energy of Si/Si oxide systems [38,41,42]. Here, the role of a particular mechanism on promoting or counteracting phase separation is determined by whether the corresponding Gibbs free energy contribution decreases or increases with the increase in x .

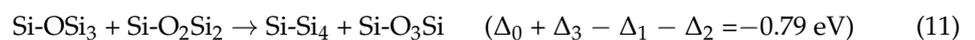
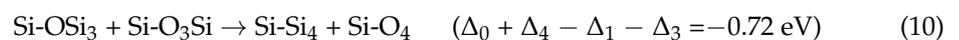
As demonstrated in both experimental and theoretical investigations, the phase separation in nonstoichiometric Si oxides is consistent with the redistribution of oxygen atoms from the oxygen poor to the oxygen rich Si–O_ySi_{4–y} tetrahedral units that compose the SiO_x microstructure [31,66–68]. In particular, it was shown [31] that too low values of Si diffusivity in Si oxide do not allow the description of the experimental very fast kinetics of SiO_x separation (~ 1 s at 1000 °C) using the mechanism of Si diffusion and agglomeration. On the other hand, IR absorption studies revealed [66] that during the annealing of SiO_x, weakly oxidized Si–O_ySi_{4–y} units (basically Si–OSi₃) become Si–Si₄ by losing oxygen atoms, which are captured by strongly oxidized complexes, such as Si–O₃Si. Oxygen in various configurations is a fast diffuser in Si oxide, and its diffusivity agrees with the experimental phase separation kinetics [31]. It was hypothesized, therefore [66], that the oxygen release at the nano-Si/Si oxide interfaces, and its diffusion into the matrix bulk, should define the phase separation of SiO_x films, and the consistency of this hypothesis was confirmed by kinetic simulations [67,68].

The character of the composition change in Si oxide by oxygen redistribution between the Si–O_ySi_{4–y} tetrahedral units may be easily understood, by referring to the unit penalty energies Δ_y (see Section 2.1). Namely, the transition of an oxygen atom between two Si–O_ySi_{4–y} units reduces their total penalty energy, only if the difference between their oxidation degrees (values of *y*) increases. Therefore, the transformation of an initially homogeneous nonstoichiometric Si oxide into a composite, consisting of separated Si and SiO_x phases, is caused by the tendency to minimize the penalty energy of the entire Si/Si oxide system as the principal mechanism. A complete separation into the stoichiometric Si and SiO₂ would reduce the total penalty energy to zero. Considering this mechanism alone, van Harpert et al. [69] concluded that the equilibrium state in Si/Si oxide systems corresponds to the coexistence of the Si and SiO₂ phases, as providing zero total penalty energy of all the Si–O_ySi_{4–y} tetrahedral units.

Moreover, taking into account the values of Δ_y, we may also be able to explain the evolution of an initial Si oxide by the separation of purely Si nano-inclusions in the Si oxide matrix, with a gradually increasing stoichiometry index instead of the formation of two Si oxide phases, the one with a gradually decreasing, and the other with a gradually increasing, stoichiometry index. Indeed, imagine the transition of an oxygen atom between two Si–O₂Si₂ units, according to the following reaction:



As a result, the Gibbs free energy changes by Δ₁ + Δ₃ – 2Δ₂ = –0.3 eV. The reaction products may further evolve, according to the following reactions:



where the change in the Gibbs free energy in each reaction is provided in parenthesis.

The reactions (10)–(12) show that when a Si–O₂Si₂ tetrahedral unit loses an oxygen atom, it is energetically favorable to lose the remaining oxygen atom, converting to the Si–Si₄ unit of a pure Si phase. Hence, the local separation of pure Si in the form of nanoparticles takes place. On the other hand, when a Si–O₂Si₂ unit acquires an oxygen atom, the next atom would be taken by another unit of the same composition, rather than by the freshly formed Si–O₃Si one. Therefore, no local inclusions of the SiO₂ composition form, and the stoichiometry index of the Si oxide matrix evolves homogeneously. The processes described by the reactions (10)–(12), together with the respective energy changes, are schematically depicted in Figure 10.

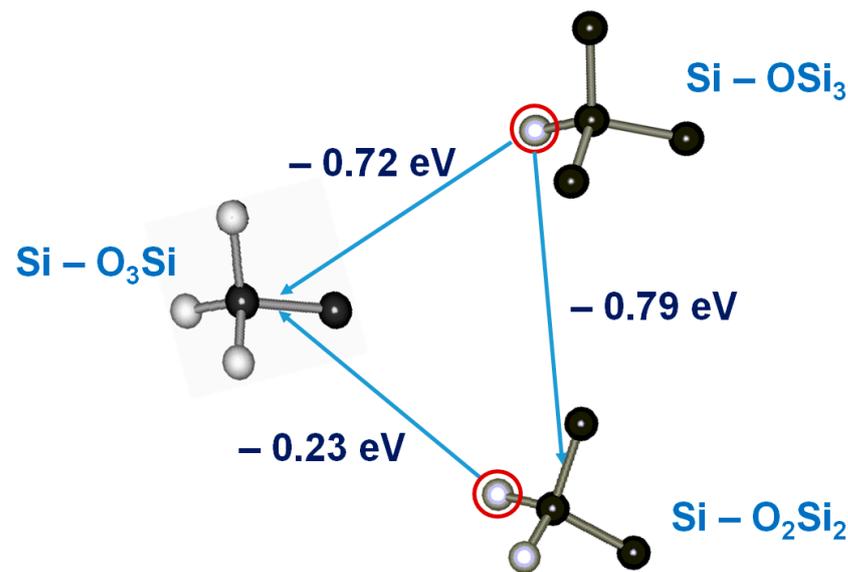


Figure 10. A schematic representation of the processes, according to the reactions (10)–(12), with respective changes in the penalty energy of the participating Si–O_ySi_{4–y} tetrahedral units. The Si atoms are shown in black, and white corresponds to oxygen atoms.

The separation of Si and Si oxide (the increase in the value of x) also leads to a decrease in the configuration entropy, due to the reduction in the number of arrangements of oxygen atoms between the pairs of Si atoms in the Si oxide phase. The entropy decrease results in the growth in the respective contribution to the Gibbs free energy. Another Gibbs free energy term increasing with x is related to the separation of the amorphous Si phase (see expression (2)). Therefore, both mechanisms counteract the phase separation of nonstoichiometric Si oxides. At this, the changes in the corresponding terms with x are noticeably smaller, compared to the total penalty energy change (for example, the absolute value of the change in the total penalty energy upon transformation of an initial SiO_{1,0} into the Si/SiO_{1,9} system at 900 °C is equal to about 0.17 eV/atom, while the entropy and amorphous Si related contributions change at this by about 0.06 and 0.02 eV/atom, respectively). Therefore, the role of the former mechanisms on the formation of the equilibrium states in Si/Si oxide systems is substantially weaker than that of the latter mechanism. The configuration entropy contribution alone defines the temperature dependence of the excess Si concentration (solubility limit) in SiO₂ in equilibrium with crystalline Si, while, together with the a-Si related term, it defines the solubility of a-Si in SiO₂, which is noticeably higher than that of c-Si [38].

It should also be mentioned that the formation of interfaces between the nano-Si inclusions and the Si oxide matrix introduces a contribution to the Gibbs free energy, three to four orders of magnitude smaller than the penalty-energy-related term (see Section 2.2). Therefore, although this process counteracts phase separation, it plays a minor role on equilibrium states in nano-Si/Si oxide systems, and may not be considered.

As demonstrated in Section 2.3, the appearance of internal stress is the key mechanism that causes an incomplete separation into the Si and SiO_x phases, and a remarkable dependence of the equilibrium Si oxide stoichiometry on the annealing temperature. We have to note that up to now, we have not been able to propose a unique unambiguous model of stress formation in phase separated Si/Si oxide systems. The main problem we encounter is that each developed model contains a number of fitting parameters no less than the semi-empirical description presented in Section 2.3. This leaves the question about the correctness of a particular model open, and at the same time offers no advantages in calculating the stress-related Gibbs free energy contribution, compared to using the function $\chi(T)$.

The mechanisms of stress formation during the phase separation of nonstoichiometric Si oxides may be discussed as follows. Let us consider oxygen out-migration from the regions where nano-Si inclusions form, into the surrounding Si oxide matrix, as illustrated schematically in Figure 11 for a single nanoinclusion case. Si atoms, which will constitute the Si nanoparticle, are located in a certain volume 2 of the initial Si oxide, as indicated in the left-hand side of Figure 11. As oxygen atoms leave this volume, the latter may shrink, as shown in the right-hand side of Figure 11, ideally down to the volume 4 of a fully relaxed Si phase. If, however, no complete Si relaxation occurs, and the volume 3 of the separated Si phase remains in excess to that of the relaxed Si, tensile stress is exerted on the Si nanoparticle. In turn, the redistributed oxygen atoms incoming into the Si oxide matrix around the formed nanoinclusion increase the total atomic concentration within it, leading to the appearance of compressive strain and corresponding stress, if only partial matrix relaxation is achieved.

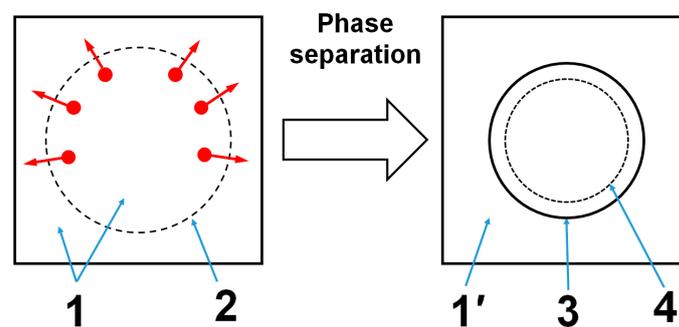


Figure 11. The formation of amorphous Si nanoinclusion by the out-migration of oxygen, during the phase separation of nonstoichiometric Si oxide. Left part: (1) the initial Si oxide phase, (2) the boundary of the volume from which oxygen out-migration takes place. Red disks schematically represent oxygen atoms, while red arrows indicate the directions of their redistribution. Right part: (1') the Si oxide phase with increased stoichiometry index, compared to the initial one, (3) the boundary of the formed Si nanoinclusion with exerted tensile stress, (4) the boundary of the fully relaxed Si nanoinclusion.

The simplest model of stress formation during phase separation in SiO_x films [40] assumes that the volume of the Si oxide phase does not change with new incoming oxygen atoms, and also that the Si phase is fully relaxed (region 4 in Figure 11). Therefore, only the compressive stress in the Si oxide matrix is considered. According to Hook's law, the stress-related energy per unit volume is calculated as follows:

$$G_{stress} = \frac{1}{2} K_{\text{SiO}_x} \left(\frac{\Delta V}{V_x} \right)^2 = \frac{1}{2} K_{\text{SiO}_x} \left(\frac{V_x - V_{x0}}{V_x} \right)^2 \quad (13)$$

where V_x is the volume that the SiO_x phase with the stoichiometry index x would have in a relaxed state; V_{x0} is the actual volume of the Si oxide phase corresponding to the initial stoichiometry index x_0 ; and $K_{\text{SiO}_x} = 2.53 \times 10^{10}$ Pa is the bulk modulus of the Si oxide phase [70], assumed not to depend on the stoichiometry index x , respectively.

The dependence of the SiO_x volume on its stoichiometry may be written using the composition expansion of Si oxide with a constant number of Si atoms $\eta = \frac{1}{V_0} \frac{\partial V_x}{\partial x}$ as follows:

$$V_x = V_0(1 + \eta x) \quad (14)$$

Here, $\eta = \frac{V_{\text{SiO}_2} - V_{\text{Si}}}{2V_{\text{Si}}} \approx 0.6$ is calculated, taking into account that the volume of Si oxide at $x = 2$ corresponds to the volume of the stoichiometric SiO_2 phase, V_{SiO_2} , while at $x = 0$, it is the volume of the Si phase, V_{Si} , respectively, as well as $\frac{V_{\text{SiO}_2}}{V_{\text{Si}}} \approx 2.2$ as follows from the experimentally observed swelling of the Si volume by about 2.2 times, after the thermal oxidation of the Si wafers [71].

Therefore, the stress-related energy per unit volume of the Si oxide phase takes the following form:

$$G_{stress} = \frac{1}{2} K_{SiO_x} \eta^2 \frac{(x - x_0)^2}{(1 + \eta x)^2} \quad (15)$$

For $\eta x \ll 1$, the expression (15) is fully equivalent to the stress-related Gibbs free energy per unit volume introduced in [37], except that there, a linear, not a bulk, deformation was considered.

In the proposed description of the stress origin, the function $\frac{K_{SiO_x} \eta^2}{2(1 + \eta x)^2}$ in the expression (15) must be equivalent to the function $\chi(T)$ in the expression (5). The temperature dependence of the former function is caused by the respective temperature dependence of η or, more particularly, of the volumes V_{SiO_2} and V_{Si} . The calculations [40] show, however, that the temperature dependence of the function in the expression (15) is negligible, compared to that of $\chi(T)$ obtained in Section 2.3, and does not allow us to explain the experimentally observed variations of x_{eq} with the annealing temperature. This means that the stress decreases with temperature, not only due to the different values of the thermal expansion coefficients of Si and SiO₂, but also due to the action of additional mechanisms of stress relaxation.

Further developments in the presented model include accounting for other possible stress contributions, such as the hydrostatic tensile stress in Si nanoparticles, when the nano-Si volume 3 remains larger than the volume 4, corresponding to the fully relaxed case (see Figure 11), and the stress related to maintaining coherency at the Si/Si oxide interfaces. Each iteration of the model complicates its expressions, and introduces new fitting parameters that take into account, for example, the different degrees of Si and SiO_x relaxation, the redistribution of strain between the Si and SiO_x phases caused by a large difference in their elastic modules [72], the degree of incoherency at the Si/Si oxide interfaces, etc., which makes the calculation of the strain-related Gibbs free energy completely inefficient. It is advised, therefore, to keep in mind a basic understanding of the mechanism of the stress origin during the phase separation in nonstoichiometric Si oxides, to use the semi-empirical expression $\Delta g_{stress} = \chi(T)(x - x_0)^2$, which requires to fit only three parameters of the function $\chi(T)$.

The descending character of $\chi(T)$ points to the enhancement of stress relaxation when the annealing temperature is increased. As may be seen from Figure 5, $\chi(T) = 0$ at about 900 °C, which constitutes complete stress relaxation and separation into Si and close-to-stoichiometric SiO₂ phases. This finding correlates with the results obtained by Lukovsky et al. [73], who investigated the behavior of SiO_x/SiO₂ interfaces during growth of SiO₂ on crystalline Si layers. It was found that a nonstoichiometric transition layer underwent separation at the temperature of about 900 °C, due to bond switching, which led to the transformation of the initially stressed transition layer into the relaxed one. This process was accompanied by an increase in the SiO₂ layer thickness. Therefore, stress relaxation in phase-separating Si oxides may be considered by bond switching at the Si/Si oxide interfaces, and in the Si oxide bulk. The probability of bond switching increases with temperature, as a certain energy barrier must be overcome. The same temperature of complete relaxation of nonstoichiometric Si oxide observed by Lukovsky et al. [73], and for achieving zero value of $\chi(T)$, strongly supports the bond-switching mechanism of stress relaxation during phase separation in SiO_x films.

The annealing of nonstoichiometric Si oxide films first leads to the separation of amorphous Si nanoinclusions. These nanoinclusions may then partially or almost fully crystallize, or remain amorphous, depending on their size and annealing temperature. The experimental results [28] supported by the theoretical calculations [43] demonstrate that the crystalline Si fraction in Si/Si oxide composites increases with the annealing temperature of SiO_x films. According to our crystallization model, outlined in Section 2.4, this increase is related to the growth in the nano-Si radii due to the increase in the amount of separated Si or the coalescence of Si nanoparticles at the temperatures above 1000 °C [28] (the relative

radius of the crystallized Si part ξ_{min} increases, and the nucleation barrier decreases, with the increase in R , see Figure 9).

The phenomenon not addressed so far is the influence of the partial crystallization of Si nanoinclusions on equilibrium in Si/Si oxide systems. The Gibbs free energy of c-Si is smaller, compared to that of a-Si (see Section 2.1). Therefore, crystallization of a part of the Si nanoparticle must lead to additional Si separation from the surrounding Si oxide matrix, resulting in the increase in nano-Si radius. In its turn, the increase in the nanoparticle radius promotes a further increase in ξ_{min} , and so forth. It may be concluded, therefore, that the crystallization process is expected to induce significant transformations of both the nanoinclusion size and crystalline state, as well as the stoichiometry of the surrounding Si oxide matrix.

Figure 12 shows the transformation of an exemplary a-Si nanoinclusion with a radius of 2 nm, embedded in a $\text{SiO}_{1.8}$ matrix obtained as a result of the phase separation of a $\text{SiO}_{1.25}$ film at 900 °C. The values of the initial and final stoichiometry indexes of the Si oxide, corresponding to the chosen temperature, are taken with reference to Figure 6b,d. The search for the minimum values of the Gibbs free energy obtained by combining the expressions (2) and (8) demonstrates that the nanoinclusion radius increases to about 2.13 nm in the equilibrium state. The relative radius of the crystallized part becomes $\xi_{min} = 0.91$, which is somewhat larger than the respective value ~ 0.89 for the crystallization of the initial a-Si nanoinclusion. The increase in the radius occurs by the separation of additional Si from the surrounding matrix. The matrix stoichiometry becomes about 1.98, which is close to that of the stoichiometric SiO_2 , and corresponds to the equilibrium between the Si oxide and the crystalline Si phase at 900 °C. The same effect was always reproduced in multiple calculations for different a-Si radii, as well as different initial and final SiO_x stoichiometries. The obtained result naturally explains an experimentally observed correlation between the appearance of the SiO_2 -related peaks in the IR absorption spectra, and the characteristic photoluminescence (PL) band of Si nanocrystals [34], implying that the crystalline Si phase and SiO_2 regions are always formed together during the phase separation of nonstoichiometric Si oxide films.

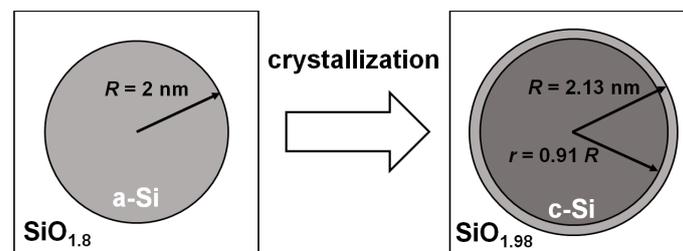


Figure 12. The transformation of a-Si nanoinclusion with a radius $R = 2$ nm, embedded in a $\text{SiO}_{1.8}$ matrix as a result of the crystallization of its internal part.

We may now use the general thermodynamic theory to discuss the peculiarities of the formation of Si/Si oxide composites by the phase separation of nonstoichiometric Si oxides as functions of the annealing temperature. Here, we will also refer to the results of experimental investigations of the temperature dependence of the characteristics of phase separated Si/Si oxide systems obtained by IR absorption spectroscopy, XPS, Raman scattering, and photoluminescence investigations [32–34,74–76].

The experimental studies report the beginning of the phase separation process at temperatures between approximately 300 and 600 °C, depending on the technology of the initial Si oxide fabrication and annealing conditions [32,33,75]. The raise of the annealing temperature leads to the increase in the amount of separated Si, which is manifested by the increase in the stoichiometry index of the Si oxide matrix, revealed by IR spectroscopy, as well as by the growth in the intensity of the Si^0 band in the XPS spectra [33,34,75], and the shift of the PL peak position toward longer wavelengths [32,34,74]. The increase in the degree of phase separation with the annealing temperature corresponds to the temperature-

enhanced stress relaxation in Si oxide films, as shown in Section 2.3, and discussed earlier in this section. Purely amorphous Si nanoinclusions form at annealing temperatures up to 800 °C, as inferred by observations in the Raman spectra of the characteristic broad band, peaked at $\sim 480 \text{ cm}^{-1}$, corresponding to the amorphous Si phase [32,76]. The Si oxide matrix of Si/Si oxide composites formed at such temperatures is essentially nonstoichiometric, without SiO₂ inclusions, as demonstrated by the presence of only the characteristic for the SiO_x ($x < 2$) elementary bands in the respective IR absorption spectra [34]. The formation of purely amorphous Si inclusions is explained by their small sizes below the crystallization threshold, as described in Section 2.4.

Raising the annealing temperature above 800 °C induces the onset of Si particle crystallization, as demonstrated in particular by the appearance in the Raman spectra of annealed films of the narrow peak at $\sim 519 \text{ cm}^{-1}$, corresponding to the crystalline Si phase [33,76]. According to the thermodynamic theory presented in this paper, Si nanoinclusions crystallize when their sizes reach the minimum crystallization size at a given temperature. By accepting the average density of Si nanoinclusions $C_{incl} = 10^{19} \text{ cm}^{-3}$, the initial stoichiometry index of SiO_x $x_0 = 1.25$ and the equilibrium stoichiometry index at 800 °C $x_{eq} = 1.7$ (see Figure 5a), the average radius of separated Si nanoparticles of $\sim 1.65 \text{ nm}$ is obtained. At the same time, the crystallization model presented in Section 2.4 provides the minimum crystallization radius at this temperature to be $\sim 1.6 \text{ nm}$. Repeating the same calculations for 700 °C, one obtains the average nanoparticle radius and the minimum crystallization radius of ~ 1.4 and more than 1.5 nm , respectively. Therefore, the temperature of crystallization starting close to 800 °C is theoretically justified.

In view of the distribution function of Si nanoinclusions on size, their crystallization does not take place at a single temperature value. The crystallization degree increases with the increase in the annealing temperature, up to about 1150 °C, when complete crystallization is obtained. Both amorphous and crystalline Si-related bands are observed in the Raman and photoluminescence spectra of SiO_x samples annealed below this temperature [32–34,76]. Along with this, the IR absorption spectra are composed by the elementary bands corresponding to Si–O_ySi_{4–y} tetrahedral complexes in the nonstoichiometric Si oxide phase, as well as Si–O₄ tetrahedra in 4- and 6-member rings of the SiO₂ phase [34]. Hence, Si/Si oxide composites obtained at the temperatures between approximately 800 and 1150 °C contain larger crystalline and smaller amorphous Si nanoinclusions, surrounded respectively by the nonstoichiometric SiO_x, and the nearly stoichiometric SiO₂ phase, formed as a result of Si crystallization, as described earlier in this section.

At higher annealing temperatures, the efficient coalescence of Si nanoparticles is observed, leading to the increase in their average size [28,30]. At such temperatures, the portion of the amorphous Si phase is small, and the signals from the Si nanocrystallites dominate in the Raman and PL spectra of annealed SiO_x films [32–34]. From a thermodynamic point of view, the major part of Si nanoparticles becomes larger than the crystallization threshold, due to coalescence, and therefore convert into Si nanocrystals. The amorphous Si-related contributions to the Raman spectra may come from the tail of the size distribution function of Si nanoparticles, and/or amorphous Si shells linking the Si nanocrystals to the surrounding Si oxide matrix.

Our theory may now be compared to the only other known thermodynamic approach to studying phase separation in nonstoichiometric Si oxide films [37]. This approach uses the phenomenological expression for the density of the Gibbs free energy of nonstoichiometric Si oxides in the following form:

$$\tilde{g}_{SiO_x}(x, x_0, T) = -\alpha(T)(x - 1)^2 + \beta(T)(x - 1)^4 + \frac{1}{2}E[\varepsilon_0(x - x_0)]^2 \quad (16)$$

where the functions $\alpha(T)$ and $\beta(T)$ are chosen based on the work of Schnurre et al. [36], to ensure the stability of the Si and SiO₂ phases, as well as the metastability of the SiO phase; E is the Young's modulus of Si oxide, $\varepsilon_0 = \frac{1}{a} \frac{\partial a}{\partial x}$ is the composition expansion coefficient of Si oxide, and a is the average atomic distance in the Si oxide, respectively.

As demonstrated in [37], the theory based on the expression (16) predicts qualitatively similar behavior in the characteristics of the nonstoichiometric Si oxides, as a function of the initial SiO_x composition and annealing temperature. However, such a theory is oversimplified, as it does not consider, for example, the free energy contribution of the separated Si phase, the microstructure of Si oxide composed of $\text{Si-O}_y\text{Si}_{4-y}$ units with different energy characteristics, the entropy transformation during phase separation, the possible crystallization of Si nanoparticles, and a number of other important aspects. Moreover, it does not provide a good quantitative agreement with the experimental data. Conversely, the thermodynamic theory developed in the present paper is comprehensive, and adequately describes all the characteristic features of the phase separation process in nonstoichiometric Si oxide films, as functions of the annealing temperature and the initial SiO_x composition.

4. Conclusions

In this paper, a thermodynamic theory of phase separation in nonstoichiometric Si oxide films (SiO_x , $x < 2$) during high-temperature anneals is developed. The theory is based on a number of thermodynamic models, addressing various aspects of the phase separation process reported in our previous publications. A brief review of these models was presented, as required in order to understand the studied process in its integrity.

The expression for the Gibbs free energy of Si oxides and amorphous (crystalline) Si/Si oxide systems is derived. The analysis of the transformations of the Gibbs free energy, with the change in the Si oxide composition during the phase separation process, as the function of the initial Si oxide stoichiometry and the annealing temperature, has enabled us to clarify the roles of different mechanisms in the formation of equilibrium states in nano-Si/Si oxide systems. It has been found that the driving force of SiO_x decomposition is the tendency toward the minimization of the total penalty energy of the $\text{Si-O}_y\text{Si}_{4-y}$ tetrahedral units composing the Si oxide microstructure. The specific values of the penalty energy of the $\text{Si-O}_y\text{Si}_{4-y}$ units with a different y cause the localized separation of the pure Si phase, as well as the homogeneous increase in the stoichiometry index of the Si oxide matrix, which is a characteristic feature of the phase decomposition in nonstoichiometric Si oxide films.

The formation of internal stress during Si and Si oxide separation is found to be the key mechanism that counteracts this process, and defines the equilibrium states in separated nano-Si/Si oxide systems (the amount of separated Si, and the stoichiometry index of the SiO_x matrix), as functions of the initial Si oxide composition and the annealing temperature. The mechanisms of stress formation in the process under study are discussed. It is demonstrated that the stress value decreases with the annealing temperature, presumably by bond switching at the nano-Si/Si oxide interfaces, and in the SiO_x bulk.

The crystallization of separated amorphous Si nanoinclusions in the Si oxide matrix is modeled. The equilibrium state of a Si nanoinclusion corresponds to incomplete crystallization in all cases, with an amorphous Si layer remaining at the crystalline Si core/Si oxide matrix interface. The relative radius of the crystallized Si part increases, and the nucleation barrier for crystallization decreases, with the increase in the Si nanoinclusion radius. It is demonstrated that the partial crystallization of an a-Si nanoparticle induces additional separation of Si from the surrounding Si oxide matrix, leading to the increase in the nanoparticle size. In its turn, this causes the relative size of the crystallized Si core to grow, etc. This process continues, until equilibrium between almost fully crystallized Si nanoinclusion, surrounded by the Si oxide matrix with the stoichiometry index $x \approx 2$, is established. This result enables us to explain the experimentally observed correlation of the presence of a-Si inclusions with the nonstoichiometric SiO_x phase, as well as c-Si inclusions with the SiO_2 phase in the Si oxide matrix of the phase-separated nano-Si/Si oxide systems.

The characteristic features of the phase separation process as the functions of annealing temperature are discussed within the framework of the general thermodynamic theory developed in this paper. At lower temperatures (600–800 °C), amorphous Si nanoinclusions, with sizes below the crystallization threshold, are formed in the non-stoichiometric Si oxide

matrix. At temperatures between approximately 800 and 1150 °C, the crystallization of Si nanoinclusions, with sizes larger than the crystallization critical size, takes place. The Si crystallization induces additional separation of Si from the Si oxide matrix, and the formation of the regions of the nearly stoichiometric SiO₂ phase within it. Finally, high annealing temperatures (above ~1150 °C) promote the coalescence of Si nanoinclusions, and their efficient crystallization, due to large sizes. The amorphous Si phase is present in the smallest nanoinclusions, and at the Si nanocrystals/Si oxide matrix interfaces.

As demonstrated in Figure 1, the thermodynamic models composing the general theory were successfully applied in the studies, beyond the thermodynamics of phase separation in SiO_x films. In particular, the analysis of the composition dependence of the Gibbs free energy of Si oxide enabled us to obtain its binodal and spinodal characteristics, and determine the stoichiometry ranges corresponding to the stability of the Si oxide phase, and phase separation, according to the nucleation and growth, and spinodal decomposition mechanisms [44]. The application of the Gibbs free energy (2) to SiO_x(N_y)/SiO₂ superlattices with nanometer thick layers made it possible to find the mechanism of layer intermixing within them, and to determine the critical layer thicknesses for intermixing as the functions of annealing temperature [47–49]. Finally, it was demonstrated, by comparing the Gibbs free energies of different Si oxynitride structures, that low stoichiometries and deposition temperatures (~300–400 °C) promote the formation of two-phase (oxide- and nitride-like) structures consistent with the random mixture model description. On the other hand, homogeneous films corresponding to the random bonding model are formed at increased stoichiometry indices and high deposition temperatures (~800–900 °C).

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Conflicts of Interest: The author declares no conflict of interest.

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