

## Mechanisms of the Phase Separation of Nonstoichiometric Si Oxide Films: What Can One Learn From Thermodynamics?

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This paper describes thermodynamic approach to the study of the mechanisms of phase separation in nonstoichiometric silicon oxide ( $\text{SiO}_x$ ,  $x < 2$ ) films during high temperature annealing, which produces the nanometer sized Si inclusions embedded in the Si oxide matrix. The expression for the Gibbs free energy of Si/Si oxide systems is derived based on the analysis of the processes taking place during the phase separation. The progress of phase separation is characterized by the evolution of the stoichiometry index of Si oxide matrix  $x$ . The mechanisms assisting and counteracting the phase separation of  $\text{SiO}_x$  films are determined based on that whether their contributions to the Gibbs free energy decrease or increase with the progress of Si and Si oxide separation (increase of  $x$ ). The mechanisms responsible for the formation of equilibrium states in the Si/Si oxide systems (equilibrium values of  $x$ ) are determined.

**Keywords:** Si nanoinclusions, Si/SiO<sub>x</sub> systems, Phase separation, Gibbs free energy, Thermodynamic equilibrium.

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### 1. INTRODUCTION

Nonstoichiometric silicon oxide films ( $\text{SiO}_x$ ,  $x < 2$ ) attract great interest of researchers in view of their potential applications in electronic devices such as light emitters [1], flash memory elements [2], and solar cells [3, 4]. These applications rely on nanosized Si inclusions, which are formed in silicon oxide matrix as a result of high temperature phase separation of such films. Experimental investigations evidence the annealing temperature and the initial stoichiometry of silicon oxide to be the main players that affect characteristics of the resulting ensembles of Si nanoinclusions and the properties of Si oxide matrix encapsulating them. Progress of phase separation process is typically characterized by the matrix stoichiometry index  $x$ ,  $x = 2$  corresponding to the complete separation into stoichiometric Si and  $\text{SiO}_2$  phases. For annealing temperatures below about 900°C this process is incomplete so that the stoichiometry index saturates at the value  $x_0 < x = x_{eq} < 2$ ,  $x_0$  being the initial silicon oxide stoichiometry [5-7]. The value of  $x_{eq}$  increases with the increase in both the  $x_0$  value and the annealing temperature  $T$  as revealed by multiple experimental studies [7-9].

Incomplete phase separation of  $\text{SiO}_x$  films is determined by thermodynamic equilibrium between the formed Si nanoprecipitates and the Si oxide surroundings. Thermodynamic theory of equilibrium states in Si/Si oxide systems has been proposed by us earlier [10]. We consider the transformations of the Gibbs free energy in the amorphous Si (a-Si)/Si oxide and crystalline Si (c-Si)/Si oxide systems with the change of the amount of separated silicon and the composition of silicon oxide phase. By minimizing the Gibbs free energy

of these systems, the equilibrium stoichiometry index of silicon oxide is derived as a function of its initial stoichiometry and temperature. However, this theory failed to explain all the details of noted above experimentally observed behavior of  $x_{eq}$  as a function of  $x_0$  and  $T$  in the systems, in which Si nanoprecipitates are formed. It was demonstrated later [11] that for correct description of the dependence of the value of  $x_{eq}$  on initial stoichiometry of silicon oxide and the annealing temperature the internal strain arising during separation of the Si and  $\text{SiO}_x$  phases should be taken into account. In this work, we discuss the mechanism of strain appearance during the phase separation and demonstrate how all the mechanisms studied up to now determine the formation of equilibrium states in the Si/Si oxide systems obtained by the phase separation of nonstoichiometric Si oxide films.

### 2. THEORY AND RESULTS

#### 2.1 Gibbs free energy of Si/Si oxide systems

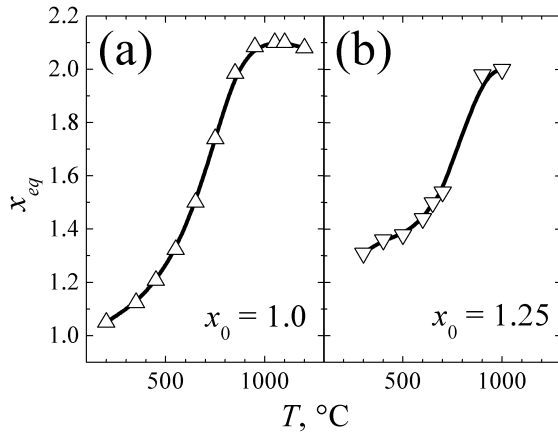
Thermodynamic theory of equilibrium states in Si/Si oxide systems considers the transformations of the Gibbs free energy of these systems with the change of the stoichiometry index of silicon oxide phase  $x$  as a result of the separation of excess Si atoms, toward its minimum values which determine the equilibrium stoichiometries  $x_{eq}$ . According to our previous works [10, 11], the expression for the reduced (i. e., not taking into account the terms that are not functions of  $x$ , see [10] for details) Gibbs free energy per one atom of the system under consideration in most general case of the amorphous state of Si phase looks as follows:

$$g'(x_0, x, T) = \frac{x_0}{1+x_0} \left\{ \frac{1}{x} \sum_{y=0}^4 \frac{4!}{(4-y)! y!} \left( \frac{x}{2} \right)^y \left[ \frac{2-x}{2} \right]^{4-y} \Delta - kT \left( \frac{2}{x} \ln \frac{2}{2-x} - \ln \frac{x}{2-x} \right) - \frac{1}{x} \frac{h_E - s_E T}{N_A} \right\} + g_{strain} \quad (1)$$

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where  $\Delta_y = \{0, 0.5, 0.51, 0.22, 0\}$  eV for  $y = \{0, 1, 2, 3, 4\}$ , respectively, is the penalty energy of  $\text{Si-O}_y\text{Si}_{4-y}$  tetrahedral units composing the  $\text{SiO}_x$  structure [12, 13],  $k$  is the Boltzmann constant,  $h_E = 13400 \text{ J}\times\text{mol}^{-1}$  is the molar crystallization enthalpy [14],  $s_E = 3.97 \text{ J}\times\text{mol}^{-1}\times\text{K}^{-1}$  is the molar excess entropy of amorphous-to-crystalline transition [15],  $N_A$  is the Avogadro constant, and  $g_{\text{strain}}$  is the strain term, respectively. The contribution from the amorphous Si state is taken into account here since in the considered temperature range of the evolution of  $x_{\text{eq}}$  below about  $900^\circ\text{C}$  amorphous Si nanoinclusions are predominantly formed [7, 8, 16].

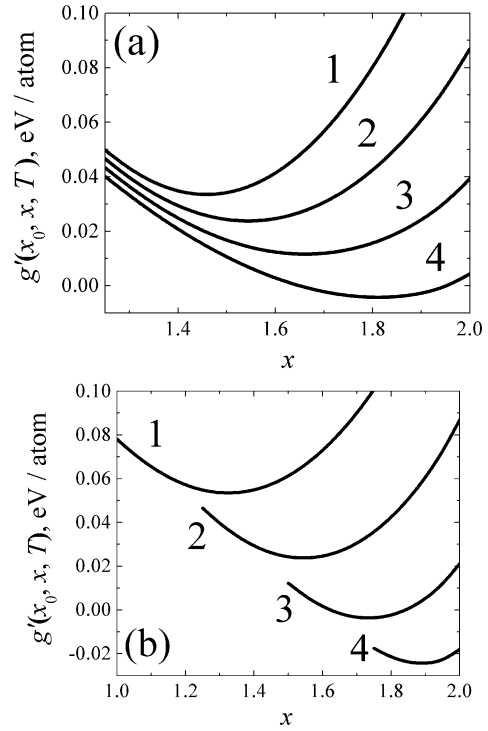
Each separate term in expression (1) corresponds to one mechanism, which drives or counteracts phase separation process in  $\text{SiO}_x$  films depending on whether respective contribution to the Gibbs free energy of Si/Si oxide system is a descending or ascending function of  $x$ . The mechanisms include: (i) the tendency to decrease the total penalty energy of  $\text{Si-O}_y\text{Si}_{4-y}$  tetrahedral units in the considered system (first term in braces), (ii) the transformation of the configuration entropy of silicon oxide (second term in braces), (iii) the appearance of amorphous Si phase (third term in braces), and (iv), as was already mentioned, appearance of the separation induced strain in the Si/Si oxide system. At this, only the first mechanism is driving to the separation of Si and  $\text{SiO}_x$  phases, while three other mechanisms counteract this process because of the growth of their contributions to  $g'(x_0, x, T)$  with the increase of the value of  $x$ .



**Fig. 1** – Temperature dependence of the equilibrium stoichiometry index of resistively evaporated  $\text{SiO}_{1.0}$  (a) and thermal vacuum sputtered  $\text{SiO}_{1.25}$  (b) films

Using Eq. (1) with the phenomenological expression for  $g_{\text{strain}}$  with parameters fitted with the use of respective experimental data we could describe the experimentally observed behavior of the equilibrium stoichiometry index  $x_{\text{eq}}$  of Si oxide phase as a function of initial stoichiometry index and annealing temperature. The details of this procedure are described in [11]. In Fig. 1, the experimental data of  $x_{\text{eq}}$  for resistively evaporated  $\text{SiO}_{1.0}$  [5] and thermal vacuum sputtered  $\text{SiO}_{1.25}$  films [6] used for fitting the parameters of  $g_{\text{strain}}$  are presented. Fig. 2 shows the respective calculated dependences of the Gibbs free energy of Si/Si oxide systems on  $x$ . As can be seen from this Figure, the minimum values of  $g'$  corresponding to equilibrium shift to higher values of  $x_{\text{eq}}$  when either  $x_0$  or  $T$  grows, which is fully in agree-

ment with available experimental data.



**Fig. 3** – Theoretical dependences of the reduced Gibbs free energy of amorphous Si/Si oxide systems on the stoichiometry index of silicon oxide phase calculated by expression (1): (a) – for different annealing temperatures,  $T$ : 1 – 600, 2 – 700, 3 – 800, 4 –  $900^\circ\text{C}$ .  $x_0 = 1.25$ . (b) – for different initial stoichiometry indexes of silicon oxide,  $x_0$ : 1 – 1, 2 – 1.25, 3 – 1.5, 4 – 1.75.  $T = 700^\circ\text{C}$

## 2.2 Formation of strain during separation of Si and Si oxide

As was already mentioned, the calculations of data presented in Fig. 2 have been carried out with phenomenological expression for  $g_{\text{strain}}$  satisfying a number of requirements to its mathematical structure but obtained without solid physical background. In this chapter, we consider the possible mechanism of the formation of strain in the Si/Si oxide system during the phase separation in it and propose a physically grounded expression for the respective Gibbs free energy contribution  $g_{\text{strain}}$ .

Phase separation in  $\text{SiO}_x$  films is known to occur by migration of oxygen atoms so that their transition takes place from the  $\text{Si-O}_y\text{Si}_{4-y}$  tetrahedral units with small  $y$  to units with high value of  $y$ . Consider the process of phase separation such that the oxygen atoms are redistributed from the regions of the formation of Si nanoinclusions into the surrounding matrix. Let us suppose that such atom redistribution does not lead to a change in the volume of remaining Si oxide phase independently upon how many new oxygen atoms have entered it from the regions of the formation of Si nanoparticles. In such case the Si oxide matrix will be exerted the strain related to the newly incorporated oxygen atoms. In addition, we suppose that the volume of Si phase relaxes so that the strain is present in the silicon oxide matrix only. According to the Hook's law, the value of strain per unit volume can be calculated as follows:

$$G_{strain} = \frac{1}{2} E \left( \frac{\Delta V}{V_x} \right)^2 = \frac{1}{2} E \left( \frac{V_x - V_{x0}}{V_x} \right)^2 \quad (2)$$

where  $V_x$  is the volume that  $\text{SiO}_x$  phase would have in relaxed state corresponding to the stoichiometry index  $x$  and  $V_{x0}$  is the actual volume of silicon oxide phase corresponding to the initial stoichiometry index  $x_0$ . Expression (2) describes thus the strain energy of  $\text{SiO}_x$  phase compressed to the volume of relaxed  $\text{SiO}_{x_0}$ .

Introducing the volume dependence on the stoichiometry index of Si oxide in the form

$$V_x = V_0(1 + \varepsilon x) \quad (3)$$

where  $\varepsilon = \frac{1}{V_0} \frac{\partial V_x}{\partial x}$  is the coefficient of the composition expansion of Si oxide with constant number of Si atoms, Eq. (2) acquires the following form:

$$G_{strain} = \frac{1}{2} E \varepsilon^2 \frac{(x - x_0)^2}{(1 + \varepsilon x)^2} \quad (4)$$

For small values of  $x$  so that  $\varepsilon x \ll 1$  this expression turns into expression for the strain contribution from [9] which was adopted and further modified in [11].

To calculate the value of  $\varepsilon$  is possible taking into account that the volume for  $x = 2$  corresponds to the volume of stoichiometric  $\text{SiO}_2$  phase,  $V = V_{\text{SiO}_2}$ , while for  $x = 0$  it is the corresponding volume of pure Si phase,  $V = V_{\text{Si}}$ , respectively. It is known that oxidation of Si wafers result in the increase of volume by about 2.2 times, i. e.  $V_{\text{SiO}_2} / V_{\text{Si}} \approx 2.2$ . Calculation from expression (3) results therefore in the following expression for  $\varepsilon$ :

$$\varepsilon = \frac{V_{\text{SiO}_2} - V_{\text{Si}}}{2V_{\text{Si}}} \approx 0.6 \quad (5)$$

Obtained value of  $\varepsilon$  provides a linear dependence of the volume of  $\text{SiO}_x$  phase with the composition  $x$  if the number of Si atoms is conserved.

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Temperature dependence of  $\varepsilon$  can be found from the respective temperature dependences of  $V_{\text{SiO}_2}$  and  $V_{\text{Si}}$  in the following general form:

$$V = V_0(1 + \beta T) \quad (6)$$

where  $V = V_{\text{SiO}_2}$  or  $V_{\text{Si}}$  and  $\beta = \beta_{\text{SiO}_2}$  or  $\beta_{\text{Si}}$  is the temperature expansion coefficient for both phases, respectively.

Temperature dependence of  $\varepsilon$  can be expressed in the following form:

$$\varepsilon(T) = \frac{V_{\text{SiO}_2}^{(0)}(1 + \beta_{\text{SiO}_2}T)}{2V_{\text{Si}}^{(0)}(1 + \beta_{\text{Si}}T)} - \frac{1}{2} \approx \frac{1.1(1 + \beta_{\text{SiO}_2}T)}{1 + \beta_{\text{Si}}T} - \frac{1}{2} \quad (7)$$

The values of  $\varepsilon(T)$  can be calculated using the values for  $\beta_{\text{SiO}_2} = 1.5 \times 10^{-6} \text{ K}^{-1}$  [17] and  $\beta_{\text{Si}} = 1.08 \times 10^{-5} \text{ K}^{-1}$  [18, 19]. However, its theoretical dependence on temperature is very weak although its values are consistent with respective values obtained from comparison with experimental data of the work [11]. This demonstrates that the temperature decrease of strain is not only determined by the different values of the temperature expansion coefficient for Si and  $\text{SiO}_x$  phases but also by the strain relaxation the easier, the higher is the annealing temperature.

## 3. CONCLUSION

In conclusion, we have demonstrated the role of the different mechanisms on the phase separation in nonstoichiometric Si oxide films during high temperature annealing. One mechanism related to the gain in the penalty energy of  $\text{Si-O}_y\text{Si}_{1-y}$  tetrahedral units composing the structure of  $\text{SiO}_x$  is the driving force of the separation of Si and Si oxide phases, while three other mechanisms counteract this process. Especial role is played by the internal strain associated with the difference in atomic densities of Si and  $\text{SiO}_2$  phases. The mechanism of strain appearance and its temperature dependence are discussed. Appearance of internal strain should be regarded as the principal mechanism that counteracts phase separation and defines the equilibrium states of nonstoichiometric Si oxides.

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