



Spinodal decomposition versus nucleation and growth mechanism of phase separation in nonstoichiometric silicon oxide films during high temperature annealing

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ABSTRACT

In this work, kinetic mechanisms of phase separation in nonstoichiometric Si oxide (SiO_x) films during high temperature annealing are studied theoretically. Analysis of the composition dependence of the Gibbs free energy of SiO_x phase is carried out to derive its binodal and spinodal characteristics. The ranges of the values of x corresponding to stability, metastability, and instability of nonstoichiometric Si oxide with respect to phase separation are determined as the functions of annealing temperature and SiO_x elastic properties. The composition-temperature regions of the spinodal decomposition and the nucleation and growth mechanisms of phase separation are presented. Obtained results open a way to a development of the kinetic theory of phase separation in SiO_x films and formation of Si quantum dots/ SiO_2 matrix composite structures.

1. Introduction

Nanocomposite structures with Si quantum dots (QDs) embedded in SiO_2 matrix are considered nowadays as the most promising candidates for realization of all-Si devices with integrated optical and electronic components [1,2]. Standard technologies for preparation of such nanocomposites make use of the phase separation of nonstoichiometric Si oxide films (SiO_x , $x < 2$) during high temperature annealing, which leads to the precipitation of excess Si from the oxide in form of amorphous or crystalline Si QDs capable of room temperature light emission. Pattern of precipitated Si is closely related to the kinetic mechanism of phase separation, which may in turn depend on the initial stoichiometry index of SiO_x film and annealing temperature. Some earlier publications [3–5] attribute this mechanism to the QDs nucleation and growth, while others claim the fulfillment of the conditions for spinodal decomposition and, hence, phase separation into Si and SiO_2 phases without energy barrier [6,7]. Also dependence of the kinetic mechanism on SiO_x composition was reported based on the results of experimental [8,9] and theoretical studies [10–12] and the estimated limits of initial excess Si concentration for nucleation and spinodal decomposition mechanism switching were provided. However, in none of these publications a detailed thermodynamic analysis of the kinetic mechanisms of SiO_x phase separation based on the dependence of the Gibbs free energy on its composition was presented. In this paper, we fill this gap by analyzing the behavior of the Gibbs free energy of SiO_x

phase proposed by us earlier [13], with respect to its stoichiometry. Such approach enables us to determine the composition-temperature regions corresponding to the stability, metastability and instability of SiO_x and fully characterize the kinetic mechanisms governing the SiO_x transformations in the entire range of x values.

2. Theory

In this section, the theoretical method of the calculation of the binodal and spinodal characteristics of nonstoichiometric Si oxide films based on the analysis of the composition dependence of their Gibbs free energy is described. The results of these calculations are used to determine the composition-temperature regions corresponding to the stability, metastability and instability of SiO_x films and in this way to identify the kinetic mechanisms of the phase separation of such films into Si and SiO_2 phases during thermal processing.

Following the approach presented in Ref. [14], the Gibbs free energy of nonstoichiometric Si oxide is considered as for solid solution of Si and SiO_2 phases corresponding to two extreme cases on the Si- SiO_2 phase diagram. The expression for the Gibbs free energy per one constituent unit of this solid solution (Si atom or SiO_2 molecule) has the following form as derived based on the analysis presented in our earlier publication [13]:

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$$G = g_{Si} X_{Si} + g_{SiO_2} X_{SiO_2} + \sum_{y=0}^4 \frac{4! X_{SiO_2}^y X_{Si}^{4-y}}{(4-y)! y!} \Delta_y + 2kT (X_{Si} \ln X_{Si} + X_{SiO_2} \ln X_{SiO_2}) \quad (1)$$

Here, g_{Si} , $X_{Si} = 1 - \frac{x}{2}$ and g_{SiO_2} , $X_{SiO_2} = 1 - X_{Si} = \frac{x}{2}$ are the Gibbs free energies and the molar fractions of Si and SiO₂ components in the SiO_x solid solution with stoichiometry index x , respectively, Δ_y is the penalty energy of Si–O_ySi_{4–y} tetrahedral complexes composing the silicon oxide structure, which characterizes energy nonequivalence of the complexes with different oxidation degrees of central Si atoms ($\Delta_0 = \Delta_4 = 0$, $\Delta_1 = 0.5$ eV, $\Delta_2 = 0.51$ eV, $\Delta_3 = 0.22$ eV) [15], k is the Boltzmann constant, and T is the annealing temperature, respectively. Third term in the expression (1) describes the contribution to the Gibbs free energy of the penalty energies of all tetrahedral complexes in the structure of Si oxide phase, while the last term is conditioned by the configuration entropy related to different arrangements of oxygen atoms between the pairs of Si atoms, respectively.

Behavior of the function (1) with respect to X_{Si} (or, alternatively, X_{SiO_2}) determines the composition regions corresponding to stability, metastability and instability of Si oxide and, hence, to different kinetic mechanisms of the phase separation of this material [14]. SiO_x films with compositions within stability regions do not undergo changes during thermal processing. Metastable SiO_x films tend to separate into Si and SiO₂ phases being annealed at high temperatures. However, such separation requires formation of critical-size Si nuclei, which involves overcoming the energy barrier for nucleation. Finally, separation of phases in the instability regions of Si oxide compositions takes place without energy barrier, i. e. spinodal decomposition mechanism is in action.

The values of X_{Si} corresponding to the binodal (or coexistence) curve, which separates the stability and metastability areas on the composition-temperature coordinate plane and defines the equilibrium compositions of Si- and SiO₂-rich phases, are determined by the minimum values of the function $G - g_{Si} X_{Si} - g_{SiO_2} X_{SiO_2}$ in the expression (1). Spinodal curve, which is a boundary between the metastability and instability regions of the Si oxide solid solution, corresponds to zero values of the second derivative of the function (1) with respect to X_{Si} , $\frac{\partial^2 G}{\partial X_{Si}^2} = 0$, when the strain formation is neglected (chemical spinodal). However, typical for early stages of spinodal decomposition is the appearance of strain (and associated stress) related to maintaining coherency at the interfaces between neighboring spatial domains with slightly differing compositions evolved as a result of material redistribution. In this case, equation of coherent spinodal curve is obtained taking into account coherency strain and additional free energy related to it.

Phase separation in nonstoichiometric Si oxide films is known to occur predominantly by migration of oxygen atoms between the Si–O_ySi_{4–y} complexes so that the complexes with higher y acquire and those with lower y loose oxygen, respectively [16]. If the redistribution of oxygen takes place as schematically shown in Fig. 1, i. e. if alternating regions of lower ($X_{Si} - \Delta X_{Si}$) and higher ($X_{Si} + \Delta X_{Si}$) Si content with respect to the initial one form in a three-dimensional pattern, the coherency strain in these regions is purely hydrostatic. In the framework of elasticity theory, the free energy per one constituent unit of Si oxide solid solution (Si atom or SiO₂ molecule) due to the hydrostatic strain caused by slight change of composition by ΔX_{Si} can be expressed as follows [17]:

$$G_{strain} = \frac{1}{2} K_{SiO_x} \varepsilon_v^2 \Omega_{SiO_x} \quad (2)$$

where K_{SiO_x} is the bulk modulus of SiO_x phase, ε_v is the volumetric strain corresponding to the value ΔX_{Si} , and Ω_{SiO_x} is the average volume per a single Si or SiO₂ constituent unit, respectively.

To calculate the volumetric strain associated with the change of Si oxide composition by ΔX_{Si} , the following general dependence of the volume of Si oxide phase on its stoichiometry index x is first considered:

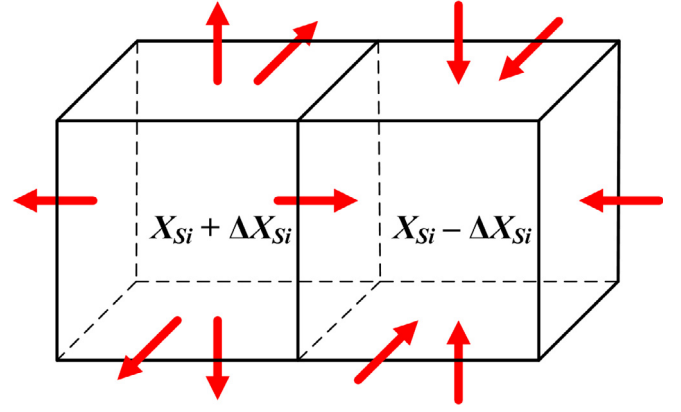


Fig. 1. Schema of the formation of spatial domains with relative Si excess and deficiency during initial stages of SiO_x spinodal decomposition. Alternation of the domains with differing Si molar fractions should be imagined to repeat in all three dimensions. Arrows indicate the pathways of net oxygen redistribution.

$$V(x) = V_0(1 + \eta x) \quad (3)$$

Here, $\eta = \frac{1}{V_0} \frac{\partial V(x)}{\partial x}$ is the coefficient of the composition expansion of Si oxide volume with fixed number of Si atoms. The value of η is calculated from the expression (3) taking into account that the volume of Si oxide at $x = 2$ corresponds to the volume of stoichiometric SiO₂ phase, V_{SiO_2} , while it is the volume of Si phase, V_{Si} , at $x = 0$, respectively:

$$\eta = \frac{V_{SiO_2} - V_{Si}}{2V_{Si}} \approx 0.6 \quad (4)$$

where $\frac{V_{SiO_2}}{V_{Si}} \approx 2.2$ has been set as follows from the observed swelling of initial Si volume by about 2.2 times as a result of thermal oxidation [18]. We note that both expressions (3) and (4) are composed for the same numbers of Si atoms in the considered phases.

Taking into account the relation between x and X_{Si} , formula (3) can be rewritten for the latter parameter, which enables to express the average volume per one SiO_x constituent unit Ω_{SiO_x} as follows:

$$\Omega_{SiO_x} = \Omega_{Si} [1 + 2\eta(1 - X_{Si})] \quad (5)$$

with Ω_{Si} being the atomic volume of Si in Si phase.

Volumetric strain ε_v in the Si oxide spatial domain having the volume $V(X_{Si})$ and Si molar fraction $X_{Si} \pm \Delta X_{Si}$ is calculated as follows:

$$\varepsilon_v = \frac{V(X_{Si} \pm \Delta X_{Si}) - V(X_{Si})}{V(X_{Si})} = \mp \frac{2\eta \Delta X_{Si}}{1 + 2\eta(1 - X_{Si})} \quad (6)$$

Therefore, expression (2) for the strain contribution to the Gibbs free energy during early stages of spinodal decomposition is converted as follows:

$$G_{strain} = \frac{4K_{SiO_x} \eta^2 \Omega_{Si}}{1 + 2\eta(1 - X_{Si})} \frac{\Delta X_{Si}^2}{2} \quad (7)$$

Coherent spinodal dependence is determined from the following equation [14]:

$$\frac{\partial^2 G}{\partial X_{Si}^2} = -\frac{2G_{strain}}{\Delta X_{Si}^2} = -\frac{4K_{SiO_x} \eta^2 \Omega_{Si}}{1 + 2\eta(1 - X_{Si})} \quad (8)$$

Condition $\frac{\partial^2 G}{\partial X_{Si}^2} > -\frac{4K_{SiO_x} \eta^2 \Omega_{Si}}{1 + 2\eta(1 - X_{Si})}$ in the vicinity of the coherent spinodal corresponds to the metastability composition regions and the Si nucleation and growth mechanism of the phase separation of SiO_x films. In its turn, condition $\frac{\partial^2 G}{\partial X_{Si}^2} < -\frac{4K_{SiO_x} \eta^2 \Omega_{Si}}{1 + 2\eta(1 - X_{Si})}$ determines the instability region of the compositions of nonstoichiometric Si oxide and the spinodal decomposition mechanism of phase separation in it.

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