

# Hydrogenated Silicon Oxycarbonitride Films.

## Part III. Thermodynamic Modeling of the Si–C–N–O–H System

A. N. Golubenko<sup>a</sup>, N. I. Fainer<sup>b</sup>, and E. F. Titova<sup>b</sup>

<sup>a</sup>Novosibirsk National Research State University, ul. Pirogova 2, Novosibirsk, 630090 Russia

<sup>b</sup>Nikolaev Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch,  
pr. Akad. Lavrent'eva 3, Novosibirsk, 630090 Russia

e-mail: nadezhda@niic.nsc.ru

Received November 10, 2014

**Abstract**—The thermodynamic modeling of the deposition of the condensed phase of a complex composition has been performed in the Si–C–N–O–H system in the broad temperature range of 300–1300 K under total pressure  $P_{\text{total}}^0 = 6-7 \times 10^{-2}$  Torr and residual air pressure in reactor  $P_{\text{res}} = 5 \times 10^{-3}$  Torr using the initial gas mixtures of organosilicon compound, hexamethyldisilazane (HMDS), with nitrogen, oxygen, air mixture ( $\text{O}_2 + 4\text{N}_2$ ), and a variable mixture of oxygen with nitrogen ( $\text{O}_2 + x\text{N}_2$ ). The temperature boundaries of multiphase ranges, where one can anticipate the deposition of silicon oxycarbonitride, silicon oxycarbides, and silicon oxynitride, have been determined.

**Keywords:** thermodynamic modeling, Si–C–N–O–H system, hexamethyldisilazane

**DOI:** 10.1134/S1087659615030062

### INTRODUCTION

This work follows a series of our works that study the opportunity of the use of volatile organosilicon compounds for the preparation of silicon-containing coatings of various compositions according to the chemical vapor deposition technique (CVD) [1–3]. The increased interest in thin films of hydrogenated silicon oxycarbonitride is related to their use in technological fields such as micro- and nanoelectronics, optoelectronics, and solar power engineering [4–11].

The interest in compounds such as hexamethyldisilazane (HMDS or bis(trimethylsilyl)amine according to IUPAC) is related to the problems of synthesis of silicon oxycarbonitride (including hydrogenated), silicon oxynitride, and silicon oxycarbides films using the gas mixtures of HMDS with additional gases, for example, with helium, nitrogen, ammonia, and oxygen (or their mixture).

A thermodynamic approach to the choice of the deposition conditions (temperature  $T$  and total pressure  $P_{\text{total}}^0$  in the reactor, composition of a particular gas mixture) of the films with various compositions from a complex gas mixture [12, 13] allows, firstly, evaluating the possibility of the use of the chosen organosilicon compound (or its mixture) to obtain the films of the required composition and, secondly, setting the variation ranges of the parameters of the system without the change of the phase and elemental composition of the coatings.

### THERMODYNAMIC CALCULATIONS

In this work, the thermodynamic analysis of the Si–C–N–O–H system was performed taking into account the use of the following initial gas mixtures: HMDS +  $\text{N}_2$  (1); HMDS +  $\text{O}_2$  (2); HMDS + (mixture  $\text{O}_2 + \text{N}_2$ ) (3). Such parameters of the system as total pressure in reactor  $P_{\text{total}}^0 = 6-7 \times 10^{-2}$  Torr and residual air pressure in reactor  $P_{\text{res}} = 5 \times 10^{-3}$  Torr were chosen by us in accordance with the experimental conditions.

Thermodynamic calculations of the considered Si–C–N–O–H system were performed using the minimization of Gibbs energy for the temperature range of 300–1300 K and chosen  $P_{\text{total}}^0$  at constant  $P_{\text{res}}$ , where  $P^0(\text{N}_2)/P^0(\text{O}_2) = 3.76$  ( $P^0$  is the initial partial pressure of corresponding gas in the gas mixture under study). The definite atomic ratios of individual components  $n^0(\text{Si}) : n^0(\text{C}) : n^0(\text{N}) : n^0(\text{O}) : n^0(\text{H})$  were determined from the given composition of the initial gas mixture, which is characterized by the parameter  $R_1^0 = P^0(\text{N}_2)/P^0(\text{HMDS}) = 0-10$ . The procedure of the calculation is described in [14].

The standard thermodynamic characteristics of individual substances were used as initial: standard enthalpy of formation  $\Delta H_{f,298}^0$ , standard entropy  $S_{298}^0$ , and standard molar heat capacity  $C_p^0(T)$ . The main source of thermodynamic characteristics is Database

(Properties of Materials of Microelectronic Technology) which was created at the Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch (IIC RAS SB) for the solution of microelectronics problems [15]. In the considered Si–C–N–O–H system, the following condensed compounds were included in the calculations: Si (solid), C (solid, graphite and diamond), SiO (solid), SiO<sub>2</sub> (solid, quartz and cristobalite), SiC (solid, two modifications), Si<sub>3</sub>N<sub>4</sub> (solid, two modifications  $\alpha$  and  $\beta$ ), H<sub>2</sub>O (liq), C<sub>4</sub>H<sub>12</sub>OSi (liq), C<sub>6</sub>H<sub>18</sub>OSi<sub>2</sub> (liq), C<sub>6</sub>H<sub>19</sub>N<sub>2</sub>Si<sub>2</sub> (liq), C<sub>8</sub>H<sub>24</sub>N<sub>2</sub>Si<sub>2</sub> (liq), C<sub>5</sub>H<sub>18</sub>N<sub>4</sub>Si (liq), C<sub>6</sub>H<sub>20</sub>N<sub>4</sub>Si (liq), C<sub>4</sub>H<sub>14</sub>N<sub>2</sub>Si (liq), C<sub>5</sub>H<sub>16</sub>N<sub>2</sub>Si (liq), C<sub>4</sub>H<sub>12</sub>N<sub>2</sub> (liq), C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> (liq), C<sub>2</sub>H<sub>8</sub>N<sub>2</sub> (liq), CH<sub>3</sub>OH (liq), and 78 gas compounds.

The absence of thermodynamic characteristics for individual ternary SiC<sub>x</sub>N<sub>y</sub> and quaternary SiC<sub>x</sub>N<sub>y</sub>O<sub>z</sub> compounds, as well as their hydrogenated forms, does not allow the strict determination of the preparation of silicon oxycarbonitride, giving only the temperature boundaries of phase ranges, which contain the mixtures of phases including all elements of these compounds.

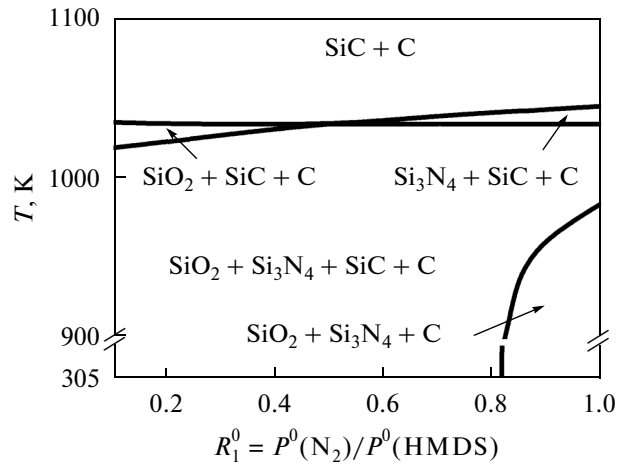
It should be noted that, although experimental processes of the layer fabrication according to the CVD technique proceed under the conditions, which are far from equilibrium, the results of thermodynamic simulation are valuable for the determination of the conditions of the preparation of the condensed phase with required composition.

Thus, the thermodynamic modeling of the utilized processes, which precedes the experiments, allows the rationalization of the choice of the initial precursor substances, determining the ranges of the conditions corresponding to the deposition of various sets of phases and, consequently, reducing substantially the program of the required expensive and long experiments.

## RESULTS OF THERMODYNAMIC ANALYSIS OF THE Si–C–N–O–H SYSTEM

*Initial gas mixture* HMDS + N<sub>2</sub> (1). Thermodynamic calculations enable one to determine the composition of the condensed phases and the gas phase, which is in equilibrium with them, under various definite pressures in the system and the chosen composition of gas mixture that is attributed by parameter  $R_1^0$ .

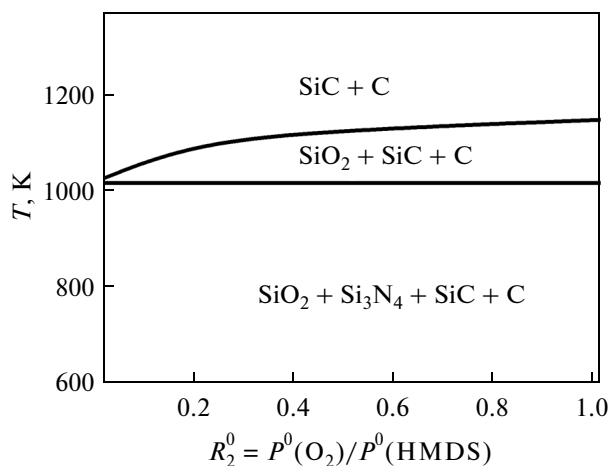
The result of the calculations is given as a section of the CVD phase diagram of Si–C–N–O–H in Fig. 1. When varying parameter  $R_1^0$  (from 0 to 1) in the temperature range of 300–1100 K within the initial gas mixture HMDS + N<sub>2</sub> (assuming residual air pressure), only the nitrogen concentration changed. In this case, the atomic ratios of the individual components can be written as  $n^0(\text{Si}) : n^0(\text{C}) : n^0(\text{N}) : n^0(\text{O}) : n^0(\text{H}) =$



**Fig. 1.** Section of the CVD phase diagram of the Si–C–N–O–H system for the initial gas mixture 1 (HMDS + N<sub>2</sub>),  $R_1^0 = P^0(\text{N}_2)/P^0(\text{HMDS})$  at  $P_{\text{total}}^0 = 6 \times 10^{-2}$  Torr and  $P_{\text{res}} = 6 \times 10^{-3}$  Torr.

2 : 6 : (x) : (5.25 × 10<sup>-2</sup>) : 19 at a particular  $R_1^0$ . As follows from Fig. 1, five phase ranges can be determined that are in equilibrium with the gas phase in the temperature range of 300–1300 K—one large four-phase (SiO<sub>2</sub> + Si<sub>3</sub>N<sub>4</sub> + SiC + C); three three-phase (SiO<sub>2</sub> + Si<sub>3</sub>N<sub>4</sub> + C), (SiO<sub>2</sub> + SiC + C), and (Si<sub>3</sub>N<sub>4</sub> + SiC + C); and a two-phase range (SiC + C)—which can be realized at elevated temperatures ( $T > 1045$  K). At 1019–1034 K and  $R_1^0$  varying from 0.1 to 0.5, the mixture of phases (SiO<sub>2</sub> + SiC + C) is in equilibrium with the gas phase; and, at  $R_1^0 > 0.5$ , in the narrower temperature range 1034–1045 K, there can be a mixture of oxygen-free phases (Si<sub>3</sub>N<sub>4</sub> + SiC + C). In the high-concentration range of nitrogen in the initial gas phase ( $R_1^0 > 0.815$ ), the existence of a three-phase range is possible in the temperature range of 300–985 K (SiO<sub>2</sub> + Si<sub>3</sub>N<sub>4</sub> + C). The total elemental composition of the condensed phase at a particular composition of the initial gas mixture  $R_1^0$  shows the increase in the carbon content with the growth of  $R_1^0$ . The limiting elemental composition at  $T > 1050$  K at various  $R_1^0$  values for the given mixture of HMDS with nitrogen corresponds to the composition Si<sub>2</sub>C<sub>5.95</sub>, and it is clear from Fig. 1 that the phase composition represents the mixture (SiC + C).

In the temperature range from 600 to ~1000 K, the elemental composition of the precipitated film practically remains constant. It should be noted that, at  $R_1^0 < 0.5$ , in the narrow temperature range, silicon oxycarbide with a small oxygen content may exist in equilibrium with the gas phase; for example, at  $R_1^0 = 0.1$  and  $T = 1019$  K, the elemental composition of the film is



**Fig. 2.** Section of the CVD phase diagram of the Si–C–N–O–H system for the initial gas mixture 2 (HMDS + O<sub>2</sub>),  $R_2^0 = P^0(\text{O}_2)/P^0(\text{HMDS})$  at  $P_{\text{total}}^0 = 6 \times 10^{-2}$  Torr and  $P_{\text{res}} = 5 \times 10^{-3}$  Torr.

$\text{Si}_2\text{C}_{8.77}\text{O}_{0.011}$ ; and, at  $R_1^0 = 0.4$  and  $T \sim 1030$  K,  $\text{Si}_2\text{C}_{5.95}\text{O}_{0.002}$ . In the narrow temperature range of 1034–1045 K, at  $R_1^0 > 0.54$ , the composition of the condensed phase would correspond to silicon carbonitride  $\text{SiC}_x\text{N}_y$ .

In the three-phase range ( $\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{C}$ ), in the temperature range of 700–985 K, the total elemental composition of condensed phase may be described as  $\text{Si}_2\text{C}_6\text{N}_{2.64}\text{O}_{0.052}$ ; in addition, Si–C bonds are not formed in this phase and there are Si–N and Si–O bonds.

The composition of the equilibrium gas phase depends on the temperature and, to a lesser extent, the

composition of the initial gas mixture, that is  $R_1^0$ . At low temperatures,  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{N}_2$ , predominate in the gas phase; in addition, nitrogen has an excessive pressure; there are also traces of  $\text{NH}_3$ . At elevated temperatures, the partial pressure of  $\text{N}_2$ ,  $\text{H}_2$  grows and  $\text{CO}$ ,  $\text{HCN}$ , and  $\text{H}$  gas molecules and traces of  $\text{C}_2\text{H}_2$ , as well as  $\text{CH}_4$ , appear.

**Initial gas mixture HMDS + O<sub>2</sub> (2).** Thermodynamic modeling of CVD processes in the Si–C–N–O–H system using the initial gas mixture HMDS + O<sub>2</sub> was performed under the same conditions as described above for the gas mixture with nitrogen. The definite composition of the initial gas phase was set using the variable parameter  $R_2^0 = P^0(\text{O}_2)/P^0(\text{HMDS})$  in the range from 0 to 1. The results of calculations are given in the CVD diagram (Fig. 2).

In contrast with the initial gas mixture (1) with nitrogen, in this case, there are three phase ranges in diagram, which are in equilibrium with the gas phase: the broad range of the four-phase mixture ( $\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$ ) up to 1000 K; and at higher temperatures, the three-phase range ( $\text{SiO}_2 + \text{SiC} + \text{C}$ ), which transfers to the two-phase range at  $T > 1150$  K ( $\text{SiC} + \text{C}$ ). The temperature boundary of the tri- and two-phase ranges is shifted to higher temperatures. It should be noted that an increase in the concentration of oxygen in the initial gas mixture (2) leads to the change of the composition of the components in the condensed phase; this can be observed from the calculated data in Table 1 for two definite values  $R_2^0$ .

Thus, we can state the possibility of the preparation of both silicon oxycarbonitride  $\text{SiC}_x\text{N}_y\text{O}_z$ , the elemental composition of which remains constant in the range of 600–1000 K at a given  $R_2^0$ , and silicon oxycar-

**Table 1.** Calculated equilibrium composition of condensed phase in the Si–C–N–O–H system using initial gas mixture HMDS + O<sub>2</sub> ( $P_{\text{tot}}^0 = 6 \times 10^{-2}$  Torr,  $P_{\text{res}} = 5 \times 10^{-3}$  Torr)

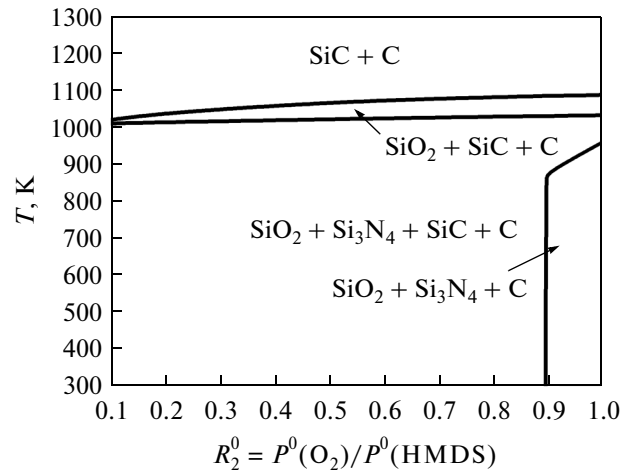
T, K	$R_2^0$		T, K	$R_2^0$	
	Atomic composition	Phase composition		Atomic composition	Phase composition
300	$\text{Si}_2\text{C}_{1.26}\text{N}_{1.14}\text{O}_{1.04}$	$\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$	300	$\text{Si}_{2.0}\text{C}_{1.26}\text{N}_{1.14}\text{O}_{2.04}$	$\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$
400	$\text{Si}_2\text{C}_{1.74}\text{N}_{1.14}\text{O}_{1.04}$		400	$\text{Si}_{2.0}\text{C}_{1.74}\text{N}_{1.14}\text{O}_{2.04}$	
500	$\text{Si}_2\text{C}_{4.79}\text{N}_{1.14}\text{O}_{1.04}$		500	$\text{Si}_{2.0}\text{C}_{4.79}\text{N}_{1.14}\text{O}_{2.04}$	
600	$\text{Si}_2\text{C}_{5.93}\text{N}_{1.14}\text{O}_{1.04}$		600	$\text{Si}_{2.0}\text{C}_{6.0}\text{N}_{1.14}\text{O}_{2.04}$	
700	$\text{Si}_2\text{C}_{5.99}\text{N}_{1.14}\text{O}_{1.04}$		700	$\text{Si}_{2.0}\text{C}_{6.0}\text{N}_{1.14}\text{O}_{2.04}$	
800	$\text{Si}_2\text{C}_{6.0}\text{N}_{1.13}\text{O}_{1.04}$		800	$\text{Si}_{2.0}\text{C}_{6.0}\text{N}_{1.14}\text{O}_{2.04}$	
900	$\text{Si}_2\text{C}_{6.0}\text{N}_{1.14}\text{O}_{1.04}$		900	$\text{Si}_{2.0}\text{C}_{6.0}\text{N}_{1.13}\text{O}_{2.04}$	
1000	$\text{Si}_2\text{C}_{5.98}\text{N}_{0.52}\text{O}_{1.02}$		1000	$\text{Si}_{2.0}\text{C}_{6.0}\text{N}_{0.52}\text{O}_{2.02}$	
1018–1127	$\text{Si}_2\text{C}_{5.55}\text{O}_{0.58}$	$\text{SiO}_2 + \text{SiC} + \text{C}$	1018–1127	$\text{Si}_{2.0}\text{C}_{5.55}\text{O}_{1.5887}$	$\text{SiO}_2 + \text{SiC} + \text{C}$
1028–1300	$\text{Si}_2\text{C}_{4.96}$	$\text{SiC} + \text{C}$	1028–1300	$\text{Si}_{2.0}\text{C}_{4.96}$	$\text{SiC} + \text{C}$

bide  $\text{SiC}_x\text{O}_z$  from the gas phase; and the mixture of the  $\text{SiC} + \text{C}$  phases, at high temperatures.

*Gas mixture* HMDS + ( $\text{N}_2 + \text{O}_2$ ) (3). After modeling CVD processes using the gas mixtures of HMDS with nitrogen (1) and oxygen (2), it was interesting to determine the composition of solid coatings using the mixture of HMDS with air. The composition of air can be represented as ( $4\text{N}_2 + \text{O}_2$ ). The composition of the condensed phase at various compositions of the initial gas mixture HMDS + air (3) was calculated in the temperature range of 300–1300 K at  $P_{\text{total}}^0 = 6 \times 10^{-2}$  Torr and  $P_{\text{res}} = 5 \times 10^{-3}$  Torr.

The initial composition of the gas phase, which is determined by the ratio of the gas flows of air to the HMDS flow, is represented by the parameter  $R_2^0 = P^0(\text{O}_2)/P^0(\text{HMDS})$ , where  $P^0(\text{O}_2)$  and  $P^0(\text{HMDS})$  are the initial partial pressures for oxygen and HMDS in the gas mixture under study, respectively. The results of thermodynamic modeling in the system (3) are represented as the CVD phase diagram in Fig. 3. In the variation range of the parameters of the system ( $T$  from 300 to 1300 K and  $R_2^0$  from 0.1 to 1.0), four phase ranges can be highlighted: a four-phase range ( $\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$ ); two three-phase ranges ( $\text{SiO}_2 + \text{SiC} + \text{C}$ ) and ( $\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{C}$ ); and, at high temperatures, a two-phase range ( $\text{SiC} + \text{C}$ ). The composition of the condensed phases at two definite values  $R_2^0 = P^0(\text{O}_2)/P^0(\text{HMDS})$  is given in Table 2. The elemental composition of the condensed phase in this system at a given  $R_2^0$  also remains almost constant in the temperature range of 600–1000 K.

The number of phase ranges in Fig. 3 (the total number is four) is intermediate between the phase

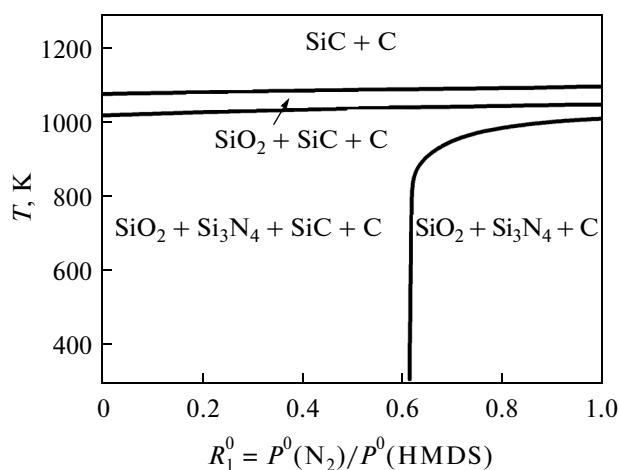


**Fig. 3.** Section of the CVD phase diagram of the Si–C–N–O–H system for the initial gas mixture 3 (HMDS + air),  $R_2^0 = P^0(\text{O}_2)/P^0(\text{HMDS})$  at  $P_{\text{total}}^0 = 6 \times 10^{-2}$  Torr,  $P_{\text{res}} = 5 \times 10^{-3}$  Torr.

ranges given in Figs. 1 and 2 for mixtures (1) and (2). The temperature boundary between high-temperature phase ranges ( $\text{SiC} + \text{C}$ )/( $\text{SiO}_2 + \text{SiC} + \text{C}$ ) for mixture (3) is below that for mixture (2) with oxygen and the temperature boundary between the ranges ( $\text{SiO}_2 + \text{SiC} + \text{C}$ )/( $\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$ ) is similar to the analogous boundary in system (2). When using the initial gas mixture (3) ( $R_2^0$  ranging from 0.9 to 1.0) at lower temperatures, there is the phase range ( $\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{C}$ ), which is similar to the three-phase range in the case of initial mixture (1) (Fig. 1), although with shifted temperature boundaries.

**Table 2.** Calculated equilibrium composition of condensed phase in the Si–C–N–O–H system using initial gas mixture HMDS + “air” ( $P_{\text{tot}}^0 = 6 \times 10^{-2}$  Torr,  $P_{\text{res}} = 5 \times 10^{-3}$  Torr)

$T, \text{K}$	$R_2^0 = 0.2$		$T, \text{K}$	$R_2^0 = 0.5$	
	Atomic composition	Phase composition		Atomic composition	Phase composition
300	$\text{SiC}_{0.56}\text{N}_{0.66}\text{O}_{0.04}$	$\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$	300	$\text{SiC}_{0.63}\text{N}_{0.90}\text{O}_{0.11}$	$\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$
400	$\text{SiC}_{0.87}\text{N}_{0.66}\text{O}_{0.04}$		400	$\text{SiC}_{0.85}\text{N}_{0.90}\text{O}_{0.11}$	
500	$\text{SiC}_{2.4}\text{N}_{0.66}\text{O}_{0.04}$		500	$\text{SiC}_{2.40}\text{N}_{0.90}\text{O}_{0.11}$	
600	$\text{SiC}_{2.96}\text{N}_{0.66}\text{O}_{0.04}$		600	$\text{SiC}_{2.97}\text{N}_{0.90}\text{O}_{0.11}$	
700	$\text{SiC}_{3.0}\text{N}_{0.66}\text{O}_{0.04}$		700	$\text{SiC}_{3.0}\text{N}_{0.90}\text{O}_{0.11}$	
800	$\text{SiC}_{3.0}\text{N}_{0.66}\text{O}_{0.04}$		800	$\text{SiC}_{3.0}\text{N}_{0.90}\text{O}_{0.11}$	
900	$\text{SiC}_{3.0}\text{N}_{0.66}\text{O}_{0.04}$		900	$\text{SiC}_{3.0}\text{N}_{0.90}\text{O}_{0.11}$	
1000	$\text{SiC}_{3.0}\text{N}_{0.34}\text{O}_{0.03}$		1000	$\text{SiC}_{3.0}\text{N}_{0.58}\text{O}_{0.97}$	
1022	$\text{SiC}_{2.98}\text{O}_{0.025}$	$\text{SiO}_2 + \text{SiC} + \text{C}$	1030	$\text{SiC}_{2.98}\text{O}_{0.08}$	$\text{SiO}_2 + \text{SiC} + \text{C}$
1047	$\text{SiC}_{2.96}\text{O}_{0.001}$		1075	$\text{SiC}_{2.90}\text{O}_{0.002}$	
1100–1300	2.96	$\text{SiC} + \text{C}$	1100–1300	$\text{SiC}_{2.89}$	$\text{SiC} + \text{C}$



**Fig. 4.** Section of the CVD phase diagram of the Si–C–N–O–H system for the initial gas mixture (4) HMDS + ( $x\text{N}_2 + \text{O}_2$ ),  $R_1^0 = P^0(\text{N}_2)/P^0(\text{HMDS})$  at  $P_{\text{total}}^0 = 7 \times 10^{-2}$  Torr,  $P_{\text{res}} = 5 \times 10^{-3}$  Torr.

The effect of the change of the composition of the initial mixture ( $x\text{N}_2 + \text{O}_2$ ), where  $x = 1, 3$ , and  $4$ , on the deposition of the condensed phases was studied. As in the cases considered above,  $P_{\text{total}}^0 = 6 \times 10^{-2}$  Torr (and also  $P_{\text{total}}^0 = 7 \times 10^{-2}$  Torr),  $P_{\text{res}} = 5 \times 10^{-3}$  Torr, and  $P^0(\text{HMDS}) = 4 \times 10^{-2}$  Torr were used in the calculations. The composition of the initial gas mixture ( $x\text{N}_2 + \text{O}_2$ ) varied in a sufficiently narrow pressure range, which corresponds to  $2.5 \times 10^{-2}$  Torr, for example, for  $P_{\text{total}}^0 = 7 \times 10^{-2}$  Torr. In the considered case, the concentration of nitrogen in the initial gas mixture grows and the concentration of molecular oxygen decreases. Fig. 4 shows the section of the CVD phase diagram for the initial gas mixture HMDS + ( $x\text{N}_2 + \text{O}_2$ ) (4) where parameters are  $T$  and  $R_1^0 = P_{\text{N}_2}^0/P_{\text{HMDS}}^0$ .

It follows from the figure that, for this initial gas mixture under the considered conditions, just as when using mixture (3), there is the same set of phase ranges and with the same number of condensed phases. The temperature boundaries between the phase ranges are in general close to those obtained for the initial gas mixture (3) (HMDS + air), although with the shift of the temperature boundary between the phase ranges ( $\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$ )/( $\text{SiO}_2 + \text{Si}_3\text{N}_4 + \text{C}$ ) by  $R_1^0$ .

The results of the integrated study of the chemical and phase compositions of the grown films using spectroscopic methods such as IR, Raman, X-ray photoelectron, and energy dispersion spectroscopy [16, 17] showed good accordance of the phase composition of these films with the composition calculated in the Si–C–N–O–H system.

## CONCLUSIONS

In this work, the results of thermodynamic modeling of the deposition of films with various compositions from the gas mixtures of hexamethyldisilazane with oxygen, nitrogen, and mixture ( $\text{O}_2 + \text{N}_2$ ) in the broad temperature range (300–1300 K) under reduced total pressure in the system are given.

The ranges of the deposition conditions of complex condensed phases, which contain silicon oxycarbonitride, silicon oxycarbide, and silicon oxynitride, were determined. Using these data, the experiments on the growth of oxycarbonitride films with various compositions were performed. It should be noted that the thermodynamic approach to the precipitation of complex films in the Si–C–N–O–H system from various compositions of volatile silicon-containing compounds showed its predictive ability.

## ACKNOWLEDGMENTS

The work was partially supported by the Russian Foundation for Basic Research (project no. 13-03-01167).

## REFERENCES

1. Fainer, N.I., From organosilicon precursors to multifunctional silicon carbonitride, *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 1, pp. 43–52.
2. Fainer, N.I., Golubenko, A.N., Rummyantsev, Yu.M., Kesler, V.G., Ayupov, B.M., Rakhlin, V.I., and Voronkov, M.G., Tris(diethylamino)silane—A new precursor compound for obtaining layers of silicon carbonitride, *Glass Phys. Chem.*, 2012, vol. 38, no. 1, pp. 15–26.
3. Fainer, N.I., Golubenko, A.N., Rummyantsev, Yu.M., Kesler, V.G., Maksimovskii, E.A., Ayupov, B.M., and Kuznetsov, F.A., Synthesis of silicon carbonitride dielectric films with improved optical and mechanical properties from tetramethyldisilazane, *Glass Phys. Chem.*, 2013, vol. 39, no. 1, pp. 77–88.
4. Zhang, D.H., Gao, Y., Wei, J., and Mo, Z.Q., Influence of silane partial pressure on the properties of amorphous SiCN films prepared by ECRCVD, *Thin Solid Films*, 2000, vols. 377–378, pp. 607–610.
5. Chen, K.H., Wu, J.-J., Wen, C.Y., Chen, L.C., Fan, C.W., Kuo, P.F., Chen, Y.F., and Huang, Y.S., Wide-band-gap silicon carbon nitride films deposited by electron cyclotron resonance plasma chemical vapor deposition, *Thin Solid Films*, 1999, vols. 355–356, pp. 205–209.
6. Gómez, F.J., Prieto, P., Elizalde, E., and Piqueras, J., SiCN alloys deposited by electron cyclotron resonance plasma chemical vapor deposition, *Appl. Phys. Lett.*, 1996, vol. 69, no. 6, p. 773.
7. Soto, G., Samano, E.C., Machorro, R., and Cota, L., Growth of SiC and  $\text{SiC}_x\text{N}_y$  films by pulsed laser ablation of SiC in Ar and  $\text{N}_2$  environments, *J. Vac. Sci. Technol., A*, 1998, vol. 16, no. 3, pp. 1311–1315.

8. Jedrzejowski, P., Cizek, J., Amassian, A., Klemberg-Sapieha, J.E., Vlcek, J., and Martinu, L., Mechanical and optical properties of hard SiCN coatings prepared by PECVD, *Thin Solid Films*, 2004, vols. 447–448, pp. 201–207.
9. Xie, E., Ma, Z., Lin, H., Lin, H., Zhang, Zh., and He, D., Preparation and characterization of SiCN films, *Opt. Mater.*, 2003, vol. 23, nos. 1–2, pp. 151–156.
10. Chen, C.W., Huang, C.C., Lin, Y.Y., Chen, L.C., Chen, K.H., and Su, W.F., Optical properties and photoconductivity of amorphous silicon carbon nitride thin film and its application for UV detection, *Diamond Relat. Mater.*, 2005, vol. 14, nos. 3–7, pp. 1010–1013.
11. Chen, C.W., Huang, C.C., Lin, Y.Y., Chen, L.C., and Chen, K.H., The affinity of Si–N and Si–C bonding in amorphous silicon carbon nitride (*a*-SiCN) thin film, *Diamond Relat. Mater.*, 2005, vol. 14, nos. 3–4, pp. 1126–1130.
12. Fainer, N.I., Golubenko, A.N., Rummyantsev, Yu.M., and Maksimovskii, E.A., Use of hexamethylcyclotrisilazane for preparation of transparent films of complex compositions, *Glass Phys. Chem.*, 2009, vol. 35, no. 3, pp. 274–283.
13. Ionescu, E., Terzioglu, C., Linck, C., Kaspar, J., Navrotsky, A., and Riedel, R., Thermodynamic control of phase composition and crystallization of metal-modified silicon oxycarbides, *J. Am. Ceram. Soc.*, 2013, vol. 96, no. 6, pp. 1899–1903.
14. Golubenko, A.N., Kosinova, M.L., Titov, V.A., Titov, A.A., and Kuznetsov, F.A., On thermodynamic equilibria of solid BN and gas phases in the B–N–H–Cl–He system, *Thin Solid Films*, 1997, vol. 293, nos. 1–2, pp. 11–16.
15. Kuznetsov, F.A., Titov, V.A., Titov, A.A., and Chernyavskii, L.I., Data bank of properties of microelectronic materials, in *Proceedings of the International Symposium on Advanced Materials, Tsukuba, Japan, September 2430, 1995*, Tsukuba, 1995, pp. 24–30.
16. Fainer, N.I., Plekhanov, A.G., Rummyantsev, Yu.M., Maksimovskii, E.A., and Shayapov, V.R., Films of hydrogenated silicon oxycarbonitride: Part I. Chemical and phase compositions, *Glass Phys. Chem.*, 2014, vol. 40, no. 5, pp. 570–577.
17. Fainer, N.I., Plekhanov, A.G., Rummyantsev, Yu.M., Yushina, I.V., Shayapov, V.R., and Kichai, V.N., Hydrogenated silicon oxycarbonitride films: Part II. Physicochemical and functional properties, *Glass Phys. Chem.*, 2014, vol. 40, no. 6, pp. 643–649.

*Translated by A.A. Muravev*