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Thermodynamic Analysis of Interface-Interaction Processes in a Silicon/Silicon Carbide Structure during Electron-Beam Treatment

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Abstract—Thermodynamic calculations of the temperature dependences of the Gibbs energy of the interface interaction of a Si melt with the surface of a SiC substrate during electron-beam treatment are conducted. The temperature regimes of phase formation are determined. According to thermodynamic analysis, a number of possible transformations of higher and lower stoichiometry carbides in SiC are proposed. The most probable reactions of SiC synthesis and dissolution in silicon are determined; it is found that the range of soluble concentrations of the substrate material is 263 ppm at $T = 1685$ K to 990 ppm at $T = 1873$ K.

Keywords: silicon carbide, thermodynamic analysis, electron-beam treatment

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INTRODUCTION

Extreme electronics devices, in particular, metal–oxide–semiconductor transistors, high electron mobility transistors, Schottky diodes, and light-emitting diodes, are produced using materials with special properties. One of these materials is silicon carbide (SiC); it is a promising material for electronic equipment, which exhibits high mechanical, chemical, and thermal resistances [1, 2]. However, the high hardness and brittleness of silicon carbide hinder the formation of a pure atomically smooth stoichiometric surface of substrates for extreme electronics and electronic equipment.

Various methods of mechanical, chemical, electrophysical, and heat treatments are used to prepare the surface of SiC substrates; these methods lead to the formation of a layer with violated stoichiometry [3, 4].

To prepare a defect-free SiC substrate surface, the method of liquid-phase dissolution of the surface layer of the substrate in silicon and in solutions of silicon with scandium is used [2]. It is reported that metal silicides and carbides can be formed; these compounds are capable of changing the kinetics of the growth/dissolution process and lead to the formation of defects in SiC single crystals. The use of pure Si as a solvent provides the formation of higher and lower stoichiometry silicon carbide.

The analysis of well-known reports on surface preparation showed that beam technologies, in particular, electron-beam treatment, are promising, because they are characterized by a local impact on the surface and a targeted change in the surface properties [3–5]. The operating-temperature range for electron-beam treatment can be 1100–2400 K.

The problems of the analysis of reactions in the Si–$Si_{1-x}C_x$ system and the formation of different compounds have not been completely solved [2, 5]. Moreover, the specified temperature ranges in the above system have been poorly studied. Therefore, studying the interface interaction of silicon carbide with silicon according to the thermodynamic analysis of a number of possible reactions in a wide temperature range (298–3000 K) is of practical and scientific interest in view of expanding physicochemical bases and outlining ways to further improve electron-beam technology for the formation of a pure atomically smooth stoichiometric surface on SiC substrates.

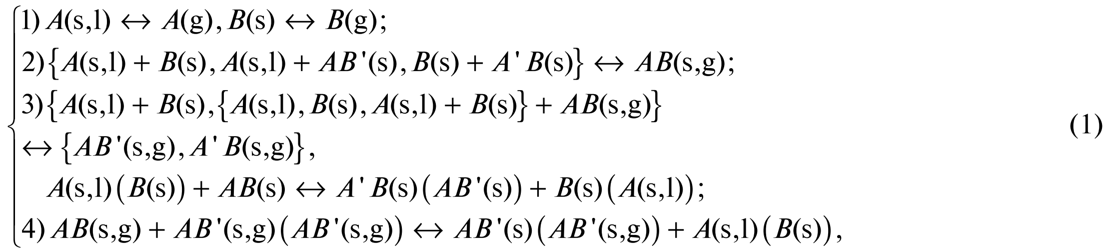
The reactions of Si with a SiC substrate involve two components (carbon and silicon), which, depending on temperature, can have different phase states. In accordance with [6–10], the following higher and lower silicon carbides ($Si_{1-x}C_x$), which can affect the interaction kinetics, can be formed in the Si–$Si_{1-x}C_x$ system: SiC_3, SiC_2, Si_2C_3, SiC, Si_2C, and Si_3C in the solid state and SiC_2, SiC, Si_2C, Si, Si_2, and Si_3 in the gaseous state.

To determine all possible directions of transformation and changes in the phase composition of the

Si–C system during heating, reactions of the formation of carbides and their interaction with single-crystal silicon carbide, silicon, and carbon in the temperature range of 298–3259 K were analyzed [11].

CALCULATION PROCEDURE

All possible interface-interaction reactions in the Si–$Si_{1-x}C_x$ system (more than 60) are presented in the form of the following system:



$$\begin{cases} 1)\, A(\mathrm{s,l}) \leftrightarrow A(\mathrm{g}),\, B(\mathrm{s}) \leftrightarrow B(\mathrm{g}); \\ 2)\{A(\mathrm{s,l}) + B(\mathrm{s}),\, A(\mathrm{s,l}) + AB'(\mathrm{s}),\, B(\mathrm{s}) + A'B(\mathrm{s})\} \leftrightarrow AB(\mathrm{s,g}); \\ 3)\{A(\mathrm{s,l}) + B(\mathrm{s}),\{A(\mathrm{s,l}),\, B(\mathrm{s}),\, A(\mathrm{s,l}) + B(\mathrm{s})\} + AB(\mathrm{s,g})\} \\ \leftrightarrow \{AB'(\mathrm{s,g}),\, A'B(\mathrm{s,g})\}, \\ \quad A(\mathrm{s,l})(B(\mathrm{s})) + AB(\mathrm{s}) \leftrightarrow A'B(\mathrm{s})(AB'(\mathrm{s})) + B(\mathrm{s})(A(\mathrm{s,l})); \\ 4)\, AB(\mathrm{s,g}) + AB'(\mathrm{s,g})(AB'(\mathrm{s,g})) \leftrightarrow AB'(\mathrm{s})(AB'(\mathrm{s,g})) + A(\mathrm{s,l})(B(\mathrm{s})), \end{cases} \tag{1}$$

where A is silicon (Si), B is carbon (C), AB is silicon monocarbide (SiC), $A'B$ is lower stoichiometry carbides (Si_2C, Si_3C), and AB' is higher stoichiometry carbides (Si_2C_3, SiC_2, SiC_3).

In system (1), the reactions of phase transitions, the formation of silicon monocarbide and higher and lower stoichiometry carbides, and the interaction of silicon monocarbide with all possible phases {silicon, carbon, carbides} are taken into account.

The amount of change in the isobaric–isothermal potential is taken as a criterion characterizing the direction and thermodynamic probability of the chemical reaction [12]:

$$\Delta G(T) = \Delta H^0_{298} + \int_{298}^{T} \Delta c_p(T)\, dT - T\Delta S^0_{298} - T\int_{298}^{T} \frac{\Delta c_p(T)}{T} dT, \tag{2}$$

where ΔG is the change in the Gibbs free energy of the reaction, ΔH^0_{298} is the change in the standard enthalpy of the reaction, ΔS^0_{298} is the change in the standard entropy of the reaction, Δc_p is the change in the heat capacity of the reaction, and T is the temperature.

In the case of silicon melting, in (2), the increment of the enthalpy of melting ΔH_m and the respective change in entropy $\Delta H_\mathrm{m}/T_\mathrm{m}$ were taken into account (T_m is the melting point of silicon).

Thermodynamic analysis of the interface-interaction processes in the Si/SiC structure (1) was conducted in accordance with the technological modes of electron-beam treatment for temperatures of 298–3259 K. The upper limit of the temperature range corresponds to the temperature of the complete decomposition of SiC [6, 10].

The calculations were conducted using reference data on the thermodynamic quantities of substances [8, 10]. For condensed $Si_{1-x}C_x$ compounds that are not provided in the reference book, data obtained by calculations by the Neumann–Kopp rule using values of the resulting components were used [6].

The Gibbs energy of the reaction of dissolution of x wt % of carbon

$$\mathrm{SiC(s)} \rightarrow \mathrm{Si(l)} + \mathrm{C}(x \text{ wt \%}, \text{in Si(l)}) \tag{3}$$

(which corresponds to $40/12x$ wt % of silicon carbide) was calculated taking into account the temperature dependence of the dissolved carbon concentration in silicon according to [7]:

$$\log \frac{C}{\text{wt \%}} = 3.66 - 9660/T \pm 0.02, \quad (T \le 1873\ \mathrm{K}), \tag{4}$$

$$\Delta G_p(T) = 1.85\times10^5 - 69.5T + \ln\left(\frac{x}{\text{wt \%}}\right)RT. \tag{5}$$

Expression (5) holds true for a carbon concentration of less than 400 ppm [7], which corresponds to 1333 ppm of SiC.

RESULTS AND DISCUSSION

To determine the phase composition of the Si–C and Si–SiC systems during electron-beam heating, the $\Delta G(T)$ dependences were calculated using equation (2) for the system of all possible reactions (1) describing interface interaction in the Si/SiC structure in the region of existence of low-temperature silicon carbides. The reactions of the formation of $Si_{1-x}C_x$ carbides most probable in terms of thermodynamics were identified (Table 1).

Analysis of the derived dependences (ΔG) of reactions (1) and the data of Table 1 in the temperature range of 298–1140 K shows that, at a temperature of about 1130 K, the higher and lower stoichiometry carbides undergo decomposition. In this case, the following reactions are thermodynamically most probable: the formation of SiC and Si_2C_3 solid-phase compounds (Table 1, Fig. 1); taking into account data on the stability of the carbide phases [6], the formation of

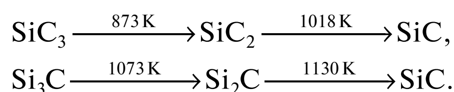
Table 1. Gibbs energy values for the most probable reactions in the region of existence of low-temperature carbides

No.	Reaction	ΔG_f (298 K), kJ/mol	ΔG_f (1140 K), kJ/mol
1	$Si + C \leftrightarrow SiC$	−69.135	−63.587
2	$2Si + C \leftrightarrow Si_2C$	−72.807	−63.564
3	$Si + 2C \leftrightarrow SiC_2$	−72.559	−63.300
4	$Si + C \leftrightarrow Si_3C$	−73.242	−63.529
5	$Si + 3C \leftrightarrow SiC_3$	−72.869	−63.157
6	$2Si + 3C \leftrightarrow Si_2C_3$	−144.150	−126.994

Table 2. Probability of reactions of the formation of gaseous substances and the liquid phase of Si in the Si–SiC system

No.	Equilibrium reaction	Change in the Gibbs energy
7	Si(s) $\leftrightarrow$ Si(l)	$\Delta G < 0$ at $T > 1685$ K
8	Si(s,g) + C(s) $\leftrightarrow$ SiC(g)	$\Delta G > 0$
9	C(s) + SiC(g) $\leftrightarrow$ SiC_2(g)	$\Delta G < 0$
10	1/2Si(s,g) + 3/2C(s) + 1/2SiC(g) $\leftrightarrow$ SiC_2(g)	$\Delta G < 0$ at $T > 2541$ K
11	Si(s,g) + SiC(g) $\leftrightarrow$ Si_2C(g)	$\Delta G < 0$
12	3/2Si(s,g) + 1/2C(s) + 1/2SiC(g) $\leftrightarrow$ Si_2C(g)	$\Delta G < 0$ at $T > 2110$ K
13	SiC(s) + Si_2C(g) $\leftrightarrow$ SiC_2(g) + 2Si(s,g)	$\Delta G < 0$ at $T > 3055$ K
14	SiC(g) + Si_2C(g) $\leftrightarrow$ SiC_2(g) + 2Si(s,g)	$\Delta G < 0$
15	SiC(s) + SiC_2(g) $\leftrightarrow$ Si_2C (g) + 2C(s)	$\Delta G < 0$ at $T < 1530$ K
16	SiC(g) + SiC_2(g) $\leftrightarrow$ Si_2C (g) + 2C(s)	$\Delta G < 0$

only SiC [11]; and the respective transformation chains of carbides in SiC (Fig. 1):



$$SiC_3 \xrightarrow{873\,K} SiC_2 \xrightarrow{1018\,K} SiC,$$
$$Si_3C \xrightarrow{1073\,K} Si_2C \xrightarrow{1130\,K} SiC.$$

Thermodynamic analysis showed that, in the preheating temperature range up to 1140 K, the likely steady-state equilibrium compound is SiC.

A further increase in the temperature of the Si/SiC structure leads to the melting of Si; for this case, the existence of a number of reactions listed in Table 2 is theoretically justified (the weight fraction of the gaseous phases Si_2(g), Si_2(g), and Si_3(g) is negligible compared with that of Si(g); therefore, their effect was not taken into account in the analysis).

Analysis of the data of Table 2 showed that reactions (13) and (15), where SiC is represented by a solid phase, are thermodynamically probable in the presence of Si_2C(g) and SiC_2(g), the formation of which by reactions (11) and (9) is determined by the presence of SiC(g). In the case of reactions (9)–(12), (14), and (16), which are thermodynamically probable in a wide temperature range, the presence of SiC(g) is required. However, reaction (8), which describes the formation of SiC(g), does not occur (Fig. 2). The absence of the SiC(g) phase in the entire temperature range suggests that, of reactions (7)–(16), only reaction (7) occurs in the forward direction.

Thermodynamic analysis showed that higher and lower stoichiometry condensed silicon carbides and

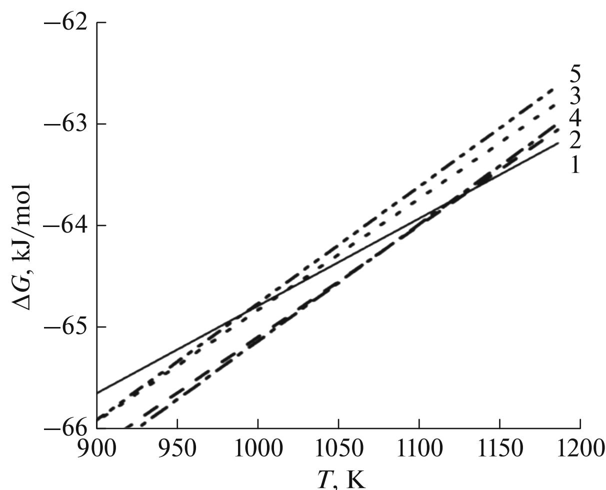


Fig. 1. Temperature dependences of the change in the Gibbs free energy of the silicon-carbide formation reactions corresponding to the numbers in Table 1.

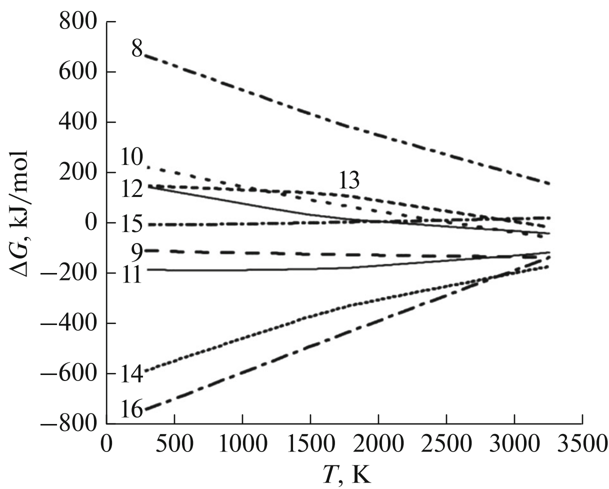


Fig. 2. Temperature dependences of the change in the Gibbs energy of the reactions for gaseous phases of $Si_{1-x}C_x$ corresponding to the numbers in Table 2.

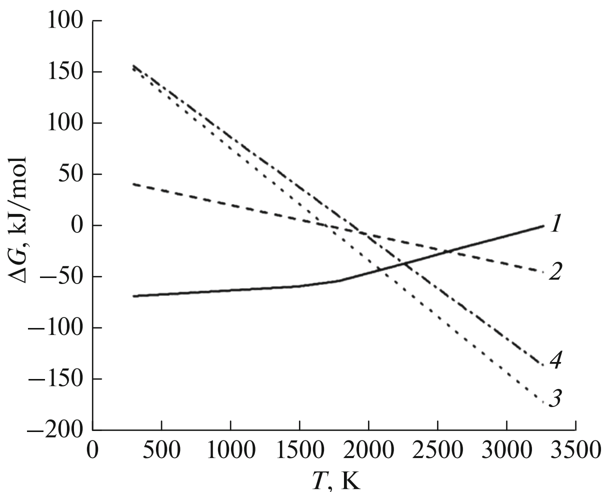


Fig. 3. Change in the Gibbs energy of the thermodynamically most probable reactions in the Si–SiC system: (*1*) SiC synthesis (reaction *1*), (*2*) Si melting (reaction *7*), (*3*) dissolution of 263 ppm of SiC, and (*4*) dissolution of 990 ppm of SiC.

gaseous phases are not formed in the $Si–Si_{1-x}C_x$ system in the temperature range of $1130 < T < 2400$ K.

At temperatures above 1685 K, in the Si melt–SiC substrate system, an equilibrium is established between the processes of the synthesis and dissolution of SiC according to expression (3); in this case, a fraction of carbon (equilibrium with respect to SiC) is dissolved in the liquid phase of Si.

Calculations in terms of the model represented by (4) and (5) show that, at a temperature of 1685 K, 79 ppm of carbon or 263 ppm of SiC are dissolved (Fig. 3). With an increase in temperature to 1873 K, 297 ppm of carbon or 990 ppm of SiC are dissolved.

Generalization of the data obtained by equation (5) and the system of thermodynamically most probable reactions (Fig. 3) revealed the following.

—There exists a temperature of equilibrium ($T \geq$ 1685 K) of the reactions of synthesis and dissolution of SiC (corresponds to the intersections of curve *2* with lines *3* and *4* in Fig. 3), at which the substrate material of a certain concentration is dissolved in the Si melt.

—The range of concentrations of the SiC substrate material dissolved in Si is 263 ppm (1685 K) to 990 ppm (1873 K).

CONCLUSIONS

Thermodynamic calculations of the temperature dependences of the Gibbs energy of the interface interaction of a Si melt with a SiC substrate during electron-beam treatment have been conducted. According to the calculations, schemes of chemical reactions that occur in the $Si–Si_xC_{1-x}$ system in the temperature range of 298–3259 K have been proposed.

The phase-formation regions have been identified. It has been found that higher and lower stoichiometry carbides undergo decomposition at a temperature of 873–1130 K. It has been shown that the gaseous phases Si_2C(g) and SiC_2(g) can be formed at temperatures above 2600 K in the presence of the SiC(g) phase, which is absent in the analyzed temperature range for the studied system. Thus, the only possible stable phases in the $Si–Si_xC_{1-x}$ system are Si(s), Si(l), and SiC(s).

The change in the Gibbs energy of the dissolution of SiC in the liquid phase of Si has been determined. The quantitative values of the solute at a given temperature have been found (263 ppm of SiC at 1685 K and 990 ppm of SiC at 1873 K).

Thermodynamic analysis has shown that solid and gaseous silicon carbides are not formed under conditions of the electron-beam treatment of Si/SiC structures in the temperature range of 1685–2400 K. The synthesis and dissolution of single-crystal silicon carbide are thermodynamically probable in accordance with the following reaction: Si(l) + C(s) $\leftrightarrow$ SiC(s).

It has been found that the range of the degree of dissolution of the substrate material is 263–990 ppm.

The fact that the synthesis of higher and lower stoichiometry silicon carbides does not occur makes Si a promising solvent of SiC in the technology of electron-beam treatment aimed at the formation of a pure atomically smooth stoichiometric surface of single-crystal silicon-carbide substrates.

Studies of the chemical processes that occur in the $Si–Si_{1-x}C_x$ system make it possible to optimize the technological parameters of the formation of this surface of SiC substrates for the manufacture of electronic devices.

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