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Phase transformations in the system Cr–Si–W–O

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ABSTRACT

Thermodynamic modelling in the system Cr–Si–W–O was carried out in order to determine the equilibrium composition of the condensed phases within temperature range 373–1273 K at under the total pressure 1 atm using the method of minimization of the free energy of the system (at fixed temperature and pressure). Within the parameter range under consideration, all condensed phases have been considered which had to be necessarily taken into account. At the given relations between the components of the system, the composition of equilibrium phases for the system Cr–Si–W–O and its subsystems Cr–Si–W–SiO_2, Cr–Si–O, Cr–Si–SiO_2 was determined.

1. Introduction

Among the transition metal disilicides, possessing semiconductor properties, Cr_xSi_y and W_xSi_y are known to be widely used in the area of new semiconductor device manufacture due to its excellent electronic properties, thermal stability and remarkable compatibility with the traditional silicon technique [1–12]. These materials can be successfully grown on silicon substrates.

Silicide layers are compatible with other materials of solid-state technology; in addition, they possess evident advantages in comparison with the conventionally used materials [11]:

- they conserve conductivity within a wider temperature range;
- they are more stable against the action of environment.

To determine the composition of transition layers, and to understand the problems connected with ageing of silicide materials and their interaction with environment, it is necessary to carry out a detailed physico-chemical, in particular, thermodynamic investigation of the systems in use. Though kinetic factors actually play an important part, purely thermodynamic consideration of the systems is not unreasonable, as thermodynamics allows one to determine the final state of the system; comparing it with the initial state, one may evaluate the degree of nonequilibrium and the directions of various relaxation processes in the system.

The present work was carried out for the purpose of determining the composition of phases formed during the growth of conducting films involving chromium, tungsten, silicon on silicon or silicon (IV) oxide in the atmosphere of oxygen. Determination of the phase composition at given temperatures and concentrations of chromium, tungsten, silicon (IV) oxide, oxygen was carried out by methods of thermodynamic modelling [12].

2. Thermodynamic modelling

The pre-condition for thermodynamic modelling, all know the phases and phase transformations which may proceed in the system. Knowing the dependence of Gibbs' energy of the system on pressure, temperature and overall composition, one may obtain the most extensive thermodynamic information. In the majority of cases these diagrams are not investigated experimentally, and only fragmentary data on the composition–temperature diagrams are available.

The authors of [12] proposed a method to compose the phase diagram on the basis of thermodynamic data on the condensed phases existing in the system. A complete summary of the data on binary compounds in the systems Cr–Si, W–Si, Cr–O, Si–O, W–O at temperatures 373–1273 K, pressure 1 atm and compositions Cr: 20–80 at.%; Si: 80–20 at.%; O: 10–50 at.%; W: 0–4 at.% is available [13–18]. The data on ternary compounds in the system Cr–Si–W–O are either absent or very fragmentary [19–21].

Constructing the diagram of state we consider all the phases coexisting in equilibrium to be the phases of constant composition. The occurrence of the regions of homogeneity in oxides, silicides and other compounds in the systems under consideration, as well as mutual solubility of substances in these systems were not taken into account assuming that these facts can hardly have a substantial effect on the qualitative conclusion concerning the existence of one

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or another combination of coexisting phases [12]. The approximation of the constant composition of the gas phase is also acceptable in this case because of the equilibrium vapor pressures and dissociation pressures of compounds formed in these systems are negligibly small and do not have a significant influence on the mass balance within the range considered in the present work.

A general method to calculate equilibrium in the system lying in the space of variables of the phase composition (n_i) is the minimization of the free energy of formation ($\Delta_f G_T^0$) (under fixed temperature and pressure, and given atomic composition (n_j^*)). Provided that the appearance of any solid solution can be neglected, the situation is represented by Eq. (1):

$$\Delta_f G_T^0 = \sum_i n_i \Delta_f G_{iT}^0 \quad (1)$$

$$\text{with limitations}: n_j{}^* = \sum \alpha_{ij} n_i \quad j = 1, \quad , m \quad (2)$$

$$n \geq 0; \quad i = 1, \quad , q \quad (3)$$

where $\Delta_f G_{iT}^0$ is the molar isobaric–isothermal potential of formation for a condensed phase i; q is the total number of phases known in the considered physico-chemical system; m is the number of components of the system; α_{ij} is the number of atoms of the element j in the molecule of the compound i.

Phase analysis of the system, leading to the minimum of function (1), is the desired solution of the problem formulated in the present work. Calculation of molar isobaric–isothermal potentials for temperatures under consideration was carried out using the known equation:

$$\Delta_f G_{iT}^0 = \Delta_f H_{iT_1}^0 + \int T_{T_1} \Delta_f C_{pi} dT - T \Delta_f S_{iT_2}^0 - T \int T_{T_2} \frac{\Delta_f C_{pi}}{T} dT \quad (4)$$

where, $\Delta_f H_{iT_1}^0$ is the enthalpy of phase formation at temperature T_1; $\Delta_f C_{pi}$ is the change of thermal capacity; $\Delta_f S_{iT_2}^0$ is the entropy of phase formation at temperature T_2.

The total hydrostatic pressure was chosen equal to 1 atm.

Minimization of function (1) and calculation of the amounts of phases coexisting in equilibrium were carried out with the help of program TUF [12], implying the use of thermodynamic information in the form in which it is conserved in the thermodynamic databases of the Bank of characteristics of materials for electronics [22].

3. Initial thermodynamic data

Initial thermodynamic data were taken from handbooks, monographs and papers [13–21]. In the cases when the data for compounds were absent from these sources, the required values were estimated using comparative or additive methods as reported in [23]. The calculations of phase equilibria have been performed with the sets of consistent data which are compiled in Tables 1 and 2.

We carried out critical analysis of all the data available from the literature on binary and ternary compounds in the system Cr–Si–W–O to obtain the set of consistent data for thermodynamic calculations and to evaluate the stability of the compounds within the required range of conditions. The principles of such critical analysis have been described in [12].

A critical analysis of binary systems W–O, Cr–O, Si–O indicated that only the compounds WO_2, WO_3, W_3O, CrO_2, Cr_2O_3, CrO_3, SiO, SiO_2 may be stable under the conditions of interest.

Enthalpies of formation for the ternary compounds in the system Cr–Si–W–O (namely Cr_2SiO_4(c), Cr_2WO_6(c), $CrWO_4$(c)) have been estimated using known [23] comparative methods. Entropies and thermal capacities were estimated using additive methods. From these estimations it was concluded that compounds Cr_2SiO_4(c), Cr_2WO_6(c), $CrWO_4$(c) are thermodynamically unstable within the temperature and pressure ranges under consideration. Therefore these compounds have not been considered in the list of basic compounds for calculations.

Separately calculations using the data both for crystalline and amorphous silicon dioxide indicated that the composition of the phases, except SiO_2, remains the same for both cases; crystal silicon (IV) oxide simply will be replaced by the same amount of the amorphous silicon (IV) oxide in the second case. A substrate made of amorphous silicon (IV) oxide was used in the experiments, so we used the data for this modification.

The chosen set of the basic thermodynamic data is presented in Tables 1 and 2. It should be noted that the level of errors for values listed in Tables 1 and 2 is rather small. Taking into account the errors we do not change the calculated ratios between condensed phases.

Additionally, temperatures (T_{tr}) and enthalpies of phase transitions (if any) for the considered compounds have to be taken into account. Within the temperature range we considered, T_{tr} and $\Delta_{tr}H$ for the following reactions which are known from the literature: Cr(cI) → Cr(cII); WO_3(cI) → WO_3(cII); WO_3(cII) → WO_3(cIII); Cr_2O_3(cI) → Cr_2O_3(cII); CrO_3(c) → CrO_3(l). Here, similarly to the Databases of the Bank of characteristics of materials for electronics (CME) [12], the states of monatomic gases of elements were chosen as the standard states.

4. Thermodynamic calculation of the equilibrium composition of condensed phases in the systems participated by silicon, chromium, tungsten, oxygen, silicon (IV) oxide

4.1. System Cr–Si–O (T = 373–1273 K)

A well investigated phase diagram is available [14] to predict the equilibrium composition of binary system Cr–Si. Thermodynamic analysis of the ternary system Cr–Si–O was carried out in [12]; on the basis of the results of that analysis, one may determine the ratios of phases in this system. Unlike for [12], we used the value for the standard enthalpy of formation of chromium monosilicide based on the results described in [24].

For better understanding of the more complicated diagram for the system Cr–Si–W–O, it is reasonable to turn to Gibbs–Rosebom diagram for the system Cr–Si–O which only slightly differs from the diagram studied in [12].

The existence of the following condensed phases was reliably established for the ternary system Cr–Si–O within temperature range 373–1273 K: Cr(cI), Cr(cII), Si(c), CrSi(c), $CrSi_2$(c), Cr_5Si_3(c), Cr_3Si(c), CrO_2(c) ($T < 700$ K), CrO_3(c) ($T < 470$ K), CrO_3(l) ($T \geq 470$ K, $T < 1000$ K), Cr_2O_3(cI), Cr_2O_3(cII), SiO(c), SiO_2(c) ($T < 1123$ K), SiO_2(am) ($T \geq 1123$ K).

Temperatures of the upper or lower boundaries of phase existence for the proper range of conditions are indicated in parentheses.

To determine the phases formed by growing chromium and silicon films on the substrates made of silicon or silicon (IV) oxide in the atmosphere of oxygen, it was necessary to perform thermodynamic modelling in the system Cr–Si–O and in its subsystem Cr–Si–SiO_2. Practically important compositions were analysed. From this point of view, altogether 18 compositions for the system Cr–Si–O and 18 compositions for the subsystem Cr–Si–SiO_2 at temperatures 373, 473, 573, 673, 773, 873, 1273 K have been considered.

Results of calculations are presented as a projection onto Gibbs–Rosenbom coordinates (Fig. 1). Here each point of the large

Table 1
Initial thermodynamic data: enthalpies and entropies of compounds.

No.	Compound	$-\Delta_f H^0$ (298.15), kJ/mol	$-\Delta_f H^0$ (T), kJ/mol	Ref.	S^0 (298.15), J/(mol·K)	S^0 (T), J/mol·K)	Ref.
1	Cr(g	0		[13]	174.202		[13]
2	Cr(cI)	397.147		[13]	23.56		[13]
3	Cr(cII)	397.147		[13]		24.604 (T = 311.5 K)	[13]
4	Si(g)	0		[13]	167.87		[13]
5	Si(c)	450.000		[13]	18.81		[13]
6	W(g)	0		[13]	173.846		[13]
7	W(c)	851.246		[13]	32.64		[13]
8	O(g)	0		[13]	160.946		[13]
9	CrSi(c)	931.877		*	45.020		[13]
10	$CrSi_2$(c)	1397.56		[13]	55.647		[13]
11	Cr_3Si (c)	1779.51		[13]	86.609		[13]
12	Cr_5Si_3(c)	3662.09		[13]	182.422		[13]
13	CrO_2(c)	1483.76		[13]	48.158		[13]
14	CrO_3(c)	1735.02		[13]	73.22		[13]
15	CrO_3(l)		1710.64 (T = 470 K)	*		143.008 (T = 470 K)	*
16	Cr_2O_3(cI)	2682.40		[13]	81.100		[13]
17	Cr_2O_3(cII)	2682.40		[13]		94.213 (T = 335 K)	[13]
18	SiO(c)	1137.11		[13]	27.213		[13]
19	SiO_2(am)	1849.92		[13]	46.861		[13]
20	WSi_2(c)	1844.96		[14]	70.260		*
21	W_5Si_3(c)	5915.03		*	219.630		*
22	W_3O(c)	3119.22		[14]	83.68		[14]
23	WO_2(c)	1937.69		[13]	50.64		[13]
24	WO_3(cI)	2440.06		[13]	81.640		[13]
25	WO_3(cII)	2440.06		[13]		88.468 (325 K)	[13]
26	WO_3(cIII)		2440.713 (T = 1013 K)	[13]		193.122 (T = 1013 K)	[13]

Gibbs–Rosenbom triangle belongs to some small triangle with the vertexes which determine the compositions of coexisting phases. A point on a line corresponds to two phases.

Practically significant trends will be described in brief below.

For the system Cr–Si–O and subsystem Cr–Si–SiO_2, the resulting sets of equilibrium condensed phases were observed to be independent of temperature. Permanent presence of SiO_2 as the third component was observed for any chromium to silicon ratio within

Table 2
Initial thermodynamic data: thermal capacities of compounds.

No.	Compound	Thermal capacity $C_p(T)$, J/(mol·K)								Ref.
		298.15	300	400	500	700	900	1100	1300	
1	Cr(g)	20.786	20.786	20.786	20.786	20.803	20.803	20.901	21.191	[13]
2	Cr(cI)	23.550	23.606							[13]
3	Cr(cII)			25.082	26.008	27.835	30.361	33.657	37.573	[13]
4	Si(g)	22.251	22.234	21.613	21.316	21.057	20.971	20.989	21.099	[13]
5	SicK)	19.789	19.855	22.301	23.610	25.124	26.135	26.974	27.737	[13]
6	W(g)	21.305	21.235	23.163	26.344	34.381	40.070	41.434	40.433	[13]
7	W(c)	24.270	24.289	25.006	25.429	26.091	26.776	27.550	28.418	[13]
8	O(g)	21.911	21.901	21.482	21.257	21.040	20.944	20.893	20.864	[13]
9	CrSi(c)	43.339	43.461	47.383	49.618	52.959	56.496	60.631	65.300	*
10	$CrSi_2$(c)	63.128	63.160	69.684	73.228	78.083	82.631	87.605	93.047	*
11	Cr_3Si(c)	90.439	90.673	97.547	101.634	108.629	117.218	127.945	140.456	*
12	Cr_5Si_3(c)	177.117	177.595	192.313	200.870	214.547	230.210	249.207	271.076	*
13	CrO_2(c)	56.997	57.195	64.547	68.624	73.591				[15]
14	CrO_3(c)	71.354	71.501	77.247						[14]
15	CrO_3(l)				113.044	113.044	113.044			[14]
16	Cr_2O_3(cI)	120.080	121.504							[13]
17	Cr_2O_3(cII)			112.993	118.880	123.945	126.411	128.421	130.614	[13]
18	SiO(c)	33.537	33.556	34.560	35.564	37.572	39.581	41.589	43.597	[13]
19	SiO_2(am)	44.350	44.560	53.094	57.907	63.806	68.057	71.726	75.144	[13]
20	WSi_2(c)	63.848	63.999	69.608	72.649	76.339	79.046	81.408	83.812	*
21	W_5Si_3(c)	180.717	181.01	191.933	197.975	205.827	221.228	218.672	225.301	*
22	W_3O(c)	88.565	88.714	94.314	97.489	101.738	105.299	108.824	112.272	*
23	WO_2(c)	55.780	55.984	63.598	67.834	73.021	76.717	79.897	82.854	[13]
24	WO_3(cI)	79.705	79.633							[13]
25	WO_3(cII)					95.321	102.848			[13]
26	WO_3(cIII)							98.876	102.133	[13]

Notes to Tables 1 and 2: 1. * – Estimated value. 2. It should be noted that the level of errors for values listed in Tables 1 and 2 is rather small. Taking the errors into account we do not change the calculated ratios between condensed phases. 3. In addition to the data present in Tables 1 and 2, in order to calculate free energy, it was necessary to know temperatures (T_{tr}) of phase transitions (if any) for the compounds participating in calculations, and the enthalpies of phase transitions ($\Delta_{tr}H$). Within the temperature range considered, T_{tr} and $\Delta_{tr}H$ for the following reactions are known from the literature[3]: Cr(cI) CrO_3(c)Cr(cII); WO_3(cI) → WO_3(cII); WO_3(cII) → WO_3(cIII); Cr_2O_3(cI) → Cr_2O_3(cII);CrO_3(c) → CrO_3(l).

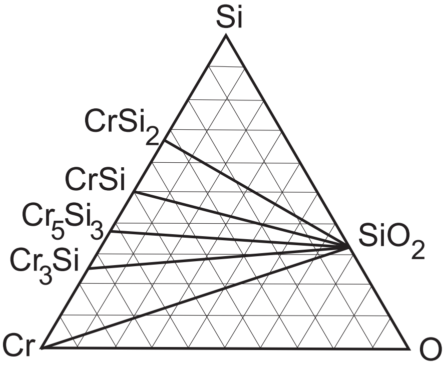

Fig. 1. Phase diagram of Cr-Si-O system (T = 373-1273 K).

the whole temperature range investigated. Further, it should be stressed that approximately the same regularity described below is actual inside each set of permanent composition for oxygen or silicon (IV) oxide, as one can see in Fig. 1. When the amount of chromium is small, the compounds with the highest silicon content are formed; these are pure silicon and chromium disilicide. With an increase in chromium content and a decrease in silicon content, compounds CrSi, Cr_5Si_3, Cr_3Si appear in the natural sequence, while pure silicon disappears. In the system Cr–Si–O, the formation of Cr_2O_3 is observed, while this compound never appears in the system Cr–Si–SiO_2. One can easily determine on the basis of the composed diagrams what will be the result of chromium agglomeration with silicon for different ratios of the initial components. It is possible to choose the compositions giving SiO_2 and silicon silicide of a definite composition. To obtain only CrSi besides SiO_s as a result of sintering, it is necessary to choose a composition corresponding to any point at the tie line CrSi–SiO_2 of the diagram (Fig. 1).

4.2. *System Cr–Si–W–O (T = 373–1273 K)*

The representation of this 4-component within the temperature range of interest has to consider compounds W(c), WSi_2(c), W_5Si_3(c), W_3O(c), WO_2(c), WO_3(c II) ($T < 1013$ K), WO_3 (cIII) ($T \geq 1013$ K) additionally to the compounds appearing in the ternary Cr–Si–O system above.

The system Cr–Si–W–O and its subsystem Cr–Si–W–SiO_2 are treated with analogously to the above-described system Cr–Si–O and its subsystem Cr–Si–SiO_2.

The principles of thermodynamic modelling of quaternary and ternary systems are similar. Calculations for 18 compositions of the system Cr–Si–W–O and 18 compositions for subsystem Cr–Si–W–SiO_2 at temperatures 573, 723, 823, 1273 K were of practical importance. Specific initial compositions and calculation results are presented in Tables 2 and 3.

Using the above-indicated results we succeeded in constructing phase diagrams both for the system Cr–Si–W–O and subsystem Cr–Si–W–SiO_2 (P and T const). These diagrams are shown in Figs. 2–4 in the plane and 3D versions. The following features have to be discussed.

Fig. 2 shows a 3D diagram of the system Cr–Si–W–O using a known representation of a four-component system in the form of a triangular pyramid. The faces of this pyramid are Gibbs–Rosenboom triangles representing ternary systems. Based on calculated results, the pyramid representing the system Cr–Si–W–O is split into 9 incorporated pyramids.

It should be noted that the governing regularities are here the same as those for the systems free from tungsten, namely: for a small amount of chromium, the phases are composed of the compounds with high silicon content; while silicon content decreases, the compounds appear as a sequence corresponding to an increase in chromium content of the compounds. For tungsten, this regularity is expressed as a gradual disappearance of tungsten silicides and the appearance of pure tungsten ($WSi_2 \rightarrow W_5Si_3 \rightarrow W$).

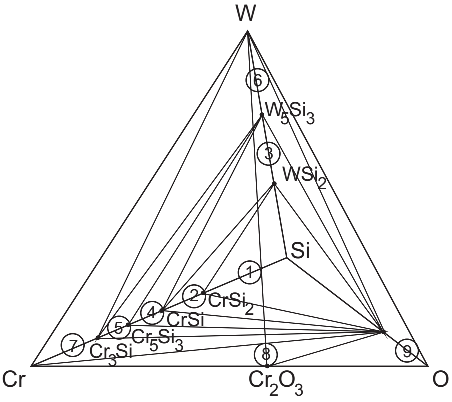

Fig. 2. Phase diagram of Cr-Si-W-O system (3D version, T = 373-1273 K)

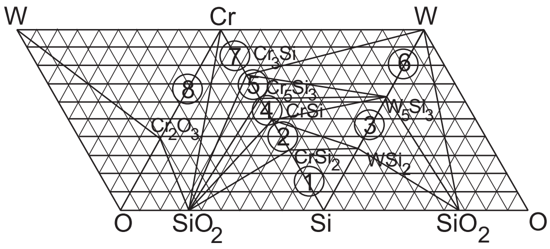

Fig. 3. Phase diagram of Cr-Si-W-O system (plane version, T = 373-1273 K).

In order to use the obtained diagram for predicting the set of phases that occurs for certain Cr:Si:W:O ratio, one can now be predicted by the following operation route. A point with the considered composition is to be fixed inside the pyramid; thereafter one can determine the small sub-pyramid which represents the phases under equilibrium conditions. However, this procedure requiring a 3D operation is complicated. That is why a projection onto planar diagrams of the systems are represented in Figs. 3 and 4. These diagrams are in fact involutes of the pyramid.

The rules governing the use of these diagrams are described below. One can easily see that to assign unambiguously the pyramid one should know one point on two of its faces. This may be also seen in Figs. 3 and 4 where each pyramid is represented by two faces abutting in two points. For instance, the pyramid SiO_2–Cr_5Si_3–CrSi–W_5Si_3 is depicted as the faces SiO_2–Cr_5Si_3–CrSi and Cr_5Si_3–W_5Si_3–CrSi having a common line Cr_5Si_3–CrSi. Phase regions Cr–Si–O and Cr–Si–W are chosen as two basic triangles. This choice is made according to the principle of the maximum of information containing on them.

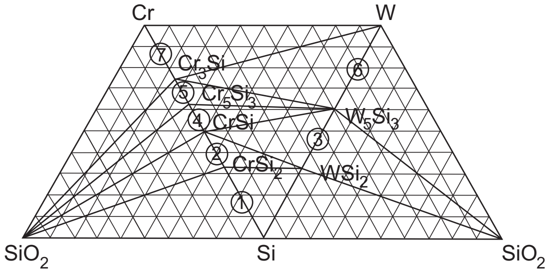

Fig. 4. Phase diagram of Cr-Si-W-SiO_2 system (T = 373-1273 K)

Table 3
Results of calculations for the system Cr–Si–W–O (*T* = 573, 723,823, 1273 K).

Initial composition as the ratios x:y:m:z in formula $Cr_xSi_yW_mO_z$				Final composition ratio of component amounts										
x	y	m	z	Cr	Si	W	CrSi	$CrSi_2$	Cr_3Si	Cr_5Si_3	Cr_2O_3	SiO_2	WSi_2	W_5Si_3
0.25	0.75	0.02	0.99		0.002			0.002				0.123	0.02	
0.25	0.75	0.02	0.5				0.093			0.006		0.245		0.004
0.25	0.75	0.04	0.25				0.02	0.16				0.12	0.04	
0.25	0.75	0.04	0.5				0.06			0.012		0.24		0.008
0.4	0.6	0.02	0.25				0.294					0.123	0.009	0.002
0.4	0.6	0.02	0.5	0.049		0.02			0.049			0.245		
0.4	0.6	0.04	0.25				0.288					0.12		0.008
0.4	0.6	0.04	0.5	0.048		0.04			0.048			0.24		
0.8	0.2	0.02	0.25	0.515		0.02			0.025			0.123		
0.8	0.2	0.02	0.5	0.196		0.02					0.098	0.098		
0.8	0.2	0.04	0.25	0.504		0.04			0.024			0.12		
0.8	0.2	0.04	0.5	0.192							0.096	0.096		

Let us consider a diagram of triangles in detail. To use the diagram, some operations are to be made. First, the given Cr:Si:W:O ratio is to be transformed, by normalizing per unity, into two ratios of basic triangles Cr:Si:O and Cr:Si:W. Then we will obtain two points in the region Cr–Si–W–O.

The case when the two points fall into the same pyramid (two faces abutting along the line) will confirm that the region exists. If the region is not found within the basis triangles, it has to be searched for in the basis triangle and in the triangle adjacent to the basis one.

An example of the search on a triangular diagram will be described below. Let the Cr:Si:W:O ratio be equal to 0.5:0.3:0.1:0.1. Two ratios for basis triangles Cr:Si:O and Cr:Si:W, normalized for unity, are: Cr:Si:O = 0.55:0.33:0.11 and Cr:Si:W = 0.55:0.33:0.11.

Point Cr:Si:O = 0.55:0.33:0.11 falls into the triangle SiO_2–Cr_3Si–Cr_5Si_3. Point Cr:Si: W = 0.55:0.33:0.11 belongs to triangle Cr_3Si–Cr_5Si_3–W_5Si_3. We obtain a coincidence of the bases of regions SiO_2–Cr_3Si–Cr_5Si_3 and Cr_3Si–Cr_5Si_3–W_5Si_3 along the line Cr_3Si–Cr_5Si_3. So, the pyramid has been found correctly.

Otherwise, if in this case the regions had no common base, an alternative procedure should be applied. Leaving the first point unchanged, we were to search for a region having the common base in triangle W–Cr–O (see Fig. 3). For this purpose, it would be necessary to assign the Cr:W:O ratio (normalized per unity), place a point in triangle Cr–W–O and see if the region found in it has a common line with the region indicated by the point in triangle Cr–Si–O.

If the pyramid was not found in this case, it would be necessary to leave point Cr:Si:W unchanged and to search for a region having the common base with the region Cr–Si–W in triangle W–Si–O (see Fig. 3).

The constructed projection of the phase diagram allows one, for a four-component system, to determine which phases will comprise the transition layers formed during growing the conducting films based on chromium, silicon, tungsten, and what the sequence of these layers will be. If the growing process is carried out on a silicon substrate (Fig. 3), a decrease in silicon concentration will be accompanied by the formation of layers each of which is composed of four phases, in the following sequence:

1. SiO_2–Si–$CrSi_2$–WSi_2
2. SiO_2–CrSi–$CrSi_2$–WSi_2
3. SiO_2–W_5Si_3–CrSi–WSi_2
4. SiO_2–Cr_5Si_3–CrSi–W_5Si_3
5. SiO_2–Cr_5Si_3–Cr_3Si–W_5Si_3
6. SiO_2–W_5Si_3–Cr_3Si–W
7. SiO_2–Cr–Cr_3Si–W
8. SiO_2–Cr_2O_3–Cr–W.

To conclude, we will describe the results of the experiment reported in [25] dealing with the growth of films in the system

Table 4
Results of calculations for the system Cr–Si–W–SiO_2 (*T* = 573, 723, 823, 1273 K).

Initial composition as the ratios x:y:m:z in formula $[(Cr_xSi_y)_nW_m](SiO_2)_z$				Final composition ratio of component amounts							
x	y	m	z	Cr	Si	W	CrSi	$CrSi_2$	Cr_3Si	SiO_2	WSi_2
0.25	0.75	0.02	0.99		0.002			0.002		0.99	
0.25	0.75	0.02	0.5		0.103			0.123		0.5	0.01
0.25	0.75	0.02	0.1		0.185			0.221		0.1	0.018
0.25	0.75	0.04	0.99		0.002			0.002		0.99	
0.25	0.75	0.04	0.5		0.08			0.12		0.5	0.02
0.25	0.75	0.04	0.1		0.144			0.216		0.1	0.036
0.4	0.6	0.02	0.99				0.002	0.002		0.99	
0.4	0.6	0.02	0.5				0.118	0.078		0.5	0.01
0.4	0.6	0.02	0.1				0.212	0.140		0.1	0.018
0.4	0.6	0.04	0.99				0.003	0.001		0.99	
0.4	0.6	0.04	0.5				0.136	0.56		0.5	0.02
0.4	0.6	0.04	0.1				0.244	0.101		0.1	0.036
0.8	0.6	0.02	0.99	0.002		0.002			0.002	0.99	
0.8	0.6	0.02	0.5	0.098		0.01			0.098	0.5	
0.8	0.6	0.02	0.17	0.176		0.018			0.176	0.1	
0.8	0.2	0.04	0.99	0.002					0.002	0.99	
0.8	0.2	0.04	0.5	0.096		0.02			0.096	0.5	
0.8	0.2	0.04	0.1	0.173		0.036			0.173	0.1	

Cr–Si–W–O. The authors of [25] carried out plasma deposition of chromium, tungsten, silicon onto the substrate made of silicon (IV) oxide in the atmosphere of oxygen under nonequilibrium conditions. In the experiments carried out at a temperature of 773 K, for compositions O: 33/44 at.%; Cr: 37/31 at.%; Si:28/24 at.%; W: 1 at.%, in addition to SiO_2, crystal fractions of the general formula Cr_nSi_m (CrSi, Cr_3Si, Cr_5Si_3) were detected in crystal layers. As the oxygen content increased within the indicated range of compositions, a transition from the CrSi–Cr_5Si_3–SiO_2 layer to the Cr_5Si_3–Cr_3Si–SiO_2 layer was observed. Though this experiment was carried out under nonequilibrium conditions, it is reasonable to compare its results with the results of calculations in the present work. According to calculation results, for the above-indicated compositions Cr, Si, W, O there should be a transition from the layer CrSi–Cr_5Si_3–SiO_2–W_5Si_3 to the layer SiO_2–Cr_3Si–Cr_5Si_3–W_5Si_3.

One can see that experiments and calculations revealed the same phases except for tungsten compounds. It should be stressed that W_5Si_3 may be present in the experimentally grown layers but it cannot be detected by means of chemical and X-ray phase analyses due to the small amount (<1 at.%) (Table 4).

5. Conclusions

1. We carried out critical analysis of all the data available from the literature on binary and ternary compounds in the system Cr–Si–W–O to obtain the set of consistent data for thermodynamic calculations

1. We carried out critical analysis of all the thermodynamic data available from the literature on binary and ternary compounds in the system Cr–Si–W–O in the temperature range of 373–1273 K and chose condensed phases which should be taken into account at calculation of phase equilibriums.
2. We carried out the critical analysis of thermodynamic data for the chosen condensed phases and choose the most reliable thermodynamic data. A large number of the data absent from the literature were estimated.
3. The thermodynamic equilibrium was calculated in the temperature range of 373–1273 K for the systems:

- silicon–chromium–oxygen;
- silicon–chromium–silicon oxide (IV);
- silicon–chromium–tungsten–oxygen;
- silicon–chromium–tungsten–silicon (IV) oxide.

References

[1] R. Radhakrishnan, S. Bhaduri, C.H. Henager, J. Miner. Metals Mater. Soc. 49 (1997) 41.
[2] K. Seo, K.S.K. Varadwai, D. Cha, J. In, J. Kim, J. Park, B. Kim, J. Phys. Chem. 111 (2007) 9072.
[3] G. Duan, H.M. Wang, J. Mater. Sci. 37 (2002) 1981.
[4] P. Zaleski, K. Szymanski, J. Przewoznik, K. Recko, S. Cottrell, L. Dobrzynski, J. Alloys Compd. 498 (2010) 5–12.
[5] P. Zaleski, K. Szymanski, M. Biernacka, S. Cottrell, K. Perzynska, K. Recko, L. Dobrzynski, J. Alloys Compd. 442 (2007) 213–215.
[6] N.G. Galkin, L. Dozsa, E.A. Chusovitin, B. Pecz, L. Dobos, Appl. Surf. Sci. 256 (2010) 7331.
[7] R.Ch. Murthy, J.K. Sonber, C. Subramanian, R.K. Fotedar, S. Kumar, M.R. Gonal, A.K. Suri, Int. J. Refract. Metals Hard Mater. 28 (2010) 529.
[8] Y.X. Yin, H.M. Wang, Mater. Sci. Eng. A 452–453 (2007) 746.
[9] K.P. Gupta, J. Phase Equilib. Diffusion 31 (2010) 300.
[10] K. Seo, K.S.K. Varadwaj, D. Cha, J. In, J. Kim, J. Park, B. Kim, J. Phys. Chem. C 111 (2007) 9072.
[11] Ya.A. Ugay, Introduction to Semiconductor Chemistry, Vysshaya Shkola, Moscow, 1965, 334p. (in Russian).
[12] G.A. Kokovin, N.A. Testova, F.A. Kuznetsov, Thermodynamic analysis of systems M–SiO_2 (M = Al, Ge, Ti, V,Ta, Cr, Mo) in connection with the problem of MOS structure stability/VINITI, Lyubertsy, 1978, 58p. Dep. in VINITI 15.12.77; No. 527, (in Russian).
[13] V.P. Glushko (Ed.), Thermodynamic Characteristics of Individual Substances, Handbook, vol. 1–4, Nauka, Moscow, 1978–1982, in Russian.
[14] V.P. Glushko (Ed.), Thermal Constants of Substances, Issue 1,4,7. Handbook, Izd. AN SSSR, Moscow, 1965–1974, in Russian.
[15] G.V. Samsonov (Ed.), Physicoche Mical Properties of Oxides. A Handbook, Metallurgiya, Moscow, 1979, 455p. (in Russian).
[16] G.B. Naumov, B.N. Ryzhenko, I.L. Khodakovsky, A Handbook of Thermodynamic Values, Atomizdat, Moscow, 1971, 238p. (in Russian).
[17] M.Kh. Karapetyantz, M.L. Karapetyantz, Basic Thermodynamic Constants of Inorganic and Organic Substances, Khimiya, Moscow, 1968, 467p. [in Russian].
[18] A.F. Kapustinsky (Ed.), Thermal Constants of Inorganic Substances. A Handbook, AN SSSR Publishing House, Moscow, Leningrad, 1949, 210p. (in Russian).
[19] E. Thommy, R.J.D. Tilley, Mater. Res. Bull. 10 (1975) 1175.
[20] Ya.A. Ugay, V.G. Kolesnikov, V.V. Anokhin, S.V. Fetisova, Neogran. Materialy 9 (1973) 173, in Russian.
[21] A.I. Tsvetkov, Z.P. Ershova, N.A. Matveeva, Ser. Geolog 2 (1964) 3, Izv. AN SSSR, (in Russian).
[22] V.A. Titov, V.I. Rakhlin, A.A. Titov, F.A. Kuznetsov, M.G. Voronkov, Zhurnal Fizicheskoi Khimii. 80 (2006) 2144–2147.
[23] V.A. Kireev, Methods of Practical Calculations in Thermodynamics of Chemical Reactions, Khimiya, Moscow, 1970, 51p. (in Russian).
[24] B.K. Voronov, L.D. Dudkin, N.I. Kiryukhina, N.I. Trusova, Neorgan. Materisly 1 (1968) 58, Izv. AN SSSR, in Russian.
[25] G. Sobe, H. Schreiber, G. Weise, Thin Solid Films 128 (1985) 149.