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Chemical vapour deposition of WSi_2 thin films: Equilibrium W–Si–H–Cl–Ar system

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Abstract

Tungsten disilicide (WSi_2) can be used in lieu of polycrystalline silicon in very large scale integrated (VLSI) circuit manufacturing; WSi_2(s) thin films have been deposited from a vapour-mix of WCl_4, SiH_2Cl_2 (or SiH_4), H_2, and an argon diluent. The present work describes an equilibrium model for the W–Si–H–Cl–Ar system: the feed-gas mixture is characterized by the atom-ratios (Ar/H), (H/Cl), and (W/Si); during the chemical vapour deposition (CVD), only the latter ratio is expected to change as one or more of condensed phases Si(s), WSi_2(s), W_5Si_3(s) and W(s) begin to form. In this work, the CVD-phase diagram was constructed by means of an *iterative method* that was coupled to the De Donder's extent of reaction formalism; the respective phase-domain boundaries Si(s) + WSi_2(s)/WSi_2(s)/WSi_2(s) + W_5Si_3(s) were computed for the temperature range of 800–1000 K at 1 atm (101.325 kPa); the SiH_2Cl_2-content of the feed-gas mixture, characterized by $F = [Si^0/(Si^0 + W^0)]$, was gradually decreased ensuring a complete sweep from the Si(s) + WSi_2(s) two-phase-domain to the phase-mixture WSi_2(s) + W_5Si_3(s) for specific (H/Cl) and (Ar/H) ratios. The results are of value in determining the CVD-phase diagrams for the growth of crystalline materials.

Keywords: Tungsten silicides; Chemical vapour deposition model; Phase diagram

1. Introduction

The tungsten–silicon equilibrium phase diagram [1] shows the presence of two stoichiometric silicide compounds: WSi_2(s) and W_5Si_3(s); and their deposition from fluoride (W–Si–H–F–Ar) or chloride (W–Si–H–Cl–Ar) systems, with the inert argon serving as the carrier-gas, have been reported in the literature [1–3]. The chemical vapour deposition of WSi_2(s) from gas mixtures consisting of tungsten hexafluoride (WF_6), silane (SiH_4), and hydrogen (H_2) is regarded feasible only within a narrow range of feed-gas compositions; contamination due to undesired co-deposition of Si(s) or W_5Si_3(s) has been reported [1]. Thomas et al. [2] studied the deposition of WSi_2(s) films using a $WCl_4 + SiH_4 + H_2 + Ar$ gas mixture at 873 K and a low pressure of 1 Torr (133 Pa); the silicon-fraction F, defined as $[Si/(Si + W)]^0$ of the feed-gas, was found to exercise a strong influence on the nature of the crystal-deposit; at $F = 0.77$, silicon deposited together with WSi_2(s); as F was decreased to 0.625, for $W^0/Si^0 = 0.6$ in feed-gas, the deposit became a WSi_2(s) + W_5Si_3(s) mixture [2]. Subsequent work of Thomas et al. [3] involved the use of a cold-wall reactor (at 873 K and 665 Pa total pressure) to grow tungsten silicide films from the W–Si–H–Cl–Ar system; the phase composition of the deposited films, determined by X-ray diffraction and electron microscopy, corresponded to the WSi_2(s)-stoichiometry.

Vahlas et al. [1] employed the method of Gibbs free energy minimization and the entailed software packages to determine the equilibrium CVD-phase diagram for the $WCl_4 + SiH_2Cl_2 + H_2 + Ar$ system, at 1000 K and 1.0 atm (101.325 kPa) total pressure, with 90 mol% argon in the feed-gas. In the present work, an iterative equilibrium constant method [4] was used together with the De Donder's extent of reaction formalism [5] to determine WSi_2(s) domain boundaries: the feed-gas mixture was constituted from WCl_4, SiH_2Cl_2, H_2 and argon with the respective atom-ratios (Ar/H) and (H/Cl) held constant (ensuring conformity with the lever rule) while the silicon-mole-fraction (F) of the $WCl_4 + SiH_2Cl_2$

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vapour-mixture, or the $[\mathrm{Si}/(\mathrm{W}+\mathrm{Si})]^0$ atom-ratio of feed-gas, was gradually decreased at fixed WCl_4.

2. Equilibrium model of the W–Si–H–Cl–Ar system

The gas-phase in equilibrium with WSi_2(s) and Si(s) or W_5Si_3(s) at high temperatures contains 11 species, represented by digital notation as follows—WCl_4: 1, SiH_2Cl_2: 2, HCl: 3, H_2: 4, $SiHCl_3$: 5, $SiCl_4$: 6, $SiCl_3$: 7, $SiCl_2$: 8, WCl_5: 9, Ar: 10, SiH_4: 11.

The Gibbs stoichiometric rule gives $r=N-C^*$; r is the number of independent reactions, N the number of species and C^* is kinds of atoms present. Depending upon the species present, the independent set (r) is chosen from the following equilibria:

$$\mathrm{WSi_2(s)} + 4\mathrm{HCl} = \mathrm{WCl_4} + 2\mathrm{Si(s)} + 2\mathrm{H_2}, \quad \varepsilon_0 \tag{0}$$

$$\mathrm{WCl_4} + 2\mathrm{SiH_2Cl_2} + 2\mathrm{H_2} = \mathrm{WSi_2(s)} + 8\mathrm{HCl}, \quad \varepsilon_1 \tag{1}$$

$$2\mathrm{HCl} + \mathrm{SiH_2Cl_2} = \mathrm{SiCl_4} + 2\mathrm{H_2}, \quad \varepsilon_2 \tag{2}$$

$$\mathrm{HCl} + \mathrm{SiH_2Cl_2} = \mathrm{SiCl_3} + 1.5\mathrm{H_2}, \quad \varepsilon_3 \tag{3}$$

$$\mathrm{SiCl_2} + \mathrm{H_2} = \mathrm{SiH_2Cl_2}, \quad \varepsilon_4 \tag{4}$$

$$\mathrm{SiHCl_3} = \mathrm{SiCl_2} + \mathrm{HCl}, \quad \varepsilon_5 \tag{5}$$

$$\mathrm{WCl_5} + 0.5\mathrm{H_2} = \mathrm{WCl_4} + \mathrm{HCl}, \quad \varepsilon_6 \tag{6}$$

$$\mathrm{SiH_4} + 2\mathrm{HCl} = \mathrm{SiCl_2} + 3\mathrm{H_2}, \quad \varepsilon_7 \tag{7}$$

$$\mathrm{WSi_2(s)} + 2.8\mathrm{H_2} = 0.2\mathrm{W_5Si_3(s)} + 1.4\mathrm{SiH_4}, \quad \varepsilon_8 \tag{8}$$

For the WSi_2(s) + Si(s) + gas system, $N=13$ and $r=8$; thus, Eqs. (0)–(7) represent the eight independent reactions. Using the extents of reactions $\varepsilon_0, \varepsilon_1, \ldots, \varepsilon_7$ and the feed-gas composition (Q_1^0, Q_2^0, Q_4^0 and Q_{Ar}^0, mol), the respective molar amounts of the 13 species are expressed by the following relations:

$$Q_1 = Q_1^0 + \varepsilon_0 - \varepsilon_1 + \varepsilon_6 : \quad \mathrm{WCl_4} \tag{9a}$$

$$Q_2 = Q_2^0 - 2\varepsilon_1 - \varepsilon_2 - \varepsilon_3 + \varepsilon_4 : \quad \mathrm{SiH_2Cl_2} \tag{9b}$$

$$Q_3 = -4\varepsilon_0 + 8\varepsilon_1 - 2\varepsilon_2 - \varepsilon_3 + \varepsilon_5 + \varepsilon_6 - 2\varepsilon_7 : \quad \mathrm{HCl} \tag{9c}$$

$$Q_5 = -\varepsilon_5 : \quad \mathrm{SiHCl_3} \tag{9d}$$

$$\begin{aligned} Q_4 = {} & Q_4^0 + 2\varepsilon_0 - 2\varepsilon_1 + 2\varepsilon_2 + 1.5\varepsilon_3 - \varepsilon_4 \\ & - 0.5\varepsilon_6 + 3\varepsilon_7 : \quad \mathrm{H_2} \end{aligned} \tag{9e}$$

$$Q_{10} = Q_{\mathrm{Ar}}^0 \tag{9f}$$

$$Q_6 = \varepsilon_2 : \quad \mathrm{SiCl_4} \tag{9g}$$

$$Q_7 = \varepsilon_3 : \quad \mathrm{SiCl_3} \tag{9h}$$

$$Q_9 = -\varepsilon_6 : \quad \mathrm{WCl_5} \tag{9i}$$

$$Q_{13\mathrm{s}} = 2\varepsilon_0 : \quad \mathrm{Si(s)} \tag{9j}$$

$$Q_8 = -\varepsilon_4 + \varepsilon_5 + \varepsilon_7 : \quad \mathrm{SiCl_2} \tag{9k}$$

$$Q_{11} = -\varepsilon_7 : \quad \mathrm{SiH_4} \tag{9l}$$

$$Q_{12\mathrm{s}} = \varepsilon_1 - \varepsilon_0 : \quad \mathrm{WSi_2(s)} \tag{9m}$$

3. Method of calculation: WSi_2(s)/Si(s) + WSi_2(s) phase-boundary

For a feed-gas composed of 4 μmol (or 4×10^{-6} mol) WCl_4, 36 μmol SiH_2Cl_2, 9766.2 μmol H_2 and 89956 μmol Ar, which together amount to a volumetric flow of 2.2362 NL/min, it is readily seen that $\mathrm{Cl}^0=88$ μmol, $\mathrm{H}^0=19604.5$ μmol, $\mathrm{Ar}^0=89956$ μmol, $\mathrm{W}^0=4$ μmol, and $\mathrm{Si}^0=36$ μmol, with the result the atom-ratios assume the values of $(\mathrm{Ar/H})^0=4.5885$; $(\mathrm{H/Cl})^0=222.78$; F, the silicon-fraction $[\mathrm{Si}/(\mathrm{W}+\mathrm{Si})]^0=0.90$ for the feed-gas. In order to fully define the equilibrium-state of this three-phase system, for specified pressure (101.325 kPa) and temperature (1000 K), the equilibrium partial pressures of 11 gaseous species must be found. An iterative method that makes use of the non-linear equilibrium constant relations together with a *successive converging approximations* scheme [4] is employed in the present computation. Using the standard chemical potential data of Knacke et al. [6], the equilibrium constants K_0, $K_1, \ldots, K_7$ for the respective reactions (0), (1), . . ., (7) were calculated. The values are 9.343×10^{-14}, 1.4684×10^{10}, 180,540, 21.667, 15.64, 3.2969×10^{-5}, 374,460, and 4.1204×10^{6}, respectively at 1000 K [6]. The species WCl_4, H_2, and Ar are chosen as *majors*; and the first iteration is begun with the following guesses for the partial pressures of the three selected species:

$$P_1 = 1.0\times10^{-26}P \ \text{for}\ \mathrm{WCl_4}, \quad P_4 = 0.098P \ \text{for}\ \mathrm{H_2},$$

$$P_{\mathrm{Ar}} = 0.90P, \quad \text{where} \quad P = 1.0\,\mathrm{atm}\,(101,325\,\mathrm{Pa})$$

The partial pressures P_3, P_2, P_6, P_7, P_8, P_5, P_9, and P_{11} of the remaining gas species were computed using the equilibrium constant data for the eight foregoing reactions:

$$P_3 = \left[\frac{P_1(P_4)^2}{K_0}\right]^{0.25}, \quad P_2 = \left[\frac{P_3^8}{K_1P_1P_4^2}\right]^{0.5},$$

$$P_6 = K_2P_2\left(\frac{P_3}{P_4}\right)^2, \quad P_7 = \frac{K_3P_2P_3}{P_4{}^{1.5}},$$

$$P_8 = \frac{P_2}{K_4P_4}, \quad P_5 = \left[\frac{P_3P_8}{K_5}\right],$$

$$P_9 = \left[\frac{P_1P_3}{K_6P_4^{0.5}}\right], \ \text{and} \ P_{11} = \left[\left(\frac{P_4^3P_8}{K_7P_3^2}\right)\right]$$

At this stage, the *three constraints* are imposed: first, the total pressure P_e is found:

$$\begin{aligned} P_e = {} & P_1 + P_2 + P_3 + P_4 + P_5 + P_6 + P_7 \\ & + P_8 + P_9 + P_{10} + P_{11} \neq P \end{aligned} \tag{10}$$

The next two constraints are the atom-ratios: for the gas-phase, the elemental molar amounts $\mathrm{CL_t}$, $\mathrm{SI_t}$, W_{tot}, H_{t}, and A_{tot} for chlorine, silicon, tungsten, hydrogen and argon, respectively, are proportional to pressure terms as the CVD flow-system is normally maintained under isothermal conditions (at 1000 K, in this instance):

$$\mathrm{CL_t} = 5P_9 + 4P_1 + 4P_6 + 3P_5 + 3P_7 + 2P_2 + 2P_8 + P_3 \qquad (11a)$$

$$W_{\mathrm{tot}} = P_1 + P_9 \qquad (11b)$$

$$\mathrm{SI_t} = P_2 + P_5 + P_6 + P_7 + P_8 + P_{11} \qquad (11c)$$

$$H_{\mathrm{t}} = 2P_2 + 2P_4 + P_3 + P_5 + 4P_{11} \qquad (11d)$$

$$A_{\mathrm{tot}} = P_{\mathrm{Ar}} \qquad (11e)$$

The gas-phase atom-ratios at the completion of the first-iteration are as follows:

$$(\mathrm{H/Cl}) = \frac{H_{\mathrm{t}}}{\mathrm{CL_t}} \neq 222.78: \quad (\mathrm{H/Cl})^0 \text{ of feed-gas} \qquad (12)$$

$$(\mathrm{Ar/H}) = \frac{A_{\mathrm{tot}}}{H_{\mathrm{t}}} \neq 4.5885: \quad (\mathrm{Ar/H})^0 \text{ of feed-gas} \qquad (13)$$

The constraints embodied in Eqs. (10), (12) and (13) are not satisfied; the approach to convergence can be quantitatively expressed by constraining ratios R_1, R_3 and R_4:

$$R_1 = \frac{P}{P_{\mathrm{e}}}: \quad \text{pressure}, \qquad R_3 = \frac{222.78\mathrm{CL_t}}{H_{\mathrm{t}}},$$

$$R_4 = \frac{4.5885 H_{\mathrm{t}}}{A_{\mathrm{tot}}}$$

At full convergence, all three approach unity within a tolerance-limit of 0.0001. The partial pressures of the *majors* are now modified to give successive increments (or declines) by means of the following convergence formulas:

$$(P_1)_{\mathrm{new}} = (P_1)_{\mathrm{old}} R_1^{0.08} \left(\frac{1.0}{R_3}\right)^{0.02}: \quad \text{for WCl}_4 \qquad (14a)$$

$$(P_4)_{\mathrm{new}} = (P_4)_{\mathrm{old}} R_1^{0.025} R_3^{0.03} \left(\frac{1.0}{R_4}\right)^{0.05}: \quad \text{for H}_2 \qquad (14b)$$

$$(P_{\mathrm{Ar}})_{\mathrm{new}} = (P_{\mathrm{Ar}})_{\mathrm{old}} R_1^{0.02} R_4^{0.01}: \quad \text{for Ar} \qquad (14c)$$

These new values for the *majors* are used together with K_0, $K_1, \ldots, K_7$ to calculate the partial pressures of the eight other species; and the computation is continued until the convergence is reached at the end of 610 iterations (*wsi3.f* code). The equilibrium data in Pascals are shown in the second column of Table 1. The elemental quantities (in mol or μmol) summed over the 11 species of the gas-phase are

$$Q_{\mathrm{Ar}} = Q^0_{\mathrm{Ar}}, \qquad Q_{\mathrm{Si}} = Q^0_2 - 2\varepsilon_1, \qquad Q_{\mathrm{W}} = Q^0_1 - \varepsilon_1 + \varepsilon_0,$$

$$Q_{\mathrm{Cl}} = 4Q^0_1 + 2Q^0_2, \qquad Q_{\mathrm{H}} = 2Q^0_1 + 2Q^0_2$$

Furthermore, defining $\mathrm{SI_t}$, W_{tot} and $\mathrm{CL_t}$ as per Eqs. (11a)–(11c), and using P_i's of Table 1:

$$\mathrm{SI_t} = 11.90179, \qquad W_{\mathrm{tot}} = 6.539 \times 10^{-20},$$

$$\mathrm{CL_t} = 89.35906\ \mathrm{Pa}$$

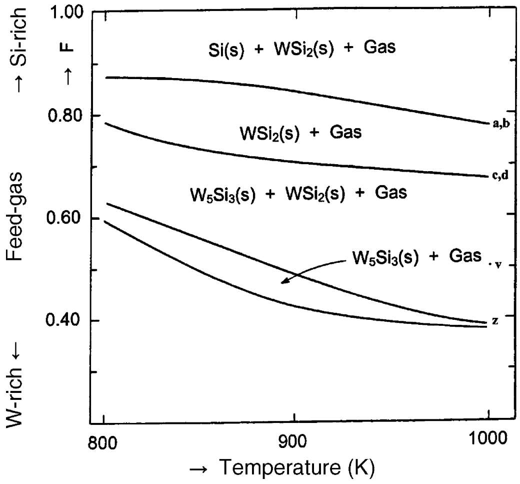

Fig. 1. Phase-boundaries in the W–Si–Cl–H–Ar chemical vapour deposition (CVD) system at 101.325 kPa (1.0 atm) for (H/Cl) = 222.78 and (Ar/H) = 4.5885.

In view of $W_{\mathrm{tot}} \approx 0$, the gas-phase tungsten $Q_{\mathrm{W}} = 0 = Q^0_1 - \varepsilon_1 + \varepsilon_0$ which yields

$$\varepsilon_1 = Q^0_1 + \varepsilon_0 = \text{ extent of reaction (1) at equilibrium} \qquad (15a)$$

$$[\mathrm{SI_t/CL_t}] = S_2 = 0.13319 = \frac{Q_{\mathrm{Si}}}{Q_{\mathrm{Cl}}} = \frac{Q^0_2 - 2\varepsilon_1}{4Q^0_1 + 2Q^0_2} \qquad (15b)$$

In Eq. (15a), the limiting value of $\varepsilon_0 = 0$ corresponds to zero-amount of Si(s) as given in Eq. (9j); consequently, ε_1 in Eq. (15b) is replaced by Q^0_1. Hence, the feed-gas that corresponds to the *boundary* between the phase-domains consists of $Q^0_1 = 4$ μmol of $\mathrm{WCl_4}$ and

$$Q^0_2 = Q^0_1 \left[\frac{2 + 4S_2}{1 - 2S_2}\right] = 13.81\ \mu\text{mol}\ \mathrm{SiH_2Cl_2} \text{ and}$$

$$F = 0.7754 \qquad (16)$$

This result is marked '**a, b**' in Fig. 1; this lies on the frontier between the two-solid $\mathrm{Si(s) + WSi_2(s)}$ domain and the single-solid $\mathrm{WSi_2(s)}$ region of stability.

4. Equilibrium gas-phase partial pressures over $\mathrm{WSi_2(s)}$

There occur the same 11 gas species in the equilibrium system containing only one solid, $\mathrm{WSi_2(s)}$; the set of independent reactions now consists of Eqs. (1)–(7) and the four constraints include the $[(\mathrm{Si–2W})/\mathrm{Cl}]^{(\mathrm{g})}$ stoichiometric ratio and the three listed earlier. The equilibrium-state is determined by the iterative equilibrium constant method [4] for a feed-gas with 4 μmol $\mathrm{WCl_4}$, 13.81 μmol $\mathrm{SiH_2Cl_2}$ and sufficient $\mathrm{H_2}$ and Ar to ensure (H/Cl) = 222.78 and (Ar/H) = 4.5885, respectively. The results are shown in column 3 of Table 1 (*wsi2.f* code). At the $\mathrm{Si(s) + WSi_2(s)/WSi_2(s)}$ *boundary*, the equality of partial pressures is evident for each gaseous species partaking in the equilibrium. Thus one can use the $\varepsilon_0 \to 0$ limit together with Eqs. (15a), (15b) and (16) to obtain a rapid determination of the boundary between the single-solid and the two-solid domains at other temperatures. The equilibrium calculations (*wsi2.f* and

Table 1
Equilibrium boundaries WSi_2(s)/Si(s) + WSi_2(s) and WSi_2(s)/WSi_2(s) + W_5Si_3(s) and partial pressures in the W–Si–Cl–H–Ar system at 101.325 kPa (1 atm) and 1000 K

	Run no.							
	#1	#2	#3	#4	#5	#6	#7	#8
F (feed-gas)	0.9000	0.7754 **b**	0.7500	0.7310	0.7125	0.6912	0.5000 **v**	0.6717 **d**
Q_1^0 (μmol)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Q_2^0 (μmol)	36.0	13.81	12.0	10.87	9.913	8.953	4.0	8.18283
Q_4^0 (μmol)	9766.2	4844.9	4443.6	4193.0	3980.7	3767.8	2669.3	3597.0
Q_{Ar}^0 (μmol)	89956	44589	40889	38579	36622	34660	24533	33085
WCl_4 (Pa)	$\approx 7 \times 10^{-20}$	$\approx 7 \times 10^{-20}$	$\approx 6 \times 10^{-19}$	$\approx 3 \times 10^{-18}$	$\approx 2 \times 10^{-17}$	$\approx 2 \times 10^{-16}$	$\approx 1 \times 10^{-14}$	$\approx 1 \times 10^{-14}$
SiH_2Cl_2 (Pa)	0.7042	0.7042	0.4347	0.2893	0.1801	0.08343	0.01504	0.01504
HCl (Pa)	51.407	51.396	60.353	67.049	73.537	80.938	87.630	87.636
H_2 (Pa)	9924.0	9922.7	9919.3	9916.6	9913.7	9910.4	9907.0	9907.7
$SiHCl_3$ (Pa)	7.0735	7.0737	5.1284	3.7932	2.5911	1.3214	0.2580	0.2581
$SiCl_4$ (Pa)	3.4115	3.4113	2.9052	2.3878	1.7895	1.0047	0.2125	0.2125
$SiCl_3$ (Pa)	0.2525	0.2526	0.1832	0.1355	0.09255	0.04721	0.00922	0.00922
$SiCl_2$ (Pa)	0.4597	0.4598	0.2839	0.1890	0.1177	0.05454	0.00984	0.00984
WCl_5 (Pa)	$\approx 3 \times 10^{-28}$	$\approx 3 \times 10^{-28}$	$\approx 3 \times 10^{-27}$	$\approx 2 \times 10^{-26}$	$\approx 1 \times 10^{-25}$	$\approx 1 \times 10^{-24}$	$\approx 8 \times 10^{-23}$	$\approx 8 \times 10^{-23}$
Ar (Pa)	91338	91339	91336	91335	91333	91331	91330	91329
SiH_4 (Pa)	4.1×10^{-4}	4.1×10^{-4}	1.8×10^{-4}	1.0×10^{-4}	5.1×10^{-5}	1.9×10^{-5}	3.0×10^{-6}	3.0×10^{-6}
$(Cl)^0$ (μmol)	88.0	43.62	40.0	37.74	35.826	33.906	24.0	32.3657
$(H)^0$ (μmol)	19604.5	9717.58	8911.12	8407.64	7981.25	7553.5	5346.7	7210.4
$(Ar)^0$ (μmol)	89956	44589	40889	38579	36622	34660	24533	33085
(H/Cl)	222.78	222.78	222.78	222.78	222.78	222.78	222.78	222.78
(Ar/H)	4.5885	4.5885	4.5885	4.5885	4.5885	4.5885	4.5885	4.5885
Fortran (program)	wsi3.f	wsi2.f	wsi2.f	wsi2.f	wsi2.f	wsi2.f	wsi4.f	wsi2.f

The letters **b**, **v** and **d** that appear in run nos. #2, #7 and #8 are shown in Fig. 1.

wsi3.f) presented in Fig. 1 show *boundary-values* of $F = 0.8389$ at 900 K and $F = 0.8729$ at 800 K, respectively. It is well to note that the amount of SiH_2Cl_2 in the feed-gas was increased with $Q_1^0 = 4$ μmol of WCl_4; and the molar amounts of H_2 and argon were suitably chosen to ensure atom-ratios $(H/Cl)^0$ and $(Ar/H)^0$ remain constant at 222.78 and 4.5885, respectively.

At 1000 K and 101.325 kPa (1 atm) pressure, the equilibrium gas-phase above the WSi_2(s) was calculated for a number of feed-gas compositions: $F = 0.750$, 0.7310, 0.7125, 0.6912, with the SiH_2Cl_2-content gradually lowered. The resulting data on the partial pressures are shown in columns 4–7 of Table 1; it is seen that the variation of pressure for any given species is smooth within the single-solid WSi_2(s) domain.

5. Phase-boundaries: WSi_2(s)/W_5Si_3(s) + WSi_2(s)/W_5Si_3(s)

The construction of the lower boundary – that separating the single-solid (WSi_2) from the two-solids ($WSi_2 + W_5Si_3$) region – in Fig. 1 is now addressed. It will be noted that the WSi_2(s) + W_5Si_3(s) + gas system at equilibrium consists of two solids and 11 gaseous species; the equilibria (1)–(8), given earlier, constitute the set of *eight independent reactions*. The four degrees of freedom possessed by this system require specification of *T*, *P*, (Ar/H), and (H/Cl) atom-ratios. For the feed-gas that is designated '**v**' in Fig. 1 (4 μmol WCl_4, 4 μmol SiH_2Cl_2, 2669.3 μmol H_2, 24533 μmol Ar), one would expect the deposition of both W_5Si_3(s) and WSi_2(s) at 1000 K and 1.0 atm (101.325 kPa) pressure; the equilibrium gas-phase composition above the two-solids was computed (*wsi4.f* code) by means of the iterative equilibrium constant method [4]. The equilibrium partial pressure data (in Pa) for the 11 species are summarized in the column 8 of Table 1; the atom-ratios (H/Cl) and (Ar/H) are 222.78 and 4.5885. The molar amounts of the 13 species are expressed in terms of ε_1 to ε_8 and Q_i^0's:

$$Q_1 = Q_1^0 - \varepsilon_1 + \varepsilon_6 : \quad WCl_4 \tag{17a}$$

$$Q_2 = Q_2^0 - 2\varepsilon_1 - \varepsilon_2 - \varepsilon_3 + \varepsilon_4 : \quad SiH_2Cl_2 \tag{17b}$$

$$Q_3 = 8\varepsilon_1 - 2\varepsilon_2 - \varepsilon_3 + \varepsilon_5 + \varepsilon_6 - 2\varepsilon_7 : \quad HCl \tag{17c}$$

$$Q_5 = -\varepsilon_5 : \quad SiHCl_3 \tag{17d}$$

$$Q_4 = Q_4^0 - 2\varepsilon_1 + 2\varepsilon_2 + 1.5\varepsilon_3 - \varepsilon_4 - 0.5\varepsilon_6 + 3\varepsilon_7 - 2.8\varepsilon_8 : \quad H_2 \tag{17e}$$

$$Q_{10} = Q_{Ar}^0 \tag{17f}$$

$$Q_6 = \varepsilon_2 : \quad SiCl_4 \tag{17g}$$

$$Q_7 = \varepsilon_3 : \quad SiCl_3 \tag{17h}$$

$$Q_8 = -\varepsilon_4 + \varepsilon_5 + \varepsilon_7 : \quad SiCl_2 \tag{17i}$$

$$Q_9 = -\varepsilon_6 : \quad WCl_5 \tag{17j}$$

$$Q_{11} = 1.4\varepsilon_8 - \varepsilon_7 : \quad SiH_4 \tag{17k}$$

$$Q_{14s} = 0.2\varepsilon_8 : \quad W_5Si_3(s) \tag{17l}$$

$$Q_{12s} = \varepsilon_1 - \varepsilon_8 : \quad WSi_2(s) \tag{17m}$$

The molar amounts of elements Si, W and Cl, evaluated from the Q_i's of the 11 gaseous species given by Eqs. (17a)–(17k), are as follows

$$Q_{\mathrm{Si}} = Q_2^0 - 2\varepsilon_1 + 1.4\varepsilon_8, \qquad Q_{\mathrm{W}} = Q_1^0 - \varepsilon_1,$$
$$Q_{\mathrm{Cl}} = 4Q_1^0 + 2Q_2^0$$

Using the data on equilibrium pressures (Table 1, column 8) for feed-gas '**v**' (Fig. 1), the values of the quantities $\mathrm{SI_t}$, W_{tot} and $\mathrm{CL_t}$ are determined by means of Eqs. (11a)–(11c):

$$\mathrm{SI_t} = 0.504615, \qquad W_{\mathrm{tot}} = 1.025 \times 10^{-14},$$
$$\mathrm{CL_t} = 89.3314\,\mathrm{Pa}$$

Since W_{tot} for the gas-phase is negligibly small, $Q_{\mathrm{W}} = 0 = Q_1^0 - \varepsilon_1$ and,

$$\varepsilon_1 = \text{equilibrium extent of reaction} = Q_1^0 \tag{18a}$$

The frontier between WSi_2(s) and W_5Si_3(s) + WSi_2(s) domains is now found using the stoichiometric ratio S_2 introduced earlier by Eq. (15b):

$$S_2 = [\mathrm{SI_t}/\mathrm{CL_t}] = 0.0056488 = \frac{Q_{\mathrm{Si}}}{Q_{\mathrm{Cl}}} = \frac{Q_2^0 - 2Q_1^0 + 1.4\varepsilon_8}{4Q_1^0 + 2Q_2^0} \tag{18b}$$

In Eq. (18b), the limiting-value $\varepsilon_8 = 0$ corresponds to zero-amount of W_5Si_3(s) in the two-solids domain, as per Eq. (17l). Solving for *boundary feed-gas* Q_2^0 of SiH_2Cl_2:

$$Q_2^0 = Q_1^0\left[\frac{2+4S_2}{1-2S_2}\right] = 8.18283\,\mu\mathrm{mol} \quad \text{and} \quad F = 0.6717 \tag{19}$$

This result is shown in Fig. 1 (as '**c**, **d**') at $T = 1000$ K and $P = 101.325$ kPa. Using a similar procedure, the boundary-limits (WSi_2/W_5Si_3 + WSi_2) at two other temperatures were determined: in Fig. 1, $F = 0.7057$ at 900 K and $F = 0.7876$ at 800 K represent the phase-boundary between solid-WSi_2 and the two-solid WSi_2 + W_5Si_3 domains.

The two-solid (WSi_2 + W_5Si_3) phase-region, with decreasing SiH_2Cl_2-content of the feed-gas, gives away to the single-solid domain W_5Si_3(s); the *boundary* between WSi_2(s) + W_5Si_3(s) and W_5Si_3(s) corresponds to zero-amount of WSi_2(s); therefore, by virtue of Eq. (17m), $\varepsilon_1 = \varepsilon_8$, which gives for the molar amount of silicon in gas-phase, $Q_{\mathrm{Si}} = Q_2^0 - 2\varepsilon_1 + 1.4\varepsilon_8 = Q_2^0 - 0.6\varepsilon_1 = Q_2^0 - 0.6Q_1^0$; and Eq. (18b) now becomes

$$S_2 = [\mathrm{SI_t}/\mathrm{CL_t}] = 0.0056488 = \frac{Q_{\mathrm{Si}}}{Q_{\mathrm{Cl}}} = \frac{Q_2^0 - 0.6Q_1^0}{4Q_1^0 + 2Q_2^0} \tag{20a}$$

The feed-gas Q_2^0 of SiH_2Cl_2 at the WSi_2(s) + W_5Si_3(s)/W_5Si_3(s) *frontier* is given by

$$Q_2^0 = Q_1^0\left[\frac{0.6+4S_2}{1-2S_2}\right] = 2.51884\,\mu\mathrm{mol} \quad \text{and} \quad F = 0.3864 \tag{20b}$$

Similar calculations at other temperatures provide $F = 0.4620$ (3.43493 μmol SiH_2Cl_2) at 900 K and $F = 0.6310$ (6.83968 μmol SiH_2Cl_2) at 800 K, respectively. Thus, the *frontier* between the two-solid (WSi_2 + W_5Si_3) and the W_5Si_3(s) regions is found.

The upper-limit of the two-solids (WSi_2 + W_5Si_3) domain in Fig. 1 is further investigated at 1000 K and 101.325 kPa (1 atm) pressure for atom-ratios (H/Cl) = 222.78 and (Ar/H) = 4.5885; the single-solid (WSi_2) region ends at limit '**c**, **d**' (Fig. 1).

The equilibrium gas-phase partial pressures over WSi_2(s) were calculated (*wsi2.f* code) for the *boundary* feed-gas consisting of 4 μmol WCl_4, 8.18283 μmol SiH_2Cl_2, 3597 μmol H_2 and 33085 μmol Ar and the data are listed in column 9 of Table 1. It is well to note that there is near perfect agreement among partial pressures (columns 8 and 9) for each of the reacting gaseous species. This confirms that $F = 0.6717$ indeed denotes the *frontier* between WSi_2(s) and WSi_2(s) + W_5Si_3(s) phase-fields at 1000 K.

6. Discussion

The application of the lever rule is illustrated by the WSi_2(s) + W_5Si_3(s) region, which at 1000 K is bounded by '**d**' and '**z**', as shown in Fig. 1; and the length '**dz**' is measured in μmol units of the SiH_2Cl_2-content of the feed-gas, with $Q_1^0 = 4$ μmol WCl_4, and atom-ratios (H/Cl) = 222.78 and (Ar/H) = 4.5885. Referring to feed-gas (point '**v**' in Fig. 1) with $F = 0.50$, listed in column 8 of Table 1, it was shown that the two-solid domain stretched from 8.18283 to 2.51884 μmol with the selected point '**v**' at 4 μmol of the SiH_2Cl_2(g). This gives length '**dz**' = 8.18283 − 2.51884 = 5.66399 μmol; and the amounts of WSi_2(s) and $WSi_{0.6}$(s) are proportional to lengths '**vz**' and '**dv**', respectively:

$$Q_{12\mathrm{s}} = Q_1^0\left[\frac{4.0 - 2.51884}{5.66399}\right] = 1.04602\,\mu\mathrm{mol\ of\ WSi_2(s)}$$

$$Q_{14\mathrm{s}} = 0.2Q_1^0\left[\frac{8.18283 - 4.0}{5.66399}\right] = 0.5908\,\mu\mathrm{mol\ of\ W_5Si_3(s)}$$

An independent verification of these results was obtained by determining the extents of reactions ε_1 to ε_8 from the data of Table 1 (column 8) as described elsewhere [4]:

$$\varepsilon_1 = 4\,\mu\mathrm{mol}, \qquad \varepsilon_3 = 2.477 \times 10^{-3}\,\mu\mathrm{mol}, \qquad \varepsilon_2 = 23\varepsilon_3,$$
$$\varepsilon_7 = 4.1356\,\mu\mathrm{mol}, \qquad \varepsilon_8 = 2.954\,\mu\mathrm{mol}$$

These upon substitution into Eqs. (17l) and (17m) yield values of 1.046 μmol for WSi_2(s) and 0.5908 μmol for W_5Si_3(s), respectively. Thus, the present work is seen to be in accord with the lever rule.

7. Conclusions

Using the iterative equilibrium constant method in combination with extent of reaction framework, the phase-boundaries between the single-solid and the two-solid regions were successfully established for W–Si–Cl–H–Ar chemical vapour deposition system. The application of lever rule was demonstrated for the two-solid W_5Si_3(s) + WSi_2(s) domain.

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