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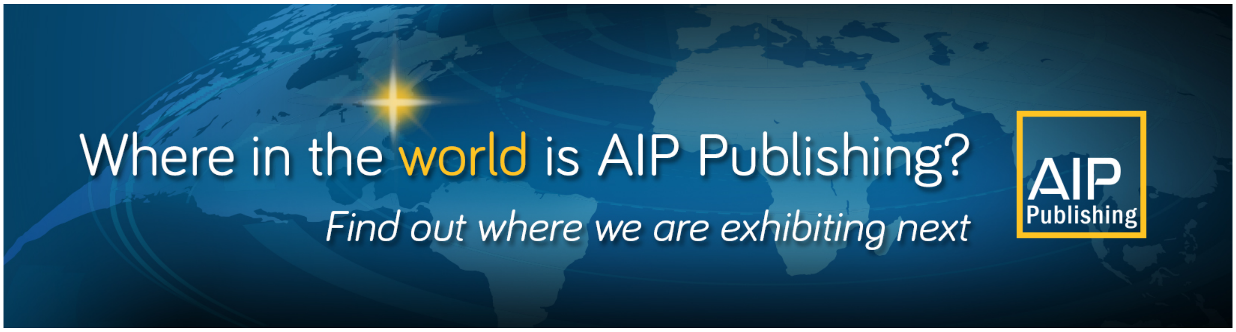

The Disilicides of Tungsten, Molybdenum, Tantalum, Titanium, Cobalt, and Nickel, and Platinum Monosilicide: A Survey of Their Thermodynamic Properties

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A critical evaluation is presented of the thermodynamic properties of six disilicides and one monosilicide that are important in the manufacture of very large scale integrated circuits. Values of the standard molar enthalpies of formation $\Delta_f H_m^\circ$ at $T = 298.15$ K and $p^\circ = 0.1$ MPa are recommended as follows: WSi_2, $-(79 \pm 5)$ $kJ \cdot mol^{-1}$; $MoSi_2$, $-(137 \pm 4)$ $kJ \cdot mol^{-1}$; $TiSi_2$, $-(171 \pm 11)$ $kJ \cdot mol^{-1}$; $CoSi_2$, $-(103 \pm 15)$ $kJ \cdot mol^{-1}$; $NiSi_2$, $-(88 \pm 12)$ $kJ \cdot mol^{-1}$; $TaSi_2$, $-(120 \pm 20)$ $kJ \cdot mol^{-1}$; and PtSi, $-(119 \pm 7)$ $kJ \cdot mol^{-1}$. Equations are given for the molar enthalpy increments of some of the silicides along with a few evaluated standard Gibbs free energies of formation. Brief descriptions of methods of synthesis and limited structural information have also been included.

Key words: chemical thermodynamics; cobalt disilicide; enthalpy increments; evaluated properties; molybdenum disilicide; nickel disilicide; platinum monosilicide; standard enthalpies of formation; standard Gibbs free energies of formation; tantalum disilicide; titanium disilicide; tungsten disilicide.

Contents

List of Tables

1. Introduction

There is a revival of interest in the chemistry of transition-metal disilicides as a result of their use as interconnects and gate materials in very-large-scale integrated (VLSI) circuits.[1] Considerable R&D efforts have been

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expended in the preparation and measurement of the electrical properties of thin films of these disilicides, but much less attention has been paid to their thermodynamic properties. Without reliable thermodynamic information for these materials, any long-term compatibility evaluation is of little value.

Schlesinger[2] recently surveyed in a general way the thermodynamic properties of metal silicides. His review covered literature references exhaustively, but critical estimates of the uncertainties in the selected values are lacking. The only other comprehensive review of the thermochemical properties of metal silicides was published about 20 years ago by Chart.[3,4]

In the present assessment, a thorough search was made of the literature of the thermodynamic properties of the crystalline disilicides of tungsten, molybdenum, tantalum, titanium, cobalt, and nickel, and of the monosilicide of platinum, because those substances appear to predominate in modern VLSI designs. The thermochemical properties: standard molar enthalpy of formation at $T = 298.15$ K, molar enthalpy increments relative to $T = 298.15$ K, and standard molar Gibbs free energies of formation are tabulated and appraised, and selected values are recommended. That is the main thrust of the effort. In addition, for each disilicide, we have included short, by no means exhaustive, sections that list methods of synthesis, structural information, and some details of the phase diagram .

2. Tungsten Disilicide

2.1. Preparative Methods

Tungsten disilicide, in common with the other disilicides discussed in this survey, is generally prepared by directly heating mixtures of stoichiometric amounts of pure specimens of Si and the appropriate second element in a vacuum or inert atmosphere to about 1500 K, followed by quenching to room temperature. Bondarenko *et al.*[5] prepared single-phase WSi_2 by the diffusion impregnation in vacuum of a tablet or thin sheet of tungsten with silicon. A number of workers[6-11] used CVD techniques to deposit thin (≤ 50 μm) films of WSi_2 on silicon substrates. Hammar *et al.*[6] laid tungsten films on predeposited polycrystalline Si in a CVD system at $p = 47$ Pa and $T = 623$ K, followed by annealing at 1073 K. Rode and Harshbarger[7] calculated the equilibrium compositions under CVD conditions for deposition of WSi_2 from two different feed gases: ($WF_6 + SiH_4 + H_2$) and ($WF_6 + SiH_2Cl_2 + H_2$) at temperatures between 473 K and 1073 K at $p = 67$ Pa. They showed that WSi_2 film was the only silicide phase formed in both cases. Blanquet *et al.*[8] examined the optimum thermodynamic conditions for CVD deposition of WSi_2 at $p = 0.1$ MPa by means of *in situ* chlorination of W-films followed by reaction with ($SiH_4 + H_2$). Dobkin *et al.*[9] obtained high-quality films of WSi_2 by CVD from ($WF_6 + Si_2H_6$) or ($SiH_4 + H_2 + N_2$) at $p = 0.1$ MPa and temperatures of the substrate between 563 K and 583 K. Zhang *et al.*[10] obtained WSi_x by low-pressure CVD from ($WF_6 + SiH_4 + Ar$), and WSi_2 by annealing on Si substrates W films formed from WF_6.[11] Tungsten disilicide and similar films prepared by CVD are usually characterized by standard surface techniques including Rutherford back-scattering.

2.2. Thermodynamic Properties

A recent assessment of the (W + Si) phase diagram by Nagender Naidu *et al.*[12] showed WSi_2 to be a congruently-melting intermediate phase that crystallized in tetragonal form (tI6, space group I4/mmm, $a = 0.3211$ nm, $c = 0.7868$ nm; melting temperature 2433 ± 4 K). The only other solid phase observed in this system was the congruently melting (at $T = 2593 \pm 10$ K) tetragonal W_5Si_3, which has a small compositional homogeneity. Apparently, W_3Si does not exist.

The direct-reaction calorimetric determination of the standard molar enthalpy of formation $\Delta_f H^\circ_m$(WSi_2, 298.15 K) by Robins and Jenkins[13] was, for many years, the only experimental result for this quantity. O'Hare[14] has recently determined $\Delta_f H^\circ_m$ by fluorine-combustion calorimetry. Several estimates[15-18] of $\Delta_f H^\circ_m$(WSi_2) have been published . Chart[19] deduced the molar Gibbs free energy of formation from Knudsen-effusion measurements. Bondarenko *et al.*[5,20] obtained the high-temperature enthalpy increments (1200 K to 2200 K) from measurements with a drop calorimeter.

All the values of the enthalpies of formation are collected in Table 1.

Robins and Jenkins[13] deduced $\Delta_f H^\circ_m$(WSi_2) from the measured total enthalpy changes when compacted samples of powdered tungsten and silicon with mole ratio

TABLE 1. The standard molar enthalpy of formation of WSi_2(cr, 298.15 K)

Source	$-\Delta_f H^\circ_m$/ kJ·mol^{-1}	Method
Robins and Jenkins[13]	93.2 ± 7.3	reaction calorimetry
O'Hare[14]	79 ± 5	reaction calorimetry
Chart[3,4]	93 ± 8.8	assessment
Searcy[15]	93.6	assessment
Niessen and de Boer[16]	33	prediction
Kaufman[17]	174	prediction
This work	79 ± 5	assessment

$n(\mathrm{W})/n(\mathrm{Si}) = 0.5$ were made to combine inside a calorimetric vessel. They reported the results of three such experiments. The standard deviation, $\pm 7.3\ \mathrm{kJ{\cdot}mol^{-1}}$, did not allow for any systematic errors. Additional effects of the enthalpy of a Thermit reaction (a pellet of aluminum and chromium sesquioxide that initiated the calorimetric reaction), the electrical energy to ignite the Thermit, and the energy of reaction of a (silicon + zirconium) cladding used to promote combination of tungsten and silicon were all included in the calorimetric measurements. Uncertainties in the enthalpies of those reactions and the identity of the zirconium silicide formed, of effects due to possible inhomogeneities in the WSi_2 product, and of impurities in the W and Si starting materials, must all be added to the standard deviation. In the absence of such important experimental details, it is very difficult to evaluate those systematic errors. Our best estimate of $\Delta_f H^\circ_m(\mathrm{WSi_2})$ from the study of Robins and Jenkins[13] is $-(93 \pm 20)\ \mathrm{kJ{\cdot}mol^{-1}}$.

A very recent investigation of the energy of combustion of high-purity, completely analyzed $WSi_{2.06}$ in a fluorine-bomb calorimeter by O'Hare[14] has given the result: $\Delta_f H^\circ_m(\mathrm{WSi_{2.06}}, \mathrm{cr}, 298.15\ \mathrm{K}) = -(80.4 \pm 4.7)\ \mathrm{kJ{\cdot}mol^{-1}}$, and for the exactly stoichiometric compound, $\Delta_f H^\circ_m(\mathrm{WSi_2})$ was estimated to be $-(79 \pm 5)\ \mathrm{kJ{\cdot}mol^{-1}}$. This value is close to that of Robins and Jenkins, but it is more precise and is preferred because the calorimetric materials and experimental procedures have been described in much greater detail.

Bondarenko *et al.*[5] calculated enthalpy increments, $H^\circ_m(T) - H^\circ_m(298.15\ \mathrm{K})$, for WSi_2 and W_5Si_3 from drop-calorimetric measurements between $T = 1173$ K and $T = 2118$ K. The following equation,[20] with the molar mass of WSi_2 taken to be $240.02\ \mathrm{g{\cdot}mol^{-1}}$, is selected as the most reliable (±5 per cent) available at present:

$$[H^\circ_m(T) - H^\circ_m(298.15\ \mathrm{K})]/(\mathrm{J{\cdot}mol^{-1}}) = 34.294(T/\mathrm{K}) + 15.41{\cdot}10^{-3}(T/\mathrm{K})^2 - 5.856{\cdot}10^{6}(\mathrm{K}/T) + 8065. \qquad (1)$$

Chart[19] used Knudsen-effusion techniques to measure the pressure of SiO(g) generated by the reaction between metal silicides and quartz cells; at the mean experimental temperature, $\Delta_f G^\circ_m(\mathrm{WSi_2}, \mathrm{cr}, 1500\ \mathrm{K}) = -(81 \pm 8)\ \mathrm{kJ{\cdot}mol^{-1}}$.

3. Molybdenum Disilicide

Even before transition-metal silicides were considered as interconnects and contacts for VLSI, molybdenum disilicide, because of its great resistance to air oxidation, was being studied as a high-temperature material and had been used as a heating element under the commercial name of Super Kanthal. Even so, published thermodynamic information[2,3,13] for $MoSi_2$ is not satisfactory. Of the seven values listed by Schlesinger[2] for $\Delta_f H^\circ_m(\mathrm{MoSi_2})$, only two are experimental in origin, and of those, one investigation[21] is described in such meager detail that the results cannot be assessed authoritatively.

3.1. Preparative Methods

Bulk $MoSi_2$ is usually synthesized by heating (Mo + 2Si) at $T \approx 1273$ K in a vacuum or inert atmosphere. Bondarenko *et al.*[22] prepared single-phase $MoSi_2$ by the reaction of ≈ 0.1-mm thick Mo plates with Si(g) in a vacuum chamber. Thin films of $MoSi_2$ were formed[23–27] by CVD methods from (silane + hydrogen + a volatile molybdenum halide) and also by the following techniques: sputtering from bulk $MoSi_2$ substrate; coevaporation of Mo and Si in a vacuum chamber; or by sequential deposition of Mo and Si, followed by annealing. Beyers[28] and Donald and Nemanich[29] examined the compatibility and mechanism of formation of such silicide films.

3.2. Thermochemical Properties

An assessment of the phase diagram of (Mo + Si) was published recently.[30] The intermediate $MoSi_2$ phase crystallizes in the tetragonal form (tI6, space group I4/mmm, $a = 0.3202$ nm, $c = 0.7851$ nm) and melts congruently at $T = (2293 \pm 10)$ K.

Since the critical reviews of the thermodynamic properties by Chart[3,4] in the early seventies, only two[21,31] additional measurements of $\Delta_f H^\circ_m$ of molybdenum disilicide have been performed.

As with WSi_2, it is difficult to estimate the uncertainty to be attached to the $\Delta_f H^\circ_m(\mathrm{MoSi_2})$ determined by Robins and Jenkins[13] by synthesis calorimetry. Unlike the (W + 2Si) experiments, an auxiliary (Zr + Si) reaction was not required to promote the formation of $MoSi_2$. For that reason, and even though the final product contained minor quantities of a compound now known to be Mo_5Si_3, the result should be less uncertain than that for WSi_2. Thus, we select $\Delta_f H^\circ_m(\mathrm{MoSi_2}) = -(131 \pm 15)\ \mathrm{kJ{\cdot}mol^{-1}}$, close to Chart's[3] recommendation of $-(132 \pm 9)\ \mathrm{kJ{\cdot}mol^{-1}}$.

Maslov *et al.*[21] electrically heated a mixture of Mo (99.47 mass per cent, with 0.24 mass per cent of oxygen and other miscellaneous contaminants) and Si (99.0 mass per cent, with the balance composed of Fe, Al, and Ca, and no reference to an oxygen impurity, although the reactants were stated to contain approximately 0.6 mass per cent of oxygen) to form $MoSi_2$ in a Calvet-type calorimeter. Surprisingly, no impurity correction appears to have been applied to the $\Delta_f H^\circ_m$ result. Furthermore, there seems to be an inconsistency between the oxygen contents of the starting materials and product silicide. We adjusted the reported result to $\Delta_f H^\circ_m(\mathrm{MoSi_2}) = -(143 \pm 3)\ \mathrm{kJ{\cdot}mol^{-1}}$ *to reflect the current molar mass of* $MoSi_2$. It is not clear whether this value came from one experiment or was the average of several. Nevertheless, the estimated uncertainty is probably optimistic in light of the quantity of impurities in the starting materials and the difference between the X-ray diffraction pattern of the product and that published for authentic $MoSi_2$, as discussed in Ref. 31.

O'Hare[31] recently used fluorine-combustion calorimetry to determine $\Delta_f H^\circ_m$ for a molybdenum silicide of composition $MoSi_{2.067\pm0.002}$, from which $\Delta_f H^\circ_\mathrm{m}(MoSi_2)$ was estimated to be $-(137.1 \pm 4.5)$ kJ·mol^{-1}. This result is believed to be the most reliable to date, because the sample was thoroughly characterized and the experimental procedure was documented fully.

The estimates of Searcy,[15] Searcy and Finnie,[32] Hultgren *et al.*,[18] and Chart[3,4] were all based in one way or another upon the determination of Robins and Jenkins.[13] All the other approximations in Table 2 were calculated.

Four high-temperature measurements that lead to the heat capacity of $MoSi_2$ have been reported.[20,22,33,34] Bondarenko *et al.*[22] measured directly the heat capacity of the silicide in an adiabatic calorimeter, and the three other studies involved drop calorimetry. Douglas and Logan[33] used an ice calorimeter to determine $H^\circ_\mathrm{m}(T)-H^\circ_\mathrm{m}(273.15\ \mathrm{K})$, where $T \leq 1173$ K, and thence derived the heat capacity as a function of T. In that research, the sample contained approximately 2 mass per cent of impurities. In addition, the authors observed some oxidation of the sample container, which contributed about ± 0.7 per cent to the overall uncertainty. Their enthalpy-increment results are approximated by the relation:

$$[H^\circ_\mathrm{m}(T)-H^\circ_\mathrm{m}(298.15\ \mathrm{K})]/(\mathrm{J{\cdot}mol^{-1}}) = 70.8937(T/\mathrm{K}) + 5.4559{\cdot}10^{-3}(T/\mathrm{K})^2 - 6356.31\ \lg(T/\mathrm{K}) - 5895.3. \quad (2)$$

Walker *et al.*[34] measured the enthalpy increments relative to 303.15 K from 383 K to 1173 K with a copper-block calorimeter. Their sample had a purity of 97.8 mass per cent and was contained in a 347 stainless-steel capsule. There are several errors in their equations for the specific enthalpy increments, which we now correct. They gave two enthalpy-increment-against-temperature relations; the terms in T^0 were interchanged, and there is an erroneous sign in the first equation. We have used a molar mass of 152.11 g·mol^{-1} for $MoSi_2$, and $[H^\circ_\mathrm{m}(303.15\ \mathrm{K})-H^\circ_\mathrm{m}(298.15\ \mathrm{K})] = 0.32$ kJ·mol^{-1} from Bondarenko *et al.*[22] to reconstruct the following $(328 \leq (T/\mathrm{K}) \leq 623)$:

$$[H^\circ_\mathrm{m}(T)-H^\circ_\mathrm{m}(298.15\ \mathrm{K})]/(\mathrm{kJ{\cdot}mol^{-1}}) = 8.48{\cdot}10^{-2}(T/\mathrm{K}) - 13.892\ \lg(T/\mathrm{K}) + 9.10 \quad (3)$$

and $(598 \leq (T/\mathrm{K}) \leq 1148)$:

$$[H^\circ_\mathrm{m}(T)-H^\circ_\mathrm{m}(298.15\ \mathrm{K})]/(\mathrm{kJ{\cdot}mol^{-1}}) = 8.94{\cdot}10^{-2}(T/\mathrm{K}) - 20.32\ \lg(T/\mathrm{K}) + 24.21. \quad (4)$$

The $MoSi_2$ studied by Bondarenko *et al.*[22] was the purest (99.95 mass per cent) sample used in the drop-calorimetric investigations, and they measured the heat capacity directly with an adiabatic calorimeter. Therefore, the selected heat capacity (± 2 per cent) is taken directly from their work:

$$C^\circ_{p,\mathrm{m}}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 67.487 + 15.522{\cdot}10^{-3}(T/\mathrm{K}) - 7.406{\cdot}10^5(\mathrm{K}/T)^2. \quad (5)$$

We have integrated Eq. (5) to obtain the following expression:

$$[H^\circ_\mathrm{m}(T)-H^\circ_\mathrm{m}(298.15\ \mathrm{K})]/(\mathrm{kJ{\cdot}mol^{-1}}) = 67.487{\cdot}10^{-3}(T/\mathrm{K}) + 7.761{\cdot}10^{-6}(T/\mathrm{K})^2 + 7.406{\cdot}10^2(\mathrm{K}/T) - 23.295\ . \quad (6)$$

Above 1200 K, the only enthalpy increments available were reported by Bondarenko[20] on the basis of drop-calorimetric experiments. His results are represented by the following:

$$[H^\circ_\mathrm{m}(T)-H^\circ_\mathrm{m}(298.15\ \mathrm{K})]/(\mathrm{kJ{\cdot}mol^{-1}}) = 26.359{\cdot}10^{-3}(T/\mathrm{K}) + 1811.63{\cdot}10^{-8}(T/\mathrm{K})^2 - 7469(\mathrm{K}/T) + 15.606\ . \quad (7)$$

Enthalpy-increment values obtained by different workers are summarized in Table 3; the agreement, usually within approximately 2 per cent, is reasonable considering the difference in sample purities and techniques.

Searcy and Tharp[35] and Chart[36] deduced the relative partial molar Gibbs free energy of Si from their Knudsen effusion studies. Searcy and Tharp measured the equilibrium partial pressures of Si(g) over $MoSi_2$ by means of the total mass loss method. The relatively small partial pressures required that the measurements be performed at quite high temperatures and that, in turn, caused interactions of the silicide with the container, sintering of the sample, and lack of equilibrium in the effusion cell. For

TABLE 2. The standard molar enthalpy of formation of $MoSi_2$(cr, 298.15 K)

Source	$-\Delta_f H^\circ_\mathrm{m}$/kJ·mol^{-1}	Method
Robins and Jenkins[13]	131 ± 10	reaction calorimetry
Maslov *et al*[21]	143 ± 3	reaction calorimetry
O'Hare[31]	137 ± 4	reaction calorimetry
Hultgren *et al*[18]	131 ± 6.2	assessment
Searcy[15]	113.7	assessment
Niessen and de Boer[16]	48	prediction
Kaufman[17]	216	prediction
Chart[3]	132 ± 9	assessment
This work	137 ± 4	assessment

those reasons, their derived $\Delta_f H_m^\circ$ at $T = 298.15$ K is not believed to be reliable.

Chart, on the other hand, measured the partial pressures of SiO(g) formed in reactions between $MoSi_2$ and SiO_2. He then derived the relative partial molar Gibbs free energies of Si in the silicide and, with the help of the Gibbs-Duhem relation, calculated $\Delta_f G_m^\circ(MoSi_2, cr) = -(128.3 \pm 7.5)$ kJ·mol^{-1}. He also recalculated the $\Delta_f G_m^\circ(MoSi_2, cr)$ result of Searcy and Tharp and found it to be between 2 to 3 kJ·mol^{-1} less negative than his own.

A careful examination of the experimental details of Chart's work indicates that his estimates of the uncertainties of $\Delta_f G_m^\circ(MoSi_2)$ were rather optimistic. He measured vapor pressures over just three alloy compositions: $x(Si) = 0.20$, 0.35, and 0.69. Each alloy sample was a two-phase mixture. In other words, he measured the equilibrium constants of the reactions:

$$Mo_3Si(s) + SiO_2 = 3Mo(s) + 2SiO(g), \qquad (8)$$

$$\tfrac{3}{4}Mo_5Si_3(s) + SiO_2(s) = 5/4Mo_3Si(s) + 2SiO(g), \qquad (9)$$

$$5/7MoSi_2(s) + SiO_2(s) = 1/7Mo_5Si_3(s) + 2SiO(g). \qquad (10)$$

Thus, in the evaluation of the partial molar Gibbs free energy of $MoSi_2$, not only must the errors from the measurement of $p(SiO)$ in reaction (8) be included, so also must those from reactions (9) and (10). Pressures varied with effusion orifice area, which suggests that thermodynamic equilibrium conditions were not realized in the effusion cells. No corrections were made to compensate for this effect. Chart's estimated uncertainties in the physical quantities that contributed to the values of $p(SiO)$ were: 1 to 2 per cent in the orifice area; ±1.5 per cent in the Clausing factor; 0.1 to 1 per cent in mass loss; and ±1.5 K in the cell temperature. These estimates are optimistic, in our opinion, when one considers that the loss in mass of the cell was the experimental parameter measured. Implicit in this method is an assumption that effusion fluxes obey the cosine distribution; such rarely happens for the total-mass-loss procedure. Chart also assumed that, in converting the measured partial pressures to Gibbs free energies, the constant errors in pressure values were cancelled. It is difficult to justify that assumption. Errors in the measurement of orifice area, temperature, mass loss rates, or the Clausing factors are not cancelled when the activities of Si are computed from two experiments, one with pure Si and the other with the silicides. Because oxygen solubility is small in the terminal solid phases, Mo(cr) and Si(cr), Chart assumed that the partial molar Gibbs free energies of Si in the silicides were not affected by the solubility of oxygen in the silicide phases. This assumption is also difficult to accept without some additional proof. In the light of these observations, the selected value $\Delta_f G_m^\circ = -(129 \pm 20)$ kJ·mol^{-1} is much more uncertain than that originally given by Chart.

There are two reports of the enthalpies of mixing of liquid Mo with Si. Arpaci and Frohberg[37] used levitation calorimetry to measure those quantities at $T = 3087$ K for $0 \leq x(Si) \leq 0.4$. They estimated the enthalpies of mixing to be uncertain by ±12 per cent. From an examination of their results and the problems associated with accurate determination of the temperature of liquid drops and the loss by vaporization of Si during the mixing process, it may be concluded that the systematic errors are larger than Arpaci and Frohberg believed. Sudavtsova *et al.*[38] also determined enthalpies of mixing in an isothermally jacketed calorimeter. Insufficient details are given in their paper to assess critically the accuracy of the measurements.

4. Titanium Disilicide

The (Ti + Si) phase diagram, probably one of the better understood for transition-metal silicides, was assessed recently by Murray.[39] The orthorhombic α-$TiSi_2$ (oF24, space group Fddd, $a = 0.8252$ nm, $b = 0.4783$ nm, $c = 0.8540$ nm) is the stable reference state from room temperature to $T = 1603$ K. The crystal structure of the high-temperature β-$TiSi_2$ modification has not yet been established.

TABLE 3. Enthalpy increments for $MoSi_2$(cr)

T/K	$[H_m^\circ(T) - H_m^\circ(298.15\ K)]$/kJ·mol^{-1}			
	Douglas & Logan[33]	Walker *et al.*[34]	Bondarenko *et al.*[5]	Bondarenko[20]
400	6.79 ± 0.14	6.87 ± 0.12	6.79 ± 0.14	67.1 ± 1.3 (1200 K)
500	13.76 ± 0.28	14.01 ± 0.24	13.87 ± 0.28	74.7 ± 1.5 (1300 K)
600	20.95 ± 0.42	21.39 ± 0.39	21.23 ± 0.42	82.7 ± 1.7 (1400 K)
700	28.32 ± 0.57	28.98 ± 0.57	28.81 ± 0.58	90.9 ± 1.8 (1500 K)
800	35.86 ± 0.71	36.74 ± 0.69	36.59 ± 0.73	99.5 ± 2.0 (1600 K)
900	43.55 ± 0.87	44.64 ± 0.88	44.57 ± 0.89	108.4 ± 2.4 (1700 K)
1000	51.38 ± 1.03	52.65 ± 1.01	52.71 ± 1.05	117.8 ± 2.6 (1800 K)
1100	59.36 ± 1.19	60.75 ± 1.18	61.03 ± 1.22	127.2 ± 2.7 (1900 K)
1200	67.46 ± 1.35	68.92 ± 1.30	69.51 ± 1.39	137.1 ± 2.9 (2000 K)

4.1. Preparative Methods

Bulk $TiSi_2$ is generally prepared by direct heating of stoichiometric amounts of the elements in a vacuum or inert atmosphere. Trambukin and Munir[40] synthesized titanium silicides by the self-propagating high-temperature combination of Ti and Si in which the exothermicity of the reaction was sufficient to carry the process to completion. Thin films of $TiSi_2$ have been prepared by CVD methods. The most common procedure is to deposit first a thin layer of Ti and then Si or to codeposit Ti and Si by means of titanium chloride, hydrogen, silicon chloride, or silane mixtures. Generally, the deposition of these layers is followed by annealing. Variations of this procedure have been described recently. Maex *et al.*[41] examined the thermodynamic criteria for the deposition of thin films of $TiSi_2$ or $CoSi_2$ on boron- or arsenic-doped substrates. Their calculations showed the absence of any stable tie-lines between $TiSi_2$(cr) and solid solutions of B or As in Si. They studied the redistribution of dopants during the formation of $TiSi_2$ film. This analysis underscores the importance of thermodynamic information for silicides used as gates or interconnects on VLSI circuits. Richter *et al.*[42] studied the formation of thin films of $TiSi_2$ on silicon and the effects of either furnace annealing or rapid thermal annealing on the final structures. Mercier *et al.*[43] deposited $TiSi_2$ layers from mixtures of $TiCl_4$, SiH_4, and H_2 without any consumption of the silicon substrate. Dahan *et al.*[44] studied the formation of layers of a ternary phase, $(Ti,Ta)Si_2$, by sputter depositing Ti and Ta on silicon wafers followed by annealing.

4.2. Thermodynamic Properties

The standard molar enthalpy of formation $\Delta_f H^\circ_m(TiSi_2)$ was determined in four calorimetric,[13,45–47] and one equilibrium[48] study. Four other assessments or estimates of this quantity have also been published.[17,18,49] Table 4 contains a summary of these values.

Robins and Jenkins[13] were the first to obtain $\Delta_f H^\circ_m(TiSi_2)$ from the direct, solid-state reaction. Different sources of systematic error in their experiments, discussed earlier in the present document, are not adequately accounted for in the standard deviation of ± 1.9 kJ·mol^{-1}. Golutvin[45] derived a value of $-(179.5 \pm 18.8)$ kJ·mol^{-1} by combustion calorimetry in oxygen of a sample that had the composition $Ti_{1.066}Si_{1.934}$ and contained 1 mass per cent of oxygen. Savin[46] reported $\Delta_f H^\circ_m(TiSi_2) = -(180.7 \pm 6.3)$ kJ·mol^{-1} from calorimetric measurements of the enthalpy of reduction with Na of $(TiCl_4 + 2SiCl_4)$. Recently, Topor and Kleppa[47] employed a Calvet-type calorimeter operating at $T = (1400 \pm 2)$ K to measure the enthalpy changes for the reactions:

$$0.05TiSi_2(\alpha,\ 298.15\ K) + 0.85Pd(cr,\ 298.15\ K) = Pd_{0.85}Si_{0.10}Ti_{0.05}(l,\ 1400\ K), \tag{11}$$

$$0.05Ti(cr,\ 298.15\ K) + 0.10Si(cr,\ 298.15\ K) + 0.85Pd(cr,\ 298.15\ K) = Pd_{0.85}Si_{0.10}Ti_{0.05}(l,\ 1400\ K). \tag{12}$$

The combined enthalpy changes of these two reactions gave $\Delta_f H^\circ_m(TiSi_2) = -170.9$ kJ·mol^{-1}, but the estimated error, ± 8.3 kJ·mol^{-1}, may be too small.

Brewer and Krikorian[48] estimated $\Delta_f H^\circ_m(TiSi_2) = -(234 \pm 42)$ kJ·mol^{-1} on the basis of equilibrium studies of several metal silicides, and de Boer *et al.*[49] used a semi-empirical model to predict a value of -183 kJ·mol^{-1}.

The selected $\Delta_f H^\circ_m(TiSi_2, \alpha, 298.15\ K) = -(171 \pm 11)$ kJ·mol^{-1} is the result obtained by Topor and Kleppa with an expanded error limit. Note, however, that within the combined uncertainties the $\Delta_f H^\circ_m$s obtained by Golutvin and Savin are in very good agreement with the recommended value.

There have been two measurements of enthalpy increments of $TiSi_2$, both by drop calorimetry. At 1200 K, the temperature of closest approach, the results of Golutvin[50] (from 407 K to 1181 K) and Bondarenko[20] (from 1200 K to 1700 K) shown in Table 5 agree to no better than about 5 per cent. According to the chemical analyses quoted by the authors, the titanium disilicide samples had different compositions, one being hyperstoichiometric and the other hypostoichiometric, and that could account for part, at least, of the discrepancies in the enthalpy values. "As a result of such variations," according to Schlesinger,[2] "more complete thermodynamic data for the titanium silicides cannot be recommended with any degree of confidence."

TABLE 4. The standard molar enthalpy of formation of $TiSi_2$(cr, α, 298.15 K)

Source	$-\Delta_f H^\circ_m$/kJ·mol^{-1}	Method
Topor & Kleppa[47]	170.9 ± 8.3	mixing calorimetry
Robins & Jenkins[13]	134.7 ± 1.9	reaction calorimetry
Golutvin[45]	179.5 ± 18.8	reaction calorimetry
Savin[46]	180.7 ± 6.3	reaction calorimetry
Brewer & Krikorian[48]	234 ± 42	equilibrium studies
Hultgren *et al.*[18]	134.3	assessment
de Boer *et al.*[49]	183	prediction
Kaufman[17]	134.4	prediction
Present work	171 ± 11	assessment

5. Cobalt and Nickel Disilicides

Disilicides of nickel (α-$NiSi_2$) and cobalt ($CoSi_2$) exhibit the fluorite structure with lattice constants only slightly different from those of Si. Thus, one would expect these two silicides to grow epitaxially on single-crystal silicon substrates, and a number of workers[51–55] have recently studied such growth. But the thermodynamic information available for these materials is sparse. The phase diagram of (Ni + Si) was reviewed recently,[56] and that of (Co + Si)[30] was critically assessed.

5.1. Preparative Methods

Disilicides of nickel and cobalt may be prepared by heating stoichiometric mixtures of the powdered components in vacuum or an inert atmosphere. Thin films are grown on silicon substrates by depositing the respective metals in vacuum followed by annealing at temperatures between 1073 K and 1173 K. Chang *et al.*[51] prepared $NiSi_2$ films epitaxially on (111) and (100) silicon substrates by depositing nickel from a plating solution at T = 363 K and pH = 9, followed by annealing in dry nitrogen. Werner *et al.* prepared epitaxial $NiSi_2$ films on a similar substrate, followed by rapid thermal annealing. Lindner and Tekat[53] formed $NiSi_2$ on silicon by implanting 6 MeV nickel ions into silicon, followed by annealing, while Barbour *et al.*[57] prepared layers of epitaxial $CoSi_2$ on silicon by ion implanting the cobalt ions and then annealing.

5.2. Thermodynamic Properties

Schlesinger[2] listed five values for the enthalpy of formation of α-$NiSi_2$ and six for the enthalpy of formation of $CoSi_2$ but, in each case, only one was obtained experimentally, the others having been assessed or calculated from various models. Oelsen and coworkers[58,59] determined $\Delta_f H^\circ_m$ for $NiSi_2$ and $CoSi_2$ by direct-reaction calorimetry. Molten Si and the appropriate molten metals were mixed together in a calorimeter at room temperature. Measurements of $\Delta_f H^\circ_m$ of Ni_2Si and NiSi were made, and from them $\Delta_f H^\circ_m(NiSi_2)$ was estimated to be ≈ -88 kJ·mol^{-1}. It is very difficult to evaluate the probable error in $\Delta_f H^\circ_m$; we have taken it to be ± 12 kJ·mol^{-1}. The Si and Ni were of technical grade and inferior purity by present-day standards. Cobalt of comparable purity was used in measurements of the reaction of molten cobalt and silicon to form $CoSi_2$. We have taken $\Delta_f H^\circ_m(CoSi_2) = -103$ kJ·mol^{-1} directly from Oelsen and Middel and, as with $NiSi_2$, estimate the uncertainty to be ± 12 kJ·mol^{-1}. Experimental, assesssed, and estimated values are summarized in Table 6.

TABLE 5. Enthalpy increments for $TiSi_2$

T/K	$[H^\circ_m(T) - H^\circ_m(298.15\ K)]$/kJ·mol^{-1} Golutvin[50]	T/K	$[H^\circ_m(T) - H^\circ_m(298.15\ K)]$/kJ·mol^{-1} Bondarenko[20]
407	6.37	1200	71.6
500	12.68	1300	79.6
596	20.22	1400	88.3
690	27.51	1500	97.7
804	37.57	1600	107.7
847	41.57	1700	118.4
969	49.71		
1072	58.45		
1181	75.23		

TABLE 6. The standard molar enthalpies of formation of $CoSi_2$(cr) and $NiSi_2$(α, cr) at 298.15 K

Source	$CoSi_2$	$NiSi_2$(α)	Method
	$-\Delta_f H^\circ_m$/kJ·mol^{-1}	$-\Delta_f H^\circ_m$/kJ·mol^{-1}	
Oelsen *et al*[58,59]	103 ± 12	88 ± 12	calorimetry
Chart[3]	99 ± 12	94 ± 12	assessment
Kaufman[17]	201	195	prediction
Machlin[76]	118.5		prediction
Pasturel *et al.*[60]	104		prediction
Mey[77]		82	prediction
Niessen *et al.*[61]	45	51	prediction
This work	103 ± 15	88 ± 12	assessment

Kalishevich *et al.*[62] measured the heat capacities of $NiSi_2$ and $CoSi_2$ to 300 K. They calculated the standard molar entropies: $S^\circ_m(NiSi_2, \alpha, 298.15\ K) = (65 \pm 6)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ and $S^\circ_m(CoSi_2, 298.15\ K) = (64 \pm 6)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$. Because the lowest temperature of the measurements was only 60 K, the uncertainties in $C^\circ_{p,m}$ may be large. Kalishevich *et al.*[63] used drop calorimetry to determine the enthalpy increments of $NiSi_2$ and $CoSi_2$ from $T = 298.15$ K to $T = 1560$ K. Chart[3] reviewed these results and selected $H^\circ_m(T) - H^\circ_m(298.15\ K)$ for both silicides; the assessed values in Table 7 are essentially those given by him.

A few measurements of the relative partial molar Gibbs free energies of Si are available for the liquid alloys. Those quantities were obtained by Schwerdtfeger and Engell[64,65] for (Ni + Si)(l) and (Co + Si)(l) by means of e.m.f. techniques, and by Martin-Garin *et al.*[66] for (Co + Si)(l) by distribution measurements followed by Gibbs-Duhem integration. Such molar Gibbs free energies of formation show large negative deviations from ideal solution behavior.

6. Tantalum Disilicide

Hexagonal tantalum disilicide (hP9, space group P6222, $a = 0.47821$ nm, $c = 0.65695$ nm) is one of four intermediate phases in the (Ta + Si) phase equilibrium system.[30] Experimental thermodynamic information on $TaSi_2$ is sparse. Chart[3,4] reviewed the data available in the early seventies.

6.1. Preparative Methods

Bulk samples of $TaSi_2$ may be prepared by heating mixtures of the elements in an inert atmosphere or in vacuum; thin films have been prepared by a number of CVD techniques. Blanquet *et al.*[8,67] used the thermodynamic properties to calculate the optimum conditions for CVD deposition of $TaSi_2$. They obtained $TaSi_2$ films at atmospheric pressure by generating tantalum chlorides *in situ* by direct reaction of Ta and Cl_2(g) at one end of the reactor and heating with different (SiH_4 + H_2) mixtures, followed by annealing at the other end. Several other workers[68–70] prepared thin films of $TaSi_2$ by high-pressure and low-pressure CVD, and from ($TaCl_5$ + $SiCl_4$ + H_2) mixtures in hot-wall reactors.

6.2. Thermodynamic Properties

Table 8 gives the experimental and estimated values for $\Delta_f H^\circ_m(TaSi_2)$. As discussed previously, the measurements of Robins and Jenkins[13] are subject to a number of systematic errors. Myers and Searcy[71] measured the dissociation pressures of $TaSi_2$ as a function of temperature by means of the total mass loss Knudsen effusion method and calculated the molar Gibbs free energy of formation at $T = 1500$ K. They assumed $\Delta C^\circ_{p,m} = 0$, and evaluated $\Delta_f H^\circ_m(TaSi_2)$. Levine and Kolodney[72] calculated $\Delta_f G^\circ_m(TaSi_2)$ at $T = 1300$ K from galvanic cell measurements. In both determinations of $\Delta_f G^\circ_m$, more than one equilibrium constant had to be calculated and the cumulative errors make the final values somewhat uncertain. Furthermore, uncertainties introduced by estimated auxiliary thermodynamic functions are difficult to estimate. Thus, the selected $\Delta_f H^\circ_m$ shown in Table 8 has quite large error limits.

There are two reports[73,74] that deal with the enthalpy increments of $TaSi_2$; both formed the basis of Chart's[3,4] recommendations, which are accepted.

7. Platinum Monosilicide

The (Pt + Si) phase diagram is not yet completely understood, but it is clear[30] that PtSi is a congruently melting intermediate phase of the system.

7.1. Preparative Methods

PtSi(cr) may be prepared directly by melting equimolar amounts of pure Pt and Si in a BN container at $T = 1575$ K under an inert gas atmosphere. This substance crystallizes in an orthorhombic habit (oP8, space group Pnma, $a = 0.5916$ nm, $b = 0.3587$ nm, $c = 0.5577$ nm), and its melting temperature is (1502 ± 5) K.

TABLE 7. Enthalpy increments for $CoSi_2$(cr) and $NiSi_{1.857}$(α, cr)

T/K	$[H^\circ_m(T) - H^\circ_m(298.15\ K)]/kJ{\cdot}mol^{-1}$ $CoSi_2$(cr)	 $NiSi_{1.857}$(α, cr)
400	7.03	6.81
500	14.44	13.87
600	22.22	21.28
700	30.25	28.81
800	38.66	36.58
900	47.20	44.47
1000	55.86	52.60
1100	74.06	60.73
1200	83.35	68.98

7.2. Thermodynamic Properties

Topor and Kleppa[75] measured the enthalpy changes that occurred when appropriate amounts of (platinum + silicon) and (platinum + platinum silicide) at room temperature were dropped into a BN cup at $T = (1400 \pm 2)$ K in a Calvet-type calorimeter. From the experimental enthalpy changes of the reactions:

$$0.72\mathrm{Pt}(\mathrm{cr}, 298.15\ \mathrm{K}) + 0.28\mathrm{Si}(\mathrm{cr}, 298.15\ \mathrm{K}) = \mathrm{Pt_{0.72}Si_{0.28}}(\mathrm{l}, 1400\ \mathrm{K}), \quad (13)$$

$$0.44\mathrm{Pt}(\mathrm{cr}, 298.15\ \mathrm{K}) + 0.28\mathrm{PtSi}(\mathrm{cr}, 298.15\ \mathrm{K}) = \mathrm{Pt_{0.72}Si_{0.28}}(\mathrm{l}, 1400\ \mathrm{K}), \quad (14)$$

$\Delta_f H^\circ_m(\mathrm{PtSi}, \mathrm{cr}, 298.15\ \mathrm{K}) = -(118.7 \pm 5.2)\ \mathrm{kJ{\cdot}mol^{-1}}$ was calculated. This uncertainty is the standard deviation of the measurements rather than an indication of their overall accuracy. Platinum and silicon, both of 99.99 mass per cent purity as used in the experiments of Topor and Kleppa, were sufficiently pure with respect to trace metals, but no account was taken of possible nonmetallic contaminants such as oxygen. The calibration standard was copper and its $[H^\circ_m(T) - H^\circ_m(298.15\ \mathrm{K})]$, taken from Hultgren *et al.*,[18] was arbitrarily adjusted by one per cent to allow for heat losses during its transfer from room temperature to the calorimeter at $T = 1400$ K. Insufficient details were given to assess other systematic errors reliably. Our selected $\Delta_f H^\circ_m(\mathrm{PtSi})$ is $-(119 \pm 7)\ \mathrm{kJ{\cdot}mol^{-1}}$, where the uncertainty has been estimated.

Topor and Kleppa also measured the enthalpy changes of the reaction:

$$(1-x)\mathrm{Pt}(\mathrm{cr}, 298.15\ \mathrm{K}) + x\mathrm{Si}(\mathrm{cr}, 298.15\ \mathrm{K}) = \mathrm{Pt}_{1-x}\mathrm{Si}_x(\mathrm{l}, 1400\ \mathrm{K}) \quad (15)$$

for $0.20 \leqslant x \leqslant 0.40$ and $0.62 \leqslant x \leqslant 0.70$. From their experiments, the enthalpy of mixing for:

$$(1-x)\mathrm{Pt}(\mathrm{l}, 1400\ \mathrm{K}) + x\mathrm{Si}(\mathrm{l}, 1400\ \mathrm{K}) = \mathrm{Pt}_{1-x}\mathrm{Si}_x(\mathrm{l}, 1400\ \mathrm{K}) \quad (16)$$

was obtained as a function of composition, and a distinct minimum was observed at $x(\mathrm{Si}) = 0.33$. They combined $\Delta_{\mathrm{mix}} H^{\mathrm{l}}_m$ with $\Delta_f H^\circ_m(\mathrm{PtSi})$ to calculate $\Delta_{\mathrm{fus}} H^\circ_m(\mathrm{PtSi}) \approx 47\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_{\mathrm{fus}} S^\circ_m(\mathrm{PtSi}) \approx 31.2\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

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TABLE 8. The standard molar enthalpy of formation of $\mathrm{TaSi_2}$(cr, 298.15 K)

Source	$-\Delta_f H^\circ_m/\mathrm{kJ{\cdot}mol^{-1}}$	Method
Robins and Jenkins[13]	116 ± 4	calorimetry
Myers and Searcy[71]	97 ± 30	equilibrium
Chart[3]	119 ± 13	assessment
Searcy and Finnie[32]	105 ± 18	prediction
Niessen and de Boer[16]	132	prediction
Brewer and Krikorian[48]	107 ± 26	prediction
Levine and Kolodney[72]	68 ± 17	galvanic cell
This work	120 ± 20	assessment

TABLE 9. The standard molar enthalpy of formation of PtSi(cr, 298.15 K)

Source	$-\Delta_f H^\circ_m/\mathrm{kJ{\cdot}mol^{-1}}$	Method
Topor and Kleppa[75]	118.7 ± 5.2	solution calorimetry
Chart[3]	184	estimation
Searcy and Finnie[32]	58	prediction
Machlin[76]	157	prediction
Pasturel *et al.*[60]	138	prediction
Niessen and de Boer[16]	166	prediction
This work	119 ± 7	assessment

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