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Thermodynamics of Phase Formation of the Cobalt Silicides

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Vaporization thermodynamics in the cobalt−silicon binary system has been studied by both reactive and simple Knudsen effusion mass spectrometry. The equilibrium partial pressures of SiO(g) over mixtures of CoSi + $CoSi_2$ and Co_2Si + CoSi with SiO_2 have been measured over the temperature range ca. 1190−1450 K. The equilibrium vapor pressure of Co(g) over a Co_2Si + CoSi two-phase mixture has been measured over the temperature range of ca. 1420−1560 K. Standard reaction enthalpy and entropy changes for the appropriate vaporization reactions, within the temperature ranges of the experiment, were determined from the temperature dependence of the measured vapor pressures. They were used, together with published and estimated heat capacity and standard entropy values, in a third-law evaluation of standard reaction enthalpy changes at 298 K. Standard enthalpies of formation of the intermediate compounds were found by a Hess' law combination of the standard reaction enthalpy values at 298 K. The results obtained are as follows: $^1/_3Co_2Si$, −41.0 ± 2.0 kJ mol^{-1}; $^1/_2CoSi$, −47.3 ± 2.0 kJ mol^{-1}; $^1/_3CoSi_2$, −32.9 ± 2.0 kJ mol^{-1}. These results are compared to previous measurements and estimates and are discussed in relation to processing $CoSi_2$ for microelectronics applications.

Introduction

Silicides of the transition metals have a number of properties of potential interest in materials applications. Their thermal stability and oxidation resistance make them materials of choice for corrosion-resistant coatings and high-temperature furnace elements.[1] Transition-metal silicides also find application in electronic device technology, where low electrical resistivity and adhesion to silicon have resulted in their use in contacts and interconnects for integrated circuitry.[2] Cobalt disilicide, $CoSi_2$, is one of the most promising silicides for VLSI and ULSI applications because of its very low resistivity (10−18 $\mu\Omega$ cm) and excellent lattice match (1.2% mismatch) with silicon that allows for its epitaxial growth on silicon substrates.[3]

Silicide materials, including $CoSi_2$, are often deposited on silicon substrates by means of chemical vapor deposition (CVD) techniques; however, group VIII silicides for electronics applications are usually formed in a self-aligned process[3] in which a deposited film is reacted with underlying silicon from which native oxide has been removed in a selective manner. Prediction of the compounds that will form under a given set of process variables and modeling of those processes requires accurate high-temperature Gibbs free energy of formation values for the reactants and all possible products. Modeling is often limited by a lack of data or their questionable reliability. In addition to these practical considerations, studying the Co−Si system as a part of a larger body of transition metal−silicon systems improves the understanding of thermodynamic stability and bonding trends in transition-metal silicides.

The thermodynamics of the Co−Si system[4] which, in addition to $CoSi_2$, contains two other intermediate phases CoSi and Co_2Si, has been reviewed by Chart,[5] Schlesinger,[6] and Choi.[7] The most recent review[8] is limited to $CoSi_2$. The only experimental data available are the standard enthalpies of formation of Co_2Si, CoSi, and $CoSi_2$ obtained by Oelsen et al.[9] using a direct reaction calorimetry technique in which molten silicon and cobalt were mixed in a sand-lined steel cylinder which was then immersed in a quantity of water whose temperature increase was measured. Their uncertainties were estimated by Chandrasekharaiah et al.[8] to be ±12 kJ mol^{-1}. The high-temperature (400−1800 K) heat capacity of Co_2Si has been measured by Frolov et al.[10] There are no low, i.e., subambient, temperature heat capacity data for Co_2Si. Both high (273−1850 K) and low (54−300 K) temperature heat capacities of CoSi have been obtained by Kalishevich et al.[11] High-

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temperature (500−1800 K) heat capacity of $CoSi_2$ has been determined by Kalishevich et al.[12] Low-temperature (60−300 K) heat capacity of $CoSi_2$ was obtained by Kalishevich et al.[13] All of the above heat capacities were determined by adiabatic calorimetry with uncertainties reported to be ca. 1%.

The data of Oelsen et al. indicate that $CoSi_2$ is marginally stable relative to CoSi; a difference of about 5 kJ mol^{-1} in the enthalpy of formation of $CoSi_2$ (more positive) or of CoSi (more negative) would make $CoSi_2$ unstable with respect to disproportionation to CoSi and Si. This difference is considerably less than the uncertainty in the data. Given this subtle situation, it is clear that further investigation of this system is warranted.

This paper reports the results of high-temperature vapor pressure measurements over two-phase cobalt silicide mixtures and thermodynamic stabilities of cobalt silicides derived from these measurements.

Experimental Technique

Cobalt silicide samples were prepared by arc-melting elemental cobalt (99.9+% Co, Johnson Matthey) and silicon (99.9999% Si, metals basis, Alfa Products) on a water-cooled copper hearth under an argon atmosphere. Sample weight loss due to arc-melting was less than 0.5%. The resulting ingots were crushed in a tool steel mortar and annealed for 6 h in a vacuum induction furnace. The temperatures were kept at about 100 K below the respective eutectic temperature for each sample. The annealed samples were ground in an agate mortar and subjected to X-ray powder diffraction experiments. The observed X-ray diffraction patterns were compared to patterns computed[14] from structural data in the literature.[15] At a given temperature and at equilibrium the thermodynamic activities of both cobalt and silicon will be fixed and independent of sample composition within the respective two-phase region. Hence, in simple Knudsen effusion experiments the presence of the two desired phases in equilibrium in the sample is a necessary and a sufficient condition for a successful experiment. Diffraction peaks that belong to both phases must appear in the diffraction pattern. In the case of reactive Knudsen effusion a second reactant ($SiO_2(s)$) must be added to the sample. Its amount relative to the amount of the material under investigation is not completely arbitrary and should be the same for all samples. Following Chart[16] we chose to use stoichiometric amounts of the silicide and SiO_2, respectively. To be able to prepare the stoichiometric mixtures the composition of the silicide samples must be known. A two-phase Rietveld refinement of the X-ray patterns was performed using the PC GSAS package[17] and the phase composition of some of the silicide samples determined.

Two series of experiments were performed with nonidentical samples. The samples of the first series had nominal compositions 60.1 and 39.9 mol % Si, respectively. Second series samples had nominal compositions 60.0 and 42.8 mol % Si, respectively, whereas the compositions obtained from the Rietveld refinement were 60.5 and 42.2 mol % Si, respectively. This indicates that arc-melting does not lead to significant composition changes which is consistent with the low sample weight loss during arc-melting. Sample characteristics as well as the type of experiments performed with each sample are summarized in Table 1. As a result of these sample preparation procedures, samples were obtained with known compositions within the $CoSi-CoSi_2$ and $Co_2Si-CoSi$ two-phase regions, respectively. Silicide samples for reactive effusion were then mixed with a stoichiometric (in terms of eqs 1 and 2, see below) amount of SiO_2(99.9% SiO_2, metals basis, Alfa Products). To maximize the interfacial area between the silicide and silica the samples were compacted in a $^1/_2$ in. steel dye under a pressure of 800 MPa.

Table 1. Cobalt Silicide Sample Characteristics

sample composition	mol % Si		temp (K)	experiment type[b]
	nominal	determined		
$CoSi/CoSi_2$	60.1		1190−1450	RE
$CoSi/CoSi_2$	60.0	60.5/RR	1190−1450	RE
$Co_2Si/CoSi$	39.9		1280−1450	RE
			1450−1560	SE
$Co_2Si/CoSi$	42.8	42.2/RR	1280−1450	RE
			1470−1540	SE

[a] RR, Rietveld refinment. [b] RE, reactive Knudsen effusion; SE, simple Knudsen effusion.

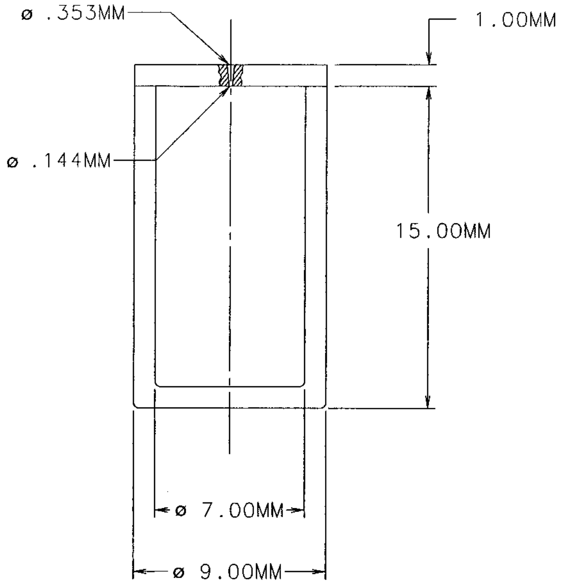

Figure 1. Fused silica glass Knudsen cell.

The Knudsen cell assembly used for the reactive effusion experiments consisted of a cylindrical molybdenum holder and a fused silica Knudsen cell that could be inserted inside the molybdenum part producing a tight fit. The current design of the Knudsen cell was arrived at after a series of experiments with different designs that revealed severe problems with achieving thermodynamic equilibrium within the cell. Similar problems were reported earlier.[10] To decrease the ratio of the effective orifice area to the sample surface area and, thus, approach the equilibrium more closely, a fused silica cell with an extremely small orifice was proposed that would also address any sample-container material compatibility concerns. The cell was manufactured by Quartz Scientific, Inc., and is depicted in Figure 1. The bottom part of the Knudsen cell was a flat bottom cup, 15 mm high, with an outside diameter of 9 mm and inside diameter of 7 mm. The top of the cup was cut flat and ground to ensure a good seal with the lid. The lid was a fused silica disk, 1 mm thick, with the effusion orifice in the center. The effusion orifice was a conical channel resulting from a failed attempt to manufacture a cylindrical channel orifice by a laser beam. The average dimensions of the two openings were 0.144 ± 0.007 and 0.353 ± 0.009 mm, respectively. They were determined by measuring a microphotograph of both sides of each lid taken with an optical microscope before every experiment. The Clausing factor, K_c, for this orifice was determined by interpolation from published

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data[18] and is equal to 0.41 making the effective orifice area 0.0067 mm^2, which is comparable to parameters achieved earlier with a more complicated cell design.[19] Individual orifices differed from each other insignificantly. The orifice was used in the diverging direction, i.e., with the smaller opening facing the sample. The cell was filled with the sample and placed into a copper heat sink. The ground top was carefully cleaned from any mechanical impurities such as the remains of the sample, etc. The lid was then placed on top of the cup and was welded to the latter by an oxygen-gas microtorch while being lightly pushed down with a graphite rod. Obtaining a good seal between the lid and the cup is essential. Any imperfections increase the effective area through which the effusate can escape from the Knudsen cell and, thus, render the small orifice ineffective.

The simple effusion Knudsen cell assembly consisted of a molybdenum cell with cylindrical effusion orifice 1.3 mm long and 0.5 mm in diameter. The sample was contained in a round-bottom fused silica cup, 13 mm high, with an inside diameter of 5 mm and an outside diameter of 7 mm that was placed inside the molybdenum part.

All vaporization experiments were performed using a Nuclide Model 12-90-HT mass spectrometer.[20] This is a magnetic deflection instrument in which a molecular beam effusing from a Knudsen cell at high temperature is directed into an electron impact (EI) ionization source. The positive ions formed by EI are electrostatically accelerated and brought into focus on a channeltron detector by a tunable magnetic field. A shutter operated via a linear motion feedthrough attached to a computer-controlled stepper motor was placed in the system between the Knudsen cell and the EI source, permitting automatic background measurements. The difference between the readings obtained with the beam shutter open and closed, respectively, gives the desired ion intensity and is a function of the electron kinetic energy in the EI source. Measurements of ion intensity due to SiO(g) and Co(g) were made using electron energies of 15 and 20 eV, respectively, which were found to give the best shutter open to shutter closed signal ratios. The progress of every experiment is fully computer controlled, including temperature control, beam shutter operation, and data aquisition. The temperature of the Knudsen cell was determined by a type K thermocouple inserted into the bottom of the molybdenum holder or the bottom of the molybdenum Knudsen cell, respectively. The thermocouple was calibrated in situ by sighting an optical pyrometer directly into the effusion orifice through a calibrated viewport. The extremely small size of the reactive effusion orifice made accurate pyrometer readings somewhat difficult.

In a Knudsen effusion mass spectrometry experiment, the vapor pressure of the ith species, p_i, is related to the observed ion intensity, I_i, via the relation $p_i = k_i I_i T$ where the proportionality factor, k_i, must be determined by calibration. The value of k_{SiO} for the reactive effusion experiments was obtained by comparison of SiO(g) ion intensities measured over a stoichiometric Si(s) + SiO$_2$(s) mixture versus temperature to vapor pressure data calculated from published[21] standard entropies at 298 K, heat capacities and standard enthalpies of formation at 298 K of Si(s), SiO$_2$(s), and SiO(g). The factor k_{Co} for simple effusion was calculated by measuring Co(g) ion intensities versus temperature over elemental cobalt and comparing to literature vapor pressure data.[22]

Thermodynamic Calculations

The thermodynamic analysis of the vapor pressure data was based upon the assumption that the intermediate silicide phases Co$_2$Si, CoSi, and CoSi$_2$ are stoichiometric. That is true for CoSi$_2$, and it is a very good approximation for Co$_2$Si and CoSi which exhibit narrow homogeneity ranges of 33.0−33.6 mol % Si between 700 and 1000 °C and 49.0−50.6 mol % Si between 800 and 1000 °C, respectively.[23] The following high-temperature vaporization reactions were considered.

For the reactive effusion:

$$\mathrm{CoSi_2(s) + SiO_2(s) \rightarrow 2SiO(g) + CoSi(s)} \qquad (1)$$

$$\mathrm{2CoSi(s) + SiO_2(s) \rightarrow 2SiO(g) + Co_2Si(s)} \qquad (2)$$

The following reference reaction was also considered:

$$\mathrm{Si(s) + SiO_2(s) \rightarrow 2SiO(g)} \qquad (3)$$

For simple effusion:

$$\mathrm{Co_2Si(s) \rightarrow Co(g) + CoSi(s)} \qquad (4)$$

The following reference reaction was also considered:

$$\mathrm{Co(\alpha) \rightarrow Co(g)} \qquad (5)$$

The temperature range covered was 1190−1450 and 1420−1560 K for reactive and simple effusion experiments, respectively. Standard enthalpy and entropy changes ($\Delta_r H°_T$ and $\Delta_r S°_T$) can be determined for T within the experimental temperature interval from least-squares fits of log(p/p_0) versus $1/T$ according to the equation

$$\log\frac{p_{\text{SiO}}}{p_0} = \frac{\Delta_r S°_T}{2 \times 2.303R} - \frac{\Delta_r H°_T}{2 \times 2.303R}\frac{1}{T}$$

for reactions 1 and 2 and according to the equation

$$\log\frac{p_{\text{Co}}}{p_0} = \frac{\Delta_r S°_T}{2.303R} - \frac{\Delta_r H°_T}{2.303R}\frac{1}{T}$$

for reaction 4, assuming that both $\Delta_r H°_T$ and $\Delta_r S°_T$ are constant over the experimental temperature interval. The standard pressure, p_0, is 1 bar. Using these values, the Gibbs free energy change for each of the reactions 1, 2, and 4 can be computed at the temperature T*, which approximately corresponds to the average of experimental $1/T$ values. T^* was selected to be 1350 K for reactions 1 and 2 and 1500 K for reaction 4 according to the equation

$$\Delta_r G°_{T^*} = \Delta_r H°_T - T^* \Delta_r S°_T$$

Standard enthalpy changes at 298 K ($\Delta_r H°_{298}$) for all three reactions are then derived by the third-law method from the Gibbs free energy changes for the high-temperature reactions:

$$\Delta_r H°_{298} = \Delta_r G°_{T^*} + T^* \Delta_r \Phi'_{T^*}$$

where $\Delta_r \Phi'_{T^*}$ is the change in the "free energy function" for the reaction defined as

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$$\Delta_r\Phi'_T = -\Delta_r\left(\frac{G°_T - H°_{298}}{T}\right)$$

Its evaluation for reactions 1, 2, and 4 requires heat capacity data for $CoSi_2$(s), SiO_2(quartz), and SiO(g) from 298 to 1350 K and for Co_2Si(s), CoSi(s), and Co(g) from 298 to 1500 K as well as standard molar entropies at 298 K as can be seen from the following equation:

$$\Delta_r\Phi'_T = \Delta_r S°_{298} + \int_{298}^{T}\frac{\Delta_r C_p}{T}\,dT - \frac{1}{T}\int_{298}^{T}\Delta_r C_p\,dT$$

Standard molar entropies at 298 K of CoSi(s) and $CoSi_2$(s) were obtained from Kalishevich et al.[11,13] In the absence of low-temperature heat capacity data for Co_2Si(s) the value of $S°_{298}$ for Co_2Si(s) was estimated by linear interpolation on a mole of atoms basis between the values for CoSi(s) and Co(s), with the latter obtained from *JANAF Tables*.[22] High-temperature heat capacities of the cobalt silicides were obtained from Frolov et al.[10] and Kalishevich et al.[11,12] Standard molar entropy of Co(g) at 298 K was taken from ref 22. Standard molar entropies of SiO_2(quartz) and SiO(g) at 298 K were taken from *Thermodynamic Properties of Individual Substances*.[21] Heat capacity data for Co(g) were obtained from ref 22, and those for SiO_2(quartz) and SiO(g) from ref 21.

Standard enthalpy changes at 298 K for the reference reactions 3 and 5 were calculated using standard enthalpy of formation at 298 K values for Co(g) from ref 22 and SiO_2(quartz) and SiO(g) from ref 21. Standard enthalpies of formation of the intermediate silicide phases Co_2Si, CoSi, and $CoSi_2$ were found by a Hess' law combination of $\Delta_r H°_{298}$ values of reactions 1, 2, and 4 and the reference reactions 3 and 5.

All thermochemical parameters used in the calculations are summarized in Table 4.

Results and Discussion

The attainment of a steady state within the cell that closely approaches thermodynamic equilibrium was demonstrated by measuring SiO(g) ion intensities with different amounts of the Si(s)−SiO_2(s) stoichiometric mixture in the Knudsen cell. Within the experimental error, the ion intensities did not depend upon the amount of the sample, which varied from 0.0903 g through 0.2076 g to 0.4585 g. Hence, the ratio of the effective orifice area to the sample surface area was sufficiently small that the measured ion intensities could be related to the equilibrium partial pressures. Two different silicide samples were studied by reactive effusion in every two-phase region considered using sample amounts that differed by a factor of 2. The SiO(g) partial pressures measured in the first and second experiment, respectively, agreed within the experimental error, thereby justifying the equilibrium assumption for the silicide samples as well.

Two series of vapor-pressure measurements were performed. Each series consisted of a reactive effusion calibration run with a Si(s) + SiO_2(s) mixture, two reactive effusion experiments (in the Co_2Si/CoSi and CoSi/$CoSi_2$ two-phase regions), a simple effusion calibration run with Co(s), and a simple effusion experiment in the Co_2Si/CoSi two-phase region. The results are presented in the log(p/p_0) vs $1/T$ plots in Figure 2a,b. A least-squares analysis of the vapor pressure data yielded the standard reaction enthalpy and entropy changes for the high-temperature vaporization reactions 1, 2, and 4. Significant differences between the $\Delta_r H°_{T*}$ and the $\Delta_r S°_{T*}$ values obtained from series 1 and 2, respectively, are due to the shortness of the experimental temperature interval (ca. 270 K for reaction 1, ca. 170 K for reaction 2, and only ca. 100 K for reaction 4) and strongly support the analysis of the data by the third-law method. The standard reaction Gibbs free energy changes were then obtained at 1350 K for reactions 1 and 2 and at 1500 K for reaction 4. The agreement in $\Delta_r G°_{T*}$ values between series 1 and 2, respectively, is excellent. All high-temperature thermodynamic functions for reactions 1, 2, and 4 are presented in Table 2. The third-law treatment of the average $\Delta_r G°_{T*}$ from the two experiment series yielded the standard reaction enthalpy changes at 298 K, which, together with the standard reaction enthalpy changes at 298 K for the reference reactions 3 and 5, are also presented in Table 2. The standard enthalpy of formation at 298 K of the three intermediate silicide phases as determined by a Hess' law combination of $\Delta_r H°_{298}$ values for reactions 1−5 are presented in Table 3, together with data previously reported in the literature. The uncertainties of ±2.0 kJ mol^{-1} of atoms originate from the errors in the least-squares estimates of $\Delta_r G°_{T*}$ values for reactions 1, 2, and 4 shown in Table 2 and from uncertainties in the Knudsen cell temperature determinations estimated to be ±5 K.

The conversion of the experimental high-temperature standard reaction Gibbs free energy changes to standard reaction enthalpy changes at 298 K requires heat capacity and standard molar entropy data. Hence, the values used in our calculations are presented in Table 4. Standard enthalpies of formation at 298 K of Co(g), SiO_2(quartz), and SiO(g) employed in calculations of $\Delta_r H°_{298}$ for the reference reactions 3 and 5 have also been included in Table 4.

A comparison of the present results with data reported in literature is given in Table 3 and Figure 3. The agreement of our values of $\Delta_f H°_{298}$ with the direct calorimetry measurements of Oelsen et al.[10] is excellent, a somewhat surprising result given the nature of the earlier technique. The differences do not exceed 3.0 kJ mol^{-1} of atoms with the uncertainties on the order of ±4.0 and ±2.0 kJ mol^{-1} of atoms, respectively. The agreement with assessed data of Chart[5] and Chandrasekharaiah[8] is good, which is not surprising since both assessments were based largely on data taken from Oelsen et al. The agreement with modeled results of Machlin[6] for CoSi and $CoSi_2$, Pasturel et al.[6] for CoSi and $CoSi_2$, and Niessen et al.[6] for Co_2Si and CoSi is acceptable. The values of Pasturel for Co_2Si and Niessen et al. for $CoSi_2$ are quite different from the results reported here. All data of Kaufman[6] are about twice as large in magnitude and more negative than our results. This indicates that, although yielding reasonable results in some cases, the various models used for $\Delta_f H°_{298}$ predictions are in need of improvement.

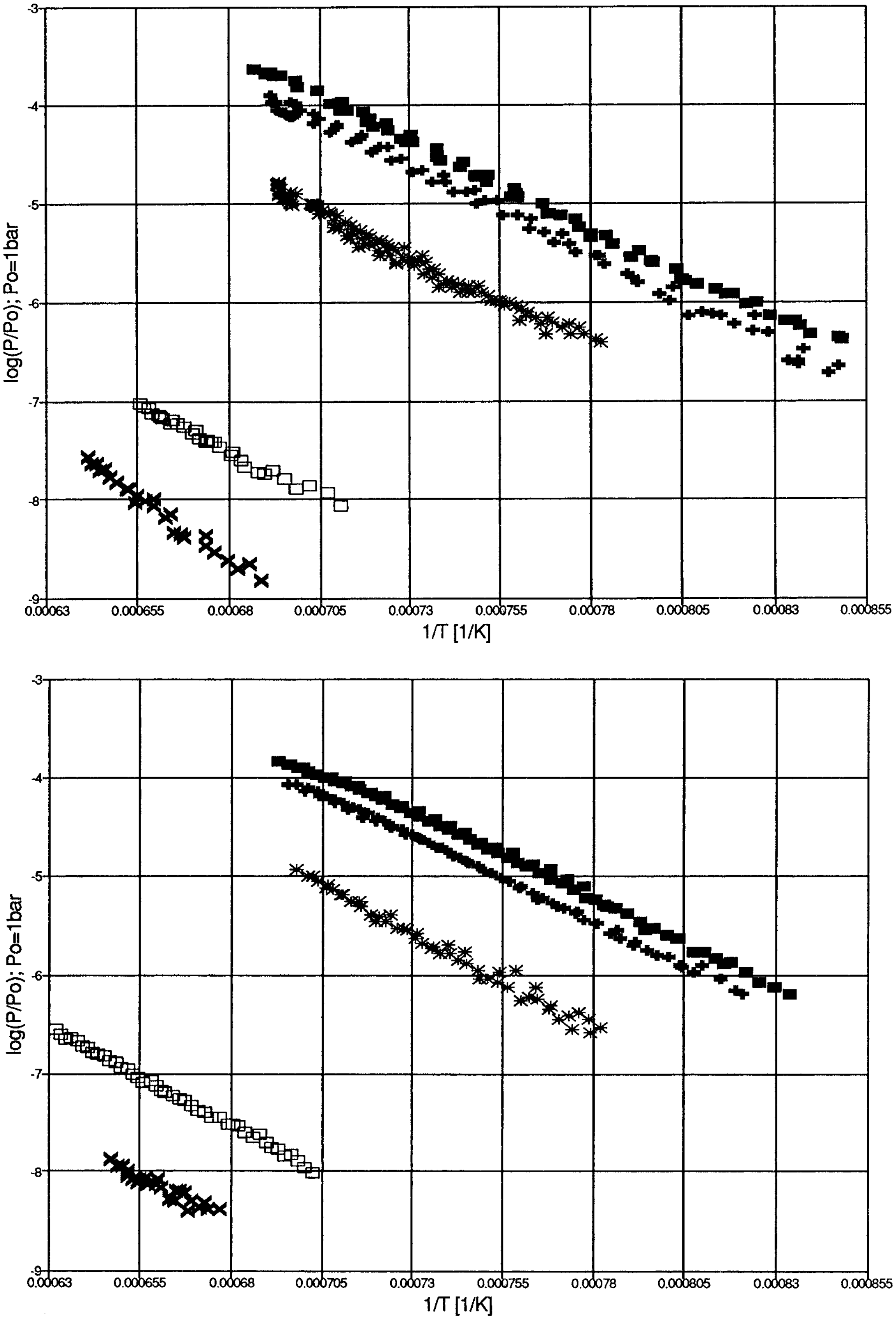

Figure 2. (a, top) Measured vapor pressures Over Co–Si alloys; series 1: (■) Si(s) + SiO_2(s) → 2SiO(g); (+) $CoSi_2$(s) + SiO_2(s) → 2SiO(g)+CoSi(s); (*) 2CoSi(s) + SiO_2(s) → 2SiO(g) + Co_2Si(s); (□) Co(s) → Co(g); (×) Co_2Si(s) → Co(g) + CoSi(s). (b, bottom) Measured vapor pressures over Co–Si alloys; series 2: (■) Si(s) + SiO_2(s) → 2SiO(g); (+) $CoSi_2$(s) + SiO_2(s) → 2SiO(g) + CoSi(s); (*) 2CoSi(s) + SiO_2(s) → 2SiO(g) + Co_2Si(s); (□) Co(s) → Co(g); (×) Co_2Si(s) → Co(g) + CoSi(s).

Engqvist et al.[24] have shown in the case of $TiSi_2$ deposition that the CVD models are extremely sensitive to the thermodynamic data employed in the computations. Even though the proposed adjustments to the thermodynamic parameters of cobalt silicides are relatively small, there may be important implications for

Table 2. Thermodynamic Parameters of Vaporization Reactions

	$\Delta_rH°_T$/kJ mol^{-1}	$\Delta_rS°_T$/J K^{-1} mol^{-1}	$\Delta_rG°_{T^*}$/kJ mol^{-1}	$\Delta_rH°_{298}$/kJ mol^{-1}
reactive effusion ($T^* = 1350$ K)				
$Si(s) + SiO_2(s) \rightarrow 2SiO(g)$				713.0 ± 2.0[21]
$CoSi_2(s) + SiO_2(s) \rightarrow 2SiO(g) + CoSi(s)$				
series 1	676.1 ± 5.3	315.7 ± 3.9	249.9 ± 3.2	
series 2	661.8 ± 3.1	306.8 ± 2.3	247.7 ± 1.2	
average			248.8 ± 2.2	717.2±2.2
$2CoSi(s) + SiO_2(s) \rightarrow 2SiO(g) + Co_2Si(s)$				
series 1	690.1 ± 8.3	291.2 ± 6.1	297.0 ± 3.2	
series 2	737.6 ± 12.6	324.7 ± 9.3	299.3 ± 2.9	
average			298.1 ± 3.1	779.2 ± 3.1
simple effusion ($T^* = 1500$ K)				
$Co(s) \rightarrow Co(g)$				426.7 ± 2.1[22]
$Co_2Si(s) \rightarrow Co(g) + CoSi(s)$				
series 1	499.5 ± 14.3	174.7 ± 9.6	237.5 ± 1.5	
series 2	325.4 ± 24.4	58.6 ± 16.3	237.4 ± 1.5	
average			237.5 ± 1.5	455.2 ± 1.5

Table 3. Standard Enthalpies of Phase Formation $\Delta_fH°_{298}$ (kJ mol^{-1})

	$^1/_3Co_2Si$	$^1/_2CoSi$	$^1/_3CoSi_2$	method[a]
this work	−41.0 ± 2.0	−47.3 ± 2.0	−32.9 ± 2.0	KREMS/KEMS
Oelsen et al.[9]	−38.5 ± 4.0	−50.2 ± 4.0	−34.3 ± 4.0	DRC
Chart[5]	−37.7	−47.5	−32.8	ASD
Kaufman[6]	−58.9	−72.4	−67.0	MOD
Machlin[6]		−44.4	−39.5	MOD
Pasturel et al.[6]	−33.1	−44.8	−34.7	MOD
Niessen et al.[6]	−38	−48	−15	MOD
Chandrasekharaiah et al.[8]			−32.8	ASD

[a] KREMS, Knudsen reactive effusion mass spectrometry. KEMS, Knudsen effusion mass spectrometry. DRC, direct reaction calorimetry. ASD, assessed. MOD, modeled.

Table 4. Literature Heat Capacity Parameters,[a] Standard Entropies and Standard Enthalpies of Formation

	Co(g)	$Co_2Si(s)$	CoSi(s)	$CoSi_2(s)$	Si(s)	$SiO_2(\alpha/\beta\text{-quartz})$[b]	SiO(g)
A	27.0146	70.785	49.16	70.86	23.698	−122.698/58.422	27.1584
10^3B	−0.6434	27.138	12.1	18.66	3.305	592.567/10.326	13.5863
$10^{-5}C$	3.4343	7.32900	7.54000	9.93000	4.351	−29.755/−1.927	0.8117
10^6D	0.3372	0	0	0	0	−367.971/0	−4.8826
10^9E	0	0	0	0	0	−558.489/0	0
$10^{12}F$	0	0	0	0	0	590.415/0	0
$S°_{298}$/J K^{-1} mol^{-1}	179.52 ± 0.01	73.3 ± 6.0	43.2 ± 6.0	64.2 ± 6.0	18.810 ± 0.080	41.46 ± 0.20	211.597 ± 0.010
$\Delta_fH°_{298}$/kJ mol^{-1}	426.7 ± 2.1					−910.7 ± 1.0	−98.8 ± 2.0

[a] c_p/J K^{-1} mol^{-1} = $A + BT - C/T^2 + DT^2 + ET^3 + FT^4$. [b] α-quartz 298.15−848 K; β-quartz 848−1696 K.

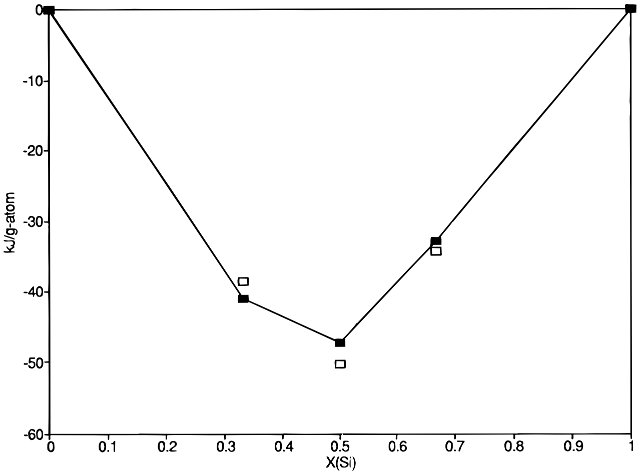

Figure 3. Enthalpies of formation, $\Delta_fH°_{298}$, of cobalt silicides, $Co_{1-x}Si_x$: (□) Oelsen et al.;[7] (■) this work.

processing. For example, Murarka and Vaidya[25,26] have studied the properties of cosputtered cobalt silicides on silicon and silicon dioxide substrates. Among other observations they note that when $CoSi_2$ deposited on silicon dioxide is sintered in an inert ambient at temperatures above 1000 °C, it undergoes decomposition to CoSi and silicon which is "lost in the furnace".[26] As pointed out above, the partial vapor pressure of silicon above a two-phase mixture of $CoSi_2$ and CoSi is much too low to account for this observation. However, at 1400 K, the partial pressure of SiO is of the order of 10^{-6} atm, which may provide a mechanism for the loss of silicon.

Generally, it is found that there is a correlation between the magnitude of the standard enthalpy of formation at 298 K and the melting point of an intermediate compound. In first-row transition-metal silicides, only those of manganese do not obey this general rule. Cobalt silicides are seen to conform to the rule by considering their melting points $T_m(Co_2Si) = 1334$ °C, $T_m(CoSi) = 1460$ °C, $T_m(CoSi_2) = 1326$ °C, and their standard enthalpies of formation $\Delta_fH°_{298}(^1/_3Co_2Si) = -41.0$ kJ mol^{-1}, $\Delta_fH°_{298}(^1/_2CoSi) = -47.3$ kJ mol^{-1}, and $\Delta_fH°_{298}(^1/_3CoSi_2) = -32.9$ kJ mol^{-1}.

Conclusion

The thermodynamic stabilities of three intermediate cobalt−silicon phases have been measured by applying the reactive Knudsen effusion mass spectrometry method

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(24) Engqvist, J.; Myers, C. E.; Carlsson, J. O. *J. Electrochem. Soc.* **1992**, *139*, 3197−3205.

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(26) Murarka, S. P. *Thin Solid Films* **1986**, *140*, 35.

to the CoSi–$CoSi_2$ and Co_2Si–CoSi two-phase regions. Simple Knudsen effusion mass spectrometry was used to study the Co_2Si–CoSi two-phase region. The standard enthalpies of formation of Co_2Si, CoSi, and $CoSi_2$ at 298 K were obtained from a combination of the experimental data with published heat capacity and published and estimated standard molar entropy values. Results are compared to literature stability data, and implications for processing of $CoSi_2$ in thin films are suggested.

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