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REACTION OF THIN METAL FILMS WITH SiO_2 SUBSTRATES†

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Abstract—Thin films of Co, Cr, Cu, Fe, Hf, Mn, Nb, Ni, Pd, Pt, Ti, V and Zr vacuum-deposited on SiO_2 substrates of thermally oxidized Si wafers and/or fused quartz were annealed under vacuum at about 800°C for 3 hr and then analyzed by backscattering spectrometry and scanning electron microscopy. It is found that Hf, Nb, Ti, V and Zr react with SiO_2. The result is a thin layer of metal silicide sandwiched between the substrate and a top layer of metal oxide. The other investigated metals apparently do not react. A table of the standard heats of formation for metal silicides has been compiled. These values were used to calculate the free energy change during reaction. The thermodynamic predictions are consistent with experimental observation. The results can also be correlated with the mean electronegativity of the metal, which offers a convenient empirical method to predict whether a metal will react with SiO_2. It is found that metals with an average electronegativity (average of Allred–Rochow, relative compactness and Pauling electronegativities) of less than 1.5 on the Pauling scale react with the SiO_2 substrate.

INTRODUCTION

Metallization schemes are of importance for bonding purposes in the ceramics industry and for creating contact layers and durable electrically conducting paths on insulating substrates for semiconductor devices. There are, however, many factors that affect the adherence of metal layers to a substrate. Tungsten, for instance, is often used for metallizing integrated circuits because its coefficient of expansion closely matches that of silicon, while titanium is used because of its strong adherence to oxides[1]. It has been suggested that strong adherence between certain metals and oxides is the result of a chemical reaction which can be predicted using thermodynamic data[2, 13].

The reaction of thin Ti, V and Nb films of a few thousand Angström with SiO_2 substrates has been investigated previously using Rutherford backscattering of 2 MeV ^4He particles and glancing angle X-ray diffraction[3–5]. In each case, a metal rich silicide and a metal oxide are formed. Although the silicide was identified, no identification of the oxide was made. An interesting result of these investigations was that the silicide layer is always in contact with the SiO_2 substrate after annealing, while the metal oxide is at the surface of the sample.

In this work, we have investigated the chemical reaction of a series of transition metals (Co, Cr, Cu, Fe, Hf, Mn, Nb, Ni, Pd, Pt, Ti, V and Zr) with SiO_2 substrates at temperatures of 800°C using Rutherford backscattering and scanning electron microscopy (SEM) as the primary analytical tools. We have tried to correlate the results with the adherence of the metallization layer to the SiO_2 substrate and have also calculated the heats of reaction between metals and SiO_2 which lead to the formation of silicides and oxides. Because of the difficulty in identifying the oxides, the heats of reaction were calculated for all combinations of metal oxides and silicides for which heats of formation data were available.

EXPERIMENTAL PROCEDURE

Silicon dioxide substrates were prepared by thermal oxidation of polished single crystal Si wafers at 1100°C in wet oxygen with SiO_2 thickness ranging from 2000 to 3000 Å. Commercially available quartz substrates obtained from Amersil were also used. Both types of substrates were first lightly etched in dilute *HF* and thoroughly rinsed in deionized water before electron-gun evaporation of the desired metal in a oil-free vacuum of approx. 5×10^{-7} torr. After evaporation, the samples were annealed in a quartz-tube furnace evacuated to better than 5×10^{-6} torr. Annealing was carried out at 800°C for times ranging from 2 to 4 hr. All samples were analyzed by Rutherford backscattering of 2 MeV ^4He[6], and the lateral uniformity of the samples was determined by optical and scanning electron microscopy.

RESULTS AND DISCUSSION

Titanium, zirconium, and hafnium (group IVB in the periodic table), and vanadium and niobium (group VB in the periodic table) all reacted with the SiO_2 substrate. Assuming that the reaction products are a metal silicide and a metal oxide, the chemical reaction can be expressed as:

$$SiO_2 + M_x = M_ySi + M_{x-y}O_2 \quad (1)$$

where M is the metal. Kräutle *et al.*[5] have shown that

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in the case of V, the silicide formed is V_3Si. The chemical nature of the metal oxide has not been determined and is probably complex. As long as unreacted metal is in ample supply, the reaction proceeds at a linear rate in time. The vanadium silicide forms towards the substrate side of the metal film, while the metal oxide forms on the surface. We found that this was true for all the metals which reacted. In addition, we have analyzed an annealed Ti film by Auger electron spectroscopy to establish depth profiles of Ti, O and Si for a sample case. The results confirmed the interpretation of the reaction described above, except that some oxygen was found uniformly distributed throughout the silicide layer. Whether this indicates the presence of a mixed phase of silicide and oxide of Ti, or the existence of a ternary compound is not clear. For the latter, eqn (1) is incorrect, but the relatively small amount of oxygen present would not materially alter the conclusions drawn below. The layers containing the reaction products in all cases were rather uniform and maintained adhesion to the substrate during and after annealing. All the metal films deposited on fused quartz behaved identically to those deposited on thin SiO_2 layers on Si.

Typical backscattering spectra of Cr on fused quartz and of V on a Si/SiO_2 substrate before and after annealing are shown in Fig. 1. The dashed line is the spectrum before annealing. In the case of Cr (see Fig. 1(a)), the backscattering spectra before and after annealing are indistinguishable, thereby indicating that there is no detectable reaction between the Cr and SiO_2. The depth resolution of these backscattering spectra are, however, about 200 Å, and it is conceivable that some chemical or physical changes may have taken place at depths less than 200 Å. In the case of vanadium, there is a significant change in the backscattering spectrum after annealing (see Fig. 1(b)), indicating reaction between V and SiO_2. For ease of interpretation, various areas under the energy spectra, which correspond to different layers, have been shaded. The formation of two distinct layers (V_3Si and VO_x) and the remaining part of the SiO_2 can readily be distinguished. The movement of part of the oxygen signal to the surface position of oxygen after annealing, shows that the vanadium oxide layer is on the surface of the sample.

The metals of the first transition period to the right of vanadium, i.e. Cr, Mn, Fe, Co, Ni and Cu, as well as Pd and Pt showed no signs of reacting with SiO_2. With the exception of Cr, these metals tended to coalesce or to "ball up" into islands on the substrate surface. Figure 2 (top) shows a typical scanning electron micrograph of such a film after annealing. In this case the coalescing of Pd into balls with diameters less than a micron, can clearly be seen. Because of the lateral nonuniformity, the backscattering spectra taken on such samples were difficult to interpret and were of no use in establishing the presence or absence of a reaction. The formation of metallic balls indicates poor adhesion, and our interpretation of this result is that no reaction took place. We cannot exclude the possibility that the metals reacted with the SiO_2 substrate over very shallow depths, but the interpretation of the results given below is more consistent with the idea that a reaction does not actually take place. That the islands as seen in Fig. 2 (top) consist of essentially pure metal and do not contain substantial amounts of oxide or silicide was established by electron microprobe analysis. The bottom part of Fig. 2 shows an SEM micrograph for a metal (Zr) which has reacted with SiO_2. In such cases it can be seen that no "balling up" has taken place and that the layer is rather uniform, except for some slight rugosity of the surface.

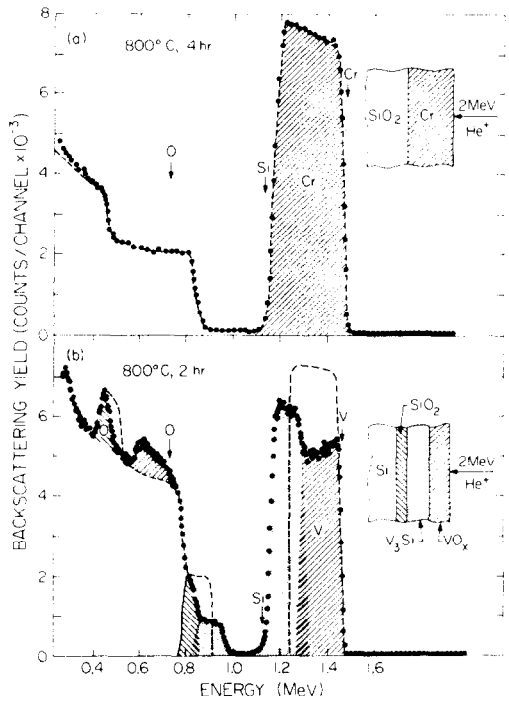

Fig. 1. Rutherford backscattering spectra measured with 2 MeV $^4He^+$ particles. The arrows show the energy of particles scattered from surface atoms of the corresponding element. (a) 2700 Å Cr on a fused quartz substrate measured before annealing (dashed line) and after annealing (closed dots) at 800°C, for 4 hr. The fact that there is no difference between these spectra indicates that no detectable chemical reaction has taken place between Cr and SiO_2. (b) 2100 Å V on a thermally oxidized silicon wafer (Si/SiO_2) measured before (dashed line) and after annealing (closed dots), at 800°C for 2 hr. Chemical reaction between V and SiO_2 can clearly be seen. The V_3Si may contain some O_2.

It is of interest to know how our results correlate with thermodynamic considerations. The reaction between the metal layer and SiO_2 takes place at constant temperature and pressure, and the change in the Gibbs free energy ΔG, is thus given by:

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

where ΔH is the change in enthalpy (or heat of reaction) during the reaction at temperature T, and ΔS is the change in entropy. In our case, the annealing temperature is usually well below the melting points of the reactants or products so that the volume changes are negligibly small. For such reactions in the solid state, $\Delta S \simeq 0$, and the change in Gibbs free energy ΔG is thus approximated by the change in enthalpy ΔH, during the

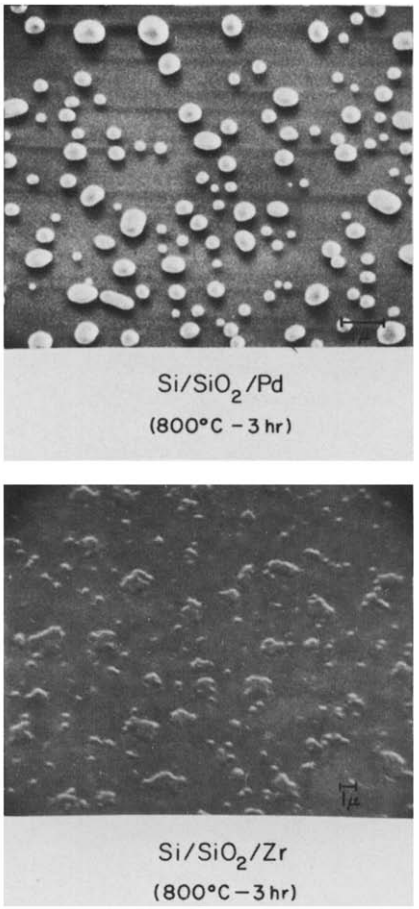

Fig. 2. Secondary electron micrographs of Pd (top) and Zr (bottom) on a Si/SiO_2 substrate. In the case of Pd no reaction has taken place and the metal has coalesced into balls of metal less than 1 μm in diameter. In the case of Zr reaction has taken place and a rather uniform layer with slight wrinkles is formed.

reaction[7, 8]. If ΔG (or ΔH in this case) is less than zero, reaction between the metal and SiO_2 is thermodynamically possible.

The heats of reaction (ΔH) for a certain system is given by the difference between the enthalpy of the products at temperatures T and the enthalpy of the reactants at the same temperature. Thermodynamic data on metal silicides are difficult to find. A survey of the literature was made and the standard enthalpy $\Delta Hf°$ (or standard heats of formation) of various metal silicides and oxides are given in Table 1. From these values, the standard heat of reaction ($\Delta H°$) at 25°C for one of the reactions that vanadium may, for instance, undergo with SiO_2, can be calculated as follows:

$$\begin{array}{lllll} 13V + 3SiO_2 & \longrightarrow & 3V_3Si + 2V_2O_3 & & (3) \\ 13(0)\ \ 9(-68.5) & & 12(-6.8)\ \ 10(-60.0) & & \\ \therefore\ \Delta H° = -65.1/22 = -3.0\ \text{kcal/gatom}. & & & & \end{array}$$

Because $\Delta H°$ is negative, this reaction is thermodynamically expected to occur. Heats of reaction were calculated for all possible combinations of silicides for which heat formation data were available. As an example, the calculated standard heats of reaction for vanadium are given in Table 2. If the value of −71.9 kcal/gatom rather than −68.5 kcal/gatom is used

Table 1. Standard heats of formation $\Delta Hf°$ of silicides and oxides at 25°C (kcal/gatom)

Element	Compound	Silicides $\Delta Hf°$	References†	Compound	Oxides $\Delta Hf°$	References†
Ca	Ca_2Si	−38.7	*g*	CaO	−75.7	*d, g*
				CaO_2	−52.2	*d, g*
Co	Co_2Si	−9.2	*a, i, k, l*	CoO	−28.6	*a, d, g, i, k*
	CoSi	−12.0	*a, g, i, k, l*	Co_3O_4	−30.0	*a, d, g, i, k*
	$CoSi_2$	−8.2	*a, i, k, l*			
	$CoSi_3$	−6.4	*i, k*			
Cr	Cr_3Si	−8.3	*b, g, j, k, l*	Cr_2O_3	−53.9	*a, d, g, i*
	Cr_5Si_3	−9.8	*b, g, j, k, l*	CrO_2	−46.3	*a, g*
	CrSi	−9.5	*b, g, j, k, l*	CrO_3	−34.2	*a, g*
	$CrSi_2$	−9.6	*b, g, j, k, l*			
Fe	Fe_3Si	−5.6	*k*	FeO	−31.8	*a, d, f, g, i, k*
	Fe_5Si_3	−4.6	*a*	Fe_3O_4	−38.1	*a, d, f, i, k*
	FeSi	−9.6	*a, g, h, k, l*	Fe_2O_3	−39.3	*a, d, f, g, i, k*
	$FeSi_2$	−5.6	*a, g, k, l*			
Hf	Hf_5Si_3	−27.4	*a*	HfO	+6.0	*k*
				HfO_2	−89.3	*a, d, k*
Ir	IrSi	−8.0	*j*	IrO_2	−15.3	*a, d, g, i*
	$IrSi_2$	−6.1	*j*			
	$IrSi_3$	−4.6	*j*			
La	LaSi	+15.0	*g*	LaO (gas)	−14.9	*g*
	$LaSi_2$	+14.8	*g*	La_2O_3	−85.8	*d, g*
Mg	Mg_2Si	−6.2	*f, g, l*	MgO	−71.8	*d, f, g*
				MgO_2	−49.6	*d*
Mn	Mn_3Si	−6.8	*c, g*	MnO	−46.0	*a, d, i, k*
	Mn_5Si_3	−6.0	*a, c, g*	Mn_3O_4	−47.3	*a, d, g, i, k*
	MnSi	−13.3	*c, g*	Mn_2O_3	−46.4	*a, d, g, i, k*
	$MnSi_2$	−2.6	*c*	MnO_2	−41.5	*a, d, g, i, k*
				Mn_2O_7	−19.3	*a, g*
Mo	Mo_3Si	−5.8	*a, g, j, k, l*	MoO_2	−43.3	*a, d, f, g, i*
	Mo_5Si_3	−8.5	*a, g, k, l*	MoO_3	−45.1	*a, d, f, g, i*
	$MoSi_2$	−9.3	*a, g, i, j, k, l*			
Nb	Nb_5Si_3	−7.9	*a, j*	NbO	−58.0	*a, g, i*
	$NbSi_2$	−7.3	*a, j*	NbO_2	−63.7	*a, g, i*
				Nb_2O_5	−66.1	*a, d, g, i*
Ni	Ni_3Si	−8.9	*g, i*	NiO	−29.2	*a, d, g, i, k*
	Ni_5Si_2	−10.3	*i*	Ni_2O_3	−23.4	*k*
	Ni_2Si	−10.5	*a, i, k, l*			
	Ni_3Si_2	−10.7	*a, i*			
	NiSi	−10.2	*a, i, k, l*			
	$NiSi_2$	−6.9	*i*			
Os	OsSi	−7.8	*j*	OsO_2	−20.5	*g*
				OsO_3	−11.4	*i*
				OsO_4	−16.0	*a, d, g, i*
Pd	Pd_2Si	−6.9	*j*	PdO	−10.5	*a, d, i, k*
	PdSi	−6.9	*j*			
Pt	Pt_2Si	−6.9	*j*	PtO	−8.5	*g*
	PtSi	−7.9	*j*	Pt_3O_4	−5.6	*g, k*
				PtO_2	−10.7	*a, g, k*
Re	Re_5Si_3	−4.8	*a, j*	ReO_2	−33.7	*a, g, i*
	ReSi	−5.1	*a, j*	ReO_3	−36.8	*a, g, i*
	$ReSi_2$	−5.5	*a, g, j*	Re_2O_7	−33.3	*a, d, g, i*
				Re_2O_8	−30.8	*d, g*

Table 1. (*Contd*)

Element	Silicides Compound	$\Delta Hf°$	References†	Oxides Compound	$\Delta Hf°$	References†
Rh	RhSi	−8.1	*j*	Rh_2O	−7.6	*d, i*
				RhO	−10.8	*d, i*
				Rh_2O_3	−13.7	*a, d, i*
Ru	RuSi	−8.0	*j*	RuO_2	−17.7	*a, d, g, i*
				RuO_4	−11.5	*g*
Si				SiO_2	−68.5	*d*‡, *f*
Ta	Ta_2Si	−10.1	*a, e, i, j, l*	Ta_2O_5	−71.4	*a, d, g, i*
	Ta_5Si_3	−9.0	*a, e, i, j, l*			
	$TaSi_2$	−8.0	*a, e, g, i, j, l*			
Th	Th_3Si_2	−13.0	*e*	ThO	−72.5	*g*
	ThSi	−14.5	*e*	ThO_2	−97.3	*a, d, g*
	Th_3Si_5	−14.0	*e*			
	$ThSi_2$	−13.9	*a, e, g, i, j*			
Ti	Ti_5Si_3	−17.3	*a, e, i, j, k*	TiO	−67.5	*a, g, i, k*
	TiSi	−15.5	*a, e, g, i, j, k*	Ti_2O_3	−75.0	*a, d, g, i, k*
	$TiSi_2$	−10.7	*a, e, g, i, j, k*	Ti_3O_5	−73.4	*a, d, g, i, k*
				TiO_2	−73.0	*a, d, g, i, k*
U	U_3Si_2	+8.2	*g*	UO_2	−85.0	*a, d, g*
	USi	+10.1	*g*	U_3O_8	−76.8	*a, d, g*
	U_3Si_5	+10.6	*g*	UO_3	−72.8	*a, d, g*
	USi_2	−10.3	*g*			
	USi_3	−10.4	*g*			
V	V_3Si	−6.8	*g, j, k, l*	VO	−53.0	*a, g, i*
	V_2Si	−12.3	*a, g, i, k*	V_2O_3	−60.0	*a, d, g, i*
	V_5Si_3	−12.0	*g, j, k, l*	VO_2	−58.7	*a, g, i*
	VSi_2	−24.6	*g, j, k, l*	V_2O_5	−54.7	*a, d, g, i*
W	W_5Si_3	−5.0	*a, j*	WO_2	−45.4	*d, g, i, k*
	WSi_2	−7.5	*g, j, l*	W_2O_5	−48.3	*d*
				WO_3	−50.2	*d, g, i, k*
Zr	Zr_2Si	−13.0	*e, k*	ZrO	−87.3	*a, d, g, i, k*
	Zr_2Si	−16.7	*a, e, g, i, j, k*			
	Zr_5Si_3	−17.2	*a, e, g, i, j, k*			
	Zr_3Si_2	−18.4	*e, j, k*			
	Zr_6Si_5	−18.6	*e, g, i, k*			
	ZrSi	−18.5	*a, e, i, j, k, l*			
	$ZrSi_2$	−12.7	*a, e, g, i, j, k, l*			

†The given standard heat of formation is from the underlined reference.

‡The value quoted in Ref. *f* is −71.9 kcal/gatom and is to be preferred (comment of a reviewer).

[a]H. J. Goldschmidt, *Interstitial Alloys*. Plenum Press, New York (1967); [b]Yu. M. Golutvin and L. Chin-k'uei, *J. Phys. Chem. U.S.S.R.* **35**, 1 (1961); [c]Yu. M. Golutvin, T. M. Kozlovskyay and E. G. Maslennikova, *J. Phys. Chem. U.S.S.R.* **37**, 6 (1963); [d]*Handbook of Chemistry and Physics* (Edited by R. C. Weast) 52nd Edn. Chemical Rubber Company, Cleveland (1971); [e]R. Hultgren, L. O. Raymond, P. D. Anderson and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys*. Wiley, New York (1963); [f]*JANAF Thermochemical Tables*, 2nd Edn, National Standard Reference Data Service, National Bureau of Standards (U.S.) Vol. 37, June, 1971; [g]M. Kh. Karapet'yants and M. L. Karapet'yants, *Thermodynamic Constants of Inorganic and Organic Compounds*. Ann Arbor-Humphrey Science Publishers, Ann Arbor (1970); [h]K. K. Kelley, *U.S. Bureau of Mines Bulletin* **476** (1949); [i]O. Kubaschewski and J. A. Catterall, *Thermochemical Data of Alloys*. Plenum Press, London (1956); [j]A. W. Searcy and L. N. Finnie, *J. Am. Ceramic Soc.* **45**, 268 (1962); [k]*Selected Values of Chemical Thermodynamic Properties*, Technical Notes 270-3, 270-4, 270-5, 270-6, 270-7, National Bureau of Standard, U.S.; [l]C. J. Smithells [Ed.], *Metals Reference Book*, 4th Edn. Plenum Press, New York (1967).

for the standard heat of formation $\Delta Hf°$ of SiO_2 (see Table 1), the resulting heat of reaction $\Delta H°$ will increase but by less than 3.1 kcal/gatom in all cases. It is clear that reactions leading to certain combinations of silicides and oxides can take place while others cannot, the range of $\Delta H°$ values varying from −7.9 to +3.7 kcal per gram atom.

Heats of reaction calculated from a table of standard heats of formation such as those given in Table 1, apply only for a pressure of 1 atm and a temperature of 25°C. The pressure dependency of free energy (and enthalpy in the case of solids) for an isothermal change in pressure from P_1 to P_2 is given by[9]:

$$\Delta G = \int_{P_1}^{P_2} V \, dP. \tag{4}$$

In order to integrate this equation, the variation of volume, V, with pressure must be known. As shown in Appendix I, for SiO_2 the change in free energy for a pressure change from 1 to 0 atm is certainly much less than the inaccuracy in G and, hence, is negligible. We therefore ignored this contribution to ΔG in our calculations.

Table 2. Standard heats of reaction $\Delta H°$ for vanadium with SiO_2 leading to the formation of various silicides and oxides. The values calculated for these 16 different reactions of V with SiO_2 are those reported in Fig. 3 for V at 1.43 Pauling units. Data given there for other metals were obtained similarly

Metal	Products Silicide	Products Oxide	$\Delta H°$ (kcal/gatom)
V	V_3Si	VO	−4.2
		V_2O_3	−3.0
		VO_2	+0.3
		V_2O_5	+3.7
	V_2Si	VO	−6.2
		V_2O_3	−5.0
		VO_2	−1.2
		V_2O_5	+2.7
	V_5Si_3	VO	−5.8
		V_2O_3	−4.4
		VO_2	−0.5
		V_2O_5	+3.7
	VSi_2	VO	−7.9
		V_2O_3	−6.5
		VO_2	−1.7
		V_2O_5	+3.6

The temperature dependence of enthalpy can be calculated if the heat capacities C_p (at constant pressure) of the reactants and products are known. The relationship between enthalpy and temperature is given by:

$$H_T - H_{298} = \int_{298}^{T} C_p \, dT \qquad (5)$$

where C_p is usually expressed by an empirical relationship such as:

$$C_p = a + (b \times 10^{-3})T + (c \times 10^{-6})T^2 + \frac{(d \times 10^5)}{T^2} \qquad (6)$$

where a, b, c and d are constants which have been determined experimentally, theoretically or semi-empirically[10]. It is clear that if the reactants and products have the same heat capacities there will be no change in the heat of reaction as a function of temperature.

Although the heat capacities for the metal oxides are generally available, heat capacity data could only be found for the silicides of Mn, Fe, Co and Ni. The heat of reaction for these metals with SiO_2 was calculated for a temperature of 800°C and compared with the calculated values at 25°C. It can be seen from Table 3 that the differences between $\Delta H°$ at 25°C and ΔH at 800°C never exceed 3 kcal/gatom, except for iron. The heat of reaction at 25°C is thus a good approximation to ΔH at 800°C. For this reason and because of the limited thermodynamic data available for silicides, $\Delta Hf°$ at 25°C, which is given in Table 1, was used for the analysis rather than ΔHf at 800°C.

The assumption that the entropy term in eqn (2), $T\Delta S$, contributes negligibly to the change in Gibbs free energy is confirmed by the fact that the heats of reaction, ΔH, vary only slightly with temperature because $\Delta S \cong 0$ requires that ΔG and ΔH do not vary with temperature ($d\Delta G = -dT\Delta S$ at constant pressure).

Table 3. Comparison of heats of reaction ΔH for some metals with SiO_2 at 25°C and 800°C

Products Silicide	Products Oxides	ΔH at 25°C (kcal/gatom)	ΔH at 800°C (kcal/gatom)	References Silicide	References Oxide
Co_2Si	CoO	+9.1	+6.4	*f*	*d*
	Co_3O_4	+11.2	+8.5		*d*
CoSi	CoO	+11.2	+9.2	*f*	*d*
	Co_3O_4	+13.9	+12.0		*d*
$CoSi_2$	CoO	+14.3	+12.5	*f*	*d*
	Co_3O_4	+17.6	+15.9		*d*
$CoSi_3$	CoO	+15.5	+13.8	*f*	*d*
	Co_3O_4	+19.0	+17.5		*d*
Cr_3Si	Cr_2O_3	−1.0	−3.7	*b*	*d*
	CrO_2	+4.8	+2.9†		*a, d*
	CrO_3	+12.2	+9.6		*a, d*
Cr_5Si_3	Cr_2O_3	−0.05	−2.0	*b*	*d*
	CrO_2	+7.1	+5.5†		*a, d*
	CrO_3	+16.5	+14.8		*a, d*
CrSi	Cr_2O_3	+1.3	−0.4	*b*	*d*
	CrO_2	+9.5	+8.0†		*a, d*
	CrO_3	+20.4	+19.1		*a, d*
$CrSi_2$	Cr_2O_3	+2.4	+1.0	*b*	*d*
	CrO_2	+11.6	+10.1†		*a, d*
	CrO_3	+24.0	+23.1		*a, d*
FeSi	FeO	+6.6	+9.7‡	*e*	*d*
	Fe_3O_4	+6.1	+8.0‡		*d*
	Fe_2O_3	+6.8	+11.9‡		*d*
Mn_3Si	MnO	−0.7	−3.2	*c*	*d*
	Mn_3O_4	+1.7	−0.9		*d*
	Mn_2O_3	+3.2	+0.6		*d*
	MnO_2	+7.7	+5.0		*d*
Mn_5Si_3	MnO	+0.8	−1.5	*c*	*d*
	Mn_3O_4	+3.9	+1.5		*d*
	Mn_2O_3	+5.8	+3.4	*c*	*d*
	MnO_2	+11.5	+8.9		*d*
MnSi	MnO	−0.8	−2.1	*c*	*d*
	Mn_3O_4	+2.4	+1.1		*d*
	Mn_2O_3	+4.5	+3.3		*d*
	MnO_2	+10.9	+9.6		*d*
$MnSi_2$	MnO	+3.2	+1.7	*c*	*d*
	Mn_3O_4	+7.2	+5.7		*d*
	Mn_2O_3	+9.7	+8.2		*d*
	MnO_2	+17.1	+16.5		*d*
Ni_3Si	NiO	+6.6	+3.3	*f*	*d*
Ni_5Si_2	NiO	+7.0	+4.0	*f*	*d*
Ni_2Si	NiO	+8.2	+5.1	*f*	*d*
Ni_3Si_2	NiO	+9.5	+6.9	*f*	*d*
NiSi	NiO	+11.4	+9.3	*f*	*d*
$NiSi_2$	NiO	+14.2	+12.8	*f*	*d*

†ΔH at 427°C—decomposition of CrO_2.
‡ΔH at 627°C—decomposition of FeSi.
[a]H. J. Goldschmidt, *Interstitial Alloys*. Plenum Press, New York (1967); [b]Yu. M. Golutvin and L. Chin-k'uei, *J. Phys. Chem. U.S.S.R.* **35**, 1 (1961); [c]Yu. M. Golutvin, T. M. Kozlovskaya and E. G. Maslennikova, *J. Phys. Chem. U.S.S.R.* **37**, 6 (1963); [d]*Handbook of Chemistry and Physics* (Edited by R. C. Weast) 52nd Edn. Chemical Rubber Company, Cleveland (1971); [e]K. K. Kelley, *U.S. Bureau of Mines Bulletin* **476** (1949); [f]O. Kubaschewski and J. A. Catterall, *Thermochemical Data of Alloys*. Pergamon Press, London (1956).

Searching for the necessary thermodynamic data in the literature and the subsequent calculations is usually tedious. For many elements, such data do not exist. It is thus desirable to have a simpler and more generally applicable way of predicting whether a particular metal

will react with SiO_2. We have found that the electronegativity of the metal serves this purpose quite well. In Fig. 3, we have plotted all our calculated standard heats of reaction $\Delta H°$, as a function of the average of the three electronegativities (average of relative compactness, Pauling, and Allred–Rochow electronegativities) of the metals as listed by Sanderson[11]. It can be seen that there is quite a good linear correlation between the calculated standard heats of reaction and the average electronegativities of the metals. The slope of the dashed straight line fitted to the most negative $\Delta H°$ values is about 65 kcal/gatom per Pauling unit and crosses the abscissa at an average electronegativity of about 1.5. It would thus be expected that metals with average electronegativity values smaller than 1.5 on the Pauling scale will react with SiO_2.

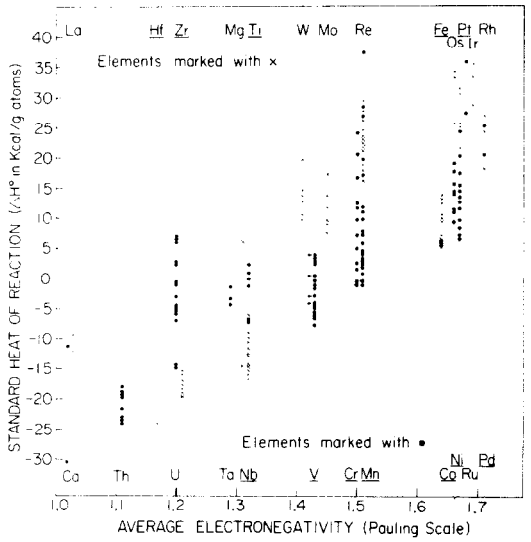

Fig. 3. Calculated standard heats of reaction ($\Delta H°$) for the reaction of various metals with SiO_2, leading to all the possible combinations of metal oxides and silicides for which thermodynamic data was available, plotted against the average electronegativity (average of Allred–Rochow, Relative Compactness and Pauling electronegativities) of the metal. The underlined metals are those that were studied experimentally in this investigation.

Our experimental results correlate quite well with thermodynamic considerations assuming the reaction given in eqn (1). A summary of these results is given in Table 4 in which the average electronegativity of each metal, the range of $\Delta H°$ values calculated for reaction of the metal with SiO_2 and the experimental outcome of whether a chemical reaction took place, is listed. The elements underlined in Fig. 3 are those that were investigated experimentally. Thermodynamically, one expects that Hf, Zr, Ti and Nb will react with SiO_2. For V, some of the reactions are excluded, but the majority of those considered are possible (see Table 2); V is thus expected to react. The heats of reaction for those reactions leading to V_3Si (which has been identified as the silicide which forms) and the four vanadium oxides are indicated with arrows in Fig. 3. Chromium and manganese are borderline cases; and for both of these metals, virtually all the possible reactions save one or two are thermodynamically excluded. We thus believe that Cr and Mn should not react with SiO_2 as was confirmed experimentally. It is interesting to note in this connection that Cr does indeed have a special position in terms of the experimental outcome, namely, that no "balling up" occurred as was the case for all the other metals which did not react. All the other metals that we investigated experimentally, namely, Fe, Co, Ni, Pt and Pd should clearly not react. The thermodynamic arguments are thus in accord with the experimental facts. Conceptually, this means that our experimental procedures (cleanliness of the metal–SiO_2 interface, duration of the anneal, control of the ambience during anneal, etc.) were sufficient to allow for a comparison with thermodynamic considerations. However, reactions between Cr or Mn and SiO_2, which were thermodynamically favorable, yet not observed, could have been limited by kinetic considerations and might be observed under other experimental conditions.†

Table 4. Summary of results when heating a thin metal layer on a SiO_2 substrate for several hours in vacuum. A comparison is made with the average electronegativity of the metal and the calculated heats of reaction $\Delta H°$ (at 25°C and 1 atm pressure)

Metal	Average electronegativity Pauling scale	Standard heats of reaction range ($\Delta H°$) (kcal/gatom)	Chemical reaction‡
Hf	1.17	−23.9	Yes
Zr	1.21	−18.7 to −15.6	Yes
Ti	1.32	−16.6 to −6.6	Yes
Nb	1.32	−7.1 to +2.2	Yes
V	1.43	−7.9 to +3.7	Yes
Cr	1.50	−1.0 to +24.0	No
Mn	1.51	−0.7 to +37.3	Not
Fe	1.64	+6.1 to +13.7	Not
Co	1.66	+9.1 to +19.0	Not
Ni	1.67	+6.6 to +24.2	Not
Pt	1.67	+21.5 to +31.5	Not
Pd	1.71	+20.4 to +25.0	Not
Cu	1.80	—	Not

†Balled up.
‡All samples vacuum-annealed at 800°C for 2–4 hr.

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†There is a paper by C. W. Nelson[13] in which the connection between adhesion of metals to oxide ceramics or glass and the free energies of formation of the metal oxides is clearly spelled out. Experiments with evaporated thin films similar to ours, and involving crude mechanical tests, are mentioned as having been performed in 1954–56.

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APPENDIX I

The Gibbs free energy is a function of pressure and can be obtained by expanding ΔG at constant temperature

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= \Delta(E + PV) - T\Delta S \\ &= \Delta E + P\Delta V + V\Delta P - T\Delta S, \end{aligned} \tag{1A}$$

where P is the pressure and V is the specific volume at temperature T given by

$$V = 1/\rho \frac{\text{cm}^3}{\text{mol}}$$

and ρ is the density.

Since $\Delta E = T\Delta S - P\Delta V$, eqn (1A) reduces to

$$\Delta G = V\Delta P \tag{2A}$$

which can be integrated to give

$$G_{P2} - G_{P1} = \int_{P1}^{P2} V\,dP. \tag{3A}$$

The experiments reported in this paper were performed in vacuum so the free energy should be evaluated for $P2 \cong 0$. The relationship between the volume V and pressure P for a solid is given by

$$V(P) = V_0(1 - \beta(P - 1)) \tag{4A}$$

where V_0 is the specific volume at 1 atm and 25°C and β is the isothermal compressibility. In the temperature range between 300 to 1200 K, the isothermal compressibility is approximately a linear function of temperature as is the specific volume. The change in specific volume between 300 and 1200 K for SiO_2 is less than 15% and the change in β is less than a factor of 2[12]. As whown later, it is adequate to approximate the volume and the isothermal compressibility in these calculations by their values at 25°C rather than using the values at 800°C where the experiment was performed. The specific volume at 1 atm and 25°C for SiO_2 is 23.1 cm^3/mol[12] and the isothermal compressibility at 25°C is $2.53 \times 10^{-6}\ \text{atm}^{-1}$[12].

$$V(P) = 23.1\ \text{cm}^3/\text{mol}\,(1 - 2.53 \times 10^{-6}\ \text{atm}^{-1}(P - 1)). \tag{5A}$$

For any value of P between 0 and 1 atm $V(P)$ can be approximated by

$$V(P) \approx 23.1\ \text{cm}^3/\text{mol}.$$

β is very small compared to 1, hence, the approximation of β to within a factor of 2 in eqn (5A) is justified. Evaluating eqn (3A) for SiO_2 gives

$$\begin{aligned} G_{1\,\text{atm}} - G_{0\,\text{atm}} &= -23.1 \frac{\text{atm cm}^3}{\text{mol}} \\ &= -0.55 \frac{\text{cal}}{\text{mol}}. \end{aligned}$$

This value is about 10^4 times smaller than the typical values for the Gibbs free energy at 1 atm; and since the free energies are not accurately known to four significant figures, this correction can be ignored. The example was worked for the free energy of SiO_2. However, the conclusion is valid for all the materials discussed since the specific volume varies between the materials by less than a factor of 20.