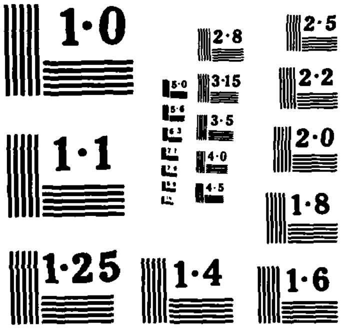
AD-A158 294   AN EXTENSION OF THE ENGEL-BREWER METALLIC CORRELATION   1/1
TO TRANSITION METAL SILICIDES(U) RENSSELAER POLYTECHNIC
INST TROY NY S SIVARAM ET AL. AUG 85 N00014-81-K-0605

UNCLASSIFIED   F/G 20/12   NL

END
FILMED
DTIC


1·0
2·8
2·5
3·15
2·2
3·5
2·0
1·1
4·0
4·5
1·8
1·25
1·4
1·6

②

AN EXTENSION OF THE ENGEL-BREWER METALLIC CORRELATION TO TRANSITION METAL SILICIDES

S. Sivaram, P. J. Ficalora, and K. C. Cadien

Department of Materials Engineering and the
Center for Integrated Electronics
Rensselaer Polytechnic Institute
Troy, New York 12181

To be published in the
JOURNAL OF APPLIED PHYSICS
August 1985

Partially supported by
ONR Contract No. N00014-81-K-0605

AN EXTENSION OF THE ENGEL-BREWER METALLIC CORRELATION TO TRANSITION METAL SILICIDES

S. Sivaram, P. J. Ficalora, and K. C. Cadien

Department of Materials Engineering and the
Center for Integrated Electronics
Rensselaer Polytechnic Institute
Troy, New York 12181

ABSTRACT

The Engel Brewer theory for transition metals has been extended to transition metal silicides. It is shown that the promoted electronic state correlates well with the properties of the silicides. From these correlations we are able to predict the effect of deviations from stoichiometry on disilicide resistivity, and the existence of other silicides crystal structures.

1. INTRODUCTION

Transition metal silicides are of considerable technological importance. In integrated circuits, they are used as gate electrodes, Schottky barriers and as ohmic contacts [1]. Inspite of the large amount of research being done on these materials, there is very little understanding of the physical and chemical factors that determine the material properties. The reason for the lack of progress is best demonstrated by considering the crystal structure. The crystal structures of all transition metal silicides fall into just four crystal systems (cubic, hexagonal, orthorhombic and tetragonal). However, any analysis is made extremely difficult by the complexity of the different atom coordinations. In addition, the ground state electronic configurations of the gaseous atoms do not necessarily represent the electronic states of the atoms in the solid compounds. Thus, predicting electrical properties based on the ground state configuration leads to erroneous results.

Cont'd

Murarka [1, 2] has tried to correlate the thin film resistivity and crystal structure to the number of `d´ electrons in the metal ground state configuration. In Figure 1, we have plotted the resistivity of disilicides against the elements in the row of the periodic table. This figure includes values for all transition metal disilicides for which data is available. It is evident that no pattern is discernible. Murarka attributes the increase in resistivity along the row, in groups IVB, VB and VIB to increasing number of `d´ electrons. But the next two groups VIIB and VIII do not have higher resistivities. He also explains the reduction in the relative change in resistivity in the same group from IVA to VIA through increasing atom sizes. Again, the remaining elements in the transition group do not fit this trend. Attempts at correlating crystal structure and resistivity in a straight-forward manner have not been successful either.

In this paper, we extend the well-known Engel-Brewer correlation for transition metals to transition metal silicides. Properties, such as resistivity, crystal structure, thermodynamic stability, bulk density, heat of formation and thermal expansion coefficient will be correlated to the promoted electronic state. We will show this correlation to be a useful predictive mode. The next section contains a brief description of the Engel-Brewer Correlation.

II. THE ENGEL-BREWER CORRELATION

The basis for the crystal structure, electrical properties and stability of a material is the electronic configuration of the atom in the solid[13]. The ground state of a gaseous atom, however, is often not consistent with the properties of the solid. For example, the ground state of gaseous atomic magnesium (s^2) is inconsistent with the fact that magnesium is an electrical conductor; the ground state of silicon (s^2p^2) is inconsistent with the crystal structure of solid silicon. In both cases, the inconsistencies are removed by promoting the atom to a higher energy state. In the first case, the electrons in solid magnesium begin to fill the second Brillouin zone before completing the first. In the second case, silicon is promoted to the sp^3 hybrid[4]. In both cases the energy input necessary to cause the promotion is offset by the gain the bonding energy as illustrated in Figure 2. Thermodynamic and spectroscopic data[5] have comfirmed this balancing between bonding energy, promotion energy and the heat of sublimation.

Engel and Brewer have used this approach to show that the BCC, HCP, and FCC structures of transition metals can be correlated with the d^ns^1, $d^ns^1p^1$, and d^nsp^2 configurations. Only integral configurations need be considered at this point. Hence, the structure is determined by the s and p levels while the stability is determined largely by the number of electrons in the d level. Because of the increasing bonding energy per electron, stability increases up to the d state of maximum multiplicity (d^5). Internal pairing then causes the d^{5+x} to be equivalent to the d^x state. Since the nucleus is progressively shielded as the 3d, 4d, and 5d levels are occupied, the bond energy per electron increases from 3d to 5d (5d>4d>3d).

Engel-Brewer approach to silicides

Engel and Brewer [6] atom average `d´ and `sp´ electrons in the individual atoms to get the structures of the intermetallic compounds. Applying the same method to silicides, one can get the `d´ and `sp´ electron values corresponding to each silicide. Thus, for example, Ti in its HCP structure has a $3d^2 4sp$ structure and Si has a $4sp^3$ structure. Hence, $TiSi_2 \rightarrow 1/3\{(d^2sp) + 2(sp^3)\} = d^{.67}sp^{2.33}$. Table I lists the `d´ and `sp´ values of all silicides. In the following results and discussions, we will always be referring to these `d´ and `sp´ values.

III. RESULTS

(i) Resistivity:

It is well known that `d´ band position can greatly affect the conductivity of transition metals [7]. The `d´ band has a large and narrow density of states and the `d´electrons are tightly bound to the nucleii. If a `d´ band level is present near the Fermi-level, it could act as a scattering site for the itinerant `sp´ electrons which are responsible for conduction in these metals. Pecora and Ficalora [8] have demonstrated this effect. They have also explained the drop in resistivity after the d^5 through the equivalence of d^{5+x} and d^x states.

Since transition metal silicides which conduct by electrons have the same conduction mechanism as the metals, one would expect an increase in resistivity with increasing `d´ electrons and decreasing `sp´ electrons. However, silicides which conduct by holes should show the opposite behavior, i.e., increasing resistivity with decreasing `d´ electrons and increasing `sp´ electrons. The variation of disilicide resistivity with majority carrier type, and the number of `sp´ and `d´ electrons is shown in Table II. Also included in this table is the resistivity divided by the number of `sp´ electrons. This $\rho$/`sp´ parameter factors-out the effect of the `sp´ electrons and allows the effect of `d´ electrons to be unambiguously determined. Figure 3 shows the `sp´ reduced resistivity plotted against the disilicides of the elements arranged in the increasing order of `d´ electrons. Where the number of `d´ electrons are the same, the elements have been plotted in order of increasing orbital number. This is consistent with the observed increased stability with increasing principal quantum number [4]. It is clear from Figures 3(a) and (b) that a trend exists. For electron conductors $\rho$/`sp´ increases with increasing `d´ electrons. The opposite effect is observed for hole conductors. No effort was made to separate extrinsic and intrinsic components of the resistivity. All resistivity data are for room temperature. The correlation does not predict the electrical properties of semiconducting silicides since the conductivity of these materials is determined by dopant concentrations. For example, $CrSi_2$ is a semiconductor with a band gap of approximately 1.3eV[10]. Several investigators have reported resistivities varying between 250 and 6000 micro ohm-cm for this material [14]. It is apparent that these large discrepancies are due to unintentional dopant incorporation during growth and small variations in stoichiometry.

(ii) Crystal Structure of Silicides

The E-B theories were originally developed to allow a semi-empirical prediction of crystal structures. It was shown that crystal structure was determined solely by the number of ˋsp´ electrons, and that each crystal structure has a particular ˋsp´ range over which it exists. If similar limits on ˋsp´ electrons in silicides could be shown the extension of the E-B theories to silicides would be valid.

Table III lists the crystal structures of all silicides. Comparing Tables I and III one does find limits within which each of the four structures exist. These are:

(i)	Tetragonal		2-2.6 ˋsp´ electrons
(ii)	Hexagonal		2.75-3 ˋsp´ electrons
(iii)	Orthorhombic		3-3.33 ˋsp´ electrons
(iv)	Cubic	β-W types	1.75 ˋsp´ electrons
		all other types	3.33-3.67 ˋsp´ electrons

It is evident that ˋd´ electrons, which vary widely in each silicide, do not effect the crystal structures. Silicides of all stoichiometries obey these limits.

(iii) Thermodynamic Stability of Silicides

Predictions of the stability of silicides is made difficult by differing coordination numbers in each crystal type. The

E-B prediction for metallic structures is that increasing `d´ electrons up to d^5 would increase stability, and 5d metals would melt at higher temperatures than 4d, and 4d than 3d for the same coordination.

Picking a set of metal-like silicides with the same crystal type, say Mn_5Si_3 type, one sees the effect of increasing `d´ electrons and of going from 3d to 4d to 5d.

Ti_5Si_3	1.25	`3d´ electrons	$T_m = 2120°C$
V_5Si_3	2.5	`3d´ electrons	$T_m = 2150°C$
Zr_5Si_3	1.25	`4d´ electrons	$T_m = 2250°C$
Nb_5Si_3	2.5	`4d´ electrons	$Tm = 2440°C$
Ta_5Si_3	2.5	`5d´ electrons	$T_m = 2500°C$

Even amongst hole conducting silicides, the 3d<4d<5d rule seems to hold true:

Cr_5Si_3	3.125	`3d´ electrons	$T_m = 1600°C$
Mo_5Si_3	3.125	`4d´ electrons	$T_m = 2100°C$
W_5Si_3	3.125	`5d´ electrons	$T_m = 2320°C$

(iv) Other Physical Properties

Some physical properties of the same set of silicides considered in the stability analysis have been plotted in figures 4, 5, and 6. The curves show the variation of bulk density, heat of formation from the elements and the thermal expansion coefficients of these silicides with increasing `d´ electrons and with increasing orbital numbers for the `d´ electrons. Though this variation reflects the periodicity among elements to an extent, such a smooth variation is not found among silicides which do not have the same crystal types. Thus, for example, the heats of formation among disilicides do not fit into the same scheme. The effect of the `d´ electrons on the bonding characteristics is thus clearly demonstrated, and this explains, in part, how the periodicity arises. A more comprehensive study of the physical properties of silicides is made difficult by the absence of reliable data.

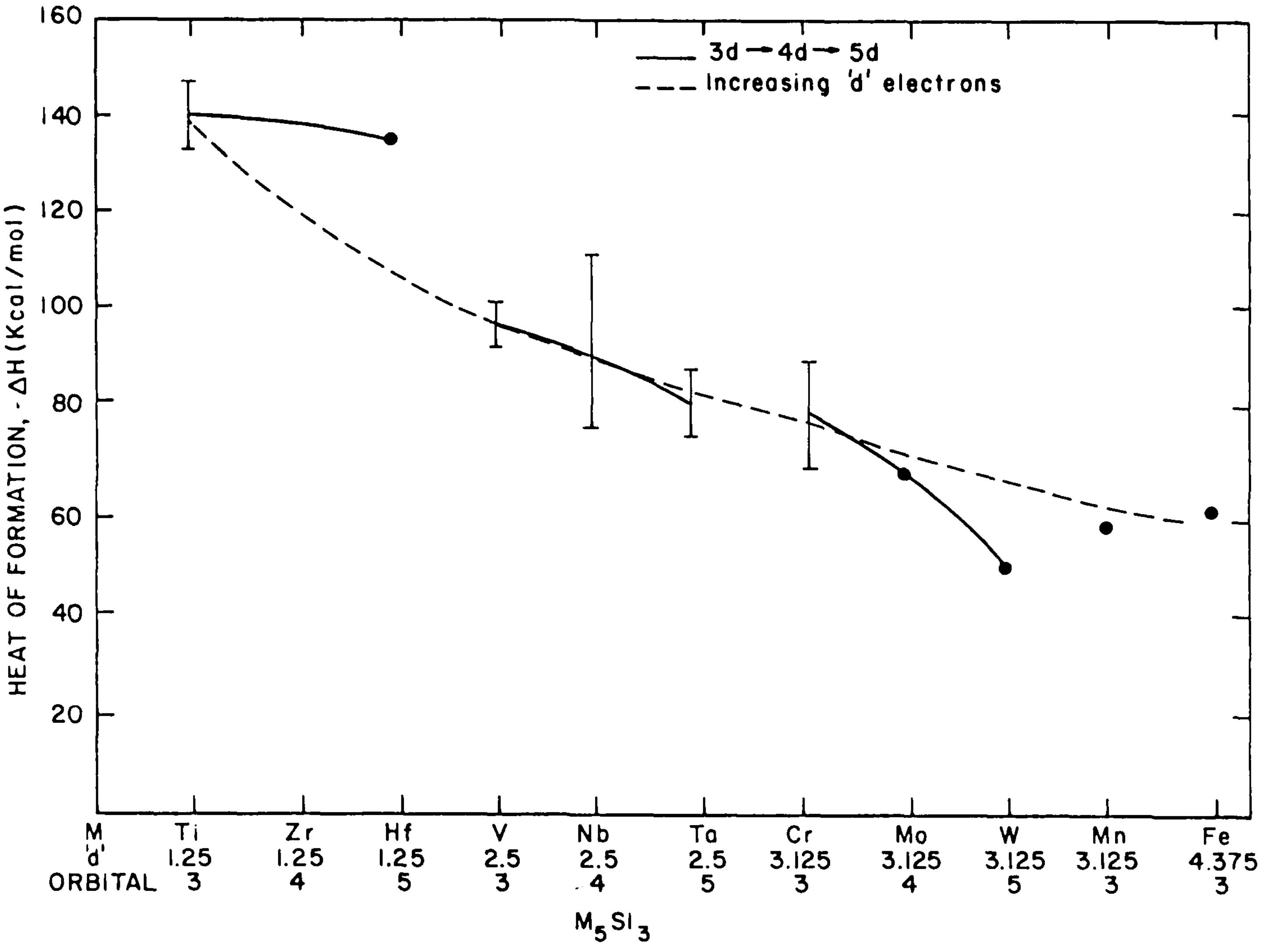
IV. DISCUSSION AND CONCLUSIONS

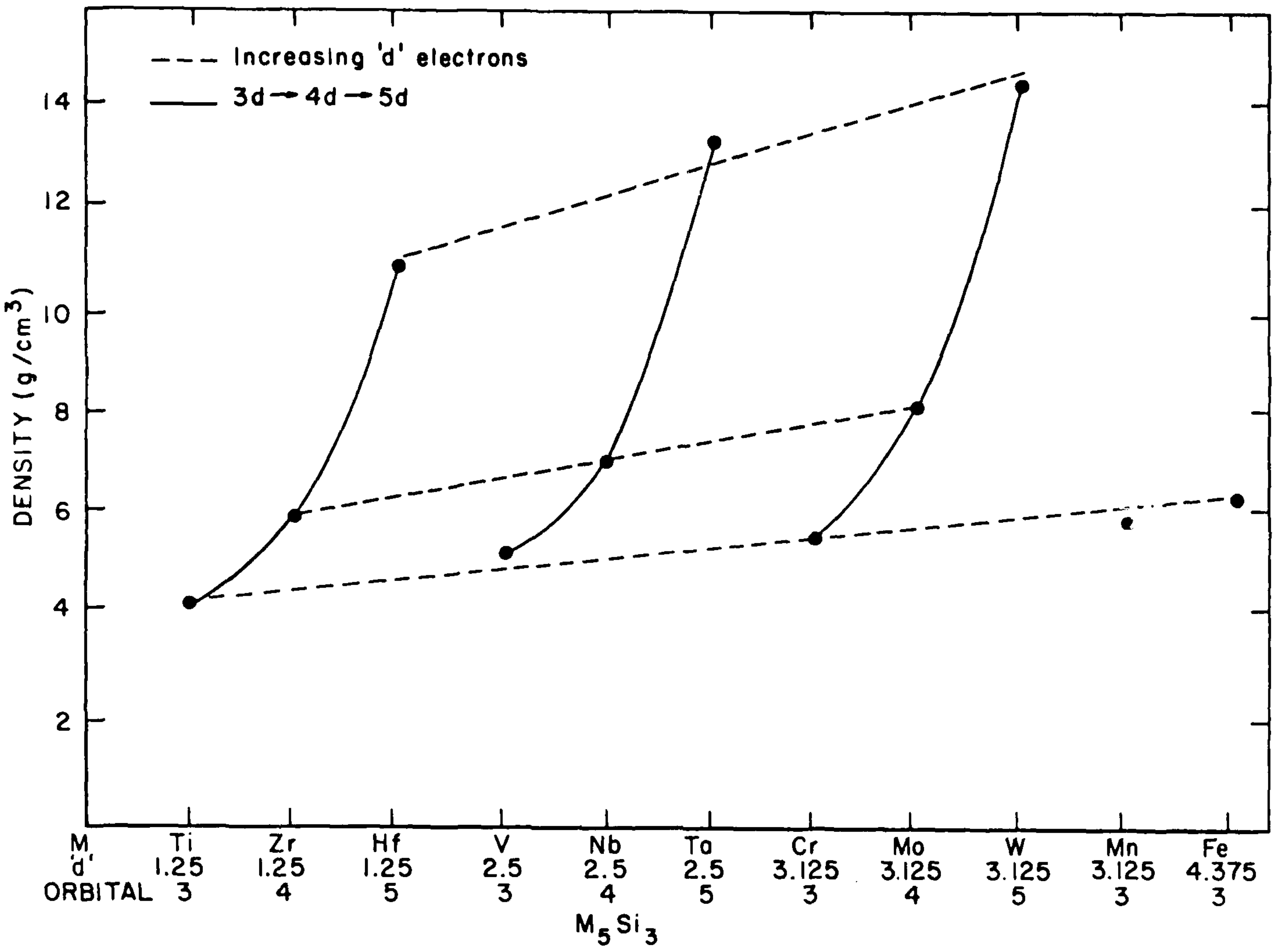
We have shown that the Engel-Brewer correlation for transition metals can be extended to transition metal silicides. The correlation between electrical resistivity, crystal structure, stability, and the number of electrons in the `d´ and `sp´ orbitals is excellent. Based on these correlations, two predictions can be made pertaining to the effect of deviations in stoichiometry on the resistivity of silicides, and the existence of other silicide crystal structures.

During the deposition of silicide thin films, it is possible for the silicide stoichiometry to deviate from the stoichiometric value. Our correlation predicts that for single phase disilicides;

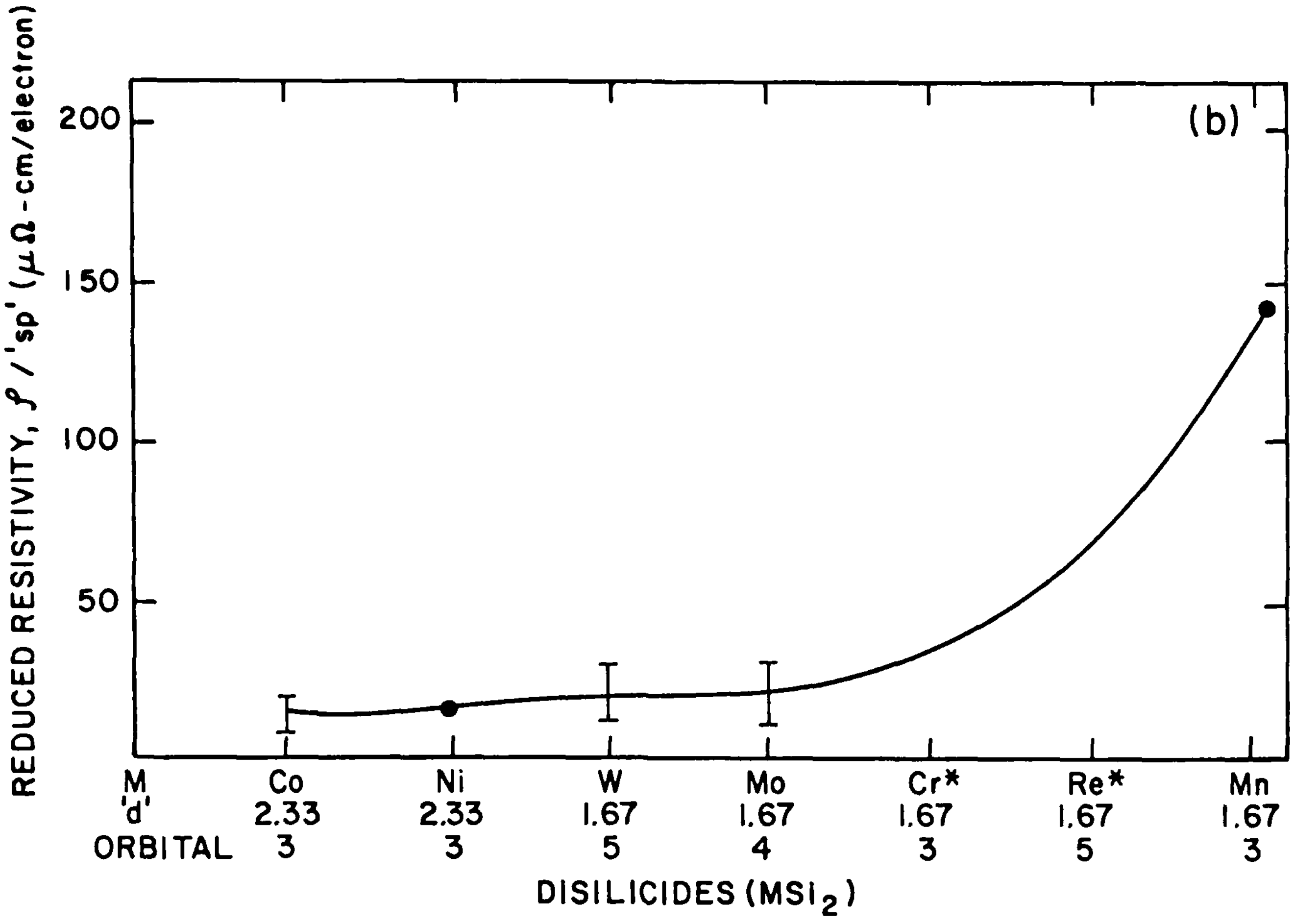
	stoichiometric	excess Si	Si deficient
Si:	2.0	>2.0	<2.0
electron conductors	ρ_e	$\rho_e\downarrow$	$\rho_e\uparrow$
hole conductors	ρ_h	$\rho_h\uparrow$	$\rho_h\downarrow$

For example, for $TiSi_2$, an electron conductor, we predict a lowering of the resistivity if there is an excess of Si. This excess would reduce the number of `d´ electrons, thus, lowering ρ . This explains a recent observation of Malhotra, et. al. [11] that excess Si in $TiSi_2$ does in fact lower ρ. In addition, WSi_2 and $MoSi_2$, hole conductors have been shown to be more resistive if the films are silicon-rich [12, 13], in agreement with our

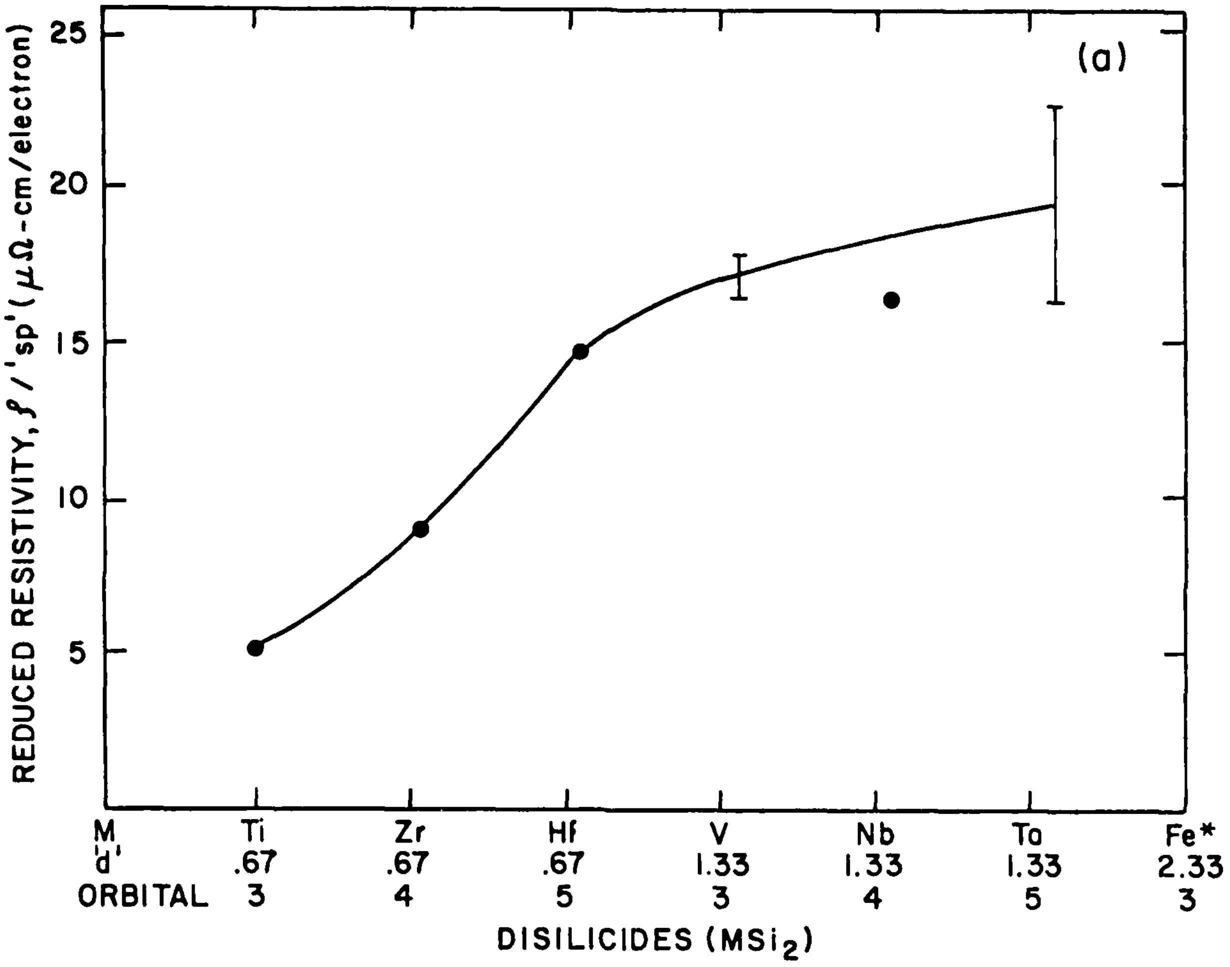

3d → 4d → 5d
Increasing 'd' electrons
HEAT OF FORMATION, - ΔH (Kcal/mol)
160
140
120
100
80
60
40
20
M
'd'
ORBITAL
Ti 1.25 3
Zr 1.25 4
Hf 1.25 5
V 2.5 3
Nb 2.5 4
Ta 2.5 5
Cr 3.125 3
Mo 3.125 4
W 3.125 5
Mn 3.125 3
Fe 4.375 3
M_5Si_3



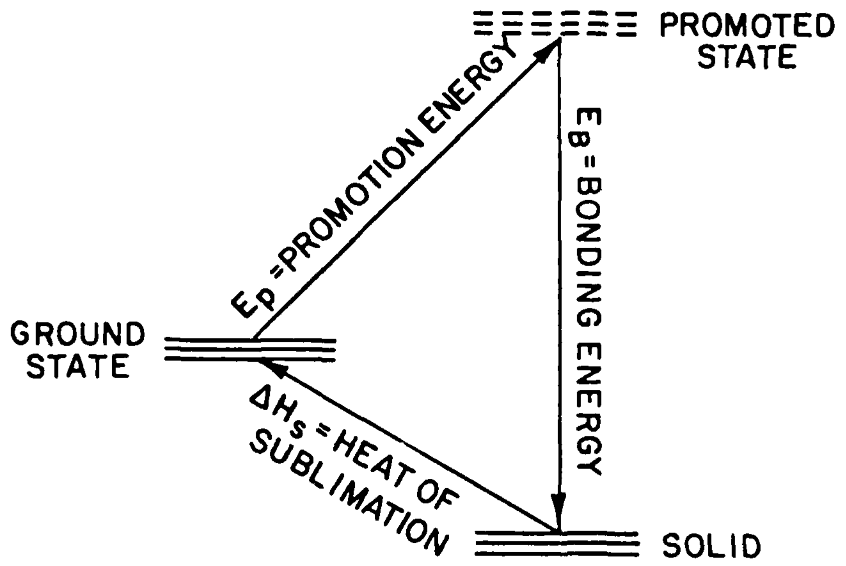
--- Increasing 'd' electrons
— 3d → 4d → 5d
DENSITY (g/cm³)
14
12
10
8
6
4
2
M
'd'
ORBITAL
Ti 1.25 3
Zr 1.25 4
Hf 1.25 5
V 2.5 3
Nb 2.5 4
Ta 2.5 5
Cr 3.125 3
Mo 3.125 4
W 3.125 5
Mn 3.125 3
Fe 4.375 3
M5Si3



*Semiconducting Silicide



* Semiconducting Silicide


PROMOTED STATE
E_p =PROMOTION ENERGY
E_B = BONDING ENERGY
GROUND STATE
ΔH_s = HEAT OF SUBLIMATION
SOLID

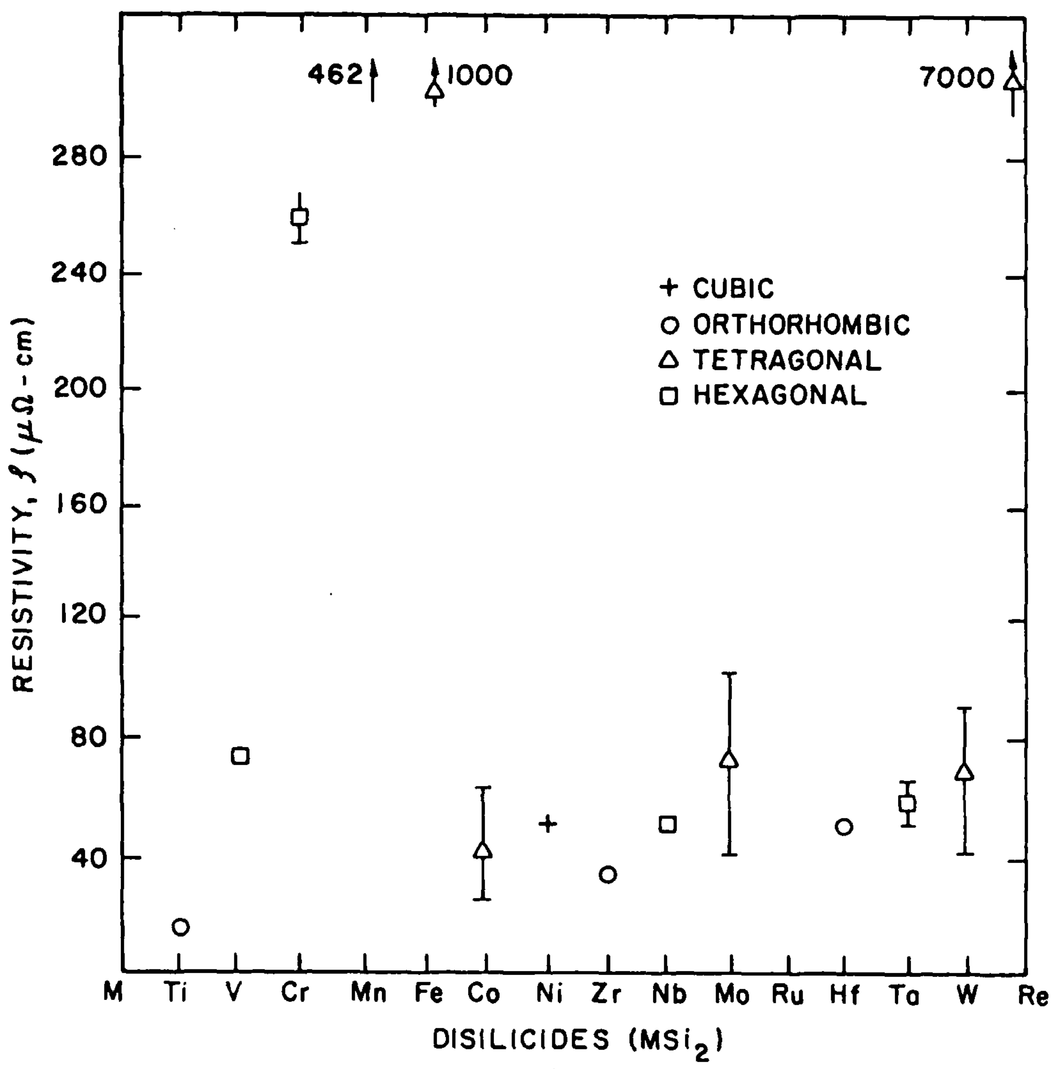

462
1000
7000
280
240
200
160
120
80
40
RESISTIVITY, ρ (μΩ-cm)
+ CUBIC
○ ORTHORHOMBIC
△ TETRAGONAL
□ HEXAGONAL
M
Ti
V
Cr
Mn
Fe
Co
Ni
Zr
Nb
Mo
Ru
Hf
Ta
W
Re
DISILICIDES (MSi₂)

Figure Captions

Fig. 1 Resistivities and crystal structures of transition metal disilicides, from ref. 15. Error bars indicate scatter in published data.

Fig. 2 Schematic of the balance between bonding energy, promotion energy, and the heat of sublimation, as proposed by the Engel-Brewer theory.

Fig. 3 Variation of the `sp´ reduced resistivity of
(a) silicides which conduct by electrons and
(b) silicides which conduct by holes.

Fig. 4 Bulk densities of M_5Si_3 type transition metal silicides.

Fig. 5 Heats of formation of M_5Si_3 type silicides.

Fig. 6 Thermal Expansion Coefficients of M_5Si_3 type silicides.

TABLE III

TABLE OF SILICIDE STRUCTURES

STOICHIOMETRY ->	$M_{>4}Si$	M_3Si	M_2Si	M_5Si_3	MSi	MSi_2
Ti				H	R[d]	R
Zr			T[c]	H	R	R
Hf			T	H	R	R
V		C[b]	T	T, H		H
Nb				T, H		H
Ta	H[a]		T	T, H		H
Cr		C		T, H	C	H
Mo		C		T, H		T
W		C		T, H		T
Mn		C		H	C	
Re				T	C	T
Fe		C			C	T
Co			R		C	T
Ni		C	H, R		R	C
Rh					C	
Pd					R	
Pt					R	

[a] H: hexagonal
[b] C: cubic
[c] T: tetragonal
[d] R: orthorhombic

TABLE II

RESISTIVITIES OF DISILICIDES

	`sp´ electrons	`d´ electrons	ρ, μΩ-cm	ρ/`sp´	Type
$TiSi_2$	3.33	.67	16.9	5.07	e[a]
$ZrSi_2$	3.33	.67	35	10.5	e
$HfSi_2$	3.33	.67	50	15	e
VSi_2	3	1.33	50-55	16.6-18	e
$NbSi_2$	3	1.33	50.4	16.8	e
$TaSi_2$	3	1.33	50-70	16.6-23	e
$FeSi_2$	3	2.33	1000[c]	333	e
$CoSi_2$	3.33	2.33	25-64	7.5-20	h[b]
$NiSi_2$	3.67	2.33	50	15	h
WSi_2	3	1.67	40-90	13-30	h
$MoSi_2$	3	1.67	40-100	13-33.3	h
$CrSi_2$	3	1.67	250-1000[c]	80-2000	h
$MnSi_2$	3.33	1.67	462	138.6	h
$ReSi_2$	3.33	1.67	7000[c]	2300	h

[a] e:conduction by electrons

[b] h:conduction by holes

[c] Semiconductor

TABLE I

`sp´ & `d´ electrons in Silicides

STOICHIOMETRY ->	M		$M_{>4}Si$		M_3Si		M_2Si		MSi		MSi_2		M_5Si_3	
	d	sp	d	sp	d	sp	d	sp	d	sp	d	sp	s	sp
Ti	2	2							1	3	.67	3.33	1.25	2.75
Zr	2	2					.8	2.6	1	3	.67	3.33	1.25	2.75
Hf	2	2					.8	2.6	1	3	.67	3.33	1.25	2.75
V	4	1			3	1.75	2.67	2			1.33	3	2.5	2.125
Nb	4	1	3.1	1.6							1.33	3	2.5	2.125
Ta	4	1	4	1.54							1.33	3	2.5	2.125
Cr	5	1			3.75	1.75	2.67	2	2.5	2.2	1.67	3	3.125	2.125
Mo	5	1			3.75	1.75					1.67	3	3.125	2.125
W	5	1			3.75	1.75					1.67	3	3.125	2.125
Fe	7	1			5.25	1.75			3.5	2.5	2.33	2.35		
Co	7	2					4.67	2.67	3.5	3	2.33	3.33		
Ni	7	3			5.25	3.25	4.67	3.33	3.5	3.5	2.33	3.33		
Rh	6	3							3	3.5				
Pd	7	3					4.67	3.33	3	3.5				
Pt	7	3					4.67	3.33	3	3.5				
Si	0	4												

REFERENCES (con't)

13. S. P. Murarka, D. B. Fraser, T. F. Retajczhk, Jr., and T. T. Sheng, J. Appl. Phys., 51, 5380 (1980).

14. S. P. Murarka, IEEE IEDM Conf., 454 (1979).

15. F. Mohammadi, Sol. St. Technol., 24(1), 65 (1981).

16. G. V. Samsonov, "High Temperature Materials: Property Index No. 2",(Plenum Press, New York 1964).

17. S. P. Murarka, M. H. Read, and C. C. Chang, J. Appl. Phys., 52, 7450 (1981).

18. T. P. Chow, A. J. Steckl, and D. M. Brown, J. Appl. Phys., 52, 6331 (1981).

19. J. Aubry, R. Duval, and B. Roques, C. R. Hebd. Acad. Sci. 261, 2665 (1965); Chem. Abst. 64, 1430b (1966).

20. Y. A. Kocherzhinskii, Coloq. Int. Cent. Nat. Rech. Sci. No. 205, 47 (1972); V. N. Svechnikov, Y. A. Kocherzhinskii, and L. M. Yupko, Dopov. Akad. Nauk Ukr. RSR, Ser. A32, 553 (1970).

REFERENCES

1. S. P. Murarka, J. Vac. Sci. Technol., 17, 775 (1980).
2. S. P. Murarka, "Silicides for VLSI Applications", (Academic Press, New York 1983).
3. L. Brewer, "Prediction of High Temperature Metallic Phase Diagrams", URC-10701, Rev. 2, University of California, Berkeley (1964); L. Brewer in "High Strength Materials", ed. Victor F. Zackay,(John Wiley & Sons, Inc., New York, 1965) p. 12.
4. W. Hume-Rothery, Prog. in Mat. Sci., 13, 229 (1967).
5. C. E. More, "Atomic Energy Levels", Vols. I-III,(U.S. Govt. Printing Office, Washington, 1949, 1952, 1958).
6. L. Brewer, Acta Met., 15, 553 (1967).
7. G. V. Samsonov, I. F. Pryadko, and L. F. Pryadko, "A Configurational Model of Matter",(Consultants Bureau, Plenum Publishing Co., New York, 1973).
8. L. M. Pecora and P. J. Ficalora, J. Sol. St. Chem., 27, 239 (1982).
9. S. P. Murarka, M. H. Read, C. J. Doherty and D. B. Fraser, J. Electrochem. Soc., 129, 293 (1982).
10. G. V. Samsonov and I. M. Vinitskii, "Handbook of Refractory Compounds",(IFI/Plenum, New York, 1980).
11. V. Malhotra, T. L. Martin, and J. E. Mahan, J. Vac. Sci. Tech., 2B, 10 (1984).
12. R. J. Miller, Thin Solid Films, 72, 427 (1980).

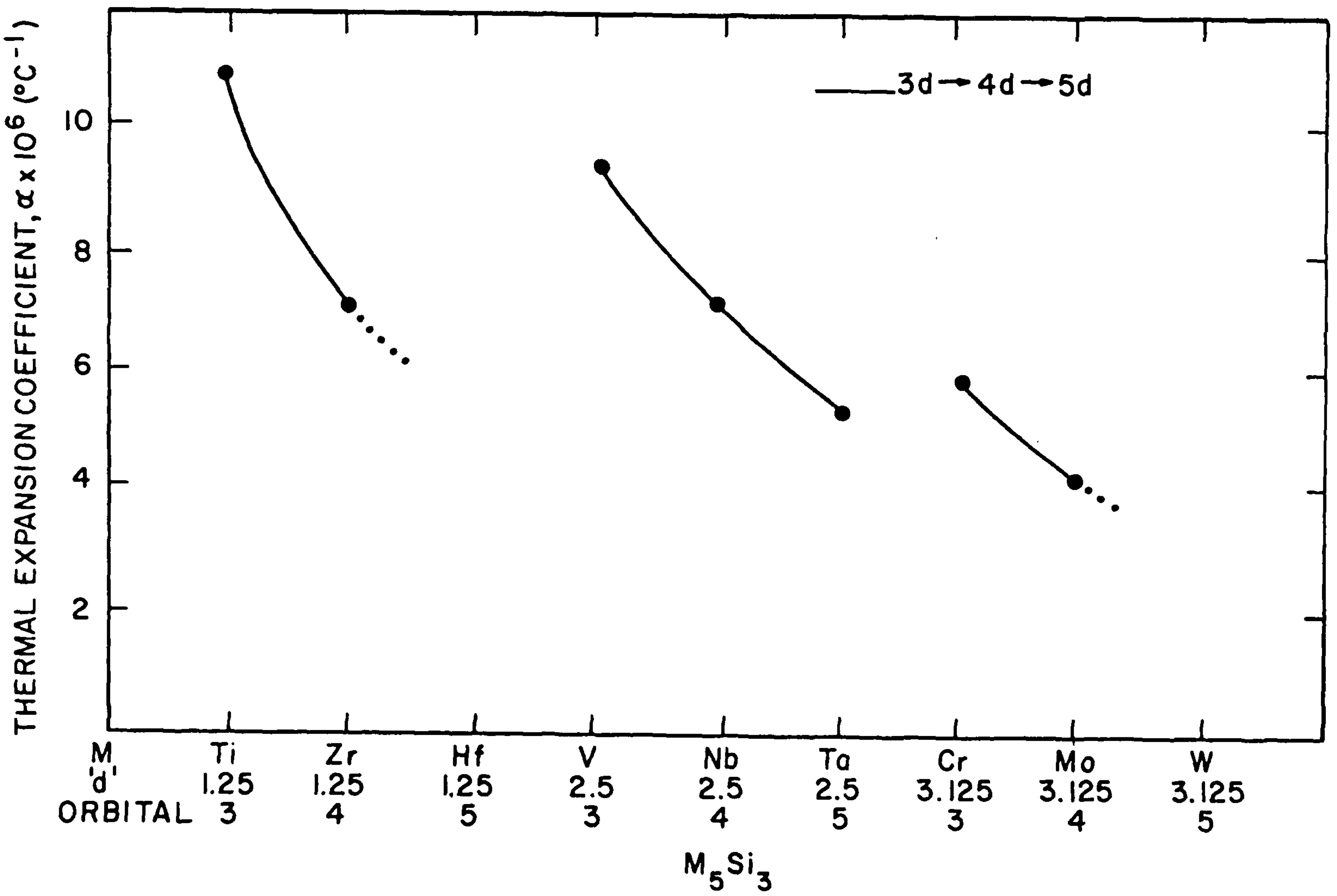
ACKNOWLEDGEMENTS

Dr. K. C. Cadien and Mr. S. Sivaram were partially supported by the Office of Naval Research under Contract No. N00014-81-K-0605.

predictions. The sensitivity of the resistivity of disilicides to stoichiometry is a possible explaination for the dependence of silicide resistivity on growth technique[14].

The correlation between crystal structure and the number of `sp´ electrons, shown in an earlier section, is unambiguous for all silicides except $WSi_2$ and $MoSi_2$. Both silicides have 3 `sp´ electrons and, thus, should be hexagonal like $CrSi_2$, which also has 3 `sp´ electrons. However, the reported structure of WSi_2 and $MoSi_2$ is tetragonal[15, 16]. Therefore, we would predict that hexagonal phases of these disilicides should exist. Hexagonal phases of these materials have been reported in sputter deposited thin films[17, 18], and stable bulk hexagonal phase of $MoSi_2$ has also been identified[19, 20].

The presence of the limits on `sp´ electrons for each crystal structure places an added constraint on the sequence of phases with stoichiometry in these systems. It is seen that there is a gap between the electron ranges of tetragonal and hexagonal crystal structures. No such gap exists between hexagonal and orthorhomibc, and orthorhombic and cubic structures. Thus, the presence of an additional phase between hexagonal and orthorhombic or orthorhombic and cubic structures is forbidden. An example would be the Co-Si system, where the Co_2Si phase is orthorhombic and the CoSi phase is cubic. Hence, this sequence forbids the presence of a Co_5Si_3 phase. All phase diagrams in the transition metal-silicon binary obey this phase sequence rule.


THERMAL EXPANSION COEFFICIENT, α x 10⁶ (°C⁻¹)
10
8
6
4
2
3d → 4d → 5d
M
'd'
ORBITAL
Ti 1.25 3
Zr 1.25 4
Hf 1.25 5
V 2.5 3
Nb 2.5 4
Ta 2.5 5
Cr 3.125 3
Mo 3.125 4
W 3.125 5
M5Si3