

Electronic structure of vanadium silicides

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The first electronic-band calculation for VSi_2 , the phase produced by the interface reaction between silicon and vanadium, has been performed using a linear combination of atomic orbitals approach in the extended Hückel approximation. The A15 compound, V_3Si , also has been investigated. The chemical bond in both compounds is found to be determined mainly by the p - d (Si-V) interaction. The d - d (V-V) interaction is also important in determining the physical properties of the compound. These interactions increase in strength with the metal concentration. The small charge transfer found in these compounds indicates a metallic bond picture. These results are used to interpret spectroscopic measurements of ultraviolet and synchrotron-radiation photoemission.

I. INTRODUCTION

The current interest in the properties of transition-metal silicides is due to their use in integrated circuits for Schottky barriers, Ohmic contacts, and low-resistance gates and interconnections.¹ Within the last few years substantial progress has been made in understanding the interfacial reaction between silicon and thin metal films.²⁻⁵ The products of these reactions are now well characterized and their physical, thermodynamic, and electrical properties have been studied. Spectroscopic techniques, such as Auger electron spectroscopy,⁶ ultraviolet photoemission spectroscopy,⁷⁻⁹ and x-ray photoemission spectroscopy,¹⁰ have been used to investigate the basic nature of the chemical bond in these complex silicide compounds. The early stage of the reaction at the Si-metal interfaces has been recently investigated using both conventional¹¹⁻¹⁵ and synchrotron radiation^{9,16,17} photoemission spectroscopy techniques.

The electronic structure of the refractory metal silicides has attracted attention because of the low resistivity and high-temperature stability of these silicides.^{18,19} In this paper we present the result of a theoretical investigation of the electronic structure of two vanadium silicides: VSi_2 and V_3Si .

Vanadium disilicide is produced by the reaction of V films with Si substrates.^{4,5} Owing to its complex structure (6 Si and 3 V atoms per unit cell), no electronic-band-structure calculation has been attempted heretofore, to the best of our knowledge.

The metal-rich silicide, V_3Si , has been as a product of the reaction between V and SiO_2 .⁴ The interest in this A15 compound arises mainly from its

high superconducting transition T_c (17 K).²⁰ Its anomalous structural, electrical, magnetic, and elastic properties are generally attributed to unusually fine features of the electronic density of states at the Fermi level. Various methods, including photoemission spectroscopy²¹⁻²⁴ and positron annihilation,²⁵⁻²⁷ have been used to study its electronic structure. Recently, a self-consistent electronic-band-structure calculation has been made for VSi_3 .^{28,29} The known structural properties of VSi_2 and V_3Si are listed in Table I.

II. METHOD OF CALCULATION

The calculations were made using the linear combination of atomic orbitals (LCAO) method in the extended Hückel³⁰ approximation (EHT). This semiempirical approach simplifies the computation of the electronic bands of very complex systems, such as the bulk silicides, which cannot be studied using first-principles methods; in addition, this method can be used to calculate the electronic properties of the interface between silicon and silicides.

In the EHT scheme the Coulomb integrals $\alpha_i = \langle \phi_i | H | \phi_i \rangle$ are set equal to the negative of the valence orbital ionization potential (VOIP) I_i ,^{31(a)} for the ϕ_i orbital. The resonance integrals are approximated by the expression.

$$B_{ij} = \langle \phi_i | H | \phi_j \rangle = -K\sqrt{I_i I_j} S_{ij}, \quad (1)$$

which is the geometric version of the Wolfsberg-Helmoltz approximation.^{31(b)} The overlap integral is denoted by S_{ij} . We choose $K=2.5$, which is the value used for metallic systems by Breeze and Perkins.³²

TABLE I. Structural properties of vanadium silicides.

	VSi ₂	V ₃ Si
Crystal structure	hexagonal C40	cubic A15
Space group	<i>P</i> 6 ₂ 22	<i>Pm</i> 3 <i>n</i>
Lattice parameters (Å)	<i>a</i> =4.571 <i>c</i> =6.372	<i>a</i> =4.7253
Unit cell volume Å ³	115.30	105.51
Number of molecules per unit	3	2
Number of shells within 8.5 Å		
Si-Si	30	5
Si-V	18	6
V-V	12	12
Nearest-neighbor distance (Å)		
Si-Si ^a	2.501	4.092
Si-V	2.501	2.462
V-V ^b	3.121	2.363

^a2.351 Å in silicon.^b2.619 Å in vanadium.

The atomic wave functions are expressed in terms of Slater-type orbitals. As pointed out by Messmer *et al.*,³³ the arbitrariness in parametrization used in the EHT scheme may lead to unphysical results for charge transfer. Following the suggestion of the above authors, we have adjusted the Slater orbital exponents to reproduce the

known electronic bands of pure silicon and vanadium.

Table II contains the orbital exponents and the VOIP data used in our calculation. Figure 1 shows the density of states of vanadium as determined by the parameters of Table II. The parameters for silicon are the same as used by Bisi and Calandra³⁴ for near-noble metal silicides.

The iterative procedure is set up by allowing the I_i 's to vary as functions of the excess charge q on the atom:

$$I_i(q) = C_i + B_i q. \quad (2)$$

Owing to the non-orthogonality of our basis, the charge q is calculated through a Mulliken population analysis.³⁵ Further details of our calculation may be found in Ref. 34.

We terminated the iteration when the charge variation between two successive iterations was less in magnitude than 0.005 e /atom, where e is the magnitude of the electron charge. Convergence was achieved after 6 (VSi₂) or 7 (V₃Si) iterations. During the iterative procedure the charge was evaluated using a mesh of 6 (VSi₂) or 10 (V₃Si) points in the irreducible part of the Brillouin zone (IBZ).

III. RESULTS

A. VSi₂

The density of states (DOS) of VSi₂ has been evaluated for a mesh of 210 points in the IBZ. The total DOS, together with the contribution of V d and Si states, is presented in Fig. 2.

The energy spectrum may be divided into several

TABLE II. Input parameters for silicon vanadium.

Orbital	Si			V	
	3s	3p	4s	4p	3d
Coefficient	1.0	1.0	0.5015	1.0	0.3739
Exponent (a.u. ⁻¹)	2.25	1.65	2.81	1.47	4.04
Coefficient			0.5783		0.7458
Exponent (a.u. ⁻¹)			1.62		1.74
VOIP					
C_i (eV)	14.82	7.75	6.32	3.43	6.37
B_i (eV)	1.39	10.13	6.71	5.63	10.79

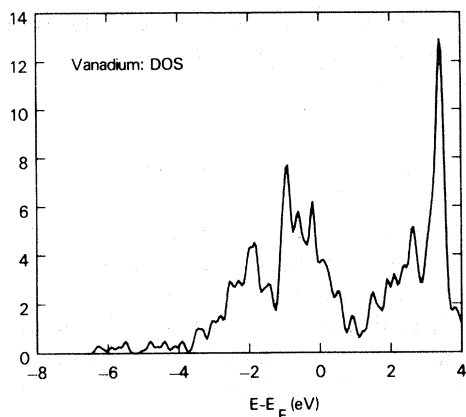


FIG. 1. Density of states (DOS) for V computed with the parameters of Table II.

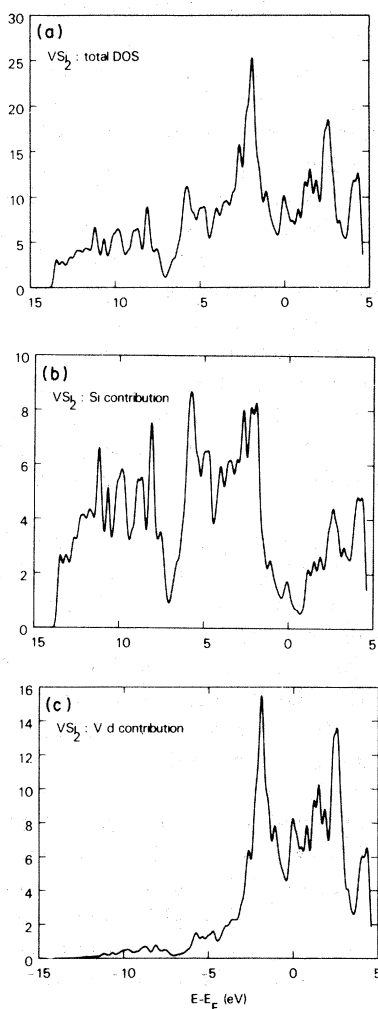


FIG. 2. Theoretical total DOS (a) and partial Si (b) and V d state (c) DOS for VSi_2 .

intervals depending on the predominant character of the states involved. Starting from higher binding energies (BE) we have four regions.

(i) The structure between -13.6 and -7.1 eV accommodates 3.9 e /molecule whose Si s -state contribution is 68% (to be compared with 23% for the Si p states). The Si s states are thus found to be dehybridized and not much is involved in the bonding with the metal.

(ii) The bonding interaction between Si p states and V d states is found in the energy region between -7.1 and -1.5 eV. Between -7.1 and -4.4 eV the Si p -state character is predominant, while close to E_F the d -state character is dominant. Nearly 2 p electrons per Si atom and 3.6 d electrons per V atom are found in this region.

(iii) Nonbonding d states are found at the Fermi level.

(iv) The region for energies greater than E_F is characterized by antibonding p - d (Si-V) interaction.

If we compare the V-metal DOS (Fig. 1) with the vanadium d -state contribution of Fig. 2, we see that the changes of d states are due to mixing with silicon. For pure V the strong d - d bonding-antibonding interaction splits the d bands into two groups of states which straddle the Fermi energy. In VSi_2 the V-V first nearest-neighbor distance is increased by $\sim 20\%$ (see Table I) and the p - d (Si-V) interaction becomes the dominant feature. As a result we have essentially the same d -band width as in pure V but the shape of the DOS is different, particularly near E_F .

The computed excess charge indicates that there is no significant ionic contribution to the chemical bond. We found an excess of 0.017 electrons per Si atom, indicating a charge transfer from V to Si.

B. V_3Si

The DOS of V_3Si has been evaluated for a mesh of 165 points in the IBZ. Figure 3 shows the total DOS and the various orbital contributions. We can distinguish four different regions in the spectrum.

(i) At higher binding energy, separated by a gap of 2.7 eV from the remaining structure of the DOS, there is a peak which accommodates 2 electrons/molecule. The predominant Si s -state character of these states indicates a full dehybridization of the Si orbitals.

(ii) The bonding interaction between Si p states and V d states is found in the energies between -5

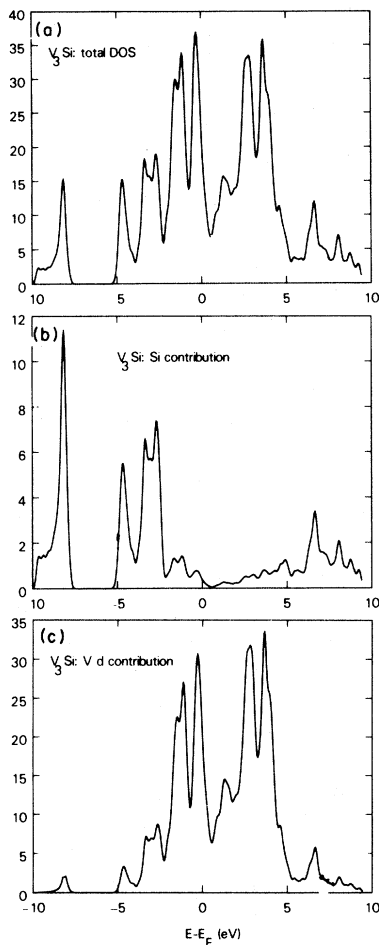


FIG. 3. Theoretical total DOS (a) and partial Si (b) and V d state (c) DOS for V_3Si .

and -2.3 eV. The structure in this region accommodates nearly 2 p electrons per Si atom and 0.8 d electrons per V atom.

(iii) The V d states constitute a strongly structured band from -2.3 to $+5$ eV.

(iv) The p - d (Si-V) antibonding states are found in the region between $+5$ and $+10$ eV.

These results show that in V_3Si both the p - d (Si-V) and d - d (V-V) interaction are important. The d states are split into bonding and antibonding bands separated by a region near E_F where the density of states is small. The details of the d -state contribution to the V_3Si DOS may be understood in terms of its $A15$ structure. The V atoms lie along three orthogonal chains with their nearest-neighbor distance being reduced by $\sim 10\%$ relative to pure vanadium. This explains the strong singularities in V_3Si and the same d -state bandwidths in V_3Si and in pure V. As for VSi_2 ,

we found for V_3Si a small charge transfer from V to Si. The excess charge on Si is 0.073 electron/atom.

IV. DISCUSSION

As mentioned, due to its complex structure, no electronic-band-structure calculation is available for VSi_2 . A synchrotron radiation photoemission study⁹ identified two structures in VSi_2 ; d -state bands at -1.56 to -1.6 eV and ~ 0.8 eV. These data may be explained in terms of the main d -state structure we found between -3 and -0.5 eV, especially the prominent peak -1.95 eV.

The same authors found a minimum between the d bands and the Si-derived bands at ~ 4 eV and three structures associated with the Si states at -5.5 , -7.2 , and -10.4 eV, respectively. These results are in close agreement with our theoretical densities of states, the -4 -eV minimum being interpreted as the separation (calculated to be at -4.4 eV) between the Si p -state peak, which is centered at -5 eV, and the predominantly d -state structures. The emission features at -7.2 and -10.4 eV can be associated with Si s -derived states. The negligible V $3p$ -state and Si $2p$ -state core-level shift⁹ is found to be in agreement with the very small computed charge transfer.

The good agreement between our results and the experimental data is evidence of the reliability of the VSi_2 electronic-band structure which we have obtained. Further support of our approach comes from our calculation for the simpler V_3Si structure.

Our calculation for V_3Si can be compared with the self-consistent augmented plane waves²⁸ and the linear muffin-tin orbital²⁹ calculations. Our results compare well with both regarding the position of the main peaks and the partial content of the DOS. Figure 4 shows a direct comparison between the results of Ref. 29 and our calculation.

We will not present a detailed comparison with the spectroscopic data²¹⁻²⁴ since the agreement has already been pointed out in Refs. 28 and 29.

The one-dimensional transition-metal chain, characteristic of the $A15$ structure, produces a substantial accumulation of bond in the charge along the chains. This high degree of anisotropy makes it difficult to determine the charge transfer from the charge-density distribution.

From x-ray diffraction data, Standenman³⁶ estimated a charge transfer of 1.8–2.4 electrons from every Si atom to V in V_3Si . Similar results

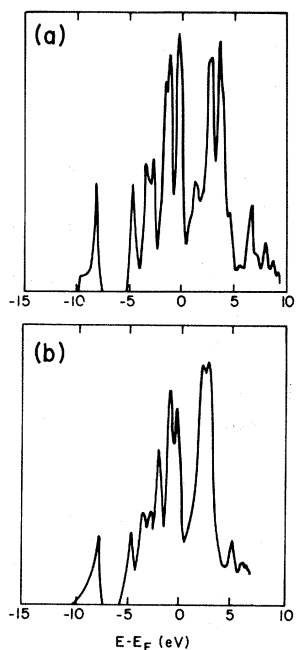


FIG. 4. Comparison between the total DOS of V_3Si (a) and the LMTO DOS (b) of Ref. 29.

have been obtained recently from theoretical electronic charge densities computed using self-consistent linear augmented plane waves.³⁷

These conclusions, which are in conflict with simple considerations of the electronegativities of the two atoms, have been questioned by Ho *et al.*³⁸ These authors interpreted their *A15* pseudopotential charge densities in terms of a metallic bonding picture. We found a charge transfer of 0.024 electron from every V atom to every Si atom. The small value of this charge transfer is in agreement with the metallic bond picture and its sign with electronegativity arguments. A similar charge transfer has been found in V_3Si with Cu_3Au structure.⁹ This result is supported by the data for the core-level shift if we interpret this shift as mainly chemical effects. The Si $2p_{3/2}$ binding energy is 98.5 ± 0.2 eV in V_3Si ,³⁹ to be compared with 99.2 ± 0.15 eV in Si(111)-(2 \times 1) (value relative to E_F , which is 0.3 eV above E_p , the top of the valence band).³⁹ The vanadium $3p$ -state peak is

found at 37.0 ± 0.1 eV,³⁹ in comparison with 37.2 ± 0.2 eV in elemental V.⁴⁰

In conclusion, the main point to be drawn from this theoretical analysis is that the chemical bond in vanadium silicides is determined mainly by the *p-d* (Si-V) interactions. Furthermore we found that this interaction increases with increasing metal concentration, resulting in an increase of the separation between the bonding-antibonding peaks. The overall picture of refractory metal silicides is similar to that of near-noble-metal silicides,^{7,9,34} the major difference being the position of the *d* band. In refractory metal silicides, the center of gravity of the *d* band is near the Fermi level, and so very peculiar features, such as *A15* structure and semimetallic behavior ($CrSi_2$) (Ref. 41) may occur. The *d-d* (V-V) interaction is thus more important in the determination of the physical properties of these compounds than for the near-noble metal silicides (for which the center of gravity of the *d* band lies well below the Fermi level).

The agreement with previous theoretical calculations and photoemission data for V_3Si and VSi_2 shows the feasibility of using a semiempirical method to study the electronic properties of these compounds. This capability to investigate the properties of very complex compounds, which at present cannot be studied using first-principles approaches, is necessary to understand the essential features of the chemical bond and the variation in electronic properties with crystal structure. Calculations of the intermixed interfaces between silicon and transition metals, i.e., between silicon and silicides, are also feasible.

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