

ELECTRONIC STRUCTURE OF TITANIUM SILICIDES^①

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ABSTRACT

Band structure and density of states(DOS) for five Ti-Si binary solid Ti_3Si , Ti_5Si_3 , Ti_5Si_4 , $TiSi$, $TiSi_2$ were calculated by use of extended Huckel tight-binding method. The bonding characters and electronic structure of titanium silicides were described. Some trends of their bonding character variation as a function of composition were also discussed here.

Key words: titanium silicides electronic structure density of state

1 INTRODUCTION

In recent years, considerable efforts^[1, 14] have been devoted to understanding the structure and microscopic properties of transition metal (TM) silicides. Spectroscopy techniques^[11, 14] such as Auger electron spectroscopy, synchrotron radiation photoemission spectroscopy, X-ray photoemission and its inverse process, bremsstrahlung isochromat spectroscopy (BIS) were used in researches on silicides of 3d, 4d and 5d TM in periodic table^[12]. There were also some results of theoretical investigation by methods such as augmented spherical wave procedure^[11] and extended Huckel technique^[5]. Some good explanation for experimental spectroscopy data was reported as well^[14]. In spite of so much work done, most of which just dealing with monosilicides or disilicides, the energy band and density of state(DOS) calculation for real crystals of TM silicides was still quite limited. As far as Ti-Si system is concerned, little work has been done to investigate the whole stable phases in phase diagrams of Ti-Si binary compounds^[16]. Moreover, the microscopic mechanism of bonding in silicides has not been sufficiently understood, and the role of Si s states in bonding, for example, is still in controversy^[1, 10, 11]. In this paper, we presented the results of theoretical calcula-

tion for silicide phases Ti_3Si , Ti_5Si_3 , Ti_5Si_4 , $TiSi$ and $TiSi_2$ in phase diagram^[15, 16] of bulk Ti-Si binary system using extended Hückel tight binding method. The electronic structure and bonding characters in these crystals and the variation tendencies of bonding characters as functions of composition in these silicides were also discussed here.

2 CRYSTAL STRUCTURE AND CALCULATION METHOD

$TiSi$ and $TiSi_2$ are orthorhombic crystal. Ti_3Si and Ti_5Si_4 are tetragonal, and Ti_5Si_3 is hexagonal (Table 1).

Except for $TiSi$ which has a simple cubic structure, the structure of the remainders is more complex. It is difficult to calculate a very complex solid system by strict methods in Quantum Chemistry such as ab initio. Thus in theoretical research of solid state chemistry, semiempirical approaches^[17, 18], which can simplify the computation and give reasonable results to satisfy semiquantitative description, are frequently used. So in this work, we used the tight binding energy band method with extended Huckel approximation. The valence orbitals 3d, 4s, 4p of Ti and 3s, 3p of Si were chosen to be a set of atomic orbital basis functions and the

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Table 1 Crystal structure of titanium silicides^[19-24]

	Ti ₃ Si	Ti ₃ Si ₃	Ti ₅ Si ₄	TiSi	TiSi ₂	Ti	Si
Crystal system	tetragonal	hexagonal	tetragonal	orthorhombic	orthorhombic	hexagonal	cubic
Space group	P42/n	P63/mcm	P4 ₁ 2 ₁ 2	Pnma	Fddd	p3ml	Fd3m
Lattice parameters / Å	<i>a</i> = 10.193 <i>b</i> = 10.193 <i>c</i> = 5.175	<i>a</i> = 7.448 <i>c</i> = 5.114	<i>a</i> = 6.713 <i>c</i> = 12.171	<i>a</i> = 6.540 <i>b</i> = 3.630 <i>c</i> = 4.990	<i>a</i> = 8.236 <i>b</i> = 4.773 <i>c</i> = 8.523	<i>a</i> = 2.950 <i>c</i> = 4.680	<i>a</i> = 5.420
<i>N_m</i>	8	2	4	4	8	4	
<i>N_e</i>	128	64	144	32	96	16	
<i>V_c</i>	537.67	283.69	548.48	118.46	335.04	40.73	159.22
Ti-Ti*	2.27	2.55	2.84	3.22	3.19	2.89	
Ti-Si*	2.57	2.50	2.45	2.59	2.53		
Si-Si*		3.10	2.32	2.17	2.53		3.84

Notes: *N_m* — number of molecules per unit; *N_e* — number of valence electrons per unit; *V_c* — unit cell volume (Å³); * — distance between nearest neighbor atoms (Å).

crystal orbital basis function set was composed of Bloch functions of these atomic orbitals. The linear combination of Bloch functions was performed in Schrodinger equation of silicide system. Table 2 contains the atomic orbital exponents, ionization potential data and other parameters used in our calculation.

Table 2 Extended Huckel parameters

orbitals	VOIP/eV	ζ_1	ζ_2	C_1	C_2
4s	-8.97	1.50			
Ti	4p	-5.44	1.50		
	3d	-10.81	4.55	1.40	0.426 0.7839
Si	3s	-17.30	1.38		
	3p	-9.20	1.38		

Considering the influence of neighbor cells on the unit cell, only those overlap integrals in which the distance from neighbor cell atom to unit cell atom was longer than 12.5 Å were neglected by our program. So that for some small unit cells such as TiSi, two or three nearest neighbor cells were considered in the computation. A set of 108 *K*-points generated according to the method of Pack and Monkhorst^[25] were used throughout the calculation.

3 RESULTS AND DISCUSSION

3.1 Bonding Characters in Titanium Silicides

The band structure, density of state (DOS) and the contribution of single atom or atomic orbitals to DOS (partial DOS) were obtained in our calculation. We also evaluated the crystal orbital overlap population (COOP) which clearly showed the bonding and antibonding properties of states. Each of five silicides, metal Ti and elemental Si were calculated in the same procedure. A large number of data were collected, and it was found that there were some similar results in them. Taking Ti₅Si₄ for example, the result of which is shown in Fig. 1.

Fig. 2 is the COOP curves for Ti-Ti, Ti-Si and Si-Si bonds in Ti₅Si₄. Amplitudes of these curves depend on the number of states, the coupling overlap and magnitude of the coefficient in crystal orbitals.

It is easy to see from Figs. 1 and 2 that;

(1) There is significant overlap between Ti and Si *s*, *p* states. The COOP in this overlap region is bonding. so there are *s* and *p* bonds between Ti and Si in Ti₅Si₄.

(2) The *s* states of Si are mainly located in the energy region of -25 ~ -16 eV and distributed in two peaks, one for bonding, the other for antibonding. It is obviously the result of interaction among Si atoms in crystal.

(3) The *d* states of Ti in energy region near Fermi level are also divided into two peaks as a result of strong bonding between Ti *d* state and Si *p*

state. The peak below ϵ_F corresponds to bonding of $d(\text{Ti})-p(\text{Si})$ bonds, and that above, antibonding. This is the general feature in TM silicides.

(4) Since strong $d(\text{Ti})-p(\text{Si})$ bonding and antibonding states lie just below and above ϵ_F , there should be a clear energy gap between them. However, as illustrated in Fig. 1, only what is referred to as a quasi gap can be seen due to the existence of significant Ti $d-d$ interaction. This may be a common feature in silicides of early TM in periodic table, because their d orbital wave functions show large spatial extension.

(5) F in Fig. 1 shows that there is overlap between s and p state in elemental Si, which is consistent with the general idea of Si sp^3 hybridization. But the situation in Ti_5Si_4 is different, there is virtually no Si p mixing with Si s . Therefore, it seems that Si s and p orbitals do not hybridize to interact with Ti and other Si atoms. The role of Si s state may be $s(\text{Si})-s(\text{Si})$ bonding, $s, p(\text{Ti})-s(\text{Si})$ bonding and $d(\text{Ti})-s(\text{Si})$ bonding. It is interesting that there is a quasi gap instead of normal due to the existence of metal d nonbonding state at ϵ_F , which may be the reason why a lot of TM silicides have good electric conductivity and low contact ohmic resistance.

3.2 Electronic Structure Variation Trend as a Function of Composition

According to the sequence Ti_3Si , Ti_5Si_3 , Ti_5Si_4 , TiSi , TiSi_2 , the silicon content increases from 25% to 66.7%. Comparing the calculation results for five silicides, metal Ti and elemental Si, it can be found that the composition of Ti silicides has a strong influence on the chemical bonding and hence on the electronic structure. The variation of bonding characters can be regarded as a function of silicon content.

Figs. 3, 4 and 5 show the d -DOS of Ti and s -DOS, p -DOS of Si in five silicides. We can see that the total DOS of these silicides is similar to each other, so their bonding mechanism should also be similar. Checking the partial DOS in detail, however, one can find that there is some regular electronic structure variation in sequence from Ti_3Si to TiSi_2 . As the silicon content increases,

four trends can be observed:

(1) Strengthened $d(\text{Ti})-p(\text{Si})$ bonds and weakened metal $d-d$ interaction in silicides are shown by more separated $d-p$ bonding peak from antibonding one and the reduction in density of state at quasi gap. The d -DOS of Ti in Ti_3Si is much more similar to that in metal Ti, but not in others, which is because the number of nearest neighbour Ti-Ti contacts is reduced. The coordination number of Ti is 12 in metal Ti and 7 in Ti_5Si_4 with 6

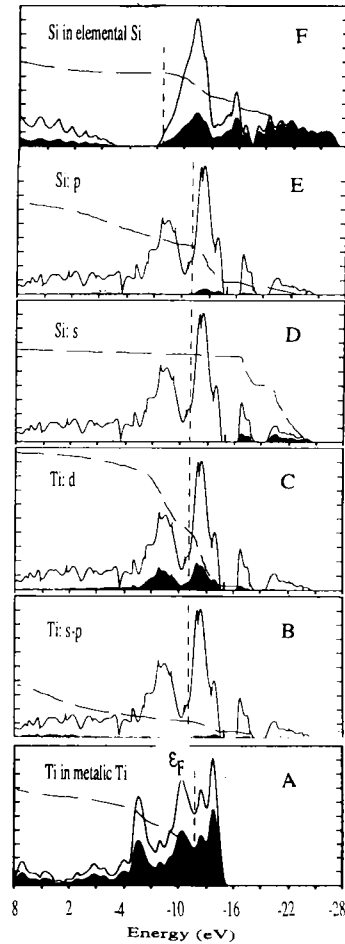


Fig. 1 Contribution (shadow area) of Ti s, p (b), d (c) orbitals and Si s (d), p (e) orbitals to total DOS (solid curve) of Ti_5Si_4 . (a) and (f) represent separately the contribution of Ti and Si atoms to total DOS of metallic Ti and elemental Si. Dashed line shows Fermi level (ϵ_F) while dotted curve is an integration of relative orbital occupation on a scale of 0~100%.

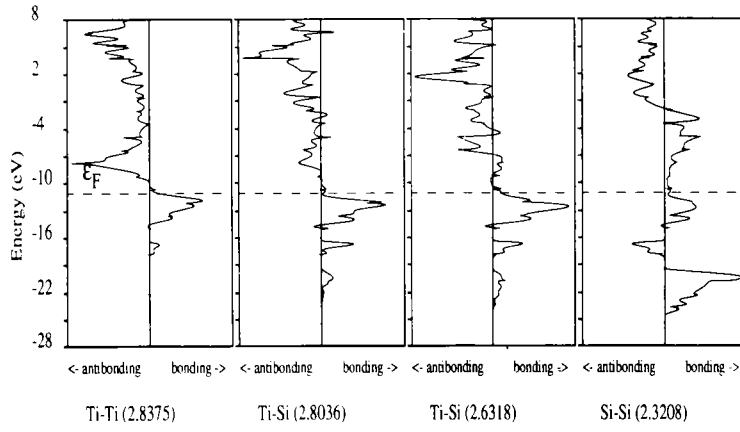


Fig. 2 Crystal orbital overlap population curves for Ti-Ti, Ti-Si, Si-Si bonds in Ti_3Si_4 . Peaks on the right side of the dashed line represent bonding states, and that on the left, antibonding.

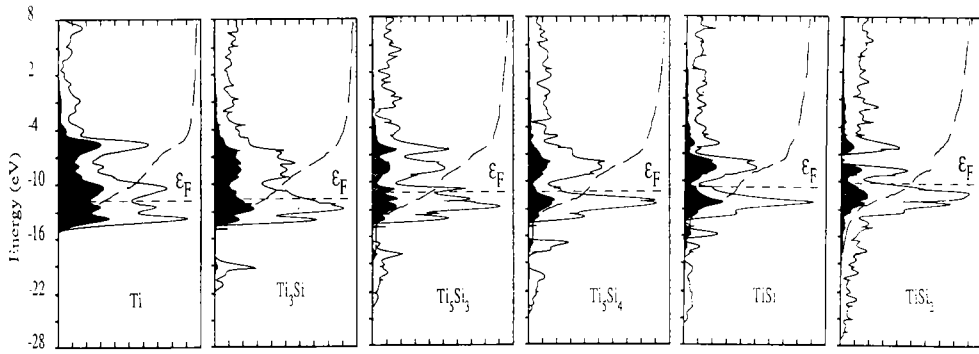


Fig. 3 Titanium *d* orbital contribution to total DOS of metallic Ti and that of five silicides in Ti-Si binary system

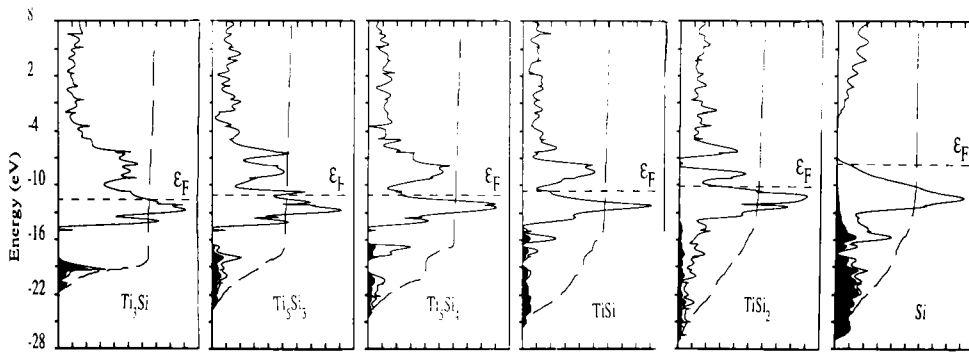


Fig. 4 Silicon *s* orbital contribution to total DOS of elemental Si and that of five silicides in Ti-Si binary system

silicon atoms surrounding a central Ti atom. Also, the separation of TM atoms in many silicides is larger than that in the pure metal due to the participa-

tion of Si atoms in bonding. The Ti-Ti bond length in Ti_3Si_4 , for instance, is 2.93 \AA , while in metal Ti, 2.89 \AA .

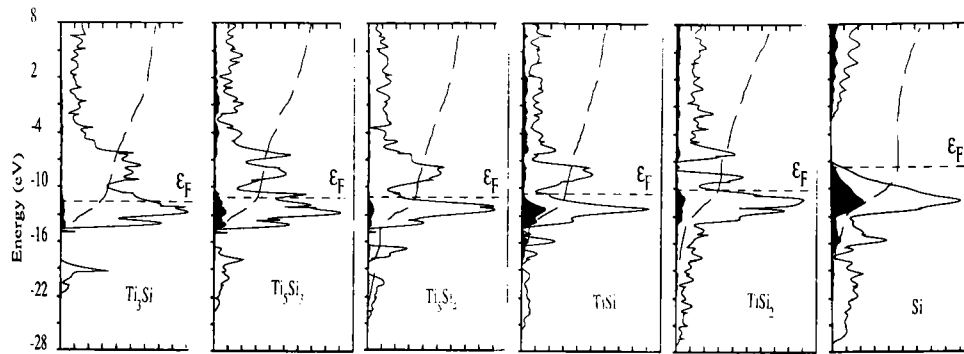


Fig. 5 Silicon p orbital contribution to total DOS of elemental Si and that of five silicides in Ti-Si binary system

(2) The d -DOS extends to the energy region where Si s state is predominant. Moreover, the width of valley between d (Ti)- p (Si) bonding and antibonding peak becomes larger gradually. This means that the increase of silicon content is favourable for d (Ti)- s (Si) and d (Ti)- p (Si) bonding. The advantage can also be seen from the interaction between Si s and Ti s , p states.

(3) From Ti_3Si to $TiSi_2$, Si s -DOS shift to higher binding energy region, which implies that s (Si)- s (Si) bond becomes more stable.

(4) The s and p states of Si in elemental Si overlap well, and there is sp^3 hybridization. This feature can also be observed in $TiSi_2$ and $TiSi$, but it becomes indistinct in Ti_3Si_1 . While for Ti_3Si_3 and Ti_3Si , there is no s - p overlap at all. So it can be concluded that the extent of Si sp^3 hybridization in TM silicides is depended on the silicon content. The silicon content in $TiSi$ and $TiSi_2$, for instance, exceeds 50%, so Si s - p hybridization exists definitely.

We can understand the four trends above in a simple way. Silicon content in TM silicides increases with increasing number of silicon atoms, which leads certainly to separate Ti atoms, weaken Ti-Ti interaction and strengthen Ti-Si bonds. The more silicon atoms there are, the more possible it is to enhance Si-Si interaction and s - p hybridization of Si.

Besides, our calculation indicated that the Fermi energy level of metal Ti was at -11.6618 eV while that of elemental Si was at -7.6616 eV. All Fermi levels of Ti silicides should lie in the energy region between them. Our results have shown

that the Fermi levels of Ti silicides shift progressively to higher energy direction as the silicon content increasing, which was also observed in our recent study on Fe silicides. Therefore, it can be concluded that in TM silicides, the larger the content of component with high Fermi level in its elemental crystal, the higher the system's Fermi level.

4 CONCLUSIONS

(1) Over the full range of DOS distribution, the largest DOS is located near Fermi level. States regarded as frontal orbitals of crystal are composed of d (Ti)- p (Si) bonding, antibonding and d - d non-bonding orbitals with respect to Ti-Si interaction. The d (Ti)- p (Si) bond is the strongest chemical force in silicides, while the existence of quasi gap would be considered as a reason for good electric conductivity of TM silicides. At the bottom of valence band are the bonding states of Si s and Ti s , p , especially d states overlapping. Their antibonding states are undoubtedly at the top of conduct band.

(2) The s states of Si in Ti silicides have three roles, i. e., s (Si)- s (Si) bonding, s (Si)- d (Ti) bonding and bonding with s , p states of Ti. If the silicon content is less, Si s and p orbitals would not hybridize. Such hybridization will become apparent when the number of silicon atoms in silicides increase.

(3) The composition of TM silicides has a strong influence on the chemical bonding and hence on the electronic structure. As the silicon content

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affects the residence time of bubbles in ASH but also affects the collision and adherence of bubbles with particles, so in the operation of ASH, the inlet flowrate and the underflow pipe diameter should be adjusted to a comprehensive optimum range to get a satisfied separation.

4 CONCLUSIONS

(1) Liquid column is one of the essential characteristics in a well operated ASH. The height of liquid column (H) is preferred to be $H = (1 \sim 2)D$. There exist inner helical flow and outer helical flow in liquid column.

(2) The tangential velocity component of liquid in swirl layer decreases rapidly when the axial coordinate Z increased, while the axial velocity component decreases slowly. And the tangential velocity component of liquid in swirl layer increases rapidly with the inlet velocity.

(3) It is reasonable to design an ASH with a small length/diameter ratio.

(4) It is not proper to sparge compressed gas in the section of ASH wall near the pedestal baffle, and the ASH wall near the pedestal baffle should be designed with solid wall other than porous wall.

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increasing, the Fermi level would move to the position close to ε_F of elemental Si, TM $d-d$ interaction would become weak, and Ti-Si interaction would become strong. In addition, the bottom of valence band would shift to higher binding energy region. Thus Si $s-s$ interaction would be intensified, and the interaction between Ti d, s, p states and Si s state would be strengthened as well.

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