Theoretical study of structural characteristics, mechanical properties and electronic structure of metal (TM = V, Nb and Ta) silicides

Biao Wan a, b, Furen Xiao a, Yunkun Zhang a, Yan Zhao a, Lailei Wu a, *, Jingwu Zhang a, Huiyang Gou b, **

a Key Laboratory of Metastable Materials Science and Technology, College of Material Science and Engineering, Yanshan University, Qinhuangdao 066004, China
b Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China

1. Introduction

Transition metal silicides possess excellent physical and chemical properties, e.g. high melting points, low densities, resistance to oxidation and good creep to tolerance, endowing them with multiple applications in high-temperature device, catalysis and very large scale integrated (VLSI) circuit technology [1–3]. For example, as an early transition metal silicides with 5:3 stoichiometry, Ti₅Si₃ is an excellent candidate for coating materials in wear resistant composite material due to the high melting point (2130 K) [4]. Zr₃Si₂ satisfies the requirements for gas fast reactors due to its good thermal conductivity [5]. MoSi₂ and WSi₂ are promising materials for high temperature device [6–8]. Among these silicides, VB transition metal silicides (TMSiₓ, TM = V, Nb, Ta) exhibit various stoichiometries, and thus received continual attentions due to their intriguing electronic and thermodynamic characteristics. The A15 type V₃Si, Nb₃Si and Ta₃Si were well studied as high-Tc superconductors with transition temperatures, 17 K, 18 K and 9.3 K, respectively [9–12]. Au₂Cu type Ta₂Si can be used to be SiC field-effect transistors, with prolonged the stable operation at 500 °C [13]. Three different structure types, D₈h (Cr₅B₃ prototype), Dm₃ (W₅Si₃ prototype) and D₈ (Mn₅Si₃ prototype) with 5:3 ratio have been observed in experiment. The low-temperature phase is D₈m for V₅Si₃, and D₈ for Nb₅Si₃ and Ta₅Si₃, all of them possess perfect thermal stability, good mechanical property, high hardness and compatibility with complementary metal-oxide-semiconductor (CMOS) devices [14–17]. P₆₃m-TMSi₂ is found to be widely applied in thin films for microelectronics, due to their high electrical conductivity, corrosion resistance, and good ability to contact with silicon.

Theoretically, elastic properties and electronic structure of vanadium silicides, V:Si = 3:1, 5:3, 6:5 and 1:2, were calculated by Thieme and Gemming using the projector augmented wave method [18]. The thermal and physical properties of Nb:Si (Ti₃P type), α-Nb:Si (Cr₃B₃ type), β-Nb:Si (W₅Si₃ type) and NbSi in Nb:Si system were evaluated by Papadimitriou [19] and Chen et al. [20].

* Corresponding author.
** Corresponding author.
E-mail addresses: will@ysu.edu.cn (L. Wu), huiyang.gou@gmail.com (H. Gou).

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thermodynamical stability, mechanical properties and electronic structures for various stoichiometries of TM-Si (TM = V, Nb and Ta) is still rare. In this work, we perform first-principles calculations on VB transition metal silicides, over a wide stoichiometry range, (TM:Si = 3:1, 2:1, 5:3, 3:2, 5:4, 6:5, 1:1, 1:2 and 1:3), which aims to provide a fundamental understanding of the structural characteristics, mechanical properties and electronic structure of studied silicides.

2. Computational method

The structural optimization, electronic structure have been performed within CASTEP [22] code based on density functional theory (DFT). The exchange and correlation functional were considered by generalized gradient approximation of Perdew-Burke-Emzerhof (GGA-PBE) [23]. The valence electrons of the elements are treated as, 3s3p2 for Si; 3d4s2 for V, 4d5s2 for Nb and 5d6s2 for Ta, respectively. A cutoff energy of 500 eV and dense Monkhorst-Pack K meshes were selected to ensure the total energy converged within 1 meV per formula unit. The pin polarized was included for metal-rich phases. The magnetism was found to be neglected. To construct the convex hull, extensive structures (stoichiometric ratio, TM:Si ranging from 3:1 to 1:3) were considered here, namely experimental phases (Pn3m-Ni3Si3, P63/mcm-Si3V3, I4/mcm-V3Si3, I4/mcm-Si3V3, I4/mcm-Ta3Si3) and P6222-VO3Si2 in V-Si system, Pn3 m-Nb3Si3, P42/mmb-Nb3Si3, P4/mmm-Nb3Si3, P4/mmm-Nb3Si3 and P6222-Nb2Si2 in Nb-Si system, P42/mn-Ta3Si, I4/mcm-Ta3Si, I4/mcm-Ta3Si, P622-Si3Ta2 and P6222-Ta2Si2 in Ta-Si system), and chemically related compounds of III-V B transition metal borides, carbides, silicides, nitrides, phosphides, and arsenides. All of the structures were fully relaxed without any symmetry and stress constraint. The elastic constants were calculated from evaluation of stress tensor generated small strains. The elastic modulus and Poisson’s ratio were derived from Voigt-Reuss-Hill approximations [27,28]. Phonon spectra of new proposed phases were calculated through finite displacement methods [27,28]. Structure figures were obtained by using VESTA package [29].

3. Results and discussion

3.1. Thermodynamic stability

The calculated lattice parameters, and formation enthalpies $\Delta H_f$ (eV/atom) of TM-Si systems are listed in Table 1, Fig. 1 and Fig. S1 in the Supporting Information. In general, the obtained lattice parameters are well consistent with previous experimental and theoretical results within the error of 3.5%, except for Nb3Si2 [30], which was proved to be Nb3Si3 in experiment [15]. $\Delta H_f$ for TM3Si were determined by the following equation:

$$\Delta H_f(TM_3Si_y) = \left( E_{TM_3Si_y} - x E_{TM} - y E_{Si} \right) / (x + y),$$

where $E$ is the total energy of a compound or a constituent element, here cubic V, Nb, Ta (Space group Im3 m) and diamond Si were selected as the reference structures. In V-Si system, as shown in Fig. 1a, Pn3 m-Ni3Si3, I4/mcm-V3Si3 and P622-VO3Si2 are just lying on the convex-hull, perfectly explaining the observations at low temperature in experiment [31]. Similar results can also be obtained for I4/mcm-Nb3Si3, P622-Nb2Si2 in Nb-Si system, and P42/mn-Ta3Si, I4/mcm-Ta3Si, I4/mcm-Ta3Si and P622-Si3Ta2 in Ta-Si system. Especially, W3Si4-type V3Si3, Cr3B2-type Nb3Si3 and Ta3Si3 show the lowest the formation enthalpies ($-0.632$, $-0.706$ and $-0.637$ eV/atom) in V-Si, Nb-Si and Ta-Si system, respectively.
Fig. 1. Formation enthalpies of V-Si (a), Nb-Si (b) and Ta-Si (c) compounds, calculated at zero temperature and zero pressure. Each red solid circle represents an individual experimental phase and each blue solid square represents an individual theoretical phase. The brown tie line is convex hull. Experimental phases V₃Si, V₅Si₃ and VSi₂ of V-Si system, Nb₅Si₃ and Nb₆Si₅ of Nb-Si system and Ta₃Si, Ta₅Si₃ and TaSi₂ of Ta-Si system are located at convex hull indicating they are ground state phases, and marked by solid green circle.

For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

suggesting that they are more easily to be synthesized. It should be noted that, in the Nb-Si system, the formation enthalpy of U₁Si₂-

3 type Nb₅Si₃ is very close to the convex-hull line, reasonable inter-

terpreting that it has been proposed by different researchers [15,32].

Meanwhile, the formation enthalpies of the high temperature phases in experiment, P₆₃/mcm-V₅Si₅, Ibam-V₆Si₆, and I4/mcm-V₆Si₆ in V-Si system, P₆₃/mcm-Nb₅Si₃, P₆₃/mcm-Nb₆Si₅, and P63/mcm-Nb₅Si₃ in Nb-Si system, β-Nb₆Si₅ and P63/mcm-Ta₅Si₃ in Ta-system, are also negative, but above the convex-hull. Therefore, their stability under high temperature should ascribe to the great contribution of entropy. On the other hand, formation enthalpies of all the new proposed phases (e.g., V₃Si, V₅Si₃, V₆Si₂, V₂Si₂, V₂Si₃ and VSi₃ in V-Si system, Nb₅Si₃, Nb₆Si₅, Nb₅Si₃, Nb₆Si₅ and Nb₆Si₃ in Nb-Si system, Ta₃Si, Ta₅Si₃, Ta₆Si₅, Ta₅Si₃ and Ta₆Si₅ in Ta-Si system, as shown in Fig. 1) show negative values. Therefore, they may be synthesized under some nonequilibrium conditions, e.g., high temperature or high pressure, as the high temperature phases verified by experiment. Particularly, the formation enthalpy of the proposed Nb₅Si₃, Nb₆Si₅, Nb₆Si₃ and Ta₅Si₃ are very close to the convex hull, indicating their good thermodynamic stability and may be more likely to be realized in experiment. Dynamic stability of the new predicted phases were further checked by calculating their phonon spectra. As shown in Fig. S2, except VSi₂, no imaginative frequency can be observed for the phonon dispersion curves in the whole Brillouin zone, implying that they are dynamic stable at zero temperature and zero pressure.

3.2. Structure property

The crystal structure of the experimental and hypothetic phases in TM-Si system present in Fig. S2, representative phases TM₃Si₂, P₆₃/mcm-TM₃Si₁ Ibam-TM₃Si₁ and TMSi₂ are listed in Fig. 2. Optimized atomic positions of TM-Si newly predicted phases are tabulated in Table S1. As shown in Fig. 2 and Fig. S2, the patterns of Si atoms in the crystal can be classified into four different types, i.e., isolated atoms, Si₂ pairs, chains (linear or zigzag) and three dimensional network. In TM₃Si, HT phase P₆₃/mcm-TM₃Si₁ (Fig. 2a), proposed P2₁3-VSi₂ and P2₁3-TaSi₁, the Si atoms are isolated from each other with the Si-Si distance larger than 3 Å. Si₂ pairs appeared in α-Nb₅Si₃ and α-Ta₅Si₃, TM₃Si (Fig. 2b), TM₅Si₃ and the Si-Si bond length is 2.403 and 2.432 Å, for α-Nb₅Si₃ and α-Ta₅Si₃; 2.355, 2.434 and 2.437 Å for V₃Si, V₅Si₃ and V₆Si₂; 2.408, 2.485, 2.511 Å for V₆Si₂, Nb₅Si₃ and Ta₅Si₃, respectively. Linear silicon chains can be observed in TM₃Si, I4/mcm-V₅Si₅, β-Nb₆Si₅ and β-Ta₅Si₃, I4/mcm-V₆Si₆. The chains run along [001] direction with a unique bond length of 2.432, 2.560 and 2.565 Å for V₃Si, Nb₅Si₃ and Ta₅Si₃; 2.357, 2.531 and 2.575 Å for I4/mcm-V₅Si₅, β-Nb₆Si₅, β-Ta₅Si₃ and alternative bond lengths 2.391 and 2.544 Å for I4/mcm-V₆Si₆, respectively. A general feature can be found that the Si-Si bond length is monotonously increased from vanadium silicides to tantalum silicides, due to the increasing atomic radius from V to Ta. V₆Si₅, Nb₅Si₃ and Ta₅Si₃ (Fig. 2c) with Ibam symmetry have the mixing Si atomic motifs of isolated atoms, linear chains and zigzag chains. Both linear and zigzag chains run along [001] direction. The Si-Si bond lengths in linear/zigzag chains are 2.769/2.421 Å, 2.610/2.517 Å and 2.644/2.514 Å, for Ibam-V₆Si₆, Nb₅Si₃ and Ta₅Si₃ respectively. Infinite zigzag Si chains along [010] direction can also be found in Pbma-NbSi with unique bond length, 2.429 Å. In the hypothetical TM₃Si₁ and TMSi₂, Si atoms adopt three dimensional network with Si-Si bond lengths varying from 2.424 to 3.068 Å. Intriguing, the Si atoms in TMSi₂ (Fig. 2d) adopt DNA-like double helix chains, the Si-Si bond lengths in helix chain are 2.492 (VSi₂), 2.573 (NbSi₂) and 2.579 Å (TaSi₂), and a couple of helix chains are connected together by Si-Si bond length of 2.657 (VSi₂), 2.651 (NbSi₂) and 2.852 Å (TaSi₂). The unique structural feature should play important role for the stability of TMSi₂.

3.3. Mechanical property

The calculated elastic constants (Cᵢⱼ) of considered phases at zero temperature and zero pressure are shown in Tables 2–4, together with available theoretical and experimental results. According to Born-Huang stability criterion [38,39], the mechanical stability were firstly judged by C₆₆. As shown in Tables 2–4, C₆₆ of all the new predicted phases satisfy Born-Huang stability criterion, indicating their mechanical stability. However, HT phases P₆₃/mcm-V₅Si₅ and Ta₅Si₃, Pm₃ m-Nb₅Si are mechanical unstable (negative C₄₄ for P₆₃/mcm-V₅Si₅ and P₆₃/mcm-Ta₅Si₃, and C₁₁ < C₄₄ for Pm₃ m-Nb₅Si), implying they are hardly recoverable at ambient conditions, consistent with previous reports [20,33]. Besides of C₃₃ value of V₃Si (133 GPa), generally, C₁₁, C₂₂ and C₃₃ values of TM₃Si are greater than that of element Si, and close or higher than that of metal V, Nb and Ta, indicating a relatively strong interaction between TM and Si. The largest individual elastic constant among V-Si, Nb-Si and Ta-Si system, C₃₃ of VSi₂, NbSi₂ and TaSi₂ is 404 GPa, 456 GPa and 461 GPa, respectively, indicating the most compression resistance along [001] direction, which should contribute to their unique double helix chains running along c axis.

To better understand the mechanical properties of those compounds, the bulk modulus (B), shear modulus (G) derived from the
Voigt-Reuss-Hill (VRH) approximation and Poisson’s ratio are shown in Table 3 and Fig. 3, the Young’s modulus ($E$) and Poisson’s ratio ($\nu$) estimated by the following relations are also listed.

$$E = \frac{9BG}{3B + G} \quad (2)$$

$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (3)$$

Our results are excellent agreement with previous studies, further verifying the reliability of our calculations. As shown in Fig. 3(a)–(c), a general trend of the bulk modulus of TM$_x$Si$_y$ is V-Si < Nb-Si < Ta-Si. Moreover, the bulk modulus firstly increase slowly with the increasing concentration of silicon, varying from 180 GPa (metal V) to 189 GPa (I$_4$/mcm-V$_5$Si$_3$) for V-Si system, 174 GPa (metal Nb) to 193 GPa (I$_4$/mcm-Nb$_5$Si$_3$) for Nb-Si system and 190 GPa (metal Ta) to 207 GPa (Ta$_2$Si) for Ta-Si system, then decrease to the lowest value, 84 GPa for diamond-like silicon. However, there is no general tendency for $G$ values. First higher value appears at TM$_5$Si$_3$ (121 GPa for I$_4$/mcm-V$_5$Si$_3$, 129 GPa for I$_4$/mcm-Nb$_5$Si$_3$ and 129 GPa for I$_4$/mcm-Ta$_5$Si$_3$), and the highest $G$ value is for TM$_2$Si$_2$ (156 GPa for VSi$_2$; 132 GPa for NbSi$_2$ and 137 GPa for TaSi$_2$). Similar tendency can also be found for the Young’s modulus. HT Ibam-V$_6$Si$_5$ and newly predicted Ibam-Nb$_6$Si$_5$ and Ta$_6$Si$_5$ phases also possess high shear modulus and Young’s modulus, 116 GPa ($G$) and 286 GPa ($E$) for Ibam-V$_6$Si$_5$, 107 GPa ($G$) and 269 GPa ($E$) for Ibam-Nb$_6$Si$_5$ and 103 GPa ($G$) and 263 GPa ($E$) for Ta$_6$Si$_5$, respectively.
To provide a straightforward way to describe the elastic anisotropy of TM5Si3, TM6Si5 and TMSi2, the Young’s moduli in three dimensions (3D) and corresponding 2D projections of H/ mcm-V5Si3, \(\alpha\)-Nb5Si3, Nb6Si5 and NbSi2 are calculated as a function of the crystallographic directions [43] (as shown in Fig. 3). For isotropic materials, the shape of 3D curved surface is sphere, and the corresponding 2D projections are circle. The deformation extent of 3D curved surface from sphere depends on the linear dimensions of covalent bonds. As shown in Fig. 3c, for isotropic materials, the shape of 3D curved surface is sphere, and the corresponding 2D projections are circle. The deformation extent of 3D curved surface from sphere depends on the linear dimensions of covalent bonds.

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The Poisson’s ratio \(\nu\) is connected with the rate of expansion or shrink when the material being stretched or compressed, and it provides a valuable information about covalent bonding character of materials [44]. The metal rich phases TM5Si3 and TM6Si5 possess high values of \(\nu\) (larger than 0.282), due to metallic characteristic. Contrarily, TMSi2 have the smallest value of \(\nu\), 0.130 for VSi2, 0.200 for NbSi2 and 0.195 for TaSi2, respectively, indicating relatively strong covalent interactions exiting in these phases. Additionally, Pugh ratio \(G/B\) [45] was also calculated to distinguish the brittle or ductile materials, the critical value is 0.571. Thus \(Ibam-V6Si5, Immm-V6Si5\) and VSi2 in V-Si system, \(\alpha\)-Nb5Si3, \(\beta\)-Nb5Si3 and NbSi2 in Nb-Si system, \(\alpha\)-TaSi3 and TaSi2 of Ta-Si system are brittle, all the others are ductile.

Debye temperature \(\Theta_D\) is an important fundamental parameter related to many physical properties (e.g. Heat capacity and stiffness). Which can be estimated by using the following equation [46]:

\[
\Theta_D = \frac{h}{K} \left( \frac{3n}{4T} \frac{N_A \rho}{M} \right)^{1/3} \mu_m
\]

where \(h\) is Plank constant, \(K\) is Boltzmann’s constant, \(N_A\) is the Avogadro’s number, \(\rho\) is the density, \(M\) is the molecular weight, \(\mu_m\) is average sound velocity in a polycrystalline system and can be evaluated by Ref. [46].
\[ \nu_m = \left( \frac{2}{3} \frac{1}{\nu_l^2} + \frac{1}{\nu_t^2} \right)^{-1/3} \]  

(5)

where \( \nu_t \) and \( \nu_l \) are the mean transverse and longitudinal sound velocities, which can be related to the shear and bulk moduli by the Nabier’s equations [47]:

\[ n_l = \left( \frac{3B + 4G}{3\rho} \right)^{1/2} \text{ And } n_t = \left( \frac{G}{\rho} \right)^{1/2} \]  

(6)

As shown in Table 3, the calculated Debye temperature is well consistent with experimental results [14,32]. From Fig. 3d, the calculated Debye temperatures are following the sequence of V-Si > Nb-Si > Ta-Si, probably caused by the density of TM-Si systems is V-Si < Nb-Si < Ta-Si in corresponding stoichiometric ratio. Further, TMSi\(_2\) exhibit the largest values, 810 K for VSi\(_2\), 651 K for NbSi\(_2\) and 526 K for TaSi\(_2\), respectively.

3.4. Electronic structure

To elucidate the bonding nature of TM\(_x\)Si\(_y\), the total and partial
density of states (TDOS and PDOS) are calculated and plotted in Fig. S4—6. As shown in Fig. S4—6, all the phases considered here show metallic characters, due to the finite values of DOS at Fermi level ($E_F$). From TM$_3$Si to TMSi (Figs. S4a—h, 5a—j and 6a—j), a general feature is that the valence band is dominated by Si-3s states in the vicinity of $-9$ eV, Si-3p states in the middle zone ($-6$ eV $-3.5$ eV), and TM-d states at the higher energy. To get a good view of the influence of silicon concentration on electronic structures, the DOS profile of TM$_2$Si, TM$_3$Si, TM$_5$Si$_3$ and TMSi$_2$ are presented in Fig. 4. From Fig. 4, for TM$_3$Si (Fig. 4a, e and i), due to the low silicon concentration, each Si atom is separated by TM atoms, introducing highly localization of Si-s band. On the other hand, a relatively weaker hybridization between Si-3p and TM-d orbital can be observed with a narrow overlapping, about 1.6 eV for V$_3$Si, 2.3 eV for P$_4$J$_{1/2}$/Nb$_3$Si and 3.0 eV for Ta$_3$Si. Furthermore, the Fermi level in TM$_3$Si catches the edge of TM-d peak, resulting extremely high $E_F$ values, which should contribute to their outstanding superconducting characters in A15 type superconductors [48, 49].

Different from TM$_3$Si, there is a small band gap of Si-s orbital, around $-9$ eV for V$_2$Si (Fig. 4b) and Nb$_2$Si (Fig. 4f), $-9.8$ eV for Ta$_2$Si (Fig. 4j), formed by the hybridization between the Si-s and Si-p orbital, resulting from the infinite Si-Si chains configuration. As for TM$_5$Si$_3$ (Fig. 4c, g and k), the hybridization between Si-3p and TM-d orbital is relatively strong with overlapping range about 4.5 eV. Especially, there is a deep pseudogap around Fermi level for $\alpha$-Nb$_5$Si$_3$ ($-0.41$ eV) and $\alpha$-Ta$_5$Si$_3$ ($-0.43$ eV), caused a special stability for these phases. We focus on another ground state structure TMSi$_2$ (Fig. 4d, h and l), significantly strong hybridization in the whole valence band can be observed, $(-13)eV$ $-6$ eV) adopted by s-p hybridization of Si atoms and $(-6eV-0$ eV) dominated by p-d hybridization between Si and TM atoms, respectively. As a result, strong Si-Si $\sigma$ bond in the double helix chains and Si-TM covalent bond are formed, which plays a crucial role for their perfect mechanical property and structural stability. As for the new proposed TMSi$_3$, the s-p-d hybridization can also be found, however, which is much less than that in TMSi$_2$, introducing much lower elastic modulus.

To get further visualization of the bonding characters in I4/mcm-V$_5$Si$_3$, $\alpha$-Ta$_5$Si$_3$ and TaSi$_2$, the valence electron charge density distributions are shown in Fig. 5. For I4/mcm-V$_5$Si$_3$, there are significant electronic accumulations in the linear Si chain, implying strong nonpolar Si-Si $\sigma$ bonding. Additionally, higher charge density between V and Si atoms is also visible, indicating the covalent V-Si interactions. On the other hand, in $\alpha$-Ta$_5$Si$_3$ and TaSi$_2$, less electronic accumulation between the Si$_2$ pairs (for $\alpha$-Ta$_5$Si$_3$) and in the double helix silicon chains can be found, along with increasing electronic accumulation between Ta-Si atoms, indicating relatively weaker Si-Si and enhanced Ta-Si covalent bonding. Interestingly, a rather strong Ta-Ta bond can be found in $\alpha$-Ta$_5$Si$_3$, as shown in Fig. 5c, the relative bond strength is also evaluated by calculating Mulliken overlap populations (MOP). For I4/mcm-V$_5$Si$_3$, the calculated Si-Si MOP value in the linear chain is 0.74 and MOP for V-Si has the maximum value of 0.39. For $\alpha$-Ta$_5$Si$_3$, MOP values for Si-Si bond in Si$_2$ pairs (for $\alpha$-Ta$_5$Si$_3$) and in the double helix silicon chains (for TaSi$_2$) are 0.28 and 0.31, respectively, smaller than that in I4/mcm-V$_5$Si$_3$. The MOP value of Ta-Si bond in $\alpha$-Ta$_5$Si$_3$ and TaSi$_2$ is comparable to that of V-Si bond with maximum value 0.38 ($\alpha$-Ta$_5$Si$_3$) and 0.39 (TaSi$_2$). Analogous results can also be acquired for $\alpha$-Nb$_5$Si$_3$, VSi$_2$ and NbSi$_2$ (not shown here), because of their similar atomic arrangement.

4. Conclusions

In conclusion, the crystal structure, stability, mechanical
property and electronic structure of TM$_5$Si$_3$ (1:3 ≤ x:y ≤ 3:1) were systematically studied by using the first-principles calculations. Although V, Nb and Ta belong to the same VB group, the V-Si, Nb-Si and Ta-Si systems display very different phase equilibrium behavior. The ground state structures are Pnma for Nb$_3$Si, I4/mcm-V$_5$Si$_3$ and P6$_2$22-VSi$_2$ for V-Si system, a-Nb$_5$Si$_3$, P6$_2$22-Nb$_5$Si$_3$ for Nb-Si system, and P4$_2$/nIa$_3$Si, P6$_2$22-Ta$_5$Si$_3$, a-Ta$_5$Si$_3$, P6$_2$22-Ta’Si$_2$ for Ta-Si system, respectively. Except for the experimental phases, many others with different stoichiometry are also predicted to be energetically, dynamically and mechanically stable at zero temperature and zero pressure, they should be recoverable at room conditions. Importantly, the hypothetical phases, P4/mmb-Nb$_4$Si$_2$, P4$2_12$-Nb$_5$Si$_3$, Ibam-Nb$_5$Si$_3$, Pnma-Nb$_5$Si$_3$ and P4/mmb-Ta$_5$Si$_3$ are mechanically and dynamic stable, and close to the convex-hull, they should be more likely to be realized in experiment. For the most energetic phases at corresponding stoichiometric ratio, bulk modulus show a general tendency Ta-Si > Nb-Si > V-Si, while shear modulus, Young’s modulus and Debye temperature at TM$_5$Si$_3$ and P6$_2$22-TM$_5$Si$_3$ are greater than others. Further electronic analysis identified that both Si-Si and TM-Si covalent interactions plays crucial roles for the good structural stability and mechanical property for ground state structure of TM-Si systems. We expected that present work can provide a better understanding of group VB silicides.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2016.04.253.

References


Fig. 5. Electron charge densities of I4/mcm-V$_5$Si$_3$ (a), a-Ta$_5$Si$_3$ (b) and Nb$_5$Si$_3$ (c). The isovalue line was set 0.317 eV for I4/mcm-V$_5$Si$_3$, 0.2514 eV for a-Ta$_5$Si$_3$ and 0.2842 eV for Ta$_5$Si$_3$ respectively.


