Versatile Titanium Silicide Monolayers with Prominent Ferromagnetic, Catalytic, and Superconducting Properties: Theoretical Prediction

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Supporting Information

ABSTRACT: On the basis of global structure search and density functional theory calculations, we predict a new class of two-dimensional (2D) materials, titanium silicide (TiSi, TiS, and TiSi) monolayers. They are proved to be energetically, dynamically, and thermally stable and own excellent mechanical properties. Among them, TiSi is a ferromagnetic metal with a magnetic moment of 1.37 μB/cell, while TiSi is an ideal catalyst for the hydrogen evolution reaction with a nearly zero free energy of hydrogen adsorption. More importantly, electron–phonon coupling calculations suggest that TiSi is a robust 2D phonon-mediated superconductor with a transition temperature of 5.8 K, and the transition temperature can be enhanced up to 11.7 K under a suitable external strain. The versatility makes titanium silicide monolayers promising candidates for spintronic materials, hydrogen evolution catalysts, and 2D superconductors.

Since the discovery of graphene,1 the family of two-dimensional (2D) materials2 has aroused tremendous interest due to their peculiar physical/chemical properties, as well as promising applications in electronics, optoelectronics, energy storage and conversion, hybrid materials, and so on.3–5 However, these existing 2D materials still cannot meet all practical demands, making it desirable to search new 2D functional materials for accelerating material innovation. Great efforts have been devoted to this field in the past decade, during which theoretical computation won the favor of scientists because it is time- and cost-saving.6–11 In fact, many newly synthesized 2D materials such as silicene,12 germanene,13,14 and borophene15,16 were first predicted theoretically.17–22

Silicon (Si) is the second most abundant element in the Earth’s crust (about 28% by mass)23 and the dominating material in semiconducting electronics. Its 2D form and related layered materials have attracted much attention because they have great advantage of compatibility with the current Si-based electronics industry.24 To date, except for silicene, which was successfully synthesized via a chemical vapor deposition method,25 it was predicted computationally that Si can form 2D binary monolayers or few-layer compounds with many nonmetal elements, such as B, C, N, O, P, and S.26–31 These new 2D binary materials show diverse structural, physical, and chemical properties by controlling atomic ratios. For example, 2D Si,C monolayers with varying Si concentration (0 ≤ x ≤ 1) present two structural phases, a homogeneous phase with well-dispersed Si (or C) atoms and an in-plane hybrid phase, which have distinct electronic properties.31 Silicon phosphide monolayers (Si,Pₙ) exist at stoichiometries of y/x ≥ 1, and their band gaps can be tuned in a wide range by altering the number of layers.30 2D SiS monolayers possess suitable direct band gaps and good mobilities for solar cells and nanoelectronics, good flexibility, and air stability.32,33 Moreover, Si can form binary monolayers with transition metal (TM) elements named TM silicides. Very recently, a Cu₂Si monolayer with planar hexacoordinate copper and silicon was predicted theoretically.34

In this Letter, 2D titanium silicide monolayers are globally searched by carrying out particle swarm optimization (PSO) simulations and further studied by density functional theory (DFT) calculations. Titanium (Ti) is selected because it has an equivalent valence electron number of four to Si and may form versatile 2D compounds with Si under different atomic ratios. Among searched structures, Ti, TiSi, TiSi, and TiSi are found to be dynamically and thermally stable and own excellent mechanical properties. Moreover, they are all metallic, and TiSi is ferromagnetic with a magnetic moment of 1.37 μB/cell while TiSi is an ideal hydrogen evolution catalyst with a nearly zero hydrogen adsorption free energy. Most interestingly, TiSi is predicted to be a 2D phonon-mediated superconductor with a transition temperature (Tc) of 5.8 K, and the Tc can be further increased up to 11.7 K under suitable external strain. If synthesized, titanium silicide monolayers will greatly enrich the family of 2D materials.

Figure 1a–c displays the optimized structures of Ti,Si, TiSi, and TiSi. In Ti,Si, each unit cell contains one Si atom and two

Received: August 3, 2016
Accepted: September 7, 2016

Ti atoms. This monolayer is in tetragonal symmetry, and its lattice constants are \(a = b = 2.73 \) Å, belonging to space group \(P4/mmm\). \(\text{TiSi}_2\) and \(\text{TiSi}_4\) have the same symmetry as that of \(\text{Ti}_2\text{Si}\), with the Ti atoms located in the middle. In particular, for \(\text{TiSi}_4\), the Ti layer is sandwiched by two completely parallel silicon layers at each side. Detailed structural information on \(\text{Ti}_2\text{Si}\), \(\text{TiSi}_2\), and \(\text{TiSi}_4\) is given in Table S1. Bader charge analysis shows that there is apparent charge transfer from Ti atoms to Si atoms (see Table S1), indicating the ionic nature of Ti–Si bonds. Interactions among in-plane Si atoms are clearly weakened due to the elongation of the Si–Si bond length (equal to corresponding lattice constants) in comparison to those in a Si single crystal (2.35 Å). There is one exception, that is, the short bonds between Si atoms in the topmost layer and those in the second layer (2.40 Å) in \(\text{TiSi}_4\) make their bonding completely covalent.

To evaluate the stability of these titanium silicide monolayers, we computed the cohesive energy, defined as

\[
E_{\text{coh}} = (1-x)E_{\text{Ti}} + xE_{\text{Si}} - E_{\text{Ti}_1-x\text{Si}_x} (0 \leq x \leq 1),
\]

where \(E_{\text{Ti}}\), \(E_{\text{Si}}\), and \(E_{\text{Ti}_1-x\text{Si}_x}\) are the total energies of a single Ti atom, a single Si atom, and corresponding titanium silicide monolayers, respectively. The cohesive energies of \(\text{Ti}_2\text{Si}\), \(\text{TiSi}_2\), and \(\text{TiSi}_4\) are 5.07, 4.96, and 4.84 eV/atom, respectively. To give a much more realistic picture, we made a simple cohesive energy diagram, as shown in Figure 1d. The data points for \(\text{Ti}_2\text{Si}\), \(\text{TiSi}_2\), and \(\text{TiSi}_4\) are located very close to or above the line connecting that for bulk Ti and bulk Si, indicating their high stability and feasibility of synthesis.

Figure 1. (a–c) Top views (up panels) and side views (bottom panels) for 2 × 2 supercells of \(\text{Ti}_2\text{Si}\) (a), \(\text{TiSi}_2\) (b), and \(\text{TiSi}_4\) (c). Red squares in (a–c) stand for primitive cells. (d) Cohesive energies \(E_{\text{coh}}\) versus composition \(x\) for titanium silicide monolayers as listed in Figure S1. Data points for bulk Ti and bulk Si are connected with a solid gray line. Comparisons with that of bulk Ti and bulk Si are drawn. Data points for \(\text{Ti}_2\text{Si}\), \(\text{TiSi}_2\) and \(\text{TiSi}_4\) are labeled in red.

(ε–g) Phonon dispersions for \(\text{Ti}_2\text{Si}\) (e), \(\text{TiSi}_2\) (f), and \(\text{TiSi}_4\) (g).

The existence of strong covalent bonding in \(\text{TiSi}_4\) directly brings about excellent mechanical property. The computed in-plane stiffness (see the methods in the Supporting Information) of \(\text{TiSi}_4\) is as high as 292 N/m, which is comparable to that of graphene (342 N/m). Even for \(\text{Ti}_2\text{Si}\) and \(\text{TiSi}_2\), without strong covalent bonding, the in-plane stiffness reaches about 120 N/m, almost the same as that of MoS\(_2\) (125 N/m), and twice greater than that of Siene (61 N/m). Further calculations of stress–strain relations for different cells under equi-biaxial strain (see Figure S4) show that the strain at maximum stress is around 0.11–0.14 for predicted titanium silicide monolayers, again demonstrating their prominent mechanical properties.

Besides their excellent mechanical properties, can these titanium silicide monolayers own other fantastic electronic or magnetic properties? As clearly shown in Figure 2, number of bands across the Fermi Level, indicating that these monolayers are all metallic. The density of states (DOS) further reveals that the bands around the Fermi level are mainly from Ti 3d orbitals (see the inset in Figure 2a). Note that the ferromagnetism of \(\text{Ti}_2\text{Si}\) is rather robust. DFT+U calculations indicate that the energy difference between the ferromagnetic state and antiferromagnetic state (or nonmagnetic state) is enlarged with the increase of the U value, and the magnetic moment is enhanced as well (up to ~2.0 \(\mu_B\)/cell).

Very recently, it was found that turning semiconducting 2H-MoS\(_2\) into metallic 1T-MoS\(_2\) can greatly enhance the hydrogen evolution reaction (HER), which is derived from the large DOS at the Fermi level and a number of active sites in the 1T phase. As the titanium silicide monolayers are all intrinsically metallic and have similar sandwich structures as MoS\(_2\), they may hold excellent HER catalytic activity as well. Theoretically,
It is known that an increase in the coverage of H adsorption may damage the catalytic activity, as has been identified in many TM dichalcogenide monolayers such as MoS_{2}, VS_{2}, and NbSe_{2}.^{41,42} Thus, it is vital to design new catalysts that can maintain good activity under high H coverage, as perfectly presented in the Pt catalyst.^{40} The effect of H coverage, defined as the ratio of the number of adsorbing H atoms with respect to the number of exposed Si atoms, on the HER efficiency is explored by using a 4 × 4 supercell of TiSi_{2}. The lowest energy profiles of H atom adsorption are depicted in Figure S6. Clearly, TiSi_{2} remains in good shape upon adsorption of H atoms, implying that it also has good chemical stability. The calculated \( \Delta G_{\text{H}} \) is no larger than 0.1 eV for most coverages, as shown in Figure 3b, suggesting that TiSi_{2} has comparable HER performance with the Pt surface even under high H coverage.^{40}

In fact, a complete HER is a multistep reaction that includes electrochemical hydrogen adsorption (Volmer reaction) and electrochemical desorption (Heyrovsky reaction) or chemical desorption (Tafel reaction). The above discussion belongs to the Volmer reaction. Generally speaking, the catalyst that has high activity for the Volmer reaction will have the same catalytic activity for the Heyrovsky reaction. Therefore, TiSi_{2} with a small \( \Delta G_{\text{H}} \) is an active catalyst for the Heyrovsky reaction as well. To verify whether TiSi_{2} is also good for the Tafel reaction, we further consider the dynamic process of two H atoms desorbing from the surface of TiSi_{2}. The Gibbs free energy \( \Delta G_{\text{H}} \) of the second H atom is still close to 0 eV, and the desorbing process only needs to overcome a low energy barrier of 1.28 eV (see Figure 3c), making the Tafel reaction possible. Therefore, we can conclude that TiSi_{2} may be a good alternative to precious Pt for the HER as it owns nearly zero free energies of hydrogen adsorption under different coverages, a low desorption energy barrier, and high electron mobility.

MgB_{2} is a conventional superconductor with a high \( T_{c} \) of \( \sim 40 \) K. Its superconductivity is mainly due to boron, which strongly binds in covalent bonding.^{55} The metallic nature and existing strong covalent bonding between Si atoms in TiSi_{4} inspire us to explore its electron–phonon coupling (EPC) and potential superconductivity. The EPC calculations were performed based on Bardeen–Cooper–Schrieffer (BCS) theory^{45} and derived Migdal–Eliashberg theory.^{46,47} Eliashberg spectral functions (details can be found in the Supporting Information) for TiSi_{4} are plotted in Figure 4a. All vibrational modes above 50 cm\(^{-1}\) contribute to the EPC indicated by the similarity between \( F(\omega) \) and \( \alpha^{2}F(\omega) \). The calculated EPC strength \( \lambda \) is 0.59, which is comparable to that of bulk CaC_{6},^{48} indicating reasonably strong EPC in TiSi_{4}.

The superconducting \( T_{c} \) is estimated using the Allen–Dynes modified McMillan equation^{49,50}

\[
T_{c} = \frac{\omega_{\text{log}}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^{*}(1 + 0.62\lambda)} \right]
\]

where \( \mu^{*} \) is the Coulomb pseudopotential and \( \omega_{\text{log}} \) is the logarithmically averaged frequency. A typical value of \( \mu^{*} = 0.1 \) is used in the McMillan equation because there is no exact method to determine this parameter yet (the effect of \( \mu^{*} \) on \( T_{c} \) is given in Figure S7). The calculated \( T_{c} \) is 5.8 K, exceeding the boiling point of liquid helium (4.2 K) and comparable to \( T_{c} \) of graphite intercalated compounds,^{51,52} suggesting that TiSi_{4} is an intrinsic BCS-type superconductor.

It is widely reported that external strain may greatly enhance the superconductivity.^{53–55} Before probing the strain influence...
Figure 3. (a) Gibbs free energies of hydrogen adsorption $\Delta G_H$ for $\text{Ti}_2\text{Si}$, $\text{TiSi}_2$, and $\text{TiSi}_4$. A comparison with that of $\text{MoS}_2$ and Pt surface is drawn. (b) $\Delta G_H$ for different coverages in a $4 \times 4$ supercell of $\text{TiSi}_2$. The dashed lines denote the $\Delta G_H$ of the Pt surface ($-0.09$ eV) and its absolute value. (c) Calculated energy profiles involved in the recombination of two hydrogen atoms. The initial, transitional, and final structures along the paths are also given.

Figure 4. Superconductivity of $\text{TiSi}_4$. (a) Eliashberg spectral functions for $\text{TiSi}_4$. (b) Electronic DOS around the Fermi level for $\text{TiSi}_4$ under strain. (c) EPC $\lambda(\omega)$ for strained $\text{TiSi}_4$. (d) EPC strength $\lambda$ and $T_c$ of $\text{TiSi}_4$ as functions of equi-biaxial strains. The percentages in (b,c) denote equi-biaxial strains applied to $\text{TiSi}_4$. 
on the superconductivity of TiSi4, it is required to find out when the dynamical instability will occur prior to the mechanical failure, as has been well studied in graphene systems.\textsuperscript{56,57} To verify this, compressive equi-biaxial strain of $\varepsilon_{xx} = \varepsilon_{yy} = -1\%$ is first applied, and TiSi4 remains dynamically stable. However, a further increase in compressive strain ($\varepsilon_{xx} = \varepsilon_{yy} = -2\%$) causes imaginary frequencies near the $\Gamma$ point of the Brillouin zone, as shown in Figure S8. Tensile biaxial strains are also considered following the same thought. TiSi4 can bear a tensile strain up to $\varepsilon_{xx} = \varepsilon_{yy} = +2\%$ (see Figure S8), which can be readily realized by employing suitable substrates. Figure 4b shows that the electronic DOS at the Fermi level is elevated with the increase of the tensile biaxial strain, implying the possible enhancement of EPC. We further calculate $\lambda(\omega)$ for strained TiSi4 and find that both $\lambda$ and $T_c$ indeed increase with the tensile strain, as displayed in Figure 4c. The $\lambda$ and $T_c$ can be enhanced to be 0.96 and 11.7 K under a strain of +2% (see Figure 4d), which is very impressive for 2D superconductors.

In summary, we have predicted a new class of 2D materials, Ti$_x$Si$_y$, TiSi$_2$, and TiSi$_4$, based on a PSO global structure search and DFT calculations. They are energetically, dynamically, and thermally stable and show excellent mechanical properties. Particularly, Ti$_2$Si is found to be a robust ferromagnetic metal with a magnetic moment of 1.37 $\mu_B$/cell. TiSi$_2$ is a highly active catalyst for HER with nearly zero free energies of hydrogen adsorption independent of the adsorption coverage, the low desorption energy barrier, and its high electron mobility. Most interestingly, TiSi$_4$ is a 2D phonon-mediated superconductor with comparable in-plane stiffness to graphene. Its transition temperature can be enhanced up to 11.7 K by applying a suitable strain. The versatility endows titanium silicide monolayers promising prospects for spintronic, catalytic, and superconducting applications.

**COMPUTATIONAL METHODS**

The PSO algorithm implemented in CALYPSO code\textsuperscript{58,59} was employed to search 2D titanium silicide structures. In our PSO simulations, a variety of Ti$_x$Si$_y$ ($x = 1$–4 and $y = 1$–4) compounds were taken into consideration. The population size and number of generation were set to be 20 and 30, respectively. For a given Ti$_x$Si$_y$, 14 atoms were considered at most in the simulation cell. For each simulation, hundreds of structures were generated, and the 6–10 energetically most favorable structures were further optimized by DFT calculations. Then, about 20 structures with energy preference and structural reasonability were further assessed by phonon dispersion calculations (see Figure S1 in the Supporting Information). Among them, only Ti$_x$Si, Ti$_2$Si$_y$, and TiSi$_4$ are dynamically stable, and their thermal stabilities were further verified by AIMD simulations. Structure relaxations were performed with projector-augmented wave (PAW)\textsuperscript{60} potentials and Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA)\textsuperscript{61} as implemented in the Vienna ab initio simulation package (VASP).\textsuperscript{62} We considered $3p^63d^24s^2$ and $3s^23p^6$ configurations as valence electrons for Ti and Si, respectively. Phonon dispersions were calculated based on density functional perturbation theory (DFPT)\textsuperscript{63} as embedded in the Phonopy program.\textsuperscript{64} AIMD simulations were performed using the Nosé–Hoover method\textsuperscript{65} to control temperatures. Additionally, the climbing-image nudged elastic band (CI-NEB) method was applied to locate the minimum-energy paths and the transition states.\textsuperscript{66} The QUANTUM ESPRESSO package\textsuperscript{67} was used to carry out EPC calculations. More computational details are given in the Supporting Information.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01731

Methods in detail, atomic structures and phonon dispersions of monolayers searched by CALYPSO, vibrational modes and corresponding analyses, AIMD snapshots, stress–strain relations, configurations for hydrogen adsorptions, $T_c$ as a function of $\mu^*$, and phonon dispersions for strained TiSi$_4$ (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is sponsored by the NSFC (21525311, 21373045, 11404056) and NSF of Jiangsu (BK20130016) and SRFDP (20130092110029, 20130092120042) in China and the Fundamental Research Funds for the Central Universities of China. The authors acknowledge computational resources at SEU and the National Supercomputing Center in Tianjin.

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