Electronic, optical, and water solubility properties of two-dimensional layered SnSi₂N₄ from first principles

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In this work, we identify a two-dimensional layered nitridosilicate $SnSi_2N_4$ in hexagonal structure via firstprinciples calculations. From the total energy calculations, $SnSi_2N_4$ is thermodynamically stable. The dynamic stabilities are demonstrated by the phonon spectrum and molecular-dynamics simulations. The $SnSi_2N_4$ exhibits semiconducting behavior with a direct band gap of 3.70 eV (GW₀), Young's modulus of 478 GPa and breaking strength of 47 GPa, and electron mobility of 2736 cm² V⁻¹ s⁻¹ (Perdew-Burke-Ernzerhof). According to the absorption spectra, $SnSi_2N_4$ presents good absorption of ultraviolet light with high energy. The chemical stability of aqueous solution is verified by the molecular-dynamics simulations.

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I. INTRODUCTION

Two-dimensional (2D) layered semiconductors have attracted burgeoning interest because of their unique properties and high potential in various applications [1,2]. At present, the common 2D semiconductors including transition-metal dichalcogenides (TMDs) [3], transition-metal monochalcogenides [4,5], black-phosphorus [6,7], and other derivates [8] have spurred many theoretical and experimental investigations. Single-layer TMDs, such as MoS₂ and WS₂, demonstrate extraordinary mechanical flexibility, electrical conductivity, and optical transparency [9]. However, these materials usually suffer from poor surface stability to surrounding environment [10,11] and island growth during the production [12]. Of note, layer growth tends to occur in those 2D materials when the surface energy is smaller than the growth substrate; therefore, reducing the surface energy is essential to achieve the uniform layer growth. Designing new 2D layered materials with high strength and stability is of major importance to enrich the current pool of TMDs.

The strength and stability depend on the electronic structure of the material. Ren and co-workers introduced elemental silicon to synthesize $MoSi_2N_4$ and efficiently passivate the surface of TMDs as verified by theoretical calculations and experimental results [13]. It is not uncommon for nitridosilicate compounds to be found in various applications. For instance, cubic spinel phase of Si_3N_4 , with a direct band gap of 3.45 eV and 280-GPa bulk modulus, exhibits a great potential application in structural material and semiconductor device [14]. The compound cubic spinel nitridosilicates $SiGe_2N_4$ and $GeSi_2N_4$ present semiconductor behavior (band gap 1.85 and 2.56 eV) and high strength (between 258 and 280 GPa) [15–17]. Of particular significance, these two nitridosilicates can form solid solutions, which might be tailored for specific applications [15].

Recently, numerous 2D materials, including topological insulators [18], semiconductors [19], and metals [20], have been successfully predicted by first principles. The crystal structure, electronic, optical, and stability properties can be determined from first-principles calculations, which drive materials discovery and spur experimental investigations.

In this work, we identify a 2D layered semiconductor, SnSi₂N₄, with hexacoordinate stannum and tetracoordinate silicon in a hexagonal structure by first-principles calculations. This structure, with seven atoms in a unit cell, is built up by septuple atomic layers of N-Si-N-Sn-N-Si-N, as a SnN₂ layer sandwiched between two Si-N bilayers. Total energy calculation results at 0 K exhibit energetic stability with respect to possible binary decomposition products, nitrides and silicides. The dynamic stability is verified by phonon calculations and molecular-dynamic simulations. Electronic band-structure calculations show that SnSi₂N₄ is a semiconductor with a direct band gap 3.70 eV (GW₀). The intrinsic electron and hole mobilities are 2736 and 441 cm² V⁻¹ s⁻¹, respectively. The relevant calculations show that Young's modulus and breaking strength of monolayer SnSi₂N₄ are about 478 and 47 GPa, respectively. From the absorption spectra calculations, SnSi₂N₄ exhibits high absorption of ultraviolet light. The aqueous solution stability of SnSi₂N₄ is verified by the molecular-dynamics simulations. The structural, elastic, electronic, and optical properties of this compound can provide useful reference for the theorists and experimentalists on this material.

II. METHODOLOGY

The crystal structure of $SnSi_2N_4$ was predicted by the element substitution method and the particle-swarm optimization method [21]. First-principles calculations were performed by

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FIG. 1. Crystal structure of hexagonal $SnSi_2N_4$, AIMD simulations, and phonon dispersion. (a) The upper is the top view of the predicted structure, and the lower is the side view. AIMD simulations at (b) 300 K and (c) 1500 K for 10 000 steps (10 ps). The AIMD optimized structures at (d) 300 K and (e) 1500 K. (f) Calculated phonon dispersion curves of $SnSi_2N_4$.

using the Vienna Ab initio Simulation Package (VASP) [22,23] based on the density-functional theory (DFT). The generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) [24] was employed to describe the exchange correlation. The cutoff energy for the wave function was 500 eV for both the monolayer and the bulk calculations. The tetrahedron method with Blöchl corrections was used to calculate the total energy. The K-point sampling grids in both structural relaxation and self-consistent process were $15 \times 15 \times 1$ and $15 \times 15 \times 3$ for the monolayer and the bulk, respectively. Both ions and cells were fully relaxed until the energy and force convergence to less than 10^{-6} eV and 0.001 eV/Å, respectively. Phonon spectrum calculations were conducted to analyze the lattice vibration using the PHONOPY package [25] with the density perturbation functional theory method. A $6 \times 6 \times 1$ supercell with 252 atoms was adopted and the q grid was $5 \times 5 \times 1$ for phonon spectrum calculations. To further confirm the structural stability of SnSi₂N₄, ab initio molecular dynamics (AIMD) method treated by the canonical (NVT) ensemble, was carried out on a $4 \times 4 \times 1$ supercell. Two temperatures of 300 and 1500 K were calculated, lasting 10 000 steps with each step of 1 fs. The nonlocal Heyd-Scuseria-Ernzerhof (HSE06) [26] hybrid functional and GW₀ [27] were used to obtain a precise estimation of the band gap. The band-gap and band-edges positions of valence-band maximum (VBM) and conduction-band minimum (CBM) were obtained by GW₀. Both the number of bands and number of frequency points were 60 for GW₀ calculations. During the optical absorption calculations, the number of bands and density of states were 72 and 2000 with $25 \times 25 \times 5$ Γ centered K points, respectively. A 20-Å-thickness vacuum region was built in order to minimize the interactions between the periodic layers along the (001) direction. The van der Waals (vdW) functional was taken into account and the optPBE-vdW method was adopted [28]. PBE was used to predict Young's modulus and breaking strength. Based on the deformation potential theory [29], the intrinsic carrier mobility μ of monolayer SnSi₂N₄ was calculated as the following



FIG. 2. Electronic structure and levels of monolayer $SnSi_2N_4$. Electronic band structure by (a) PBE, (b) HSE06, and (c) GW₀.

TABLE I. Calculated electronic levels of monolayer $SnSi_2N_4$. The vacuum level is set as 0 eV.					
Vacuum level (eV)	Fermi level (eV)	CBM (eV)	VBM (eV)	Work function (eV)	Electron affinity (eV)
0	-6.20	-3.76	-7.46	6.20	3.76

equation:

$$\mu = q \frac{\sum_{i} \int_{BZ} \tau(i\mathbf{k}) \upsilon^{2}(i\mathbf{k}) \left| \frac{\partial f_{i\mathbf{k}}}{\partial E_{i\mathbf{k}}} \right| d\mathbf{k}}{\sum_{i} \int_{BZ} f_{ik} d\mathbf{k}}, \qquad (1)$$

where q, $\tau(i\mathbf{k})$, i, \mathbf{k} , υ , and f represent the charge, the relaxation time, the band index, the wave vector, the velocity, and the occupation distribution at equilibrium, respectively. Young's modulus E was calculated using the following equation:

$$E = \frac{1}{V_0} \left(\frac{\partial^2 U(\varepsilon)}{\partial \varepsilon^2} \right)_{\varepsilon=0},\tag{2}$$

where V_0 is the equivalent continuum volume of the unit cell without strain, ε is the strain, and $U(\varepsilon)$ is the energy potential corresponding to the strain ε . The adsorption energy was defined as

$$E = E_{\text{total}} - (E_{\text{SnSi}_2\text{N}_4} + E_x), \qquad (3)$$

where E_x , $E_{\text{SnSi}_2N_4}$, and E_{total} represent the free energy of X (X is H or O or H₂O), the free energy of SnSi₂N₄, and the free energy of X adsorbed on SnSi₂N₄, respectively. Both zero-point energy and entropy energy were taken into consideration.

III. RESULTS AND DISCUSSION

The predicted SnSi₂N₄ crystallizes in hexagonal space group $P\bar{6}m^2$ and possesses the lattice parameters of a = b =3.0282 Å, and c = 10.6457 Å by PBE-vdW (Fig. 1). The Sn, Si, and O atoms are occupied Wyckoff positions at 1 f (0.667, 0.333, 0.500), 2h (0.333, 0.667, 0.222), and 2h (0.333, 0.667, 0.382) as well as 2g (0.000, 0.000, 0.178), respectively. Each stannum atom and silicon atom coordinates to six and four nitrogen atoms, forming a triangular prism and a tetrahedron environment, respectively. The Sn-N distances are 2.166 Å, which are about 2.5% shorter than those in SnN [30], indicating the stronger interaction between layers in SnSi₂N₄. Without vdW correction, the computed lattice constants are a = b = 3.0275 Å, c = 11.0033 Å. The lattice parameters of a axis and b axis remain the same as that with vdW correction, while the c axis is 3.36% larger than that with vdW correction.

To evaluate the thermodynamic stability of $SnSi_2N_4$ at 0 K, the calculations of decomposition energy are performed. The corresponding decomposition into binaries are assumed with two typical reactions as follows:

$$\text{SnSi}_2\text{N}_4 \rightarrow \text{Si}_2\text{N}_3 + \text{SnN},$$
 (4)

$$\text{SnSi}_2\text{N}_4 \to \frac{2}{3}\text{Si}_3\text{N}_4 + \frac{1}{3}\text{Sn}_3\text{N}_4.$$
 (5)

The structures of related binaries are obtained from the Inorganic Crystal Structure Database [31]. The total energy calculations show the reaction energy of 272 meV/atom for Eq. (4), indicating the possible synthesis of $SnSi_2N_4$ from

this parent binary phase. However, the reaction energy of Eq. (5) is -45 meV/atom, demonstrating that the predicted SnSi₂N₄ may be decomposed into Si₃N₄ and Sn₃N₄ at 0 K. Nevertheless, the reaction energy is relatively low, implying that it can be stabilized by entropic effects [32] and exists as the newly discovered 2D semiconductor $MoSi_2N_4$ and WSi_2N_4 with a metastable structure [13]. AIMD simulations for 10 000 steps (10 ps) are implemented to further estimate the thermal and dynamic stability of this structure. The averaged mean-squared displacements (MSDs), from AIMD calculations at both 300 K [Fig. 1(b)] and 1500 K [Fig. 1(c)], show that Sn, Si, and N atoms have ignorable values. The AIMD optimized structures of SnSi₂N₄ at 300 K and 1500 K [Figs. 1(d) and 1(e)] are in a good agreement with that at 0 K, demonstrating satisfied thermodynamic stability. The phonon calculation [Fig. 1(f)] reveals that there are no imaginary frequency modes in the Brillouin zone, further confirming the dynamic stability of this structure.

After determining the thermal and dynamic stability of $SnSi_2N_4$, the electronic structure, carrier mobility, and breaking strength are calculated by first principles. The electronic band structure of monolayer $SnSi_2N_4$ calculations is carried out with PBE functional, hybrid HSE06 functional, and GW_0 . Both above calculations show that the predicted $SnSi_2N_4$ is a semiconductor with a direct band gap of 2.03 eV (PBE) [Fig. 2(a)], 3.19 eV (HSE06) [Fig. 2(b)], and 3.70 eV (GW_0) [Fig. 2(c)], similar to other photocatalysts like ZnO [33] and TiO₂ [34]. The band gap is slight affected without vdW correction by PBE (1.99 eV). The electronic levels, such as Fermi level, vacuum level, work function, and electron affinity are of paramount importance to the semiconductor, hence these parameters are calculated by GW_0 (Table I). GW_0 calculations reveal that the work function, CBM, VBM,



FIG. 3. The optical absorption of SnSi₂N₄.



FIG. 4. The stability of aqueous solution and schematic diagrams of H, O and H_2O adsorbed on $SnSi_2N_4$. The structures of $SnSi_2N_4$ with nine molecules of water (a) before and (b) after AIMD simulations at 300 K for 5 ps. (c) MSDs for Sn, Si, N, H, and O atoms from AIMD simulations at 300 K for 5 ps. (d) Site I. (e) Site II. (f) Site III. (g)–(i) The absorption of H, O, and H_2O on $SnSi_2N_4$. The white and red spheres represent the H and O atoms, respectively.

and electron affinity of monolayer $SnSi_2N_4$ are 6.20, -3.76, -7.46, and 3.76 eV, respectively. The small electron affinity indicates strong electron donors. Moreover, the carrier mobility calculations reveal that the intrinsic electron and hole mobilities of monolayer SnSi₂N₄ at Gamma point are 2735.97 and 441.17 cm² V⁻¹ s⁻¹, respectively. The electronic mobility of SnSi₂N₄ is 37 times greater than that of monolayer MoS_2 (72.16 cm² V⁻¹ s⁻¹) [35] and 10 times larger than that of monolayer MoSi₂N₄ (261.96 cm² V⁻¹ s⁻¹) [13]. The hole mobility of SnSi₂N₄ is 2 times in comparison to monolayer MoS_2 (200.52 cm² V⁻¹ s⁻¹) [35]. Moreover, Young's modulus [36] and breaking strength [37] of monolayer $SnSi_2N_4$ is analyzed by theoretical calculations. Theoretical results show that Young's modulus and breaking strength are 478.1 and 47.3 GPa, respectively. These values are much greater in contrast to 2D MoS₂ (270.0 and 22.0 GPa) [35] and 2D Ti₃C₂ T_x Mxene (333.0 and 17.3 GPa) [38], and similar to these of 2D MoSi₂N₄ (479.1 and 49.1 GPa) [13].

The calculation of optical properties provides an assessment of the photoabsorptive capability. Therefore, further calculations are conducted to obtain the optical absorption spectra of SnSi₂N₄. Results reveal that SnSi₂N₄ exhibits high ultraviolet light spectroscopy absorptivity [Fig. 3(a)]. There are two common methods to tailor the photoabsorption of semiconductor: band-structure regulation (including doping and defects) and integrating with other semiconductors with small band gaps. For instance, NaTaO₃ photocatalyst with Fe³⁺ doping shows a redshift of the absorption edges from the ultraviolet light to the visible range [39]. Both NaTaO₃/NiO heterojunction [40] and MoS₂/CdS heterojunction [41] exhibit wider light absorption range than NaTaO₃ and MoS₂.

To evaluate the chemical stability of the aqueous solution, AIMD simulations are carried out at 300 K for 5 ps. The vacuum slab is built with 20-Å thickness and contains nine molecules of water [Fig. 4(a)]. AIMD simulations show that the structure of $SnSi_2N_4$ remains unchanged with no bonding behavior of water molecules [Fig. 4(b)]. This result ensures its stability of aqueous solution. Besides, the averaged MSDs from AIMD simulations show that the MSDs for Sn, Si, and N atoms have constant small values near zero, indicating the structural stability and aqueous solution stability [Fig. 4(c)], in accord with similar compound of $MoSi_2N_4$ [13]. Of note, a video is made to visualize the total process of AIMD simulations, shown in the Supplemental Video. Furthermore, the active sites of SnSi₂N₄ for H, O, and H₂O adsorption are calculated. Three major possible active sites, including above the hollow sites between three Si atoms and three N atoms [site I, Fig. 4(d)], above Si atoms [site II, Fig. 4(e)], and above N atoms [site III, Fig. 4(f)] are considered. DFT calculations show that the absorption energy of H adsorbed above N atoms is 1.06 and 1.10 eV lower than that of other two sites, respectively. It means that N atoms are the most possible active sites for H adsorption [Fig. 4(g)]. However, O atoms favor adsorption above the bridge site between N and Si atom based on the result of structural relaxation. Its absorption energy is about 1.25 and 1.26 eV lower than other two sites, respectively, indicating that the bridge site between N and Si atom is the active site for O adsorption [Fig. 4(h)]. DFT calculations show that the absorption energy of H₂O adsorbed above Si atoms is 0.013 and 0.029 eV lower than that of other two sites, respectively. It means that Si atoms are the most possible active sites for H_2O adsorption [Fig. 4(i)]. Besides, the application in water splitting is explored in the Supplemental Material [42] (see also Refs. [43–47] therein).

IV. CONCLUSION

In summary, a two-dimensional layered nitridosilicate $SnSi_2N_4$ in hexagonal structure is discovered by first-

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principles calculations. The structure is composed of stacking layers of N-Si-N-Sn-N-Si-N with hexacoordinate stannum and tetracoordinate silicon. Total energy calculations exhibit thermodynamic stability of SnSi₂N₄ with respect to possible binary decomposition products. The dynamic stability of SnSi₂N₄ is verified by the phonon spectrum and AIMD simulations. The calculation of electronic band structure reveals that SnSi₂N₄ is a semiconductor with a direct band gap of 3.70 eV (GW₀). The intrinsic electron and hole mobilities of $SnSi_2N_4$ are 2736 and 441 cm² V⁻¹ s⁻¹, and Young's modulus and breaking strength are 478.1 and 47.3 GPa, respectively. SnSi₂N₄ presents high absorption of ultraviolet light based on the absorption spectra calculations. From the molecular-dynamics simulations, SnSi₂N₄ exhibits excellent aqueous solution stability. It is envisioned that this work can provide reference for future investigations and application of this material.

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