Electronic supplementary information

Two-Dimensional Superhard Silicon Nitrides with Widely Tunable Bandgap, High Carrier Mobilities and Hole-Doping-Induced Robust Magnetism

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Part I

The isomeric structures of Si₃N₄ via sublayer geometric combination



Fig. S1 Schematic diagram of the isomeric structures of Si_3N_4 (the difference between the different structures lies in the relative positions of N and Si, as shown by the green and red lines).

According to the relative positions of selected atoms in different layered substructure unit as indicator for different layer stacking patterns, a suffix of '(*xy*)' (*x* or y = a, b) is labeled for identification, of which the '*x*' represents the first attachment of SiN₂ sublayer and one SiN sublayer, and the '*y*' represent the second SiN sublayer attached to the SiN₂-SiN bi-sublayer; And the 'a' or 'b' represents that the selected atoms are 'staggered' or 'eclipsed', respectively. For T and H series, the selected atoms for '*x*' is the N atom in SiN sublayer (noted as 'N_{CN=3}') and the hexa-coordinated Si (Si_{CN=6}), and they are the N_{CN=3} of the second SiN sublayer and Si_{CN=6} for '*y*'. Therefore, there are three stacking methods of aa, ab and bb within symmetry limit for H and T series. For OT and OH series, the selected atoms for '*x*' is also the N_{CN=3} of the second SiN sublayer and the Si_{CN=4} of the first SiN sublayer for '*y*'. And there are four stacking modes of aa, bb, ab and ba for OT and OH series. Thus, 14 structure patterns are systematically constructed and labeled as shown in Fig. S1.

Si ₃ N ₄ - series	<i>a/b</i> (Å)	Δ_Z (Å)	Space group	Energy (eV/atom)	E_{gap} (eV)	Young's stiffness (N/m)	Poisson's ratio
H-aa	2.858	6.812	P-6m2	-7.807	2.154(I)	484.29	0.28
H-ba	2.858	6.814	<i>P</i> 3 <i>m</i> 1	-7.807	2.329(I)	480.45	0.29
H-bb	2.857	6.821	P-6m2	-7.804	2.228(I)	495.33	0.27
T-aa	2.876	6.518	<i>P</i> -3 <i>m</i> 1	-8.068	3.859(I)	487.25	0.26
T-ba	2.874	6.532	<i>P</i> 3 <i>m</i> 1	-8.065	3.492(I)	491.02	0.26
T-bb	2.872	6.546	<i>P</i> -3 <i>m</i> 1	-8.061	3.233(I)	497.83	0.26
OH-aa	2.882	7.148	<i>P</i> 3 <i>m</i> 1	-7.344	metal	358.84	0.36
OH-ab	2.888	7.142	<i>P</i> 3 <i>m</i> 1	-7.332	metal	149.36	0.73
OH-bb	2.887	7.153	<i>P</i> 3 <i>m</i> 1	-7.342	metal	342.92	0.39
OH-ba	2.882	7.152	<i>P</i> 3 <i>m</i> 1	-7.354	metal	342.80	0.39
OT-aa	2.904	6.707	<i>P</i> 3 <i>m</i> 1	-7.584	metal	162.66	0.70
OT-ab	2.907	6.723	<i>P</i> 3 <i>m</i> 1	-7.569	metal	237.87	0.56
OT-bb	2.901	6.747	<i>P</i> 3 <i>m</i> 1	-7.579	metal	124.12	0.78
OT-ba	2.902	6.718	<i>P</i> 3 <i>m</i> 1	-7.586	metal	311.66	0.44

Table. S1 The lattice constant (a/b), thickness (Δz) , space group, Energy (eV/atom), bandgap (E_{gap} , (I) means the indirect band gap) Young's stiffness (Y) and Poisson's ratio (v) of isomeric structures of Si₃N₄.

Part II

Global structure search by CALYPSO code

The particle-swarm optimization (PSO) scheme, as implemented in the CALYPSO code¹, is employed to search for low energy 2D Si₃N₄, which has been successfully and widely applied in global structure reach for new materials. In our PSO calculations, the population size and the number of generations are set as 30 and 20 (600 different structures), respectively. The global minimum and the other metastable isomers are shown in Fig. S1. Based on the rank of the structures in order of enthalpy as shown in Fig. S2, the global minimum structures for 2D Si₃N₄ is expected the T-aa phases in our work.



Fig. S2 The Si_3N_4 (T-aa) and isomers of 2D Si_3N_4 found by the CALYPSO structure search, where the number indicate the energies in ascending order.



Fig. S3 The energy difference between Si_3N_4 (T-aa) and 2D isomers of Si_3N_4 .

Part III

Difference/deformation charge density

Here, the difference (as well as deformation) charge density $(\Delta \rho)$ is defined as the difference between the electron cloud density (ρ) of the Si₃N₄ (T-aa) monolayer and the electron cloud density of the N and Si atoms composing its structure, i.e.

 $\Delta \rho = \rho_{Si_3N_4} - \rho_{Si} - \rho_N \#(1)$

Lattice dynamics stability



Fig. S4 The phonon dispersion of Si_3N_4 (T-aa) structure.

Thermal stability



Fig. S5 The snapshots of Si₃N₄ (T-aa) structure after AIMD simulations.



Fig. S6 Energy evolution of the Si_3N_4 (T-aa) structure subjected to AIMD simulations at distinct temperatures: (a) 500 K, (b) 1000 K, (c) 2000 K, (d) 3000 K, and (e) 4000 K. The structural snapshots (f) of Si_3N_4 (T-aa) post-AIMD simulations at 4000 K over a simulation time of 20 ps.

To investigate the thermal stability of the Si_3N_4 (T-aa) nanosheet, a $4 \times 4 \times 1$ supercell is used for Ab Initio Molecular Dynamics (AIMD) simulations. The calculated result reveals that the system's total energy displays stable fluctuations throughout the AIMD simulations from 500 K to 4000 K, as shown in Fig. S6. Notably, during the AIMD simulation at 4000 K with extended time scale of 20 ps, only minor in-plane structural deformations can be observed. This demonstrates the excellent thermal stability of the 2D-Si₃N₄ monolayer up to 4000 K.

Mechanical properties

For 2D structure, the Young's stiffness (*Y*) and Poisson's ratio (v) can be calculated by the equation as below^{2, 3}:

$$Y_{x} = \frac{C_{11}C_{22} - C_{12}^{2}}{C_{22}}, Y_{y} = \frac{C_{11}C_{22} - C_{12}^{2}}{C_{11}} \#(2)$$

$$v_{12} = \frac{C_{12}}{C_{11}}, v_{21} = \frac{C_{21}}{C_{22}} \#(3)$$

Where the C_{11} , C_{12} and C_{22} indicate the elastic constant.

Part IV

GW calculation

To ensure the accuracy and reasonable output of the GW method, we first validated it with the silicon bulk, where we computed the GW band gap to be 1.08 eV (parameters: k: $8 \times 8 \times 8$, two atoms in unit cell, 60 empty bands, ENCUTGW = 160 eV). This is in good agreement with the experimental result of 1.1 eV.⁴

In the case of 2D systems, the GW band gap is generally influenced by several factors: the number of empty bands (N), the grid density (n × n for k-points), the energy cutoff for response functions (ENCUTGW), and the length of the vacuum layer (Lz) in computation.⁵ Therefore, we performed several tests to verify the convergence of these parameters: (i) the energy cutoff for the response functions is 150 eV ($\Delta E = 0.003$ eV, vs. 200 eV); (ii) the empty band number (N) is 56 with a total number of bands (NBANDS) equal to 96, which resulted in a small energy shift ($\Delta E = 0.008$ eV, vs. NBANDS = 192); (iii) k-point is 12 × 12 ×1 ($\Delta E = 0.001$ eV, vs. 15 × 15 × 1). Additionally, we calculated GW0 bandgap with different values of Lz (12, 14, 16, 20, 24 Å) and extrapolated to the case of an infinite vacuum layer (1/Lz = 0),^{6, 7} as shown in Fig. S7.



Fig. S7 Dependence of the GW0 band gap on Lz for extrapolation to the bandgap limit (ENCUTGW = 150 eV, k-points: $12 \times 12 \times 1$, NBANDS = 96)



Fig. S8 The band structure of Si_3N_4 (T-aa) by GW method (ENCUTGW = 150 eV, k-points: $18 \times 18 \times 1$, NBANDS = 96, Lz = 20 Å)



Electronic properties of isomeric structures of Si₃N₄

Fig. S9 Calculated band structure and DOS of isomeric structures of Si_3N_4 at PBE level.



Fig. S10 (a) The top and side views of Si_3N_4 (T-aa) structure under +12% and +14% biaxial strain, and the phonon dispersion of Si_3N_4 under +12% biaxial strain.



Fig. S11 The change ratio (%) of each chemical bond relative to the original bond length under different (a) electric field strengths (range of 0 to 0.74 V/Å) and (b) biaxial strains (range of -6% to +12%).

Table. S2 The change ratio (%) of each chemical bond relative to the original bond length under different electric field strengths (range of 0 to 0.74 V/Å). Where N(1) is tri-coordinated N, N(2) is tetra-coordinated N, Si(1) is tetra-coordinated Si, and Si(2) is hexa-coordinated Si.

Electric	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.72	0.74
field	V/ Å	V/ Å	V/ Å	V/ Å	V/ Å	V/ Å	V/ Å	V/ Å	V/ Å	V/ Å
N(1)-Si(1)	0	0.02%	0.03%	0.04%	0.07%	0.10%	0.08%	0.10%	0.11%	0.13%
N(2)-Si(1)	0	0.01%	0.01%	0.03%	0.05%	0.07%	0.04%	0.06%	0.08%	0.08%
N(2)-Si(2)	0	0.02%	0.02%	0.04%	0.06%	0.09%	0.07%	0.09%	0.10%	0.11%

Table. S3 The change ratio (%) of each chemical bond relative to the original bond length under different biaxial strains (range of -6% to +12%).

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Biaxial strain	-6%	-4%	-2%	2%	4%	6%	8%	10%	12%
N(1)-Si(1)	-3.74%	-2.59%	-1.35%	1.45%	2.94%	4.51%	6.12%	7.82%	9.43%
N(2)-Si(1)	-4.51%	-3.00%	-1.51%	1.49%	2.98%	4.47%	5.97%	7.45%	8.94%
N(2)-Si(2)	-3.68%	-2.46%	-1.24%	1.28%	2.56%	3.85%	5.17%	6.45%	7.80%



Fig. S12 The partial charge density of the VBM and CBM of 2D Si_3N_4 (T-aa) at vertical electric field.

Carrier mobilities

The charge carrier mobilities of the system can be calculated using the variable situation (DP) theory,⁸ which has been widely used in a variety of two-dimensional structures for the prediction of carrier mobilities.⁹⁻¹¹ According to DP theory, the mobility of specific carrier in a two-dimensional material can be calculated by the following equation.

$$\mu_{2d} = \frac{e\hbar^{3}C_{2d}}{k_{B}Tm^{*}m_{d}(E_{1}^{i})^{2}}\#(4)$$

where e, \hbar, k_B and T are the electron charge, reduced Planck constant, Boltzmann constant and Kelvin temperature, respectively. m^* denotes the effective mass of the carrier at VBM and CBM; m_d is the average effective mass, defined as $m_d = \sqrt{m_x^* m_y^*}$. C_{2d} is the stiffness of elasticity; E_l^i is the deformation potential constant, which is calculated by the following equation.

$$E_l^i = \frac{\partial E_{edge}}{\partial \left(\Delta l/l_0\right)} \#(5)$$

where E_{edge} denotes the band edge. In this calculation, a narrow $\Delta l/l_0$ ranging from - 0.6 % to +0.6 % is selected to fit E_l^i . All results are shown in Table S4.

Table. S4 Effective mass m^* of charge carrier, average effective mass m_d , deformation potential constant E_l and carrier mobility μ_{2d} along the *a*- and *b*-directions of Si₃N₄ (T-aa) lamellar structure at 300 K. (m_e is the rest mass of electron.)

)	(· c)	
Si ₃ N ₄	h(<i>a</i>)	h(b)	e(<i>a</i>)	e(b)
<i>C</i> _{2d} (N/m)	519	519	519	519
E_l (eV)	1.917	1.819	5.112	4.833
$m^*(m_e)$	2.334	0.542	0.363	0.565
$m_{\rm d} (m_{\rm e})$	1.125	1.125	0.453	0.453
μ(1148	5490	2578	1853
$cm^2V^{-1}s^{-1})$				

Table. S5 Effective mass m^* of charge carrier, average effective mass m_d , deformation potential constant E_l and carrier mobility μ_{2d} along the *a*- and *b*-directions of Ge₃N₄ lamellar structure at 300 K. (m_e is the rest mass of electron.)

Ge ₃ N ₄	h(a)	h(b)	e(<i>a</i>)	e(b)
$C_{2d}(N/m)$	392	392	392	392
E_l (eV)	2.157	1.727	9.427	7.760
$m^*(m_e)$	3.276	0.469	0.194	0.193
$m_{\rm d} (m_{\rm e})$	1.239	1.239	0.193	0.193
μ(443	4824	2507	3719
$cm^2V^{-1}s^{-1})$				

Table. S6 Effective mass m^* of charge carrier, average effective mass m_d , deformation potential constant E_l and carrier mobility μ_{2d} along the *a*- and *b*-directions of SiGe₂N₄ lamellar structure at 300 K. (m_e is the rest mass of electron.)

SiGe ₂ N ₄	h(<i>a</i>)	h(b)	e(<i>a</i>)	e(b)	
$C_{2d}(N/m)$	420	420	420	420	
$E_l (\mathrm{eV})$	2.327	1.397	7.923	9.130	
$m^*(m_e)$	5.192	0.429	0.255	0.254	
$m_{\rm d}$ ($m_{\rm e}$)	1.492	1.492	0.255	0.255	
μ(214	7171	2200	1663	
$cm^2V^{-1}s^{-1})$					

Table. S7 Effective mass m^* of charge carrier, average effective mass m_d , deformation potential constant E_l and carrier mobility μ_{2d} along the *a*- and *b*-directions of GeSi₂N₄ lamellar structure at 300 K. (m_e is the rest mass of electron.)

GeSi ₂ N ₄	h(<i>a</i>)	h(b)	e(<i>a</i>)	e(b)
$C_{2d}(N/m)$	482	482	482	482

E_l (eV)	2.027	3.597	6.130	6.783
$m^*(m_e)$	2.512	0.492	0.368	0.577
$m_{\rm d}$ $(m_{\rm e})$	1.111	1.111	0.461	0.461
μ(896	1453	1614	841
$cm^2V^{-1}s^{-1})$				

Magnetism raised by charge doping



Fig. S13 Calculated magnetic moment and magnetic energy (E_{Mag}) of the 2D Si₃N₄, Ge₃N₄ Sn₃N₄, Ge(Si₂)N₄, Sn(Si₂)N₄ and Sn(Ge₂)N₄ as a function of carrier density, where negative and positive values correspond to electron- and hole-doping densities, respectively.

It is noteworthy that, for Si_3N_4 and $Ge(Si_2)N_4$, there have an obvious magnetic moment change near the carrier concentration of 0, but the E_{Mag} is almost to 0, we believe that they are in an unstable state of magnetization and non-magnetization, so it is considered as non-effective magnetization raised by charge-doping.



Fig. S14 The calculated band structure of Si_3N_4 at hole concentration of 7.00×10^{14} cm⁻².

Magnetic Ground State, Magnetic Anisotropic Energy (MAE), and Curie Temperature Analysis

For the magnetic orders in Si_3N_4 and Sn_3N_4 with heavy hole doping, both ferromagnetic (FM) and antiferromagnetic (AFM) coupling orders are considered to determine the magnetic ground state, within accounting only the nearest neighbor magnetic exchange interactions (as shown in Fig. S15a and S15b). Calculated results show that Si_3N_4 (T-aa) and Sn_3N_4 with hole-doping of 1h⁺ per cell both exhibit a FM ground state as half-metals, with the energy difference between AFM and FM is 90.3 meV per unit cell (meV/uc) and 53.1 meV/uc, respectively (HSE06 level).

The magnetic anisotropy energy (MAE) of magnetized Si_3N_4 and Sn_3N_4 are calculated with the HSE06 + SOC method along the *x*-, *y*-, and *z*-directions, as listed in Table. S8. The easy axis (EA) of Si_3N_4 and Sn_3N_4 is found to along with the in-plane *x*-direction. The calculated MAEs for the *y*- and *z*- are 0.3 and 1.0 μ eV/uc for Si_3N_4 , 0.1 and 12.9 μ eV/uc for Sn_3N_4 , respectively. This result suggests that the MAE of magnetized Si_3N_4 and Sn_3N_4 is almost ignorable, indicating that the magnetic interaction within the system could be described by the Heisenberg model. The spin

$$H = E_0 + \sum_{ij} J_{ij} M_i M_j$$

Hamiltonian can be expressed as

Where E_0 is the energy without magnetic coupling, J is the nearest exchange parameters, and M is the unit spin vector of 1 µB. The energy profiling results of the two magnetic configurations (Fig. S15c) for each unit cell are as follows: $H_{FM} = E_0 + 3J$ $H_{AFM} = E_0 - J$

Utilizing the energy difference between the AFM and FM states, the magnetic exchange energy J is approximately 22.6 meV/uc for Si_3N_4 and 13.3 meV/uc for Sn_3N_4 .

Furthermore, Monte Carlo simulation results are used to fit the temperaturedependent magnetization intensity given by $M(T) = (1 - T/T_c)^{\beta}$. The method of predicting Curie temperature (Tc) has been widely employed.^{12, 13} The simulation structure used measures 40 nm × 40 nm, with 40000 equilibrium steps and 80000 averaging steps carried out in the VAMPIRE software.¹⁴ The T_c of Si₃N₄ and Sn₃N₄ is calculated to be 298 K and 180 K (Fig. S15d), respectively, much higher than that in CrI₃ monolayer (45 K in experiment,¹⁵ 50 K in simulation with same method¹²). This suggests that Si₃N₄ and Sn₃N₄ has potentially promising application in spintronics.



Fig. S15 The spin density (the isosurfaces is set as 0.005 e/Bohr^3) of (a) ferromagnet and (b) antiferromagnet configuration of Si₃N₄ (T-aa), Yellow and blue region represent spin-up and spin-down, respectively. (c) The FM and AFM configurations. (d) Normalized magnetization of Si₃N₄ (blue) and Sn₃N₄ (black) as a function of temperature by Monte Carlo simulation.

Table. S8 The magnetic properties date of Si_3N_4 and Sn_3N_4 . The energy of FM and AFM state (FM, AFM eV/uc), the magnetic exchange energy (*J*, meV), the critical temperature (T_c , K), the relative energy between the magnetization direction and easy axis (*x*, *y*, *z*, μ eV/uc).

	FM	AFM	J	$T_{\rm c}$	x	У	Z
Si ₃ N ₄	-67.8134	-67.7231	22.6	298	0	0.3	1.0
Sn_3N_4	-54.2176	-54.1645	13.3	180	0	0.1	12.9

Part V

Structures of 2D nitride analogues

The extended study of analogues of nitrides of IV_A analogues of Si_3N_4 (Si, Ge, Sn and Pb) are carried out. Based on the Si_3N_4 (T-aa) nanosheet, two characteristically different structural types are investigated, including the A(B₂)N₄-type structure with equivalent upper and lower surfaces and the A(AB)N₄-type structure with nonequivalent upper and lower surfaces (i.e., Janus structure). Here, the A atoms outside the bracket represent the hexa-coordinated atoms in the inner layer, while those inside the bracket represent the tetra-coordinated atoms in the outer layer, as shown in Fig. S16-S18.



Fig. S16 Top and side view of A_3N_4 (A = Si, Ge, Sn and Pb)



Fig. S17 Top and side view of $A(B_2)N_4$ (A and B = Si, Ge, Sn and Pb)



Fig. S18 Top and side view of $A(AB)N_4$ (A and B = Si, Ge, Sn and Pb)

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Structures	<i>a/b</i> (Å)	Δ_Z (Å)	Space group	
Si ₃ N ₄	2.876	6.517	<i>P</i> -3 <i>m</i> 1	
Ge ₃ N ₄	3.065	7.021	<i>P</i> -3 <i>m</i> 1	
Sn_3N_4	3.391	7.758	<i>P</i> -3 <i>m</i> 1	
Pb_3N_4	3.574	8.315	<i>P</i> -3 <i>m</i> 1	
Si(Ge ₂)N ₄	2.994	6.952	<i>P</i> -3 <i>m</i> 1	
$Si(Sn_2)N_4$	3.221	7.689	<i>P</i> -3 <i>m</i> 1	
Si(Pb ₂)N ₄	3.308	8.204	<i>P</i> -3 <i>m</i> 1	
Ge(Si ₂)N ₄	2.946	6.615	<i>P</i> -3 <i>m</i> 1	
$Ge(Sn_2)N_4$	3.297	7.683	<i>P</i> -3 <i>m</i> 1	
Ge(Pb ₂)N4	3.395	8.201	<i>P</i> -3 <i>m</i> 1	
$Sn(Si_2)N_4$	3.055	6.823	<i>P</i> -3 <i>m</i> 1	
Sn(Ge ₂)N ₄	3.174	7.184	<i>P</i> -3 <i>m</i> 1	
$Sn(Pb_2)N_4$	3.495	8.250	<i>P</i> -3 <i>m</i> 1	
$Pb(Si_2)N_4$	3.111	6.998	<i>P</i> -3 <i>m</i> 1	
$Pb(Ge_2)N_4$	3.239	7.335	<i>P</i> -3 <i>m</i> 1	
$Pb(Sn_2)N_4$	3.414	7.934	<i>P</i> -3 <i>m</i> 1	
Si(SiGe)N ₄	3.005	6.825	<i>P</i> 3 <i>m</i> 1	
Si(SiSn)N ₄	3.224	7.350	<i>P</i> 3 <i>m</i> 1	
Si(SiPb)N ₄	3.337	7.736	<i>P</i> 3 <i>m</i> 1	
Ge(GeSi)N ₄	2.934	6.745	<i>P</i> 3 <i>m</i> 1	
Ge(GeSn)N ₄	3.286	7.496	<i>P</i> 3 <i>m</i> 1	
Ge(GePb)N ₄	3.407	7.862	<i>P</i> 3 <i>m</i> 1	
Sn(SnSi)N ₄	3.033	7.194	<i>P</i> 3 <i>m</i> 1	
Sn(SnGe)N ₄	3.177	7.397	<i>P</i> 3 <i>m</i> 1	
Sn(SnPb)N ₄	3.512	8.088	<i>P</i> 3 <i>m</i> 1	
Pb(PbSi)N ₄	3.058	7.483	<i>P</i> 3 <i>m</i> 1	
Pb(PbGe)N ₄	3.213	7.682	<i>P</i> 3 <i>m</i> 1	
Pb(PbSn)N ₄	3.440	8.004	<i>P</i> 3 <i>m</i> 1	

Table. S9 The lattice constant (a/b), thickness (Δz) and space group of A₃N₄, A(B₂)N₄ and A(AB)N₄ (A and B = Si, Ge, Sn and Pb)

Stabilities of 2D nitride analogues

To confirm the stabilities of 2D nitride analogues, we first calculated the phonon spectra for Ge₃N₄, Sn₃N₄, and Pb₃N₄, as shown in Fig. S19. Apart from Pb₃N₄, no imaginary frequencies appear at any k-point for Ge₃N₄ and Sn₃N₄, suggesting good lattice dynamical stability for these structures. To further examine their thermal stability, we conducted 10 ps Ab Initio Molecular Dynamics (AIMD) simulations for Ge₃N₄ and Sn₃N₄ at 500 K. The simulations reveal only slight structural deformations in these two materials throughout the simulations, while the total energy fluctuations remain stable, thus demonstrating their excellent thermal stability at 500 K (Fig. S19). Furthermore, we have calculated the elastic constant tensor matrix for both Ge_3N_4 and Sn₃N₄ (T-aa) structures, as listed in Table. S10. Considering the mechanical stability criterion for 2D structures, specifically $C_{11}C_{22}$ - $C_{12}C_{21} > 0$ and $C_{66} > 0$, both Ge₃N₄ and Sn₃N₄ (T-aa) structures also exhibit mechanical stability. The calculations for Young's stiffness and Poisson's ratio show $Y_x = Y_y = 361$ N/m and 0.28 for Ge₃N₄ (T-aa) sheet, and $Y_x = Y_y = 253$ N/m and 0.34 for Sn₃N₄, respectively. These results indicate that both Ge₃N₄ and Sn₃N₄ are softer than Si₃N₄ (T⁻aa). Further calculation of the phonon spectra of other non-Pb-containing $A(B_2)N_4$ and Janus $A(AB)N_4$ (A = Si, Ge, and Sn, B = Si, Ge, and Sn) structures reveals that all nitride structures do not exhibit any imaginary frequencies at k-points other than near the Γ point (Fig. S20), indicating their good lattice dynamical stability.



Fig. S19 The phonon dispersions of (a) Ge_3N_4 , (b) Sn_3N_4 , and (c) Pb_3N_4 . The energy evolution and structural snapshots of the Ge_3N_4 and Sn_3N_4 subjected to AIMD simulations at distinct temperatures of 500 K in simulate time of 10 ps.



Fig. S20 The phonon dispersions of $A(B_2)N_4$ and Janus $A(AB)N_4$ structures.

Table. S10 The elastic constant $C_{11/22}$, $C_{12/21}$, C_{66} , and Young's stiffness (Y_x/Y_y) and Poisson's ratio (v) of A_3N_4 (A = Si, Ge, and Sn)

	C_{11}/C_{22} (N/m)	C_{12}/C_{21} (N/m)	C ₆₆ (N/m)	$Y_{\rm x}/Y_{\rm y}$ (N/m)	v	
Si_3N_4	520	137	192	487	0.26	
Ge ₃ N ₄	392	110	141	361	0.28	
$\mathrm{Sn}_3\mathrm{N}_4$	287	98	94	253	0.34	

Part VI

Formation energy, electronic properties and analysis of 2D nitride

analogues.

To examine the thermodynamic stability of these structures, the formation energy has been carried out. For the chemical general formula $ABCN_4$, their formation energies (E_f) is calculated according to the following equation.

$$E_f = \frac{E_{ABCN_4} - E_A - E_B - E_C - 4E_N}{7} \#(6)$$

where E_A , E_B and E_C denote the average energy per atom in the most stable bulk phase materials corresponding to elements A, B and C, and E_N denotes the average energy of an N atom in nitrogen.

As shown in Fig. 5c and 5d, there are 10 structures (including Si₃N₄) with negative formation energy, mostly between -0.3 and -0.7 eV/atom, and the rest are four slightly negative structures (-0.1 eV/atom $\langle E_f \langle 0 eV/atom \rangle$). Both A(B₂)N₄ and A(AB)N₄ structures have the same phenomenon: the position is closer to the left upper corner of the table, the formation energy is more negative with higher stability; while the position is closer to the bottom right of the table, the formation energy is more positive with less stability. In other words, they satisfy two rules at the same time: (a) the lower the number of elements leads to more stability; (b) the larger the proportion of low-number element in the composition results in more stability. For A = B, the formation energy of Si, Ge, Sn and Pb is -0.991, -0.033, 0.218, and 1.065 eV/atom, respectively. When A \neq B, the formation energy of the system is roughly equal to the linear combination of respective A₃N₄ nanosheet with deviation range of from 0.010 eV/atom to 0.383 eV/atom, as shown in Fig. S24a and S24b.

The electronic properties are explored at PBE and HSE06 level, as shown in Fig 5e, 5f (including Si₃N₄) and Fig S21, S22, and S23. At PBE level, most of the structures are semiconductors (24/28) and have indirect bandgap (18/24). Only a few of them are metallic (4/28). But, all of them are semiconductors at HES06 level, with many indirect bandgap (22/28), and a few direct bandgap (6/28). The value and types of bandgap of the A(B₂)N₄ and A(AB)N₄ structures are similar overall. The largest/smallest indirect bandgap is 5.347/0.195 eV for Si(SiGe)N₄/Pb₃N₄, and the largest/smallest direct bandgap is 3.087/0.972 eV for Si(SiSn)N₄/Pb(SiPb)N₄, respectively. Similar to the formation energy results, the bandgap values also satisfy two rules at the same time: (a)

the lower the number of elements in the structure leads to a larger bandgap; (b) the larger the proportion of low number elements in the composition leads to a larger bandgap. Similarly, when A = B, the bandgap of the system becomes smaller as the atomic number becomes larger: Si (5.273 eV) > Ge (3.363 eV) > Sn (1.522 eV) > Pb (0.195 eV); when A \neq B, the bandgap of the system can also be considered as a roughly linear combination of bandgap of the respective A₃N₄ nanosheet but with larger deviation, as shown in Fig. S24c and S24d.

Ultimately, these two phenomena likely result from the inert electron pair effect, where the relatively inner valence *s*-orbital of the IV_A atom turns more passivated as the period of the element becomes larger to leads increasingly difficulty to participate in bond formation to leads to smaller bonding energy (i.e., higher formation energy) and less orbital-hybridization splitting (i.e., smaller bandgap), as shown in Fig. S25. Among them, the Pb-*6s* is the most significant and difficult to participate in bonding, while Si-*3s* is the least significant and most easy one. This results in that there is a strong bonding ability (wide bandgap) between (in) Si and N, a slightly weaker bonding ability (moderate bandgap) between (in) Pb and N. In general, the nitride analogues of Si₃N₄ have a wide bandgap distribution range (0.195 -5.347 eV), which have a significant expansion effect relative to Si₃N₄ (T-aa) and effectively enrich the variety and electronic properties for the material family.



Fig. S21 Calculated band structure and DOS of isomeric structures of A_3N_4 (A = Si, Ge, Sn and Pb) at PBE level.



Fig. S22 Calculated band structure and DOS of isomeric structures of $A(B_2)N_4$ (A and B = Si, Ge, Sn and Pb) at PBE level.



Fig. S23 Calculated band structure and DOS of isomeric structures of $A(AB)N_4$ (A and B = Si, Ge, Sn and Pb) at PBE level.



Fig. S24 The deviation of linear combination of respective A_3N_4 for formation energies and bandgap (HSE06 level) of (a)&(c) A(B₂)N₄ and (b)&(d) Janus structure A(AB)N₄, where the color of the blocks indicates the degree of deviation of formation energy and bandgap.



Fig. S25 The partial DOS and integral DOS (IDOS) of the orbital-*s* (a) and orbital-*d* (b) of A_3N_4 structure (A = Si, Ge, Sn and Pb), the Fermi level is set as 0.

Part VII

Magnetism raised by charge doping.



Fig. S26 Spin-resolved projected density of states at a hole concentration of 2.00×10^{14} cm⁻². The inset depicts are the corresponding spin density (the isosurfaces is set as 0.001 e/Bohr³). The Fermi level is indicated by a dashed line at 0 eV.



Fig. S27 The spin density of 2D Sn_3N_4 at a hole concentration of (a) +0.1, (b) +0.2, (c) +0.3 and (d) +1.0 h⁺/cell, respectively.

	R_{MDC}	E_{Mag}
	$(\times 10^{13} \text{ cm}^{-2})$	(meV/carrier)
Si ₃ N ₄	41.9 ~ 139.6	59.3
Ge ₃ N ₄	24.3 ~ 121.4	97.3
Sn_3N_4	0.1 ~ 100.2	103.8
Ge(Si ₂)N ₄	39.8 ~ 132.7	83.5
$Sn(Si_2)N_4$	0.1 ~ 123.6	83.6
Sn(Ge ₂)N ₄	0.1 ~ 113.5	100.7

Table. S11 The range of magnetization doping concentration (R_{MDC}) and magnetic energy (E_{Mag}) of Si₃N₄, Ge₃N₄, Sn₃N₄, Ge(Si₂)N₄, Sn(Si₂)N₄ and Sn(Ge₂)N₄

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