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Electronic and optical properties of silicon based porous sheets

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Si based sheets have attracted tremendous attention due to their compatibility with the well-developed Si-based semiconductor industry. On the basis of state-of-the-art theoretical calculations, we systematically study the stability, electronic and optical properties of Si based porous sheets including $g-Si_4N_3$, $g-Si_3N_4$, $g-Si_3N_3$ and $g-Si_3P_3$. We find that the $g-Si_3N_3$ and $g-Si_3P_3$ sheets are thermally stable, while the $g-Si_4N_3$ and $g-Si_3N_4$ are unstable. Different from the silicene-like sheets of SiN and Si_3N which are nonplanar and metallic, both the porous $g-Si_3N_3$ and $g-Si_3P_3$ sheets are planar and nonmetallic, and the former is an indirect band gap semiconductor with a band gap of 3.50 eV, while the latter is a direct band gap semiconductor with a gap of 1.93 eV. Analysis of the optical absorption spectrum reveals that the $g-Si_3P_3$ sheet may have applications in solar absorbers owing to its narrow direct band gap and wide range optical absorption in the visible light spectrum.

The study of two dimensional (2D) monolayer materials has been a topic of high interest since the discovery of graphene¹ showing superior physical and chemical properties.² Among them, graphitic carbon nitrides C3N3, C3N4 and C4N3 catch considerable attention due to their novel mechanical, electronic, magnetic, and photocatalytic behaviors.³⁻⁹ For example, Xie's group reported the first finding of a carbon nitride with graphite-like lamellar structure.¹⁰ Li et al. synthesized a single layer of carbon nitride sheet labeled as g-C₃N₃ through the reaction of C₃N₃Cl₃ and Na by a simple solvothermal method.¹¹ Chai et al. found that g-C₃N₃ can exhibit optical absorption anisotropy and it may be used as a photocatalyst to split water.¹² Qiu *et al.* suggested that if each of the carbon atoms in g-C₃N₃ adsorbs a hydrogen atom, the hydrogenated structure (g-H₃C₃N₃) can display ferromagnetic properties with 100% half-metallicity around Fermi energy.¹³ Ma et al. observed that g-C₃N₃ monolayer has high H₂ permeability and selectivity with a potential for H₂ purification.¹⁴ Since silicon is in the same group as carbon in the periodic table, some intriguing questions arise: if C is replaced by Si, are these 2D Si-N sheets still stable? What properties do they have?

In fact, three dimensional (3D) Si–N materials are found to have some unique properties. Silicon nitride (Si_3N_4) is a light, hard, and strong engineering ceramic¹⁵ at high temperatures, and it has high strength applications owing to its outstanding mechanical features.^{16,17} There are two common forms of silicon nitride: α -Si₃N₄ and β -Si₃N₄. Both of them have hexagonal structures, but different in stacking modes.18 Theoretical studies were carried out to explore the electronic structures, charge distribution, charge transfer and optical properties of these two phases.^{19,20} In 1999 a new phase, labeled as c-Si₃N₄, was successfully synthesized²¹ and first-principles calculations suggested its hardness being comparable to that of the hardest known oxide.²² Although great efforts have been made to study 3D Si–N materials, less attention is paid to 2D Si–N sheets. Very recently silicene-like sheets of SiN and Si₃N were investigated theoretically²³ and both of them were found to exhibit metallic behaviors but have different geometries: SiN sheets prefer the washboard-like buckled conformation, while Si₃N sheets have chair-like buckled conformation. To the best of our knowledge there are no studies reported on 2D porous Si-N sheets like g-Si₃N₃, g-Si₃N₄, and g-Si₄N₃. In this paper, we systematically study the stability, electronic and optical properties of these designed 2D sheets.

First principles calculations were carried out by using density functional theory (DFT) as implemented in the Vienna ab initio Simulation Package (VASP code).²⁴ The electronic exchange– correlation functional was treated using the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) parametrization.²⁵ The interactions between electrons and nuclei were treated using projected augmented wave (PAW) potentials. Hybrid functionals in the Heyd–Scuseria–Ernzerhof (HSE06) form²⁶ were also used to achieve greater accuracy of the electronic and optical absorption properties. The energy cutoff was set at 500 eV. The convergence criteria for energy and force were set as 0.0001 eV and 0.01 eV Å⁻¹, respectively. The Brillouin zones were represented with 9 × 9 × 1 Monkhorst–Pack special



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Fig. 1 Optimized structure of the g-Si₃N₃ sheet. Si and N atoms are represented by yellow and blue balls, respectively. The unit cells are marked by purple rhombus.

k-point meshes.²⁷ The vacuum space in the normal direction of the sheets was taken to be 20 Å, which is sufficient to avoid the interaction between the two neighboring layers. To confirm their dynamic stability, phonon calculations were performed using finite displacement method as implemented in the phonopy program.²⁸

We first study a g-Si₃N₃ sheet where the initial geometry is generated from a g-C₃N₃ sheet by replacing C with Si. Fig. 1 shows the fully optimized geometrical structure which has a high symmetric space group of *P*6/*mmm* (D_{6h}^1 , 191). The equilibrium lattice constant of the g-Si₃N₃ sheet is a = b = 9.65 Å, which is larger than the value of 7.11 Å of g-C₃N₃ sheet¹³ and even larger than that of g-C₄N₃ sheet⁹ due to the larger size of Si atoms and the porosity of this structure. The Si–Si and Si–N bond lengths in the ground state structure are 2.35 Å and 1.67 Å, respectively, indicating a feature of single σ bonds.

We then examine the stability of the g-Si₃N₃ sheet. To confirm its dynamic stability, we performed calculations of phonon spectra as displayed in Fig. 2(a), where no imaginary frequencies exist, indicating that the g-Si₃N₃ is dynamically stable. This is different from the cases of g-Si₃N₄ and g-Si₄N₃ which are found to be unstable from the calculations of phonon dispersions. The phonon instability of g-Si₃N₄ and g-Si₄N₃ implies that there might be some local distortion induced buckling in these nanosheets, which can be attributed to pseudo-Jahn–Teller distortion.²⁹ Such out-of-plane distortion has been suggested in previous studies on silicene³⁰ and g-C₄N₃.³ Here, we focus



Fig. 2 (a) Phonon dispersions and (b) energy fluctuation with respect to time in MD simulations at 300 K for the $g\text{-}Si_3N_3.$

only on the stable planar g-Si₃N₃ nanosheet. To further confirm the thermal stability of g-Si₃N₃ sheets at finite temperature, a larger 3 × 3 supercell containing 108 atoms was used to reduce the constraint of the lattice. *Ab initio* molecular dynamics (MD) simulations were carried out with a Nosé thermostat³¹ at 300 K for 5000 steps with a time step of 1 fs. The fluctuations of total energy with simulation time are plotted in Fig. 2(b). After 5000 steps, we found that no obvious structure destruction occurred, and the average value of total energy remains nearly constant during the simulation, confirming that the g-Si₃N₃ is thermally stable at room temperature.

To compare the stability of g-Si₃N₃ with other silicon based sheets, we calculated the formation energy³² of other 2D Si–N systems including SiN and Si₃N sheets. The calculated results show that the formation energy of g-Si₃N₃ sheet (0.47 eV) is smaller than those of SiN sheet (1.02 eV) and Si₃N (0.64 eV) sheets²³ due to its porosity, indicating that the g-Si₃N₃ sheet is energetically metastable. We note that the structural unit of g-Si₃N₃ is the Si₃N₃ ring. Therefore, this newly designed nanosheet could be synthesized by polymerization reaction using the synthesized C₂₁H₂₄F₃N₃Si₃ or C₁₂H₃₀F₃N₃Si₃ molecules which contain the hexagonal Si₃N₃ cores.^{33,34} A similar procedure was reported to fabricate the g-C₃N₃ architectures.¹¹

To study the electronic properties of the g-Si₃N₃ sheet, we calculated the electronic band structure and corresponding partial density of states (PDOS). The results are shown in Fig. 3(a) and (b), respectively. The g-Si₃N₃ sheet is found to be nonmagnetic due to zero spin polarization, while the silicene-like SiN structure is metallic resulting from the abundance of p-electrons of N elements, according to previous studies.²³ The band structure shows that the g-Si₃N₃ is an indirect band gap semiconductor with a band gap of 2.30 eV, because the valence band maximum (VBM) is located at the Γ point and the conduction band minimum (CBM) is located at the *K* point in the Brillouin zone. This is different from g-C₃N₃, which has a smaller direct band gap of 1.5 eV at the *K* point in the Brillouin zone.¹³ We note that the VBM is quite flat, which would lead to



Fig. 3 (a) Electronic band structures of the $g-Si_3N_3$ calculated using GGA-PBE (blue lines) and HSE06 hybrid functional (red lines). (b) PDOS of the $g-Si_3N_3$ at GGA-PBE level. The Fermi energy level is shifted to 0.00 eV.

a large effective mass of holes. This can be understood from the fact that the tops of valence bands (VB) are comprised of the N 2p orbitals, as shown in Fig. 3(b). Previous studies on α - and β -Si₃N₄ phases manifested that both of them are semiconductors and the tops of their VB are also flat since they are derived from the more delocalized nonbonding N 2p orbitals,¹⁹ indicating that the 2D and 3D Si-N systems have similar electronic properties to each other. As standard DFT calculations are well known to underestimate the band gap, we repeated the band structure calculations using the screened hybrid functional HSE06²⁶ which has been demonstrated to be more accurate in describing the exchange-correction energy of electrons. The results are also plotted in Fig. 3, showing both the GGA and HSE06 functionals lead to similar dispersion curves of the valence and conduction bands. However, the conduction bands are up-shifted, while the VB are down-shifted at the HSE06 level, resulting in a larger band gap of 3.50 eV, as compared to that obtained with the GGA. While the 3D α - and β -Si₃N₄ have band gaps at 4.63 and 4.96 eV,¹⁹ respectively. Thus, we see that the electronic properties of Si-N based systems can be tuned by changing dimensionality.

Graphitic carbon nitrides are widely used for optical applications.^{35,36} Therefore, it would be intriguing to investigate the optical properties of its new counterparts. We first study the optical absorption of the g-Si₃N₃ structure. The dielectric function is defined as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, respectively. From the calculated $\varepsilon_2(\omega)$, we obtained the optical absorption curve, which is displayed in Fig. $4(a_1)$. The curve shows a sharp increase at about 290 nm (corresponding photon energy is 4.30 eV), which originates from the π - π * electronic transitions. The wide absorption ranging from about 100 to 250 nm is derived from the electronic transitions between the inner non-bonding orbitals and π^* orbitals. Compared with g-C₃N₃,¹² which has a main peak situated at 297 nm and a weak broad absorption from 78 to 114 nm, the g-Si₃N₃ also has a strong optical absorption in ultraviolet wavelengths but a wider



Fig. 4 Calculated optical absorptions (a_1) and (b_1) , and refractive index (a_2) and (b_2) of the g-Si₃N₃ and g-Si₃P₃ sheets, respectively.

range of optical absorption. Compared with the 3D Si₃N₄ system,¹⁹ where the optical absorption curves for both α - and β -Si₃N₄ have three relatively sharp peaks around 113, 127 and 159 nm (corresponding photon energies are 11.0, 9.8 and 7.8 eV, respectively), the 2D g-Si₃N₃ undergoes a red shift. Thus, we see the effect of dimensionality on the optical properties in the Si-N based system. Usually, in a semiconductor, if the photon energy is greater than the band gap of the material, then electrons are excited onto the conduction bands. Thus there is an upper limit for wavelength, which is defined as $\lambda_{\text{max}} = 2\pi \hbar c/E_{g}$, where \hbar , c, and E_{α} represent the Planck constant, light speed, and electronic band gap, respectively. The HSE06 calculations provide a band gap of 3.50 eV. Hence, as expected, all the absorption peaks are within the value of maximum light wavelength λ_{max} of 355 nm, which is consistent with the calculated optical spectrum, as shown in Fig. $4(a_1)$.

We then calculate the refractive index using the relation:

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + \operatorname{Re}\varepsilon(\omega)}{2}}$$

The results are plotted in Fig. $4(a_2)$. We see that the minimum value of the refractive index lies at a light wavelength of 116 nm, and the curve has gradual growth as wavelength increases and approaches the peak value of 1.5 at light wavelength of 306 nm in the ultraviolet region.

Since phosphorus and nitrogen are in the same group in the periodic table, we then carried out similar calculations on a g-Si₃P₃ sheet constructed by replacing N with P in the optimized structure of g-Si₃N₃. The fully optimized geometrical structure is plotted in Fig. 5. It also has a planar 2D hexagonal primitive cell but has a larger lattice constant of 10.70 Å, as compared to the g-Si₃N₃ sheet due to the bigger size of P atoms. The relaxed Si–Si and Si–P bond lengths are 2.35 Å and 2.16 Å, respectively. MD simulations confirm that the g-Si₃P₃ sheet is thermally stable at room temperature.

The electronic band structure of the g-Si₃P₃ is displayed in Fig. 6(a). It shows that the g-Si₃P₃ is a nonmagnetic semiconductor, while the silicene-like SiP sheet is metallic.²³ Different from the g-Si₃N₃ sheet, the g-Si₃P₃ sheet is a direct band gap semiconductor as both the VBM and CBM are located at the *K* point



Fig. 5 Optimized structure of the g-Si $_3P_3$ sheet. Si and P atoms are represented by yellow and pink balls, respectively. The unit cells are marked by purple rhombus.



Fig. 6 (a) Electronic band structures of the $g-Si_3P_3$ using GGA-PBE (blue lines) and HSE06 hybrid functional (red lines). (b) PDOS of the $g-Si_3P_3$ at GGA-PBE level. The Fermi energy level is shifted to 0.00 eV.

in the Brillouin zone from both the GGA and HSE06 level calculations. The calculated band gap is 1.41 eV and 1.93 eV, respectively, from these two functionals. The corresponding PDOS of the g-Si₃P₃ is plotted in Fig. 6(b), showing that the VBM and CBM come from the p orbitals of both the Si and P atoms. For comparison, the optical absorption curve of $g-Si_3P_3$ is also given in Fig. 4(b₁). We note, unlike the g-Si₃N₃, that the absorption curve of g-Si₃P₃ starts at about 100 nm with the first peak at 212 nm (corresponding photon energy is 5.9 eV) and the second peak at 501 nm (corresponding photon energy is 2.5 eV), namely, the absorption spectrum of the g-Si₃P₃ covers a wider range in visible light wavelength as compared to that of the g-Si₃N₃. Since the preferable energy window for photocatalytic materials is in the range of 400 to 770 nm, the g-Si₃P₃ would be suitable for solar absorbers. The calculated work function of g-Si₃P₃ is 5.57 eV, which is approximately the same value as a graphene sheet functionalized with OH groups,32 showing its potential application in water-splitting. When excited by light, the electrons would jump into the conduction band enabling the reduction of H₂O for H₂, while holes in the valance band would oxidize H₂O for O₂. The calculated results of refractive index are also plotted in Fig. 4(b_2), showing that the peak value of the g-Si₃P₃ shifts to the visible light range, which differs from the g-Si₃N₃.

In summary, a detailed first-principles DFT study on the stability, electronic and optical properties of the monolayer g-Si₃N₄, g-Si₄N₃, g-Si₃N₃ and g-Si₃P₃ sheets is performed. Their dynamical and thermal stabilities are examined by carrying out phonon calculations and MD simulations. The g-Si₃N₃ sheet is found to be stable, while the first two structures are dynamically unstable, indicating that the stability of 2D Si–N sheets can be manipulated by changing the stoichiometric ratio of Si : N. We find that unlike the previously studied silicene-like SiN and Si₃N sheets which are metallic, the g-Si₃N₃ is semiconducting with an indirect band gap of 3.50 eV (at the HSE06 level). We have shown that the 2D sheet has a larger effective mass of holes, a smaller band gap, and a red shift of the optical absorption in ultraviolet wavelengths, as compared to the

3D Si₃N₄ structure, suggesting that in Si-based materials the electronic and optical properties can be tuned by changing dimensionality. When N is replaced by P forming a g-Si₃P₃ sheet, the system is also stable and becomes a semiconductor with a smaller energy direct band gap of 1.93 eV, as compared with the g-Si₃N₃ sheet. It has a main optical absorption peak at 501 nm in the visible light region, suggesting that the g-Si₃P₃ sheet may be a potential material for solar absorption. We hope that this work will provide some useful physical insights for experimental studies in this direction.

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