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Research Article

Formation and atomic-scale characterization of an interfacial β -Si₃N₄ nanolayer in a C/SiC composite

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Abstract

β -Si₃N₄ combines attractive mechanical, thermal, and dielectric properties, yet experimental characterization of its local atomic arrangement and bonding-related electronic structure is often complicated by the sintering additives and intergranular phases present in bulk ceramics. Here, a continuous, sintering-additive-free β -Si₃N₄ nanolayer was formed at the C/SiC interface through reactive infiltration of molten Si into a nitrogen-containing, glucose-derived carbon framework. The nanolayer exhibits micrometer-scale lateral continuity within the examined interfacial region, with a local thickness on the order of 20 nm, providing a resolvable crystalline interior that remains accessible to site-specific atomic-scale analysis. Correlative HAADF-STEM and iDPC-STEM observations along multiple crystallographic directions resolved both the projected Si framework and the light-element N sublattice, and consistently identified the characteristic ABAB stacking and corner-sharing SiN₄ tetrahedral network of β -Si₃N₄. The N *K*-edge and Si *L*_{2,3}-edge electron energy-loss near-edge structures were further examined using reference spectra and density-functional-theory-based simulations. Their principal features were associated with complementary N- and Si-

projected components of the hybridized unoccupied states in the tetrahedral Si-N framework. Projected densities of states, charge-density redistribution, and band-structure calculations further revealed N-weighted occupied bonding states, predominantly Si-derived unoccupied states with finite N 2*p* contributions, partial charge transfer from Si to N, and directional covalent bonding. Together, these results provide correlated atomic-scale structural and bonding-sensitive spectroscopic characterization of the interfacial β -Si₃N₄ nanolayer, with first-principles calculations supporting the interpretation of the principal ELNES features.

Keywords: β -Si₃N₄; C/SiC interface; Atomic-resolution STEM; Electron energy-loss near-edge structure; Si-N bonding

1 Introduction

β -Si₃N₄ possesses a unique combination of high strength and hardness, excellent thermal and chemical stability, low dielectric constant, and potentially high thermal conductivity, making it an important structural and functional ceramic for demanding applications, including high-temperature structural components, thermal-management substrates, and dielectric materials [1–6]. These properties originate from its highly ordered atomic framework and the strong, directional Si-N bonds within the corner-sharing SiN₄ tetrahedral network [7–10]. The local coordination of Si and N, the stacking of the tetrahedral layers, and the associated electronic states therefore provide the structural basis for understanding the performance of β -Si₃N₄. Establishing a reliable experimental correspondence between its atomic configuration and bonding-

related electronic features is consequently important for interpreting how composition, defects, interfaces, and additive-related local environments modify the structure and properties of silicon nitride ceramics.

The crystallographic and electronic structures of β -Si₃N₄ have been extensively described using diffraction-derived structural models and first-principles calculations [7–9]. These studies have established the characteristic ABAB stacking of the β polymorph, the tetrahedral coordination of Si by N, and the mixed covalent–ionic character of the Si–N bonds. Experimental investigations of β -Si₃N₄ commonly involve bulk ceramics consolidated through additive-assisted liquid-phase sintering. The extremely low self-diffusion coefficients associated with the strong and highly directional Si–N bonds make the densification of Si₃N₄ difficult without the use of oxide additives, such as Al₂O₃, MgO, CaO, Y₂O₃ or other rare-earth oxides [11–19]. During sintering, these additives react with surface silica and silicon nitride to form an oxynitride liquid phase, which facilitates densification but may remain as intergranular glassy phases or nanoscale grain-boundary films after cooling [11–15,20]. Additive elements may also segregate at interfaces or enter the Si or N related sublattices in chemically modified silicon nitride structures [16–18]. Consequently, the local atomic arrangement and spectroscopic response measured from practical ceramics may contain contributions from additive-derived phases, compositional variations, and grain-boundary environments in addition to those of the β -Si₃N₄ framework itself. Obtaining an experimentally accessible β -Si₃N₄ region with reduced interference from these

extrinsic chemical environments remains challenging. Atomically thin nitride interphases and surface-grown structures can be directly examined at high spatial resolution, but their atomic and electronic structures may be strongly influenced by adjacent phases, structural termination, or substrate interactions. Conversely, conventional bulk grains contain an extended crystalline interior but are generally produced through additive-assisted processing. As such, the quest to prepare a continuous β - Si_3N_4 nanolayer that spans micrometer-scale distances while retaining a nanoscale thickness, and is formed without conventional sintering additives, is essential. It is expected that such a β - Si_3N_4 nanolayer would contain a sufficiently developed crystalline region for examining the β - Si_3N_4 framework while remaining accessible to site-specific atomic-scale structural and spectroscopic analysis. Such a system would help connect the periodic descriptions of ideal β - Si_3N_4 with the more chemically complex environments encountered in practical Si_3N_4 ceramics. Correlating atomic configuration with bonding-related electronic response is important for understanding β - Si_3N_4 at the local scale. Resolving both the Si framework and the light-element N sublattice enables identification of the characteristic tetrahedral stacking of the β polymorph, while element-specific near-edge spectra provide complementary information on the local coordination and unoccupied electronic states of Si and N [21–29]. Combined with reference data and first-principles calculations, these measurements allow the experimentally resolved atomic arrangement to be examined together with the associated bonding-related spectroscopic features within the same

crystalline region. Such a β - Si_3N_4 nanolayer offers a local system in which the atomic arrangement and bonding-sensitive spectroscopic characteristics of β - Si_3N_4 can be examined with high spatial resolution.

In this work, a process was deliberately designed to prepare a sintering-additive-free β - Si_3N_4 nanolayer at the C/SiC interface through reactive melt Si infiltration into a nitrogen-containing, glucose-derived carbon framework [34–37]. Within the examined interfacial region, the β - Si_3N_4 nanolayer extends continuously for more than 3 μm and exhibits a local thickness on the order of 20 nm, thereby combining micrometer-scale lateral continuity with nanoscale thickness. Its spatial extent exceeds that of an atomically confined interphase and provides a resolvable crystalline region, while this high-temperature stable polymorph of Si_3N_4 was formed without intentional addition of conventional oxide sintering additives. Complementary atomic-resolution observations along multiple crystallographic directions reveal the projected Si framework, N sublattice, and characteristic ABAB stacking of β - Si_3N_4 within the examined crystalline region. Element-specific N K -edge and Si $L_{2,3}$ -edge ELNES are further analyzed together with reference spectra, first-principles spectral simulations, and electronic-structure calculations. This correlative analysis combines atomic-resolution structural characterization of the interfacial β - Si_3N_4 nanolayer with bonding-sensitive analysis of its principal ELNES features.

2 Experimental and theoretical methods

2.1 Experimental

To prepare a sintering-additive-free β - Si_3N_4 nanolayer, a process was deliberately designed as illustrated in Fig. 1. In this process, a nitrogen-containing hydrogel precursor was prepared first. The nitrogen-containing hydrogel precursor was subsequently pyrolyzed to form a porous carbon framework, followed by reactive infiltration with molten Si to form SiC and the sintering-additive-free β - Si_3N_4 nanolayer.



Briefly, the process involved the preparation of a nitrogen-containing hydrogel precursor, vacuum pyrolysis to form a porous carbon framework, and subsequent vacuum reactive melt infiltration with molten Si. In order to form an interfacial Si_3N_4 nanolayer, D-(+)-glucose monohydrate (98%, Aladdin) and deionized water (Type 1, Milli-Q system) were used as the carbon source and solvent, respectively. Acrylamide (AM, AR, Aladdin) was introduced as the monomer and nitrogen-containing component, while N,N'-methylenebisacrylamide (MBAM, 99%, J&K) acted as both the cross-linking agent and an additional nitrogen-containing component. 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (AIBA, 97%, Aladdin) was used as the radical initiator. Firstly, Glucose, AM and MBAM were dissolved in deionized water with mass ratios of glucose/deionized water = 3.00, AM/glucose = 0.25, and MBAM/AM = 0.01. Secondly, the mixture was heated at 70°C under magnetic stirring until a homogeneous transparent solution was obtained. AIBA was then added at 0.05

wt.% relative to AM. After complete dissolution, the precursor solution was transferred into a Petri dish and kept at 80°C in a blast drying oven for gelation. During this step, AM polymerization and MBAM-assisted cross-linking produced a three-dimensional hydrogel network containing nitrogen-bearing groups. The chemical structures and cross-linking reactions involving acrylamide and N,N'-methylenebisacrylamide during the preparation of glucose-derived carbon materials are shown in Fig. 2, which have been described in previous related studies in the authors' group [34,37].

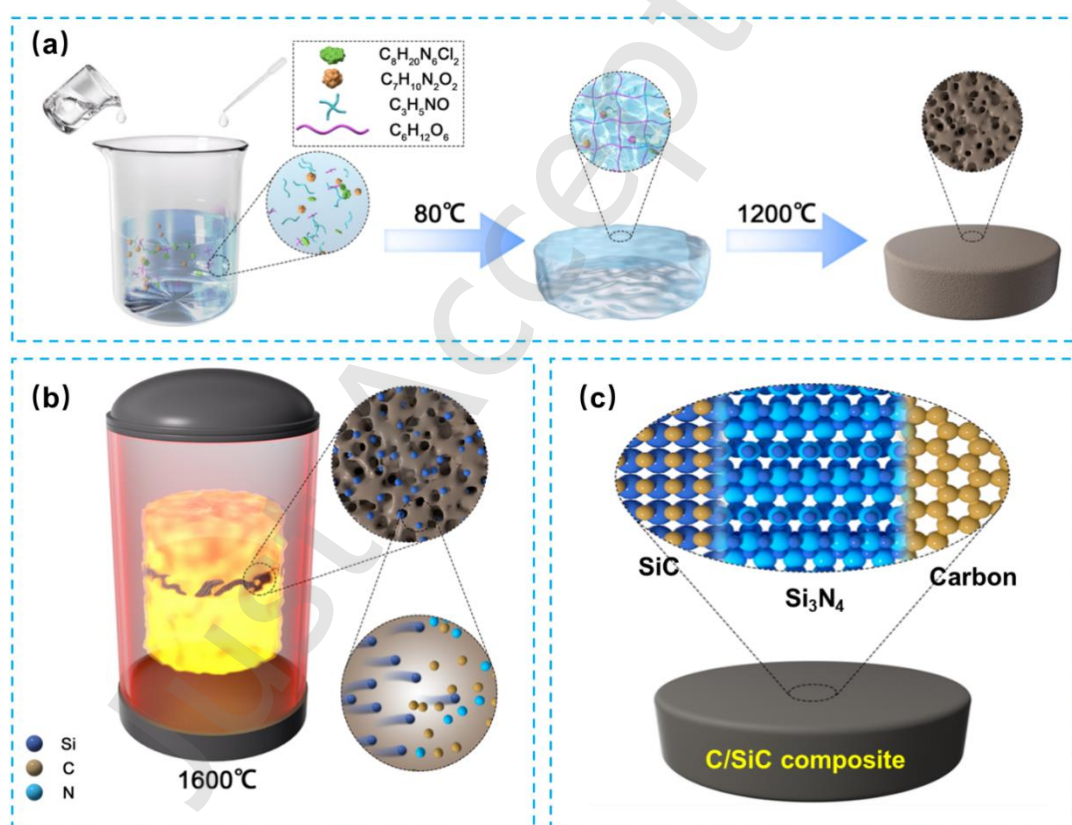


Fig. 1. Schematic illustration of the process designed for the synthesis of the sintering-additive-free β - Si_3N_4 nanolayer within the C/SiC composite. (a) Preparation of the nitrogen-containing hydrogel precursor followed by high-temperature carbonization to form the porous carbon framework. (b) The reactive melt infiltration (RMI) of Si at

1600 °C into the porous carbon framework. (c) Conceptual representation of the resulting C/SiC composite, wherein a β -Si₃N₄ nanolayer was formed at the C/SiC interface.

The obtained hydrogel was pre-carbonized in a blast drying oven using a gradient heating program from 100 °C to 240 °C for 28 h. The pre-carbonized body was then pyrolyzed in a vacuum pyrolysis furnace at 1200°C for 4 h to yield a porous carbon block. Subsequently, the carbon block was embedded in high-purity Si powder (purity $\geq 99.99\%$, -325 mesh, HWRK CHEM, Beijing, China) and heated to 1600 °C at a rate of 5°C/min under vacuum, followed by a dwell time of 30 min. During vacuum reactive melt infiltration, molten Si penetrated the porous carbon framework and reacted with carbon to form SiC, while an interfacial nanolayer developed between the SiC and carbon regions. No conventional oxide sintering additives, such as Al₂O₃, MgO, CaO, Y₂O₃, or other rare-earth oxides, were intentionally introduced during precursor preparation, vacuum pyrolysis, or reactive melt infiltration.

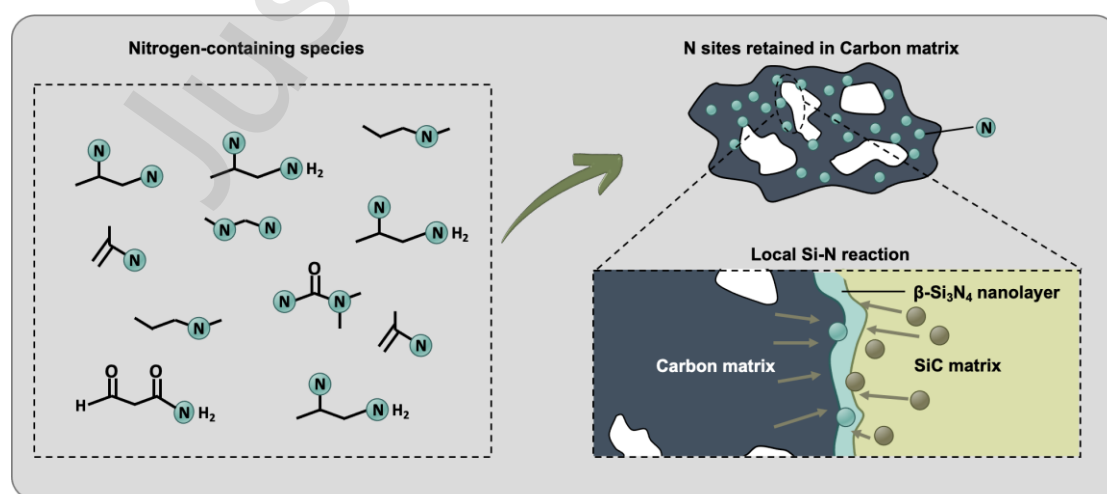


Fig. 2 Schematic illustration of the proposed formation pathway of the β -Si₃N₄

nanolayer at the C/SiC interface during reactive melt infiltration.

To meet the stringent requirements of high-resolution transmission electron microscopy, targeted site-specific sampling and thinning of the interfacial region were performed using focused ion beam (FIB) milling to prepare electron-transparent lamellae. Electron-transparent TEM lamellae were prepared using a focused ion beam/scanning electron microscope system (Dual Beam, Helios 5 CX, Thermo Fisher, USA). Final thinning was performed at 2 kV, followed by low-voltage cleaning to reduce surface damage. Atomic-scale morphological and crystallographic characterization was conducted on an aberration-corrected scanning transmission electron microscope (AC-STEM, Spectra Ultra, Thermo Fisher, USA) operated at 300 kV. HAADF-STEM, BF-STEM, ABF-STEM, and iDPC-STEM imaging were performed with a probe current of 80 pA and a beam convergence semi-angle of 28.0 mrad. The HAADF collection semi-angle was 54-200 mrad, while the collection semi-angles for ABF and iDPC imaging were 22 mrad and 8-40 mrad, respectively. The camera length was 110 mm for HAADF/BF imaging and 175 mm for iDPC imaging. HAADF-STEM imaging was used to examine the interfacial morphology and Z-contrast structural features, while BF-STEM and ABF-STEM imaging provided complementary contrast for examining the interfacial region. iDPC-STEM imaging was employed to visualize the projected atomic columns with improved sensitivity to light elements, especially the N sublattice in β -Si₃N₄. Atomic-resolution images acquired along selected zone axes were compared with crystallographic models of α -Si₃N₄ and

β -Si₃N₄. STEM-EDS elemental mapping was performed using an Ultra-X EDS detector to examine the spatial distributions of Si, C and N across the interfacial region. Electron energy-loss spectroscopy was performed separately in STEM mode to examine the bonding-sensitive near-edge features of the interfacial β -Si₃N₄ nanolayer. For the spectrum-image dataset used in the Si $L_{2,3}$ -edge analysis, the microscope was operated at 200 kV. A 270×270 -pixel spectrum image was acquired with a spatial sampling of $0.984 \text{ nm pixel}^{-1}$, a dwell time of 5 ms pixel^{-1} , and a single-pass raster scan. The energy dispersion was $0.300 \text{ eV channel}^{-1}$, and the energy-loss scale was referenced to the zero-loss peak at 0 eV. The spatially integrated zero-loss peak exhibited a full width at half maximum of approximately 1.4 eV, which was taken as the effective energy resolution of this dataset. The N K-edge and Si $L_{2,3}$ -edge ELNES were analyzed from crystalline regions within the interfacial β -Si₃N₄ nanolayer identified by atomic-resolution STEM. The experimental spectra were compared with reported reference spectra and DFT-based ELNES calculations for qualitative interpretation of the principal near-edge features. A short pixel dwell time and single-pass acquisition were used to reduce prolonged electron-beam exposure during spectrum imaging.

2.2 Theoretical methods

First-principles calculations were carried out within density functional theory using the CASTEP code implemented in Materials Studio [38]. The electron energy-loss near-edge structures (ELNES) of the N K-edge and Si $L_{2,3}$ -edge of β -Si₃N₄ were calculated using the method developed by Gao [39] to assist the interpretation of the

experimental EELS spectra. The β - Si_3N_4 unit cell was first optimized using the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange–correlation functional (GGA–PBE) [40] and on the fly generated (OTFG) ultrasoft pseudopotentials [41]. The plane-wave cutoff energy was set to 500 eV. The self-consistent field convergence threshold was set to 1.0×10^{-6} eV per atom, and the force convergence criterion was 0.01 eV $\text{\AA}^{-1}$.

Following structural optimization, core-level spectral calculations were performed for the N K -edge and Si $L_{2,3}$ -edge. The spectral intensity was evaluated from the transition matrix elements between the corresponding core states and unoccupied electronic states under the electric-dipole selection rules. Accordingly, the N K -edge predominantly probes transitions from the N $1s$ core level to unoccupied states with N p character, whereas the Si $L_{2,3}$ -edge reflects transitions from the Si $2p$ core levels to the corresponding dipole-allowed unoccupied states [26]. To account for the perturbation of the local electronic structure caused by the core-excited final state, a core-hole pseudopotential was introduced on the corresponding absorbing atom. A $2 \times 2 \times 2$ supercell was constructed from the optimized β - Si_3N_4 unit cell to reduce the artificial interaction between periodically repeated core holes. Separate calculations were performed for the N K -edge and Si $L_{2,3}$ -edge by placing the core hole on the corresponding excited N or Si atom. The exchange–correlation functional and plane-wave cutoff energy were kept consistent with those used for structural optimization, and Brillouin-zone integration was performed using a $2 \times 2 \times 2$ Monkhorst–Pack k -

point mesh. A sufficient number of unoccupied states was included to cover an energy range extending to 40 eV above the absorption threshold. The calculated spectra were broadened using a Gaussian function with a width of 0.2 eV and aligned with the corresponding experimental absorption onsets by an energy-axis shift to facilitate comparison. The comparison focused on the principal near-edge features and their overall spectral evolution, providing a qualitative basis for interpreting the experimental ELNES. Because the calculations employ the PBE exchange-correlation functional within a finite supercell, differences in absolute excitation energies and relative spectral intensities may arise from the exchange-correlation approximation and finite-size effects, as well as from local structural variations in the experimental nanolayer.

3 Results and discussion

3.1 Formation of the interfacial β -Si₃N₄ nanolayer

Scanning transmission electron microscopy (STEM) was employed to examine the morphology of the Si₃N₄ nanolayer formed in the C/SiC composite. Both the low-magnification high-angle annular dark-field STEM image in Fig. 3a and the corresponding bright-field STEM image in Fig. 3b reveal a narrow and continuous interfacial nanolayer between the adjoining SiC and carbon regions. Within the examined interfacial region, the Si₃N₄ nanolayer can be followed continuously over a distance exceeding 3 μ m, with a local thickness on the order of 20 nm. The contrast of this nanolayer is clearly distinct from those of the neighboring SiC and carbon regions,

indicating the formation of a compositionally and structurally different interfacial Si_3N_4 product [42]. Slight thickness variations are observed along the interface, while lateral continuity is maintained throughout the field of view. It therefore combines the micrometer-scale continuity with the nanoscale thickness, being suitable for microstructural analysis. The low-magnification STEM-EDS elemental mappings in Fig. 3c-e, acquired from the same field of view as Fig. 3a and b, further reveal the spatial distribution of the interfacial nanolayer. The N signal forms a narrow enriched band along the C/SiC boundary and follows the interfacial contrast throughout the examined field of view. The corresponding Si and C maps delineate the adjacent SiC- and carbon-rich regions, respectively. The spatial correspondence between the interfacial contrast and the localized N enrichment supports the formation of a nitrogen-containing product at the C/SiC boundary.

During hydrogel preparation, AM and MBAM introduce nitrogen-containing groups into the cross-linked glucose-derived network [34,37]. Related polyacrylamide-derived systems have been reported to retain precursor-derived nitrogen in carbonaceous products after carbonization [47,48]. During subsequent reactive melt infiltration, molten Si penetrates the porous carbon framework and SiC develops along the advancing Si/C reaction front. Residual nitrogen-containing species associated with the carbon framework could encounter the infiltrating Si within this interfacial reaction zone, providing a local nitrogen source for Si-N formation. The spatial confinement of this reaction zone is consistent with the narrow N-enriched band following the C/SiC

boundary and with the observed layer-like morphology.

Based on this spatial relationship, a possible formation pathway of the β - Si_3N_4 nanolayer is illustrated in Fig. 2. After reactive melt infiltration at 1600 °C, the interfacial crystalline product is identified as β - Si_3N_4 by the structural analyses described below. Previous phase-transformation studies have shown that β - Si_3N_4 is the thermodynamically favored polymorph at elevated temperature and that $\alpha \rightarrow \beta$ transformation behavior is sensitive to the local chemical environment and thermal history [42,43]. The β - Si_3N_4 observed here is therefore consistent with the high-temperature interfacial reaction environment during RMI. The interfacial β - Si_3N_4 nanolayer was formed during the 1600 °C RMI treatment without intentional addition of conventional oxide sintering additives. Within the examined region, the nanolayer combines micrometer-scale lateral continuity with nanoscale thickness.

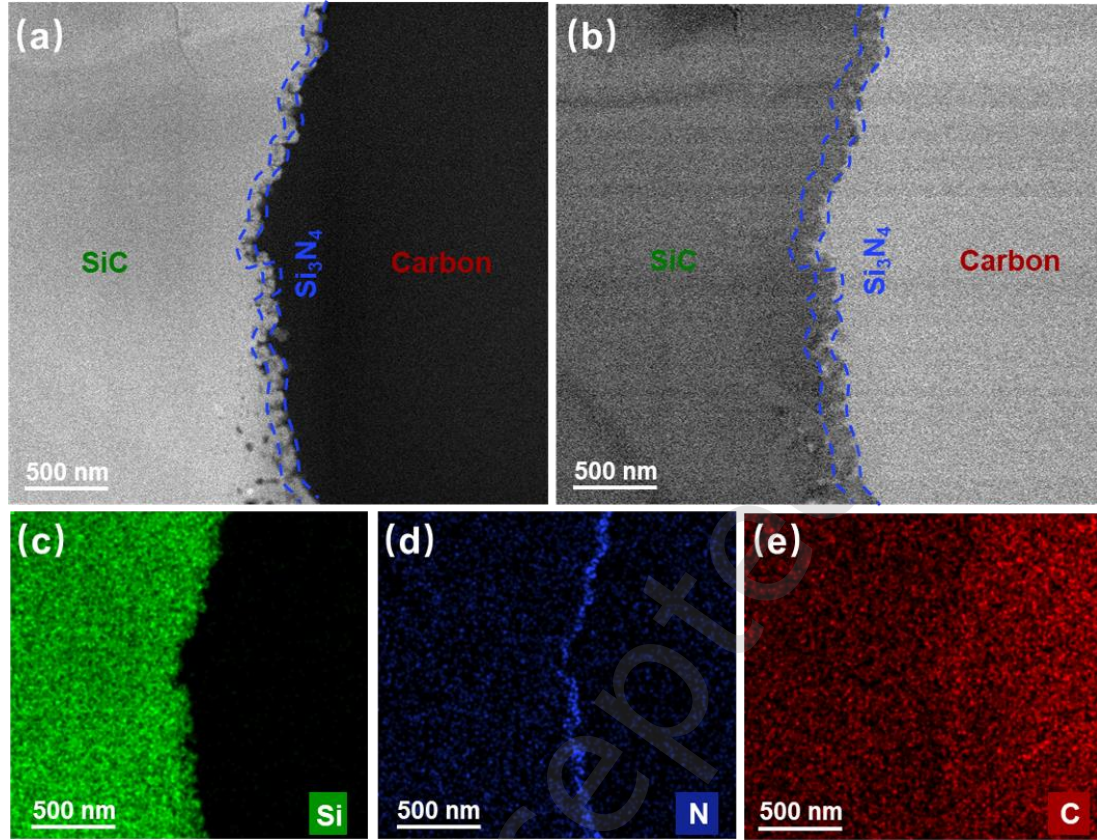


Fig. 3 Low-magnification STEM characterization and elemental distributions of the C/SiC interfacial region containing the β -Si₃N₄ nanolayer. (a) HAADF-STEM image and (b) BF-STEM image of the same interfacial region; the scale bars are 500 nm. In the HAADF-STEM image, the contrast is primarily sensitive to atomic number and mass-thickness, providing compositional contrast between the SiC, interfacial nanolayer, and carbon-rich regions, whereas the BF-STEM image provides complementary diffraction/thickness contrast across the interface. The blue dashed lines indicate the boundaries of the interfacial nanolayer. (c-e) Corresponding STEM-EDS elemental maps of Si, N, and C, respectively, acquired from the same field of view; the scale bars are 500 nm.

3.2 Atomic structure identification of the interfacial β - Si_3N_4 nanolayer

Atomic-resolution STEM imaging was performed to determine the crystal structure of the interfacial β - Si_3N_4 nanolayer. The BF-STEM image in Fig. 4a shows clear and continuous lattice fringes throughout the examined region, indicating a well-crystallized structure of the interfacial nanolayer. The diffraction pattern obtained from the same area is consistent with crystalline silicon nitride along the $[0001]$ zone axis, which cannot distinguish α - Si_3N_4 from the β -polymorph. The phase identity was further established by comparing the experimentally resolved atomic arrangements with the projected structures of the α and β - Si_3N_4 polymorphs. The projected structural models of β - Si_3N_4 and α - Si_3N_4 are presented in Fig. 4b. Both polymorphs are constructed from corner-sharing SiN_4 tetrahedra, but they differ in the stacking sequence of the tetrahedral layers along the $[0001]$ directions. The α polymorph follows an ABCD stacking sequence, whereas β - Si_3N_4 exhibits the characteristic ABAB sequence [1]. This crystallographic difference produces distinct projected atomic arrangements and provides the structural basis for distinguishing the two polymorphs in atomic-resolution images. Crystalline $\text{Si}_2\text{N}_2\text{O}$ has an orthorhombic structure (space group $\text{Cmc}2_1$) composed of interconnected SiN_3O tetrahedra [52]. In the $[0001]$ projection, the atomic contrast in the HAADF-STEM image shown in Fig. 4c agrees with the projected Si framework of β - Si_3N_4 . Because HAADF contrast is strongly dependent on atomic number, the image predominantly reflects the arrangement of the heavier Si atomic columns, whereas the lighter N columns are less pronounced. In the iDPC-STEM image

acquired from the same orientation (Fig. 4d), both the Si framework and the N sublattice can be resolved within the projected structure [21–24], wherein SiN_4 tetrahedra are clearly seen and their arrangement coincides well with the corresponding $\beta\text{-Si}_3\text{N}_4$ structural model. To further confirm the crystal structure of the interfacial Si_3N_4 nanolayer has the β -type structure, additional atomic-resolution observations were conducted along the $[\bar{1}2\bar{1}3]$ and $[2\bar{1}\bar{1}3]$ zone axes, as shown in Fig. 4e-h. The HAADF-STEM images reveal the projected Si-column arrangements, while the corresponding iDPC-STEM images provide complementary information on both the Si and the N sublattice. In both projections, the experimentally resolved atomic configurations agree with the projected $\beta\text{-Si}_3\text{N}_4$ structures as overlaid on the iDPC-STEM images in Fig. 4f and Fig. 4h. The alternating SiN_4 tetrahedral layers display the characteristic ABAB stacking sequence of the β polymorph, rather than the ABCD sequence associated with $\alpha\text{-Si}_3\text{N}_4$. The consistent structural correspondence obtained from diffraction and multiple crystallographic projections identifies the examined crystalline region of the interfacial nanolayer as $\beta\text{-Si}_3\text{N}_4$.

Taken together, the diffraction result establishes the crystalline nature of the interfacial Si_3N_4 nanolayer, while the atomic-resolution observations provide the decisive structural evidence for phase identification. The projected Si-column arrangements resolved by HAADF-STEM, together with the N sublattice visualized by iDPC-STEM, consistently reproduce the corner-sharing SiN_4 tetrahedral framework of $\beta\text{-Si}_3\text{N}_4$. More importantly, the characteristic ABAB stacking sequence is observed

along multiple crystallographic directions, distinguishing the interfacial nanolayer from the ABCD-stacked α polymorph. These mutually consistent observations support the β - Si_3N_4 assignment for the examined crystalline regions of the interfacial nanolayer.

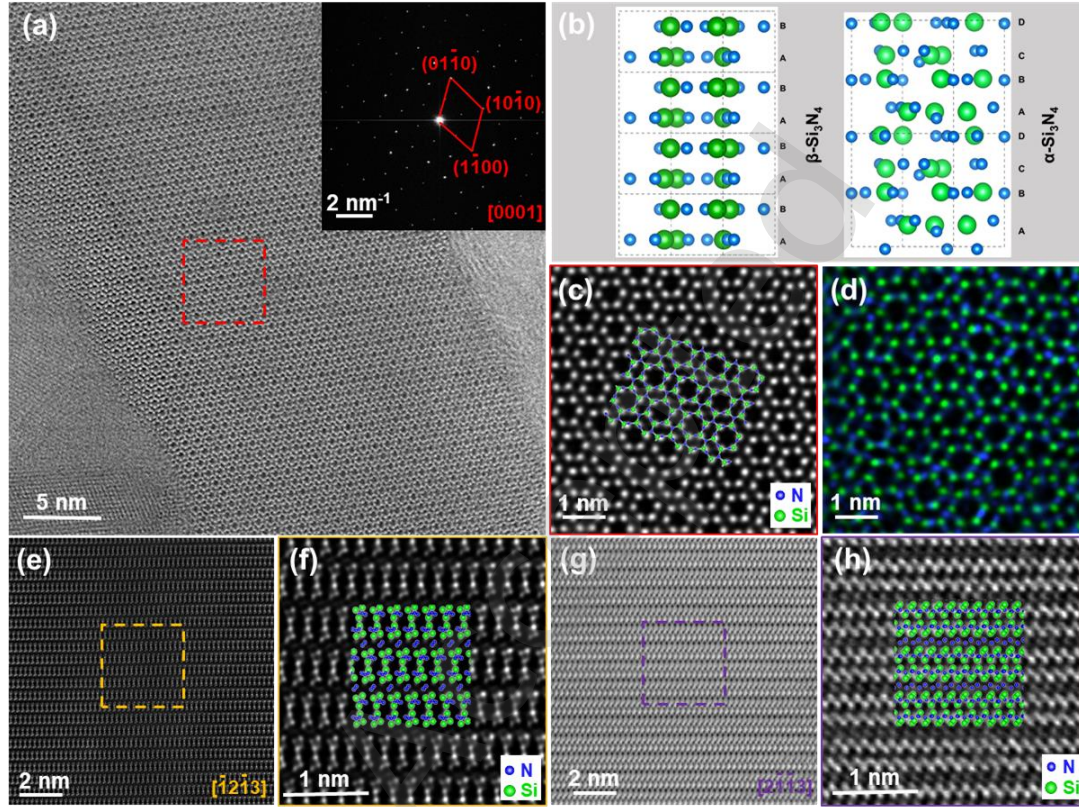


Fig. 4 Atomic-scale structural characterization of the interfacial β - Si_3N_4 nanolayer. (a) BF-STEM image acquired along the $[0001]$ zone axis, showing continuous lattice contrast within the interfacial nanolayer; the scale bar is 5 nm. The inset shows the corresponding indexed diffraction pattern with a reciprocal-space scale bar of 2 nm^{-1} . (b) Projected structural models of β - Si_3N_4 and α - Si_3N_4 viewed along $[0001]$, illustrating the characteristic ABAB and ABCD stacking sequences, respectively. (c) HAADF-STEM image acquired along $[0001]$, in which the Z-sensitive contrast predominantly reveals the projected Si-column framework; the scale bar is 1 nm. The β - Si_3N_4 atomistic model is overlaid on the experimental image, with Si and N represented by green and

blue spheres, respectively. (d) iDPC-STEM image acquired along $[0001]$, resolving both the Si framework and the lighter N sublattice; the scale bar is 1 nm. (e, g) HAADF-STEM images acquired along the $[\bar{1}2\bar{1}3]$ and $[2\bar{1}\bar{1}3]$ zone axes, respectively; the scale bars are 2 nm. (f, h) Corresponding iDPC-STEM images from the two crystallographic orientations, with scale bars of 1 nm. The projected β - Si_3N_4 atomistic models are overlaid on the experimental images, with Si and N represented by green and blue spheres, respectively, showing the characteristic ABAB stacking of the SiN_4 tetrahedral framework. The dashed boxes in (e) and (g) indicate the regions corresponding to the higher-magnification views in (f) and (h), respectively.

3.3 Bonding-related spectroscopic features and electronic structure of β - Si_3N_4

Electron energy-loss spectroscopy was further used to examine the bonding-related unoccupied states of the interfacial β - Si_3N_4 nanolayer formed between SiC and C. The spectra were acquired from the crystalline region marked in Fig. 5a, located within the β - Si_3N_4 domain identified by the atomic-resolution observations in Fig. 4. The experimental N K -edge spectrum is characterized by a weak low-energy feature at approximately 403-405 eV, followed by a pronounced main resonance and broader near-edge structures at higher energies (Fig. 5b). Its overall profile agrees with the previously reported reference spectrum of β - Si_3N_4 [25]. After alignment at the absorption onset, the calculated spectrum reproduces the principal near-edge features observed experimentally (Fig. 5c), providing a qualitative basis for interpreting the measured ELNES in relation to the electronic structure of β - Si_3N_4 . The dominant N K -

edge resonance is assigned primarily to transitions from the N $1s$ core level into unoccupied states with N $2p$ character involved in the antibonding states of the tetrahedrally coordinated Si-N framework. The strong σ^* related response therefore reflects unoccupied states distributed predominantly along the Si-N bond directions. The overall agreement with the reference spectrum and the calculated ELNES supports the assignment of the principal N K -edge features to the characteristic Si-N bonding environment of β -Si₃N₄. In addition to the dominant N K -edge resonance, a weak pre-edge shoulder is observed at approximately 403-405 eV. This feature is absent from the calculated spectrum of ideal β -Si₃N₄ and is much less pronounced in the reported reference spectrum. Geometric phase analysis of the corresponding region reveals minor local lattice modulation within the β -Si₃N₄ nanolayer, as shown in the inset of Fig. 5a [44]. The coexistence of the weak pre-edge shoulder and the local lattice modulation is consistent with a locally perturbed Si-N coordination environment. Such a perturbation may modify the distribution of low-energy N $2p$ -projected unoccupied states and contribute to the additional pre-edge intensity. Considering the weak intensity of this feature and the present experimental resolution, it is interpreted qualitatively as a local perturbation-sensitive spectral feature. The dominant resonance and the overall N K -edge profile remain characteristic of the tetrahedrally coordinated β -Si₃N₄ framework.

The close agreement between the present spectra and the reported β -Si₃N₄ reference spectrum [25] is consistent with the local nature of ELNES. The dominant N

K -edge and Si $L_{2,3}$ -edge features are determined primarily by the short-range tetrahedral Si-N coordination within the crystalline β -Si₃N₄ framework. In additive-assisted ceramics, oxide-derived species are commonly concentrated in intergranular films or segregated boundary regions. Their influence on the dominant ELNES features is therefore limited when the acquisition volume lies within the crystalline grain interior, although appreciable changes may occur when the probe intersects an additive-rich boundary or a chemically substituted site. Composition-dependent shifts in the Si $L_{2,3}$ -edge ELNES have indeed been reported for intergranular films in Si₃N₄ ceramics [45]. The similarity of the dominant ELNES features to the reported β -Si₃N₄ reference spectrum is consistent with their primary sensitivity to the short-range tetrahedral Si-N coordination within the crystalline region. Local structural and compositional perturbations may introduce additional modifications to the near-edge response. Accordingly, the weak pre-edge shoulder is treated here as a perturbation-sensitive spectral feature within the present experimental resolution.

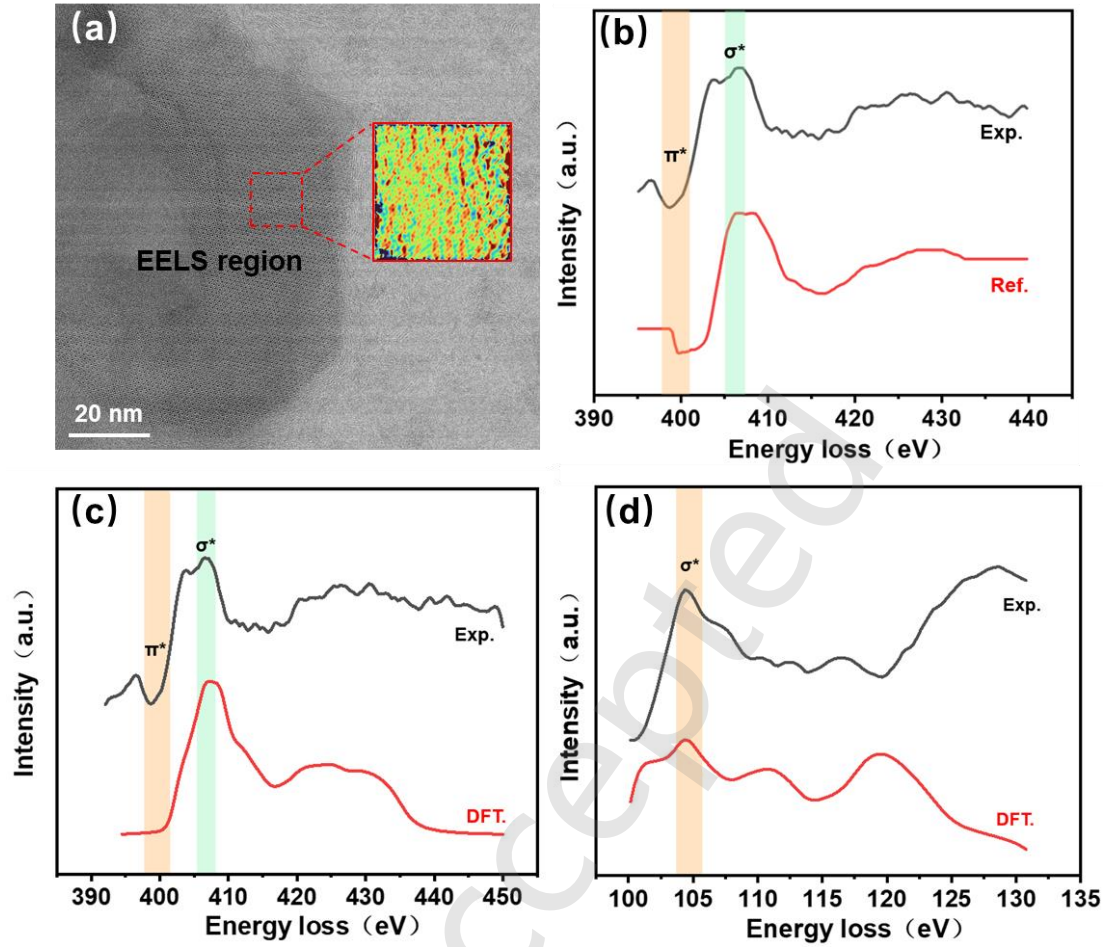


Fig. 5. EELS characterization of the interfacial β - Si_3N_4 nanolayer. (a) STEM image showing the region used for EELS analysis within the interfacial β - Si_3N_4 nanolayer; the scale bar is 20 nm. The red dashed box marks the region used for the geometric phase analysis (GPA), and the enlarged inset shows the corresponding GPA result. (b) Experimental N K -edge spectrum compared with the reported reference spectrum. (c) Experimental and calculated N K -edge ELNES. (d) Experimental and calculated Si $L_{2,3}$ -edge ELNES.

The bonding-related ELNES features in Fig. 5 can be further interpreted in light of the calculated electronic structure of β - Si_3N_4 . The total and projected densities of states in Fig. 6a show that the occupied states are separated into two principal energy

regions with distinct orbital characters. The deeper valence band, extending approximately from -18 to -13 eV, is dominated by N $2s$ states. The relatively narrow energy distribution and limited contribution from Si orbitals indicate that these states are comparatively localized around the N sites. A weak overlap with Si $3s$ and $3p$ states is nevertheless present, showing that even this deeper valence region is not completely atomic-like. The upper valence band, extending approximately from -10 eV to the valence-band maximum, is dominated by N $2p$ states, while Si $3s$ and Si $3p$ components occur over the same energy range. In particular, the coincident peak structures of N $2p$ and Si-derived states indicate that these orbitals are electronically coupled within the SiN_4 tetrahedral network. Because the valence-band states are occupied, this overlap is associated mainly with the bonding combinations formed between N $2p$ and Si $3s/3p$ orbitals. The predominance of N $2p$ character in this region also indicates that the occupied bonding states are weighted toward the N sublattice, consistent with the higher electronegativity of N and the polar character of the Si-N bond. Thus, the upper valence band represents a set of Si-N bonding states with stronger N-site projection. A pronounced depletion of the density of states around the Fermi level separates these occupied bonding states from the unoccupied conduction-band manifold. The conduction-band states beginning at approximately 4-5 eV are dominated by Si $3p$ orbitals, with additional Si $3s$ and weaker N $2p$ contributions. Compared with the upper valence band, the relative weight shifts markedly from N toward Si. This reversal in orbital character across the band gap is consistent with the separation between

predominantly N-weighted bonding states below the gap and predominantly Si-weighted antibonding states above it. The finite N $2p$ contribution in the conduction band, however, shows that the unoccupied states are not purely localized on Si. They remain hybridized across the Si-N framework, with the relative Si and N contributions varying among different conduction-band energies. This bonding–antibonding separation provides a more direct electronic basis for interpreting the N K -edge and Si $L_{2,3}$ -edge ELNES. The N K -edge arises primarily from transitions from the N $1s$ core level into the N $2p$ -projected components of the unoccupied Si-N states. Consequently, its principal near-edge resonances reflect how the N-centred p character is distributed within the conduction-band manifold. The Si $L_{2,3}$ -edge probes the dipole-allowed Si-centred components of the same unoccupied electronic framework. Although the two edges obey different core-level transition rules and emphasize different orbital projections, their principal features are linked because both originate from the unoccupied states generated by the same tetrahedrally coordinated Si-N network. The correspondence between the two edges therefore reflects complementary elemental projections of a common hybridized conduction-band structure. The charge-density-difference map on the (0001) plane in Fig. 6b provides the corresponding real-space description of this orbital interaction. Electron accumulation is concentrated predominantly around the N atoms, whereas electron depletion is observed around Si, directly indicating a net redistribution of valence charge from Si toward N. This transfer shifts the bonding electron density toward the N end of each Si-N linkage and accounts

for the polar contribution to the bond. At the same time, the redistributed charge is not confined to approximately spherical regions around the N atoms. Continuous and anisotropic charge redistribution is also visible in the regions connecting neighboring Si and N sites. This bond-directed feature indicates that the electronic interaction retains substantial orbital-overlap character and is consistent with polar-covalent bonding. The Si-N bonds in β -Si₃N₄ are more appropriately understood as polar covalent bonds, in which partial Si to N charge transfer coexists with directional electron sharing along the tetrahedral Si-N connections. The band structure in Fig. 6c is consistent with this picture. A wide band gap separates the occupied and unoccupied states, consistent with previous first-principles descriptions of Si₃N₄ as a wide-band-gap insulator [46]. The deeper N 2s-dominated bands show comparatively limited dispersion, consistent with their more localized nature. In contrast, the upper valence and conduction bands display stronger dispersion along the sampled crystallographic directions, reflecting the extended electronic coupling through the corner-sharing SiN₄ tetrahedral framework. Together with the PDOS, the band structure shows that the bonding and antibonding states are distributed throughout an extended three-dimensional Si-N network.

Overall, the calculated electronic structure reveals a clear redistribution of orbital character across the band gap. The occupied states near the valence-band maximum are predominantly N 2p-derived but contain substantial Si 3s/3p contributions, whereas the unoccupied states are mainly Si-derived while retaining finite N 2p character. This complementary distribution reflects the formation of hybridized Si-N bonding states

below the gap and corresponding antibonding states above it. The charge-density redistribution on the (0001) plane further shows that this hybridization is accompanied by partial electron transfer from Si to N and directional charge sharing along the Si-N bonds. These results provide the electronic-structure basis for the principal N *K*-edge and Si *L*_{2,3}-edge responses observed experimentally.

From a materials perspective, these bonding and electronic characteristics also provide a qualitative link to the established properties of β -Si₃N₄. The directional polar-covalent Si-N network revealed by the PDOS and charge-density redistribution is consistent with the strong and rigid tetrahedral framework underlying the mechanical robustness and thermal/chemical stability of silicon nitride. Meanwhile, the wide band gap obtained from the calculated band structure is consistent with its low electronic conductivity and insulating character, which are relevant to the dielectric applications of β -Si₃N₄. For the present C/SiC composite, the formation of such a nanolayer therefore introduces an interfacial region whose local bonding and electronic structures differ from those of the adjacent carbon and SiC phases. From a mechanical perspective, the β -Si₃N₄ nanolayer may also provide a transition in local interfacial stiffness. Representative Young's moduli reported for Si₃N₄ ceramics and sintered β -SiC are approximately 300-330 GPa [49] and 395 ± 10 GPa [50], respectively, while glassy carbon exhibits a substantially lower modulus of approximately 20-40 GPa [51]. These literature values suggest a possible intermediate-stiffness role for the β -Si₃N₄ nanolayer, potentially alleviating local mechanical mismatch and stress concentration at the C/SiC

interface. Together, these interfacial characteristics may influence interfacial stability as well as local mechanical, electrical, and dielectric responses.

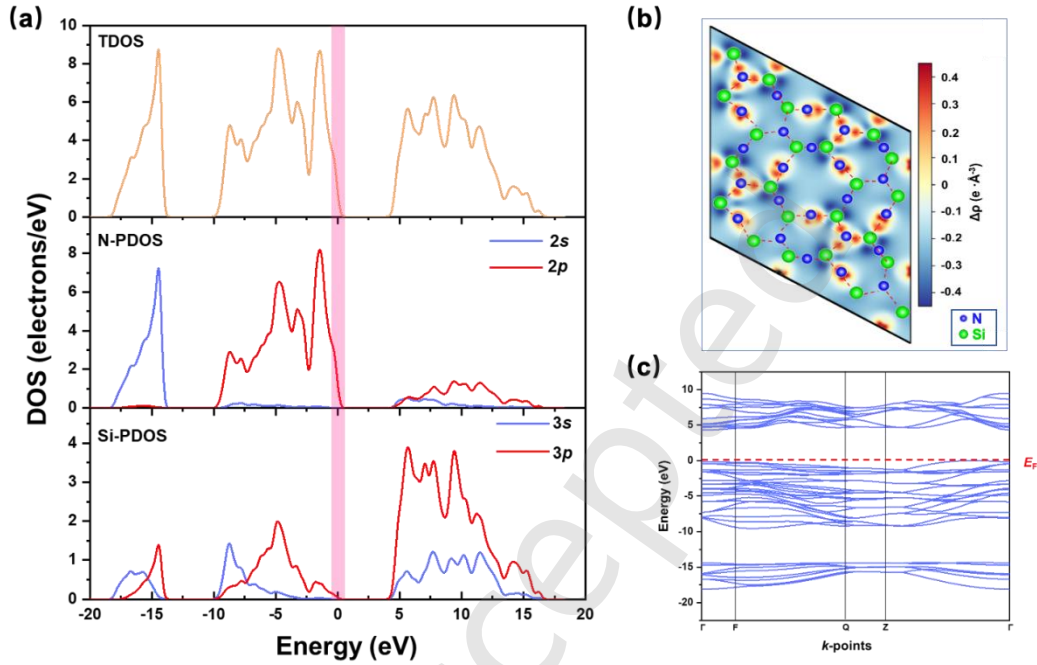


Fig. 6. Electronic-structure analysis of β - Si_3N_4 . (a) Total density of states (TDOS) and projected density of states (PDOS) of N and Si. (b) Two-dimensional charge density difference map of β - Si_3N_4 on the (0001) plane. (c) Electronic band structure of β - Si_3N_4 .

4 Conclusions

A continuous interfacial β - Si_3N_4 nanolayer was formed in situ between C and SiC in a C/SiC composite through reactive melt infiltration of Si into a nitrogen-containing, glucose-derived carbon framework. Within the examined interfacial region, the β - Si_3N_4 nanolayer exhibits micrometer-scale lateral continuity and a local thickness on the order of 20 nm, providing a resolvable crystalline region for site-specific atomic-scale structural and spectroscopic characterization. The interfacial β - Si_3N_4 nanolayer was

formed without intentional addition of conventional oxide sintering additives commonly used in liquid-phase sintering of Si_3N_4 . The combination of lateral continuity, nanoscale thickness, and a comparatively clean local environment makes this nanolayer directly accessible to site-specific atomic-scale structural and spectroscopic examination. This crystalline domain enables the atomic configuration of $\beta\text{-Si}_3\text{N}_4$ to be examined together with its bonding-related electronic response within the same local interfacial region. Atomic-resolution observations along multiple crystallographic directions resolved both the projected Si framework and the light-element N sublattice within the same domain. The experimentally observed atomic arrangements reproduce the characteristic ABAB stacking and projected connectivity of the corner-sharing SiN_4 tetrahedral network, thereby presenting the Si-N atomic configuration of $\beta\text{-Si}_3\text{N}_4$ in real space. On this structural basis, the principal N K -edge and Si $L_{2,3}$ -edge ELNES features were related to the N- and Si-projected components of the hybridized unoccupied states within the same tetrahedral framework. The calculated charge redistribution, characterized by electron accumulation around N, depletion near Si, and directional localization along the Si-N bonds, is consistent with the polar and covalent character of the bonding.

Together, the atomic-resolution structural observations and bonding-sensitive spectroscopic results provide a correlated description of the interfacial $\beta\text{-Si}_3\text{N}_4$ nanolayer, revealing the local Si-N coordination and associated electronic characteristics within the examined crystalline region.

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