

Regulating graphene growth behavior through surface chemical modification of SiC fibers

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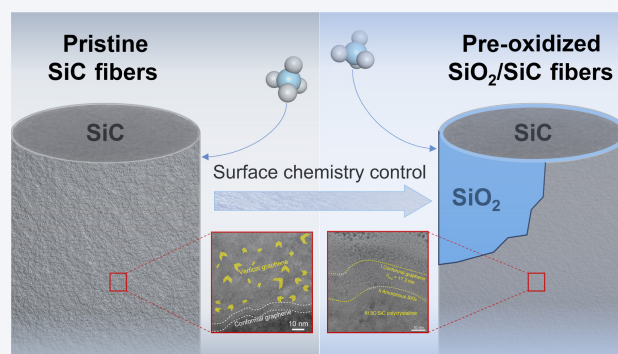
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ABSTRACT: The interphase in continuous SiC fiber-reinforced ceramic matrix composites is critical to their mechanical reliability, and graphene is a promising interphase material. However, the effect of substrate surface condition on graphene growth on SiC fibers remains unclear. Here, graphene grown by chemical vapor deposition on pristine SiC fibers and pre-oxidized SiO₂/SiC fibers is systematically compared. Experiments show that pristine SiC promotes early multi-point nucleation and an outward-propagating Stranski–Krastanov (SK)-like mode, whereas the pre-oxidized surface favors conformal layer-by-layer growth, leading to a smoother Frank–van der Merwe (FM)-like morphology. First-principles calculations reveal that SiC more strongly catalyzes carbon-source cracking and generates active carbon species, while SiO₂ is more favorable for carbon diffusion and conformal growth. In addition, graphene edges, steps, and curved regions tend to act as secondary nucleation sites, inducing disordered multilayer growth at later stages. These results provide guidance for tailoring graphene interphases on SiC fibers by surface pretreatment.

KEYWORDS: graphene, SiC fiber, chemical vapor deposition (CVD), surface chemical modification, density functional theory (DFT)



1 Introduction

Continuous silicon carbide fiber-reinforced silicon carbide matrix composites (SiCf/SiC) have emerged as an advanced material system that integrates structural load-bearing capability with multifunctional characteristics, owing to their exceptional high-temperature strength [1–3], low density [4, 5], and favorable thermal stability [6]. From a structural perspective, the incorporation of continuous SiC fibers significantly enhances the

load-bearing capacity, fracture toughness, damage tolerance, and fatigue resistance of the composites through synergistic fiber–matrix interactions [7, 8]. From a functional perspective, the SiC matrix itself possesses high thermal conductivity [9, 10], excellent oxidation resistance [6, 11, 12], and low neutron absorption cross-section [13, 14], making this material system highly attractive for applications involving thermal management, oxidation protection, and nuclear irradiation environments. In addition, through rational fiber orientation, textile design, and interface engineering, the electromagnetic properties of SiCf/SiC can also be tailored, further demonstrating their potential for structural–functional integration in applications such as thermal protection and electromagnetic shielding [2, 7, 15]. Owing to this unique combination of mechanical, thermal, and functional advantages, SiCf/SiC composites have been widely considered for cutting-edge technological applications, including hot-section

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components in next-generation aero-engines and advanced nuclear energy systems [6].

In SiCf/SiC composites, the interface between the fiber and the matrix is a critical determinant of their mechanical performance, particularly fracture toughness and fatigue resistance [16, 17]. The interface enables efficient load transfer from the matrix to the fibers while also governing the overall fracture behavior by controlling crack initiation, crack propagation path, and energy dissipation mechanisms [18–20]. The interphase must not only balance load transfer with toughness but also be controllable and stable under complex service conditions such as high temperatures and cyclic loading [21, 22]. Therefore, achieving precise interface design and reproducible fabrication constitutes a core challenge in enhancing the reliability and engineering applicability of SiCf/SiC composites.

Against this backdrop, two-dimensional materials, particularly graphene, have garnered significant attention as highly functional interfacial layers due to their high specific strength [23, 24], excellent thermal conductivity [25, 26], and tunable interfacial adhesion. As an interfacial modifier, graphene can provide moderate interfacial adhesion to facilitate interfacial sliding and fiber pullout, thereby enhancing fracture toughness [27–30]. Furthermore, its number of layers, orientation, or chemical functionalization can be tailored to modulate interfacial adhesion and thermal and electrical transport properties, simultaneously addressing both mechanical and functional requirements. Currently, direct chemical vapor deposition (CVD) growth of graphene on SiC fibers surfaces via CVD represents one of the most widely investigated routes, offering relatively simple process and enabling intimate contact between graphene and the fiber substrate [31–34]. However, this growth process is strongly influenced by the surface state of the SiC substrate (e.g., crystallographic orientation and surface termination), which subsequently influences the quality of the as-grown graphene and the resulting graphene–fiber interfacial performance [35].

To overcome the challenges associated with direct graphene growth and to further enhance the tunability of graphene as an interface material, researchers have recently adopted an intermediate-layer strategy. An example of this strategy involves forming a dense oxide layer (SiO_2) onto the SiC fibers surface [36, 37]. This oxide layer can modify the substrate surface energy and catalytic activity. As a result, it regulates the decomposition of carbon precursors and promotes surface diffusion of active carbon atoms, thereby improving the quality of the as-grown graphene. Moreover, it can act as a diffusion barrier during high-temperature growth [38, 39], protecting the SiC fibers from excessive etching or thermal damage. This provides a viable pathway for obtaining graphene interphases with desirable morphologies and structures under milder conditions.

Although these two approaches exhibit distinct features, current research has largely focused on process optimization for single methods. A lack of comparative studies has hindered a fundamental understanding of how the surface chemical state influences the graphene growth mode. Specifically, the surface chemistry of the substrate (e.g., surface energy and catalytic activity) may dictate the growth mechanism and interfacial morphology of graphene [40, 41]. However, existing studies often overlook the profound impact of differences in surface properties on the growth mode [42]. Consequently, a systematic comparison of the graphene growth process, resulting microstructure, and interfacial characteristics on different surfaces remains an open question.

This study aims to address this gap by conducting a comparative study of graphene growth via chemical vapor deposition on pristine SiC fibers and SiC fibers with a pre-oxidized SiO_2 layer. The growth parameter space, resultant graphene morphologies, microstructures, and interfacial characteristics on the two substrates are systematically compared. Based on these comparisons and supported by theoretical calculations, we propose and validate the strategy of pre-oxidizing the SiC fiber surface to form a SiO_2 layer prior to growth. This approach enables the tuning of surface chemistry and the diffusion behavior of active carbon atoms to achieve a more continuous and controllable graphene layer. This strategy provides a robust scientific foundation for the rational design and controlled fabrication of interphases in high-performance SiCf/SiC composites. It also offers direct process guidance for optimizing the mechanical performance of these composites and has significant implications for interface engineering in high-temperature structural materials and nuclear energy applications.

2 Experimental details and simulation methods

The third-generation SiC fibers used for graphene growth were first subjected to a solvent-based desizing treatment at room temperature to remove the surface organic sizing and obtain clean and well-dispersed fiber substrates. Subsequently, graphene was grown on the desized SiC fibers in a quartz-tube CVD furnace under atmospheric pressure. For the direct-growth route, the chamber was heated to 1100 °C at a rate of 10 °C/min under an Ar atmosphere. After the target temperature was reached, a gas mixture of CH_4 , H_2 , and Ar with a flow ratio of 1:10:10 was introduced into the chamber, and growth was maintained isothermally for 5 h, followed by natural cooling under Ar protection. For the pre-oxidized route, the desized SiC fibers were first oxidized at 800 °C for 2 h to form a surface SiO_2 layer, and were then heated to 1100 °C for graphene growth under the same gas composition and atmospheric-pressure conditions. After growth, the furnace was allowed to cool naturally to room temperature under Ar flow, and the resulting samples were collected for subsequent characterization. Based on the optimized growth parameters, graphene-coated SiC fibers with different graphene thicknesses were further prepared by varying the growth duration.

The surface morphology of the samples was characterized by scanning electron microscopy (SEM, FEI Quattro S, operating at 10 kV). The surface roughness and topography were further analyzed by atomic force microscopy (AFM, Bruker Dimension Icon with ScanAsyst mode). Cross-sectional microstructures, lattice orientation, and elemental distribution were investigated by transmission electron microscopy (TEM, JEM 2100 F), high-resolution TEM (HRTEM), inverse fast Fourier transform (IFFT), and energy-dispersive X-ray spectroscopy (EDS, JEM 2100 F). These techniques were used to analyze the growth morphology, layered structure, and interfacial characteristics of graphene on SiC fibers.

All first-principles calculations were carried out within the framework of density functional theory (DFT) using the Vienna *ab initio* simulation package (VASP) [43]. The interaction between ions and electrons was described by the projector augmented-wave (PAW) method, while the exchange-correlation energy was treated using the Perdew–Burke–Ernzerhof (PBE) functional within the

generalized gradient approximation (GGA). A plane-wave cutoff energy of 400 eV was adopted for all calculations. During structural relaxation and charge-density calculations, the electronic self-consistent convergence criterion was set to 1×10^{-4} eV, and the force threshold on each atom was converged to 0.01 eV/Å. Brillouin-zone sampling was performed using a $1 \times 1 \times 1$ Γ -centered k -point mesh. Transition states along the reaction pathways were determined using the climbing-image nudged elastic band (CI-NEB) method.

3 Results and discussion

During the CVD process, the substrate material and its surface state exert a decisive influence on the nucleation density, growth rate, and final morphology of graphene. To ensure the controllability and reproducibility of the growth process, appropriate pretreatment of the SiC fibers is particularly critical. Commercial SiC fibers are typically coated with an organic sizing to enhance processability and tow integrity. This sizing can pyrolyze during subsequent high-temperature growth, leaving behind carbonaceous species that severely interfere with graphene growth. To eliminate this interference, all SiC fibers were first subjected to a solvent-based desizing treatment at room temperature. This process yielded substrates with well-dispersed individual filaments, clean surfaces, and uniform chemical states, laying the foundation for subsequent controlled graphene growth.

To systematically investigate the influence of different surfaces on the growth morphology, a comparison was made between graphene grown on SiC fibers subjected only to desizing treatment (pristine SiC fibers) and those that were subsequently pre-oxidized

to form a SiO₂ layer (pre-oxidized SiO₂/SiC fibers). The specific growth processes and corresponding characterizations are illustrated in Fig. 1. For pristine SiC fibers (direct growth route, Fig. 1(a)), the temperature was ramped to 1100 °C at 10 °C/min in an Ar atmosphere. Subsequently, a gas mixture of CH₄:H₂:Ar = 1:10:10 was introduced, and growth was conducted isothermally for 5 h, followed by natural cooling. SEM images (Fig. 1(b)) revealed that the fiber surface became significantly rougher after growth, with AFM (Fig. 1(c)) measuring an average surface roughness (R_a) of 19.61 nm. In contrast, fibers were first oxidized at 800 °C for 2 h to form a SiO₂ layer. The pre-oxidized surface with reduced roughness (Fig. S1 in the Electronic Supplementary Material (ESM)) is expected to facilitate the surface migration of active carbon species and promote more conformal graphene growth. The fibers were then heated to 1100 °C for growth under the same gas composition (Fig. 1(d)). SEM images of the resulting samples (Fig. 1(e)) showed a markedly smoother surface, and AFM (Fig. 1(f)) yielded an R_a value of 4.50 nm. These quantitative results demonstrate that the pre-oxidized SiO₂ layer significantly reduces the surface roughness after graphene growth and enables a more uniform surface morphology within a shorter growth time. This indicates that the pre-oxidized SiO₂ layer is beneficial for obtaining a smoother graphene layer.

To gain a deeper understanding of the growth mechanism of graphene on different substrate surface states, a detailed structural and morphological characterization was performed on graphene grown directly on pristine SiC fibers and on pre-oxidized SiO₂/SiC fibers. Figure 2(a) presents a low-magnification transmission electron microscopy (TEM) image, revealing that the substrate surface is covered by vertically oriented graphene with a flake-like

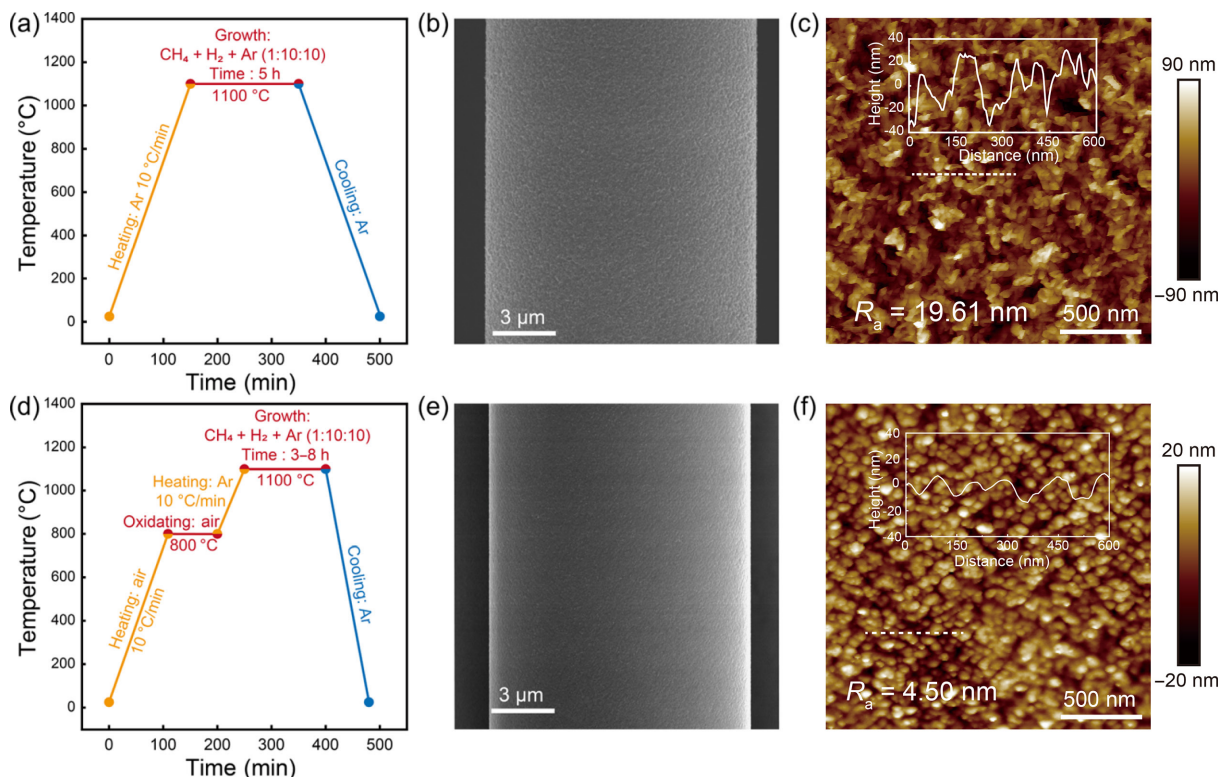


Figure 1 Graphene growth on SiC fibers and corresponding characterization results. (a) Parameters for direct graphene growth on the pristine SiC fibers using CH₄ as the carbon source. (b) SEM image of graphene grown directly on pristine SiC fibers. (c) AFM image of graphene grown directly on pristine SiC fibers. (d) Parameters for graphene growth on pre-oxidized SiO₂/SiC fibers. (e) SEM image of graphene grown on the pre-oxidized SiO₂/SiC fibers. (f) AFM image of the fiber surface after graphene growth on pre-oxidized SiO₂/SiC fibers.

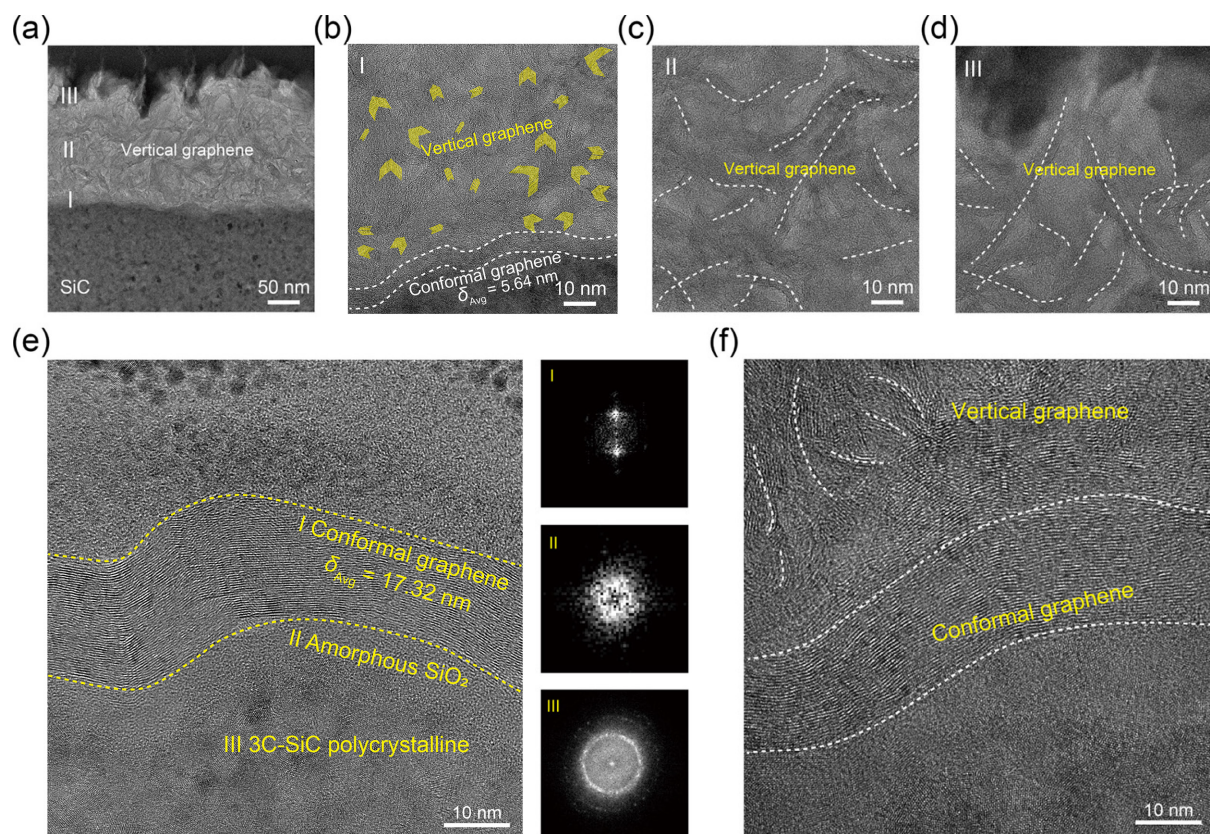


Figure 2 (a) TEM image of graphene grown directly on pristine SiC fibers. (b)–(d)) Enlarged views of regions I–III marked in (a), respectively. (e) TEM image at the early growth stage on pre-oxidized SiO₂/SiC fibers, showing initial conformal layered growth. (f) TEM image at the later growth stage, where wrinkling and corrugation appear as the graphene thickness increases.

morphology. Localized magnified observations of regions I–III, marked in Fig. 2(a), are shown in Figs. 2(b)–2(d). A layered structure with an average thickness of ~ 5.64 nm can be clearly observed near the substrate (region I, Fig. 2(b)). Inverse fast Fourier transform (IFFT) analysis of this region (Fig. S2(a) in the ESM) yielded an average interplanar spacing of 0.351 nm, which is consistent with the interlayer spacing of graphene, confirming that this layered structure is indeed graphene. However, in the region above this layer and further away from the substrate (regions II and III, Figs. 2(c) and 2(d)), the layered characteristics diminish and disappear, with only scattered and irregular vertical structures visible. A bright-field TEM image (Fig. S3(a) in the ESM) serves as a morphological reference, and the corresponding EDS elemental mapping for C and Si (Figs. S3(b)–S3(d) in the ESM) shows significant carbon enrichment in the flake-like structures, while the Si signal remains confined to the substrate region. This provides direct evidence linking the elemental distribution to the spatial characteristics of the layered and vertical structures.

In contrast, the morphological evolution of graphene grown on pre-oxidized SiO₂/SiC fibers differed significantly from that of direct growth on pristine SiC fibers. HRTEM images of samples grown for 0.5 and 2 h (Fig. S4 in the ESM) show that no obvious multilayer graphene domains or vertical graphene structures are observed during the early growth stage before complete surface coverage, suggesting a conformal and layer-by-layer growth tendency on the pre-oxidized surface. Figure 2(e) shows an HRTEM image at an early growth stage (3 h), revealing a continuous layered structure with a uniform thickness of approximately 17.32 nm covering the surface. No evident vertical

graphene nanosheets were observed at this stage. With increasing growth time, scattered and irregular vertical structures began to appear above the layered structure (Fig. 2(f)). IFFT analysis of the layered region measured an average interlayer spacing of 0.348 nm, similar to 0.351 nm obtained for direct growth, further supporting the identification of the observed layered structures as graphene [44, 45]. Bright-field TEM images and corresponding EDS elemental maps (Figs. S3(e)–S3(h) in the ESM) show oxygen enrichment in the surface SiO₂ layer formed by pre-oxidation and significant carbon enrichment in both the layered and vertical structures, while silicon remains confined to the fiber interior. This elemental spatial distribution clearly verifies the correspondence between the surface pre-oxidized SiO₂ layer and the subsequent graphene overcoat.

To further elucidate the microscopic mechanisms by which different substrate surfaces influence graphene growth behavior at the atomic scale, systematic DFT calculations were performed in this study. The calculations focused on the key steps of graphene growth, using representative SiC(110) and SiO₂(001) surfaces to comparatively investigate the decomposition kinetics of CH₄, the adsorption and residence behavior of decomposition products, the distribution of active carbon species on the surfaces, as well as key parameters such as substrate surface energy and carbon atom migration barriers. This enables establishing correlations between microscopic energy parameters and macroscopic growth modes from both thermodynamic and kinetic perspectives. First, as shown in Fig. 3(a), the adsorption behavior of CH₄ and its decomposition products on the two surfaces was compared. The results indicate that CH₄ exhibits low adsorption energy and short adsorption

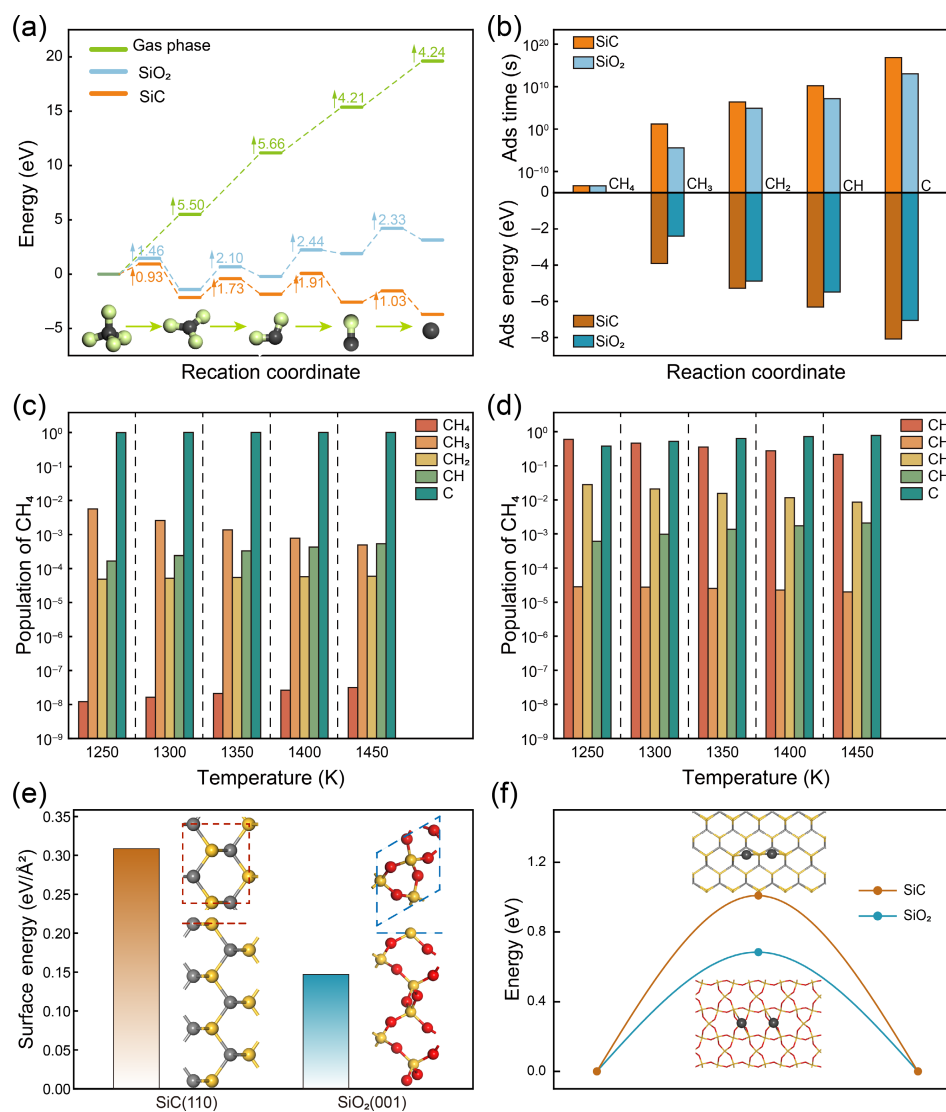


Figure 3 (a) CH₄ decomposition barriers on the SiC surface, the SiO₂ surface, and in the gas phase. (b) Adsorption energies and lifetimes of CH₄ and its reactive carbon species on the SiC and SiO₂ surfaces (Ads = adsorption). (c) Relative distribution of reactive carbon species on the SiC surface. (d) Relative distribution of reactive carbon species on the SiO₂ surface. (e) Surface energies of common exposed surfaces, including SiC(110) and SiO₂(001). (f) Migration barriers of carbon atoms on SiC and SiO₂ surfaces.

lifetime on both surfaces, making stable adsorption difficult. In contrast, its decomposition products demonstrate stronger adsorption strength and longer adsorption lifetime, enabling their participation in subsequent growth reactions. Comparative analysis reveals that both the adsorption energy and adsorption lifetime of CH₄ and its decomposition products are generally higher on the SiC surface than on the SiO₂ surface, indicating that SiC possesses a stronger adsorption strength for carbon species. Adsorption behavior on other common exposed surfaces shows the same trend, with relevant results presented in Fig. S5 in the ESM. Analysis of the CH₄ decomposition pathways (Fig. 3(b)) shows that the decomposition barrier in the gas phase is the highest (rate-determining step up to 5.66 eV), while the barriers required for this process are significantly reduced on both solid surfaces, confirming that both substrates exhibit catalytic effects on CH₄ decomposition. Notably, the decomposition barrier on the SiC surface is the lowest (rate-determining step of 1.91 eV), whereas the corresponding barrier on the SiO₂ surface is higher (2.44 eV), indicating that the SiC surface possesses a stronger ability to promote CH₄

decomposition. Analysis of the distribution of carbon species on the surfaces at different temperatures (Figs. 3(c) and 3(d)) further reveals that active C atoms dominate on the SiC surface across all temperatures, whereas on the SiO₂ surface, the predominant carbon species shifts from CH₄ to C atoms with increasing temperature. This result similarly confirms that the SiC surface exhibits stronger catalytic activity for the further decomposition of carbon precursors. Furthermore, surface property calculations (Fig. 3(e)) show that the surface energy of SiO₂(001) (0.17 eV) is lower than that of SiC(110) (0.32 eV), indicating that the oxide surface is more stable. Calculation results on other common surfaces are consistent with this trend (Fig. S6 in the ESM). Meanwhile, the migration barrier for carbon atoms on the SiO₂ surface (0.68 eV, Fig. 3(f)) is significantly lower than that on the SiC surface, demonstrating that carbon atoms exhibit higher surface diffusion mobility on the pre-oxidized SiO₂ layer.

Based on the above calculation results, systematic correlations can be established between theoretical parameters and experimental observations. For the SiC surface, its lower CH₄ decomposition

barrier and higher concentration of reactive carbon species facilitate the rapid formation of localized carbon-rich regions near the substrate, thereby triggering fast and multi-site nucleation and vertical stacking [46]. This mechanism directly corroborates the phenomena observed in Fig. 2: Only a thin graphene layer forms in the vicinity of the substrate, while a large number of irregular vertical graphene nanosheets cover the region above. It also accounts for the higher R_a observed in Fig. 1. Together, these features indicate rapid nucleation and a pronounced tendency toward three-dimensional growth at the early stage. In contrast, for the SiO_2 surface, the higher structural stability of the pre-oxidized SiO_2 layer and the lower migration barrier for carbon atoms favor long-range surface diffusion of carbon species, thereby promoting a more ordered two-dimensional lateral growth. This is in excellent agreement with the uniform layered structure observed in Fig. 2(f).

The aforementioned DFT results explain, from an energetic standpoint, the reasons for the different growth modes on SiC and SiO_2 surfaces. However, in practical CVD growth, the nucleation and evolution of graphene often originate at heterogeneous nucleation sites such as edges, steps, and locally exposed substrate

regions. To delve deeper into the influence of these local structures on growth, this study further investigated the adsorption stability of carbon atoms at different local sites based on single-atom adsorption analysis, aiming to reveal the microscopic growth preferences and evolutionary trends. First, to simulate the realistic interface at the initial growth stage, we constructed models of SiC and SiO_2 substrates partially covered by graphene (Figs. 4(a) and 4(b)). These models comprise exposed substrate, graphene-covered regions, and well-defined graphene edges. For each system, five representative types of adsorption sites were selected for calculation: (1) far from the edge on graphene, (2) near the edge on graphene, (3) at the graphene edge, (4) on the exposed substrate near the edge, and (5) on the exposed substrate far from the edge. The calculated adsorption energies reveal that graphene edge regions (site (3)) and exposed substrate areas (sites (4) and (5)) possess relatively high stability and show stronger adsorption capacity toward carbon atoms. To examine the generality of this behavior, additional calculations were performed on substrates fully covered by either one or two graphene layers with locally introduced edges (Fig. S7 in the ESM). Regardless of substrate type or graphene thickness, edge

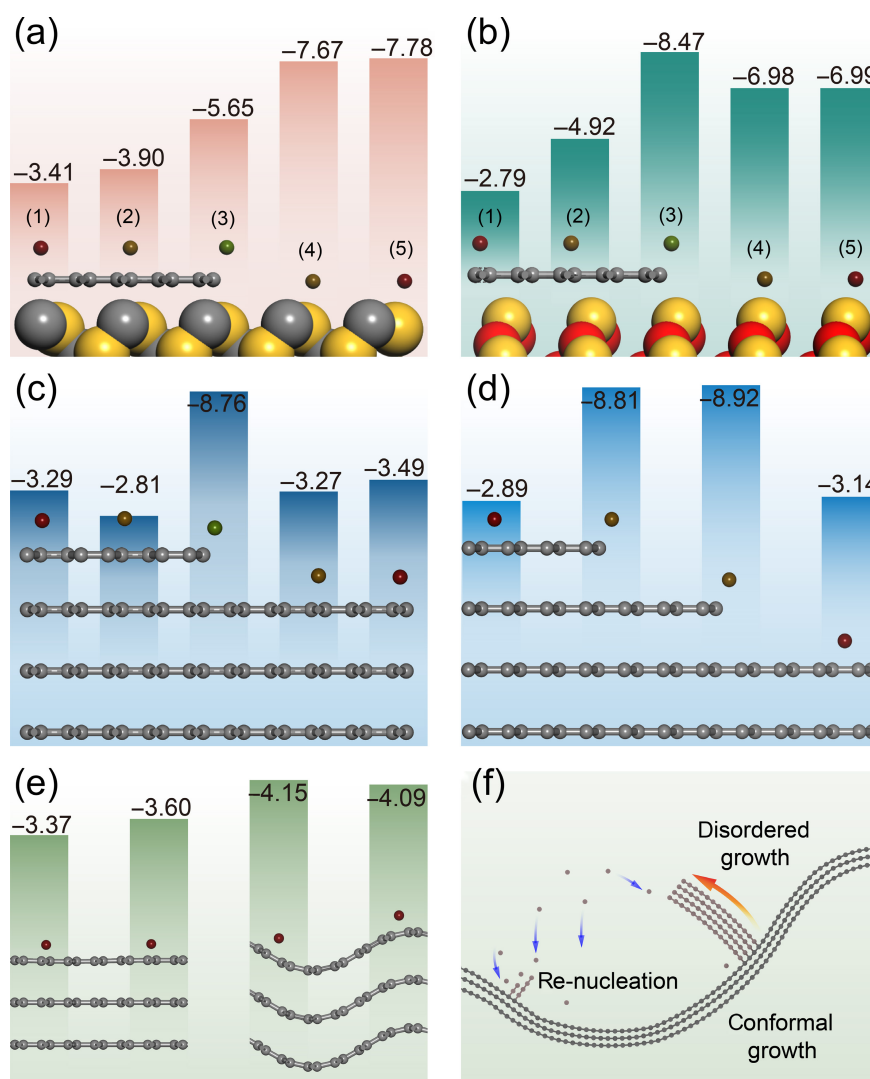


Figure 4 ((a) and (b)) Adsorption energies of carbon atoms at different sites in partially graphene-covered models on pristine SiC and pre-oxidized SiO_2 substrates. (c) Adsorption behavior on multilayer graphene and partially covered structures under substrate-free conditions. (d) Adsorption energies of carbon atoms at edges at different layers in a multilayer graphene step structure. (e) Adsorption energies of carbon atoms on flat and curved graphene surfaces. (f) Schematic illustration of secondary nucleation induced by curved regions and edges, leading to disordered growth.

sites consistently exhibit significantly higher adsorption stability than flat surfaces, while differences among non-edge sites remain minor. This confirms the structural robustness of edge-dominated carbon capture behavior.

To decouple substrate effects and simulate later growth stages involving graphene thickening, adsorption on multilayer graphene and partially covered structures atop it was investigated under substrate-free conditions (Fig. 4(c)). Even in purely graphene systems, edge sites retain much stronger adsorption stability than flat regions, indicating that edge-dominated growth is an intrinsic energetic property of graphene. Step structures with different layer widths were further constructed (Fig. 4(d)) to model interlayer edges during multilayer growth. Graphene edges at all levels exhibit significantly enhanced adsorption stability, whereas intact graphene basal planes, even near edges, exhibit relatively weak adsorption. This suggests that graphene growth preferentially propagates along existing edges or step sites rather than nucleating randomly on flat terraces. Additionally, local curvature was found to significantly affect adsorption behavior. As shown in Fig. 4(e), curved graphene surfaces exhibit markedly enhanced adsorption energy compared to flat regions. This implies that curvature induced by layer thickening or stress may create new active sites, promoting secondary nucleation.

Based on these findings, a growth evolution model is proposed (Fig. 4(f)): Carbon atoms preferentially adsorb at curved regions, triggering secondary nucleation and leading to multilayer and multidirectional growth. This mechanism satisfactorily explains the experimentally observed evolution of vertical or disordered graphene clusters above the initial layered structure. More importantly, it reveals a gradual shift in the growth mechanism, from substrate effects to being dominated by graphene's intrinsic geometric and structural characteristics during the later stages.

By integrating the experimental characterization results with

DFT calculations, a unified understanding of the graphene growth modes on the two substrate surfaces can be established. On the pristine SiC surface, CH_4 decomposes more readily, continuously generating active C atoms. Concurrently, the decomposition products exhibit strong adsorption, but the high migration barrier for carbon atoms restricts surface diffusion. This characteristic of “high supply, low diffusion” leads to the rapid local accumulation of carbon species, inducing multi-site nucleation. Although a limited conformal layer forms during the initial growth stage, continued supply of the carbon source favors secondary nucleation atop the existing structures, which subsequently grow outward, ultimately evolving into vertical graphene nanosheets. This evolutionary pathway closely resembles a typical Stranski–Krastanov (SK)-like growth mode (Fig. 5(a)).

In contrast, on the surface with a pre-oxidized SiO_2 layer, the CH_4 decomposition is less favorable, resulting in a lower generation rate of reactive carbon species. However, the migration barrier for carbon atoms is significantly reduced, enhancing their surface diffusion mobility. Under this “low-supply/high-diffusion” regime, carbon species tend to migrate along the surface and incorporate into existing nuclei/layers, preferentially forming a continuous and uniform layered structure at early stages and achieving layer-by-layer lateral growth. As growth proceeds and the surface becomes progressively covered by graphene, new nucleation sites may still emerge in local regions due to edge effects, defects, or curvature, subsequently inducing the formation of a limited number of vertical graphene nanosheets. This morphological evolution can be classified as a Frank–van der Merwe (FM) growth mode, i.e., layer-by-layer conformal growth (Fig. 5(b)).

In summary, the intrinsic differences between the two substrate surfaces in terms of catalytic activity for carbon source decomposition, adsorption behavior, and carbon atom diffusion collectively dictate the divergent pathways from initial nucleation to

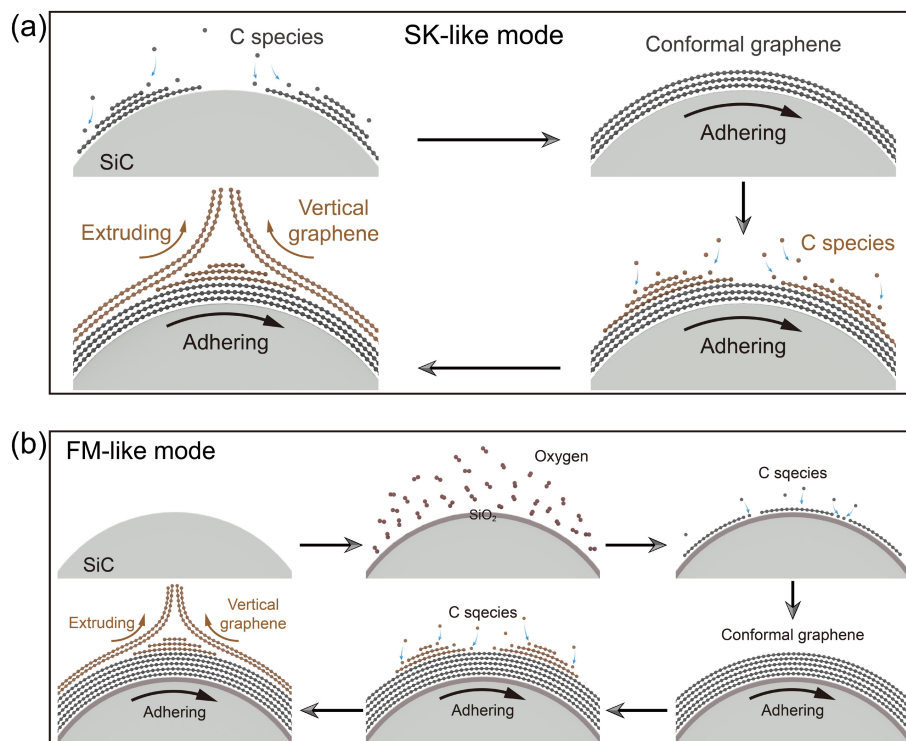


Figure 5 (a) Schematic illustration of the SK-like growth mode of graphene directly grown on pristine SiC fibers. (b) Schematic illustration of the FM-like growth mode of graphene grown on SiC fibers with a pre-oxidized SiO_2 layer.

final morphological evolution of graphene. This study demonstrates that by tailoring the surface chemical state of the substrate, the growth pathway and final morphology of graphene can be effectively modulated, providing important theoretical insights and design principles for the controlled fabrication of interfacial structures in composite materials.

4 Conclusions

A systematic investigation was conducted into the morphological differences and underlying mechanisms of graphene grown via CVD on pristine SiC fibers and on SiC fibers with a pre-oxidized SiO₂ layer through a combination of experiments and first-principles calculations. During direct growth on pristine SiC, only a thin conformal layer (average thickness of ~ 5.64 nm) formed near the substrate, accompanied by a rough surface and a high density of irregular vertical graphene nanosheets ($R_a \approx 19.61$ nm), consistent with an SK-like growth mode. In contrast, on the pre-oxidized SiO₂ layer, a thicker and more continuous conformal graphene layer (~ 17.32 nm) was obtained during the early growth stage, resulting in a macroscopically smoother surface ($R_a \approx 4.50$ nm) and displaying a tendency toward FM-like layer-by-layer conformal growth. The interlayer spacing measured by IFFT (~ 0.35 nm) further confirmed that the observed layered structures were graphene.

First-principles calculations provided the thermodynamic and kinetic basis for the observed differences in graphene growth behavior. The decomposition barrier for CH₄ is the highest in the gas phase, whereas it is significantly reduced on solid surfaces due to their catalytic effects. The SiC surface exhibits superior catalytic activity for CH₄ decomposition compared to SiO₂, leading to a higher propensity for generating active C atoms and promoting the formation of localized carbon-rich regions and multi-site nucleation. In contrast, the SiO₂ surface displays lower surface energy and a smaller migration barrier for C atoms, facilitating surface diffusion and ordered layer-by-layer lateral growth. Site-specific adsorption calculations further indicated that graphene edges, steps, and curved regions act as preferential trapping sites for carbon atoms, thereby promoting secondary nucleation and triggering disordered and multilayer growth at later stages.

In summary, introducing a pre-oxidized SiO₂ layer on SiC fibers promotes a more continuous and smoother conformal graphene layer by reducing the local carbon-source decomposition rate and enhancing the surface diffusion of carbon atoms, a strategy with direct processing relevance and engineering significance for interface design. It should be noted, however, that edges, steps, and curved regions can still induce local secondary nucleation and disordered growth at later stages. Therefore, further suppression of later-stage secondary nucleation by tuning adsorption strength, carbon flux, or introducing additional surface modification strategies may enable more precise control over the interfacial morphology of graphene on fibers.

Electronic Supplementary Material: Supplementary material (further computational, structural, and experimental details) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908906>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary

Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work. Author Zhongfan Liu is the advisory board member of this journal, but he is not involved in the peer-review or decision of this article.

Author contribution statement

Z. Y. J.: Investigation, data curation, methodology, formal analysis, visualization, writing – original draft. W. H. W.: Investigation, formal analysis, visualization, experimental design, writing – review & editing. J. J. S.: Writing – review & editing. C. J. Y.: Writing – review & editing. J. Q. W.: Writing – review & editing. M. C.: Writing – review & editing. Y. Q. S.: Funding acquisition, writing – review & editing. X. L. S.: Investigation, conceptualization, methodology, writing – review & editing. Z. F. L.: Funding acquisition, investigation, conceptualization, methodology, writing – review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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