

Stepwise growth of graphene on silicon carbide: Decoupling formation buffer layer from graphene growth

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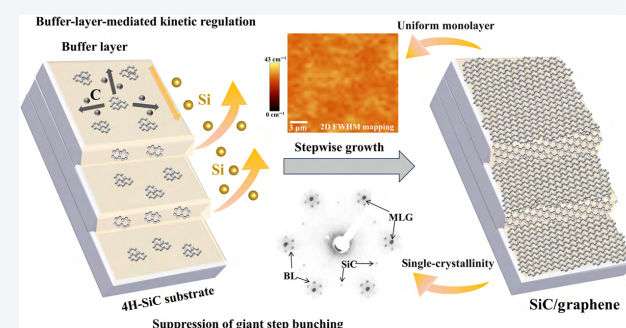
 Cite this article: Nano Research, 2026, 19, 94908882. <https://doi.org/10.26599/NR.2026.94908882>

ABSTRACT: Epitaxial growth of graphene on silicon carbide (SiC) offers a promising route to high-quality and wafer-scale graphene directly on a wide bandgap semiconductor, eliminating transfer-induced contamination. Conventional growth, however, relies on extremely high temperatures that often provoke severe step bunching on the SiC surface, impairing graphene uniformity and device performance. To overcome this limitation, we present a stepwise growth strategy that exploits buffer-mediated kinetic control, with first-principles calculations confirming its thermodynamic feasibility. The process employs a carefully controlled two-stage temperature program. First, a continuous buffer layer is formed on SiC(0001) at a relatively low temperature. This layer acts as a diffusion barrier, confining sublimated Si atoms to step edges and suppressing terrace-scale atomic migration, thereby inhibiting giant step bunching and stabilizing the surface morphology. In the second stage, raising the temperature drives graphene growth. The pre-formed buffer layer serves as a carbon reservoir, delivering a uniform supply of precursors across terraces and enabling dual-site nucleation at both steps and terraces. This promotes rapid lateral expansion of monolayer graphene while further suppressing step bunching. Compared with conventional high-temperature direct growth, this stepwise approach substantially reduces giant step bunching, disrupts the step-edge-dominated nucleation paradigm, and yields more controllable nucleation alongside a stabilized surface morphology. As a result, large-area, uniform, and high-quality monolayer single-crystal graphene can be reliably obtained.

KEYWORDS: graphene, silicon carbide (SiC), buffer layer, step bunching, stepwise growth, nucleation

1 Introduction

Supported by continued progress in wafer-scale crystal growth and cost reduction, wide-bandgap semiconductor silicon carbide (SiC) [1–3] has increasingly attracted attention as a material platform for



next-generation electronic systems. It provides a unique foundation for integrating low-dimensional materials with conventional semiconductor technologies. Beyond its established role in power and high-frequency electronics [4, 5], the combination of high thermal conductivity [6, 7], chemical stability [8], and optical transparency [9] has positioned SiC as an enabling substrate for advanced electronic and optoelectronic applications [10], driven in particular by the rapid emergence of optical and augmented-reality (AR) technologies [11, 12]. Graphene, as a two-dimensional (2D) atomic crystal, exhibits high carrier mobility [13] and optical transparency [14] together with exceptionally high in-plane thermal transport [15]. Direct epitaxial growth of graphene on SiC forms an integrated material system that naturally couple graphene's intrinsic

Received: March 25, 2026; Revised: May 16, 2026

Accepted: May 26, 2026

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properties with the thermal stability, scalability, and optical functionality of the SiC substrate, creating opportunities to simultaneously address heat dissipation, electronic performance, and optical integration.

Epitaxial growth of graphene on SiC(0001) offers a promising route toward the direct fabrication of wafer-scale, large-area, and high-quality single-crystalline monolayer films with uniform and controllable thickness. This approach avoids the introduction of defects, such as contamination, damage, and wrinkles, that are commonly associated with transfer processes [16–18]. Moreover, the SiC substrate is intrinsically compatible with established semiconductor technology, thereby enabling seamless integration into device fabrication and supporting the development of structurally integrated functionalities. In a typical epitaxial growth, high-temperature annealing drives preferential silicon sublimation from the SiC surface, with the excess carbon reconstructing into graphene [19, 20]. Graphene grown on the SiC(0001) exhibits superior layer-number controllability compared to that on the SiC(000 $\bar{1}$) [21]. Moreover, a reconstructed carbon layer (buffer layer) preferentially forms on SiC(0001), in which approximately one-third of the C atoms are covalently bonded to the Si atoms of the SiC [22, 23]. The strong covalent bonding at this epitaxial interface, in contrast to the weak van der Waals interactions in mechanically stacked heterostructures, significantly promotes phonon transport across the interface. As a result, interfacial thermal resistance is markedly reduced, enhancing the efficiency of heat dissipation from the graphene layer into the SiC substrate.

However, the elevated growth temperature inevitably leads to pronounced surface migration of both carbon and silicon atoms, resulting in the formation of irregular step bunching [24, 25]. Particularly on SiC substrates with an miscut angle exceeding 0.2°, step bunching leads to macro steps with heights reaching several tens of nanometers. These morphological irregularities severely degrade the continuity and uniformity of the graphene film, making it challenging to achieve wafer-scale and atomically flat monolayer graphene. Moreover, such pronounced step bunching contributes to localized increases in electrical resistance and induces anisotropic electronic transport along versus across the step edges [26]. It also elevates the interfacial thermal resistance, which impedes efficient vertical heat dissipation and promotes localized hot spots, thereby compromising the long-term reliability and operational lifetime of electronic devices [27].

To address these growth-related challenges, recent experimental and theoretical studies have increasingly focused on the growth mechanism of epitaxial graphene on the SiC(0001). Han et al. proposed a thermal shock annealing method based on the Joule heating mechanism, which enables kinetically regulated epitaxy of graphene on SiC at high temperatures within an ultra-short duration. This approach effectively suppresses the step bunching commonly encountered in conventional annealing and achieves a surface roughness of 0.956 nm [28]. Through theoretical modeling, Huang et al. revealed an unconventional near-equilibrium nucleation mechanism on SiC(0001), showing that carbon clusters exhibit greater stability on terraces than at step edges, an insight that expands the current understanding of nucleation in epitaxial graphene systems [29]. Sato et al. developed two-step growth techniques for SiC epitaxial graphene. The method of preparing a buffer layer via vacuum low-temperature annealing can effectively suppress step bunching, significantly reduce the surface atomic diffusion rate, and enable graphene growth on 4° off-axis substrates

[30]. Chen et al. systematically investigated the growth of epitaxial graphene on 4H-SiC(0001) under low-pressure conditions, identifying anisotropic expansion from step edges in the form of nanoribbons as a key growth mode [31]. Despite these advances, epitaxial graphene formation on SiC(0001) remains a highly complex process governed by multiple interdependent factors, and a coherent understanding of step bunching dynamics and the overall growth mechanism is still incomplete.

In this work, we present a stepwise growth approach for epitaxial graphene on SiC(0001) that decouples buffer layer formation from graphene growth, elucidating a buffer-mediated mechanism for growth kinetics control. By prefabricating a continuous buffer layer, its physical shielding effect confines the diffusion of sublimated Si atoms primarily to step edges, thereby suppressing long-range atomic transport across terraces and significantly mitigating giant step bunching during epitaxy. Moreover, the buffer layer alters the conventional nucleation landscape by breaking the step-edge dominated mode characteristic of direct growth. The resulting uniform carbon adlayer facilitates simultaneous nucleation across terraces and steps, shifting the system toward near-equilibrium growth conditions and preventing heterogeneous nucleation density distributions. This stepwise strategy provides enhanced control over nucleation uniformity and surface morphological stability, ultimately enabling the reproducible synthesis of large-area, homogeneous, single-crystal monolayer graphene.

2 Experimental

2.1 4H-SiC substrate preparation

Semi-insulating and on-axis 4H-SiC single crystal substrates with miscut angles ranging from 0.02° to 0.45° were fabricated using methods developed by our laboratory [32]. The substrates were subsequently processed through chemical-mechanical polishing (CMP) and standard radio corporation of America (RCA) cleaning prior to further pretreatment.

2.2 Experimental section on graphene growth

The 4H-SiC substrates were loaded in a custom-built induction-heated epitaxial growth system, and epitaxial graphene was grown on the (0001) face via medium-frequency induction heating. The typical substrate size was 10 mm × 10 mm. Prior to the growth, the SiC substrates were etched in a H₂ atmosphere at 1300–1400 °C for 20 min to remove surface damage and form uniform and regular etched steps, which served as preferential nucleation sites for subsequent graphene growth. The growth was then carried out under an Ar atmosphere using a two-stage annealing process: First, holding at 1500–1600 °C for 1 h to grow the buffer layer, followed by holding at 1650–1750 °C for 0.5–1 h to complete graphene growth. For comparison, conventional growth of SiC epitaxial graphene was performed by direct annealing in Ar atmosphere at 1750–1850 °C for 2 h. Throughout the growth process, the chamber pressure was maintained near atmospheric pressure (800–1000 mbar).

2.3 Characterizations

Surface morphology was characterized using a Park NX20 atomic force microscopy (AFM) in non-contact mode, with a noise level below 0.5 Å, enabling sub-angstrom roughness measurement. Graphene layer number and quality were characterized using a

WITec alpha 300R confocal Raman spectrometer (excitation wavelength = 532 nm, objective numerical aperture (NA) = 0.90, and spot size $\approx 0.8 \mu\text{m}$). The laser power was kept below 15 mW during testing to avoid sample damage. The lateral spatial resolution was approximately $0.36 \mu\text{m}$, the longitudinal resolution was about $0.9 \mu\text{m}$, and spectral reproducibility reached 0.15 cm^{-1} . The optical transmittance of the SiC/graphene was measured with a Lambda 750 ultraviolet–visible–near infrared (UV–Vis–NIR) spectrophotometer. C 1s X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher ESCALAB 250 Xi spectrometer with Al K α monochromatic X-rays under ultra-high vacuum ($< 10^{-7}$ Pa). The single-crystal quality of the epitaxial graphene on the SiC substrate was characterized by low-energy electron diffraction (LEED) patterns acquired at an acceleration voltage of 65 eV. The morphological evolution of the graphene at different growth stages was examined using a Gemini SEM560 at an acceleration voltage of 2 kV. The electrical properties of the graphene were characterized using a CH-50A Hall effect measurement system (Beijing Cuihaijiacheng Co., Ltd.).

2.4 Computational methods

A three-layer SiC(0001) slab was constructed with the bottom two layers fixed for optimization. Zigzag and armchair nanoribbons were modeled on the Si-terminated side, while the C-terminated side was H-passivated. Two carbon growth modes, lateral and vertical, were then designed to validate the decoupling mechanism. Our first-principles calculations were based on the density functional theory (DFT) [33–36] within the Perdew–Burke–Ernzerhof (PBE) [33] approximation for the exchange–correlation functional. The core–valence interactions were described by the projector augmented wave (PAW) potentials [34], as implemented in the Vienna *ab initio* simulation package (VASP) code [35]. The DFT–D3 dispersion correction with BJ-damping was applied to correct the weak interaction and improve the calculation accuracy [37]. Plane waves with a kinetic energy cutoff of 400 eV were used as the basis set. Slab calculations were carried out using periodic supercells [36]. During the structural relaxation, an energy convergence criterion of 10^{-5} eV and a force convergence criterion of 10^{-2} eV/Å were adopted.

3 Results and discussion

As shown in Fig. 1(a), conventional epitaxial graphene growth approach on SiC substrates is based on the preferential sublimation of Si atoms during direct high-temperature annealing of hydrogen-etched surfaces. Under such conditions, the rapid and spatially non-uniform sublimation of Si atoms, predominantly from step edges and buffer-layer-free regions, induces strongly divergent step motion rates. This disparity in mobility drives the formation of pronounced step bunching, whose severity is strongly influenced by both growth conditions and the initial surface step morphology (substrate miscut angle) [19, 23]. Under such conditions, graphene nucleation is concentrated at step edges, resulting in uneven growth across the SiC surface. As a result, the conventional direct growth is commonly accompanied by giant step bunching as well as thickness non-uniformity of graphene film, posing a major obstacle to the realization of wafer-scale, uniform monolayer graphene on SiC substrate. Monolayer graphene tends to form preferentially on larger bunched steps, while adjacent smaller steps often retain only a buffer layer structure due to growth suppression by the dominant macro steps. As growth continues, buffer-covered regions evolve into monolayer graphene, whereas pre-existing monolayer areas thicken further, increasing the proportion of bilayer graphene.

To overcome these limitations, we developed a stepwise epitaxial approach that decouples buffer layer formation from graphene synthesis via precise two-stage temperature control. This strategy suppresses giant step bunching, stabilizes step morphology, and enables the growth of continuous and homogeneous monolayer graphene. As illustrated in Fig. 1(b), a continuous buffer layer is first formed at a lower temperature, which moderates Si sublimation and step migration, while acting as a diffusion barrier that confines subsequent Si release predominantly at step edges rather than terraces. This effectively pins the surface morphology during the subsequent high-temperature growth stage. Upon further heating, graphene growth is initiated on the prefabricated buffer layer, which alters the nucleation landscape and enables concurrent nucleation on both step edges and terraces. This dual-site nucleation mechanism increases graphene nucleation density and promotes rapid lateral expansion of monolayer domains. Together, the stepwise process offers a controllable route to large-area,

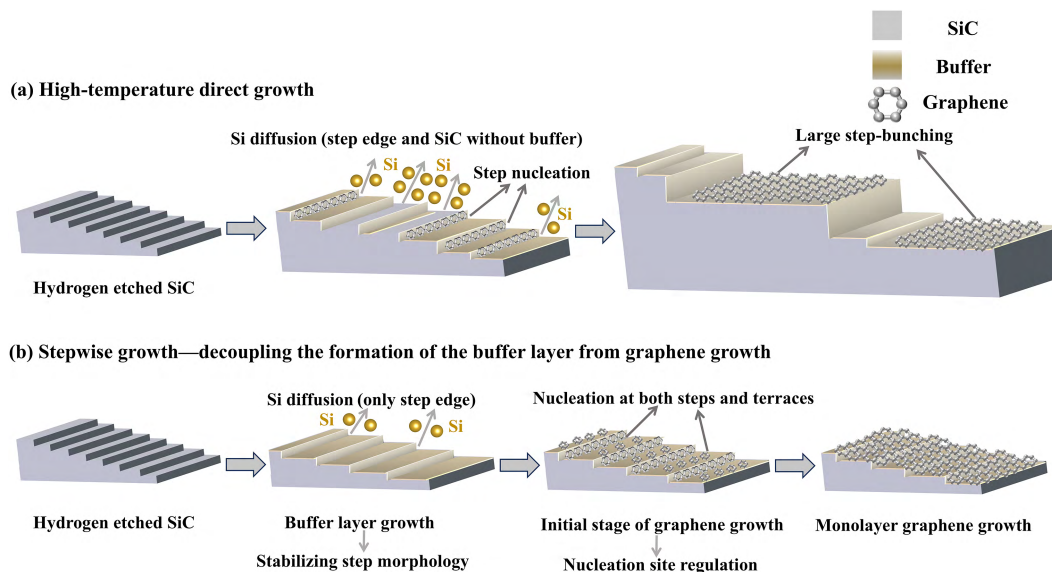


Figure 1 Schematic diagram of conventional high-temperature direct growth versus the proposed stepwise growth method for epitaxial graphene on SiC substrates.

smooth, and fully covered monolayer graphene with improved uniformity.

The pristine 4H-SiC substrate (miscut angle of $0.25^\circ \pm 0.02^\circ$), was initially subjected to H_2 etching to eliminate surface scratches and generate well-defined surface steps. As shown in the AFM image in Fig. 2(a), the surface exhibits uniform and straight steps with a height of 2–3 nm and a width of $\sim 0.5 \mu\text{m}$. After conventional direct growth, the sample exhibits pronounced giant step bunching with the maximum step height exceeding 25 nm, more than an order of magnitude larger than that of the initial etched steps (Fig. 2(b)). These bunched macro steps evolve into irregular and island-like features, coexisting with smaller, straight, and parallel steps that retain their original regularity. Such step instability originates from the rapid sublimation and diffusion of Si atoms during high-temperature growth, which preferentially escape from step edges and regions incompletely covered by the buffer layer. As a result, the severely degraded surface uniformity significantly hinders the large-area synthesis of graphene across the substrate.

Then the surface morphology of graphene grown by the stepwise approach was characterized. Figures 2(c) and 2(d) present the surface step morphology after the first and second growth stages, respectively. After the first growth stage, the buffer layer exhibits uniform and parallel steps with step heights of ~ 5 nm and widths of 3–4 μm , without the emergence of irregular step bunching. Notably, after the second high-temperature growth stage, the step morphology remains essentially unchanged, retaining comparable step heights and widths. In sharp contrast to conventional direct

high-temperature growth (Fig. 2(b)), the stepwise growth method effectively suppresses macro steps formation throughout the entire growth process. Additionally, the overall graphene growth temperature is reduced by approximately 100°C , which further limits high-temperature-induced surface reconstruction and contributes to the stabilization of the step morphology.

Figure 2(e) clearly reveals the presence of giant step bunching across the macroscopic area, where large steps encompass smaller steps. Raman spectra acquired from these large-step and small-step regions are shown in Fig. 2(f). The characteristic G and 2D peaks of graphene near 1580 and 2700 cm^{-1} , respectively, are detected exclusively within the macro steps. The full width at half maximum (FWHM) of the 2D peak is 34 cm^{-1} . Applying the empirical relation $\text{FWHM}_{2\text{D}} = -45(1/N) + 88$ (where N is the number of graphene layers) confirms that the graphene is monolayer [38]. This indicates the preferential growth of monolayer graphene in the bunched step regions. In contrast, no graphene signals are detected on the adjacent small steps; instead, only the characteristic G_B peak of the buffer layer near 1500 and 1580 cm^{-1} are observed [39, 40]. The Raman mapping images of the 2D peak FWHM and position (Figs. 2(g) and 2(h)) further corroborate the non-uniform graphene growth inherent to direct high-temperature growth. The growth of graphene on the small steps is suppressed by the adjacent macro steps, making it difficult to obtain a fully covered and continuous graphene sample. The step bunching phenomenon during high-temperature growth typically degrades the overall uniformity of the graphene film.

The graphene grown by the stepwise method was similarly

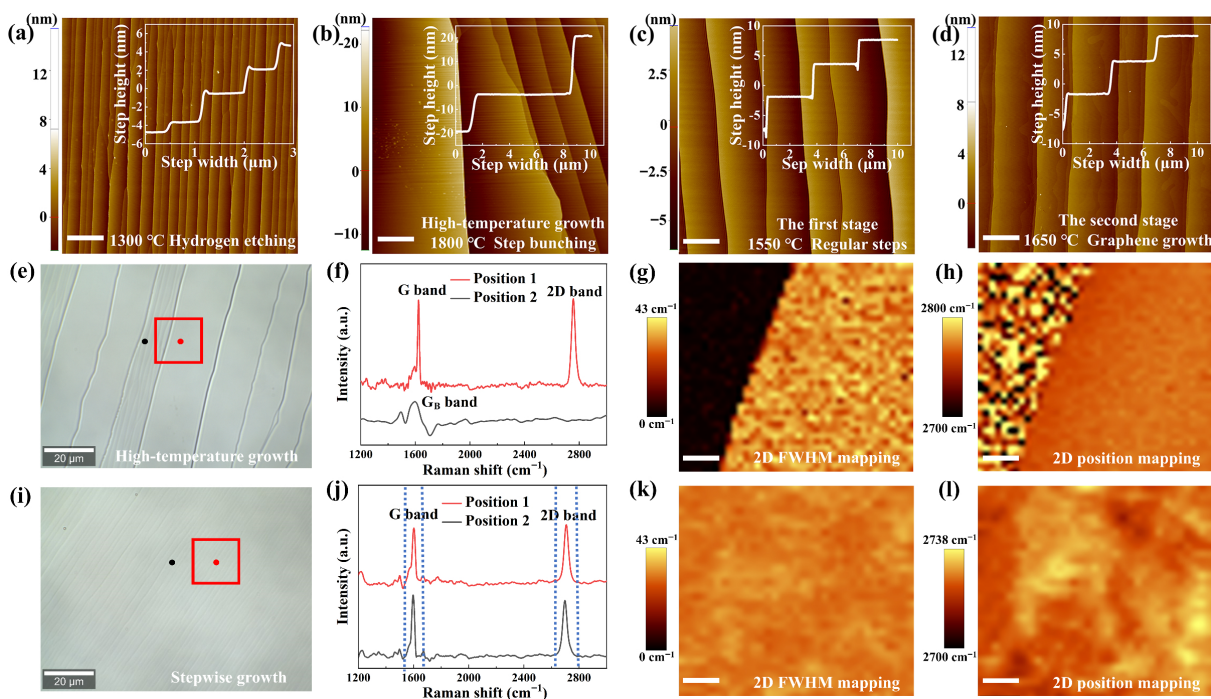


Figure 2 Comparative analysis of high-temperature direct growth versus stepwise growth of graphene. ((a)–(d)) AFM topography images representing the initial morphology after H_2 etching, the final morphology after high-temperature direct graphene growth, and the morphology after stepwise method decoupled growth of the buffer layer and graphene, respectively. ((e)–(h)) Optical microscopy and Raman characterization of high-temperature directly grown graphene: (e) macro surface step morphology image, (f) representative single-point Raman spectra (red and black spectra correspond to typical measurements on bunched macroscopic steps and adjacent small step regions, respectively), all Raman spectra are background-subtracted against a bare SiC substrate, and ((g) and (h)) Raman mapping images of the 2D peak FWHM and peak position, respectively, for the region marked by the red square in (e) at the boundary between giant step bunching and small steps. The raw Raman spectra are provided in Fig. S2 in the ESM. ((i)–(l)) Optical microscopy and Raman characterization of stepwise grown graphene: (i) macroscopic surface step morphology image, (j) representative single-point Raman spectra (red and black spectra from similar step regions), and ((k) and (l)) Raman mapping images of the 2D peak FWHM and peak position, respectively, for the region within the red square in (i). All AFM and Raman scan areas are $20 \mu\text{m} \times 20 \mu\text{m}$. The scale bar is $3 \mu\text{m}$.

characterized. Prior to this, a stable buffer layer was first formed at a relatively low temperature. Its complete coverage was confirmed by Raman mapping (Figs. S7(g)–S7(i) in the ESM), thereby stabilizing the step morphology before graphene growth. The optical microscopy image in Fig. 2(i) shows a uniform and smooth surface over a macroscopic area after graphene growth, with no evident giant step bunching. Raman spectroscopy analysis of the stepwise-grown graphene is presented in Figs. 2(j)–2(l). Figure 2(j) displays individual spectra from adjacent locations, showing distinct graphene G and 2D peaks. The 2D peak FWHM of 38 and 33 cm^{-1} confirm monolayer graphene. Notably, the 2D peak position at $\sim 2700 \text{ cm}^{-1}$ is closer to that of quasi-free-standing graphene compared to the directly high-temperature grown graphene ($\sim 2760 \text{ cm}^{-1}$), indicating lower strain in the stepwise-grown graphene. Furthermore, the absence of a noticeable D peak near 1350 cm^{-1} attests to its high quality. Raman mapping of the 2D peak FWHM and position within the red boxed region (Figs. 2(k) and 2(l)) show values concentrated in the ranges of 30–40 and $2700\text{--}2738 \text{ cm}^{-1}$, respectively, demonstrating the overall uniformity of the monolayer graphene. In summary, the stepwise growth method yields a graphene with more uniform surface step morphology and ensures a completely covered, homogeneous monolayer. These observations directly demonstrate that decoupling buffer-layer formation from graphene growth kinetically stabilizes the SiC surface, preventing step bunching even under subsequent high-temperature annealing.

XPS was employed to probe the chemical and structural characteristics of graphene samples synthesized by both high-temperature direct growth and stepwise growth methods. The inset in Fig. 3(a) displays the deconvoluted C 1s spectrum of the stepwise growth sample, which was fitted with four distinct components. The dominant peaks at binding energies of approximately 283.8 and 284.8 eV are assigned to carbon atoms in the SiC substrate and graphene (C–C bonds), respectively [41–43]. Two additional peaks situated near 285.0 and 285.7 eV correspond to the S1 and S2 components of the buffer layer [44]. In accordance with the established buffer layer model, approximately one-third of the carbon atoms are covalently bonded to the underlying SiC substrate [22]. The integrated area ratio of the S1 to S2 peaks is approximately 1:2, consistent with sp^3 -hybridized and sp^2 -hybridized carbon atoms within the buffer layer, respectively. Comparative analysis of the C 1s spectra reveals a progressive enhancement in the intensity of the graphene related peak at 284.8 eV from the buffer layer to direct grown graphene (Fig. 3(a)), and further to the stepwise growth sample. Given that direct growth results in incomplete graphene coverage, especially on narrow terraces adjacent to bunched steps due to severe step bunching, the XPS results corroborate that the stepwise growth method achieves superior graphene coverage across the substrate. The transmittance of SiC and stepwise-grown graphene/SiC was measured across the spectral range of 200–2500 nm using a UV–Vis–NIR spectrophotometer (Fig. 3(b)). Except for the intrinsic absorption of

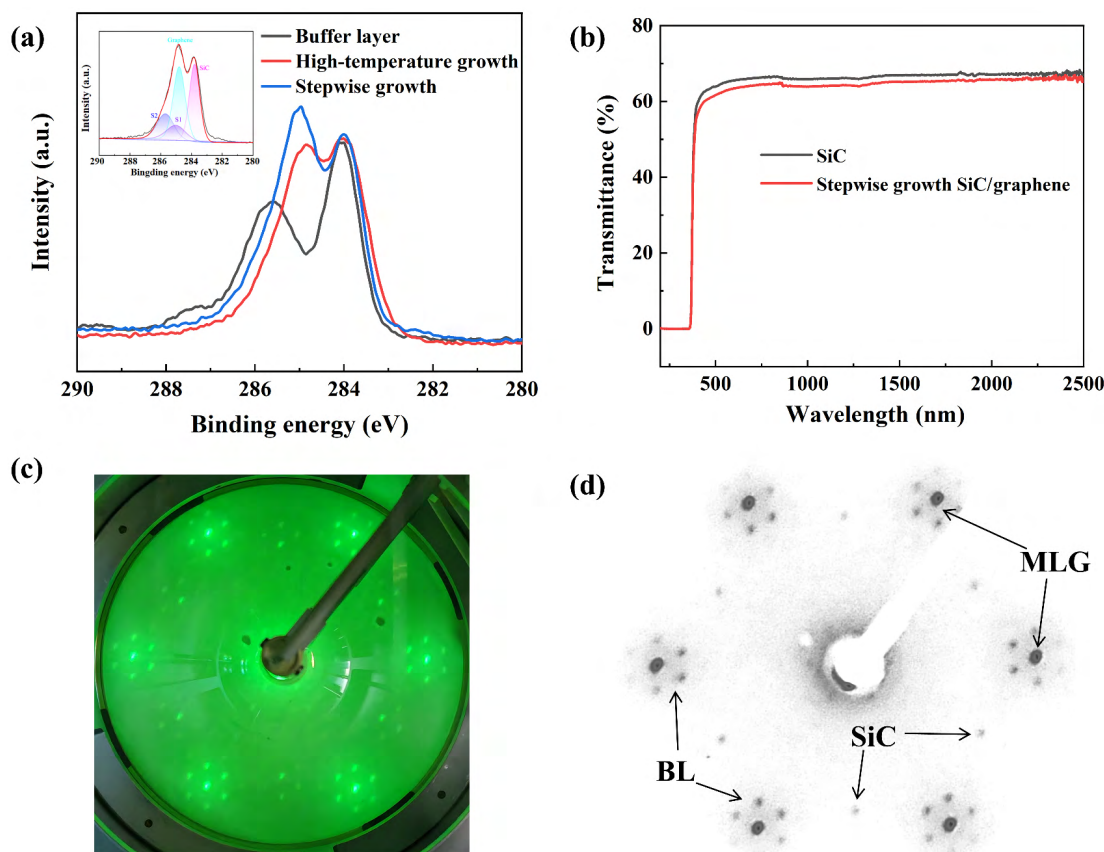


Figure 3 (a) Comparative XPS analysis of graphene grown by direct high-temperature growth and by the stepwise method. The inset in (a) shows the peak-fitting of the C 1s spectrum for the stepwise-grown graphene sample. (b) Optical transmittance spectra of bare SiC and stepwise-grown graphene/SiC measured over the wavelength range of 200–2500 nm. (c) Series of LEED patterns acquired from the stepwise-grown graphene sample at an incident beam energy of 65 eV. (d) Processed diffraction spot pattern derived from the LEED data.

4H-SiC in the ultraviolet region below 380 nm, the SiC substrate exhibits high broad-spectrum transparency, maintaining a transmittance of $\sim 68\%$ from 400 to 2500 nm, making it an ideal material for ultraviolet-to-infrared broadband optical windows. Owing to the high optical transmittance of monolayer graphene ($\sim 97.7\%$), the directly epitaxial graphene on SiC still achieves a transmittance as high as $\sim 66\%$, only about 2% lower than that of bare SiC. This integrated material system therefore enables an excellent synergy between optical transparency and electrical conductivity.

Furthermore, LEED was conducted to assess the long-range crystalline order and epitaxial alignment of graphene synthesized via the stepwise growth. As shown in Figs. 3(c) and 3(d), the LEED patterns exhibit well-defined and sharp diffraction spots, indicative of a high degree of structural order and long-range coherence. The pattern consists of three distinct sets of diffraction spots corresponding to the SiC substrate, the $(6\sqrt{3} \times 6\sqrt{3})$ R30° reconstructed buffer layer, and the epitaxial monolayer graphene. The outermost six bright spots originate from the graphene layer. Notably, the graphene-derived diffraction spots form a single set of sharp sixfold-symmetric features without evidence of rotational variants or ring-like diffuse scattering, indicating the absence of rotational domains and confirming a single crystallographic orientation across the probed area. The additional satellite spots surrounding the graphene diffraction, arise from the superperiodic structure of the buffer layer. Besides, the six slightly weaker spots are attributable to the SiC substrate. The buffer layer is rotated by 30° relative to the SiC substrate, while the graphene layer is aligned with the buffer layer (0° orientation). Their in-plane lattices achieve coherent registry via a supercell mechanism, resulting in an indirect 30° rotation between graphene and the SiC substrate. The graphene-derived diffraction manifests a sharp sixfold symmetric arrangement, and consistent patterns were obtained at multiple locations across the sample surface (Fig. S3 in the ESM), confirming that the stepwise growth strategy enables the formation of continuous, wafer-scale monolayer graphene with high crystallinity and long-range orientational uniformity.

To further validate the feasibility of our stepwise growth strategy, we first examine the role of temperature through experimental observations. As shown in Fig. S6 in the ESM, when the growth temperature is increased to $\sim 1700^\circ\text{C}$, the buffer layer formation and graphene growth become strongly coupled, indicating that temperature is the dominant parameter controlling the coupling or decoupling between these two growth stages. From an energetic perspective, the temperature dependence of the underlying growth kinetics can be quantitatively described by the Arrhenius equation

$$\ln k = -\Delta E_a/RT + \ln A \quad (1)$$

where k represents the rate constant of the relevant process, ΔE_a denotes the activation energy barrier, A is the pre-exponential factor (frequency factor), R is the universal gas constant, and T is the absolute temperature. According to the Arrhenius equation, increasing temperature accelerates both growth processes, but the extent of acceleration is determined by their respective activation energy barriers ΔE_a .

To evaluate the activation energy barriers associated with the different growth modes, we employed a formation energy approach based on first-principles calculations. This method is justified because both formation energy and activation energy quantify the energetic cost of transitioning between distinct atomic

configurations and in many kinetically controlled processes, such as nucleation and growth, and the formation energy of key intermediates often correlates strongly with (or serves as a proxy for) the effective activation barrier.

The calculations in this study simulate the early growth stage, in which the buffer layer has only begun to form and most of the SiC surface remains exposed, and all carbon atoms involved in the growth process originate from the thermal decomposition of the exposed SiC substrate. We implemented a computational protocol in which 1–6 carbon atoms were systematically added to a three-layer SiC(0001) nanoribbon model, considering both lateral (in-plane) and vertical (out-of-plane) incorporation directions. Formation energies were then calculated for each resulting configuration. The formation energy E_f is defined as

$$E_f = E_{\text{tot}} - E_{\text{sub}} - N_C \times \varepsilon_C \quad (2)$$

where E_{tot} is the total energy of a carbon cluster on the substrate, E_{sub} is the energy of the substrate, N_C represents the number of carbon atoms in the cluster, and ε_C is the chemical potential of one carbon atom in perfect graphene.

As shown in Figs. 4(a)–4(d) (with full calculation details and optimized structures provided in Figs. S4 and S5 in the ESM), the formation energies for configurations C1–C6 exhibit a clear and consistent trend across both armchair and zigzag nanoribbon edges: Vertical growth modes possess markedly higher formation energies, ranging approximately from 3.2 to 12.0 eV (detailed formation energy data are provided in Table S2 in the ESM), whereas lateral modes display much lower values, spanning from about -1.6 to 1.6 eV over the range of added carbon atoms. This large energetic disparity, typically on the order of several eV, demonstrates a strong thermodynamic preference for lateral carbon incorporation, which implies a substantially higher intrinsic growth rate for lateral expansion at all temperatures. Nevertheless, the vertical growth mode exhibits a markedly stronger temperature dependence in its kinetics. Owing to its significantly higher effective activation barrier (as mirrored by the elevated formation energies), the vertical process becomes increasingly activated with rising temperature. It only emerges as experimentally observable above a critical temperature threshold, at which point it begins to coexist and compete with the dominant lateral growth. This competition leads to simultaneous buffer-layer formation and nucleation of true sp^2 -hybridized graphene, marking the onset of coupled growth.

The observed temperature-driven transition between laterally dominant and coupled growth regimes defines a distinct “temperature window” for achieving selective and decoupled control of the two stages. This computational insight is fully consistent with our experimental results (Fig. S6 in the ESM), which reveal the onset of coupled growth near 1700°C .

Additionally, from an energetic perspective, the buffer layer stabilized in the first growth stage represents a thermodynamically favored configuration rather than a transient growth byproduct. Previous reports have shown that the epitaxial buffer layer on SiC(0001) exhibits an opened bandgap of ~ 0.6 eV, suggesting that it may serve as a functional semiconductor interface with high carrier mobility [45, 46], further highlighting the significance of its controlled formation in the stepwise growth process.

In the stepwise graphene growth approach, the initial low-temperature formation of the buffer layer dictates the final surface step morphology. Pyrolysis of the SiC substrate initiates the diffusion of Si atoms and the reorganization of C atoms. The

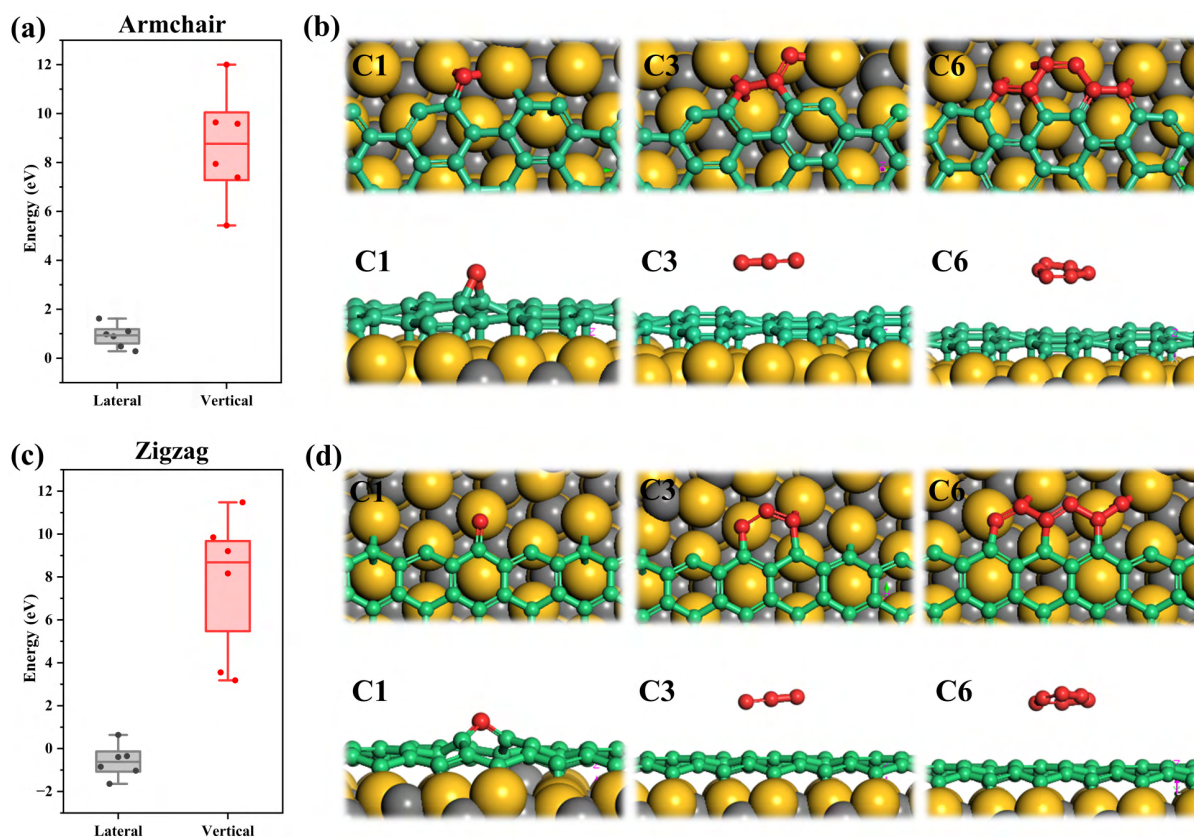


Figure 4 Calculated formation energies and atomic structures for the lateral buffer layer expansion and the vertical graphene growth on 4H-SiC(0001). (a) Formation energies for the lateral expansion and vertical growth modes of armchair-edged buffer layer. (b) Representative atomic configurations with 1, 3, and 6 additional carbon atoms (C1, C3, and C6) incorporated at or above the armchair-edged buffer layer. (c) Formation energies for the lateral expansion and vertical growth modes of zigzag-edged buffer layer. (d) Representative atomic configurations with 1, 3, and 6 additional carbon atoms (C1, C3, and C6) incorporated at or above the zigzag-edged buffer layer.

inherent atomic-scale steps on the substrate serve as natural sites for the step bunching during growth, a process whose extent is predominantly governed by temperature. Therefore, precise regulation of the buffer layer growth temperature is essential for achieving a desirable surface step topography.

Figures 5(a)–5(e) show AFM images of surfaces obtained after the first growth stage at temperatures ranging from 1350 to 1800 °C (held for 1 h). The step morphology undergoes a marked evolution with increasing temperature, characterized by a sequence of “orderly–disordered–regular–giant step bunching”. Corresponding Raman mapping of the integrated intensity for characteristic peaks (Figs. 5(f)–5(j)) provides further insight. At 1350 °C, no decomposition of the SiC substrate is observed, and consequently, no carbon layer forms. The AFM morphology closely resembles the ordered step structure of the H₂-etched substrate (compared with Fig. 2(a)). At 1450 °C, the step arrangement becomes comparatively disordered. In these disordered regions, the step height increases from 2 to 4–5 nm. Raman characterization indicates that areas with greater step height typically correlate with the buffer layer’s G_B peak, corresponding to the yellowish-green regions in Fig. 5(g). Within the optimal temperature range of 1550 °C (Figs. 5(c) and 5(h)), the surface evolves into a uniform buffer layer with regular steps of ~ 5 nm in height. Raman confirms complete buffer coverage without graphene formation, indicating ideal conditions for subsequent conversion. A significant increase in temperature to 1700 °C intensifies Si sublimation and diffusion, promoting the merger of adjacent steps via Si atom migration. Pronounced step

bunching emerges, with maximum step heights exceeding 10 nm, leading to markedly degraded step uniformity. While Raman signatures of graphene are detected on bunched steps (orange areas in Fig. 5(i)), the overall graphene coverage remains low. At 1800 °C, giant step bunching is further accentuated, yielding step heights over 20 nm, often flanked by smaller steps at their edges. Although Raman mapping reveals increased graphene formation, the surface coverage remains incomplete. Proceeding to the second growth step from this state would compromise graphene uniformity, promoting the conversion of initial monolayer areas into bilayer graphene.

Statistical analysis of step height and width from AFM images (Figs. 5(k) and 5(l)) reveals that at lower temperatures (1350–1550 °C), steps exhibit smaller dimensions with only slight merging [23], maintaining good overall uniformity. In contrast, at temperatures exceeding the optimal buffer layer growth range (≥ 1700 °C), a sharp increase in both step height and width is observed. The step size distribution broadens significantly, resulting in a co-existence of large and small steps and deteriorated uniformity. Similarly, analysis of multiple Raman maps (additional data in Figs. S7 and S8 in the ESM) quantifying the coverage of the buffer layer and graphene (Figs. 5(m) and 5(n)) shows that stable and complete buffer layer coverage is achieved at 1550 °C. At higher temperatures, graphene nucleation initiates preferentially on large steps, with its coverage increasing progressively. However, a complete and homogeneous monolayer cannot be obtained solely via this first step. Optimal monolayer graphene coverage is ultimately achieved following the second growth step.

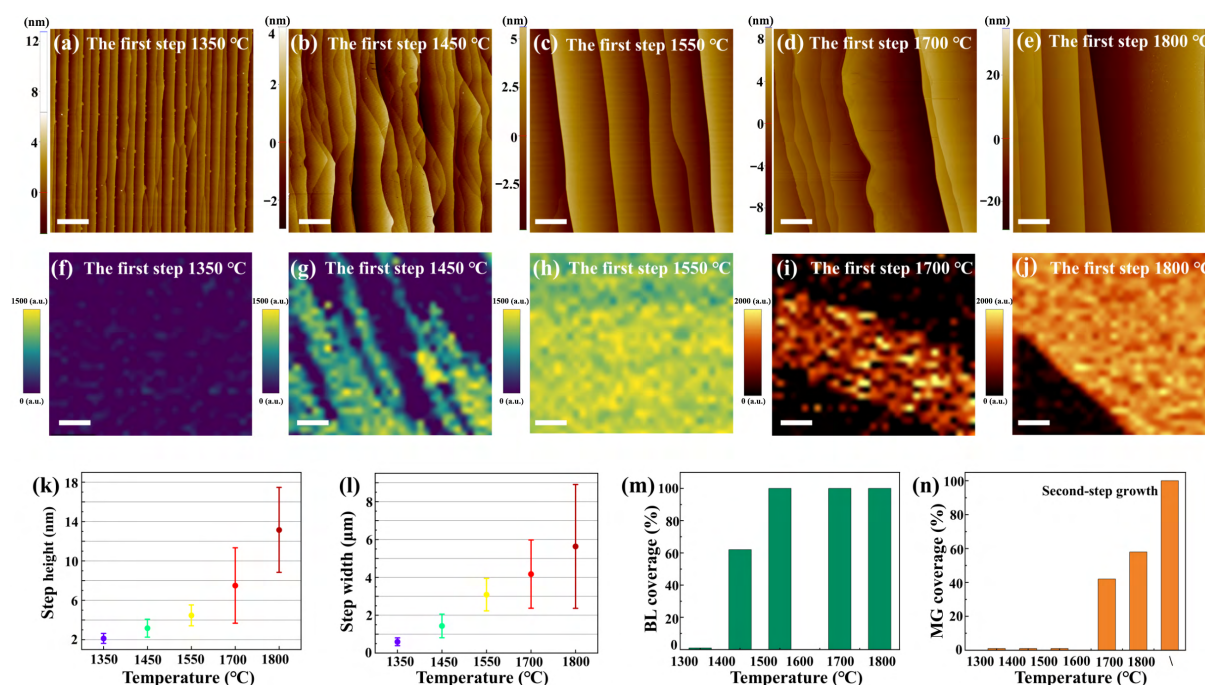


Figure 5 Comparative AFM and Raman analysis for different first-step growth temperatures. ((a)–(e)) AFM topography images after the first growth stage at temperatures of 1350, 1450, 1550, 1700, and 1800 °C, respectively, demonstrating significant variations in step morphology with temperature. ((f)–(j)) Corresponding Raman mapping images sequentially corresponding to ((a)–(e)): ((f)–(h)) show mapping of the integrated intensity of the buffer layer G_B peak, while (i) and (j) present mapping of the integrated intensity of the graphene 2D peak, characterizing the growth states at different temperatures. ((k) and (l)) The distributions of step height and width, respectively, across different growth temperatures. ((m) and (n)) Summarizing the coverage of the buffer layer and graphene, respectively, at various temperatures. All AFM and Raman measurements were performed over an area of 20 μm × 20 μm. The scale bar is 3 μm.

In summary, step bunching represents a significant and persistent challenge in the epitaxial growth of graphene on SiC, arising primarily from the migration and rearrangement of surface atoms, particularly Si, which drive adjacent steps to merge via atomic flow to minimize surface energy. During the initial transition from an etched substrate to a buffer layer, the surface undergoes moderate reorganization, resulting in limited step coalescence. However, because the buffer layer is synthesized at substantially lower temperatures than graphene, the diffusivity of Si atoms is markedly reduced. Consequently, step bunching at this stage is significantly suppressed relative to direct high-temperature graphene growth from an etched substrate. Once established, the buffer layer functions as an efficient physical barrier, resembling a continuous “rigid capping layer” over the SiC surface. This shielding effect is comprehensive: Sublimated Si atoms are confined to diffuse primarily from step edges rather than across terraces, thereby restricting atomic mobility on terraces and preventing step coalescence through migration. As a result, step bunching is effectively mitigated during the subsequent transformation from buffer layer to graphene. In contrast, during conventional high-temperature direct growth, which lacks a defined buffer formation stage, graphene can occur locally before the buffer layer fully covers the surface. Under these conditions, Si is released not only from step edges but also from exposed terrace regions, while the elevated temperature further accelerates Si diffusion. This combination promotes rapid step migration and pronounced giant step bunching.

Moreover, the buffer layer passivates dangling bonds on the Si-face of SiC and reduces the overall surface energy [47]. By decoupling the buffer layer and graphene growth stages, a structurally coherent and energetically favorable interlayer is

obtained, which plays a key role in stabilizing the step morphology and enabling the growth of uniform monolayer graphene.

The second stage of the stepwise method involves graphene formation. In conventional direct high-temperature growth, graphene nucleation is strongly step-edge-dominated, owing to the relatively weaker Si–C bonds at step edges, which promote preferential decomposition of SiC at these sites, while nucleation on terraces remains largely suppressed. As shown in the SEM images in Figs. 6(a) and 6(b), recorded after 60 min of direct high-temperature growth on SiC, graphene first covers step edges and then extends in dendritic [31] or ribbon-like [48] morphology perpendicular to the step direction. The schematic in Fig. 6(c) illustrates that graphene nucleates rapidly along step edges in the [1100] direction (parallel to the steps), followed by lateral expansion across the terraces in the [1120] direction (perpendicular to the steps). Nucleation along step edges is typically spatially inhomogeneous. Regions with high nucleation density evolve rapidly into continuous graphene ribbons, whereas elsewhere nucleation remains sparse or even absent (detailed nucleation and growth pathways are provided in Figs. S9(a)–S9(d) in the ESM. This non-uniform nucleation distribution not only yields irregular graphene coverage but also induces local variations in step motion, further exacerbating morphological instability.

In contrast, the pre-formed buffer layer plays a critical role in regulating the kinetics of graphene growth. Figures 6(d) and 6(e) show SEM images acquired after 3 and 10 min of second-step growth, respectively. Compared to direct high-temperature growth, the buffer layer shifts nucleation from exclusive step-edge initiation to a dual-site mode, with simultaneous nucleation at step edges and on terraces. While graphene adopts a dendritic morphology at step edges, terraces exhibit a higher density of nucleation sites. With

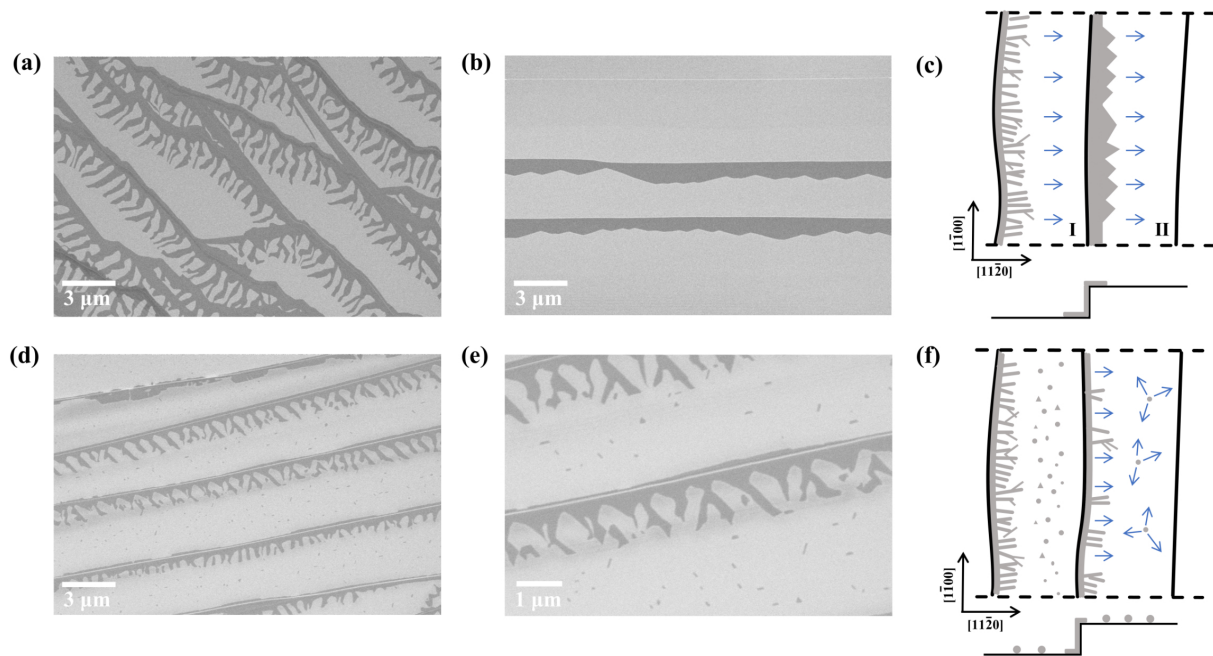


Figure 6 SEM images of graphene grown by direct high-temperature annealing and by the second stage of the stepwise method at different growth time. ((a) and (b)) SEM images of two typical morphologies observed after 60 min of direct high-temperature growth, where graphene extends from step edges in dendritic and ribbon-like forms, respectively. (c) The corresponding growth pathway for direct high-temperature growth. ((d)–(f)) SEM images after 3 min of growth in the second stage of the stepwise process, along with a schematic of the growth pathway: (d) SEM image of the sample after 3 min of the second stage in the stepwise process, (e) an enlarged view of the corresponding region, and (f) The proposed growth pathway during the stepwise growth.

extended growth, dendritic branches from step edges advance perpendicularly onto terraces, while terrace-based nuclei evolve into islands that expand radially (detailed nucleation and growth pathways are provided in Figs. S9(e)–S9(h) in the ESM). As illustrated in Fig. 6(f), these two growth fronts eventually coalesce into a continuous and uniform monolayer. This strategy yields a more spatially uniform nucleation distribution and a higher nucleation density, eliminating regions where nucleation is suppressed. As a result, graphene coverage becomes more homogeneous and complete. The pre-grown buffer layer fundamentally alters the growth mechanism of graphene, breaking the inherent step-edge-dominated nucleation mode. The formation of the buffer layer saturates the dangling bonds on pristine SiC, particularly at step edges, and significantly narrows the differences in both dangling bond density and chemical reactivity between step edges and terraces. Through this coverage effect, the buffer layer suppresses Si atom sublimation at step edges, thereby reducing the discrepancy in sublimation rates between steps and terraces and leading to a more uniform distribution of surface carbon chemical potential. Furthermore, the buffer layer serves as a carbon-supply layer that delivers a uniform flux of precursors across the surface. This prevents localized carbon accumulation at step edges and promotes concurrent nucleation at steps and terraces. The resulting homogeneous carbon distribution drives the system toward near-equilibrium growth conditions [29], increases the fraction of terrace-based nucleation, and further suppresses step bunching during growth.

Furthermore, the miscut angle of SiC substrates is a critical factor governing the final surface morphology of epitaxial graphene. The miscut angle, defined as the inclination angle between the actual substrate surface and the ideal (0001) crystallographic plane, determines the initial step density of the substrate. Substrates with larger miscut angles generally possess higher and denser initial

steps, and the step migration behavior during high-temperature annealing ultimately results in distinct final surface states. In this work, we systematically investigated the surface step morphologies of graphene grown on SiC substrates with different miscut angles (0.02° , 0.25° , and 0.45°) under identical experimental conditions using two growth strategies: direct high-temperature annealing growth and our optimized stepwise growth method. Figure S10 in the ESM presents the surface step morphologies of samples grown via direct high-temperature growth with different miscut angles. Regardless of the miscut angle, varying degrees of irregular step coalescence occur during graphene growth, and the height of coalesced steps generally increases with rising miscut angle. Although a near-zero miscut angle typically corresponds to wider initial terraces and smaller step heights (Figs. S12(a) and S12(b) in the ESM), the vigorous step migration during high-temperature annealing inevitably causes step aggregation and reconstruction. Nevertheless, the degree of step coalescence is relatively weaker in this case, and giant steps with heights of tens of nanometers are usually not formed. Figure S11 in the ESM shows the surface morphologies of graphene grown on substrates with different miscut angles using stepwise growth method, which decouples the growth stages of the buffer layer and graphene. The graphene grown via the stepwise approach exhibits a much smoother surface with significantly reduced roughness. Compared with direct high-temperature growth, irregular step coalescence is effectively suppressed, and the overall uniformity and straightness of the steps are remarkably improved, which is highly beneficial for achieving high-uniformity epitaxial graphene.

For SiC substrates with a small miscut angle (approximately 0.02°), we systematically investigated the epitaxial growth of graphene by optimizing the growth parameters, and by adopting the same stepwise growth strategy that decouples the buffer layer and graphene growth stages. After graphene growth, AFM

measurements reveal that the typical surface step height is 0.5 nm (Figs. S12(c) and S12(d) in the ESM), corresponding to two C-Si atomic layers, which is significantly lower than that obtained on substrates with larger miscut angles. Such minimal step heights effectively suppress the formation of non-(0001) oriented bilayer graphene inclusions, facilitating the realization of uniform monolayer single-crystal graphene. Raman spectroscopy characterization, including both single-point spectra and spatial mapping (Figs. S12(e)–S12(g) in the ESM), further confirmed the monolayer nature of the graphene, as evidenced by the line shape and position of the 2D band. The absence of a discernible D peak indicates high crystalline quality and excellent spatial uniformity across the sample. In general, the use of low miscut substrates is highly advantageous for the epitaxial growth of graphene on SiC. However, inevitable deviations in miscut angle during substrate slicing and processing, as well as step-flow evolution during bulk crystal growth, can alter the initial surface morphology. These variations often lead to severe giant step-bunching during high-temperature epitaxial growth. The two-stage growth method developed herein effectively mitigates such morphological degradation, thereby significantly broadening the tolerance toward SiC substrate selection. Besides, we demonstrated graphene growth on 6-inch wafer-scale SiC substrates, and characterized the graphene uniformity via multi-region Raman mapping (Fig. S13 in the ESM). The stepwise growth method enables the epitaxial growth of wafer-scale uniform monolayer graphene on SiC substrates, which well meets the requirements for industrialization and mass production.

In addition, by decoupling the synthesis process into two distinct stages, buffer layer formation and subsequent conversion, we not only enable epitaxial graphene growth via thermal annealing in the second step but also facilitate the production of quasi-free-standing monolayer graphene through hydrogen intercalation. This technique involves the introduction of hydrogen atoms to disrupt the covalent bonds between the buffer layer and the SiC substrate. Hydrogen saturates the silicon dangling bonds on the Si-face SiC(0001) surface, while the sp^3 hybridized carbon atoms within the buffer layer revert to sp^2 hybridization, effectively converting the buffer layer into a quasi-free-standing graphene sheet. The initial growth of a complete and uniform buffer layer is critical, as it ensures the formation of a continuous and homogeneous quasi-free-standing graphene monolayer. Corresponding characterization by Raman spectroscopy and AFM, provided in Fig. S14 in the ESM, confirms the successful formation of high-quality and uniform quasi-free-standing graphene.

4 Conclusions

This study establishes a stepwise growth strategy that decouples buffer layer formation from graphene growth through precise temperature control. A continuous and stable buffer layer is first formed at a reduced temperature to kinetically stabilize the SiC surface, followed by a higher-temperature stage that drives graphene growth. First-principles calculations confirm that the lateral expansion of the buffer layer is energetically far more favorable than vertical growth graphene formation, validating the thermodynamic basis for this separation of growth stages. The buffer layer plays a dual kinetic role by suppressing step coalescence through confinement of Si sublimation to step edges and by reshaping the graphene nucleation landscape. Acting as a uniform

carbon reservoir, it mitigates step-edge-dominated nucleation and promotes concurrent nucleation on terraces, shifting the growth regime toward near-equilibrium conditions. Consequently, large-area, uniform, and single-crystalline monolayer graphene is achieved and with markedly improved step morphology stability. Beyond enabling high-quality graphene synthesis, this work also identifies buffer-layer-mediated kinetic regulation as a general mechanism for controlling surface morphology and nucleation during SiC-based epitaxy, deepening the fundamental understanding of epitaxial graphene on SiC(0001) and paving the way for wafer-scale integration of epitaxial graphene in electronic and optoelectronic devices.

Electronic Supplementary Material: Supplementary material (additional experimental, electrical data from van der Pauw–Hall measurements, characterization, and computational details) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908882>.

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.

Acknowledgements

This work was supported by the Shandong Province Key Research and Development Program (No. 2025CXPT203), the National Natural Science Foundation of China (No. U23A20569), and the Shandong Provincial Natural Science Foundation (No. ZR2025MS754).

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

X. C. J.: Data curation, formal analysis, validation, writing – original draft. Y. Y. W.: Data curation, software. T. C.: Methodology, software. Q. H. W.: Validation. C. L.: Resources, validation. J. Q. J.: Investigation. B. G.: Investigation. X. C. S.: Methodology, software. L. S.: Supervision, project administration. Q. D.: Supervision, project administration. K. H. L.: Resources, project administration. W. C. Y.: Funding acquisition, formal analysis, writing – review & editing. H. Y. R.: Funding acquisition, formal analysis, writing – review & editing. X. F. C.: Resources, supervision. X. G. X.: Project administration, supervision. All the authors have approved the final manuscript.

Use of AI statement

None.

References

- [1] Nakamura, D.; Gunjishima, I.; Yamaguchi, S.; Ito, T.; Okamoto, A.; Kondo, H.; Onda, S.; Takatori, K. Ultrahigh-quality silicon carbide single crystals. *Nature* **2004**, *430*, 1009–1012.

- [2] Widmann, M.; Lee, S. Y.; Rendler, T.; Son, N. T.; Fedder, H.; Paik, S.; Yang, L. P.; Zhao, N.; Yang, S.; Booker, I. et al. Coherent control of single spins in silicon carbide at room temperature. *Nat. Mater.* **2015**, *14*, 164–168.
- [3] Koehl, W. F.; Buckley, B. B.; Heremans, F. J.; Calusine, G.; Awschalom, D. D. Room temperature coherent control of defect spin qubits in silicon carbide. *Nature* **2011**, *479*, 84–87.
- [4] She, X.; Huang, A. Q.; Lucia, Ó.; Ozpineci, B. Review of silicon carbide power devices and their applications. *IEEE Trans. Ind. Electron.* **2017**, *64*, 8193–8205.
- [5] Eddy, C. R. Jr.; Gaskill, D. K. Silicon carbide as a platform for power electronics. *Science* **2009**, *324*, 1398–1400.
- [6] Cheng, Z.; Liang, J. B.; Kawamura, K.; Zhou, H.; Asamura, H.; Uratani, H.; Tiwari, J.; Graham, S.; Ohno, Y.; Nagai, Y. et al. High thermal conductivity in wafer-scale cubic silicon carbide crystals. *Nat. Commun.* **2022**, *13*, 7201.
- [7] Li, S.; Zheng, Q. Y.; Lv, Y. C.; Liu, X. Y.; Wang, X. Q.; Huang, P. Y.; Cahill, D. G.; Lv, B. High thermal conductivity in cubic boron arsenide crystals. *Science* **2018**, *361*, 579–581.
- [8] Morkoç, H.; Strite, S.; Gao, G. B.; Lin, M. E.; Sverdlov, B.; Burns, M. Large-band-gap SiC, III–V nitride, and II–VI ZnSe-based semiconductor device technologies. *J. Appl. Phys.* **1994**, *76*, 1363–1398.
- [9] Woods-Robinson, R.; Han, Y. B.; Zhang, H. Y.; Ablekim, T.; Khan, I.; Persson, K. A.; Zakutayev, A. Wide band gap chalcogenide semiconductors. *Chem. Rev.* **2020**, *120*, 4007–4055.
- [10] Woon, W. Y.; Kasperovich, A.; Wen, J. R.; Hu, K. K.; Malakoutian, M.; Jhang, J. H.; Vaziri, S.; Datye, I.; Shih, C. C.; Hsu, J. F. et al. Thermal management materials for 3D-stacked integrated circuits. *Nat. Rev. Electr. Eng.* **2025**, *2*, 598–613.
- [11] Chen, B. Q.; Li, C.; Li, X. X.; Fang, C. T.; Chen, Y. G.; Zhao, D.; Cai, L.; Du, K. K.; Qiu, M. SiC diffractive waveguides for augmented reality: Single-layer, full-color, rainbow-artifact-free display with vision correction. *eLight* **2025**, *5*, 21.
- [12] Li, Y.; Li, H. H.; Wu, F.; Wang, M. G.; Xiang, Z. Y.; Zheng, Z. R. Single-layer full-color SiC diffractive waveguide AR glasses with large FOV and rainbow effect suppression. *Photonics* **2025**, *12*, 952.
- [13] Zhang, Y. B.; Tan, Y. W.; Stormer, H. L.; Kim, P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* **2005**, *438*, 201–204.
- [14] Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J. H.; Kim, P.; Choi, J. Y.; Hong, B. H. Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature* **2009**, *457*, 706–710.
- [15] Dai, W.; Lv, L.; Lu, J. B.; Hou, H.; Yan, Q. W.; Alam, F. E.; Li, Y. F.; Zeng, X. L.; Yu, J. H.; Wei, Q. P. et al. A paper-like inorganic thermal interface material composed of hierarchically structured graphene/silicon carbide nanorods. *ACS Nano* **2019**, *13*, 1547–1554.
- [16] Li, X. S.; Cai, W. W.; An, J.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E. et al. Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science* **2009**, *324*, 1312–1314.
- [17] Reina, A.; Jia, X. T.; Ho, J.; Nezich, D.; Son, H.; Bulovic, V.; Dresselhaus, M. S.; Kong, J. Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Lett.* **2009**, *9*, 30–35.
- [18] Xu, X. Z.; Zhang, Z. H.; Dong, J. C.; Yi, D.; Niu, J. J.; Wu, M. H.; Lin, L.; Yin, R. K.; Li, M. Q.; Zhou, J. Y. et al. Ultrafast epitaxial growth of metre-sized single-crystal graphene on industrial Cu foil. *Sci. Bull.* **2017**, *62*, 1074–1080.
- [19] Yang, D.; Ma, F.; Bian, X. L.; Xia, Q. F.; Xu, K. W.; Hu, T. W. The growth of epitaxial graphene on SiC and its metal intercalation: A review. *J. Phys.: Condens. Matter* **2024**, *36*, 173003.
- [20] Yin, H.; Hutter, M.; Wagner, C.; Tautz, F. S.; Bocquet, F. C.; Kumpf, C. Epitaxial growth of mono- and (twisted) multilayer graphene on SiC(0001). *Phys. Rev. Mater.* **2025**, *9*, 044003.
- [21] Pitsch, S. A.; Sumathi, R. R. Effect of polar faces of SiC on the epitaxial growth of graphene: Growth mechanism and its implications for structural and electrical properties. *Crystals* **2023**, *13*, 189.
- [22] Stanishchev, V.; Armakavicius, N.; Bouhafs, C.; Coletti, C.; Kühne, P.; Ivanov, I. G.; Zakharov, A. A.; Yakimova, R.; Darakchieva, V. Critical view on buffer layer formation and monolayer graphene properties in high-temperature sublimation. *Appl. Sci.* **2021**, *11*, 1891.
- [23] Kruskopf, M.; Pierz, K.; Pakdehi, D. M.; Wundrack, S.; Stosch, R.; Bakin, A.; Schumacher, H. W. A morphology study on the epitaxial growth of graphene and its buffer layer. *Thin Solid Films* **2018**, *659*, 7–15.
- [24] Ciochoń, P.; Marzec, M.; Olszowska, N.; Kołodziej, J. Reversible graphitization of SiC: A route towards high-quality graphene on a minimally step bunched substrate. *Appl. Surf. Sci.* **2020**, *528*, 146917.
- [25] Ridene, M.; Wassmann, T.; Pallecchi, E.; Rodary, G.; Girard, J. C.; Ouerghi, A. Epitaxial graphene on step bunching of a 6H-SiC(0001) substrate: Aromatic ring pattern and Van Hove singularities. *Appl. Phys. Lett.* **2013**, *102*, 111610.
- [26] Schumann, T.; Friedland, K. J.; Oliveira, M. H. Jr.; Tahraoui, A.; Lopes, J. M. J.; Riechert, H. Anisotropic quantum Hall effect in epitaxial graphene on stepped SiC surfaces. *Phys. Rev. B* **2012**, *85*, 235402.
- [27] Chen, L. X.; Wang, H. S.; Kong, Z. Q.; Zhai, C. W.; Wang, X. J.; Wang, Y. B.; Liu, Z. T.; Jiang, C. X.; Chen, C.; Shen, D. W. et al. Gaseous catalyst assisted growth of graphene on silicon carbide for quantum Hall resistance standard device. *Adv. Mater. Technol.* **2023**, *8*, 2201127.
- [28] Han, Y. C.; Yin, S. H.; Zheng, J. R.; Hu, Y. F.; Sun, L.; Zhang, L.; Tian, Z. Q.; Yi, J. Epitaxial growth of graphene on SiC by thermal shock annealing within seconds. *Adv. Funct. Mater.* **2024**, *34*, 2307298.
- [29] Huang, H. J.; Ren, Z. B.; Xue, X.; Guo, H. Y. C.; Chen, J. Y.; Guo, Y. L.; Liu, Y. Q.; Dong, J. C. Unconventional near-equilibrium nucleation of graphene on Si-terminated SiC(0001) surface. *Angew. Chem., Int. Ed.* **2025**, *64*, e202417457.
- [30] Sato, K.; Maekawa, T.; Oku, Y.; Nakahara, K.; Norimatsu, W. Suppression of step bunching in graphene growth on 4° off-axis SiC(0001) by a two-step growth technique. *Appl. Phys. Lett.* **2025**, *127*, 081602.
- [31] Chen, J. D.; Sun, C. Z.; Lin, D. Q.; Chen, X. P.; Zhang, Y. N.; Zhang, F.; Fu, D. Y.; Zhang, R. Anisotropic growth mechanism of epitaxial graphene on 4H-SiC. *Appl. Surf. Sci.* **2025**, *690*, 162596.
- [32] Chen, X. F.; Yang, X. L.; Xie, X. J.; Peng, Y.; Xiao, L. F.; Shao, C.; Li, H. D.; Hu, X. B.; Xu, X. G. Research progress of large size SiC single crystal materials and devices. *Light Sci. Appl.* **2023**, *12*, 28.
- [33] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [34] Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- [35] Kresse, G.; Furthmüller, J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- [36] Cohen, M. L.; Schlüter, M.; Chelikowsky, J. R.; Louie, S. G. Self-consistent pseudopotential method for localized configurations: Molecules. *Phys. Rev. B* **1975**, *12*, 5575–5579.
- [37] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- [38] Adelman, B.; Hellmann, R. A study of SiC decomposition under laser irradiation. *Appl. Phys. A* **2017**, *123*, 454.
- [39] Fromm, F.; Oliveira, M. H. Jr.; Molina-Sánchez, A.; Hundhausen, M.; Lopes, J. M. J.; Riechert, H.; Wirtz, L.; Seyller, T. Contribution of the

- buffer layer to the Raman spectrum of epitaxial graphene on SiC(0001). *New J. Phys.* **2013**, *15*, 043031.
- [40] Milenov, T.; Rafailov, P.; Yakimova, R.; Shteplyuk, I.; Popov, V. Raman fingerprint of the graphene buffer layer grown on the Si-terminated face of 4H-SiC(0001): Experiment and theory. *J. Raman Spectrosc.* **2024**, *55*, 416–424.
- [41] Maeda, F.; Takamura, M.; Hibino, H. Core-level photoelectron spectroscopy study on the buffer-layer formed in approximately atmospheric pressure argon on n-type and semi-insulating SiC(0001). *Surf. Sci.* **2023**, *733*, 122292.
- [42] Mastropasqua, C.; El Alouani, A.; Paillet, M.; Portail, M.; Koudia, M.; Abel, M.; Cordier, Y.; Jouault, B.; Berbezier, I.; Juillaguet, S. et al. Self-limited monolayer graphene growth on SiC with propane-hydrogen CVD. *npj 2D Mater. Appl.* **2025**, *9*, 32.
- [43] Chen, X. N.; Wang, X. H.; Fang, D. A review on C1s XPS-spectra for some kinds of carbon materials. *Fuller. Nanotub. Carbon Nanostruct.* **2020**, *28*, 1048–1058.
- [44] Jabra, Z. B.; Berbezier, I.; Michon, A.; Koudia, M.; Assaf, E.; Ronda, A.; Castrucci, P.; De Crescenzi, M.; Vach, H.; Abel, M. Hydrogen-mediated CVD epitaxy of graphene on SiC: Implications for microelectronic applications. *ACS Appl. Nano Mater.* **2021**, *4*, 4462–4473.
- [45] Zhao, J.; Ji, P. X.; Li, Y. Q.; Li, R.; Zhang, K. M.; Tian, H.; Yu, K. C.; Bian, B. Y.; Hao, L. Z.; Xiao, X. et al. Ultrahigh-mobility semiconducting epitaxial graphene on silicon carbide. *Nature* **2024**, *625*, 60–65.
- [46] Nair, M. N.; Palacio, I.; Celis, A.; Zobelli, A.; Gloter, A.; Kubsky, S.; Turmaud, J. P.; Conrad, M.; Berger, C.; de Heer, W. et al. Band gap opening induced by the structural periodicity in epitaxial graphene buffer layer. *Nano Lett.* **2017**, *17*, 2681–2689.
- [47] Kruskopf, M.; Pakdehi, D. M.; Pierz, K.; Wundrack, S.; Stosch, R.; Dziomba, T.; Götz, M.; Baringhaus, J.; Aprojanz, J.; Tegenkamp, C. et al. Comeback of epitaxial graphene for electronics: Large-area growth of bilayer-free graphene on SiC. *2D Mater.* **2016**, *3*, 041002.
- [48] Luxmi; Srivastava, N.; He, G. W.; Feenstra, R. M.; Fisher, P. J. Comparison of graphene formation on C-face and Si-face SiC{0001} surfaces. *Phys. Rev. B* **2010**, *82*, 235406.



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