Controlled Growth of Single-Crystal Graphene Films

Jincan Zhang, Li Lin, Kaicheng Jia, Luzhao Sun, Hailin Peng,* and Zhongfan Liu*

Grain boundaries produced during material synthesis affect both the intrinsic properties of materials and their potential for high-end applications. This effect is commonly observed in graphene film grown using chemical vapor deposition and therefore caused intense interest in controlled growth of grain-boundary-free graphene single crystals in the past ten years. The main methods for enlarging graphene domain size and reducing graphene grain boundary density are classified into single-seed and multiseed approaches, wherein reduction of nucleation density and alignment of nucleation orientation are respectively realized in the nucleation stage. On this basis, detailed synthesis strategies, corresponding mechanisms, and key parameters in the representative methods of these two approaches are separately reviewed, with the aim of providing comprehensive knowledge and a snapshot of the latest status of controlled growth of single-crystal graphene films. Finally, perspectives on opportunities and challenges in synthesizing large-area single-crystal graphene films are discussed.

1. Introduction

Graphene, the thinnest carbon material with atoms arranged in a honeycomb lattice, possesses unique and extraordinary mechanical, electrical, and thermal properties.[1,2] A variety of eye-catching applications of graphene are being pursued by academia and industry and it has many advantages when used in ultrahigh-speed electronics,[3] flexible transparent conductive films,[4–5] solar cells,[5] separation membranes,[6] and transmission electron microscopy (TEM) imaging.[7] To date, the best quality graphene (considering the concentration of defects) has been obtained by mechanically exfoliating highly oriented pyrolytic graphite.[8] However, this method is limited by poor scalability considering the limited size of graphene flakes and the difficulty in carefully controlling the number of layers.[1] Various methods to synthesize graphene have been developed to address these challenges, among which chemical vapor deposition (CVD) has emerged as the most promising technique, owing to its capability to provide high-quality, large-area production, controllability of the number of layers, and good repeatability.[9–12] Large-area graphene films have been acquired on the surface of certain substrates, among which, Cu is considered as one of the best metal substrate materials because of its low carbon solubility, well-controlled surface, and low cost. And a high-quality single-layer graphene film was successfully synthesized on Cu for the first time in 2009.[9]

Graphene grain boundaries (GGBs), which form in regions where graphene domains with different orientations merge, are observed as line defects in graphene film. These line defects often consist of pentagonal, heptagonal, and octagonal rings along the edges of the merging graphene domains (Figure 1a–c) and result in degradation of the thermal, electrical, and chemical properties of graphene (Figure 1d–f).[13–18] For instance, the electrical performance of graphene is degraded by the additional scattering centers induced by GGBs; causing a reduction in the carrier mobility and conductivity of graphene.[19] Lee et al. used the nanoindentation method to analyze the influence of GGBs on the mechanical properties of suspended graphene films and found that the mechanical strength of graphene in the region of the GGBs highly decreased.[20] Specifically, the fracture loads were ≈20–40% smaller in the GGBs than in the center of single-crystal domains,[20–22] especially in small-angle defect configurations (Figure 1f),[23] which exhibited a higher defect density and were more difficult to heal.[24,25] By systematically comparing the thermal and electrical conductivities of polycrystalline graphene samples with different domain sizes, Cheng’s group further confirmed the negative influence of GGBs on the thermal and electrical properties of graphene.[14] Overall, to improve the quality of CVD-grown graphene films, there is a great need to synthesize large-area single-crystal graphene.[11,14]

Over the past ten years, numerous efforts have been devoted to growing monolayer graphene samples with larger domain sizes and reduced GGBs. Following the first synthesis of centimeter-sized graphene single crystal by Ruoff’s group in 2013,[26] meter-sized[27] and wafer-sized[28] single-crystal graphene samples have been successfully synthesized on Cu foil...
and Cu film substrates in 2017, respectively. The methods used in these studies can be classified into two approaches depending on whether the single-crystal graphene films were grown from one seed or multiple seeds, as shown in Figure 2. In the single-seed approach, control of the nucleation density is vital to acquire graphene domains as large as possible.\cite{26} As for the multiseed approach, control of the grain orientation is critical to ensure alignment of the graphene domains, which further leads to the seamless stitching of adjacent domains.\cite{29}

Here, we focus on the controlled CVD growth of single-crystal graphene films, especially on Cu substrates. First, the elementary steps of graphene growth are carefully discussed and the nucleation step is identified as being vital in acquiring single-crystal graphene. Next, attention is devoted to current synthesis strategies, key parameters, and representative results of single- and multiseed approaches in enlarging graphene domain sizes. In detail, for the single-seed method, we discuss the significance of reducing the nucleation density by pretreating the substrate and regulating the feedstock. For the multiseed method, the epitaxy relationship between graphene and the underlying single-crystal metal substrate are analyzed, followed by the discussion on seamless merging of well aligned graphene domains. In particular, the main strategies to prepare single-crystal metal substrates (sub-micrometer thin films and tens of micrometer thick foils) are comprehensively summarized. The final section compares the single-seed and multiseed approaches and provides the outlook on the opportunities and challenges in terms of the mass production of high-quality single-crystal graphene films for the high-end applications.

2. Graphene Growth via CVD

In this section, we mainly focused on the growth dynamics and elementary steps of graphene growth on Cu surfaces. Because of the low solubility of carbon in Cu and the weak Cu–C interaction, the growth of graphene on Cu is a self-limiting surface reaction.\cite{30} That is, when the Cu surface is fully covered by graphene and the Cu catalyst is no longer exposed to hydrocarbons, the catalytic growth of graphene by Cu is terminated, due to its self-limiting growth mechanism.\cite{31} Meanwhile, recent reports concerning the synthesis of single-crystal graphene films on CuNi alloys,\cite{31,32} where the Ni content is no higher than 20%, are also based on the surface-mediated mechanism.

The CVD process for growing graphene mainly includes four steps: heating, annealing, growth, and cooling.\cite{33} The annealing and growth steps are the most important steps for synthesizing high-quality graphene crystals; annealing is required to pre-clean and flatten the substrate, whereas the growth step can be controlled by changing the precursors,\cite{34} substrate types,\cite{12} growth pressure,\cite{35} and other parameters.\cite{33} Generally, after the annealing step, carbon feedstocks are introduced into the CVD system for graphene growth via gas flow control.\cite{36} Then, growth of graphene film on the Cu surface can be divided into seven elementary steps (Figure 3). Active carbon species are formed both on the Cu surface and in the gas phase after dehydrogenation of the carbon sources. Meanwhile, there is a dynamic balance between the adsorption and the desorption of active carbon species from Cu surface. The active carbon species then diffuse over the Cu surface and agglomerate at the active sites on Cu surface to form graphene nucleation seeds and then diffuse to the edge of graphene nuclei to enlarge graphene domain size. It should be noted that the nucleation step is vital, to the control over both the nucleation density and lattice orientation with regard to synthesizing large-area single-crystal graphene films.
The decomposition of carbon feedstock molecules (e.g., CH₄) would supply active carbon species for graphene nucleation and growth. The first dehydrogenation reaction of methane is highly endothermic,[37] and its reaction energy is as high as 4.8 eV. Compared with the gas phase reaction, dehydrogenation of the carbon feedstock would become more favorable on metal substrates. The dehydrogenation of methane on Cu surfaces has already been systematically investigated. All hydrogenation steps are endothermic with an activation energy barrier ranging from 1.0 to 2.0 eV (Figure 1a).[37–39] The decomposition process for other carbon sources (e.g., C₂H₄) is also endothermic. The Cu surface can adsorb active carbon species and accelerate the dehydrogenation reaction of CH₄. Unlike the hydrogenation on more active metal substrates, such as Pd,[40] Ru,[41] and Ni,[42] CH cannot decompose into H and C atoms on the Cu surface because of its relatively weak catalytic activity. Instead, partially dehydrogenated species (e.g., CHₓ) would react with each other as a result of their unfavorable dehydrogenation thermodynamics before generating hydrogen-free products. Considering the intermediate species on metal substrates, the carbon dimer is the dominant feeding species in the epitaxial growth and morphological phase transition of graphene on different Cu substrates.[43] Snapshots from molecular dynamics (MD) simulations of a CH-covered Cu(111) surface showed that C₂H₂ groups were easily formed.[37] Typically, the reaction of two CH species is exothermic (emitting 1.94 eV of energy) with an activation barrier of only 0.3 eV. Further combination of C₂H₂ with an additional CH is also exothermic, with reaction energy of 0.98 eV (Figure 1b). The final dehydrogenation process occurs when the CH species adhere to the edges of the graphene nuclei. The occurrence of this process is supported by both MD simulations of C₂H₂ stability on a Cu surface to produce C atoms and experimental observations of C–H bond breakage after the formation of C₂H₄.[44] Therefore, this phenomenon also indicates that dehydrogenation is involved in the overall graphene growth process, as confirmed by isotope-labeling experiments.[30] In addition, desorption of active carbon species from Cu surface is non-negligible and the gas phase compositions might also influence the nucleation behaviors of graphene.[36,45,46]

The formation energy of carbon clusters on Cu(111) surfaces can be described by Equation (1)

\[ E_{\text{form}} = \left( E_{\text{tot}} - E_{\text{Cu(111)}} - N \times E_{\text{C,alone}} \right) / N \]

(1)

where \( E_{\text{tot}} \) is the total energy of the system after relaxation, \( E_{\text{Cu(111)}} \) is the energy of the Cu(111) phase after relaxation, and \( E_{\text{C,alone}} \) is the energy per C atom. When \( N \) is smaller than 13, the formation energy of linear structures, where only two terminal atoms bond with the surface, is always smaller than that of 2D ring structures (Figure 5a,b).[47,48] Because the C–C interaction is stronger than the C–Cu interaction, structures with fewer C–Cu bonds would be more stable. The largest difference appears when \( N = 4 \) or 8, as these structures cannot...
form closed hexagonal shapes. However, a further increase in the number of carbon atoms results in a compact configuration composed of pentagons, hexagons, and heptagons that impart greater stability.[49] These formed sp²-C hybridized carbon clusters on the metal surface have been investigated using both in situ scanning tunneling microscopy (STM)[48] and density functional theory (DFT) simulations.[50] For example, low temperature in situ STM images of graphene growth intermediates, including carbon dimers, carbon rectangles, and zigzag and armchair-like carbon chains, could be observed during the high-temperature CVD growth of graphene on Cu surfaces.[51]

The transition of the carbon cluster from a 1D chain to a 2D compact structure must overcome a significant energy barrier when CH attaches to a magic carbon cluster during the final dehydrogenation process.[52] Therefore, even though the formation energy decreases as the number of carbon atoms for small carbon clusters increases, a nucleation barrier still exists. Ding’s group found that with an increasing number of carbon atoms, a compact configuration composed of pentagons, hexagons, and heptagons further increases in stability, leading to the formation of graphene with a closed hexagonal structure.

---

**Figure 2.** Two approaches for the controlled growth of single-crystal graphene. The upper is the single-seed approach, where control of the nucleation density is critical to grow graphene single crystals as large as possible and the lower is the multiseed approach where the orientation of graphene nuclei should be aligned to guarantee the seamless merging of adjacent graphene islands without forming defective GGBs.

**Figure 3.** Growth mechanism of graphene on Cu. I: Gas reaction. II: Adsorption and desorption of active species from the substrate surface. III: Dehydrogenation of carbon sources on the Cu surface. VI: On-surface diffusion of active species. V: Graphene nucleation. VI: Lateral growth of graphene islands. VII: Merging of adjacent graphene domains.
atoms (C₃), the configuration for large carbon clusters changed from a chain to a compact shape. They also calculated the ground state structure of adsorbed magic carbon clusters with 16–26 atoms and found that the high symmetry (C₃v) core–shell structured C₂₁ is very stable on Rh(111), Ru(0001), Ni(111), and Cu(111) surfaces (Figure 5c,d).

The nucleation process consists of four main steps (Figure 6): (1) adsorption and decomposition of the carbon source with an energy barrier of $E_{\text{ad}}$; (2) diffusion of the active carbon species produced in the first step with an energy barrier of $E_d$; (3) desorption of the active carbon species from the substrate surface with an energy barrier $E_{\text{des}}$; and (4) attachment of the active carbon species to the edges of graphene islands with an energy barrier $E_{\text{att}}$. In the low-temperature region, graphene growth is mainly capture controlled, as described by Equation (2), whereas in the high-temperature region, it is...
Figure 6. Dependence of graphene nucleation and growth on the concentration of active carbon species. Schematic illustration of nucleation and the growth mechanism of graphene on Cu. The decomposition of methane leads to the supersaturation of carbon atoms on the Cu surface. When \( c_{\text{Cu}} \) reaches a critical supersaturation point \( (c_{\text{nuc}}) \) graphene domains nucleate and begin to grow, possibly involving multiatom carbon cluster formation and attachment of the clusters. Reproduced with permission. Copyright 2012, American Chemical Society.

mainly desorption controlled, where the desorption step needs to be included, as shown in Equation (3)

\[
N^2_\text{nuc} \sim P_{\text{CH}_4} \times \left( \frac{2E_{\text{ad}} - E_{\text{d}} - E_{\text{sl}}}{kT} \right)
\]

\[
N^2_\text{nuc} \sim P_{\text{CH}_4} \times \exp \left( \frac{E_{\text{ad}} + E_{\text{m}} - E_{\text{d}} - E_{\text{sl}}}{kT} \right)
\]

For the critical nucleation size \( N^0 \), as shown in Equation (4), the nucleation barrier can be defined as

\[
G(N) = E(N) - \Delta \mu \times N
\]

where \( \Delta \mu \) is the chemical potential difference between the carbon surface and graphene lattice, and \( E(N) \) is the formation energy of carbon clusters on metal substrates, which can be obtained using Equation (5)

\[
E(N) = E(C_N@M) - E(M) - N \times E_C
\]

where \( E(C_N@M) \) is the energy of the carbon clusters on metal surfaces for the number of carbon atoms \( N \), \( E(M) \) is the energy of the metal substrates, and \( E_C \) is the energy of single carbon atoms. Hence, the nucleation barrier can be calculated.

As shown in Equation (6), the chemical potential of C and H can be expressed as

\[
\mu_C = -2\mu_{H_2} - 10.152 + 0.112\ln \chi
\]

where \( \chi \) is the ratio of the partial pressures of \( H_2 \) and \( \text{CH}_4 \), \( \mu_C \) and \( \mu_{H_2} \) are the chemical potentials of C and H, respectively, and \( \mu_{H_2} \) is directly related to the partial pressure of hydrogen gas in the ideal gas state. In the case of fixed \( \mu_C \), \( \mu_{H_2} \) is also related to the partial pressure of hydrogen; if the chemical potential of carbon clusters is larger than \( \mu_C \), they will react with hydrogen. Generally, with increasing \( \text{CH}_4/\text{H}_2 \) ratio, the number of carbon atoms required for forming stable nuclei would gradually decrease. For example, the number of carbon atoms for stable nucleation decreased from 24 to 6 when the \( \text{CH}_4/\text{H}_2 \) partial pressure ratio increased from 1/20 to 20.

As expressed by Equation (7), a higher \( E_d \) value results in a lower nucleation rate and thus a longer nucleation time

\[
k = A e^{-\frac{E_d}{RT}}
\]

where \( k \) is the nucleation rate constant, \( T \) is the growth temperature, \( A \) is the pre-exponential factor, and \( R \) is the ideal gas constant. Meanwhile, the collision frequency of active carbon species increases as the carbon concentration increases. Therefore, the nucleation barrier and local carbon source concentration are two key factors determining the nucleation density of graphene, both of which affect the critical size of the stable graphene nuclei.[53,54]

After nucleation, individual graphene islands begin to extend laterally. Because the concentration and energy barrier for graphene growth is much lower than that required for new nucleation, the growth rate is higher than the nucleation rate. Defect healing is another microreaction for enabling the growth of high quality CVD-grown graphene. Vacancy or bivacency defects within graphene lattices can be easily healed with the assistance of metal substrates to minimize the total energy of the system. However, in the case of grain boundaries, although small-angle graphene domains can easily coalesce with a lower defect density after relaxation, it is impossible for these defects to be completely healed.[55] Thus, it is the nucleation step that decides the final quality of the graphene film, especially in regards to the density of graphene grain boundaries.

In all, the nucleation step is important for both single-seed and multiseed approaches (Figure 2). For the single-seed approach, control of the nucleation density is critical to grow graphene single crystals as large as possible and the metal substrates are commonly polycrystalline, since its graphene domain can cross metal grain boundaries without changing its orientation.[56] By contrast, for the multiseed approach, the single-crystal metal substrates satisfying good lattice matching relationship with graphene seeds are required for the aligned nucleation, epitaxy growth, and following seamless merging of graphene domains to avoid the formation of defective graphene grain boundaries.[58]

3. The Single-Seed Approach

Drastically reduction of the graphene nucleation density is a direct and simple approach for growing large graphene single crystals with improved film quality. In this review, we classified the main strategies toward reduced nucleation density into two types: one focuses on the control of active sites by modulation of
surface characteristics of the metal substrates before graphene growth, and the other one mainly concerns about the control of carbon source supply during graphene growth (Figure 7).

### 3.1. Control of Active Sites

#### 3.1.1. Reduction of Active Sites

Active sites are generally reported to be the sites with higher surface roughness or covered by impurity or contamination on the surface.\[^{57,58}\] For example, Ding’s group also found that the graphene nucleation barrier on the terrace was ≈2 eV higher than that on Cu step.\[^{49}\] Therefore, flattening and cleaning the substrate surface, which are generally simultaneously fulfilled by surface pretreatment processes, are necessary to suppress the graphene nucleation. In the past ten years, numerous methods have been reported to pretreat substrates to grow large graphene single crystals, including surface rinsing, etching, polishing, and annealing (Table 1). These methods can be divided into ex situ and in situ pretreatment processes, according to whether they are conducted in the CVD chamber.

The ex situ pretreatment methods include surface rinsing, etching, and polishing. In the early stage, some researchers successively rinsed Cu foils with acetone, isopropanol, and deionized water to remove the surface organic contamination\[^{59,60}\] while others used acid solution to etch away the oxide-containing layer (e.g., CuO and Cu$_2$O).\[^{60,61}\] For example, the first reported centimeter-scale graphene crystal was grown on Cu foil whose surface was exposed to acetic acid for 8 h.\[^{26,62}\] Besides, Cu surface can also be etched by FeCl$_3$, Na$_2$S$_2$O$_8$, H$_2$O$_2$, KOH, and HNO$_3$ solutions by etching both Cu and oxide (e.g., CuO and Cu$_2$O) on the surface.\[^{60,61}\] More importantly, polishing processes, including electrochemical polishing\[^{65}\] and chemical mechanical polishing (CMP) methods,\[^{54,66,67}\] have been widely used to pretreat metal substrates for growing large graphene single crystals. The constituents of the polishing agent and specific treatment conditions significantly influence the flatness of the Cu foil. Recently, a dramatic reduction in the roughness of a Cu substrate by 99% was achieved using an optimized double-plateau Cu surface planarization method.\[^{68}\]

High-temperature annealing is an efficient in situ way to reduce the nucleation density of graphene on the substrate surface, which is often conducted after ex situ pretreatment process. Generally, higher annealing temperature, longer duration, and higher pressure can be expected to produce more suitable substrates for reducing the nucleation density.\[^{69}\] The annealing temperature is usually higher than the premelting point of Cu, and it can even exceed the melting point of Cu (1082 °C).\[^{70}\] Considering the high vapor pressure of Cu (≈10$^{-7}$ bar), the sublimation of Cu is significant, especially in low-pressure CVD (LPCVD) systems, which would increase the surface roughness of the metal substrates.\[^{71}\] To solve this, James Tour group synthesized millimeter-sized single-crystal graphene based on a CVD system with controlled chamber pressure. That is, they annealed the polished Cu foil for 7 h at a high pressure to efficiently suppress the sublimation of Cu and then grew large graphene single crystals at a low pressure (Figure 8a,b).\[^{72}\] Moreover, the introduction of novel Cu enclosure or stacking structures to decrease the evaporation loss of Cu was also

### Table 1. Representative substrate pretreatment methods.

| Methods            | Key parameters                                      |
|--------------------|-----------------------------------------------------|
| Rinsing            | Acetone, isopropyl alcohol, deionized water\[^{59,60}\] |
| Chemical etching   | FeCl$_3$, Na$_2$S$_2$O$_8$\[^{63,64}\]               |
|                    | CH$_3$COOH, HNO$_3$, HCl, HF, KOH\[^{61,62}\]         |
| Electrochemical polishing | H$_2$PO$_4$-ethylene glycol (3:1 volume ratio), 1.0–2.0 V working voltage, 20–30 min\[^{65}\] |
|                    | H$_2$O (100 mL) + ortho-phosphoric acid (50 mL) + ethanol (50 mL) + isopropyl alcohol (10 mL) + urea (1 g), 4.8 V working voltage, 1 min\[^{72}\]/8 V working voltage, 1–2 min\[^{44}\] |
| CMP                | Cu film deposited on the wafer and pressed against a rotating pad through a slurry, which contains a fine abrasive grain (colloidal SiO$_2$ particles, 13 nm in diameter, 30 vol%), oxidizer (H$_2$O$_2$, 3 wt%), complex agent (glycine, 3 wt%), inhibitor (benzotriazole, 0.5 × 10$^{-3}$ M), surfactant (hydroxethyl cellulose, 0–0.003 wt%), and HNO$_3$ as regulator to make pH = 4\[^{47}\] |
| Annealing          | H$_2$, 7 h, atmospheric pressure\[^{72}\]               |
|                    | Nonreduction atmosphere, 7 h, low pressure\[^{72}\]     |
|                    | Cu stacking/enclosure structure, low pressure\[^{72}\] |

---

**Figure 7.** Strategies toward large single-crystal graphene via single-seed approach. Strategies i and ii focused on the modulation of surface characteristics of the metal substrates to reduce (strategy i) or passivate (strategy ii) the active sites, which are the sites with lower energy barrier for graphene nucleation on the substrate surface. For the former, the active sites disappeared, while for the latter the active sites still exist but lose their preferential nucleation functions. Strategies iii and iv focused on the modulation of carbon source supply by controlling the supply quantity and positions. In detail, decreased carbon source supply resulted in a decreased possibility to overcome the nucleation barriers as shown in Figure 6 while the local feeding method can define the sites for graphene nucleation and growth without generating other nuclei elsewhere.
shown to effectively increase the smoothness of the Cu surface under low-pressure conditions (Figure 8c–f)\cite{70,34,71,73,74}. For example, after growth for 6 h, 5 mm sized graphene single crystals were observed on the inner surface of the Cu enclosure (Figure 8c,d).\cite{71} Under free molecular flow, fast growth of sub-centimeter-sized graphene domains were also achieved on monocrystallized Cu(100) surface (Figure 8e,f).\cite{74}

Various gases (e.g., Ar, N\textsubscript{2}, H\textsubscript{2}, CO\textsubscript{2}, and O\textsubscript{2}) have been utilized for substrate annealing in order to remove impurities (e.g., native Cu oxides and carbon impurities), and flatten the substrate surface.\cite{75–77} For example, the graphene nucleation density on the Cu surface was notably reduced using an extended pregrowth annealing process in a hydrogen atmosphere to obtain sub-millimeter-sized graphene single crystals.\cite{78} Typically, the reduction of Cu after significant surface oxidation more efficiently decreases the nucleation density because the Cu surface smoothness is increased by both the reduction of preformed CuO\textsubscript{x} and the oxidation of carbon impurities on the surface or in the bulk of Cu foils.\cite{79}

The utilization of Cu film in the liquid state is also beneficial for reducing the roughness of the Cu surface and growth of large-size single-crystal graphene. The groups of Liu and Warner both demonstrated the fabrication of Cu surfaces with increased smoothness after performing the reaction above the melting point of Cu (1084 °C).\cite{80,81} A comparison of the root-mean-square (RMS) roughness extracted from atomic force microscopy (AFM) images revealed that the melted and resolidified Cu surface has an RMS value of only 8 nm, whereas the as-received, thermally annealed, and electropolished samples had values of 166, 81, and 48 nm, respectively.\cite{70} To further decrease the nucleation density and increase the domain size, Gu and co-workers developed a melting-solidification pretreatment process to obtain smooth Cu foil before nucleation. This facile method was used to successfully grow millimeter-sized, hexagonally shaped, monolayer, graphene single crystals on commercial metal foils (Figure 9a–c).\cite{70} When using the noble metal Pt, extensive annealing steps are also practical for growing millimeter-sized single crystals, as reported by Cheng’s group in 2012.\cite{76} Moreover, the introduction of a thin, liquid silicon-containing layer on the Pt surface can more efficiently reduce the influence of defects, roughness, and crystallographic orientation. Indeed, the formation of a Pt\textsubscript{1}Si\textsubscript{x} liquid wetting film can screen the platinum lattice and fill topographic defects to increase the crystallinity and uniformity of millimeter-sized single-crystal graphene (Figure 9d–f).\cite{82}

### 3.1.2. Passivation of Active Sites

The methods discussed above are concentrated on reducing the surface roughness or increasing the surface cleanliness to decrease the number of active sites and thus control the nucleation density of graphene on Cu surfaces. In contrast with the strategies utilized to reduce the amount of active nucleation sites by cleaning and flattening the substrate surface, preoccupying these active sites using other agents before graphene nucleation is also effective to reduce the nucleation density of graphene. We named this strategy as “passivation of the active sites” and the introduction of passivators, such as O\textsubscript{2} and melamine, is more efficient and time saving for growing large graphene single crystals.

Oxygen passivation is an efficient strategy to reduce nucleation density, since O\textsubscript{2} is able to more actively occupy the active sites on Cu, thus prohibiting the formation of graphene nuclei, owing to the inferior catalytic ability of CuO\textsubscript{x} compared to that of Cu. Ruoff’s group systematically compared the nucleation density, growth rate, and domain size of graphene grown on Cu foil with and without the assistance of oxygen and variations...
in the nucleation density of up to several orders of magnitude was observed. Centimeter-sized graphene single crystals were produced for the first time using oxygen rich Cu foil or by deliberately introducing oxygen during the CVD process (Figure 10a–d). Duan's group reported a pathway for growing millimeter-sized single-crystal graphene on a Cu substrate using pregrowth ramping/annealing in a nonreducing environment at a low pressure, taking advantage of the traces of oxygen in Ar (Figure 10e). The as-formed Cu$_2$O layer decreased the nucleation density by more than five orders of magnitude and 5 mm graphene single crystals were obtained after 48 h of growth. Luo's group also proved the effect of oxygen by demonstrating that the nucleation density depended on the annealing time after introduction of trace amounts of oxygen.

Wang et al. further studied the impact of trace amounts of gaseous oxidants in the CVD system, including water and oxygen, and found that they were responsible for graphene etching, which further modulated the nucleation and growth behavior of graphene. By introducing KOH to absorb unwanted H$_2$O impurities in the gas, and optimizing the concentration of O$_2$ and the relative ratios of O$_2$/CH$_4$ and O$_2$/H$_2$, centimeter-scale domains were achieved with good repeatability. Liu's group also reported that the introduction of O$_2$ assisted not only in transforming the Cu surface from a rough polycrystalline state into a flat monocristalline Cu(100) plane, but also in reducing the nucleation density. As a result, millimeter-sized graphene crystal patterns were formed on Cu surface (Figure 8f).

The melamine pretreatment process was developed to passivate active sites and control graphene nucleation on Cu surfaces to achieve the growth of centimeter-sized graphene single crystals (Figure 11a,b). The control over nucleation density also relies on introducing foreign species to passivate Cu active sites. Surprisingly, the nucleation density decreases nearly four orders of magnitude after the introduction of melamine pretreatment. Generally, the entire process of graphene growth on melamine-pretreated Cu foil can be classified into three stages. First, the carbon- and nitrogen-containing species preferentially accumulate at the active sites on the Cu surface, which led to the passivation of these active. For example, Auger electron spectroscopy (AES) confirmed the spatial accumulation of these compounds in regions of Cu grain boundary. After the melamine pretreatment, the formation of graphene nuclei is only possible on a flat surface, rather than at defective sites on the Cu surface, indicating that the passivation effect is preserved (Figure 11c,d). Finally, during the sequential graphene growth stage, nitrogen-containing compounds are gradually released from these active sites, which in turn avoid the introduction of heteroatoms into the graphene lattice (Figure 11e).
Similar with melamine, 2-amino-4-methoxy-6-methyl-1,3,5-triazine (AMOMT, one of the ramifications of melamine), has also been proven efficient in the passivation of active sites on Cu foil. Based on the thermogravimetric curves of these molecules, the heating temperatures range from 170 to 250 °C with an optimal passivation time of ≈10 min.

**Figure 10.** Growth of large graphene single crystals based on passivation of active sites with the assistance of oxygen. a) Photographic image of centimeter-sized single-crystal graphene on Cu foil after weak oxidation. b) Comparison of graphene nucleation density without (black) and with (red) oxygen exposure. c,d) Typical SEM images of graphene nuclei on a Cu surface with the same CH₄ to H₂ ratio and growth time with (c) and without (d) the introduction of oxygen. a–d) Reproduced with permission.[26] Copyright 2014, American Association for the Advancement of Science. e) Photographic image of millimeter-sized graphene single crystals transferred onto a 300 nm SiO₂/Si substrate. Inset: optical image of a graphene single crystal transferred on a 300 nm SiO₂/Si substrate. Reproduced with permission.[77] Copyright 2012, American Chemical Society. f) Photographic image of millimeter-sized single-crystal graphene prepared via the O₂ passivation approach. g) Dependence of the nucleation density on annealing time with the introduction of trace amounts of oxygen. f,g) Reproduced with permission.[83] Copyright 2013, American Chemical Society.

**Figure 11.** Growth of large graphene single crystals based on passivation of active sites using melamine. a) Illustration of the effect of melamine to passivate active sites. b) Photographic image of a centimeter-sized single crystal of graphene transferred onto a 300 nm SiO₂/Si substrate. c,d) Comparison of graphene nucleation density without (c) and with (d) melamine passivation. e) AES analysis of nitrogen element at the Cu grain boundary before, during, and after graphene growth. a–e) Reproduced with permission.[85] Copyright 2016, American Chemical Society.
that the collaborative passivation of oxygen and AMOMT can collaboratively decrease the nucleation density, from 600 to 0.57 cm$^{-2}$.[86]

### 3.2. Controlling the Supply of Carbon Species

#### 3.2.1. Repeated Growth–Etch–Regrowth and Multistage Carbon Supply

Control of the supply of carbon species, e.g., by decreasing the flow rate of carbon source or increasing the supply of carrier gas, is effective to reduce the formation of active carbon species to further control the graphene nucleation density.[78] This strategy can be applied to all metal substrates in both atmospheric pressure CVD (APCVD) and LPCVD systems, and is also compatible with other types of carbon sources in CVD systems.[34,87] For example, ethane, with a lower energy barrier for decomposition, was used to grow sub-centimeter-sized graphene single crystals at an increased growth rate after precise control the flow rate ratio of hydrogen to ethane.[34] Moreover, the low partial pressures of ethanol vapor were proven to be efficient for growing 5 mm hexagonal single-crystal graphene on a preoxidized Cu surface.[87]

In 2011, the Ruoff’s group reported the growth of sub-millimeter-sized graphene grains using LPCVD with low carbon source supply content to reduce the nucleation density, which resulted in increased growth time.[71] In 2012, the groups of Cheng[76] and Wang[78] reported the growth of millimeter-sized graphene single crystals by increasing the flow ratio of hydrogen to methane, but this also extended the growth time considerably. For example, attempts to grow graphene domains on polycrystalline Pt substrates in an APCVD system, as the flow ratio of CH$_4$/H$_2$ decreases from 20/400 to 4/700, resulted in the enhanced size of the graphene grains from 50 to 1300 µm.[76] Combined with the repeated growth–etch–regrowth process, larger graphene domains can be subsequently possible by gradually decreasing the carbon supply during graphene growth (Figure 12a–d).[88]

In 2011, the Ruoff’s group reported the growth of sub-millimeter-sized graphene grains using LPCVD with low carbon source supply content to reduce the nucleation density, which resulted in increased growth time.[71] In 2012, the groups of Cheng[76] and Wang[78] reported the growth of millimeter-sized graphene single crystals by increasing the flow ratio of hydrogen to methane, but this also extended the growth time considerably. For example, attempts to grow graphene domains on polycrystalline Pt substrates in an APCVD system, as the flow ratio of CH$_4$/H$_2$ decreases from 20/400 to 4/700, resulted in the enhanced size of the graphene grains from 50 to 1300 µm.[76] Combined with the repeated growth–etch–regrowth process, larger graphene domains can be subsequently possible by gradually decreasing the carbon supply during graphene growth (Figure 12a–d).[88]

In 2011, the Ruoff’s group reported the growth of sub-millimeter-sized graphene grains using LPCVD with low carbon source supply content to reduce the nucleation density, which resulted in increased growth time.[71] In 2012, the groups of Cheng[76] and Wang[78] reported the growth of millimeter-sized graphene single crystals by increasing the flow ratio of hydrogen to methane, but this also extended the growth time considerably. For example, attempts to grow graphene domains on polycrystalline Pt substrates in an APCVD system, as the flow ratio of CH$_4$/H$_2$ decreases from 20/400 to 4/700, resulted in the enhanced size of the graphene grains from 50 to 1300 µm.[76] Combined with the repeated growth–etch–regrowth process, larger graphene domains can be subsequently possible by gradually decreasing the carbon supply during graphene growth (Figure 12a–d).[88]

Generally, with the increasing coverage of graphene film, the weak catalytic ability of Cu results in a slower growth rate and even incomplete graphene coverage.[89] To solve this, a two-step CVD method was developed by supplying excess carbon source during the final stage of graphene growth to ensure complete coverage.[89] However, it is difficult to avoid defects and secondary nucleation in the merging regions. On the other hand, large graphene domains were obtained by gradually increasing the partial pressure of methane from 8 to 18 ppm over 3 h while maintaining that of hydrogen at the same level.[35,90] Using this approach, Fulvio’s group synthesized sub-millimeter sized graphene crystals in an APCVD system.[35] Using the second passivation and multistage carbon supply strategy, Liu’s group achieved the rapid growth of 5 mm sized graphene crystals in an LPCVD system (Figure 12e–h).[65] After the first passivation step controlling the initial nucleation density, the second passivation step was conducted both to etch away unstable nuclei and suppress secondary nuclei when enhancing the carbon supply.

#### 3.2.2. Local Feeding of Carbon Source

The concept of “local feeding” of a carbon source was reported in 2017 by Xie’s group using a specific system design.[11] In this work, 1.5 in. sized graphene monolayer single crystals were
synthesized within 2.5 h using methane as a carbon source and optimized Cu$_{85}$Ni$_{15}$ alloy as the growth substrate (Figure 13a–c). Control of the nucleation density was achieved by locally feeding carbon precursors to a desired position through a quartz nozzle. Graphene growth was boosted by Ni-mediated isothermal segregation and enhanced catalytic ability of the CuNi alloy, together with a gradual increase in the feedstock concentrations. The novel design of growth substrates can also be used to optimize local carbon feeding. For example, a hole-pocket method was also developed to grow large-area single-crystal graphene on the inner surface of folded Cu foil, in which small holes were made to regulate permeation and the adsorption of gas.\cite{91} This was achieved by using perforated Ni foil above the Cu foil substrate to enable the selective nucleation of graphene on regions not covered by Ni (Figure 13d,e).\cite{92} Moreover, placement of other plain metal foils (e.g., W, Mo, or Ni) below the Cu foil that can dissolve additional carbon species also assist in decreasing the nucleation densities and synthesize large graphene single crystals with improved the uniformity and coverage of monolayer graphene.\cite{92,93} Deposition of these metal films on the backside of Cu foils also has similar effect. Recently, a new approach was reported to synthesize monolayer single-crystal graphene films on polycrystalline substrates based on “self-selection” of the fastest growing domain orientation, which eventually yields a continuous foot-long 2D film (Figure 13f,g).\cite{12} The key parameters in this approach included a high-velocity flow of buffer gas (mixture of H$_2$ and Ar) and Cu$_{80}$Ni$_{10}$ alloy substrate at a high temperature. Taken together, these parameters produce a sharp concentration gradient at the growth front of the graphene domains and undesired seeds are prevented from forming. Under such conditions, single-crystal graphene films can be prepared via smooth movement of the substrate at a sufficiently slow rate and with optimized precursor concentrations. The combination of local control of feed gases and high-velocity buffer gas in the direction of substrate movement may be also applicable to the growth of other 2D materials.

In all, the nucleation density is influenced by both the density of active sites and local carbon source concentration, wherein the distribution of active sites on surface is mainly related with the surface characteristics while the carbon source concentration can be precisely controlled via changing the gas flow conditions. Therefore, controlling both the active sites and carbon supply is more effective to decrease the nucleation density of graphene. Meanwhile, single-seed approach exhibits high repeatability and compatibility to grow large graphene single crystals, as verified by the works listed in Table 2. The representative works reporting the synthesis of graphene single crystals with sizes larger than 1 mm are summarized in Table 2 based on their publication time, with the main strategies and key parameters extracted.
4. The Multiseed Approach

Although suppressing the graphene nucleation is an effective approach for reducing density of GGBs, the corresponding lower growth rate and longer time for growing full-coverage graphene films greatly decreased the growth efficiency. By contrast, simultaneous growth and seamless merging of well-aligned graphene domains can reduce the growth time, which is suitable for large-area growth of single-crystal graphene with high efficiency. In this regard, monocrystallized metal substrates having an appropriate symmetry relationship with the lattice of graphene are used for epitaxial growth of aligned graphene seeds towards a continuous graphene film (Figure 14).

4.1. Orientation Dependence of Graphene on the Substrate

The orientation dependence of graphene on the substrate surfaces, which is vital to the aligned nucleation of graphene islands, is mainly determined by the interaction and the

Table 2. Representative works on the growth of large graphene single crystals using single-seed approach.

| Year | Domain size | Method | Detailed growth condition | Journal | Group |
|------|-------------|--------|---------------------------|---------|-------|
| 2011 | 0.5 mm      | Cu enclosure Low carbon supply | LPCVD, large-domain graphene was grown inside Cu enclosure at 1035 °C[71] | J. Am. Chem. Soc. | R. S. Ruoff |
| 2012 | 0.2 mm      | Melted Cu on W | APCVD, annealing, and growth above the melting point of Cu at 1090 °C[69] | ACS Nano | J. H. Warner |
|      | 0.4 mm      | Long time annealing | APCVD, Cu foils annealed at 1045 °C, 3 h in Ar (300 sccm) and H2 (50 sccm)[78] | J. Am. Chem. Soc. | W. J. Zhang |
|      | 1.3 mm      | Long time annealing Low carbon supply | APCVD, the flow ratio of CH4/H2 = 4/700 at growth temperature of 1040 °C on Pt substrate[79] | Nat. Commun. | H. M. Cheng |
|      | 2.3 mm      | Long time annealing with controlled pressure | APCVD, annealing at high pressure and growth at low pressure with 0.15 sccm CH4 and 70 sccm H2 on Cu foils[72] | ACS Nano | J. M. Tour |
| 2013 | 1 mm        | Cu melting and resolidification | APCVD, Cu foils melting at 1100 °C and then resolidifying at 1075 °C before graphene growth[72] | ACS Nano | G. Cu |
|      | 2 mm        | Annealing to flatten Cu surface | LPCVD, Cu tubes formed out of Cu foil for graphene growth[72] | Adv. Mater. | R. S. Ruoff |
|      | 5 mm        | Oxygen assistance Low carbon supply | LPCVD, nonreducing environment annealing to form Cu2O and growth graphene with high H2/CH4 ratio[73] | Nat. Commun. | X. F. Duan |
|      | 5.9 mm      | Oxygen assistance | APCVD, Ar annealing to form CuO seeds as graphene nucleation sites[83] | ACS Nano | Z. L. Luo |
|      | 10 mm       | Oxygen assistance | LPCVD, O2 treating Cu substrate and CH4 pressure about 1 × 10⁻³ torr[74] | Science | R. S. Ruoff |
| 2014 | 1.9 mm      | Suppressing Cu evaporation Repeated growth–etching–regrowth | Circumfluence CVD, inserting a copper foil into a tube with one close end[69] | Sci. Rep. | L. Wang |
|      | 3 mm        | Oxygen assistance | APCVD, introducing CH4 for initial graphene growth, then cutting off CH4 to induce graphene etching, after which CH4 was reintroduced for graphene regrowth[72] | ACS Nano | H. M. Cheng |
| 2015 | 1.4 mm      | Surface amorphization | APCVD, coating Pt foils with the liquid silicon-containing film[82] | Nat. Commun. | N. Grobert |
| 2016 | 0.5 mm      | Local feeding of carbon precursor | APCVD, Ni–Cu–Ni sandwich structure at growth temperature of 1075 °C[92] | ACS Nano | H. Ago |
|      | 1.5 in.     | Local feeding of carbon precursor | APCVD, local carbon precursor feeding on an optimized Cu64Ni15 alloy[11] | Nat. Mater. | X. M. Xie |
|      | =3 cm       | | | | |
|      | 3 mm        | Cu stacking structure, oxygen assistance | LRPCVD, graphene growth on the pretreated Cu foil after surface monocrystallization[76] | Adv. Mater. | Z. F. Liu |
|      | 4 mm        | Substrate second passivation | LPCVD, vacuum annealing twice to etch away the unstable nuclei and control the nucleation density[75] | Adv. Mater. | Z. F. Liu |
|      | =1 cm       | Melamine passivation | LPCVD, melamine powders heated at 120 °C for the transportation of the melamine to the Cu foil before graphene growth[75] | ACS Nano | Z. F. Liu |
|      | 10 mm       | Oxygen assistance | APCVD, a gas purifier to absorb H2O vapor impurity and controlling the O2 content[75] | Adv. Mater. | S. Wang |
|      | =1 cm       | Substrate passivation | | | |
|      | 6 mm        | Substrate passivation | APCVD, vertically stacked Cu foil and trace O2 treatment for Cu(100) surface | Nano Res. | Z. F. Liu |
| 2017 | 5 mm        | Ethane as the carbon feedstock | LPCVD, stacked Cu foils and Ar/O2 treatment before graphene growth | Small | Z. F. Liu |
|      | 5 mm        | Substrate second passivation | LPCVD, vertically stacked Cu foil and trace O2 treatment for Cu(100) surface | Nano Res. | Z. F. Liu |
| 2018 | Foot long   | Evolutionary selection growth | APCVD, advancing local control of the feed gases and high-velocity buffer gas above Cu64Ni15 substrate[12] | Nat. Mater. | S. N. Smirnov |
lattice matching degree between graphene and underlying substrates.\cite{94} To date, epitaxial growth of graphene has been reported on the surfaces of Cu(111),\cite{95} Au(111),\cite{96} Pt(111),\cite{97} Ni(111),\cite{98} Ge(110),\cite{29} Ru(0001),\cite{99} Ir(111),\cite{100} Mo(110),\cite{101} Rh(111),\cite{102} In,\cite{103} Sn,\cite{104} and CuNi alloy.\cite{11} Among these, Cu(111) plane is highly advantageous for aligned nucleation and growth of graphene domains as its hexagonal lattice symmetry matches the honeycomb lattice of graphene well (lattice mismatch $\approx 4\%$), thereby enabling epitaxial growth of graphene. Considering the high temperature and premelted state of the Cu(111) base, Lee’s group used an embedding model for understanding interaction of graphene and underlying substrates.\cite{66} Larger graphene islands (e.g., C$_{54}$) are strongly confined to the orientation at 0° when embedded in a Cu(111) surface due to the higher energy barrier to rotate (3 eV). Rotation is therefore unlikely to occur and is similar to the growth step observed at relatively high temperature (Figure 15a,b).\cite{66} In addition, the energy difference between different misorientation angles is relatively small for the graphene on Cu(100) and Cu(110) surfaces, implying a broad distribution of misorientation angles, consistent with experimental observations.

For comparison, large quantities of computational modeling of graphene clusters on Cu(101), Cu(111), and Cu(100) surfaces were conducted, all of which verified that the affinity of the hexagonal graphene lattice varied for different orientations of Cu surfaces and that minimizing the lattice mismatch between graphene and Cu is critical during domain formation. Grobert’s group proved that the C$_{28}$ cluster prefer to align in one direction on Cu(111) surfaces but preferentially aligned with zigzag edges parallel to [110] or [−110] owing to the symmetrical lattice of Cu(100), resulting in graphene domains with two 90° rotations.\cite{105} This result corresponded well with the conclusion given in Figure 15c–f, where the lowest formation energy of graphene domains on Cu(100) surfaces appears when the rotation angle is 0° and 30°,\cite{106} making growth of twin crystals with 30° intersection angles inevitable during the CVD growth.\cite{86,107} This is because that graphene ZZ edge has the lowest formation energy when it binds along the [110] or [−110] direction of the Cu(100) surface and the two optimal binding orientations of a ZZ edge lead to two equivalent stable orientations of hexagonal graphene domains on the Cu(100) surface. Hence, the coalescence of merging two graphene grains can induce the formation of a polygon with line defects if only one is rotated by 30°.\cite{108}
Therefore, neither Cu(100) nor Cu(110) is an ideal substrate to obtain single crystals via the multiseed method. An approach that was proposed to solve this problem is to apply external strain; specifically, to compress the Cu(100) surface along the [110] or [−110] direction in order to break the symmetry of the Cu(100) surface,[101] which is supported by DFT calculations but nevertheless requires further experimental confirmation.

In addition to structural characteristics of underlying substrates, the growth dynamics of graphene are also very sensitive to thermodynamic variables such as temperature and pressure. The domain orientation of monolayer graphene on Cu(111) is highly sensitive to temperature because the thermal energies and Cu surface structures vary at different temperatures. At a relatively low growth temperature (900 °C), two orientations are observed, whereas at a higher temperature (1000 °C) only one orientation survives, consistent with the underlying Cu(111) lattice.[95] An investigation of the growth dynamics indicated that, at relatively low temperatures (i.e., 900–1030 °C), the orientation of as-grown graphene was identical with that of the underlying Cu(111) lattice.[95] An investigation of the growth dynamics indicated that, at relatively low temperatures (i.e., 900–1030 °C), the orientation of as-grown graphene was identical with that of the underlying Cu(111) lattice. However, when graphene was grown above 1040 °C, a new stable configuration of graphene rotated by 3.4° predominated. This slight rotation is attributed to: (i) different domain sizes due to strong dependence on the growth temperature; and (ii) enhanced thermal fluctuation of the Cu lattice at high-temperature CVD. A further increase in the CVD temperature resulted in graphene rotation with wide distributions of lattice orientation, suggesting enhanced thermal fluctuation of the Cu lattice.[106]

Amorphization of metal substrates is another alternative method for unifying the orientation of graphene nuclei. When growing graphene on a liquid Cu surface, the electrostatic interactions between small graphene domains would play a pivotal role in determining the orientation of graphene seeds. Liu’s group reported the growth of graphene at the melting point of Cu and they observed enhanced coverage of graphene on the Cu surface; the orientation of hexagonal graphene flakes tended to be well aligned owing to spatial constraints (Figure 16a–c).[81] Specifically, hexagonal graphene flakes with similar sizes can translate and rotate on a liquid Cu surface to minimize the total surface/edge energy. Thus, well-separated nuclei evolve into closely packed structures and then into a continuous film to form large single crystals of graphene. The rotation of isolated graphene islands was also systematically investigated by Fu’s group.[109,110] The isotropic Cu surface obtained by melting the growth substrate does not induce specific grain orientation growth in a certain preferential direction; thus, isotropic growth of graphene single crystals is possible (Figure 16d,e). The as-obtained isotropically round graphene grains had randomly mixed smooth edges with high activity. Limited rotation due to steric hindrance of the isotropic grains facilitates atom delocalization; therefore, adjacent grains can self-adjust to achieve smooth stitching. Furthermore, it was also proposed that, when the mutual electrostatic force between adjacent crystals is modulated (assisted by airflow-induced hydrodynamic forces on the liquid metal surface), super-ordered graphene structures could be obtained via self-assembly of high-quality graphene single crystals.[70]

4.2. Preparation of Single-Crystal Substrates

Single-crystal metals with hexagonally symmetrical planes and the lattice closely corresponding to graphene lattice, such as...
Cu(111),[28,64,66,111,112] Ni(111),[98,113,114] and Co(0001),[115,116] have enabled the epitaxial growth of large-area high-quality single-crystal graphene by CVD. Initially, bulk single crystals were used to adjust the orientation of graphene seeds, mainly in mechanistic studies.[95,117,118] As expected, graphene grown on Cu single crystals is more homogeneous than that grown on commonly used polycrystalline Cu foil.[119] However, single-crystal metal substrates are usually size-limited, expensive, and inappropriate for industrial production. Recently, large-area production of single-crystal Cu substrates was achieved and the representative works are summarized in Table 3. According to the thickness of metal substrate and the preparation principles, we classified them into two states, foil and film. The monocrystallization of metal foils is mainly based on the spontaneously transformation into grains with a {111} surface because of surface energy minimization, while the preparation of single-crystal thin metal films (usually sub-micrometer thick) is fulfilled based on their epitaxial growth on top of specific single-crystal inorganic substrates, such as α-Al2O3(0001),[120–122] spinel(111),[111] MgO(111),[107] and Si(110).[29]

### 4.2.1. Preparation of Large-Area Single-Crystal Metal Foils

Although conventional cold-rolled copper foils are known to be predominantly Cu(100),[123,124] longer annealing time before the growth under a hydrogen atmosphere can induce the formation of Cu(111) based on the mechanism of abnormal grain growth.[125] The process of high-temperature annealing and recrystallization results in the formation of new dislocation-free grains, which are thermodynamically more favorable to reduce the total grain boundary energy. In this case, normal grain growth gives way to abnormal grain growth. Thus, a few giant grains would selectively grow by consuming smaller adjacent ones via grain boundary migration. The Cu(111) crystallographic orientation would be naturally adopted, because it is the most thermodynamically stable crystal plane for face-centered cubic (fcc) metals.[126,127]

Recrystallization of Cu foil via extended annealing (12 h) at a temperature close to its melting point produces a single Cu(111) domain with a spatially uniform in-plane orientation over an entire 12 cm long foil, as first reported in 2014 (Figure 17a).[112] Lee’s group further found that extended annealing (6 h) after
CMP resulted in larger Cu domains owing to Oswald ripening, leaving the closely packed Cu(111) surface with large-scale domains.\(^{[66]}\) Controlling the Cu evaporation inside a foil pocket also helped induce the transformation of polycrystalline Cu domains to a centimeter-sized Cu(111) surface.\(^{[91]}\) However, high-temperature annealing over extended periods of time are both energy- and time-consuming.

In 2017, Liu’s group and collaborators proposed a new concept for preparing meter-sized single-crystal Cu(111) foil using a temperature-gradient-driven annealing method similar to that used for the preparation of Si single crystals (Figure 17b–d).\(^{[27]}\) Specifically, the process involved slowly moving polycrystalline Cu foil with a tapered end through a hot zone near the center of a quartz tube, where the peak temperature was 1030 °C (55 °C lower than the melting point of Cu), resulting in large single-crystal Cu(111) foil. The temperature gradient around the central hot zone provided the driving force for continuous motion of the grain boundaries in the Cu foil. Typically, the Cu atoms near a grain boundary were loosely bonded, and at 1300 K the grain boundaries transformed into the premelting state to drastically facilitate mobility and diffusion of Cu atoms.\(^{[128]}\) Furthermore, it was found that sliding the foil through the central hot zone promoted movement of the grain boundaries between the single- and polycrystalline regions. This concept is similar to the traditional “Czochralski method,” in which the temperature gradient at the interface between a liquid and a solid phase acts as the driving force for growing a single-crystal silicon ingot. Note that the initial tipped Cu(111) grain is very important for further monocrystallization of the entire Cu foil to avoid additional nucleation of Cu grains. The single-crystal Cu(111) grain grew to an area of 5 × 50 cm\(^2\) within 50 min at a sliding rate of 1.0 cm min\(^{-1}\). The sample size is only currently limited by the size of the furnace tube and the size of commercially available Cu foil.

The group of Ruoff developed a contact-free annealing method to acquire large single-crystal metal foils by minimizing contact stresses. A preferred in-plane and out-of-plane crystal orientation is observed, driven by surface energy minimization during the rotation of the crystal lattice followed by “consumption” of neighboring grains (Figure 18a,b).\(^{[32,108,129]}\) They successfully prepared Cu(111), Ni(111), Co(0001), Pt(111), and Pd(111) single-crystal foils with a large grain size up to 32 cm\(^2\) using this strategy.\(^{[129]}\) The introduction of hydrogen to the metal during the annealing process would increase the vacancy concentration in the bulk by reducing its vacancy-formation energy and promote the grain rotation and transformation from the \{112\}\{111\} to the \{111\}\{112\} orientation for the single-crystal fcc foils. On this basis, single-crystal CuNi alloy foils were also successfully prepared by electroplating a desired amount of Ni on both sides of the Cu(111) foil and heat-treatment of the Ni-plated Cu(111) foil, as reported by Ruoff’s group.\(^{[32]}\) In addition, control of the tension during single

---

**Figure 17.** Preparation of large-area single-crystal Cu foil for the growth of single-crystal graphene films. a) Schematics showing the graphene growth process on a Cu(111) foil after extended annealing steps. Insets: Laue diffraction images of preannealed (left) and annealed (right) Cu foils. Reproduced with permission.\(^{[112]}\) Copyright 2014, American Chemical Society. b) Schematics of the experimental design for the continuous production of a single-crystal Cu(111) foil with a hot temperature zone at the central area of a furnace tube. c) Evolution of Cu(111) grain in the foil during high-temperature dynamic annealing. Inset in (c): typical LEED pattern from a single-crystal Cu(111) foil. d) Formation of a single-crystal Cu(111) nucleus at the tapered end of the foil. e) Gradually expanding of Cu(111) grain to the width of the Cu foil. f) Photograph of large-area single-crystal Cu(111) region continuously progressed during continuous sliding of the foil. b–f) Reproduced with permission.\(^{[27]}\) Copyright 2017, Elsevier Ltd.
crystallization of Cu foils to activate Cu grain boundary migrate was also helpful to acquire large-area Cu single crystals, even with adjustable crystal planes (Figure 18d–e).[130,131] This technique is compatible with the roll-to-roll synthesis of high-quality graphene films as it is based on vertically suspended Cu foils loaded with a weight to provide controllable tension.

4.2.2. Preparation of Large-Area Single-Crystal Metal Films

C-plane sapphire is an excellent mother substrate for the preparation of Cu(111) films, because it has an acceptable lattice mismatch of 8.6% with the Cu(111) lattice, allowing epitaxial growth of single-crystal Cu film (Figure 19a).[132–134] The sufficiently different lattice mismatch provides the stresses required for easy peel-off, reliably providing a flat surface (in direct contact with the sapphire) to achieve a uniform, easily reduced, and exclusively Cu(111)-oriented film. In addition, sapphire has a relatively low cost available in sizes up to 15 in., has excellent tailorable interfacial properties, and its insulating properties make it compatible with electrochemical processes.[64] Even Mo(110) can be epitaxially grown on an α-Al₂O₃(0001) substrate.[106] A MgO substrate can also be used to prepare Cu(111) films.[98] Moreover, single-crystal spinel (111) substrates have been shown to be good candidates to avoid twin formation in Cu(111) films.[111,122]

Both thermal evaporation and sputtering methods have been reported for preparing metal films, but the latter is considered superior as the developed film is denser, and evaporation of the metal vapor during high-temperature annealing and growth stages can be more efficiently inhibited.[121] However, the special attention are required because of the intense evaporation of Cu at the premelting temperature (especially at a low pressure) and induced reconstruction of the metal surface. Furthermore, a thin film (50 nm) on an electroplated Cu foil was observed to undergo reconstruction after high-temperature annealing. Thus, to date, the growth of wafer-sized graphene films on large-area single-crystal Cu(111) films was mainly attained on Cu/sapphire surfaces via APCVD.[135]

The formation of grain boundaries in Cu or Ni films is usually caused by the appearance of twin structures from ABC and ACB stacking, resulting in the loose arrangements of Cu atoms at the border and high surface fluctuation (Figure 19b). Thus, the suppression of twin crystals is crucial for producing large-area single-crystallinity substrates. The hydroxyl layer bonded to the Al₂O₃ surface affects twin formation; however, it is difficult to remove.[136,137] Hence, bombardment with Ar ions at 200 to 1000 eV followed by a high-temperature (>650 °C) process was required to recrystallize the damaged surface.[137]

A recent report described the exposure of Cu film to a pre-annealing process in a weakly oxidizing atmosphere before
sputtering.\textsuperscript{[28]} The adsorption of O\textsubscript{2} contributed to the formation of CuO, which can effectively release the strain induced by the lattice mismatch between the Cu film and Al\textsubscript{2}O\textsubscript{3} (Figure 19c–f). The monocrystalline nature of as-obtained Cu film was confirmed using X-ray diffraction (XRD), low energy electron diffraction (LEED), and EBSD analyses. Moreover, when using the bubble transfer method without etching Cu, these substrates can be reused for growing graphene. The bonding mechanism at the Cu/Al\textsubscript{2}O\textsubscript{3} interface has long been the subject of extensive research.\textsuperscript{[138–140]} The epitaxy and bonding of Cu films on oxygen-terminated α-Al\textsubscript{2}O\textsubscript{3}(0001) surfaces can be fulfilled using oxygen plasma treatment at a high temperature (≈750 °C), as reported in 2006.\textsuperscript{[121]}

Single-crystal Ni films can also be synthesized. For example, reactive sputtering from an Al target in a mixture of 40% O\textsubscript{2} in Ar at a total pressure of 0.67 Pa (5 mtorr) to remove OH was used to obtain a 97% single orientation Ni film with a smooth and well-ordered surface on Al\textsubscript{2}O\textsubscript{3} with a reactivity sputtered seed layer to improve the film adhesion.\textsuperscript{[122]} As for MgO(111) substrates, even though highly crystalline Ni films can be grown on the surface at high temperatures, the lattice mismatch of 16% between Ni(111) and MgO(111) causes twin formation in large grains with macroscopic boundaries. Low-temperature growth can suppress twin formation but at the expense of film crystallinity.\textsuperscript{[141]} To compensate, a low-temperature buffer layer of 50 nm thick Ni was deposited at 300 °C to form small, particle-like Ni structures. The crystal orientation is therefore locked to the MgO host, thereby suppressing twin formation before the sputtering deposition of 100 nm thick Ni at 600 °C onto the crystalline structure of the as-deposited Ni buffer layer, in order to provide a flat surface and good continuity. After subsequent high-temperature annealing at 800 °C, high-quality heteroepitaxial Ni thin films were successfully grown on MgO(111). The concept of introducing a buffer layer is similar to that for the growth of GaN on sapphire.\textsuperscript{[142]} And this method can also be applied to a MgO substrate with less accurate surface orientation.\textsuperscript{[111]}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure19.png}
\caption{Preparation of wafer-sized single-crystal Cu films for the growth of single-crystal graphene films. a) Schematic illustration of the preparation of a Cu(111) single-crystal film on a sapphire substrate to prepare single-crystal graphene. Reproduced with permission.\textsuperscript{[134]} Copyright 2012, American Chemical Society. b) XRD pattern of a Cu film on sapphire, showing the well-defined Cu(111) out-of-plane orientation. Inset: EBSD map of the Cu thin film on α-Al\textsubscript{2}O\textsubscript{3}, with the existence of twin crystals. Reproduced with permission.\textsuperscript{[111]} Copyright 2015, American Chemical Society. c) Photographic image of a 4 in. single-crystal Cu(111) thin film on sapphire. d) EBSD map of the single-crystal Cu thin film on α-Al\textsubscript{2}O\textsubscript{3} without twin crystals. e) High-resolution XRD azimuthal off-axis ϕ scan of Cu(111) using Cu(200) as the Bragg position and of α-Al\textsubscript{2}O\textsubscript{3}(0001) using α-Al\textsubscript{2}O\textsubscript{3}(022̅4) as the Bragg position. f) Schematic illustration of the orientation relationship between Cu(111) and an oxygen-terminated α-Al\textsubscript{2}O\textsubscript{3}(0001) substrate. g) STEM image of the interface regions of Cu/α-Al\textsubscript{2}O\textsubscript{3} along the zone axis of [110]\textsubscript{Cu} and [1010]\textsubscript{α-Al\textsubscript{2}O\textsubscript{3}}. h,i) SAED images obtained from the Cu film (h) and α-Al\textsubscript{2}O\textsubscript{3} substrate (i). c–i) Reproduced with permission.\textsuperscript{[28]} Copyright 2017, American Chemical Society.}
\end{figure}
Moreover, single-crystal CuNi alloy thin film can also be prepared using two-step sputtering method by sputtering Ni on the preformed Cu(111) single-crystal film or sputtering Cu on the preformed Ni(111) film, one-step sputtering using CuNi alloys as the target and cosputtering method using Cu and Ni targets. For example, after annealing Ni film sputtered on the single-crystal Cu(111) thin film on oxygen-terminated α-Al2O3(0001) as the target, 4 in. sized twin-free CuNi(111) film was acquired, which was proven to possess more smooth surface and higher catalytic ability for the fast growth of single-crystal graphene film (Figure 20a–c).[143] On this basis, scalable growth of single-crystal graphene wafers on 4 in. CuNi(111) substrates was then achieved in Peking University and Beijing Graphene Institute (Figure 20d,e). Besides, using one-step sputtering method, 6 in. sized single-crystal graphene film was also successfully synthesized by Xie’s group on the surface of CuNi thin film substrates, with growth temperature lowered to 750 °C (Figure 20f).[31]

4.3. Seamless Stitching of Aligned Graphene Domains

Seamlessly stitching of aligned graphene domains on Cu(111) surfaces and determined a rotational alignment of 0.5° using the experimental μ-angle-resolved photoelectron spectroscopy (ARPES) Fermi surface.[112] The long-range crystallinity of Cu foil and optimization of the growth parameters for reduced reactivity both contribute to the generation of graphene domains with an alignment that exceeds 95%, as confirmed by dark field optical microscopy (DF-OM), dark-field transmission electron microscopy (DFTEM) (Figure 21a,b), and ARPES. Zero misorientation angle was observed for nearly 98% of the grains on a polished Cu(111) surface, in which the remaining 2% were misoriented by 5°–10°, presumably because of impurities or artifacts on the Cu(111) surfaces. Individual hexagonal graphene islands on sub-monolayer graphene fabricated by Liu’s group showed an improved alignment greater than 99% (from the examination of over 3400 individual domains). LEED patterns are another powerful tool for determining lattice orientation of graphene domains.[27] Liu’s group also obtained 1200 randomly selected LEED patterns of graphene films and found the alignment of all of these films to be nearly identical within 0.5°.

Both microscopic and macroscopic methods have been used to characterize the aligned orientation and seamless merging of graphene islands. From the view of microscopic characterization, both STM (Figure 21c) and TEM (Figure 21a,b) have been used to evaluate whether the atomic structures were identical.
nonepitaxial graphene, did not allow the formation of wrinkles, was approximately two orders of magnitude larger than that of large frictional force between graphene and the substrate, which increasing the stability of graphene films on the Cu(111) surface. Besides, for epitaxial graphene grown on Cu(111), the very stitching regions are defect-free and very stable, further evidenced by both theoretical and experimental observations, seamless stitched regions are defect-free.

Remarkably, strong interactions between Cu(111) and graphene make it difficult to oxidize Cu(111) underneath the graphene layer, irrespective of whether the graphene domains are isolated or seamlessly merged. Apart from this, compressive strain in the epitaxial regions (0.3–0.6%) is higher than that in nonepitaxial regions (0.2–0.3%), as determined from Raman and STM data, as well as molecular dynamics simulations. Furthermore, the small lattice mismatch between Cu(111) and graphene was reported to decrease the defect density of graphene, and thus enhance the electrical properties. In addition, as evidenced by both theoretical and experimental observations, seamlessly stitched regions are defect-free and very stable, further increasing the stability of graphene films on the Cu(111) surface. Besides, for epitaxial graphene grown on Cu(111), the very large frictional force between graphene and the substrate, which was approximately two orders of magnitude larger than that of nonepitaxial graphene, did not allow the formation of wrinkles, even though the compressive strain was higher (0.25–0.40%).

Single-crystal Ge is another good candidate for the growth of single-crystal graphene, with the obvious advantages of suitable catalytic ability, extremely low carbon solubility, well-defined and anisotropic atomic arrangement, and small differences in thermal expansion coefficients. To date, large-area single-crystal Ge has been prepared via solid phase epitaxial growth on Si(110) wafers. Vaporized Ge is used as a precursor in the CVD chamber, followed by thermal annealing at 600 °C to increase the crystallinity of the Ge film. As reported by Whang’s group in 2014, single-crystal graphene has been grown on the wafer scale based on the seamless merging of multiple nucleation with perfect unidirectional alignment on the Ge(110) surface. Specifically, graphene islands at the early stage of growth on H-terminated Ge(110) surfaces were uniaxially aligned along the [−110] direction of the underlying substrate. Further investigations revealed the underlying mechanism of the necessary coalignment of nucleating graphene islands on the Ge(110) surface. The presence of natural step patterns is necessary for the emergence of coaligned graphene islands resulting from the strong chemical bonding between the edges of the graphene island and the atomic steps on the Ge(110) surface (Figure 21). The anisotropic twofold symmetry of the Ge(110) surface allowed multiple seeds to be unidirectionally aligned, which would be merged to uniform single-crystal graphene with a predefined orientation. The hydrogen-terminated Ge(110) overlayer on a Si substrate.
adopts a weakly interacting graphene monolayer for seamless stitching of graphene domains to form wafer-sized monocrystalline graphene (Figure 22i).

5. Conclusions and Outlook

This paper presented an in-depth review of the controlled CVD synthesis of single-crystal graphene films, covering the most recent and significant results in this field. In the past ten years, large-area single-crystal graphene films have been prepared on metal substrates under various growth conditions. Cu is the most commonly used metal substrate to synthesize high-quality single-crystal graphene films, based on the surface-mediated growth mechanism. After decomposition of the carbon feedstocks, active species would diffuse on the substrate surface and migrate to the active sites to form graphene nuclei, which would continue the lateral growth and then merge with adjacent graphene domains. Thereinto, the nucleation step plays a vital role in deciding the monocrystallinity of the large-area graphene films. Generally, based on the inhibition the formation of GGBs, these synthesis methods can be classified into two types: single-seed and multiseed approaches. The comparisons between these two approaches are listed in Table 4 and Figure 23.
The single-seed approach involves growing a single graphene crystal as large as possible by efficiently decreasing the nucleation density. This can be achieved by pretreating the substrate to reduce or passivate the active nucleation sites or by optimizing the critical growth parameters, especially the carbon source supply. In addition, local feeding of carbon feedstock has been utilized to grow 1 in. sized to foot-long sized graphene single crystals on stationary and traveling substrates, respectively. However, the single-seed approach is considerably time-consuming. Alternatively, the multiseed approach involves achieving the same orientation of graphene nuclei, which is mainly dependent on the monocrystallinity of the underlying metal substrates (e.g., Cu, Ni, Ge, Co, and some alloys). In this case, seamless merging of adjacent graphene domains ensures the formation of graphene single crystals within shorter time.

In addition, the electrostatic force modulation between adjacent crystals also contributes to the aligned orientation and seamless merging of graphene domains.

The preparation of large-area single-crystal graphene in a low-cost manner is still our pursuit. Large graphene single crystals grown from a single seed have the highest quality among CVD-grown graphene ever reported; however, the growth rate remains relatively low, e.g., it might take over 10 h to acquire a millimeter-sized graphene crystal. Even though oxygen has been reported to decrease the energy barrier for carbon source cracking and accelerate the nucleation and growth of graphene crystals, the high nucleation density resulting from the excessive carbon supply in the initial stages prevents the growth of single crystals larger than millimeter-size. The trade-off between low nucleation density and high growth rate might be addressed to a certain extent, by the evolutionary growth of graphene films from one seed on traveling substrates, where it is necessary to ensure the perfect matching of the substrate movement rate and amount of carbon source supply. This work provides new insight and lays the foundation for other forms of localized control during graphene CVD growth, such as providing localized high-temperature via inductive or infrared heating to further lower the production cost. However, the maximum size is still limited, as inhibition of secondary nucleation on meter-sized substrates is still challenging and the evolution from one seed to a meter-sized film is still time-consuming.

The multiseed approach significantly shortens the graphene growth time to form large-area continuous single-crystal films by merging well aligned isolated islands, whose nucleation happens simultaneously. However, the aligned nucleation depends mainly on the monocrystalline metal substrates and the preparation of these single-crystal substrates involves the expensive sputtering and time-consuming annealing processes, which increases the cost in the early stage. To lower the cost, etching-free clean transfer methods to exfoliate graphene from the substrate surface need to be developed for the cycle utilization of the substrates. Meanwhile, the existing unaligned graphene islands (typically 0.1–5%) cannot be completely eliminated because of the imperfection of the underlying monocrystallized metal substrates and the disturbance in the high-temperature CVD system. On the other hand, electrostatic force modulation between the adjacent crystals has been reported to facilitate the seamless merging of adjacent graphene domains; however, the overall size of the single-crystal film is still very limited. Therefore, new strategies are still in need focusing on both the modulation of boundary layer and optimization of the underlying substrates.

Admittedly, there is room for improving the quality of single-crystal graphene. Even though the above-mentioned methods enabled a significantly decreased grain boundary density, much work is still required to obtain “perfect graphene.” The structural defects of graphene include not only GGBs, but also wrinkles, impurities, adatoms, point defects, and adlayers. The defect-related D peak is undetectable for most CVD-grown graphene.
films by Raman spectroscopy, indicating great progress in this respect over the past ten years. However, there still remains a gap between mechanical exfoliated graphene and CVD-grown graphene. A high temperature is necessary to guarantee sufficient catalytic ability during graphene growth; however, the difference in the thermal expansion coefficients between graphene and the underlying substrates would lead to the formation of wrinkles. Recently, Peng and co-workers synthesized 4 in. sized wrinkle-free graphene single-crystal film on strain-engineered single-crystal Cu(111)/sapphire for the first time. This strategy is applicable to scalable and fast growth of graphene single-crystal wafers on CuNi(111)/sapphire substrates. A pilot-scale CVD system was designed and built for the mass production of single-crystal graphene wafers, with productivity of 25 pieces in one process cycle. Very recently, Xie et al. reported the growth of 6 in. sized wrinkle-free graphene single-crystal film on (111) Cu$_2$Ni$_{31}$/sapphire substrate at 750 °C. But to date, wrinkle-free graphene films on foil substrates have not yet been reported. In addition, the formation of adlayers, impurities, and contaminants on the as-grown graphene surfaces might be attributed to the complex gas phase reactions in the CVD system but has not been rigorously studied. Therefore, further attention and efforts are required to elucidate the growth mechanism of imperfect graphene and synthesize large-area high-quality graphene films.

Good repeatability and controllability are critical for the industrialization of graphene production. Even though CVD has proven advantageous in these respects, the conditions may be more complex and uncontrollable during the mass production of large-area graphene films. Regulation of the key points toward the synthesis of large-sized single-crystal graphene, such as pretreatment of the substrate surfaces, preparation of single-crystal substrates and control of the carbon source supply becomes more difficult or even ineffective, especially considering the uniformity in different regions of the growth substrate. In addition, clear relationships between the structure features and properties of graphene films need to be illustrated. Meanwhile, fast and large-area nondestructive methods to prepare graphene samples on various functional substrates and evaluate their performances are also needed for further applications.

Since the past ten years, exploration of the “killer applications” of graphene films, the so-called “star material” of the 21st century, has been ongoing. Graphene has proven to be a good candidate for ultrahigh-speed electronics, transparent and flexible electronics, solar cells, separation membrane, and TEM imaging. In the future, quality control of large-area graphene films should consider the specific requirements of practical application fields. Even though most properties of graphene films improve with increased domain size, the balance between the maximum domain size and production cost need to be found. Moreover, take the development trends of carbon fiber, Si, and plastic (currently the three most commonly used materials) as reference, more patience and attention should be given in the exploration of graphene applications.

**Acknowledgements**

This article is part of the Advanced Materials Hall of Fame article series, which recognizes the excellent contributions of leading researchers to the field of materials science. This work was financially supported by the Beijing Municipal Science & Technology Commission (No. Z181100004831800), the National Basic Research Program of China (No. 2016YFA0200101), and the National Natural Science Foundation of China (Nos. 21525310, 51432002, and 51520105003).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

chemical vapor deposition, grain boundaries, single-crystal graphene, thin films

Received: May 22, 2019
Revised: July 23, 2019
Published online: October 3, 2019

[1] K. S. Novoselov, V. I. Fal’ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, *490*, 192.
[2] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
[3] L. Banszerus, M. Schmitz, S. Engels, J. Dauber, M. Oellers, F. Haupt, K. Watanabe, T. Taniguchi, B. Beschoten, C. Stampfer, *Sci. Adv.* **2015**, *1*, e1500222.
[4] H. Jang, Y. J. Park, X. Chen, T. Das, M. S. Kim, J. H. Ahn, *Adv. Mater.* **2016**, *28*, 4184.
[5] G. Zhao, X. Li, M. Huang, Z. Zhen, Y. Zhong, Q. Chen, X. Zhao, Y. He, R. Hu, T. Yang, R. Zhang, C. Li, J. Kong, J. B. Xu, R. S. Ruoff, H. Zhu, *Chem. Soc. Rev.* **2017**, *46*, 4417.
[6] S. M. Fatemi, Z. Abbasi, H. Rajabzadeh, S. A. Hashemizadeh, A. N. Deldar, *Eur. Phys. J. D* **2017**, *71*, 194.
[7] J. Zhang, L. Lin, L. Sun, Y. Huang, A. L. Koh, W. Dang, J. Yin, M. Wang, C. Tan, T. Li, Z. Tan, Z. Liu, H. Peng, *Adv. Mater.* **2017**, *29*, 1700639.
[8] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
[9] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science* **2009**, *324*, 1312.
[10] S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong, S. Iijima, *Nat. Nanotechnol.* **2010**, *5*, 574.
[11] T. Wu, X. Zhang, Q. Yuan, J. Xue, G. Lu, Z. Liu, H. Wang, H. Wang, F. Ding, Q. Yu, X. Xie, M. Jiang, *Nat. Mater.* **2016**, *15*, 43.
[12] I. V. Vlassiouk, I. Stehle, P. R. Pudasaini, R. R. Unocic, P. D. Rack, F. Haupt, K. Watanabe, T. Taniguchi, B. Beschoten, C. Stampfer, *Sci. Adv.* **2015**, *1*, e1500222.
[13] I. V. Vlassiouk, Y. P. Chen, *Nat. Nanotechnol.* **2014**, *9*, 755.
[14] T. Ma, Z. Liu, J. Wen, Y. Gao, X. Ren, H. Chen, C. Jin, X. L. Ma, N. Xu, H. M. Cheng, W. Ren, *Nat. Commun.* **2017**, *8*, 14486.
[15] D. L. Duong, G. H. Han, S. M. Lee, F. Gunes, E. S. Kim, S. T. Kim, H. Kim, Q. H. Ta, K. P. So, S. J. Yoon, S. J. Chae, Y. W. Jo, M. H. Park, S. H. Chae, S. C. Lim, J. Y. Choi, Y. H. Lee, *Nature* **2012**, *490*, 235.
[16] W. Lee, K. D. Khim, H. G. Kim, S. Shin, C. Lee, J. S. Park, S. Cheon, O. M. Kwon, G. Lim, W. Lee, *Nano Lett.* **2017**, *17*, 2361.
[17] D. Wang, Z. H. Zhang, X. Q. Deng, Z. Q. Fan, G. P. Tang, *Carbon* **2016**, *98*, 204.
[129] S. Jin, M. Huang, Y. Kwon, L. N. Zhang, B. W. Li, S. Oh, J. C. Dong, D. Luo, M. Biswal, B. V. Cunning, P. V. Bakharev, I. Moon, W. J. Yoo, D. C. Camacho-Mojica, Y. J. Kim, S. H. Lee, B. Wang, W. K. Seong, M. Saxena, F. Ding, H. J. Shin, R. S. Ruoff, Science 2018, 362, 1021.

[130] I. Jo, S. Park, D. Kim, J. S. Moon, W. B. Park, T. H. Kim, J. H. Kang, W. Lee, Y. Kim, D. N. Lee, S.-P. Cho, H. Choi, I. Kang, J. H. Park, J. S. Lee, B. H. Hong, 2D Mater. 2018, 5, 024002.

[131] H. Chun, S. M. Na, J. H. Yoo, M. Wuttig, A. B. Flatau, J. Appl. Phys. 2011, 109, 07A941.

[132] C. P. Khattak, F. Schmid, J. Cryst. Growth 2001, 225, 572.

[133] F. Schmid, C. P. Khattak, D. M. Felt, Am. Ceram. Soc. Bull. 1994, 73, 39.

[134] H. Ago, Y. Ogawa, M. Tsuji, S. Mizuno, H. Hibino, J. Phys. Chem. Lett. 2012, 3, 2228.

[135] V. L. Nguyen, Y. H. Lee, Small 2015, 11, 3512.

[136] P. J. Eng, T. P. Trainor, G. E. Brown, G. A. Waychunas, M. Newville, S. R. Sutton, M. L. Rivers, Science 2000, 288, 1029.

[137] C. Scheu, M. Gao, S. H. Oh, G. Dehm, S. Klein, A. P. Tomsia, M. Ruhle, J. Mater. Sci. 2006, 41, 5161.

[138] G. Dehm, M. Ruhle, G. Ding, R. Raj, Philos. Mag. B 1995, 71, 1111.

[139] K. Matsunaga, T. Sasaki, N. Shibata, T. Mizoguchi, T. Yamamoto, Y. Ikuhara, Phys. Rev. B 2006, 74, 125423.

[140] T. Mizoguchi, T. Sasaki, S. Tanaka, K. Matsunaga, T. Yamamoto, M. Kohyama, Y. Ikuhara, Phys. Rev. B 2006, 74, 235408.

[141] P. Sandstrom, E. B. Svedberg, J. Birch, J. E. Sundgren, J. Cryst. Growth 1999, 197, 849.

[142] H. Amano, N. Sawaki, I. Akasaki, Y. Toyoda, Appl. Phys. Lett. 1986, 48, 353.

[143] B. Deng, Z. Xin, R. Xue, S. Zhang, X. Xu, J. Gao, J. Tang, Y. Qi, Y. Wang, Y. Zhao, L. Sun, H. Wang, K. Liu, M. H. Rummeli, L. Weng, Z. Luo, L. Tong, X. Zhang, C. Xie, Z. Liu, H. Peng, Sci. Bull. 2019, 64, 659.

[144] D. W. Kim, Y. H. Kim, H. S. Jeong, H. T. Jung, Nat. Nanotechnol. 2012, 7, 29.

[145] R. He, L. Y. Zhao, N. Petrone, K. S. Kim, M. Roth, J. Hone, P. Kim, A. Pasupathy, A. Pinczuk, Nano Lett. 2012, 12, 2408.

[146] H. J. Shin, S. M. Yoon, W. M. Choi, S. Park, D. Lee, I. Y. Song, Y. S. Woo, J. Y. Choi, Appl. Phys. Lett. 2013, 102, 163102.

[147] G. Wang, M. Zhang, Y. Zhu, G. Q. Ding, D. Jiang, Q. L. Guo, S. Liu, X. M. Xie, P. K. Chu, Z. F. Di, X. Wang, Sci. Rep. 2013, 3, 2247.

[148] J. Y. Dai, D. X. Wang, M. Zhang, T. C. Niu, A. Li, M. Ye, S. Qiao, G. Q. Ding, X. M. Xie, Y. Q. Wang, P. K. Chu, Q. H. Yuan, Z. F. Di, X. Wang, F. Ding, B. I. Yakobson, Nano Lett. 2016, 16, 3160.