Towards Wafer-Scale Monocrystalline Graphene Growth and Characterization

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Since its discovery in 2004, graphene has boosted numerous fundamental sciences and technological applications due to its massless Dirac particle-like linear band dispersion, that causes unprecedented physical properties. Among the various methods for synthesizing graphene, chemical vapor deposition is the most suitable approach for scalable production on a wafer scale, which is a critical step for practical applications. Graphene grain boundaries (GGBs), consisting of nonhexagonal carbon rings and therefore modulating the properties of graphene films, are inevitably formed via the merging of adjacent graphene domains with different orientations. Large-area monocrystalline graphene synthesis without forming GGBs has been challenging, let alone observing such boundaries. Here, an up-to-date review is presented of how to grow wafer-scale monocrystalline graphene without GGBs. One approach is to make single domain sizes as large as possible by reducing or passivating the number of nucleation sites. Another approach is to align graphene domains in identical orientations, and then merge them atomically. The recently developed methods for observing graphene orientation and GGBs both at the atomic and macro-scales are also presented. Finally, perspectives for future research in graphene growth are discussed.
Graphene is a 2D material with atomically thin sp²-bonded carbon atoms. Due to its unprecedented physical,[1-3] electrical,[4-7] and optical properties,[8,9] graphene has attracted intense attention from scientists for both theoretical and experimental studies since it was first reported in 2004.[10] Those extraordinary properties provide opportunities for applications in field-effect transistors (FETs),[11,12] transparent and flexible electrodes,[13,14] spintronic devices,[15] and solar cells.[16] Owing to these important applications, graphene could be a better choice than any hard materials.[17,18]

The quality of graphene, from the viewpoint of defect concentration, is produced by the mechanical cleavage of highly oriented pyrolytic graphite (HOPG).[10] Highly oriented single-crystal graphene can be obtained easily with this approach, which is very necessary for fundamental studies.[19-25] Nonetheless, the number of exfoliated layers and the position of flakes are uncontrollable and obtained only by chance. Moreover, the size of flakes is typically limited to a few micrometers, which is a big challenge for industrial applications. Several approaches have been attempted to achieve reproducible and scalable graphene on a substrate. For example, graphene sheets are obtained in large quantities by exfoliation from graphite in solution.[22-24] However, this method introduces electronic disorder in graphene.

Millimeter-scale monocrystalline graphene has been realized by thermally annealing single-crystal Ru(0001).[25] At high-temperature annealing (1000 K) under ultra-high vacuum (UHV) conditions (10⁻⁷ Pa), the carbon atoms already in the Ru bulk are segregated and accumulated on the Ru surface, leading to the formation of monocrystalline graphene. This graphene film can grow continuously, regardless of step edges and terraces of the Ru(0001) surface, suggesting the possibility of large-area graphene without any breakage of its structure or symmetry. However, this graphene layer couples strongly with its Ru substrate due to the hybridization of Cp₉ orbitals with Ru d states, causing some difficulty to transfer graphene to a desired substrate for further application, let alone controlling the carbon content in the Ru bulk.[26] Wafer-scale monocrystalline graphene is also achieved by the conversion of SiC(0001) into graphene layers via the sublimation of silicon atoms at high temperature.[27-29] However, the rough SiC surface results in a nonuniform graphene thickness. Monolayer graphene is formed homogeneously on the macro SiC terraces, but bi- or tri-layer graphene exists at the downward edges of those terraces. A special method of transferring graphene from SiC substrates was also suggested: the nonuniform graphene layer, with various thicknesses, is exfoliated from the SiC wafer using a proper adhesive-stained layer (Ni) and a handling layer (thermal release tape). Due to the stronger binding energy of the Ni-Gr than that of Gr-Au (γ₃,Gr ± 2.6 γ₃,Au), the multilayer graphene (bi- or tri-layer) is selectively removed from the Ni film by second exfoliation using a Au film as an adhesive-stained layer. Finally, the remaining monolayer graphene on the Ni film is transferred to the desired substrate. As a consequence, 4-inch monocrystalline graphene with a uniform monolayer has been obtained. However, the high cost issue of Ru(0001) and SiC(0001) prohibit this approach for practical applications.

Among the methods used, chemical vapor deposition (CVD) has emerged as the most promising and inexpensive approach to obtain reproducible and scalable high-quality graphene on many transition-metal substrates such as Pt,[30] Ir,[31] Ni,[32] and Cu.[33] In particular, Cu is considered the best substrate candidate due to being inexpensive, having a well-controlled surface and low carbon solubility, which is necessary to obtain monolayer graphene.[33,34] Numerous efforts have aimed to achieve large-area monocrystalline graphene without forming grain boundaries. There are two possible approaches to realize this target. The first approach involves the growth of a single domain, as large as possible.[30,35-42] Although a centimeter-scale flake size has been obtained, this approach is not practical for wafer-scale growth due to the difficulty of controlling the number of nucleation seeds and unknown self-limiting growth factors and, to make it worse, it requires (in general) long growth times of over a day or so.[43,44] Another approach is based on the alignment of graphene domain orientations on a proper substrate and leading them to stitch atomically to form uniform monocrystalline graphene.[45,46] This approach seems to be the satisfactory for the demands of wafer-scale growth.

The CVD approach produces (in general) wafer-scale but polycrystalline graphene, which consists of many domains with various lattice orientations. Such an orientation disorder inevitably leads to the formation of graphene grain boundaries (GGBs) at the interfaces between the domains.[47-49] GGBs consist of a series of connected nonhexagonal rings of pentagons, heptagons, and/or octagons. Pristine graphene shows a rather high conductivity and is chemically inert, however, the presence of atomic-scale defect lines (or GGBs) in graphene could significantly modulate its mechanical,[1,49] electrical,[50] chemical,[52,53] and magnetic properties.[54] These defect lines are predicted to have unusual properties, which depend on the exact atomic configuration at the boundaries as well as the crystallinity of the individual grains, and can be further modulated by functionalization with different functional groups.[53] Therefore, the investigation of grain orientation and grain boundaries is critical to comprehend completely the underlying properties of graphene and to realize suitable applications.

The most challenging issue is how to observe graphene orientation and GGBs at the atomic and macro-scales. Several approaches to observe graphene orientation have been reported so far, such as dark-field transmission electron microscopy (DFTEM) [55-61] and scanning tunneling microscopy (STM) [62,63]. However, this method introduces electronic disorder in graphene.
microscopy (DF-TEM), \cite{47,48,55} low electron energy microscopy (LEEM), \cite{56} confocal Raman mapping on overlapped graphene bilayers, and polarized optical microscopy (POM) of graphene covered by nematic liquid crystal (NLC) layers. \cite{46,67,58} For detailed visualizations of the GGB structure at the atomic scale, high-resolution transmission electron microscopy (HR-TEM) \cite{47,49,55,59} and scanning tunneling microscopy (STM) observations are the most effective. Local electronic properties of GGBs are investigated by scanning tunneling spectroscopy (STS). \cite{60,63} Nevertheless, information about the GGB distribution at the macroscale is not so easily accessible with such approaches. Fortunately, several methods have been developed to enable the visualization of GGBs at the macroscale by optical microscopy \cite{64,66} scanning electron microscopy (SEM), \cite{67,68} or by using IR nano-imaging techniques. \cite{69} In this article, we discuss the up-to-date progress in graphene growth by CVD and, furthermore, the recent efforts to observe graphene grain boundaries and orientations from the nanoscale to the macroscale are discussed in detail, followed by our conclusions and an outlook for this research area.

2. Graphene Synthesis

2.1. Growth Mechanism

The growth mechanism of graphene on a Cu substrate by CVD has been well described in the literature. \cite{70} Hydrocarbon molecules are absorbed and catalytically dissociated on the Cu surface to form active carbon species by dehydrogenation reactions. Those active carbon species diffuse on the Cu surface and agglomerate on its active sites, forming graphene nucleation seeds. Although H\textsubscript{2} gas is utilized during growth, the growth mechanism is discussed without involving this hydrogen gas. \cite{44,67,51} In fact, introducing H\textsubscript{2} gas is mandatory for graphene growth in most CVD approaches. This indicates that H\textsubscript{2} plays a vital role in graphene growth. The overall process of graphene growth on copper is illustrated in Figure 1a. It is expected that there are mainly three elementary steps: i) Adsorption and decomposition, ii) diffusion and desorption, iii) nucleation and growth. Hydrocarbon molecules, for example, CH\textsubscript{4}, are observed and catalytically dehydrogenated on the Cu surface to form active carbon species such as (CH\textsubscript{3})\textsubscript{s}, (CH\textsubscript{2})\textsubscript{s}, (CH)\textsubscript{s} or (C)\textsubscript{s}, where ‘s’ signifies ‘surface-adsorbed’. If H\textsubscript{2} gas is absent in the reaction mixture, the dehydrogenation reaction of CH\textsubscript{4} occurs catalytically via chemisorption on copper substrate by \( (CH_4)_{-} \xrightarrow{Cu} (CH_{x-1})_{+} + H_2 (x = 1,2,3,4). \) However, these reactions are not thermodynamically favorable on copper. \cite{72,73}

With the presence of H\textsubscript{2} gas in the reaction mixture, hydrogen molecules dissociate on the Cu surface, forming active hydrogen atoms according to \( Cu + H_2 \rightarrow 2H_\text{ads}. \) \cite{74} The dehydrogenation reaction could now be more favorable in the presence of those active hydrogen atoms to form the active carbon species (signified by blue spots in Figure 1a) by the reaction \( (CH_4)_{+} + H_2 \xrightarrow{Cu} (CH_{x-1})_{+} + H_2 (x = 1,2,3,4). \) \cite{72,75}

Owing to the low solubility of carbon in copper (less than 0.001 at%), the active carbon species are only diffused on the surface of copper. \cite{76} At high temperatures, those active carbon species also gain kinetic energy and then may be desorbed partially from the copper surface. Numerous active sites (symbolized by red spots in Figure 1a) such as impurities, defects, and sharp wrinkles exist on the Cu surface. They are known to play a role of active heteronuclei seeds in the early stages of graphene growth. \cite{55,77,78} The active carbon species are predicted to be unstable and tend to agglomerate into thermodynamically stable species on the active sites of the Cu surface to form graphene nucleation seeds according to \( (CH_4)_{+} + \text{graphene} \rightarrow (\text{graphene} + C) + \text{H}_2 (x = 1,2,3). \) Once those seeds have formed, most of the active carbon species are captured and incorporated into the graphene lattice. The H\textsubscript{2} gas plays another role as an etching agent, that controls the size and shape of the graphene domains by the reaction \( H_1 + \text{graphene} \rightarrow (\text{graphene} - C) + (CH_4)_{+} (x = 1,2,3). \) \cite{71,79,81}

Carbon adatoms only diffuse on the surface of Cu. In order to prove this concept, isotopic labeling of carbon precursors such as \(^{13}\text{CH}_4\) and \(^{12}\text{CH}_4\) are injected sequentially during growth, as illustrated in Figure 1b. If carbon atoms do not diffuse into the metal substrate, graphene is grown laterally. Thus, the \(^{13}\text{C}\) and \(^{12}\text{C}\) distributions will reflect a sequential dosing of \(^{13}\text{CH}_4\) and \(^{12}\text{CH}_4\), respectively. Figure 1c shows the Raman mapping of the G band of \(^{12}\text{C}\). The bright (dark) areas correspond to the location of \(^{12}\text{C}\) (\(^{13}\text{C}\)). This distribution of \(^{13}\text{C}\) and \(^{12}\text{C}\) reflects exactly the sequential dosing of \(^{13}\text{CH}_4\) and \(^{12}\text{CH}_4\) precursors. It indicates that growth occurs in two dimensions and is a consequence of a surface-adsorption process, and monolayer graphene is thus controllable.

The situation is different with other transition-metal substrates with high carbon solid solubility. For example, graphene growth on Ni substrates has been believed to follow...
the bulk-mediated growth mode. Due to the high carbon solubility in Ni, carbon atoms diffuse into the Ni substrate at high reaction temperatures before segregating and precipitating to the surface upon cooling.\cite{32,34,70,82–85} As a consequence, multilayer graphene is easily formed on a Ni substrate, making it difficult to obtain uniform monolayer graphene.

With these approaches, large-area graphene can be synthesized without much difficulty where the size is limited only by the chamber size. Since multiple nucleation seeds are involved during this growth, even with a Cu substrate (and a Cu substrate itself is polycrystalline), it is inevitable to form grain boundaries and the resulting graphene is polycrystalline, with grain boundaries between domains.

### 2.2. Monocrystalline Graphene Growth

#### 2.2.1. The Single-Nucleation Approach

Based on the growth mechanism discussed above, one of the critical points for synthesizing large-scale graphene domains is to suppress or passivate the density of active nucleation sites on the copper surface as much as possible. Therefore, reducing the density of nucleation seeds is a key step in the initial growth stage: Graphene domain size is inversely proportional to the density of nucleation seeds. By terminating growth before all domains merge to form a polycrystalline film, relatively large domains could be obtained. There are three main methods to decrease the nucleation seed density:

1. Increase the \( \text{H}_2/\text{CH}_4 \) gas concentration ratio by decreasing the partial pressure of \( \text{CH}_4 \)\cite{36,71}.
2. Increase the growth temperature\cite{30,66}.
3. Passivate the active sites by decreasing the roughness\cite{35,36,38,39} or pre-oxidation\cite{42–44} of the copper surface. These factors together play a crucial role to obtain large graphene domains and will be discussed in detail here.

As-received copper foils generally involve wrinkles, step edges, and impurities, and are often coated with protection layers. These play a role as active sites for graphene heteronucleation. Therefore, pre-treatment of the copper foils is necessary to obtain smooth surfaces before graphene growth. Several methods exist in order to clean as-received copper foils such as chemical–mechanical polishing (CMP)\cite{78} or electrochemical polishing (ECP)\cite{86–88}. At low-pressure growth, the copper surface is easily evaporated, increasing the surface roughness.\cite{89} In order to suppress the loss of Cu by evaporation, the Cu foil is wrapped in a tube shape. At high temperatures, the outer copper surface becomes very rough due to the evaporation of Cu atoms (Figure 2a). Cu atoms on the inner surface are evaporated and re-deposited so that the inner surface becomes smoother. Thus, graphene nucleation seeds on the inner surface could be suppressed, leading to the formation of millimeter-sized domains (Figure 2b). At ambient-pressure growth, Cu evaporation is suppressed\cite{89}. The presence of \( \text{H}_2 \) during annealing is considered helpful to achieve smooth copper surfaces by reducing the oxide layer and defects. After 3 h annealing under \( \text{H}_2 \), graphene nucleation seeds are also significantly suppressed and sub-millimeter-sized domains are obtained.\cite{35} However, big wrinkles still exist on the Cu surface and cannot be suppressed completely by simply annealing at ambient pressure. Therefore, high-pressure annealing has been attempted.\cite{71} The controlled chamber pressure in CVD is constructed to manipulate the pressure from low to high inside the chamber by a metering valve. The polished Cu foil is annealed at high pressure (2 atm) for 7 h to minimize sharp wrinkles and defects.
on the Cu surface. After annealing at high pressure, the pressure is reduced by metering the valve for the growth stage. Annealed Cu foils become very smooth and stable at low pressure, Cu evaporation does not occur and, consequently, a 2.3 mm-sized hexagonal graphene domain is obtained, as shown in Figure 2c.

The disadvantage of these methods is that they require relatively long annealing and growth times. An approach to achieve a smooth Cu surface in a relatively short time involves a two-step process including melting and re-solidifying of the copper. The cleaned Cu foil is placed on a tungsten (W) foil to prevent de-wetting of the liquid copper during cooling. The temperature is ramped up to 1100 °C to melt the copper foil completely (melting point of bulk copper is 1084 °C). Then, the temperature is slowly ramped down to 1075 °C and the copper is re-solidified. A smooth Cu surface is obtained with a root-mean-square (RMS) roughness of 8 nm (Figure 2d), leading the formation of millimeter-sized domains, as shown in Figure 2c. This further demonstrates that the copper surface morphology is one of the most important factors to obtain large graphene domains.

In addition to copper, other noble metals could be candidates for growing large monocrystalline graphene. For example, a millimeter-sized hexagonal graphene domain has been realized successfully on Pt foil by CVD. In contrast to copper foil, carbon solubility in Pt foil is as high as 0.9 at% at 1000 °C. Nevertheless, monolayer graphene could be easily controlled. Owing to the higher catalytic ability of Pt for the dehydrogenation reaction of CH4 compared to that of Cu, graphene could be grown at a relatively low temperature (750 °C) and the growth rate of graphene on a Pt substrate is four times faster than on Cu when identical growth conditions are applied. By using low carbon concentrations (ratio of CH4/H2 of 4/700), a perfect hexagonal shape with very smooth edges and a lateral size of up to 1.3 mm was obtained at 1040 °C, as shown in Figure 2f. Pt foil is an expensive metal, but the bubbling transfer method is available and, thus, the Pt substrate could be re-used. Therefore, Pt foil is a potential candidate for high-quality graphene growth.

The aforementioned methods mainly focused on making smooth surfaces with improved quality to reduce the graphene nucleation seed density. Recently, oxygen has been found to be the best candidate for passivating the active sites on copper surfaces, resulting in a low graphene nucleation seed density, although the copper surface is very rough. Two commercial Cu foils with different oxygen impurity concentrations have been employed for this study. The oxygen concentrations are $10^{-2}$ and $10^{-6}$ at% for oxygen-rich Cu (OR-Cu) and oxygen-free Cu (OF-Cu), respectively. The two types of Cu were utilized to grow graphene under identical conditions in low pressure CVD, and the results are shown in Figure 3a,b. There are three significant differences between...

Figure 2. Large-scale graphene domain growth on a smooth copper surface. a,b) SEM images of graphene on the outer and inner surfaces of the Cu foil tube, respectively. Reproduced with permission. [39] Copyright 2013, Wiley-VCH. c) Typical optical and SEM images of as-produced graphene domains on Cu. Reproduced with permission. [71] Copyright 2012, American Chemical Society. d) AFM topographical image of a re-solidified copper surface. e) SEM image of a graphene domain. Scale bar is 0.2 mm. Reproduced with permission. [40] Copyright 2013, American Chemical Society. f) SEM images of as-produced graphene domains on a Pt substrate. Scale bar is 1 mm. Reproduced with permission. [30] Copyright 2012, Nature Publishing Group.
graphene growth on these two types of Cu substrate, which are probably induced by the presence of the oxygen impurity: i) Domain density on OR-Cu is three orders of magnitude lower than that of OF-Cu. As we discussed above, metal surface imperfections such as sharp wrinkles, step edges, and defects play a role as the active sites for graphene nucleation. They have higher d band centers at lower coordination defects, which leads to strong binding with any adsorbents. By the same reason, those active sites easily absorb oxygen impurities and are then effectively passivated, resulting in a lower domain density in the case of the OR-Cu substrate. ii) Domain shape on OF-Cu is compact hexagons with sharp edges, whereas graphene domains on OR-Cu always exhibit multibranched and rough domain edges. iii) The graphene growth rate on OR-Cu is much faster than on OF-Cu. Theoretical studies have shown that the dehydrogenation reaction could be enhanced with the introduction of O on Cu substrate through the reaction $CH_x + O \rightarrow CH_{x-1} + O$. Therefore, oxygen could reduce the adsorption barrier and facilitate C incorporation, accelerating the graphene growth rate. In order to further suppress the graphene nucleation density, both kinds of Cu substrate are exposed to oxygen at a high temperature, and then a copper oxide layer is formed on the substrate. Because H$_2$ gas can reduce the oxide layer during ramping up and short annealing, samples should be placed in a nonreducing environment (only pure argon gas) in order to maintain this oxide layer. Figure 3c shows the graphene nucleation density measured as a function of oxygen-exposure time. The nucleation density significantly decreases with increasing exposure time, with a similar trend for both Cu substrates. After 5 min exposure to O$_2$, H$_2$ and CH$_4$ are injected into the reactor at the same time, and graphene nucleation density is as low as $=0.01$ mm$^{-2}$ and the domain size is larger than 1 cm after 12 h growth, as shown in Figure 3d. These results reveal that the oxide layer plays a crucial role to effectively passivate the active sites on the Cu surface, thus providing a new pathway to synthesize single-crystal graphene on a centimeter scale.

2.2.2. The Multi-nucleation Approach

Although great achievements have been realized in the CVD synthesis of large-scale graphene domains using single-nucleation approaches, some challenges still remain. For instance, several nucleation seeds always co-exist with different orientations in one sample, and to obtain a single nucleation seed on a wafer scale is a big challenge. In practice, large individual grains require low carbon concentrations. Thus, it takes a very long time to archive large-scale domains, for example, 12 h to obtain 1 cm$^2$ or 48 h for 5 mm-sized graphene domains in another report. Moreover, those domains are terminated at a certain time during growth when the exposed Cu area is reduced. As a consequence, a complete graphene film could not be obtained.

Therefore, a feasible approach to realize monocrystalline graphene at a wafer scale is desired. Single-crystal substrates with a minimum lattice mismatch with graphene and the preferred orientation of graphene domains are necessary conditions to grow monocrystalline graphene. Another condition is to maintain epitaxial graphene growth. For this approach, instead of trying to start with a single nucleation seed, graphene nucleation density could be high, however, if the initial multiple domains of graphene have an identical orientation and coalesce together atomically, uniform monocrystalline graphene could be obtained. The size of the continuous monocrystalline graphene is restricted by the size of the single crystal substrate. This concept was first demonstrated via epitaxial graphene growth on an exfoliated hexagonal-boron nitride (h-BN) substrate. However, the size of exfoliated h-BN was limited to the microscale, which hampers graphene growth at a wafer scale on this substrate. Recently, large-area, single-crystal substrates were also utilized to prove this concept, such as hydrogen-terminated germanium and polished Cu. Consequently, wafer-scale and reproducible monocrystalline graphene growth has been demonstrated. The advantage of the multi-nucleation approach is the use of a short growth time to obtain continuous, large-area, monocrystalline graphene. This will be discussed in detail here.

Figure 3. Large-scale graphene domain growth on a pre-oxidized copper surface. a, b) SEM images of graphene domains on oxygen-free and oxygen-rich copper, respectively. c) The graphene nucleation density, measured as a function of O$_2$ exposure time. d) Optical image of centimeter-scale graphene domains on oxygen-rich Cu exposed to O$_2$. Reproduced with permission. Copyright 2013, American Association for the Advancement of Science (AAAS).
Among numerous methods of graphene growth, the hetero-epitaxial approach allows us to define the orientation of graphene by the crystallographic orientation of the substrate. Single-crystal h-BN has an hexagonal lattice structure with a lattice constant close to that of graphene.\(^9\) Thus, h-BN has been considered one of the best substrates for epitaxial graphene growth. Figure 4a illustrates the growth process. Single-crystal h-BN flakes are exfoliated onto a SiO\(_2\)/Si substrate by mechanical cleavage.\(^9\) After CH\(_4\) gas is introduced into the chamber, it is dissociated into various reactive radicals by a remote plasma source without the presence of metal catalysts. Then, graphene is nucleated and subsequently grown on the substrate. Remarkably, all of the graphene grains have an identical orientation, which is confirmed by the edge-direction of those domains (marked with white dotted lines). This alignment is also observed in other reports.\(^10-11\) These grains will be enlarged and merged together to form a continuous graphene film after a longer growth time. The identical orientation of the graphene domains is further confirmed by Moiré patterns, as shown in Figure 4c. It is clear evidence that Moiré patterns of two adjacent domains are well aligned. The lattice mismatch between graphene and h-BN is 1.8% and, thus, they could be out-of-phase during the coalescing of two adjacent domains. However, this lattice mismatch is considered negligible compared to the size of the graphene domains (a few hundred nanometers). Graphene has low friction on h-BN due to weak interactions between the graphene and h-BN. Therefore, the small angle mismatch between two adjacent domains could be relaxed by local lattice distortions or translocations of domains during coalescing. Consequently, it is energetically unfavorable to form grain boundaries or line defects between domains. Figure 4d shows an atomic-scale STM image of a merged region between two adjacent domains. There is no evidence of line defects, confirming the seamless stitching of two adjacent domains. By extending the growth time, monocrystalline graphene without grain boundaries or line defects is formed on the h-BN substrate. However, the size of this graphene film is limited by the size of the exfoliated h-BN substrate on the microscale.

Due to the problem of scalable epitaxial graphene growth on h-BN, other suitable substrates are needed. Recently, the seamless stitching concept of graphene domains was also demonstrated on hydrogen-terminated Germanium(110) film.\(^4\) This film is obtained by hetero-epitaxial growth on a Si(110) wafer using germane (GeH\(_4\)) as a precursor.\(^10\)
After deposition, the Ge layers are crystallized by thermal annealing at 600 °C. The reasons for using single-crystal Ge for graphene growth are: i) Ge can also play a role as a catalyst to lower the barrier energy for the dehydrogenation reaction of the carbon precursors. ii) Ge has an extremely low carbon solubility at its melting temperature; consequently, monolayer graphene growth is controllable. iii) Wafer scale single-crystal Ge films could be achieved by hetero-epitaxial growth on a Si wafer. iv) A small thermal expansion coefficient difference between graphene and Ge reduces the intrinsic wrinkles in the graphene film.

Figure 5a shows an SEM image of incomplete graphene growth on a H-terminated Ge film. The white arrows indicate the corners, which are formed by the edges of graphene domains. By focusing on one of those corners using HR-TEM, atomic-resolution images are obtained, as shown in Figure 5b. No defect line is observed, indicating the seamless stitching of graphene domains. Figure 5c reveals low energy electron diffraction (LEED) patterns of graphene on the Ge(110) surface. The six sharp spots (dashed red circles) indicate the monocrystalline graphene while dashed white circles correspond to Ge(110) peaks. The commensurability between graphene and the underlying Ge(110) substrate is possible even though there is a large lattice mismatch between them (Figure 5d). By analyzing the position of LEED spots of graphene and the Ge surface in Figure 5c, the periodicity of the supercell is derived as \((8 \times 10)\) in terms of a Ge(110) unit cell. Moreover, every 23 zigzag units and 16 armchair units of graphene almost perfectly coincide with 10 a\(_{\text{Ge}}\) (lattice constant of Ge) along the [001] direction and \(8 \times \sqrt{2}\) a\(_{\text{Ge}}\) along the [110] direction of the (110) facet, respectively. Due to the seamless stitching and commensurate growth with this substrate, a wafer-scale monocrystalline graphene is obtained. Surprisingly, commensurate graphene growth does not occur at 1000 °C but does not occur at 900 °C. This phenomenon requires more experiments and theoretical calculations. The large lattice mismatch between graphene and the Ge(110) film and the formation of simple defects or impurities on the Ge(110) surface could easily break the commensurate graphene growth conditions, resulting in too narrow a growth window for the synthesis of graphene with high uniformity and reproducibility.

Graphene has an hexagonal-honeycomb lattice structure and, thus, epitaxial graphene growth requires an hexagonal substrate with a minimum lattice mismatch. Normally, transition-metal foils are polycrystalline, which is not compatible with epitaxial growth. Recently, well-defined, single-crystal hexagonal structured substrates such as Co(111), Ni(111), Ir(111), Ru(111), and Cu(111) films were obtained by hetero-epitaxial deposition on single-crystal sapphire (α-Al\(_2\)O\(_3\))(0001)) or MgO(111) substrates. This approach provides highly monocrystalline metal films, which are suitable for epitaxial graphene growth on a wafer scale with a low cost and high throughput. Among those metals, Cu films are widely utilized due to their self-limiting tendency to grow large-area monolayer graphene. Figure 6a shows the schematic of monocrystalline graphene growth over the hetero-epitaxial Cu film. Firstly, hetero-epitaxial Cu films are deposited onto single-crystal sapphire (α-Al\(_2\)O\(_3\))(0001)) at 500 °C by radio frequency (RF) magnetron sputtering. At high-temperature sputtering, diffusions of deposited Cu atoms or clusters are enhanced, contributing to single, oriented Cu grains. Thus, high temperature is a crucial parameter to obtain stable and uniform single-crystal Cu films without twinning or grain boundaries. After that, the Cu films deposited on sapphire are annealed at 1000 °C to improve the metal crystallinity. Graphene films are synthesized by the typical CVD method at atmospheric pressure using CH\(_4\) as a carbon source. The electron backscattering diffraction (EBSD) image in Figure 6b clearly indicates that the deposited Cu

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**Figure 5.** Monocrystalline graphene growth on a H-terminated Ge(110) film. a) SEM image of incomplete graphene growth on Ge(110) film, where white arrows point out the corners formed by the edges of merged domains. b) High-resolution TEM image of a corner as indicated by the white arrows in (a). c) LEED patterns of monocrystalline graphene grown on a Ge(110) film: red and white dashed circles correspond to graphene and Ge peaks, respectively. d) Atomic model of commensurate growth of graphene on a Ge(110) film. The orange balls and green grid indicate the top-most Ge atom and a unit cell of the Ge(110) surface, respectively. Reproduced with permission. Copyright 2014, AAAS.
film has a (111) plane. This result confirms that the Cu film is uniform, with the absence of grain boundaries or twinning. Figure 6c shows a LEED image of as-grown graphene over the hetero-epitaxial Cu film measured at 100 eV with a spot size of 1 mm. The six sharp diffraction spots originate from both the graphene lattice (green circle) and the Cu(111) lattice (red circle). This result clearly demonstrates that the graphene film is synthesized epitaxially on the Cu(111) film. In other words, orientation of the graphene well matches with that of the underlying Cu(111) film. In order to characterize the domain structure of the graphene film, LEEM is employed. The advantage of this measurement is that it does not require a graphene transfer process and can measure a large area by simply moving the stage. The dark field (DF)-LEEM image of graphene on the hetero-epitaxial Cu(111) in Figure 6d shows a uniform contrast, which confirms the formation of a monocrystalline graphene film. These above results are distinct compared with those of graphene growth on Cu deposited on single-crystal MgO(100).[56]

Nevertheless, LEEM gives the averaged orientation of graphene domains within a large beam shot size (1 mm), thus, the orientation of the graphene film on a macroscopic level is not guaranteed. Moreover, there is no clear evidence of the non-existence of grain boundaries or line defects in these epitaxial graphene films.[116,117] In order to clarify this problem, the concept of seamlessly stitching graphene domains on polished copper (111) is demonstrated by various methods.[60] The as-received Cu foils are polished using the chemical–mechanical polishing method followed by annealing at 1075 °C in Ar/H₂ gases to remove the protection layer, sharp wrinkles, etc.[78] This process is repeated several times, until very smooth Cu(111) foils are obtained. The hexagonal shape of the graphene domains is obtained by maintaining a high ratio of H₂/CH₄ of 1600, i.e., a slow carbon feedstock that can reach energetically favorable sites. Seamless stitching of graphene domains is proved convincing not only at the macroscale but also at the atomic scale. By terminating the growth before continuous graphene films are formed, merged graphene domains can be seen in Figure 7. An example of incommensurate stitching between two hexagonal graphene domains is shown in Figure 7a. The edge directions of two hexagonal graphene domains are mismatched by 15°, which indicates misorientation between the two domains. By using UV exposure under moisture-ambient conditions, which is described clearly in a previous report,[66] a clear grain-boundary line is observed. Conversely, the edge directions of two hexagonal graphene domains are identical, which indicates the identical orientation between two domains, as shown in Figure 6b. After identical UV exposure, no grain boundary line is observed, which indicates the commensurate stitching of two hexagonal domains. The seamless stitching is further confirmed at an atomic scale in Figure 7c. The STM measurements are carried out at the corner that is formed by the two edges of merged domains. There is no evidence of
a grain boundary or of poor matching of the two domains, as shown in the right panel. In other words, the two adjacent domains are connected atomically. Remarkably, the lattice mismatch between copper (111) and graphene is 4%. The self-alignment of graphene domains is also observed in graphene growth on liquid copper, regardless of the orientation of the underlying copper substrate. However, graphene domains are locally self-aligned. During cooling, the strain energy on graphene due to the lattice mismatch cannot strongly influence the already-formed graphene lattice. This kinematical behavior requires further detailed study. By applying this seamless stitching concept, 6 cm × 3 cm monocrystalline graphene has been synthesized within an hour without forming grain boundaries on polished Cu(111) foils, which was only limited by the chamber size. This is the largest monocrystalline graphene film that has been reported so far using CVD.

3. Observations of Graphene

3.1. Graphene Orientation

3.1.1. At the Microscale

The principle of using DF-TEM for observations of the graphene orientation is shown in Figure 8a–d. Figure 8a shows a bright-field TEM (BF-TEM) image of graphene on commercial TEM grid. There is uniform contrast in this BF image, consequently, no graphene orientation is observed. The red dashed circle indicates the region for the diffraction pattern acquisition in panel (b). The scale bar is 500 nm. Figure 8b shows a bright-field TEM (BF-TEM) image of graphene prepared on a commercial quantifoil holey carbon grid. There is uniform contrast in this BF image, consequently, no graphene orientation is observed. The red dashed circle indicates the region for the selected-area electron diffraction pattern (SAED), as shown in Figure 8b. Because graphene has six-fold symmetry,
electron diffraction patterns of monocrystalline graphene generate one set of six-fold symmetry spots. The electron diffraction pattern in Figure 8b contains two sets of hexagonal patterns, indicating that the measured region contains two grains, which are rotated relative to one another by 25.6°. By transmitting only a single diffraction spot (marked by the black dashed circles ‘c’ or ‘d’), using a small objective aperture filter, a bright contrast in one grain could be enhanced. The resulting real-space images show only one grain corresponding to the transmitted diffraction spot. The DF image in Figure 8c clearly shows that there are two distinct regions divided by a sharp line feature, with the left side brighter than the right side, which corresponds to the transmitted diffraction spot ‘c’. The DF image with inverted contrast in Figure 8d corresponds to the transmitted diffraction spot ‘d’, while the yellow dashed line feature does not change. There is no overlap between the two bright regions in the two DF images (Figure 8c,d) which identifies the line feature as a grain boundary, not a local overlapping of two distinct graphene grains. By repeating these processes over an entire sample to cover multiple grains, then coloring and overlaying these DF images, the graphene orientation distributions are visualized, as shown in Figure 8e. Each color corresponds to a grain boundary, not a local overlapping of two distinct graphene grains. By repeating these processes over an entire sample to cover multiple grains, then coloring and overlaying these DF images, the graphene orientation distributions are visualized, as shown in Figure 8e. Each color corresponds to a grain boundary. The indicated angles inside each grain are the relative angles between grains measured against a reference grain in the center (overlaid in red).

Figure 9. Graphene orientation observation by Raman mapping. a–c) Optical microscopy images of top (a) and bottom (b) graphene layer before and after (c) aligned transfer. d,e) Raman mapping of the G and 2D band intensities of the region indicated by the green square in panel (c), respectively. f) The Raman spectrum in three regions indicated in panel (e). Reproduced with permission. Copyright 2014, Wiley-VCH.

There have been great achievements regarding the observation of graphene orientation in the microscale regime. However, graphene film size has approached wafer scale already. Thus, a suitable method to observe on the macroscale is extremely desirable. In the case of the DF-TEM approach, complicated sample preparations for TEM are required but are still limited to small-area observations. Confocal Raman mapping is more versatile on a larger scale by simply moving the stage to scan samples, however, another graphene domain with a similar size to the investigated sample is needed. In both approaches, the samples could not be re-used for other purposes.

Polarized optical microscopy (POM) with NLC layer assistance has emerged as the most promising tool for the visualization of graphene orientation distributions and for solving all of the problems of the previous approaches completely. It is practical on a wafer scale by simply moving the stage of the POM, and the graphene sample could be re-used
by removing the coated NLC layer using acetone. Yet ambiguity still exists with Cu domains in the first report. Based on these results, graphene orientations are perfectly matched with underneath Cu grains. However, single-crystal graphene domains can grow across Cu grain boundaries due to weak interactions with the Cu substrate. Thus, a strong correlation between graphene orientations and Cu grains is misleading. Using the same approach, graphene orientation distributions on Cu surface have been visualized precisely in recent reports, which are discussed in more detail below.

Figure 10a shows a schematic of the NLC alignment on a polycrystalline graphene surface. The NLC (4-cyano-4’-pentylbiphenyl: 5CB) molecules consist of two hexagonal benzene rings with a nitrogen atom at one end and a long carbon chain at the other end. This molecule is adsorbed onto the surface of a graphene film by a simple spin-coating method. Although two carbon rings in a free-standing molecule are twisted, they are strongly adsorbed in parallel to the graphene surface, while the tail part is repelled due to the hydrophobic nature between graphene and tail of the molecule. DFT calculations show that AB stacking between two benzene rings of NLC molecule with graphene has the strongest binding energy. It implies that NLC molecules prefer to be oriented along the graphene lattice. The NLC molecules will be oriented differently depending on the graphene lattice orientation (red arrows in Figure 10a). The orientation of aligned NLC molecules could be observed by POM and, consequently, graphene orientation distributions are visualized. For the transmittance mode of POM, graphene domains are transferred onto a glass substrate. By fixing an analyzer and a polarizer while rotating the sample stage, the absolute lattice orientation of graphene domains is featured (Figure 10b). Two hexagonal domains are stitched together with angles of 90° and 135° with respect to the x axis. More importantly, the calculated misorientation angle (45°) is the same as the edge mismatch between the two graphene domains. The graphene orientation distribution is also realized directly on the Cu substrate without any further transfer processes, using the reflection mode of POM. The observed texture (Figure 10c) of the graphene film grown on Cu(110) indicates that the orientation of the NLC molecules corresponds to various graphene orientations. Graphene film is polycrystalline in this case. In contrast, no texture is observed in the case of films grown on Cu(111) (Figure 10d), which indicates that all NLC molecules are oriented in the same direction. Therefore, the graphene film is monocrystalline.

3.2. Graphene Grain Boundaries

3.2.1. At the Atomic Scale

By visualizing graphene domain orientations, GGBs could be found located roughly between the graphene grains. However, untilted or extended GGBs can exist between two grains with identical orientation. Therefore, the aforementioned approach is not suitable for locating these kinds of GGBs. Moreover, the atomic structure and properties of GGBs are not revealed either. For these issues, TEM and STM are most frequently employed. The HR-TEM method provides the atomic configuration of GGBs directly and relatively quickly. However, this method requires complicated sample preparation processes on TEM grids, which may induce contamination or extra wrinkles in the graphene film, and graphene sample could be damaged or distorted under the high-energy radiation of the electron beam. In contrast to HR-TEM, the exact atomic configuration of GGBs could not be revealed directly in the atomic resolution of STM.
images, since the local density of states distorts the atomic image at the GGBs.\textsuperscript{[125,126]} It can only be inferred from model calculations.\textsuperscript{[60,61]} However, this drawback is also the biggest advantage of STM measurements, since the local electronic structures of the GGBs could be studied. GGBs could be investigated directly on metal substrates, but STM measurements are time-consuming because hundreds of billions of pixels would be needed for an atomic-resolution image.

Depending on the nonhexagonal carbon-ring arrangement, GGBs could be classified as periodic or aperiodic. The most-observed GGBs experimentally are aperiodic.\textsuperscript{[127–129]} Figure 11a shows an example of an aperiodic grain boundary which consists of nonhexagonal carbon rings with a random arrangement. Recently, 5–8–5 and 5–7 (Figure 11b) periodic GGBs were also observed experimentally on Ni(111) and Cu(111) substrates, respectively.\textsuperscript{[60,63]} The aperiodic GGBs play a role as carrier scattering sources and degrade the electrical conductivity of graphene, which is proven by transport measurements across the boundary.\textsuperscript{[124,130]} This is further confirmed by current–voltage (dI/dV) mapping when an STM tip is scanned across a grain boundary. Figure 11c shows that the tunneling current at the grain boundary is significantly suppressed, about an order of magnitude lower than the defect-free graphene region. Several other studies have also reported that the aperiodic grain boundary is n-type doped, while defect-free graphene regions are p-type doped.\textsuperscript{[62,127]} This forms an abrupt p–n–p junction within a few nanometers in polycrystalline graphene. This observed phenomenon may originate from the self-doping of GGBs, where charge transfer occurs between defect-free graphene and GGBs. An additional reason may come from the high chemical reactivity of GGBs, and thus functional groups or absorbents prefer to attach on them. In contrast with aperiodic GGBs, periodic GGBs are predicted to have special properties such as high mechanical strength, magnetism, and the presence of a well-defined transport gap.\textsuperscript{[131–135]} Figure 11d shows dI/ dV mapping across a periodic grain boundary. Interestingly, it reveals that the tunneling conductance along the periodic grain boundary is about three times higher than that on a defect-free graphene sheet. This phenomenon is attributed to the presence of van Hove singularity (VHS) states at the boundary, which is an effective source to enrich charge

Figure 11. Grain boundary observations by STM. a, b) Atomic-resolution STM images of aperiodic and periodic grain boundaries, respectively. Inset in (b): FFT showing the domain misorientation angle at 22.5°. Reproduced with permission.\textsuperscript{[62,63]} Copyright 2012, American Institute of Physics; Copyright 2014, American Chemical Society. c, d) Spatially resolved tunneling conductivity mapping at the aperiodic and periodic grain boundaries, respectively. Reproduced with permission.\textsuperscript{[61]} Copyright 2014, American Physical Society.
nanoparticles are deposited predominantly at the GGBs. Due to the higher chemical reactivity of the GGBs compared to pristine graphene, metal nanoparticles at GGBs. Due to the limited scan area, high-resolution TEM and STM/STS are not practical for macroscale observations of GGBs. Thus, several approaches have been developed to study their distribution over a large area. Recently, GGBs have been visualized using IR nano-imaging techniques. The infrared light is focused on the metallic tip of an atomic force microscope (AFM), generating a strong localized field around the sharp tip. This concentrated electric field induces circular surface plasmon waves around the tip. These waves are partially scattered and reflected by GGBs, causing interference between the incident and back-reflected plasmonic waves. By recording and analyzing the interference patterns, GGBs can be visualized. Figure 12a indicates multiple graphene grains (overlaid by various colors) which are defined by the twin fringes due to grain boundaries (marked as red arrows).

Another approach relies on the selective deposition of metal nanoparticles at GGBs. Due to the higher chemical reactivity of the GGBs compared to pristine graphene, metal nanoparticles are deposited predominantly at the GGBs. Base on this, Pt nanoparticles were deposited at GGBs by atomic layer deposition (ALD), forming 1D nanowires. Figure 12b shows an SEM image of graphene on a glass substrate after Pt deposition. GGBs are visualized due to the presence of Pt nanoparticles. The formation of Pt nanoparticles on GGBs is further proven convincingly by high-resolution TEM (not shown here). However, Pt nanoparticles could be also deposited on wrinkles, thus, the observed GGBs could be confused with wrinkle lines.


Another method is based on the selectively oxidized underlying Cu through GGBs, forming Cu oxide lines. These Cu oxide lines expand in volume to several hundred nanometers due to oxidation and could be observed under an optical microscope. Indirectly, GGBs distributions are obtained. Two methods to selectively oxidize Cu though GGBs have been reported so far. The first method was realized by UV irradiation in the presence of humidity. Reactive radicals such as O and OH are generated under UV irradiation. These radicals selectively penetrate GGBs and oxidize the Cu underneath. Figure 12c shows an optical microscope image of graphene on a Cu substrate after UV irradiation. These line features (as marked by red arrows) clearly indicate the distribution of GGBs. However, during UV irradiation, the graphene film is inevitably oxidized simultaneously, which is the main drawback of this method. Another approach to oxidize the underlying Cu substrate without oxidation of the graphene film has been developed. Half of the graphene film/Cu is immersed in NaCl solution. The immersed portion generates electrons by corrosion of the Cu substrate (nongraphene side). The generated electrons diffuse to the nonimmersed portion, which enhances air oxidation of the Cu substrate through GGBs under ambient moisture conditions. Consequently, Cu is only oxidized at the GGBs while maintaining the pristine property of the graphene film. Using this approach, the GGB distribution is visualized clearly, as shown in Figure 12d.

4. Conclusions and Outlook

The production of monocrystalline graphene on a wafer scale without any grain boundaries via CVD synthesis is essential for both fundamental research and industrial applications. In this review, the graphene growth mechanism and recent progress in synthesizing monolayer, monocrystalline graphene on a wafer scale have been discussed in detail. Two main approaches have been reviewed: The first approach focuses on the reduction of the nucleation seed density by suppressing or passivating the active sites on the Cu surface. Using this approach, a centimeter-sized graphene domain has been obtained after 12 h growth. The second approach is based on the seamless stitching of graphene domains, which have identical orientations on polished Cu(111) or H-terminated Ge(110). Wafer-scale monocrystalline graphene could be achieved this way during a relatively short growth time.

The properties of polycrystalline graphene could be modulated significantly due to the existence of GGBs (or defect lines). The observation and characterization of GGBs from the nano- to the macro-scale provide an understanding of the chemical and physical properties of polycrystalline graphene. As discussed in this review, high-resolution TEM and STM/STM provide clear atomic configurations and the electrical properties of GGBs. At the microscale, graphene orientations are visualized by DF-TEM and confocal Raman mapping with the assistance of another overlaid single-crystal graphene layer. Moreover, graphene orientation and GGB observation at macroscale by SEM, optical microscopy, and IR nano-imaging techniques was also discussed in detail.
Although GGB-free graphene growth on a wafer scale has been realized, there are still some challenges. Large-area, monocrystalline graphene has been grown on several transition-metal substrates such as Cu, Pt, and Au. In order to utilize graphene for electronic devices, the graphene film should be transferred onto an insulating substrate. This process can involve the introduction of wrinkles, cracks, or contaminations, which degrade graphene performance significantly. Thus, direct graphene growth onto an insulating substrate is extremely desirable. The seamless stitching of graphene domains has been demonstrated on single-crystal h-BN flakes using remote PE-CVD. Combined with the recent progress of CVD for large-area, single-crystal h-BN substrates, this will open a new window to synthesizing large-area, monocrystalline graphene on this insulating substrate. Other insulating substrates, such as sapphire and MgO(111), could be suitable for this due to their small lattice mismatch with graphene and an hexagonal symmetry.

Monolayer graphene is a semimetal with a zero bandgap.\[137–139\] Therefore, to open the bandgap of graphene while maintaining its high carrier mobility is a big challenge for graphene FETs. Several approaches have been developed to open the bandgap of graphene by preparing graphene nanoribbons, nanomeshes, or functionalizing graphene.\[20,140,141\] However, the carrier mobility of FETs using these kinds of graphene is relatively low due to edge or resonant scattering.\[142\] AB-stacked bilayer graphene is suggested to open the bandgap by 0.2–0.3 eV by applying a vertical electric field.\[143\] Although it could be possible to form monocrystalline bilayer graphene by transferring another monocrystalline graphene with a fixed orientation as described above, it will be desirable to grow bilayer graphene directly in particular with an AB stacking order. Owing to the limited carbon solubility in Cu, a uniform monolayer is well controlled. However, growing bilayers using CVD can be a challenge. One may extend the CVD approach to reach the epitaxial growth of an additional bilayer once monolayer graphene is obtained. Two issues should be resolved in such a case: One is how to increase the adsorption of the carbon species. Low temperatures can be tried, but the decomposition rate of hydrocarbon gases is reduced, which may be overcome by using a plasma source. Another issue is to maintain energetically favorable van der Waals interactions during growth to maintain the AB stacking order. This can be done also by optimizing the growth temperature so that favorable energetics prevail.

As discussed above, the conductivity of periodic GGBs is about 3 times higher than that on defect-free graphene sheets. This is in contrast with that of aperiodic GGBs. Periodic GGBs are also predicted theoretically to have peculiar properties such as high mechanical strength and magnetism. The controllable formation of periodic GGBs would be useful to engineer graphene properties and develop graphene-based devices. However, how the atomic configuration of GGBs formed when merging grains is not clear at this moment. This could depend on the graphene growth conditions or the substrate. More efforts toward in-situ growth and observations are needed to answer this question. Although monolayer h-BN (or transition-metal chalcogenides – TMDs) have a polar character and the antiphase phenomenon might occur during the merging of identical h-BN (or TMD) domains, the concept of seamless stitching in the case of graphene is still expected to be utilized for the large-area, monocrystalline growth of those 2D materials.

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