Quasistatic Equilibrium Chemical Vapor Deposition of Graphene

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This study reviews the majorly used chemical vapor deposition (CVD) with a focus on confined reaction configurations in which quasistatic equilibrium conditions are obtained for the fabrication of graphene with large size and high quality through controlled nucleation density, feedstock flux, and growth rates. The confinement configurations can also be used to tune the thickness, domain size and shape, and stacking order of the synthetic graphene. The confined CVD reaction configurations discussed include enclosure systems, inner-tube setups, sandwiched substrates, as well as other types of configurations. The advantages and limitations of the different confinement configurations are presented, along ways to optimize the operational parameters for them.

1. Introduction

Graphene has undergone a surge in development in recent decades due to its distinctive structural features and intriguing physicochemical attributes.1–3 The development of effective techniques is vital for fabricating well-defined graphene materials with controllable size, thickness, and structural integrity.4–6 In context, the confined synthesis, as an emerging concept has been viewed as an auspicious approach for design and growth of novel 2D graphene nanostructured materials. In addition, vapor blocking or containment is a concept that has been utilized for restricting gaseous moieties in a small space for a prolonged period to ensure a flow profile of quasistatic equilibrium state.7–9 This confinement approach has been established for the controlled fabrication of graphene, where the confined condition contribute to decide the shape and size of depositing nanomaterials. In addition, the restricted reactor setup offers a specific chemical environment for the stabilization of growth bearing intermediates, reduced nucleation density and controlled growth.10–12

The chemical vapor deposition (CVD) method is distinct from its alternatives, because growth can be controlled using several parameters that facilitate diversity of selection based on the synthesis conditions. In addition, the various advantages of the CVD approach include those posed by the confinement concept as well.11,13 Generally, a space-restricted configuration poses two major advantages. First, the key objective of the space-limited chamber is to reduce the carbon (C) flux and contain the growth substrate nearby for a longer period to increase the growth probability. Second, a large-domain single-crystal growth occurs with minimal secondary growth, as a lower carbon supply reduces the nucleation probability of graphene.15 In addition, such reactors also ensures the suppression of growth substrate surface vaporization. Consequently, both the effects reduce the nucleation density, which is favorable for large domain and single-crystal graphitic growth.16

The confinement configuration can be used to tune for the major portion, nucleation number, and grain size (Figure 1a–f);

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including the diverse attributes of graphene, for instance, thickness and shape, and stacking order. Moreover, it can be used to protect graphene from reactor contamination (e.g., silicon dioxide (SiO$_2$) particles. Here, it should be kept in mind that SiO$_2$ particles also help with graphene growth behave as a nucleation center or catalyst) and eliminate the impurities from the as-grown graphene in space-confined growth, especially enclosure and slot methods, thus improving graphene growth quality.[18–22] Furthermore, it can result in high-quality in situ growth of growth substrates (e.g., copper (Cu) film) and then graphene films over it.[13,24] Moreover, it reduces the interaction with the external environment/gases, thus providing isolated conditions for interactions between growth species and growth substrates and aiding favorable growth. Therefore, two configurations have been reported: first, the modification of the growth substrate itself, namely, its enclosure, tube, or stacking/sandwiching; second, the placement of the growth substrate inside an additional setup with limited space (e.g., tube, slot, or box) to control the flow around it.[16,25]

Graphene quality growth is reported by optimizing other growth parameters.[26–29] In this review article, we primarily discuss the various configuration used for controlling the flow from the perspective of their advantages and disadvantages. The various reactor configurations along with their advantages, disadvantages, growth size and thickness are listed in Table 1. As per the present authors’ knowledge, this study entails the first dedication to integrate all the efforts describing the significance of flow on graphene growth different aspects. Finally, we summarize the findings of the study with concluding remarks, and the perspective section details the existing challenges and futuristic development. This study will be used as a benchmark for CVD graphene researchers to emphasize the significance of vapor restricted CVD strategy.

2. Enclosure Configuration

In general, an enclosure configuration creates a restricted atmosphere by simply modifying the flexible growth substrate itself into an envelope without requiring any additional setup, resulting in a lower overall price. In contrast, other reactors are cost-intensive as they need additional units for enabling flow
control situations, creating a complex reactor configuration and growth process. Despite the limited supply of carbon flux at the inside surface of the reactor acting as the fabrication surface for graphene synthesis, their surface smoothness is preserved. The major function of this configuration includes the control of gaseous fluid flow to inhibit growth substrate roughness by suppressing evaporative loss. Although this configuration is not restricted to the growth of graphene, other 2D materials have been developed, e.g., hexagonal boron nitride (hBN). This work was pioneered by Rouff et al., who fabricated monocrystalline graphene where the grain reached up to 0.5 mm in size. As an alternative of a usual flat copper foil, they utilized a Cu-foil pocket as the growth surface. In particular, the Cu foil was bend into an envelope (Figure 2a), and a mono-crystal growth of graphene was realized on its inside surface (Figure 2b). Overall, the controlled synthesis of large grains in the confined conditions can be explained as follows. The confined chemical and growth environment served to reduce the number of nucleation density as well as resided the growth moieties around the growth surface for a longer period. In addition, the dendritic boundaries of the fabricated graphene grain suggest that the growth is intervened by the restrained diffusion of growth intermediates unlike that in a conventional low-pressure CVD operating in free space conditions where the growth process is led by surface regime. 

The enclosure-based setup has various forms. Not limited to only an enclosure reactor, a distinct hole in the enclosure reactor was reported by Phan et al., to restrict the dynamics of growth-bearing active gases (Figure 2c–e). Based on this reactor configuration, the deposited graphene grains were few millimeters in dimension. Furthermore, it has been noticed that some of the growth grains were merged (Figure 2f). The hole-based reactor setup maintained uniform evaporation and re-deposition rates of growth surface as well as insisted an equilibrium flow via hole to the inner of reactor (Figure 2e), thereby maintain an even inside surface. In addition, a hydrogen-annealing effect is encouraged by the holes on the pocket by adequate gas provision, which help rearrange the surface regime of copper growth surface. Hence, it is more suitable for graphene fabrication with high structural integrity and single layer thickness. In view of this finding, it is suggested that the restricted flow and improved copper surface features promoted the development of single layer graphene domains that expand further and eventually their boundaries meet together leading to large-area graphene (Figure 2f,g).

Bilayer graphene (BLG), in particular, Bernal-stacked (AB-stacked) has received major consideration owing to its tailored band gap. An enclosed structure was designed, and a piece of Cu sheet was embedded into it to establish a suppressive environment against Cu evaporation and ensure adequate smoothness of the Cu surfaces. Hence, large-size BLG and multilayer graphene (MLG) growth was enabled. Principally, the inner enclosure surface followed a single-diffusion mechanism, whereas the enclosed copper sheet surfaces are governed by a double-diffusion mechanism (one-way and two-way diffusion pathways, respectively; in the former, carbon enters into the copper thickness from one side, whereas in the latter, it enters from both sides). Based on the latter mechanism, BLG (AB-stacked) and MLG are fabricated with up to 603 and 793 µm in size, respectively. This study aimed to improve the growth integrity and crystallinity. Therefore, widen the applications limit in electronic and other disciplines.

Table 1. List of reactor configuration with advantages and disadvantages, growth size, and thickness.

| Reactor Configuration | Advantages | Disadvantages | Grain size | Thickness | Refs. |
|----------------------|------------|---------------|------------|-----------|-------|
| Enclosure            | No additional unit needed; elimination of reactor contaminations. | Increased chances of growth substrates damages; enclosure does not allow probing interior gas environment; time-consuming; not applicable to rigid substrates. | Continuous | Monolayer | [15] |
|                      |            |               | 0.5 mm     | Monolayer | [30] |
|                      |            |               | 450 µm     | Monolayer | [31] |
| Sandwich             | Limited chances of growth substrates damages; applicable to rigid/flexible substrates. | Time-effective. | Continuous | Monolayer | [16] |
|                      |            |               | 2 mm       | Monolayer | [16] |
| Tube                 | Limited chances of growth substrates damages; allows probing of interior gas environment; time-effective; applicable to rigid/flexible substrates. | Additional setup required. | Continuous | Mono/bilayer | [34] |
|                      |            |               |            |           |       |
| Box/slot             | Limited chances of growth substrates damages; applicable to rigid/flexible substrates. | Additional setup required | Continuous | Mono/bilayer | [34] |
|                      |            |               |            |           |       |
| Spiral               | Roll-to-roll (R2R) growth | More chances of growth substrate damage; only to flexible substrates. | Continuous | Multilayer | [12] |
| Channel              | Both flexible/rigid substrates. | Additional setup required. | Continuous | Monolayer | [38] |
|                      |            |               | 1072 µm    | Monolayer |       |
addition, Miseikis et al. lowered the nucleation density via the pocket method, and therefore, grew single-crystal grains over an extended growth period. Similarly, Zhao et al. explained the pocket reactor intervened diffusion mechanism and proposed that equilibrium fluid dynamics under restrained conditions can promote the development of improved graphene. Moreover, the AB bilayer graphene was studied based on the pocket route by another group of scholars, who investigated the influence of oxygen on growth and reported monocrystals AB BLG with 0.5 mm in size. In recent times, Fang et al. reported that the small domain growth of BLG on copper substrate could be resolved by using a Cu envelope. They determined that the exposed Cu inner surface served as a catalytic route to constantly supply active C to the outer surface via the copper thickness. Thus, the uneven flow conditions around the reactor surfaces can produce greater area dual layer growth on the external surface. This demonstrates that, by altering the copper surface thickness, it is possible to optimize the BLG growth. Zhao et al. verified the C diffusion process across the enclosed surface and attempted to control the nucleation density of graphene on its inside surface which on the other hand regulated the graphene layer thicknesses on the outer surface of the enclosure. The optimization of the growth conditions developed a large domain size of BLG, with an AB bilayer areas of 83% on the outer surface of the copper pocket reactor. The inhomogeneous crystalline film however, degrade the distinguished attributes of graphene, and minimize the boundary of graphene applications. Thus, it is a matter of research interest to establish a synthesis strategy that can suppress the number of grain boundaries. In this regard among many, Nanayakkara et al. used a dual treatment process, comprising an enclosure and impurity particles to favor minimal nucleation density and large domain growth. Interestingly, the dual treatment process; a copper enclosure reactor, and their exterior surface coating was used to suppress the nucleation density in chemical vapor deposition method for graphene fabrication. Thus the combined effort of confined reactor and their coated surface enabled the removal of multilayer growth and ensured graphene monocrystal deposition (Figure 3a,b). Furthermore, another group of researchers reported the influence of dual treatment, including the enclosure, as well the role of polishing. Enclosed reactor controlled the grain number and growth rate, whereas reactor surface electropolishing possibly removed surface defects. This confined setup led to monocrystalline graphene on polished Cu surface. Accordingly, Yang et al. characterized the influence of growth pressure on the dynamic balance of evaporation and deposition of copper in copper pockets to deposit single-crystal graphene using the copper pockets method. Inward surface roughness of the copper pockets reduces as the growth pressure increases. They observed a smooth and large domain growth on the inward Cu face as opposed to the outward one. Therefore, graphene single-crystal grain size can be enhanced by rising the pressure condition under vapor-trapped configuration.

A common feature of the above studies, is the adoption of an enclosure configuration which provides an environment in which gas (feedstock) flow is controlled to approximate static equilibrium conditions. In effect this provides an environment in which the C flux can be controlled and is limited. Under these circumstances it is possible to control the nucleation density which in turn allows for larger single crystal grain formation or poly-crystalline graphene comprising large domains, particularly as compared to synthetic graphene production using open CVD systems. In addition, enclosed conditions can control the stacking of bi-layer graphene, which is important for future applications based on twisted graphene (the so-called...
A potential drawback of enclosed systems is the risk of contamination, however, with appropriate steps to minimize this we do not envisage this being a serious issue. Another possible down side is the slower growth rates (as compared to open systems), however with time we believe faster growth rates will be obtained as more sophisticated setups are developed and moreover, even if growth rates are not ideal, the potential for high quality large area single crystal graphene could be attractive for niche applications.

3. Sandwich Configuration

Large-area graphene development was realized using a sandwich configuration with the growth substrate, as it is attributable to the confinement effect and the varying flow regime. More importantly, both the rigid (e.g., silicon wafer) and flexible substrates (e.g., copper foil) can be setup in a sandwich form, unlike the enclosure. Additionally, the sandwich approach has been used to fabricate other thin films, e.g., copper films and transition metal dichalcogenides. There are additional advantages of the sandwich configuration, which can be used to eliminate reactor impurities from the as-growing sample. Following this configuration, Chen et al. proposed a copper surface evaporation suppression mechanism while comparing three different space-limited configurations. Although, copper surface sublimation is common and result to poor quality growth. In these setups, interior Cu surfaces was covered with mono-crystal graphene grains growth. As opposed to, outer surface was noticed with graphene grains in reduced sizes. This varying Cu evaporation rates at the inner and outer surfaces led to such asymmetric growth conditions. Briefly, the inside face of Cu was in equilibrium between evaporation and redeposition processes at high growth temperatures, thereby leading to even surface. Contrarily, on the exposed face the evaporative rate was higher, which warranted a coarse surface. This strategy enabled graphene in large-size and single-crystal with high structural integrity on the restricted faces.

Sandwich growth assumes the form of a configuration with a spacer by creating a small slot above the growth surface. A prior study proposed that the growth on a space-limited surface is similar to that on a 3D porous template, which creates a pressure gradient and stagnant flux to favor growth. Graphene electronic features are strongly controlled by the stacking order in case of BLG. Subhedar et al. used various geometries of the reaction site to grow bilayer graphene using the restricted conditions-intervened chemical vapor deposition method and investigated the influence of the confined configurations on bilayer stacking order. A quartz/Cu/quartz sandwich reactor and the quartz plates were gaped by a spacer/gapper to create a confined environment, was used for graphene samples fabrication. In context, the gapper controlled the copper vapors sublimation and resided the growth bearing carbon species around the growth surface by generating contained conditions. Comparatively, an identical configuration but without the gapper was studied, therefore the Cu growth face directly touching the quartz plate. An AB-stacked bilayer graphene was formed by the spacer-intervened reactor, whereas twisted BLG was noticed in case of spacer free reactor configuration. The variation in the synthesis mechanisms offered by each configuration.
reactor configuration serves for the distinction in layer orientation. The development of twisted stacked graphene is mediated by diffusion mechanism. On the other hand, Bernal BLG was produced under the surface-assisted process with sufficient and continuous supply of C moieties under spacer-sandwich reactor. In view of this experimental report, graphene can be fabricated with tailored layer stacking order effectively. Under circumfluence chemical vapor deposition strategy minimal nucleation density has been acquired. Yet, the large dimension of restricted reactor condition led to high nucleation density on Cu surface. Therefore, a mini rectangular flow blocking setup was designed which guaranteed the uniformity of the nucleation density (Figure 4a). Moreover, this restrained configuration enabled the even distribution of growth intermediates and a smooth fabrication surface is preserved, which induced diffusion-based growth mechanism (Figure 4b–d). Single-crystalline graphene with high structural integrity was reported under these experimental setups (Figure 4e–i). A much smaller confined slot was set up by sitting a spacer (U-shaped tungsten spacer) between the two quartz slides (inset in Figure 4a), and the direct gas flow into the reactor was prevented by placing its opening end away from gas flow side. The objective behind this setup was to effectively minimize the growth moieties flow reaching the growth substrate surface (copper substrate in this work). Under this fabrication conditions, the reported graphene development was identical in nucleation density, size and the area covered on the deposition surface. On top of that, the small nucleation density was ascribed to the evaporation and re-deposition processes from the copper surface which was in dynamical equilibrium, thus maintained an even substrate surface. Moreover, the optimal growth parameters suppressed the nucleation density to 200 nuclei per cm². Furthermore, the simulation modeling investigation demonstrated a mass transport diffusion-intervened synthesis regime, a much decreased flow dynamic and a uniform distribution of growth active carbon forms (Figure 4b–d), all these conditions and processes were favorable for the development of single crystals and large domains of graphene.

Fabiane et al. elucidated the role of gas kinetics in the growth of graphene domain shapes by using two Si/SiO₂ wafers to sandwich a copper foil, and two growth reactor configurations were studied: 1) a copper substrate under open condition was sit at the mid chemical vapor deposition quartz tube and 2) in the second configuration, two Si/SiO₂ wafers sandwiched a copper substrate, that enable to control graphene nucleation features. As the growth results theoretically predicted, the graphene

Figure 4. a) Tubular CVD setup schematic utilized for graphene production. Inset in (a) at top-right of tube depicts the expanded view of flow confined reactor. b) Simulation result from finite element method manifests the fluid velocity on symmetry plane where the direction of fluid is indicated by white arrows. c) Colored manifestation of Fluid dynamics of gaseous moieties, where the cell Reynolds number is the function of flow width and speed. Reynolds number is the relative ratio between the flux convection and diffusion. d) The simulation of the distribution of the growth species. b–d) In each case, the flux configuration is uniform, although in the vicinity of the reactor it is modified. e) Optical image of as-grown large domain graphene after transferring to a silicon wafer. f) Corresponding Raman spectra collected at 1–7 spot illustrated in (e). g–i) Raman mappings of the highlighted square area in panel (e) corresponding to graphene 2D, G, and D bands respectively. Raman study demonstrates homogenous single layer growth. Adapted with permission. Copyright 2015, American Chemical Society.
fabrication under these confined conditions matches well with theory as well as previous CVD reports working under flow blocking regimes. In particular, monolayer domain synthesis of graphene structures is evidenced.[54]

For the large scale and commercial usage, the batch manufacturing of graphene with nonstop and uniform fashion is vital, including the simultaneous and uniform supply of carbons/flux, especially for multi-growth substrates.[55] Correspondingly, the batch sandwich method was followed by Huet et al., where they came up with an idea of using 3 inch wafers arranging in batches and produced large-area graphene with single layer thickness and high-structural integrity. Instead of sitting the wafers in horizontal fashion, a vertical and closely placed configuration favored successful development (Figure 5a). In addition, computational fluid dynamics simulation studies visualized the gas flow patterns, which aided in a greater understanding of the influence of mass transport phenomena on graphene deposition (Figure 5b–d). Thus, a significant reduction of convective gas flow is essential to provide an equivalent growth rate and uniform monocrystal graphene seeding density around each growth surface (wafers in this case). Graphene, a carbon atom thick layer can be easily fabricated under quasistatic flow conditions with the consumption of minimal C, this strategy enable to provide the required carbon to each wafer without considerably altering the growth rate across them, even stay constant for a big batch of around 25 wafers.[56] Similarly, Zhang et al. proposed a batch growth method and ensured back-to-back production via uniform distribution of growth active carbon plasma around each deposition platform. This was made possible by arranging the growth surfaces into rectangular channel via sitting in holder, which led to the even flow of feedstock gases (Figure 5e–g), and this is vital for graphene growth in even manner. A much higher uniform deposition is observed on faces under the channel configuration, and the unconfined surface displayed no growth (Figure 5h,i, respectively). Furthermore, the theoretical finding as well matches with the experimental inspections. Both results demonstrated, that growth bearing fluid dynamics and growth regimes are substantially influenced by the fashion of fabrication surfaces sitting and reaction site. Thus far, by optimizing the distribution of flow dynamical regimes, a continuous and scalable graphene sheets can be produced.[57]

Figure 5. Graphene batch growth via vapor confined setup. a) Schematic of various alignments of Cu foil. b–d) Simulation images of flow profile in case of single horizontal and vertical, and multiple vertical Cu foil, respectively. The vertical setup interrupts the flow profile more than the horizontal. Adapted with permission.[56] Copyright 2019, IOP Publishing. e) Photograph of multiple Cu foils fixed in quartz holder. f) Schematic of Cu foil holder in CVD tube for batch graphene growth. g) Schematic of parallel view of batch Cu foil with inner foils as confined regime but outer foils in unconfined regime. h) Uniform graphene grain growth under confined surface. i) No growth observed on unconfined surface. Scale bar for (h) and (i): 10 µm. Adapted with permission.[57] Copyright 2020, IOP Publishing.
reports, it is suggested that, graphene technology can soon take industrial value which can revolutionize many commercial disciplines such as, electronics and photovoltaics.

Transfer-free growth is one of the crucial reasons for industrial development, because this avoids the tedious transfer step, thus preserving growth quality and ensuring time- and cost-effectiveness. Notably, CVD allows the design of a flow-regulated setup for graphene development directly on an application-friendly substrate.[38,59] In this regard, Pang et al. established a direct growth method on sandwich substrates (Si/SiOx) under restricted reaction site. In addition, this was a self-terminating method and reported homogenous single layer of graphene in large-area (Figure 6a–e). This finding is attributable to the impact of controlled flux and significant advancement in transfer-free graphene growth.[32]

Tai et al. reproduced a similar study by Pang et al. and explained the controlled flow mechanism. The silicon platform was sat with growth face touching the heating stage, a small gap built in between the growth substrate and heater face. The asymmetric flow design of the reactor considered in this study greatly boosted the content of growth species in the vicinity of deposition surface as opposed to a regular CVD setup. Ultimately, more carbon content around the growth surface enhanced the interaction/collisions of growth intermediates with the growth surface (silicon wafer in this case which is placed upside down), hence favored graphene nucleation and growth. Herein, only the face touching the heating platform showed graphene coverage, therefore the proposed fabrication mechanism is logical. On the contrary, the exposed substrate surface was empty from graphene film, that is no growth.[60]

Recently, another group of researchers developed large-domain graphene with a gapped-sandwich configuration between substrates. Interestingly, graphene was used as the substrate on top of a silicon wafer.[61] In comparison to silicon, the sandwich configuration could produce growth on glass substrates, thereby posing application value. This aspect was matured and fulfilled by Chen et al., who reported graphene production with high crystallinity and uniformity on glass surface. In this experimental methodology the main specialty is the gap over the growth surface which is created by the frosty quartz slide touching the deposition side. In addition, the frosty top built an asymmetric fluid current over the target glass substrate. Subsequently, a gap of around 2–4 µm wide and turbulent channels over the glass substrate are attributed by the top grooved quartz slide, which significantly increased the collision frequency among carbon growth-related active plasma and with the deposition surface. Consequently, graphene fabrication rate on glass surface boosted with uniform coverage and high crystallinity in comparison to the regular flow based chemical vapor deposition method.[62]

The sandwich configuration is a less complex approach than the enclosed configuration discussed in the above section. Risks, like that from enclosed systems, from contamination remain and steps to minimize contamination are required. It is a more scalable approach though as compared to enclosed approaches. In addition, sandwich systems have been demonstrated on nonmetal substrates such as Si wafers that have obvious attractive potential. In terms of growth rates, again, they are slower than open configurations when considering metal substrates; however, when comparing Si wafers, they are similar in that graphene growth on Si wafers is also usually slow in open systems.

4. Inner-Tube Configuration

An additional tube is introduced and the copper foil is rolled inside it to create a restricted environment. Moreover, the growth feedstock flow profile is in a quasistatic equilibrium condition and remains for a longer period in close surrounding of the deposition surface. In particular, this configuration is advantageous owing to the minimal processing of copper foil, which prevents its damage as compared to the enclosure setup. Furthermore, this configuration allows probing of the inner gaseous dynamics.

In addition, a variety of growth substrate configurations, several other alternative methodologies have been presented. For instance, Zhang et al. developed a semi-closed inner tube method that restricted vapors and fabricated flower-shaped large domain and monocrystalline graphene. In this method, semi-closed additional small quartz tube reactor and copper foil
were flushed out by the carrier gases, and the flux dynamics mini reactor tube. As in conventional CVD, the carbon species by maintaining the solid precursor at the closed end inside the reactor tube. Specifically, C delivery was suppressed and generated steady equilibrium in the vicinity of the substrate. Henceforth, the varying condition of flow and reduced growth bearing asymmetric flow dynamic conditions favored by the inner surfaces with distinct morphology variation clearly suggest (Figure 7c). The fabricated graphene on the inner and outer side, the exposed Cu surface (without a confined setup) was covered with continuous graphene film with poor crystallinity (Figure 7c). The fabricated graphene on the inner and outer surfaces with distinct morphology variation clearly suggest the asymmetric flow dynamic conditions favored by the inner reactor tube. Specifically, C delivery was suppressed and generated steady equilibrium in the vicinity of the substrate. Henceforth, the varying condition of flow and reduced growth bearing carboneous intermediates ensured the fabrication of flower patterned crystalline graphene.[63]

Accordingly, a detailed study of the influence of the inner tube configuration based chemical vapor deposition was reported by Rummeli et al. (Figure 8a, b). A reactor tube with unrestricted gas flow produced graphene layers with inhomogeneous thickness. In contrast, the second flow restricted reactor tube with semi-closed end yielded a two-dimensional continuous graphene sheet with homogenous thickness (Figure 8c–e).[14]

Although the quasistatic-condition-based CVD is limited to pristine graphene, graphene derivative materials are commonly produced as well.[64] Recently, Hasan et al. loaded an additional tube with one end closed to control and ensure the laminar flux of carbon species. In this setup, the carbon flux was stagnant by maintaining the solid precursor at the closed end inside the mini reactor tube. As in conventional CVD, the carbon species were flushed out by the carrier gases, and the flux dynamics were turbulent because the growth substrate was exposed to a large amount of feedstock that resulted in inhomogeneous growth. They developed single/multilayer nitrogen–oxygen (NO) substitutionally codoped graphene. Moreover, a vapor trapping tube with both ends open was studied as well, which suggested unsatisfactory growth in comparison to the one-end closed counterparts setup.[15] Accordingly, Hasan et al. further employed this CVD setup and successfully developed single elemental bromine (Br)-doped graphene (Figure 9a). These various characterizations elucidated the high-quality crystalline growth, as presented in Figure 9b–d.[36]

Wang et al. developed a feasible and reproducible method to remarkably discourage the graphitic nucleation number on Cu surface inside CVD method. In their experimental finding, the Cu foil as the growth substrate inside the semi-closed tube suppressed the seeding density by a value of approximately >5 and nucleation density value obtained was 10 nucleus/cm². In addition, it is proposed that, under certain optimized setup, monocrystalline graphene with one-layer thickness can be deposited. Figure 10a demonstrates the schematic of the CVD for the fabrication of graphene domains with large-area. Herein, the reactor setup is analogous to the configuration used for flower shaped graphene growth described above. However, the inner reactor tube is sat in the contrary direction. Simulation study was also combined with experimental finding and the distribution of the fluid dynamics inside the reactor tube is proposed (Figure 10b). The allowed gases follow a whirled fashion at the opening and inside of the reactor tube, instead to directly flowing into it, which ensure a controlled amount of hydrocarbon gases to approach a copper substrate. The gases reaching the copper substrate follow a horizontal path above the surface, and move in a stagnant manner and their velocity is much dropped than the flow speed of gases in the outer exposed space. The graphene domains growth covered the whole surface, although a great variation in the graphene domains density is noticed along the longitudinal direction of growth surface. The number of graphitic domains directly
reflected the seeding/nucleation frequency during the process of graphene. In view of these observations it is proposed, that the nucleation number on the growth stage utilizing restricted fluid dynamical conditions could be efficiently suppressed (4 nuclei mm$^{-2}$). Significantly, such experimental configuration opens a pathway for the fabrication of large crystals of graphene (Figure 10c,d). A 1 mm in size monocrystal graphene was reported by using this methodologies.

In a similar manner, Song et al. sat a copper deposition foil in a vapor blocking quartz cuvette reactor. As reviewed above, Song's group came up with the same finding of gaseous containment, favored by the small enclosed site inside the reactor. An obvious asymmetric distribution of gaseous stream velocity was noticed, which further led to a much-reduced diffusion. This factors overall, attributed to the change in nucleation frequency and grain size. Consequently, the graphitic grain size and homogeneity of the graphene film fabrication boosted under the confinement-intervened configuration in comparison to the normal chemical vapor deposition-based environment. Interestingly, the computational fluid dynamics modeling match with the practical observations, that is, the fabrication quality of graphene can be enhanced by the controlled velocity distribution and diffusivity of the active hydrocarbons into the fabrication surface. In summary, it is proposed that a simple setup even a cuvette can be used as a flow confining reactor for controlled large-area and monocrystalline graphene growth.

Approaches that adopt specialized inner tube configurations to control the flow conditions toward equilibrium conditions are the simplest and most scalable systems. Aside from their simplicity and scalability they are less prone to contamination issues, particularly as they can be easily “cleansed” prior to the reactions through vacuum pumping and/or flushing. They are also the most likely strategy for yielding higher growth rates. We anticipate reactor configurations dominate over other approaches in the future.

5. Other Configurations

The primary objective of the space-limited chamber is to reduce and stabilize the carbon mobility around the growth substrate. Therefore, various setups were used to serve the same purpose. In this section, various reported configurations were reviewed, such as box and spiral. A box or slot configuration ensures that the growth substrate is enclosed, which limits and stagnates the flux, and it is advantageous because the box has the
plus point of elimination of reactor contamination.\cite{66} Recently, Dai et al. loaded copper deposited silicon (SiO$_2$/Si) platform as a fabrication surface into a small quartz box-like rectangular chamber (Figure 11a) and realized large-area graphene development by inserting a growth substrate inside a special box or slot. More importantly, both the rigid (silicon wafer) and flexible substrates (copper foil) can be easily subjected to this form of setup, unlike that for the enclosure and tube configurations. In addition, this was a space limited transfer-free strategy. The reactor with a small reaction room prevented copper

Figure 9. a) Schematic diagram of semi-closed inner tube configuration-based CVD setup; b) corresponding Raman spectrum of a monolayer Br-doped graphene. c) High-resolution TEM (HRTEM) of continuous monolayer graphene as indicated by hole, as represented by orange arrow. d) HRTEM of Br-doped single layer graphene with a well-formed crystalline honeycomb lattice of graphene. Adapted with permission\cite{36} Copyright 2019, Royal Society of Chemistry.

Figure 10. a) A schematic illustration of purpose-made CVD setup for the growth of larger domains of graphene under restrained additional tube condition. Constant temperature zone and gas flow is represented by red dotted line and orange arrows, respectively. b) Simulation image of whirled gas flow current in CVD tube with restricted space environment. c) Optical image of uni-crystal larger domain of graphene collected on SiO$_2$/Si platform. d) Raman spectrum of graphene measured on SiO$_2$/Si substrate. Adapted with permission\cite{65} Copyright 2014, Springer Nature.
surface roughness by discouraging the sublimation process. Henceforth, graphene with high structural integrity and mostly covered with single layer is evidenced (Figure 11b–d). Undesirably, small nucleation number lead to large crystal growth but it also drop the growth rate which takes growth period elongation. The synthesis of large-domain graphene requires a low nucleation density, which inevitably reduces the growth rate. Interestingly, Wu et al. used a facile configuration for adjusting the nucleation frequency under controlled flow regimes, thus deposited large size graphene under improved growth rate (Figure 11e). Under this pathway, centimeter-scale graphene is produced in an hour of growth period and the average fabrication rate noticed was 70 μm/min, as depicted in Figure 11f.

A novel growth substrate configuration-intervened graphene development, i.e., rolling a nickel (Ni) foil growth substrate into a coil has been established. This approach is like an enclosure configuration in which the enclosure offers both the growth surface as well as growth reactor without additional setup. As a simple method for drastically improving the productivity of chemical vapor deposition in large-area graphene synthesis with a roll-stacked Ni coil as a catalyst. This simple trick favored to steady the flow inside the gaps of rolled-stack of Ni foil as opposed to outer region which enhanced growth bearing plasma interaction with growth surface, therefore, promoted successful large-area growth. Similar to roll-to-roll production, this method under confined configuration is appropriate for scalable graphene development.

This section shows alternative configurations that have beneficial traits are possible. We envisage further novel developments that combine the traits of other configurations that in short are hybrid systems. A good example is the use of novel metal catalyst systems (outside of being a substrate) which can help improve growth rates.

6. Future Perspective

In light of the above studies, it is obvious that vapor- and space-confined reactors are well-established and versatile growth pathways to enable graphene growth on metal substrate, direct deposition on application relevant platforms, including presentation of an R2R fabrication.

Principally, the space-restricted configuration offers two major advantages. First, confined configurations are effective for building quasistatic conditions. Ultimately, growth carboneous intermediates reside for longer periods around the growth surface, which increase the chances of growth. Second, such setups control/reduce growth bearing moieties flow reaching the substrate deposition face, guaranteeing nucleation density suppression. This boosts the probability of large single crystal fabrication (Figure 12a). In addition, vapor blocking reactors also suppress growth substrate evaporation and preserve the growth surface smoothness, leading to additional nucleation density suppression and enhancing single crystal creation and high quality graphene deposition (Figure 12b).

Although controlled flow strategies are successful in depositing high quality, single crystal, and monolayer graphene, there are certain limitations to address for the sake of transport of graphene laboratory scale research into practical and durable applications.

Figure 11. a) Slot/box configuration with Cu coated Si wafer as growth substrate. b) Photograph of large area. c) Raman mapping of uniform single layer; d) high-quality single layer growth of graphene is a function of reactor entrance gap. The small entrance restricts the flow and favors the growth results. Adapted with permission. Copyright 2020, American Chemical Society. e) Cu foil mounted on quartz slide with channel configuration. f) Large grain of graphene grown with channel setup. Adapted with permission. Copyright 2017, Royal Society of Chemistry.
For the major portion, an additional setup is required, which subsequently increases the overall cost. The growth substrate itself is modified in the case of enclosure reactors, which often damage the growth substrate and inhibits proper growth, making the synthesis tedious and complex (Figure 12c). Furthermore, the reduced carboneous feedstock access to the growth surface led to a minimal growth rate, eventually causing a longer growth period (Figure 12d). Overall, these are major problems for consideration that prevent large area graphene growth with a single carbon atom thickness and single crystallinity in a scalable manner.

To address these concerns, we are encouraged to follow Rummei’s group approach,[35,69] where they used a solid precursor inside the tubular confined reactor and produced high-quality growth in a short growth period. In this method, the precursor sits inside the reactor, reducing the external flow effect, which protects it from being flushed away by the carrier gases, thus saving precursor loss and allowing its gentle decomposition and diffusion toward the growth substrate. In addition, tubular reactors allow probing of inner gaseous dynamics, which is helpful in gaining insight into flow dynamics and develop a well-established growth mechanism.[65] Therefore, we need more such strategies to obtain graphene with desired quality, size, and yield. This is not limited to graphene but extends to the fabrication of other 2D materials, e.g., transition metal dichalcogenides. Hence, the future perspective emphasizes the fact that we need methods that have more advantages and minimal limitations. In view of this, future research is required to achieve precise control on the frequency and location of nucleation number on the fabrication surfaces, and more importantly, to encourage confined approach intervened industrial scale fabrication, as shown in Figure 12e and references.[12,56] To overcome these limitations, a more detailed future study is vital, and the real-time and in situ observations can help researchers gain a closer look at the changes inside the reaction chamber during graphene growth. Therefore, the collected information could be used to improve the existing graphene growth mechanism.[70] Finally, such quasistatic methods should be encouraged to enable direct growth on application friendly substrates, e.g., silicon wafer (Figure 12f,g),[61] and to avoid a tedious transfer process and risk to the graphene quality.[59]

It is concluded that the following three points should be emphasized in future research review direction: first, there is a need for graphene single crystal synthesis with a large surface area and high structural integrity; second, direct growth on application relevant substrates should be promoted; finally, R2R fabrication should be encouraged to promote graphene to an industrial level.

7. Summary

This review article discusses the various strategies used for creating equilibrium or quasi-equilibrium flow conditions, such as enclosures, sandwiches, tube restrictions, and slot configurations. In light of the above studies, it is evident that a confined setup is remarkable for creating quasistatic and asymmetric flow conditions, which maintains the growth moieties in the
growth substrate vicinity for a longer period and also reduces the access of the carbonaceous species to the growth substrate. The confined design further reduces the evaporative fabrication surface loss, thereby maintaining its smoothness. These effects can lead to suppressed nucleation densities that result in the synthesis of large single crystal graphene and bi-layer graphene with high quality. In conclusion, it is proposed that modifying the reactor design most probably will have the greatest impact in the future for tuning the gaseous flow profile and stabilizing the fabrication surface smoothness, graphene stacking, layer number, grain size and substrate flexibility. Moreover, as shown, the potential of such systems being implemented for the roll-to-roll production of graphene are real. Hence, we anticipate, confined quasistatic CVD reactors to soon be implemented in commercial settings.

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Conflict of Interest
The authors declare no conflict of interest.

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[1] V. Chabot, D. Higgins, A. Yu, X. Xiao, Z. Chen, J. Zhang, Energy Environ. Sci. 2014, 7, 1564.
[2] E. P. Randivir, D. A. C. Brownson, C. E. Banks, Mater. Today 2014, 17, 426.
[3] K. S. Novoselov, D. V. Andreeeva, W. Ren, G. Shan, Front. Phys. 2019, 14, 13301.
[4] S. Zhou, L. Gan, D. Wang, H. Li, T. Zhai, Nano Res. 2018, 11, 2909.
[5] L. Lin, Z. Liu, Nat. Mater. 2016, 15, 9.
[6] J. H. Warner, F. Schäffel, A. Bachmatiuk, M. H. Rümmeli, Graphene: Fundamentals and emergent applications, Elsevier, Waltham, MA 2013.
[7] Z. Li, X. Zhang, H. Cheng, J. Liu, M. Shao, M. Wei, D. G. Evans, H. Zhang, X. Duan, Adv. Energy Mater. 2020, 10, 1900486.
[8] H.-T. Chin, J.-J. Lee, M. Hofmann, Y.-P. Hsieh, Sci. Rep. 2018, 8, 4046.
[9] Y.-Z. Chen, H. Medina, H.-W. Tsai, Y.-C. Wang, Y.-T. Yen, A. Manikandan, Y.-L. Chueh, Chem. Mater. 2015, 27, 1646.
[10] X. Chen, L. Zhang, S. Chen, Synth. Met. 2015, 210, 95.
[11] F. B. Fauzi, E. Ismail, M. H. Ani, S. N. S. A. Bakar, M. A. Mohamed, B. Y. Majlis, M. F. M. Din, M. A. A. M. Abid, J. Mater. Res. 2018, 33, 1088.
[12] H. Bong, S. B. Jo, B. Kang, S. K. Lee, H. H. Kim, S. G. Lee, K. Cho, Nanoscale 2015, 7, 1314.
[13] A. Zavabeti, A. Jannat, L. Zhong, A. A. Haidry, Z. Yao, J. Z. Ou, Nano-Micro Lett. 2020, 12, 66.
[14] J. Kraus, L. Bobel, G. Zwaschka, S. Günther, Ann. Phys. 2017, 529, 1700029.
[15] P. Zhao, A. Kumamoto, S. Kim, X. Chen, B. Hou, S. Chiashi, E. Einarsson, Y. Ikuhara, S. Maruyama, J. Phys. Chem. C 2013, 117, 10755.
[16] S. Chen, H. Ji, H. Chou, Q. Li, H. Li, J. W. Suk, R. Piner, L. Liao, W. Cai, R. S. Ruoff, Adv. Mater. 2013, 25, 2062.
[17] D. Ding, P. Solis-Fernández, H. Hibino, H. Aga, ACS Nano 2016, 10, 11196.
[18] K. M. Subhedar, I. Sharma, S. R. Dhakate, Phys. Chem. Chem. Phys. 2015, 17, 23204.
[19] W. T. Ramos, T. H. Cunha, I. D. Barcelos, D. R. Miquita, G. A. Ferrari, S. De Oliveira, L. M. Seara, E. G. S. Neto, A. S. Ferlauto, R. G. Lacerda, Mater. Res. Express 2016, 3, 045602.
[20] X. Ge, Y. Zhang, L. Chen, Y. Zheng, Z. Chen, Y. Liang, S. Hu, J. Li, Y. Sui, G. Yu, Carbon 2018, 139, 989.
[21] N. Lisi, T. Dikonimos, F. Buonocore, M. Mazzaro, R. Rizzoli, S. Marras, A. Capasso, Sci. Rep. 2017, 7, 9927.
[22] A. Bachmatiuk, F. Bornert, M. Grobosch, F. Schäffel, U. Wolff, A. Scott, M. Zaka, J. H. Warner, R. Klingeler, M. J. A. Knupfer, 2009, 3, 4098.
[23] M. Atwa, Master Thesis, The Royal Institute of Technology, Stockholm, Sweden 2016.
[24] O. J. Burton, F. C. Massabaua, V-P. Veigang-Radulescu, B. Brennan, A. J. Pollard, S. Hofmann, ACS Nano 2020, 14, 13593.
[25] W. Fang, A. L. Hsu, Y. Song, A. G. Birdwell, M. Amani, M. Dubey, M. S. Dresselhaus, T. Palacios, J. Kong, ACS Nano 2014, 8, 6491.
[26] E. Muhoz-Sandoval, J. L. Fajardo-Diaz, R. Sanchez-Salas, A. J. Cortés-López, F. López-Urías, Sci. Rep. 2018, 8, 2983.
[27] R. Muhoz, C. Gómez-Alexandre, Chem. Vap. Deposition 2013, 19, 297.
[28] R. Kumar, R. K. Singh, D. P. Singh, Renewable Sustainable Energy Rev. 2016, 58, 976.
[29] A. Hussain, S. M. Mehdi, N. Abbas, M. Hussain, R. A. Naqvi, Mater. Chem. Phys. 2020, 248, 122924.
[30] X. Li, C. W. Magnuson, A. Venugopal, R. M. Tromp, J. B. Hannon, E. M. Vogel, L. Colombo, R. S. Ruoff, J. Am. Chem. Soc. 2013, 111, 2816.
[31] K. Yang, J. Liu, R. Jiang, Y. Gong, B. Zeng, Z. Yi, Q. Gao, J. Yang, F. Chi, L. Liu, Micromachines 2020, 11, 1101.
[32] J. Pang, R. G. Mendes, P. S. Wrobel, M. D. Wlodarski, H. Q. Ta, L. Zhao, L. Giebeler, B. Trezicka, T. Gemming, L. Fu, Z. Liu, J. Eckert, A. Bachmatiuk, M. H. Rümmeli, ACSNano 2017, 11, 1946.
[33] C.-C. Chen, C.-J. Kuo, C.-D. Liao, C.-F. Chang, C.-A. Tseng, C.-R. Liu, Y.-T. Chen, Chem. Mater. 2015, 27, 6249.
[34] M. H. Rümmeli, S. Gorantla, A. Bachmatiuk, J. Phieler, N. Geissler, I. Ibrahim, J. Pang, J. r. Eckert, Chem. Mater. 2013, 25, 4861.
[35] M. Hasan, W. Meiou, L. Yulian, H. Q. Ta, L. Zhao, R. G. Mendes, S. Oswald, Z. Akhter, Z. P. Malik, N. M. Ahmad, Mater. Res. Express 2019, 6, 055604.
[36] M. Hasan, W. Meiou, L. Yulian, S. Ullah, H. Q. Ta, L. Zhao, R. G. Mendes, Z. P. Malik, N. M. Ahmad, Z. Liu, RSC Adv. 2019, 9, 13527.
[37] C.-Y. Dai, W.-C. Wang, C.-A. Tseng, F.-C. Ding, Y.-T. Chen, C.-C. Chen, J. Phys. Chem. C 2020, 124, 23094.
[38] R. Wu, J. Pan, X. Ou, Q. Zhang, Y. Ding, P. Sheng, Z. Luo, Nanoscale 2017, 9, 9631.
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