Hongtao Liu / Yunqi Liu

Controlled Chemical Synthesis in CVD Graphene

Abstract:
Due to the unique properties of graphene, single layer, bilayer or even few layer graphene peeled off from bulk graphite cannot meet the need of practical applications. Large size graphene with quality comparable to mechanically exfoliated graphene has been synthesized by chemical vapor deposition (CVD). The main development and the key issues in controllable chemical vapor deposition of graphene have been briefly discussed in this chapter. Various strategies for graphene layer number and stacking control, large size single crystal graphene domains on copper, graphene direct growth on dielectric substrates, and doping of graphene have been demonstrated. The methods summarized here will provide guidance on how to synthesize other two-dimensional materials beyond graphene.

Keywords: CVD graphene, Controlled Chemical Synthesis, Layer Number Control, Bilayer, Stacking, Large size, Single Crystal, Doping
DOI: 10.1515/psr-2016-0107

1 Introduction

Chemical vapor deposition (CVD) is a chemical process widely used to grow high-quality, high-performance thin films. CVD is the most promising method to produce large-area, high-quality graphene, among various methods of graphene synthesis, such as micromechanic exfoliation of graphite using scotch tape, thermal decomposition of silicon carbide (SiC), reduction of graphene oxide, liquid exfoliation of graphite and even bottom-up organic synthesis [1–17]. Graphene can be grown on the surface of many transition metals (e.g., Ni, Cu) and alloys. Various gaseous, liquid or solid precursors can be used as carbon source. Tuning the growth parameters, like temperature, pressure, flow of carrier gas and hydrogen and so on, can also control the growth process. It can produce large-area, high-quality graphene films and large-sized single-crystal graphene flakes with different shapes and layers by choosing appropriate catalytic substrate and finely controlling the growth parameters. At the same time, there is a reservoir of precursors being used to synthesize graphene or doped graphene that has different properties to pristine graphene. CVD method is compatible to standard semiconductor technology, and it will facilitate the commercial application of graphene in integrated circuits (ICs), solar cells, transparent conductive films (TCFs) and so on. The insights gained in CVD graphene will be helpful for manufacturing of other two-dimensional (2D) materials beyond graphene.

For thermal CVD, the growth mechanism of graphene depends on the carbon solubility in transition metal catalysts and the growth parameters. The interaction of graphene and transition metals can generally be categorized as weak, for metals with closed $d$-shells such as Cu, and strong, for metals with open $d$-shells such as Ni [18, 19]. The weak interaction will also result in low carbon solubility in the metal and preserve the linear band structure of graphene near the Fermi level. The strong interaction will lead to high carbon solubility and destroy the linear band structure of graphene. There are two main graphene growth processes corresponding with the different carbon solubility. One is carbon segregation and precipitation (Figure 1(a)) [20]. The carbon solubility in those metals is high at high temperature. No stable metal carbide forms or metastable carbide forms and later decomposes to release the carbon. When temperature drops, the carbon solubility decreases and then carbon atoms diffuse out of the metal and bond covalently forming graphite or graphene. In this case, graphene growth on Ni is a typical example. The other growth process is surface-catalyzed growth (Figure 1(b)). It applies to metals in which carbon solubility is very low, such as Cu. In this process, carbon precursor adsorbs and decomposes only on the surface of the metal. It is surface mediated and self-limited. However, despite the low carbon solubility of Cu, it has demonstrated that segregation growth of graphene indeed occurs using Cu as substrate [14]. Carbon precursor decomposes on one side of the Cu surface and diffuses through the Cu foil to the other side of the Cu surface forming bilayer or multilayer graphene. Regardless of which process graphene grows, graphene nucleation and growth require carbon concentration near the metal surface to exceed the equilibrium carbon solubility, that is, carbon supersaturation near the metal surface. Carbon supersaturation can be achieved by continued carbon precursor exposure and dissociation at the metal surface. Graphene growth in this process can be considered as isothermal growth because the temperature is usually kept constant (Figure 1(c)). Carbon
supersaturation can also be achieved by cooling the metal at a specific carbon concentration because the carbon solubility decreases due to falling of temperature (Figure 1(c)). Graphene grows via segregation and precipitation in this process. Using metals with low carbon solubility as catalyst, isothermal growth of graphene will be dominant. Whereas using metals with high carbon solubility, graphene can grow isothermally at continued carbon precursor exposure or can also grow during catalyst cooling down. So selecting metals with appropriate carbon solubility is essential to control the layer of CVD graphene.

Figure 1: Schematic diagrams of graphene growth mechanisms on transition metals. (a) Graphene growth through segregation and precipitation. (b) Graphene growth via surface-mediated reaction [21]. (c) Carbon phase diagram illustrating graphene growth via isothermal growth and precipitation upon cooling. (d) A local carbon supersaturation ($\Delta c$) near the catalyst surface leading to graphene growth, which is a competition with carbon diffusion into the bulk metal ($j_D$) [17].

Hydrocarbons are common precursors to produce graphene, and methane is the most widely used precursor. The growth mechanism can be very briefly described like this: (1) Carbon precursors diffuse to and adsorb on the metal surface. (2) Adsorbed precursors decompose into active carbons, which diffuse on the metal surface or into the bulk metal. (3) Carbon species on the surface or diffused out of the metal nucleate at high-energy sites on the metal surface forming graphene crystallites. (4) Nonactive hydrogen atoms, which desorb from the metal surface, are carried off in the form of hydrogen molecules by carrier gas. Every step is vital to graphene growth. Controllable CVD growth of graphene can be achieved by choosing appropriate metal substrate, substrate pretreatment and finely tuning the growth parameters. Here we will briefly describe the development of the control of layer number, size, direct growth on insulating substrates and doping of graphene. We will mainly focus on the graphene growth using Ni and Cu as catalysts and substrates. For Ni substrate, the layer number control will be discussed, while for Cu substrate, the controllable synthesis of large-sized single-crystal graphene and bilayer graphene with Bernal stacking (AB stacking) will be presented.

2 Layer Number Control

2.1 Layer Number Control on Ni Substrate

The process of graphene growth on transition metals with high carbon solubility, such as Ni, Co and Fe, involves the following steps: (1) carbon adsorption and decomposition on the metal surface, (2) carbon dissolution and diffusion in the bulk of the metal and (3) graphene nucleation and growth via carbon segregation and precipitation from the bulk to the surface of the metal. Carbon solubility in Ni is high and temperature dependent. Carbon segregation and precipitation from the metal is rapid during the cooling period so that single-layer and few-layer graphene form simultaneously on the metal surface. Figure 2 gives the whole graphene growth process on Ni, consisting of catalyst pretreatment, C dissolution, isothermal growth and precipitation. Carbon prefers segregating and precipitating at the step edges, defects and grain boundaries of polycrystalline Ni substrates [23, 24] [25]. Single and bilayer graphene prefer growing on the surface of terrace, while few-layer and multilayer graphene will form at the grain boundaries of Ni substrates. As a result, the layer number of
Liu and Liu

Graphene at the grain boundaries of Ni substrates is larger than within the grain boundaries. So it is challenging to synthesize uniform single-layer, bilayer or even few-layer graphene on the surfaces of metals with high carbon solubility such as Ni. Controlling the morphology of Ni is important to control the growth behavior of graphene. The diffusion of carbon to the surface of metals can also be kinetically controlled to some extent and thus uniform single-layer, bilayer or few-layer graphene will be formed.

Figure 2: Graphene growth process on Ni. Four major phases and their key factors determining the graphene growth behavior are illustrated [22].

2.1.1 Substrate

Substrate Selection
To uniformly grow monolayer (ML)/bilayer graphene on Ni, atomically smooth surfaces with large grain size or in the absence of grain boundaries will be essential [26]. It has been reported that ML/bilayer graphene preferentially grows on bulk Ni(111) single crystal [23, 27] or epitaxial Ni(111) thin films grown on MgO(111) [28] due to the absence of defects and grain boundaries and lattice mismatch. It has been respected that because of the registry between graphene and the Ni(111) lattice, there will be no grain boundaries in continuous graphene films formed by coalescence of neighboring graphene domains on single-crystal Ni. Considering the cost of single-crystal metals is high and the catalyst metals are usually etched away to transfer graphene to target substrate, polycrystalline metals should be chosen as substrates to grow large area graphene films with high productivity [10]. However, graphene growth behaviors on single crystal are quite different from those on polycrystalline metals [29]. Graphene growth under “real-world” conditions, such as ambient pressure and polycrystalline catalysts, should be carefully studied and it should not straightforwardly “extrapolate” from “ideal” conditions with ultra-high vacuum (UHV) on the surface of high-quality single crystals. Graphene cannot grow homogenously on the entire surface of Ni foil or polycrystalline Ni film due to the high carbon solubility at high temperature and nonequilibrium carbon segregation and precipitation upon cooling. Single-layer, bilayer, few-layer and/or multilayer graphene always appear simultaneously. As a result, most approaches to grow uniform graphene with controllable layers are trying to suppress the nonequilibrium carbon precipitation at highly active Ni surface sites, such as step edges, defects and grain boundaries.

Film Thickness
Carbon solubility in Ni is high especially at high temperature; therefore, the metal acts as a carbon reservoir. The film thickness of Ni determines the maximum carbon content dissolved in the metal and also the grain size of the metal. The thicker the metal film is, the more carbon will be dissolved at high temperature [31]. Few-layer graphene or even graphite will form on the surface of thick Ni film via carbon segregation and precipitation upon cooling. Kim et al. [30] found that Ni film deposited on SiO$_2$/Si by electron beam evaporation with thickness about 100 nm can be used to decrease the carbon in the metal and grow single and bilayer graphene films with a short growth time (Figure 3(b)). However, as shown in Figure 3(a), when graphene grows at high temperature for a long time, the Ni thin film tends to agglomerate forming a rough surface, which will facilitate the formation of multilayer graphene and thus give rise to an inhomogeneous graphene film [31, 32]. With the aid of plasma, ultra-thin Ni film (~50 nm or less) and low temperature can be used in a hydrogen-free plasma-enhanced CVD (PECVD) to synthesize graphene with controllable layers [33]. Low temperature determines the low carbon solubility in Ni and a thin Ni film gives a finite dissolution of carbon atoms in the Ni film,
which segregate and precipitate on the surface of Ni forming few-layer graphene and suppress the formation of multilayer graphene.

Figure 3: (a) Optical images of graphene grown on different thickness Ni film. As the film thickness decreases, it tends to agglomerate forming a rough surface during the growth process at high temperature and thus giving inhomogeneous graphene. (b) Number of graphene layers distributed on Ni thin films with different thickness [30].

Uniform single-layer graphene or graphene with controllable layers can also be grown on the surface of thick Ni films, foils or even slabs by kinetically controlled local surface saturation of carbon, without fully saturating the bulk throughout its thickness [34]. Graphene grows isothermally on the catalyst surface and the carbon diffused into the bulk will not precipitate upon cooling due to only the near-surface saturation of carbon. Carbon diffusion into the bulk metal mediates the graphene growth. Please note that this graphene growth process is implemented at low temperature (~600°C) and low pressure.

Pretreatment
Both the topography and grain orientation of Ni surface have important bearing on the layer number and domain size of CVD graphene. So, before graphene growth, it is necessary to pretreat the metal substrate. Thermal annealing will smooth the surface, increase the grain size and reduce the grain boundary of the metal, which makes the growth of graphene with controlled layer easier and decrease the thickness variation of graphene films. Annealing in H₂ can further eliminate impurities and reduce the film roughness. As a result, a thinner and more uniform graphene can be obtained on Ni surface [35]. In order to increase the percentage of Ni(111), the annealing rate of polycrystalline Ni should be deliberately controlled. It has been reported that thermal annealing of polycrystalline Ni at a slow rate favors the formation of large Ni(111) grains with less grain boundaries [23]. Larger domain size and predominated Ni(111) grains can be obtained with a prolonged annealing time. Because the morphology of graphene correlates with the metal substrate and multilayer graphene grows at the grain boundary of the metal, graphene grown on the surface of metal with large grain size will be more uniform. Moreover, graphene can also grow across the grain boundaries of the metal forming a continuous film [36–38]. All of those factors make the growing large area, uniform and thin graphene possible.

A flat Ni surface with a roughness less than 5 nm can be obtained by mechanical polish and subsequent chemical etching [39]. There are an extremely small number of graphene nucleation sites on such flat surface, and graphene can grow continuously without changing the crystal orientation over the steps and grain boundaries of the substrate. ML graphene grows at the temperature between 1,100 and 1,200 K. No graphene forms above 1,200 K and multilayer graphene grows below 1,100 K.

Alloys
In order to tune and especially to decrease the carbon content dissolved in Ni bulk and thus to suppress the formation of multilayer graphene, binary metal alloys are selected as catalysts, which preserve the catalytic properties of Ni but impart new properties to Ni [40]. However, different metals or elements added to Ni play different and important roles during graphene growth. Metals with strong metal–carbon interaction or low carbon solubility or low catalytic activity toward carbon precursor decomposition, such as Mo, Cu and Au, can be used to be alloyed with Ni. The component other than Ni in the alloy will decrease the graphene nucleation density [41] compared with the pure Ni catalyst alone by tuning the carbon content and subsequent segregation [31], or inhibiting high active sites, such as grain boundary [42]. To a certain extent, the layer number of graphene is correlated with the Ni mole fraction in the alloy, which can be modulated by the film thickness of the constituent before alloyed by thermal annealing. As a result, uniform graphene with large grain size and controllable layer number will be acquired.
Mo–Ni Alloy

Dai et al. [43] used a Mo–Ni alloy to grow uniform high-quality single-layer graphene. Ni is the catalyst to decompose carbon precursors, while Mo acts as carbon sink to trap dissolved carbons in Ni via forming stable metal carbides and to suppress the carbon segregation and precipitation (Figure 4). Graphene growth on this alloy catalyst is surface limited, like the growth behavior of single-layer graphene on the surface of Cu. Uniform single-layer graphene films with a coverage of 100% can be obtained over a wide range of growth conditions (different concentrations of carbon precursor, Mo film thickness, growth temperature and cooling rate), as long as there is enough Mo remaining in the alloy to react with carbon species and trap them. The catalytic metal Ni can be replaced with other catalytic metals such as Co or Fe, and other metals like W and V, which can form stable carbides, can be chosen as carbon trap metals.

Figure 4: (a) Schematic of graphene growth on Mo–Ni alloy [43]. (b) and (c) Optical images of graphene on Mo–Ni alloy. Graphene uniformly covers the entire surface on the alloy. (d) and (e) Optical images of graphene on Ni surface grown under different cooling rates, which distribute inhomogeneously on the Ni surface. All scale bars are 20 µm.

Graphene nucleation and growth on this kind of Mo–Ni alloy with different Mo/Ni ratio achieved by varying the Ni film thickness deposited over Mo foils have been studied by Rümmeli et al. [44]. The study of the surface structure of the Mo–Ni binary substrates shows that during graphene growth, Ni thin films diffuse into the underlying Mo foils and the Ni films break up forming Ni islands embedded in the Mo foil at the surface (Figure 5). This will take place during the annealing pretreatment. When thinner Ni thin film is deposited on Mo foil, the penetration depth and lateral density of Ni islands are smaller than that of thicker one. Spatially resolved Auger spectroscopy studies reveal that graphene nucleates only on Ni islands surface rather than on Mo islands surface. This is because stable molybdenum carbide forms on Mo surface and it cannot transform into graphene. Carbon will be depleted over and near the Mo surface and carbon is also deficient on Ni surface surrounded by Mo. So the growth of graphene on this Mo–Ni binary substrate is self-terminated. The growth of multilayer graphene is suppressed and single-layer graphene with high uniformity grows over the substrate. The density of graphene nucleation sites can be tuned by altering the Ni film thickness deposited on Mo foil. When thinner Ni film is deposited on Mo foil, the density of Ni islands at the surface decreases and there will be fewer graphene nucleation sites, thus leading to larger graphene domain size. As carbon precursor supply continues, graphene flakes grow larger and merge with each other into a continuous single-layer graphene film.

Figure 5: Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) of cross sections of Mo–Ni alloy. Ni film breaks up and diffuses into the underlying Mo foil. Ni islands form at the alloy surface. When the Ni film is thicker, the number of Ni islands and the diffusion depth are larger [44].
**Cu–Ni Alloy**

Commercial Cu–Ni foils with a fixed Cu/Ni ratio, which have moderate carbon solubility at high growth temperature and large grain size after annealing, can be used as catalysts to deposit highly uniform graphene films with controllable layer number, for example, single layer, bilayer, and few layer, through carbon segregation and precipitation by tuning the growth temperature, carbon precursor exposure time and cooling rate [42, 45]. The moderate carbon solubility in Cu–Ni alloy foil makes controlling the graphene thickness much easier. Not only the graphene layer number but also the substrate cover level can be controlled by varying the growth parameters. The surface coverage and uniformity of graphene films increase as the growth temperature increases, due to the enhanced carbon solubility and diffusivity at high temperature. The surface coverage can be attributed mainly to two factors: density of graphene nucleation sites, which is mainly temperature dependent, and the size of individual graphene sheet, which is mainly sensitive to the carbon precursor exposure time. For example, uniform ML, bilayer (about 70% coverage and mainly AB stack) and multilayer graphene films (2–5 ML) were obtained at the growth temperature of 975°C, 1,000°C, and 1,030°C, respectively, at the same cooling rate (100°C/s) for “70–30” commercial Cu–Ni foils (weight percent: 67.80% Cu, 31.00% Ni) [42]. Slow cooling rate favors the AB-stacked bilayer graphene. And a low-carbon precursor flow rate and a long exposure time will enhance the uniformity of bilayer graphene. Multilayer graphene or thick graphite will deposit when more carbon atoms dissolved into the alloy foil and when they have enough time to segregate and precipitate during the cooling period.

Cu–Ni ratio can be tuned by adjusting the thickness of the deposited Cu and Ni film before pre-annealing to form an alloy [46]. As the concentration of Cu increases in Cu–Ni alloy, graphene growth mode changes from segregation mode on pure Ni and Ni-rich surface to surface catalytic mode on pure Cu and Cu-rich surface [47]. Moreover, Cu will accumulate at the alloy surface during annealing, that is, Cu concentration at the top surface is higher than that in bulk. The Cu-rich surface suppresses the carbon diffusion into the alloy bulk. As a result, graphene with controllable layer number (ML, bilayer and trilayer) can be obtained through this surface catalytic mode at different growth pressures and carbon precursor (methane) partial pressures. And the yield of AB-stacked bilayer graphene is strongly influenced by the Cu/Ni ratio and growth temperature as shown in Figure 6, where both are achieved by changing the carbon concentration and graphene growth mode. However, surface concentration enhancement of Ni at Cu–Ni surface is also confirmed by angle-resolved X-ray photoelectron spectroscopy after graphene growth at high temperature (1,050°C), which probably results from the high vapor pressure of Cu (about three times higher than Ni) at high temperature [48]. In a word, the growth of large area, uniform graphene with controllable layer number and stacking order (>1 L) needs to optimize the metal substrate and growth conditions.

![Figure 6: Graphene growth mode and the yield of AB stacking bilayer graphene with the relationship of (a) the ratio of Cu in Cu–Ni alloy and (b) growth temperature [47]. SM, segregation mode; SCM, surface catalytic mode; HCC, high carbon concentration; LCC, low carbon concentration; OCC, optimal carbon concentration.](image)

Large-area single-crystal graphene has grown by locally feeding carbon precursor on an optimized Cu–Ni alloy [46]. Local precursor feeding through a quartz nozzle makes it possible to grow large-sized single-crystal graphene from only one nucleus and even at designated locations. In contrast, multiple site nucleation and thus polycrystalline graphene usually occur in a conventional CVD process. The optimized ratio of Cu/Ni is 85/15, which enables a nickel-mediated isothermal segregation growth of graphene at a fast rate due to the Ni-enhanced catalytic power and abundant carbon atoms dissolved in the alloy. This method avoids long-time growth of graphene and ~1.5-inch hexagonally shaped single-crystal ML graphene can be synthesized in 2.5 h at 1,100°C.

Cu–Ni alloy can also be used as substrate to grow wafer size uniform ML and bilayer graphene through segregation without introducing extraneous carbon precursors [31, 49]. Cu in the alloy was used as segregation controller, while Ni was used as carbon source and graphene thickness controller. By tuning the Cu/Ni ratio (Ni film thickness), graphene with controllable layer number was obtained at appropriate annealing temperature and segregation time, while the bilayer graphene here obtained is non-AB stacking. Carbon content in
metal substrate and layer number of subsequently precipitated graphene can also be controlled precisely by varying the fluence of the carbon ion implantation combined with Cu–Ni binary metal substrate [50]. All the carbon ions implanted in Ni-coated Cu foil are expelled toward the substrate surface and precipitate forming graphene during annealing, which is enhanced by inward diffusion of Ni and outward diffusion of Cu leading to a decreased carbon solubility in Cu-rich surface. This approach also applies to Co–Cu alloy but using an exogenous carbon source in an atmospheric pressure CVD (APCVD) system [51]. Moreover, this approach is less sensitive to the thermal history of metal substrate and cooling rate during the growth of graphene and compatible with large-scale microelectronics processing. It might be a great practical convenience to grow graphene with controllable layer number.

**Au–Ni Alloy**

Graphene growth using Au–Ni alloy catalyst can be performed at low temperature (~450°C) [34, 41]. Due to the low carbon solubility in Ni at low temperature, graphene was grown isothermally on the surface of alloy catalyst and it was not a segregation and precipitation process. Au decorates the majority active surface sites of Ni, such as step edges, and the presence of Au decreases the graphene nucleation density and thus reduces the graphene thickness variation yielding more uniform graphene films and larger domains. Being different from Mo, Au and Cu cannot react with carbon and no stable carbide is formed. As a result, there are no carbon traps in Au-Ni alloy, and multilayer graphene or even graphite will grow when more carbon is supplied.

**Calculations on Alloys for Graphene Growth**

Density functional theory (DFT) calculations of Au alloying on Ni(111) are consistent with the experimental works. It is energetically favorable for Au atoms to substitute Ni atoms at the step edges on Ni(111) due to the least coordination numbers of Ni atoms at the step edges, which will passivate the highly active step edges and makes the step edges much more like the Ni terrace in catalyzing graphene growth [52]. The uniformity of Au-modified Ni(111) step edges and clean Ni(111) terrace in carbon adsorption, diffusion and segregation will reduce the density of the nucleation centers and facilitate the growth of large area and uniform graphene film. Nevertheless, before all the Ni atoms at the step edges are replaced by Au atoms, the Au atoms begin to substitute Ni atoms on the terrace of Ni(111), because high density of Au atoms at the step edges will lead to a high formation energy which is equivalent to the formation energy of Au atoms deposited on Ni(111) terrace [52]. Au atoms modified on Ni(111) terrace can lower the energy barrier of carbon atoms incorporation onto graphene growth front and thus facilitate the growth of armchair/zigzag (AC/ZZ) graphene edges [53]. As a consequence, high-quality graphene will be obtained at a lower growth temperature on Au-alloyed Ni(111).

Calculations have also demonstrated that other metals, such as Mn, with strong metal–carbon interaction and repulsive with each other atoms on Cu(111) surface, can be alloyed in Cu forming a $3 \times \sqrt{3} R30^\circ$ superstructure [54]. Carbon clusters with only one orientation will seed on the surface of this Mn–Cu(111) superstructure due to the strong Mn–carbon interaction. Those carbon clusters subsequently grow larger and coalesce with each other into a graphene sheet with no grain boundaries. Not only the alloyed metals on the uppermost metal surface will affect the nucleation and growth of graphene, but also the subsurface alloy will also affect the graphene growth behavior by modulating the topmost metal–carbon coupling and carbon–carbon interaction. For example [55], for metal Rh(111), when it is alloyed with relatively inert transition metals right side of Rh in the periodic table, such as Pd and Ag, carbon atoms repel with each other when they get closer. They prefer separation due to the repulsive effect and graphene nucleation will be suppressed. However, alloying with those late transition metals will suppress the orientation disordering of graphene domains. When Rh(111) is alloyed with more active transition metals on the left side of Rh, such as Tc and Ru, the carbon–substrate interaction will weaken and two carbon atoms energetically and kinetically tend to form a dimer on the topmost host Rh(111), which will facilitate the nucleation of graphene, but the orientations of graphene domains will be disordering.

### 2.1.2 Growth Parameters

The correlation of hydrocarbon pressure with the epitaxial growth of graphene on Ni(111) surface will shed light on CVD growth of few-layer graphene on polycrystalline Ni catalyst [56]. There is a strong interaction between epitaxial graphene and Ni(111), which leads to a depletion of dissolved carbon close to the catalyst surface and prevents the formation of additional layer of graphene. Single-layer graphene is thus commonly achieved in a wide range of low-exposure pressures. A further increase of carbon precursor pressure, dissolved carbon accumulates in the bulk catalyst, and the concentration of dissolved carbon near the catalyst surface...
increases, which weakens the graphene–Ni interaction causing a formation of rotated graphene and enabling the nucleation and growth of additional graphene layers.

To minimize the carbon dissolved in Ni and thus reducing the graphene thickness variation, highly diluted hydrocarbon should be introduced into the growth system \[34, 36\]. Hydrogen (H\(_2\)) is also important to the graphene growth. As high H\(_2\)/CH\(_4\) ratio is used, the coverage of multilayer graphene decreases and the percentage of single-layer graphene increases \[57\]. However, no graphene grows without H\(_2\) and too much H\(_2\) will etch the graphene and suppress the formation of graphene. The amount of H\(_2\) also plays a key role in determining the layer number of graphene.

Growth temperature determines the activity of the metal catalyst, the sorption/desorption and decomposition of carbon precursors, the carbon solubility and diffusion rate of carbon in the bulk and on the surface \[31, 58\]. At high temperature (>900°C), the carbon solubility in Ni is high. When the pressure of carbon precursor is high, more carbon will be dissolved in the bulk of Ni and there is no graphene formed on the surface of Ni at such high temperature, but only dilute carbon atoms \[59\]. Graphene will form upon cooling by segregating and precipitating dissolved carbon as a consequence of decreased solubility of carbon in Ni. The majority of the graphene is rotated or mismatched with Ni(111) surface at high temperature, which, due to the weak interaction of the Ni(111) and mismatched graphene, favors the precipitation and segregation of carbon from bulk to the surface forming a second layer of surface carbide or graphene \[60\]. This process depends on the concentration of carbon in the bulk Ni. It is challenging to suppress carbon diffusion to the surface upon cooling when the carbon precursor pressure is high. Multilayer graphene will difficult to be avoided. However, at a relatively low temperature (~600°C or ~550°C), carbon dissolution into the bulk is limited. Self-limiting surface growth or isothermal growth of graphene on polycrystalline Ni film dominates and single-layer graphene will be obtained \[22\]. At a much lower temperature (<500°C), a single layer of nickel carbide forms, which inhibits the nucleation and growth of high-quality graphene \[27, 61\]. However, the role of the surface carbide is open to discussion. It has been reported that a single layer of nickel carbide could transform into graphene \[56, 60, 62\]. Graphene grown at very low temperature is usually not continuous and defective, and the majority of the graphene is in registry with Ni(111) surface. Most of the above-mentioned processes to grow graphene on the surface of Ni(111) were carried out in UHV, in which the pressure of the carbon precursors is very low and it is easy to keep the Ni surface clean. In ambient pressure growth systems, it is difficult to grow large-area graphene with controllable layers at high temperature due to the high pressure of carbon precursors and oxidation of Ni. Other metals with low carbon solubility and weak metal–graphene interaction such as Cu and Pt will be alternatives to Ni to be used as substrate to grow uniformly large-area high-quality graphene with controllable layer.

The layer number of graphene grown on the surface of Ni depends not only on the carbon content dissolved in the metal but also on the cooling rate of the metal. When low concentration of carbon precursor exposes to Ni, thus low carbon concentration in the bulk metal, the coverage of single-layer and bilayer graphene increases at a slow cooling rate (<25°C/min) \[63\]. The low carbon content in Ni will suppress the carbon segregation on the Ni surface and the slow cooling rate will promote the carbon segregation under conditions close to equilibrium. Both of those conditions favor the growth of single-layer and bilayer graphene. The density of nucleation sites of multilayer graphene decreases but the thickness of multilayer graphene increases at a slow cooling rate. The single-layer and bilayer graphene will grow across the grain boundary of the metal substrate and the size of the graphene is limited only by the size of metal film and the CVD chamber. However, when higher concentration of carbon precursor is introduced into the growth system, multilayer graphene with fewer single-layer and bilayer graphene grows on the metal surface independent of the cooling rate. Although the uniformity of CVD graphene improves using a slow cooling rate, there are still thicker-layer graphene appears among single-layer, bilayer and few-layer graphene \[43\].

It has also reported that at an extremely fast cooling rate, the dissolved carbon atoms do not have enough time to diffuse to the Ni surface (Figure 7) \[35\]. The quench effect allows no graphene to form. Graphite will form at a fast cooling rate (~20°C/s) and there are many defects in those graphite due to not enough time to crystallization at the high cooling rate. The layer number of graphite is reduced and the quality is improved with a slower cooling rate. Few-layer (less than 4) graphene can be obtained at a medium cooling rate of ~10°C/s. However, at a slow cooling rate (0.1°C/s), there is also no graphene formation because of the dissolved carbon atoms diffusing into the bulk of the metal and no carbon segregating and precipitating on the Ni surface. Those results have been verified by Kim et al. \[30\], in which a fast cooling rate (~10°C/s) can suppress the formation of multilayer graphene. So controlling the cooling rate controls not only the layer number of graphene but also the graphene quality. Because of fast cooling, the formation of graphene is also very fast. Bilayer or few-layer graphene with AB stack is energetically more favorable, and turbostratically arranged layers are usually obtained due to the nonequilibrium graphene process \[64\]. However, besides cooling rate, other factors such as carbon content in the Ni film, Ni film thickness and surface roughness are also critical to control the layer number of grown graphene.
The atmosphere in which the sample is cooled plays a key role in graphene growth too. Before cooling, exposing the Ni film to H\textsubscript{2}, carbon layers formed on the Ni surface will be removed by the etching effect of H\textsubscript{2} with the assistance of Ni at high temperature, and carbon content in bulk Ni is also reduced. Carbon segregation and precipitation from Ni bulk to the surface is strongly suppressed due to the reduced carbon content in Ni. Wafer-scale uniform layer-controlled graphene can be obtained by rapidly cooling and finely tuning the Ni film thickness, carburization and H\textsubscript{2} exposure at ambient pressure [65]. A coverage of ~90 % single-layer and ~6 % bilayer graphene can be obtained. The sheet resistance of a 3–4 layer graphene film is as low as ~100 Ω per square and ~90 % transmittance at 550 nm. The use of H\textsubscript{2} during the cooling process can also etch away the weakly bounded carbon atoms by forming hydrocarbons like methane to obtain graphene free of deposits or flakes. Nevertheless, the hydrocarbon in the system will balance the etching effect.

2.2 Bilayer Graphene and Stacking on Cu Substrate

Graphene growth behavior varies on the surface of different transition metals. Graphene growth on the surface of Cu is surface limited and is predominantly single layer [66]. When the (entire) surface is covered by graphene, the second-layer graphene cannot easily grow above (in the absence of the catalyst) or below (deficient or no carbon precursor feeding) the first graphene layer. And the stacking disorder appears when the second layer grows across the grain boundary of the first-layer graphene. Multilayer graphene always precipitated “simultaneously” on the grain boundaries and steps of Ni leading to disordered stacking of graphene [30, 36]. Therefore, controllable growth of large-area single-crystal ML graphene, which will be discussed in the next section, is the prerequisite to synthesize large-area, uniform, orderly stacked bilayer graphene.

Although consensus on the growth of the second-layer graphene on top or below the first-layer graphene has not been reached, the location of the second-layer graphene will depend on the technique and growth conditions [21]. The possible growth mechanisms of bilayer graphene are illustrated in Figure 8. It is challenging to synthesize bilayer graphene in large scale, especially for large-area uniform AB-stacked (Bernal) bilayer graphene, in which tunable band gap opens by applying a perpendicular electric field for breaking the inversion symmetry [67–71] or by chemical doping [72, 73].
Bilayer graphene has been usually synthesized by catalyst engineering, kinetic control [74–77] or a combination of both [34]. For example, as mentioned earlier, alloy substrates can be used to grow graphene with controllable layer number by carefully tuning the alloy composition and the growth conditions [31, 42, 45, 47, 49]. However, the resulting bilayer graphene often consists of a mixture of AB-stacked and randomly stacked bilayer graphene.

In a classical CVD system using Cu as a catalyst, the self-limited growth can be broken and the second-layer graphene typically grows beneath the first-layer graphene by surface reaction, that is between the Cu surface and the top graphene layer (Figure 8(b)), at a low pressure [76], high H$_2$/CH$_4$ ratio or low flux of methane with a decreased growth rate [78]. As a result, in order to obtain a large-sized bilayer graphene, a long growth time is sometimes necessary. Both graphene layers share the same nucleation center and most bilayer graphene is AB stacked due to the strong interaction of the two layers. The second-layer graphene stops growing when the first-layer graphene coalesce into a continuous film, because the carbon diffusion channel at the edges of the first graphene layer will be shut [76]. Although AB-stacked bilayer and trilayer graphene has been synthesized at atmospheric pressure by finely tuning the growth parameters, the procedures is complicated and other simple and effective methods should be developed to grow bilayer and trilayer graphene in large scale [79].

Epitaxial growth of the second-layer graphene will be the most straightforward approach to synthesize bilayer graphene. However, for Cu catalyst, the catalyst is passivated by the covered graphene. In order to grow the second-layer graphene, additional catalyst or process must be introduced to decompose the carbon precursor and generate active carbon species.

A two-step growth process has been developed to grow bilayer graphene by Yan et al. [80]. Uniform ML graphene was first grown on the surface of Cu foil serving as the substrate for the following epitaxial growth of the second-layer graphene. A fresh Cu foil was placed upstream to catalyze the decomposition of methane to feed the second-layer graphene epitaxial growth on the surface of the first-layer graphene. As the growth time increases, the lateral size of the second-layer graphene reaches several tens of micrometers and the shape changes from hexagons to hexagrams or round risks. Most bilayer graphene is AB stacked with a coverage as high as 67 % confirmed by optical microscope, transmission electron microscopy (TEM), selected area electron diffraction (SAED) and Raman. The epitaxial growth of the second-layer graphene and the low coverage can be attributed to the fact that carbon radicals or fragments generated by Cu catalytic decomposition of methane prefer to attach to the graphene edges with dangling bonds rather than on the graphene surface forming an additional layer. Liu et al. [81] have found that a relatively high H$_2$/CH$_4$ ratio, high temperature and very low pressure are required to improve the bilayer graphene coverage and AB-stacking ratio in a similar approach to epitaxially grow bilayer graphene. A relatively high H$_2$/CH$_4$ ratio will keep the balance of graphene growth and etching, which leaves the upstream Cu foil uncovered by graphene and keeps the catalytic activity. Moreover, the high ratio of H$_2$ will terminate the graphene edges by hydrogen, which allows the carbon diffuse easily and

**Figure 8**: Possible bilayer graphene growth mechanisms. (a) The second-layer graphene growth on top of the first-layer graphene. The second-layer graphene growth beneath the first-layer graphene feeding by carbon species diffused from the graphene–metal interface (b) and the bulk metal (c).
fast into the region beneath the top graphene layer and thus favors the growth of bilayer or few-layer graphene [82]. Using large-area single-crystal ML graphene as template, large-sized (up to 300 μm width) AB-stacked bilayer graphene can be achieved by using a high H₂/CH₄ ratio (4,400) [83]. The growth rate is very slow as it is a diffusion-limited growth. However, the very low pressure is not beneficial for the growth of large-sized bilayer graphene. To remedy this issue, a low-pressure (1 mbar) nucleation and high-pressure (5 mbar) growth procedure are employed to obtain a high coverage (~99%) and a high AB-stacking ratio (~90%) bilayer graphene [81]. The introduction of high ratio/concentration of H₂ will lower the growth rate of the second layer and it takes long time to obtain large-sized bilayer graphene. Using ethanol as carbon precursor, epitaxial growth of AB-stacked bilayer layer graphene can be achieved without introducing extra Cu as catalyst due to the catalytic effect of ethanol but require careful control of the growth parameters [84].

The catalytic transition metal thin film can be used as carbon delay to grow the second-layer graphene. That is, the time of carbon reaches to one surface of Cu is different. The early arrived carbon forms the first-layer graphene and the lately arrived carbon that must diffuse through the bulk metal thin film gives the second-layer graphene. In other words, one side of the Cu foil acts as the first-layer graphene growing substrate and the other side acts as catalyst to decompose carbon precursor to diffuse through the bulk foil to feed the growth of the second-layer graphene. Because of the exposed metal surface acting as catalyst to decompose the carbon precursor, it should make sure that the catalytic surface of the metal should not be fully covered or passivated by graphene before the growth of the bilayer graphene on the other side is completed. As mentioned earlier, it is very important to maintain the activity of the catalyst and control the carbon content and the precipitation time to grow large-area bilayer layer graphene.

Fang et al. [85, 86] have shown that bilayer, trilayer or quadlayer graphene can be grown on the outside surface of a Cu enclosure at low pressure. The newly formed graphene grows by capturing carbon species decomposed on the inside surface of the Cu enclosure and diffused through the Cu foil. So it is a carbon diffusion-limited growth model. The growth time, Cu foil thickness and the time of full coverage of the inside surface will determine the size, and coverage of the bilayer graphene on the outside surface. Graphene growth behavior on both sides of a Cu pocket has demonstrated once again that graphene growth on inside and outside of Cu surface is correlated, that is single layer inside versus single layer outside, bare Cu inside versus bilayer or multilayer outside. The bare inside surface of Cu allows the active carbon species to diffuse from the inside to the outside and then nucleates and grows the second-layer graphene underneath the top graphene layer [87]. The full coverage of outside Cu surface by graphene will not terminate the growth of the second-layer graphene. Therefore, graphene with different layer numbers can be obtained by this approach.

It has been demonstrated that oxygen on Cu surface plays a critical role in the growth of bilayer graphene [88]. A Cu pocket was designed to grow bilayer graphene on the outside surface (Figure 9(a)). The second-layer graphene nucleates and grows by feeding carbon atoms that are formed by complete dehydrogenation of methane with the assistance of inside surface oxygen, diffusion through the bulk Cu and segregation to the outside Cu–first graphene interface. Both the first-layer and the second-layer graphene grow isothermally rather than by precipitation as verified by isotope labeling. The weak interaction between the two-layer graphene enables the AB stacking, while grain boundary in the first graphene layer is the cause of the stacking disorder (Figure 9(b)). Analogous to the case of single-layer graphene growth, decreasing the pressure of methane will reduce the density of graphene nucleation and thus increase the domain size of the second layer graphene (Figure 9(c)). As a result, the ratio of AB stacking increases with the decrease in methane pressure (Figure 9(d)). High methane pressure will lead quickly to full coverage of graphene on the inside surface and thus sparse bilayer graphene on the outside surface. Long-time exposure of methane will grow graphene >2 layers. This work points out the key role of surface oxygen in the growth of bilayer graphene and provides the evidence of underneath growth of the second-layer graphene.
Figure 9: Bilayer graphene growth on the outside surface of an oxygen-rich Cu foil pocket [88]. (a) Optical image of the pocket. (b) Raman 2D mapping of as-grown bilayer layer graphene, in which bright areas are Bernal stacking. Bilayer graphene domain size (c) and Bernal-stacking ratio (d) as a function of methane partial pressure, \( P_{\text{CH}_4} \).

Bilayer graphene has been synthesized directly on the surface of silicon oxide using deposited Ni thin film on top of it as a catalyst (Figure 10) [89]. Various carbon precursors can be used to grow bilayer graphene. They decompose, diffuse, segregate and precipitate at the constrained Ni–silicon oxide interface, forming bilayer graphene. This growth process resembles the graphene growth behavior on the top surface of Ni, but here the constrained space plays a vital role in determining the layer number. Most of the bilayer graphene (~95%) are non-AB stacked with twist angles from 0° to 30°. Using polymers or self-assembled MLs (SAMs) on a dielectric substrate as carbon precursors and deposited Ni atop of them as catalyst, bilayer and multilayer graphene can be synthesized by tuning the film thickness or the alkyl length of the SAM [90, 91]. A similar method but using 300 nm Cu thin film as catalyst has also been developed to grow few-layer graphene [92]. AB-stacked bilayer graphene are randomly observed and other stacking configurations also exist.

Figure 10: Bilayer graphene growth on silicon oxide using solid carbon precursors and a Ni film as a catalytic buffer layer [89].

In contrast to the large number of reports on CVD growing AB-stacked bilayer graphene, twisted bilayer graphene with specified twist angles has been rarely reported. Twisted bilayer graphene has been synthesized by combining surface reaction and segregation growth on the surface of Ni(111) [93]. But this kind of bilayer graphene is a mixture of twisted bilayer graphene with different twisted angles. It has been reported that twisted bilayer graphene prefers to grow underneath the rotated graphene domains relative to a Ni(111) substrate rather than the no-rotated ones [94]. The formation of twisted bilayer graphene may be attributed to the strong interaction of graphene and Ni, which gives the carbon atoms less mobility and cannot form the thermodynamic stable configurations. Twisted bilayer graphene has also been synthesized using APCVD by optimizing growth parameters, such as temperature, \( \text{H}_2 \) pressure and \( \text{CH}_4 \) concentration [77].
3 Large-Sized Single-Crystal Graphene on Cu Substrate

Due to the surface-mediated and thus self-limited graphene growth process, as well as its low cost, availability, reliability and scalability, Cu has been considered as an ideal substrate to synthesize large-sized uniform single-layer graphene. However, graphene prepared by this CVD method is typically polycrystalline [95]. Graphene grain boundaries form when graphene flakes nucleated and grown with different lattice orientations coalesce to a continuous film. Although graphene grain boundaries have distinct properties and can be used to tailor the properties of graphene, they will deteriorate graphene’s mechanical, electrical and other physical properties [96, 97] [98]. It is important to grow large-sized single-crystal graphene without grain boundaries and it has been demonstrated that the quality of large-sized CVD graphene can be comparable to mechanically exfoliated graphene [99, 100].

In order to obtain large-sized single-crystal graphene, decreasing the graphene nucleation density, which makes graphene flakes have enough space to grow to large size, and at the same time ensuring the continuous growth of graphene without forming additional nuclei is one of the key principles [101]. Lowering the nuclei density can be achieved by pretreating the Cu substrate and carefully controlling the growth parameters, such as temperature, pressure, flow rate of carbon precursor and ratio of hydrogen and carbon precursor. Another approach is to grow graphene flakes at different nucleation sites but with same lattice orientation, suitable shape and arrangement, and then coalesce seamlessly to a continuous film free of grain boundaries [15, 102]. It should be noted that the formation and structure of graphene grain boundaries will depend on the growth model. And it should be carefully characterized before identifying the single-crystal graphene flakes, especially for graphene flakes with irregular shapes [103, 104].

3.1 Substrate

3.1.1 Facets

Cu–graphene interaction is relatively weak. Graphene growth on Cu surface generally cannot be considered as epitaxy because there is no obvious or weak correlation between the lattice of graphene and Cu. Graphene can grow continuously across the imperfections such as grain boundaries, steps, dislocations, clusters and vacancies of Cu and maintain the lattice orientation. On least mismatched Cu(111) (3.9 %), there are still rotations of lattice orientation and grain boundaries in graphene [105, 106]. The grain size, crystallographic orientation, surface roughness, purity, surface oxygen and the geometry of the Cu substrate will affect the size, shape and layer number of graphene sheet. In general, Cu substrate with large grain size, high purity and smooth surface will favor the growth of large-sized single-crystal graphene domains.

The weak correlation between the shape and orientation of graphene domains and the crystallographic orientations are simply shown in Figure 11 [107]. Zigzag edges of graphene grown on the surface of Cu(101), Cu(001) and Cu(111) tend to align parallel to the direction of Cu<101>. For Cu(101) and Cu(111), there is only one direction, that is Cu<101> (Figure 11(c) and Figure 11(e)). While for Cu(001), there are two directions, that is Cu<110> and Cu<110>, which are perpendicular to each other (Figure 11(d)). The shapes of graphene domains on different Cu facets are also different. For example, the shape of graphene domains on the surface of Cu(111) or the surface with orientations close to Cu(111) is hexagonal. Four-lobed graphene domains on Cu(101) and Cu(001) and six-lobed and star-shaped graphene domains appear on high-index Cu facets. Other experiments have also verified those findings [108–110]. Graphene nucleates and grows more easily on Cu(111) and the quality of graphene grown on Cu(111) is higher than that grown on other surface due to the high carbon diffusion rate and improved carbon adsorption [111]. Cu foil is the most popular substrate to grow graphene. However, it is polycrystalline and contains many structures, such as different facets, grain boundaries and annealing twins. Cu(111) is the lowest energy Cu surface and the (111) surface is enriched in Cu foil after high-temperature annealing [111]. Inspired by those results, we can grow graphene domains with different shapes and orientations by selecting or engineering the Cu orientation. Pretreatment of Cu foil by thermal annealing to produce Cu(111) facets will be helpful for the production of large-sized graphene. Graphene domains grown on Cu(111) with alignment in one direction will merge seamlessly and without grain boundaries into a large sheet [101, 112–114]. Nevertheless, the shape of graphene domains also largely depends on the growth parameters.
3.1.2 Roughness

The roughness of Cu foil is another factor for the growth of large-sized graphene. On the one hand, graphene should be transferred onto target substrate to realize its various applications. Wrinkles, discontinuity and damage, such as cracks and tears, occur when graphene grown on roughness surface is transferred onto a substrate. On the other hand, nuclei density decreases on smooth Cu surface and the homogeneity of graphene enhances. For example, the roughness of Cu foil reduced by a factor of 10–30 after electropolishing, leading to that uniform high-quality >95 % single-layer graphene with room temperature hole mobility enhanced by a factor of 2–5 was obtained [115]. Due to the reduction of nuclei density (from, e.g., 2.4 × 10^4 ea/mm^2 on unpolished Cu foil to 5.5 × 10^3 ea/mm^2 on polished Cu foil), the size of graphene domains increases with a higher growth rate on polished Cu foil [116]. The size of single graphene domains further extends to millimeter size (~2.3 and ~4.5 mm^2) after electrochemical polishing and then high-pressure high-temperature annealing of Cu foil by eliminating sharp wrinkles, steps and defects to improve the quality of Cu foil [117]. The quality of as-prepared graphene is comparable to that of exfoliated graphene showing a room temperature hole mobility as high as 11,000 cm^2/Vs. Seamlessly stitching oriented hexagonal graphene domains into large-area (6 cm × 3 cm) single-crystal graphene without grain boundary was achieved on Cu(111) foil pretreated by high-temperature annealing and subsequent chemical–mechanical polishing [112].

In order to grow large-sized graphene, low pressure and high temperature are typically required. At such high temperature, Cu evaporates and sublimes, which are elevated at low pressure. As a result of this, the Cu surface becomes rough, resulting in a decreased growth rate and degraded quality of graphene. To suppress the evaporation, Cu foil enclosure or tube was designed and large-sized graphene domains grow on the inside surface with a low nuclei density due to the elimination of Cu surface evolution caused by evaporation and sublimation and thus smooth surface, absence of SiO_2 particles and low pressure of carbon precursor [118, 119].

3.1.3 Liquid Metal

Liquid metal will be another selection to grow large-sized graphene [40]. The processing history as well as the imperfections (grain boundaries, steps, etc.) of Cu are eliminated forming a quasi-atomic smooth homogeneous surface in liquid state. Geng et al. [120] demonstrated that uniform, single-layer, large-sized and self-aligned hexagonal graphene flakes can be synthesized on liquid Cu surface (Figure 12). Graphene domain size larger
than 200 μm has also been produced by using liquid Cu as catalytic substrate and combining controlling the amount of hydrogen and the H₂/CH₄ ratio during growth [121]. The alignment of hexagonal graphene domains can be attributed to the epitaxial relationship with the Cu lattice. Because of the high mobility of the liquid metal, large-area continuous single-crystal graphene sheet would be obtained by seamlessly merging the aligned graphene flakes. Resolidified Cu can also be used as substrate to synthesize large-sized graphene and ~1 mm sized hexagonal ML graphene grains were obtained due to the smooth surface of the resolidified Cu [122].

![Figure 12: Hexagonal graphene domains growth and self-assembly on liquid Cu [120]. (a) Schematic of the growth process. (b)–(d) Surface coverage of graphene domains with an increasing density. At high density, graphene domains self-align into a compact ordered structure. (e) Graphene domains extend to a continuous graphene film. (f) and (g) Typical large-sized graphene domains.](image)

### 3.1.4 Surface Passivation

Annealing the Cu foil in the presence of H₂ will remove the surface oxide, impurities, contaminants and defects to suppress graphene nucleation [123]. However, passivating the active sites on Cu surface, for example, by oxidation, is an effective method to suppress the graphene nucleation density. Whereas because of the weak catalytic activity of the passivated Cu, growth time should be prolonged to obtain large-sized graphene domains. Due to the high nucleation barrier of graphene on Cu foil with native surface oxide by annealing it without H₂, graphene nucleation density greatly reduced from ~10⁶ nuclei/cm² to 4 nuclei/cm² and as large as 5 mm sized single-crystal graphene was achieved by further carefully tuning the growth parameters, for example, low pressure, high H₂/CH₄ ratio [83]. Cu surface active sites can also be effectively passivated by exposing Cu foil to O₂ during annealing pretreatment [100]. Graphene nucleation density decreases with increasing O₂ exposure, for example from 2 × 10³ mm⁻² on oxygen-free Cu foil to ~0.01 mm⁻² on Cu foil with 5 min O₂ exposure. However, it has also been reported that surface oxygen accelerates the graphene domain growth through enhancing adsorption and dissociation of hydrocarbons and thus reducing the edge attachment barrier [124]. Not only the surface oxygen but also the trace amount of gaseous O₂ introduced along with the hydrocarbon into the CVD chamber will reduce the graphene nucleation density and centimeter-sized (1 cm) single-crystalline graphene domains were produced [125]. Here, suppressing nucleation density is realized by oxide etching the metastable carbon islands and enhancing the desorption of carbon species. Other methods such as melamine pretreatment can also be used to passivate the active sites to reduce the nuclei density and grow centimeter-sized (1 cm) single-crystal graphene on Cu foil surface [126].

### 3.1.5 Seeded Growth

Seeding is another approach to control the graphene nucleation density. Graphene domains and graphene arrays with predetermined location and/or controlled layer number can be achieved by using this seeded growth. Patterned multilayer graphene [113], graphene oxide flakes [127], patterned highly oriented pyrolytic graphite (HOPG), Poly(methyl methacrylate) (PMMA) [128], coronene [129], and nanoparticles [130] can be used as
the seeds. Occasionally, multiple nucleations at one seed and random newly formed nuclei are also observed. Graphene lattice orientation might be determined by the seed and uniformly aligned graphene domains could merge into a large graphene sheet without grain boundary.

### 3.2 Growth Parameters

Growth parameters, such as $\text{H}_2/\text{CH}_4$ ratio, temperature, pressure, hydrocarbon flow rate and partial pressure, can also affect the graphene growth behavior. Figure 13 gives a typical example of graphene nucleation and size changing under different growth conditions [131]. It indicates that graphene nucleation density decreases and thus domain size increases as the temperature ($T$) increases, or methane flow rate ($J_{\text{Me}}$) decreases, or methane partial pressure ($P_{\text{Me}}$) decreases. CVD growth graphene is a complicated process. A large number of reports on graphene growth kinetics and thermodynamics can be referred to those excellent articles [5, 17, 132–136]. Some examples to produce large-sized single-crystal graphene domains are listed in Table 1.

![Figure 13](image-url)

**Figure 13:** Scanning electron microscope (SEM) images of graphene domains grown under different conditions [131]. $T$ (°C)/$J_{\text{Me}}$ (sccm)/$P_{\text{Me}}$ (mTorr): (a) 985/35/460, (b) 1035/35/460, (c) 1035/7/460, (d) 1035/7/160. Scale bars are 10 μm.
Table 1: Large size single crystal graphene produced by CVD.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>H$_2$/CH$_4$ (Ar) /sccm</th>
<th>Pressure 1</th>
<th>Temperature / °C</th>
<th>Size and shape</th>
<th>Mobility 2/cm$^2$/Vs</th>
<th>Methods or Annealing</th>
<th>Growth time</th>
<th>Ref and Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu Foil</td>
<td>LP</td>
<td>1035</td>
<td>hundreds of µm$^2$ starlike</td>
<td>16000</td>
<td>2 sccm H$_2$, 1035 °C, 20 min annealing; two-step growth</td>
<td>2.5+1 min</td>
<td>[131] 2010</td>
</tr>
<tr>
<td>2</td>
<td>Cu Foil</td>
<td>AP</td>
<td>1050</td>
<td>~15 µm hexagonal</td>
<td>&lt;10$^3$--10$^4$</td>
<td>H$_2$/Ar, 10/300 sccm, 1050 °C, 30 min annealing tuning H$_2$/CH$_4$ ratio, smooth Cu surface, 200 sccm H$_2$, 1000 °C, 30 min annealing inside surface of copper-foil enclosures</td>
<td>~10 min</td>
<td>[113] 2011</td>
</tr>
<tr>
<td>3</td>
<td>Cu Film</td>
<td>AP</td>
<td>1000</td>
<td>~5 µm equiangular hexagonal</td>
<td>1900</td>
<td></td>
<td>1.5–60 min</td>
<td>[135] 2011</td>
</tr>
<tr>
<td>4</td>
<td>Cu Foil</td>
<td>LP</td>
<td>~1035</td>
<td>0.5 mm, dendrites</td>
<td>4000 (e)</td>
<td>inside surface of copper-foil enclosures</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ni(111)</td>
<td>Propylene gas</td>
<td>UHV</td>
<td>600–680</td>
<td>millimeter size</td>
<td>Ni(111) heteroepitaxially grown on MgO(111)</td>
<td>5 min</td>
<td>[28] 2011</td>
</tr>
<tr>
<td>6</td>
<td>Pt Foil</td>
<td>AP</td>
<td>1040</td>
<td>~1.3 mm hexagonal</td>
<td>7100</td>
<td>700 sccm H$_2$, 1040 °C, 10 min</td>
<td>180 min</td>
<td>[103] 2012</td>
</tr>
<tr>
<td>7</td>
<td>Cu Foil</td>
<td>AP</td>
<td>1045</td>
<td>submillimeter, 0.4 × 0.4 mm$^2$, square</td>
<td>4200; 20000 (hBN)</td>
<td>H$_2$/Ar, 50/300 sccm, 1045 °C, 3 h</td>
<td>15.5 min</td>
<td>[123] 2012</td>
</tr>
<tr>
<td>8</td>
<td>Cu Foil</td>
<td>LP</td>
<td>1000</td>
<td>100 µm six-lobed flower</td>
<td>4200; 20000 (hBN)</td>
<td>7 sccm H$_2$, 1000 °C, 40 min; vapour trapping</td>
<td>30 min</td>
<td>[138] 2012</td>
</tr>
<tr>
<td>9</td>
<td>Liquid Cu</td>
<td>AP</td>
<td>1160</td>
<td>&gt;100 µm, hexagonal</td>
<td>1000–2500</td>
<td>200 sccm H$_2$, 1100 °C, 30 min; 100 sccm(1.3 H$_2$/Ar mix) 1090 °C, 30 min</td>
<td>~30 min 10–50 µm/ min</td>
<td>[120] 2012</td>
</tr>
<tr>
<td>10</td>
<td>Liquid Cu</td>
<td>AP</td>
<td>1090</td>
<td>&gt;200 µm, hexagonal</td>
<td>1000–2500</td>
<td>high-pressure annealing (1500 Torr, 500 sccm H$_2$, 1077 °C, 7 h)</td>
<td>~15 min</td>
<td>[121] 2012</td>
</tr>
<tr>
<td>11</td>
<td>Cu Foil</td>
<td>LP</td>
<td>1077</td>
<td>~2.3 mm, ~4.5 mm$^2$ hexagonal</td>
<td>~11000</td>
<td>electrochemical polishing and high-pressure annealing (1500 Torr, 500 sccm H$_2$, 1077 °C, 7 h)</td>
<td>125 min</td>
<td>[117] 2012</td>
</tr>
<tr>
<td>No.</td>
<td>Material</td>
<td>Dimensions</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Growth Conditions</td>
<td>Time</td>
<td>References</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>------------</td>
<td>----------</td>
<td>-------------</td>
<td>------------------</td>
<td>------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Cu Foil</td>
<td>10/0.1</td>
<td>LP</td>
<td>1035</td>
<td>centimeter-size</td>
<td>40000–65000 (1.7 K); 15000–30000 (r. t.)</td>
<td>12 h</td>
<td>[100] 2013</td>
</tr>
<tr>
<td>13</td>
<td>Cu Foil</td>
<td>Polystyrene</td>
<td>AP</td>
<td>1050</td>
<td>~1.2 mm hexagonal</td>
<td>5000–8000</td>
<td>0.1–10 Torr H₂, 1035 °C, 30 min; 1 × 10⁻³ Torr O₂, 5 min, oxygen rich surface</td>
<td>30–80 min</td>
</tr>
<tr>
<td>14</td>
<td>Cu Foil</td>
<td>10/0.1</td>
<td>LP</td>
<td>1035</td>
<td>~2 mm</td>
<td>5200</td>
<td>15000–3000 (r. t.)</td>
<td>6 h</td>
</tr>
<tr>
<td>15</td>
<td>Resolidified Cu</td>
<td>100/46/854(CH₄ diluted by Ar, 0.1%)</td>
<td>AP</td>
<td>1075</td>
<td>~1 mm hexagonal</td>
<td>1100 °C, 30 min</td>
<td>5 h</td>
<td>[122] 2013</td>
</tr>
<tr>
<td>16</td>
<td>Cu Foil</td>
<td>H₂/CH₄ (1320–8800)</td>
<td>LP</td>
<td>1070</td>
<td>~5 mm, hexagonal</td>
<td>16000</td>
<td>pulse heating polystyrene inside surface of Cu tube electropolishing H₂/Ar, 60/940 sccm</td>
<td>48 h</td>
</tr>
<tr>
<td>17</td>
<td>Cu Foil</td>
<td>21/15/320(N₂) (CH₄ diluted by Ar, 500 ppm)</td>
<td>AP</td>
<td>1050</td>
<td>5.9 mm, hexagonal</td>
<td>320 sccm Ar; Ar/H₂, 30 min; seeded growth</td>
<td>hours to tens of hours</td>
<td>[130] 2013</td>
</tr>
<tr>
<td>18</td>
<td>Ge(110)</td>
<td>CH₄ (Diluted by H₂ to 1–2%)</td>
<td>LP</td>
<td>900–930</td>
<td>wafer size</td>
<td>7250 ± 1390 (max. 10620)</td>
<td>pure Ar, maintaining native oxide, high H₂/CH₄ mechanically polishing; pure Ar, 320 sccm Ar; Ar/H₂, 30 min; seeded growth</td>
<td>5–120 min</td>
</tr>
<tr>
<td>19</td>
<td>Cu₈₅Ni₁₅</td>
<td>15/80–120/300 (0.05% CH₄ diluted by Ar)</td>
<td>AP</td>
<td>1050–1100</td>
<td>~1.5 inch</td>
<td>10,000 ~ 20,000</td>
<td>local carbon precursor feeding Cu-Ni alloy substrate, H₂/Ar 50/1000 sccm, 1050 °C, 2h</td>
<td>2.5 h</td>
</tr>
</tbody>
</table>

1. LP stands for low pressure; AP stands for ambient pressure.
2. e stands for electron mobility.
Low hydrocarbon concentration and high H$_2$/CH$_4$ ratio are typically used to reduce graphene nucleation density with or without the nucleation suppressing methods mentioned earlier. In addition, H$_2$/CH$_4$ ratio can also be used to tailor the size, shape or layer number of graphene domains due to the etching effect of H$_2$ [16, 119, 133, 137]. Generally, dendritic graphene domains are obtained at low H$_2$/CH$_4$ ratio due to diffusion (mass transport)-limited growth, while compact hexagonal graphene domains grow at high H$_2$/CH$_4$ ratio due to the edge-attachment-limited growth. The evolution of graphene domain shape is illustrated in Figure 14.

![Figure 14: Graphene domain shape evolution under different H$_2$/CH$_4$ ratio [137].](image)

From (a) to (h), the H$_2$/CH$_4$ ratios are 20, 30, 40, 60, 70, 80, 100, 120, respectively and the CH$_4$ flow rate maintains at 0.5 sccm. The flow rate of H$_2$/CH$_4$ for (i)–(l) are 200/2, 200/4, 300/5 and 300/22 sccm, respectively. All scale bars are 5 μm.

### 4 Direct Growth on Insulating Substrates

Graphene grown on transition metal substrates must be transferred onto insulating substrates to measure its optoelectronic properties and realize its various applications [2, 141]. During the transfer process, the catalytic substrates typically etched away, which will cause waste and pollution. The metal and support polymer materials such as PMMA cannot be completely removed. As a result, unintentional contaminants, cracks and wrinkles, introduced during transfer process, will degrade the electrical and mechanical properties of graphene [141]. Transferring graphene is heavily manual and time-consuming and not compatible with industrial batch processing. Although a face-to-face transfer method has been developed by Gao et al. [142], much effort has to be made to find novel transfer methods.

To overcome those challenges, direct growth graphene on dielectric substrate free of transfer is highly desirable [143, 144]. Due to the no or weak catalytic activity of insulating substrate, additional procedures, such as gaseous catalyst (e.g., metal vapor) assisted catalyzation or plasma enhancement, have to be applied to promote the carbon precursor decomposition. To date, various substrates such as SiO$_2$ [145–150], hexagonal boron nitride (hBN) [151–155], high-$k$ materials (Al$_2$O$_3$ [148, 156–158], SrTiO$_3$ [159] and Si$_3$N$_4$ [160, 161]), quartz [162] glass [163–165], oxide powders [166, 167] or even water-soluble NaCl [168] powders have been used as substrate to grow graphene. As-grown graphene always conforms to the morphology of the substrate and thus graphene with various structures can be produced. It should be noted that hBN is an ideal substrate for high-performance graphene devices, due to the atomically flat surface free of dangling bonds and charge traps [169, 170]. Graphene band structure can also be modulated by varying the crystallographic alignment with the hBN substrate [171, 172]. However, for conventional CVD, during the growth of graphene, etching of the pregrown hBN is unavoidable. Because of atomic flatness and small lattice mismatch (1.8 %), van der Waals epitaxial growth of single-domain graphene on exfoliated hBN has been achieved using PECVD [151]. Graphene lattice orientation locked into a fixed orientation with respect to the hBN substrate and the size of the well-stitched continuous single-crystalline graphene free of grain boundaries will be limited only by the size of the hBN substrate.

Cu vapor [147, 149], Ni vapor [173] and Ga vapor [165, 174] have been used as catalysts to decompose carbon precursors into active carbon species and then nucleate and grow graphene. Besides growth parameters (e.g., temperature and pressure), metal location and the distance of metal and the growth substrate also play a critical role in determining the size, quality and layer number of graphene. The graphene quality is not very well and...
nucleation seeds such as graphite debris have been introduced to improve the graphene quality [147]. Although no detectable metal residues were confirmed in as-grown graphene, it could not exclude the possibility of metal contamination. Silane and germane are another highly effective gaseous catalysts to directly grow high-quality graphene on exfoliated hBN with a high growth rate and an alignment with hBN [155]. Silicon atoms attach to the edge of graphene, thus leading to a much reduced reaction barrier. Graphene domain size as large as 20 μm with quality comparable to mechanical exfoliated graphene is obtained, which is evidenced by high hole and electron mobility of 19,000 and 23,000 cm²/Vs, respectively, and two peaks owing to the secondary Dirac cones of the graphene/hBN superlattice in transport measurement.

Catalyst-free growth of graphene on insulating substrate at low temperature can be achieved using PECVD [148, 175–177]. The plasma provides the energy for bond breaking of carbon precursors and decomposes them into highly reactive radicals and atoms, leading to the possibility of low temperature and rapid synthesis of graphene. Atomic hydrogen generated by decomposing carbon precursor or introduced H₂ acts as important etchant to remove amorphous carbon and grow high-quality graphene [178]. The growth behavior is not self-limiting. Graphene layer number or film thickness can be modulated by varying the growth time or flow rate of carbon precursor.

Other metal-free methods to promote carbon precursor decomposition or graphene nucleation include high-temperature thermal decomposition of carbon precursors [163] and surface oxygen-aided nucleation [145]. Additionally, a two-stage growth (first nucleation and then growth under different conditions) is sometimes adopted to expand the lateral size [156, 160].

No matter what method is applied, most graphene directly grown on insulating substrate typically suffers a low growth rate and long growth time, but poor quality with nonnegligible defects and grain boundaries, and the domains size are limited to several microns. Direct synthesis of high-quality, large-sized graphene on insulating substrate especially at low temperature compatible with flexible plastics still needs further study. However, graphene with inferior quality could find its suitable places for various applications, for example, defoggers [163, 165] and cell culture [164].

5 Doping

The electrical properties of graphene can be tailored by doping, rendering graphene suitable for various applications, such as n- or p-type transistors, band gap opening, sensors, work function tuning, catalyst, energy conversion and storage [179–182]. Here, we aim to briefly discuss the direct CVD synthesis of nitrogen (N) substitutional-doped graphene [180, 183–186].

Various heteroatoms, like single heteroatom, such as N [187], B [188–193], S [194–196], Si [197, 198], and binary heteroatoms, such as B:N [199, 200], S:N [201], B:P [202], N:P [203], and N:F [204], have been substitutionally doped graphene by direct CVD synthesis, among which, N-doped graphene has been extensively studied. Several nitrogen-containing compounds, such as NH₃ [177, 205–209], pyridine [210–212], s-triazine [213, 214], melamine [215, 216], acetonitrile [217], urea [218], N, N-dimethylformamide (DMF) [219] and melamines [220], and other compounds [221] can be used as nitrogen precursors to synthesize N-doped graphene. The nitrogen-containing precursors have a significant influence on the graphene growth mechanism and thus the N configuration in as-grown graphene [220, 222]. There are three common bonding configurations of N in graphene sp² carbon network, including pyridinic, pyrrolic and graphitic N (or quaternary N) [205]. A mixture of those N configurations usually appears in as-grown N-doped graphene. The doping level can be tuned by varying the ratio of nitrogen precursor and carbon precursor. As high as 8.9 % of N and graphitic N dominated few-layer graphene was produced on Cu thin film by Wei et al. using NH₃ and CH₄ as nitrogen precursor and carbon precursor, respectively [205].

Temperature has a profound effect on the doping level, N configuration and defect density of as-grown graphene [212, 216]. Typically, doping level decreases as temperature increases [214]. Low temperature creates conditions favorable to the synthesis of N-doped graphene dominated by pyridinic N but more defects, while high temperature usually leads to pyridinic N and less defects. A temperature-dependent N configuration change from pyrrolic N (~880°C) to pyridinic N (~1,050°C) has been observed [209]. Single-layer pure pyridinic N-doped graphene with atomic percentage of N up to 16 % has been synthesized on Cu foil by low-pressure CVD at 900°C using ethylene, H₂ and NH₃ as gas source [206]. N-doped graphene with two graphitic N atoms locating in the same sublattice separated by a carbon atom was grown by carefully controlling the growth parameters (growth temperature 850°C, NH₃ reaction time) [208]. Highly N-doped single-layer single-crystal graphene arrays have been grown at temperature as low as 300°C by self-assemblying of pyridine on Cu foil [211]. Almost 100 % of the as-grown graphenes are of single layer. Nitrogen content reaches as high as 16.7 % and graphitic N is dominant. Direct growth N-doped graphene on dielectric substrates by PECVD at low
temperature (435°C, using C₂H₂ and NH₃ as carbon precursor and nitrogen precursor, respectively) has also been developed by Wei et al. [177].

Nitrogen atoms randomly distribute in the graphene matrix. However, a lower N concentration or N depletion near the grain boundaries and nucleation region than that in the interior was observed by Zhao et al. (Figure 15) [223]. Different N configurations will lead to different doping types and carrier concentration [224]. Generally, N doping of graphene leads to n-type doping of graphene and enhancement of state density near the Fermi level because of N delocalizing extra electrons into the graphene lattice and shifting the Fermi level above the Dirac point [225].

![Figure 15: Nitrogen dopants distribution in graphene island [223].](image)

The extensive studies of nitrogen doping of graphene will provide important guidance for synthesizing other heteroatoms doped graphene, which we do not discuss here due to space limitations.

6 Conclusions and Perspectives

In this chapter, we briefly summarize the controllable CVD synthesis of graphene. It is challenging to grow uniform single-layer, bilayer and few-layer graphene on Ni substrates, due to the high carbon solubility in Ni and the nonequilibrium carbon precipitation. Various methods to produce uniform single-layer, bilayer and/or few-layer graphene on Ni substrate are discussed. The methods consist of substrate selection, thin-film thickness, pretreatment, alloys, growth parameters and heat/cool rate, and the overall aim of which is to obtain a large grain size, smooth Ni surface and suppress the nonequilibrium carbon precipitation at highly active Ni surface sites. For Cu substrate, the surface-mediated reaction and thus self-limited growth of graphene make it suitable to grow single-layer graphene. However, the Cu surface imperfections such as grain boundaries and steps will hinder the growth of large-sized single-crystal graphene. The approaches to synthesize bilayer graphene and large-sized single-crystal graphene domains on Cu substrate are discussed then. To grow large-sized single-crystal graphene, reducing the graphene nucleation density or (seeded) growth of oriented graphene domains and then seamlessly coalescing into a large graphene sheet free of boundaries are the fundamental principles. Bilayer layer graphene will be obtained by breaking the self-limited growth of graphene on Cu by epitaxial growth or asymmetric growth on two sides of Cu enclosure or Cu pocket. Direct growth graphene on insulating substrate through catalytically decomposing carbon precursors by gaseous catalyst and PECVD is briefly addressed. At last, doping of graphene by direct CVD synthesis using substitutional nitrogen doping as an example is presented. The relationships of doping level and nitrogen configurations with the nitrogen source and temperature are demonstrated.
Although progress has been achieved in the growth of uniform large-sized single-crystal graphene, bilayer graphene, doping as well as direct synthesis on insulating substrates, there are still various issues and challenges remaining, and much effort has to be taken to grow uniform large-sized single-crystal graphene on polycrystalline transition metals such as Ni and Cu. Wafer-scale single-crystal graphene sheet as well as bilayer or few-layer graphene with controllable stacking order will be required for various applications. The quality of graphene directly grown on insulating substrate needs further improvement, especially at low temperature compatible with flexible electronics. CVD growth doped graphene with controllable doping level, configurations and heteroatoms scattering will be helpful to further understand the structure–property relationships. Addressing those issues may offer bright future for graphene applications.

Acknowledgment

This article is also available in: Muellen, Feng, Chemistry of Carbon Nanostructures. De Gruyter (2016), isbn 978-3-11-028450-8.

References


