

Chapter 2

Controllable Synthesis of Graphene on Rh

Compared with monolayer graphene, bilayer graphene displays even more complex electronic band structures and intriguing properties. Recent studies reveal that the low-energy band structure of bilayer graphene is extremely sensitive to the stacking order. Two low-energy VHSs, which originate from the two saddle points in the band structure, were observed in the twisted graphene bilayer as two pronounced peaks in the DOS. The VHSs will induce novel physical properties, such as, superconductivity and magnetism. Therefore, the preparation of large area non-AB-stacked bilayer graphene is an efficient way to modify the energy band structure near Fermi level. Combined with the preparation methods of graphene introduced in Chap. 1, especially the growth method of bilayer graphene, I choose segregation growth as a method for preparing non-AB stacking bilayer graphene.

The first section introduces the process engineering of graphene growth and the factors that affect the segregation of graphene. I designed the carrier gas system, heating system, cooling rate control system and pressure control system of graphene growth and chose the Rh foil as a substrate for the growth of non-AB-stacked graphene.

The second section mainly introduces the growth of graphene on Rh substrate. Because Rh is a metal with a large carbon solubility, the low pressure(LP) CVD system cannot provide enough carbon source for the growth of graphene. Thus I selected the atmospheric pressure (AP) CVD system. By changing the cooling rate after the growth of graphene, monolayer, bilayer, or multilayer graphene can be obtained on Rh substrate. With the same growth system and method, I can control the preparation of monolayer and bilayer graphene on Rh(111) substrate. It is indicated that in addition to the grain boundary of the substrate, the terraces and step edges are also the graphene segregation channel. In addition, wrinkles were observed on graphene grown on Rh substrates, which are originated from the thermal expansion mismatch between graphene and Rh.

In the third section, I summarize the growth characteristics of graphene on Rh substrate. Thus, I propose that the thickness of the graphene prepared in this system has a great relationship with the cooling rate after growth. The advantages and

disadvantages of graphene growth on Rh substrate were summarized by comparison with the growth of graphene grown on other noble metal substrates (Pt, Pd) with high carbon solubility.

2.1 Experiment

I choose the metal with high carbon solubility as the substrate to grow graphene, and control the segregation process of graphene by CVD system to obtain the large-scale bilayer non-AB-stacked graphene. In order to control the growth of graphene, the basic steps of graphene growth are needed to be understood. Yan et al. [1] summarized the previous work on graphene synthesized by CVD method and proposed the process engineering of graphene growth.

2.1.1 Process Engineering for Graphene Growth

Figure 2.1a is a typical CVD system for graphene growth, consisting of carrier gas part and growth part. Carrier gases include carbon precursors (CH_4 , C_2H_4 , benzene, etc.), carrier gases (H_2 , Ar) and doped precursors (N_2 , BH_3). A surrounding resistance wire is used to heat the sample in quartz tube at temperature up to 1200°C .

A typical CVD process consists of four main elementary steps: (A) adsorption and catalytic decomposition of precursor gas, (B) diffusion and dissolution of decomposed carbon species into bulk metal, (C) segregation of dissolved carbon atoms onto the metal surface, and finally, (D) surface nucleation and growth of graphene. Absence or enhancement of each elementary step would lead to significant changes in the whole growth process. Metals with certain carbon solubility, such as nickel and cobalt, involve all four elementary steps in a typical CVD process. Copper with negligible carbon solubility provides another platform for process engineering, where both carbon dissolution and segregation steps are negligible in the CVD process. Carbon atoms decomposed from precursors diffuse on the surface and build up the thermodynamically stable honeycomb graphene lattice. As a result, graphene growth on copper is self-limited, and formation of multilayer graphene is generally prohibited. For most cases, the two growth paths are coexisting.

2.1.2 Factors for Graphene Segregation

The advantage of segregation growth is that it is easily to obtain the non-AB stacked graphene, while the disadvantage is that it is difficult to control the homogeneity of graphene. Thus how to improve the homogeneity of graphene film

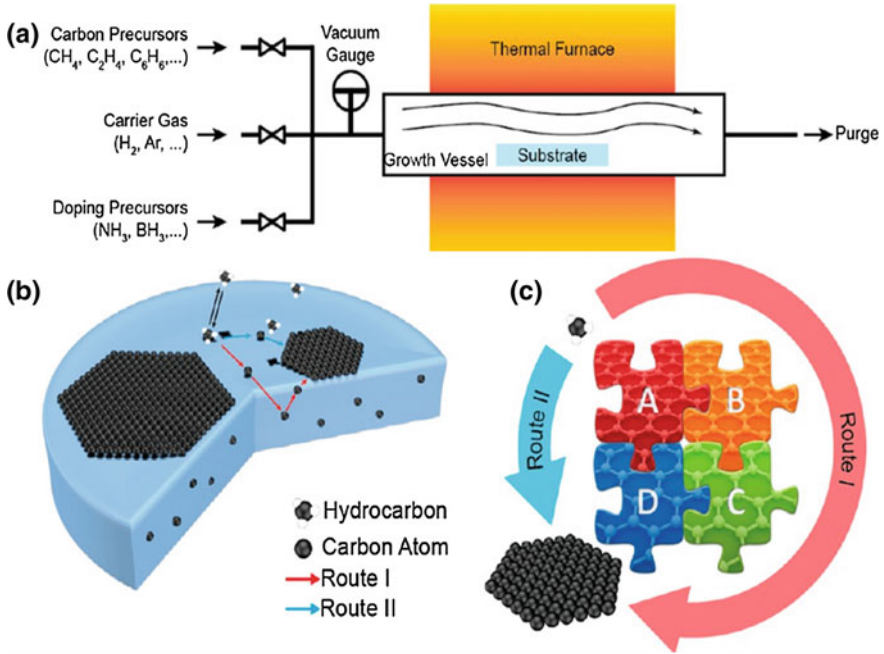


Fig. 2.1 The process engineering of graphene. **a** Typical CVD growth process of graphene. **b**, **c** Graphene growth process on different metal substrates: the red arrow and blue arrow represent the graphene growth process on metals with high carbon solubility and low carbon solubility, respectively. Reproduced with permission of [1]. Copyright [2013], American Chemical Society

becomes the most important factor for the study of graphene segregation growth. According to the process engineering of graphene growth, the result of segregated graphene is mainly related to the two steps of B and C. There are many factors to control graphene segregation process, including the basic properties of the substrate (e.g., carbon solubility, thickness and crystallization, etc.) and control parameters of graphene growth (e.g., growth temperature and cooling rate). I will briefly describe the impact of these factors on the graphene segregation process:

(1) The carbon solubility and thickness of metal substrates

The segregation growth of graphene conforms to the equation:

$$\text{Quantity of segregated carbon} \propto \Delta C \times \Delta T \times n$$

where ΔC refers to the difference of carbon solubility in the metal substrate at different temperature, ΔT refers to the temperature difference, and n refers to the thickness of the substrate. It can be seen from the equation, with the reduced carbon solubility and the thickness of the metal substrate, the amount of segregated carbon will be reduced. For example, the carbon solubility of Fe, Co and Ni at 1000 °C are 7, 1.6, 0.9 at.%, respectively. Under the same growth conditions, monolayer

graphene on Fe surface is about 40, and 15% of the substrate is bare. Monolayer graphene on Co and Ni accounted for 50 and 70%, respectively. Consequently, with the decrease of carbon solubility of metal substrate, the homogeneity of segregated graphene is improved remarkably [2]. For the same metal substrate, increased thickness of the substrate leads to increasing in the amount of dissolved carbon atoms. As a result, the segregated carbon increases. For example, graphene layer grown on Co substrate with thickness of 300 nm is very inhomogeneous and monolayer graphene is rarely observed. With the decrease of the thickness of Co substrate, the homogeneity of graphene increases, and the area of monolayer increases. The monolayer graphene grown on Co substrate with 100 nm thickness accounts for more than 70% [3]. However, the thickness of the substrate cannot be reduced indefinitely. If the thickness of the substrate layer is too thin, the metal substrate tends to be agglomerated into nanoparticles at high growth temperature at 1000 °C.

(2) The crystallization of metal substrate

From the kinetic point of view, carbon atoms preferentially diffuse from the grain boundary of substrate to form graphene films [4, 5]. Reducing the quantity of grain boundary can effectively prevent the segregated carbon atoms and improve the film uniformity. For example, the grain boundary between the different crystal faces of the polycrystalline Pd substrate is the main channel for the segregation of carbon atoms. However, due to the high carbon solubility of Pd, the graphene on grain boundary is much thicker than that on Pd crystal facet. As shown in Fig. 2.2, the grid-like graphite-coated graphene structure is formed on Pd foils. The long-term annealing of the Pd foil at 1050 °C can optimize the Pd crystal plane and reduce the number of grain boundaries. With the increasing of the optimization time, the thickness of segregated graphene at the grain boundary gradually decreases, and the homogeneity of graphene increases. What's more, uniform monolayer graphene can be obtained on Pd single crystal substrate, which has no grain boundary.

(3) Growth temperature and cooling rate

The growth temperature for graphene segregation affects the balance between the carbon dissolution into substrate bulk and carbon segregation onto substrate surface. When the equilibrium is reached, the different temperatures correspond to the different states of the metal on the metal surface [6, 7]. In the case of Ni: the carbon atoms begin to form sp^2 -hybrid fragments on the Ni surface, and small graphite domains can be obtained at 850 °C; at 1000 °C, high coverage of the graphite aggregates are obtained; at 1100 °C, monolayer graphene can be achieved; when the temperature is higher than 1150 °C, the amount of carbon atoms are dissolved in Ni substrates, thus graphene cannot be formed [2]. Consequently, 1100 °C is the optimum temperature for the segregated graphene on Ni substrates (Fig. 2.3).

The effect of cooling rate and growth temperature on graphene segregation is associated. When the equilibrium of carbon dissolution-segregation is achieved, the

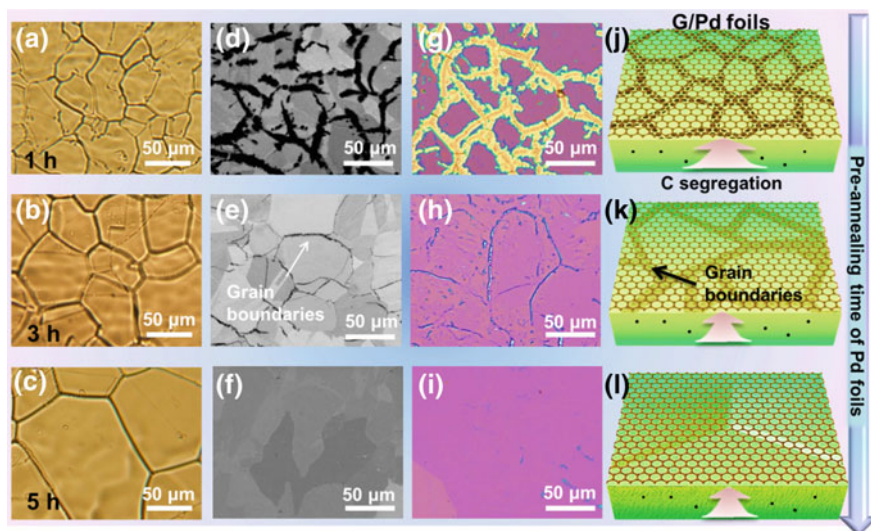


Fig. 2.2 Annealing pretreatment of Pd foils for the subsequent growth of graphene. **a–c** Optical images of Pd foils after annealing pre-treatment for 1 (**a**), 3 (**b**), and 5 (**c**) hours. **d–f** Corresponding SEM images of the subsequently grown graphene on the pretreated Pd foils. **g–i** Corresponding optical images of the graphene samples after being transferred onto SiO₂/Si substrates. **j–l** Schematics of the pre-treatment effect on the reduction of the grain boundaries and on the suppression of the excessive carbon segregation. Reproduced with permission of [4]. Copyright [2014] Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim

cooling process will break the balance. During the slow cooling process, as the temperature decreases, the carbon solubility of the metal substrate decreases, causing the excessive carbon atoms to segregate on the surface to form thick graphene layers or graphite. The rapid cooling process can maintain the equilibrium state of the system at high temperature, resulting in the uniform graphene layers at the growth temperature.

2.1.3 Substrate

The existing research on segregation growth of graphene is mainly focused on three kinds of substrates: (1) Cheap metals with high carbon solubility, such as Ni [8–10], Fe [11], and Co [12, 13]. This kind of metals can be used to prepare large-scale graphene with high coverage. However, due to the high carbon solubility, it is difficult to control the uniformity and thickness. (2) Noble metals, such as Ru(0001) [14–17] and Ir(111) [18]. Such metals can be used to prepare monolayer or bilayer singlecrystalline graphene. The preparation of graphene on noble metals is usually carried out in UHV chamber. Moreover, the singlecrystalline noble metals are expensive and the as-grown graphene is difficult to be transferred onto other

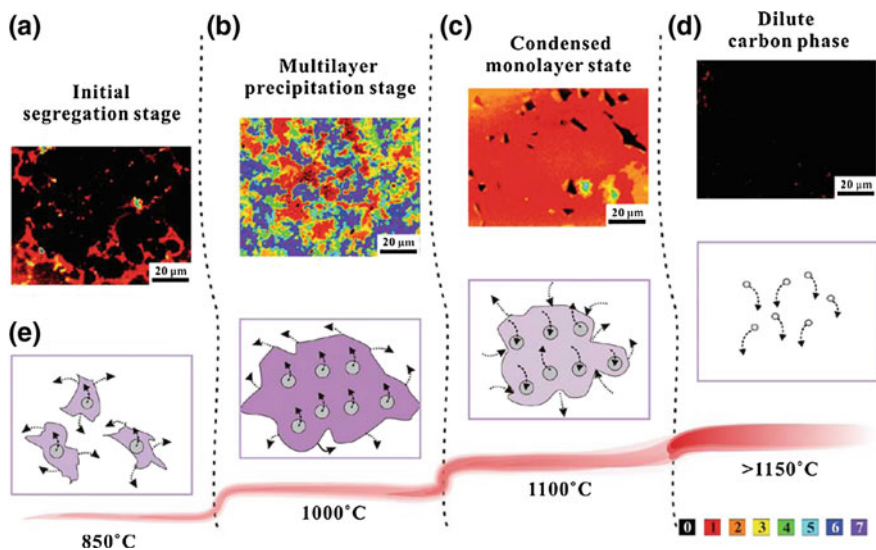


Fig. 2.3 Temperature effect on graphene segregation. **a–d** Layer distribution of graphene on 300 nm SiO₂/Si grown from 200 nm Ni at temperatures of 850, 1000, 1100, and >1150 °C, respectively. **e** Schematic illustration of various equilibrium states corresponding to temperature change during graphene segregation. Reproduced with permission of [2]. Copyright [2011], American Chemical Society

substrates for further applications. (3) Alloys, such as, Cu–Ni alloy [19–21]. This kind of alloy combines metals with high carbon solubility and low carbon solubility, thus the control of thickness of graphene can be significantly improved. The disadvantage of the alloy system is that the surface roughness is high and the quality of the prepared graphene is poor.

It is mentioned in process engineering of graphene growth that the four basic steps are all related to the metal substrates, meanwhile most of the factors that affect graphene segregation are also related to the intrinsic properties of the metal substrate. Therefore, it is essential to select a suitable substrate for the preparation of segregated graphene. The most important factor is the carbon solubility of metal substrate. In addition to the most commonly used Cu and Ni substrates, the metals of VIIIB and IB also have high carbon solubilities (up to 7 at.% at 1000 °C) and high catalytic activity for graphene growth (Fig. 2.4).

Among these transition metals, Rh has the smallest carbon solubility, between Cu and Ni, and the growth of graphene on Rh(111) singlecrystal in UHV system has been studied deeply. Monolayer graphene can be synthesized on Rh(111) substrate at 600 °C, and the lattice orientation of graphene is consistent with that of Rh(111) facet, which means the graphene shows a singlecrystalline feature [22–24]. Consequently, Rh is expected to be a good substrate for the growth of large-scale non-AB stacked bilayer graphene.

a			VIIIB			IB		
1538°C	✓	1495°C	✓	1455°C	✓	1085 °C	✗	
7%@1000°C		1.6@1000°C		0.9 @1000°C		0.04 @1000°C		
Fe		Co		Ni		Cu		
0.8	FCC/BCC	1.8	HCP	1.2	FCC	3.7	FCC	
2334°C	✗	1964°C	✗	1555°C	✗	962°C	✗	
		0.25@1000°C		3.5@1000°C		0.04		
Ru		Rh		Pd		Ag		
9.1	HCP	8.5	FCC	10.5	FCC	14.9	FCC	
3033°C	✗	2466°C	✗	1768°C	✗	1064 °C	✗	
2.1@2732°C				0.7@1000°C		0.08		
Os		Ir		Pt		Au		
10.2	FCC	9.4	FCC	11.3	FCC	14.5	FCC	

Fig. 2.4 Comparison of transition metals of VIIIB and IB on melting point, carbon solubility and the lattice mismatch with graphene

2.1.4 Experimental System

Figure 2.5 is a schematic diagram for the growth system. The sample is placed in a quartz tube in furnace; the mixed gases are carried through the pipeline into the quartz tube for the growth of graphene; after the growth, the sample is rapidly removed from the heating zone by magnet to complete the rapid cooling process.

The detailed growth process of graphene is shown in Fig. 2.6. First, the Rh foil is heated to 1000 °C in a hydrogen and argon atmosphere for 40 min. In this process, the organic impurities adsorbed on the surface of the metal substrate can be removed, and the Rh crystal facet can be optimized. Then the CH₄ is introduced into the quartz tube for the growth of graphene. After that, the system is cooled down to room temperature. It is worth noting that in the process of cooling, if a

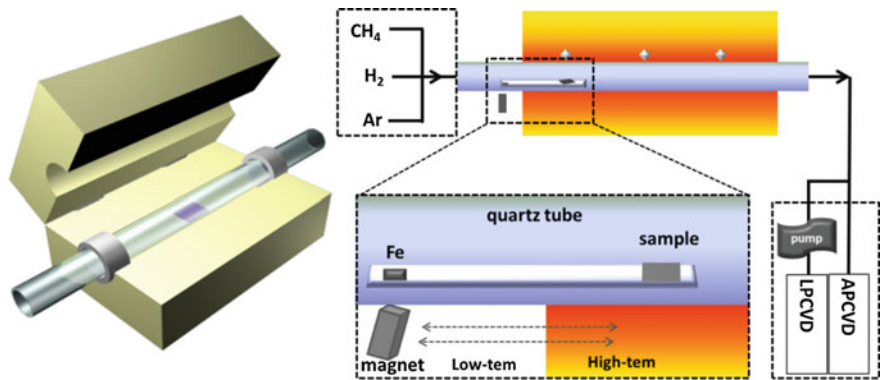
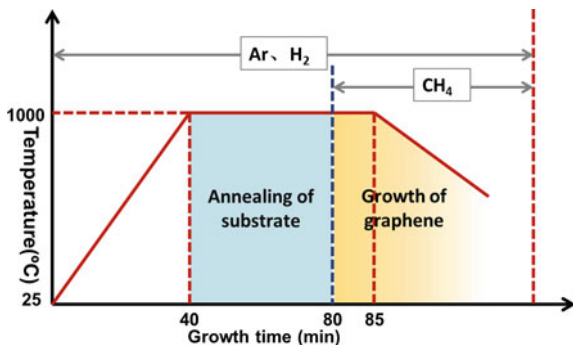


Fig. 2.5 The experimental system for graphene growth

Fig. 2.6 The growth process of graphene in APCVD system



slow cooling method is used, it is necessary to keep the CH_4 on. If the CH_4 is cut off during the slow cooling process, the graphene can be easily etched by H_2 . In opposite, there is no need for continuous access to CH_4 during the fast cooling process.

Chemical etching is the most commonly used method for graphene transferring [25]. However, Rh is insoluble in most acid, alkali or salt solutions, thus graphene on Rh cannot be transferred by chemical etching method. Graphene grown on noble metal substrate can be transferred by using the “bubble transfer method”. The bubble transfer method is proposed by the Cheng et al. in 2012 [26], that is, the graphene and substrate is separated by the interfacial bubbles generated from electrolyzed water. The graphene can be transferred onto SiO_2/Si or other substrates for further characterization and applications.

2.2 Controllable Growth of Graphene on Rh Substrates

The Rh substrate used in the experiment was purchased from Sigma-Aldrich, with a thickness of 0.025 mm and a purity of 99.9%, the picture of which is shown in Fig. 2.7a. After the Rh foil was annealing at 1000 °C, X-ray diffraction (Fig. 2.7b) shows that there are only two facets, Rh(111) and Rh(200).

In order to minimize the amount of carbon source introduced into the system and control the thickness of the segregated graphene, we first tried the low pressure (LP) CVD system, where the tail gas was connected to a rotary pump so that the sample in the quartz tube was at low pressure.

When the carrier gas is $\text{CH}_4:\text{H}_2:\text{Ar} = 20:10:50$ (here means the flow of CH_4 , H_2 and Ar are 20, 10, 50 sccm, respectively, where sccm is short for the standard cubic per minute abbreviation), the result is shown in Fig. 2.8. It is observed that the coverage of graphene is very low. After the graphene is transferred onto SiO_2/Si substrate, we find that the graphene sheets are not uniform, and the OM image shows that the thickness of graphene sheet is more than 10 layers. These results

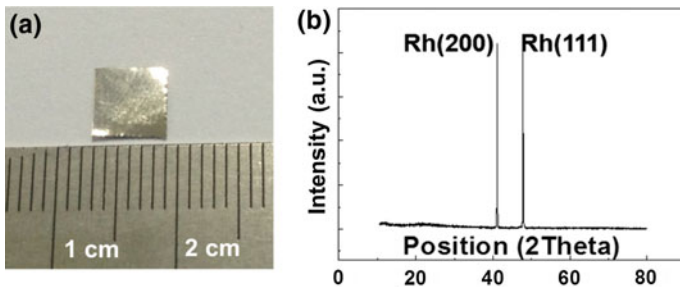
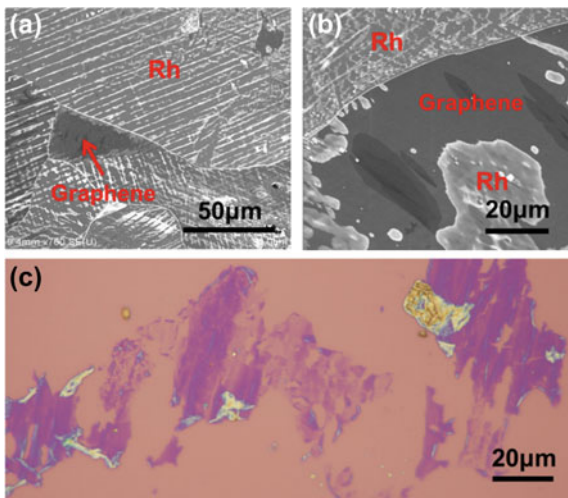


Fig. 2.7 **a** Picture and **b** XRD characterization of Rh foils after annealing at 1000 °C

Fig. 2.8 Graphene grown on Rh foils under LPCVD system. **a, b** SEM images of as-grown graphene on Rh foils. **c** OM image of graphene after transferred onto SiO₂/Si substrate



reveal that the LP system cannot provide sufficient carbon source for the growth of large-scale uniform graphene.

Therefore, we choose the atmospheric pressure (AP) CVD system for graphene growth, that is, the tail gas and the rotary pump are isolated, so that the sample in the quartz tube is at atmospheric pressure. The carrier gases are CH₄:H₂:Ar = 10:300:100 and growth temperature is 1000 °C for 5 min. After growth, the sample was rapidly cooled to room temperature at a rate of 150 °C/min. As shown in Fig. 2.9, the coverage of graphene is more than 80% and the SEM contrast is very uniform. We then transfer the graphene sample into the UHV chamber and degas at 400 °C for further STM characterizations. STM image shows that the Rh foil surface forms straight array of steps with graphene wrinkles across the steps. The width of wrinkle is ~30 nm, height ~3 nm and the length can reach several hundred nanometers. The atomic resolution of the graphene honeycomb lattices can be obtained by high-resolution STM, as shown in Fig. 2.9c. The AFM image of

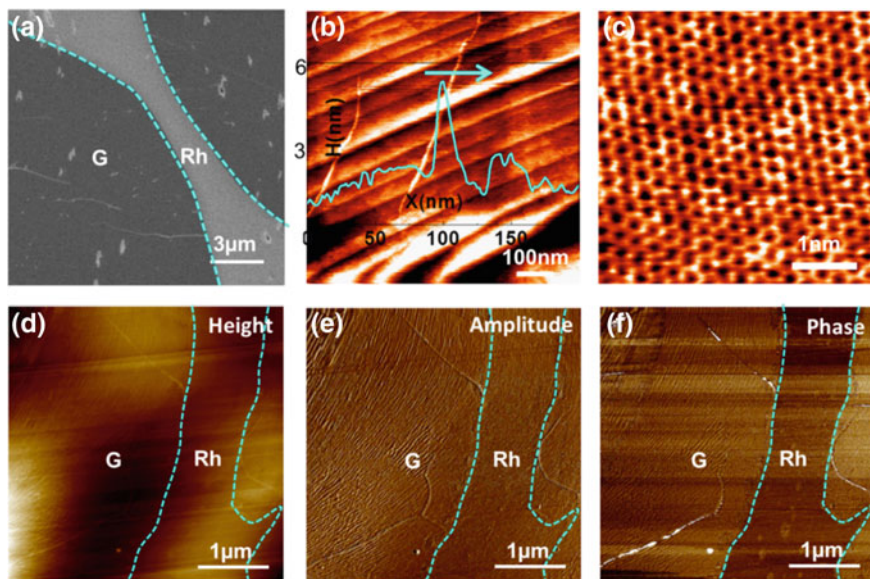


Fig. 2.9 Monolayer graphene synthesized on Rh foils through a fast cooling process after growth. **a** SEM image of graphene. **b** STM image of graphene on Rh foils. **c** Atomic resolved STM image of graphene showing honeycomb lattices. **d–f** AFM images of graphene on Rh foils, **d**, **e** and **f** corresponding to height, amplitude and phase channels, respectively

as-grown graphene on the Rh foil shows a highly corrugated surface. AFM height and amplitude images are difficult to distinguish the graphene domains. Interestingly, the AFM phase image shows different contrasts of graphene and the bare Rh foils.

We used the bubble method to transfer the graphene to SiO₂/Si substrate for further study. The graphene on the SiO₂/Si substrate shows a light purple contrast in OM image, which is corresponds to the contrast of monolayer graphene (Fig. 2.10). The Raman spectra of graphene (the wavelength of the laser is 633 nm) shows that the G peak and 2D peak of graphene appear at ~ 1584 and ~ 2650 cm⁻¹, respectively, meanwhile the 2D/G ratio is ~ 1.2 and the full width at half maximum (fwhm) of 2D peak is ~ 30 cm⁻¹, consistent with the characteristics of monolayer graphene. In addition, there is no D peak at ~ 1350 cm⁻¹, indicating a high quality of graphene. In order to further reconfirm the thickness of graphene, we transfer the graphene film onto the TEM grid to do the high-resolution measurement. Figure 2.10c is a large-scale image of TEM, and its edge fold is enlarged to show that the graphene is monolayer. The selected area electronic diffraction (SAED) on graphene shows only one set of six symmetric diffraction spots, and the second order diffraction intensity is weaker than that of the first order diffraction, again confirming that the graphene is monolayer.

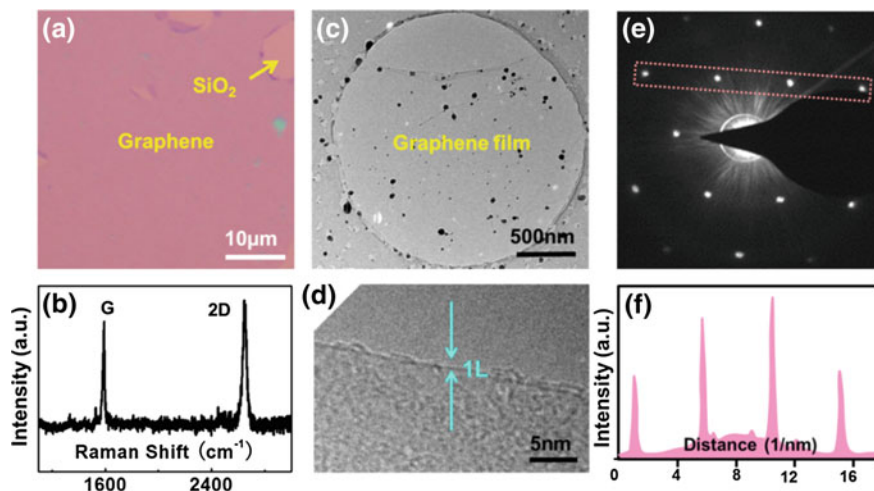


Fig. 2.10 The identification of graphene thickness. **a** OM image of graphene on SiO_2/Si . **b** Raman spectrum of graphene. **c, d** Large-scale TEM image and the magnified image of the folded edge. **e, f** The SAED of graphene shown in (c)

The experimental results reveal that graphene tends to form a uniform monolayer on Rh foils with the coverage over 80% at 1000 °C. It means that the dissolution of the carbon atoms at this temperature is greater than segregation. In order to obtain a full monolayer or bilayer graphene, it is necessary to slow down the cooling rate to apply sufficient time for carbon atoms to segregate on Rh surface.

We slow down the cooling rate to 15 °C/min, and set the precursor ratio (CH_4 : H_2 :Ar = 5:50:850 sccm), while the growth temperature and time remain unchanged. The growth results are displayed in Fig. 2.11. SEM images of the samples show that the Rh foils are fully covered with graphene, and the white wires correspond to the graphene wrinkles. The angles between the graphene wrinkles (Fig. 2.11a, b) are 60° or 120°, forming a triangular or hexagonal shape, meanwhile

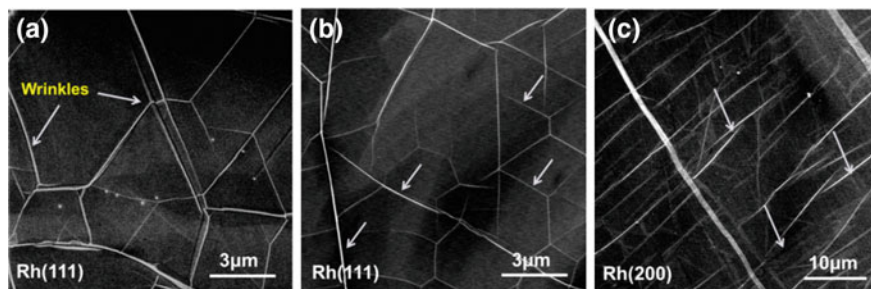


Fig. 2.11 SEM images of graphene grown on Rh foils through a slow cooling process

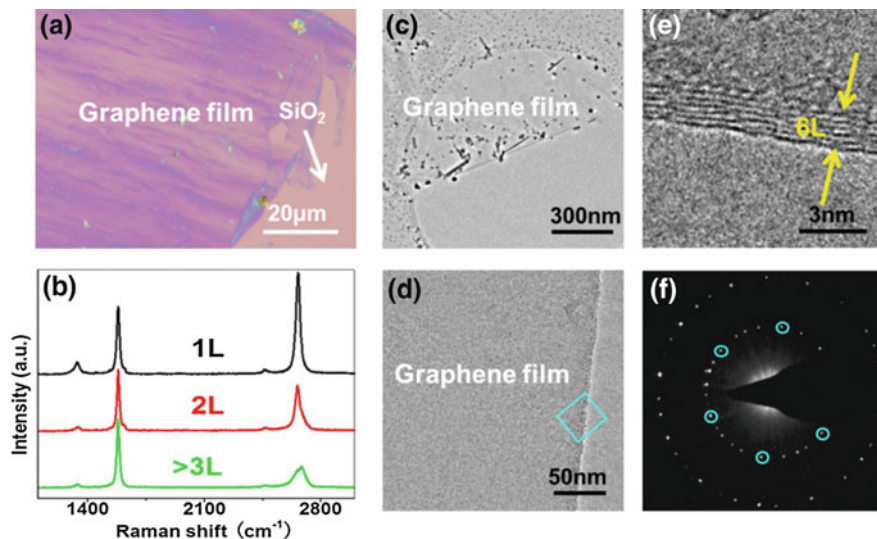


Fig. 2.12 Characterizations of graphene growth on Rh foils under slow cooling process (15 °C/min). **a** OM image of graphene after being transferred onto SiO₂/Si. **b** Raman spectra of graphene sample in (a) showing multilayer (nL) films along with a little portion of 1L and 2L regions, under a Raman excitation wavelength of 633 nm. **c–f** TEM characterization of graphene grown with a slow cooling process. TEM images of the folded regions showing 6L graphene

the angles between the graphene wrinkles in Fig. 2.11c is mostly 90°, forming a rectangular structure. The formation of wrinkles is due to the thermal expansion mismatch between the graphene and the substrate in the cooling process and the wrinkles prefer to form along the grain boundaries of the substrates. Therefore, we can infer that Fig. 2.11a, b, c represent the graphene grown on Rh(111) and Rh(200) facets, respectively (Fig. 2.12).

We transferred graphene to the SiO₂/Si substrate by bubble method to confirm the thickness of graphene. OM image shows that graphene exhibits various contrasts from light purple to purple, indicating that the thickness of graphene is less than 10 layers, but the uniformity is poor. The Raman spectra measured randomly (the wavelength was 633 nm) indicate the characteristic spectra of graphene with different thickness. Such as, characteristics of single-layer graphene shows $I_{(2D/G)} = 1.6$, and fwhm of 2D peak $\sim 30 \text{ cm}^{-1}$; bilayer graphene $I_{(2D/G)} = 0.8$, fwhm of 2D peak $\sim 45 \text{ cm}^{-1}$; few layer graphene $I_{(2D/G)} < 1$, fwhm of 2D peak $> 70 \text{ cm}^{-1}$. The graphene film was transferred to the TEM grid for further confirmation of the thickness, and the high-resolution TEM image of the graphene folded edge proves that the thickness of graphene is 6 layers. SAED image shows multiple sets of six symmetric diffraction spots with different rotation angles, indicating non-AB stacked feature of graphene films.

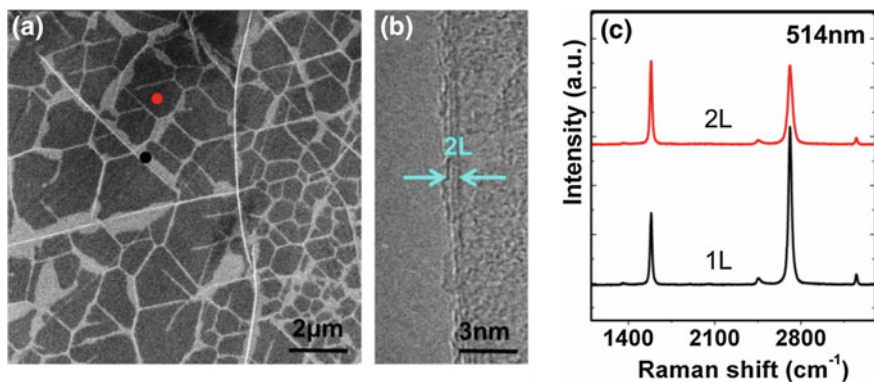


Fig. 2.13 Bilayer graphene synthesized on Rh foils **a** The SEM image, **b** high-resolution TEM image and **c** Raman spectra of bilayer graphene

The slow cooling process provides a large amount of carbon source to segregate onto the Rh surface to form few layer graphene films. In order to reduce the segregation of carbon atoms and improve the homogeneity of graphene, we change the ratio of the precursor to $\text{CH}_4:\text{H}_2:\text{Ar} = 3:300:850$. Reducing the flow of methane while increasing the flow of hydrogen is for both diluting the methane concentration and increasing the etching process. The SEM image shown in Fig. 2.13a reveals that there are only dark gray and light gray contrast in graphene region. According to the work mechanism of SEM, graphene in dark gray area is thicker than light gray. The high-resolution TEM image of the folded edge of graphene layer confirm that the thickness of graphene is bilayer. The graphene is transferred to the SiO_2/Si substrate and the Raman spectra are measured in different contrast regions. The results show that the light gray area has the characteristic of the monolayer graphene and the dark gray region has the characteristic of bilayer graphene.

By controlling the growth time from 2 to 5 min, the coverage of bilayer graphene can be controlled from 50 to 95% (Fig. 2.14a–d). In addition, we also use Rh(111) single crystal as a substrate to synthesize bilayer graphene. The growth parameters on the Rh(111) substrate are set to $\text{CH}_4:\text{H}_2:\text{Ar} = 20:50:200$, at 1000°C for 10 min and the cooling rate is $15^\circ\text{C}/\text{min}$.

The growth results are shown in Fig. 2.14e–h, and the proportion of bilayer graphene is about 60%. It is found from the gradually magnified SEM images that the segregated graphene on Rh(111) substrate has two characteristics: no wrinkle is observed on graphene; bilayer graphene has no specific nucleation sites and domain shapes. Compared with the Rh foil substrate, there is no grain boundary on Rh(111) substrate. It is generally believed that grain boundaries are the main route of graphene segregation. This work shows that in the absence of grain boundary of the metal substrate, the metal steps and the terraces are the main path for graphene segregation.

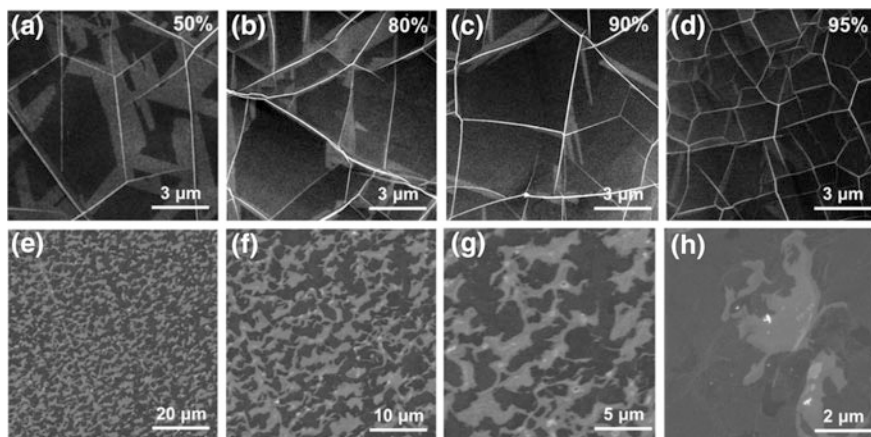


Fig. 2.14 Bilayer graphene synthesized on Rh foils and Rh(111) substrates **a–d** SEM images of bilayer graphene on Rh foils. **e–h** SEM images of bilayer graphene on Rh(111)

2.3 The Mechanism of Graphene Growth on Rh Substrates

Based on the high carbon solubility of Rh substrates and the characteristics of graphene growth under different cooling rates, I proposed a mechanism for graphene growth on Rh substrates under APCVD conditions. As shown in Fig. 2.15, at 1000 °C, CH_4 are decomposed on Rh surfaces for its perfect ability to catalyze hydrocarbon decomposition, and contemporary, carbon atoms dissolve into bulk Rh because of its high carbon solubility. In the cooling process of CVD growth, the solubility of carbon becomes lower with decreasing the sample temperature, and therefore excess carbon atoms would segregate from bulk to surface forming graphene layers. In the relative long cooling process, carbon atoms have enough time to segregate to metal surfaces to form multilayer graphene. In contrast, under fast cooling, the balance between dissolution and segregation of carbon is destroyed, and only a small amount of carbon atoms can be segregated from bulk to surface, leading to the formation of mainly monolayer graphene.

In addition to the Rh substrate, I also studied the growth of graphene on Pt and Pd substrates. The carbon solubility of Pt and Pd are higher than that of Rh. But the two metal substrates show absolutely different characteristics on graphene growth. Pt has a carbon solubility of 0.7 at.% at 1000 °C, slightly lower than Ni. However, monolayer graphene is obtained on Pt foils in the APCVD system, whether the rapid cooling or slow cooling process is used. I speculate that the reason may be due to the slow velocity or the high energy required for carbon atoms migrating in the Pt bulk, which prevents the excess carbon atoms from segregating to the Pt surface. Pd has an ultrahigh carbon solubility of 3.5 at.% at 1000 °C. We can only obtain multilayer graphene or graphite using LPCVD system on Pt foils, whether

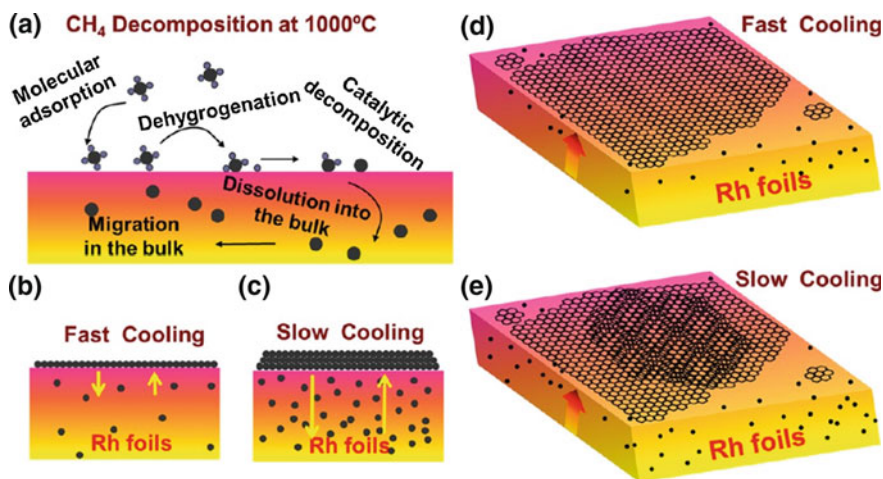


Fig. 2.15 Schematic drawing showing the growth mechanism of graphene on Rh foils. **a** CH_4 decomposition at 1000 °C, followed with carbon dissolution into Rh foils. **b–e** Side-view and 3D images of carbon atoms segregating from bulk to Rh surfaces throughout the quenching processes under fast and slow cooling, forming monolayer and multilayer graphene, respectively

rapid cooling or slow cooling process is applied. Comparing the growth of graphene on the three noble metal substrates, we can obtain monolayer, bilayer and multi-layer graphene on the Rh substrate in a controllable way, and the control window of the graphene layer is relatively wide. Consequently, Rh is the best substrate for the preparation of segregated bilayer graphene.

2.4 Conclusion

In this chapter, I summarized the factors that control the thickness of segregated graphene, and selected the Rh (with the appropriate carbon solubility) as substrate, to synthesize segregated graphene using CVD growth system.

Monolayer graphene is obtained with a cooling rate of 150 °C/min after the growth process, and the monolayer feature is confirmed by TEM, OM and Raman measurements. Combined with the control factors of graphene segregation growth, few layer graphene is obtained by reducing the cooling rate to 15 °C/min. Furthermore, bilayer graphene is obtained by reducing the ratio of CH_4/H_2 in gas precursors. Using the same growth system and method, I can also obtain bilayer graphene on the Rh(111) substrate, which indicates that in addition to the grain boundary of the substrate, the crystal terraces and steps are also segregated channel for carbon atoms.

Based on the growth characteristics of graphene on Rh substrate, I proposed the segregation growth mechanism of graphene. By comparison with the graphene growth on other noble metals of Pt and Pd, Rh substrate is the most suitable substrate for the segregation growth of bilayer graphene.

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