

Controllable Fabrication of Vertical Graphene with Tunable Growth Nature by Remote Plasma-Enhanced Chemical Vapor Deposition

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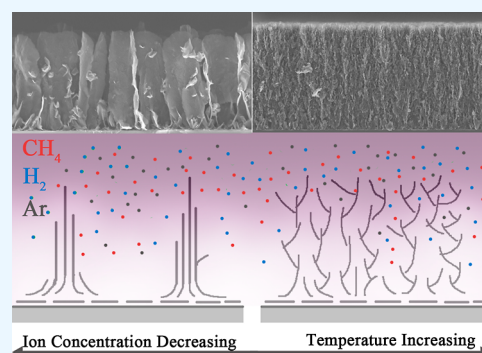
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ABSTRACT: As an important member of the graphene family, vertical graphene (VG) has broad applications like field emission, energy storage, and sensors owing to its fascinating physical and chemical properties. Among various fabrication methods for VG, plasma enhanced chemical vapor deposition (PECVD) is most employed because of the fast growth rate at relatively low temperature for the high-quality VG. However, to date, relations between growth manner of VG and growth parameters such as growth temperature, dosage of gaseous carbon source, and electric power to generate plasma are still less known, which in turn hinder the massive production of VG for further applications. In this study, the growth behavior of VG was studied as functions of temperature, plasma power, and gas composition (or chamber pressure). It was found that the growth behavior of VG is sensitive to the growth conditions mentioned above. Although conditions with high growth temperature, large flow rate of mixed gas of methane and carrier gases, and high plasma power may be helpful for the fast growth of VG, branching of VG is simultaneously enhanced, which in turn decreases the vertical growth nature of VG. High-quality VG can be achieved by optimizing the growth parameters. It was revealed that the vertical growth nature of VG is governed by the electric field at the interfacial layer between VG and the substrate, for which its strength is influenced by the density of plasma. These findings are important for the general understanding of the VG growth and provided a feasible way for the controllable fabrication of VG using the remote PECVD method which is usually believed to be unsuitable for the fabrication of VG.



1. INTRODUCTION

A vertical graphene (VG) film is composed by two-dimensional (2D) carbon units, i.e., few-layer graphene nanosheets. However, VG is distinct from planar growth graphene materials in that the 2D units are arranged in the direction normal to the graphene film, resulting in the three-dimensional (3D) morphology within the graphene film. Compared with conventional planar graphene, which is a 2D film with a basal plane, VG has fascinating advantages such as large specific surface area, plenty of chemically active edges and defects, and the highest ratio of edge atoms of any carbon allotrope. These properties ensure VG as a promising candidate for various application such as field-emission,¹ biochemical sensors,^{2,3} and supercapacitors.⁴ So, the controllable fabrication of this material has drawn intensive scientific attention in recent years. Plasma-enhanced chemical vapor deposition (PECVD) is one the most frequently used method to fabricate VG.^{5–9} It was reported that VG can be grown on various substrates by adopting the PECVD method. It was found that the growth behavior of VG is highly sensitive to growth conditions such as growth temperature, the power of plasma generator and the dosage of carbon source, but is irrespective of the substrate.^{10–}

¹⁴ High growth speed is attractive for the massive fabrication of VG materials. Wu et al. found that the growth speed of VG could reach 18.08 $\mu\text{m}/\text{min}$ when power of plasma generator is very high, e.g., 18 kW, which is the fastest rate ever reported.¹⁵ Compared with thermal CVD growth of 2D graphene, the temperature required for the growth of VG with PECVD method is much lower.^{16–19} In fact, VG can even be fabricated without the assistance of extra thermal decomposition of carbon precursors.²⁰ Although the growth temperature may be very low, the power for generation of plasma must be very high in order to decompose carbon precursors efficiently and maintain the growth speed of VG. In addition to growth conditions and growth method, the source of carbon feedstock is another parameter that was intensively studied. Historically, using methane (CH_4) as a carbon gaseous source (or

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precursor) to grow VG is a traditional recipe. Later, researchers gradually developed novel recipes using different carbon sources such as C_2H_2 and solid carbon sources.^{21–23}

Investigations suggest that the growth mechanism of VG is related to the movement of carbon ions driven by the interfacial electric field between plasma and the substrate.^{7,24–27} It was supposed that CH_4 was decomposed into CH_x which are charged particles by the radio frequency (RF) electromagnetic field. The CH_x debris move along the normal direction of the substrate surface and further reduced to form graphene sheets which are aligned perpendicular to the substrate surface. The energy of charged ions and environmental temperature can affect the growth rate and morphology. At the same time, the growth of VG and the etching effect of H^+ coexist, which together determines the final structure of VG.^{9,13,24,28,29} Studies have shown that H_2 can affect the morphology of VG, but it is not a necessary condition for VG growth. For PECVD growth of VG, the plasma power, substrate type, and even gas ratio are the factors that are mainly focused.^{15,23,30,31} However, the detail of growth manner of VG with respect to growth parameters such as growth temperature, dosage of gaseous carbon source and buffer gases such as argon and hydrogen, and electric power to generate plasma are still lacking.

In this work, we investigated the evolution of growth manners of VG with growth temperature, RF power, and ratio between carbon precursor and carrier gas. It was found that the morphology of the VG film is significantly influenced by the growth temperature, while the branching behavior is sensitive to the ratio between carbon precursor and carrier gas. By contrast, both morphology and the branching behavior of VG were influenced by the power of the RF generator. These observations imply an electric-field-directed growth of VG tuned by the density of plasma.

2. METHODS

The VG samples were fabricated on a homemade PECVD system, whose diagram is shown in Figure 1. Carbon precursor

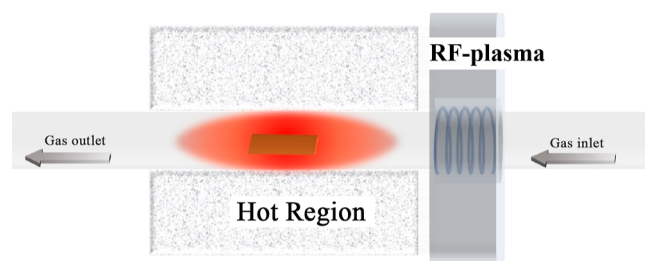


Figure 1. Schematic diagram of the RF-plasma enhanced chemical vapor deposition system used for the deposition of VG.

such as methane was inlet into the CVD chamber through flow controller and then decomposed by the RF electromagnetic field generated by a RF generator with maximum power of 500 W. NO other gas was used otherwise mentioned. The decomposed carbon debris was transported to the hot-region which was heated by the oven and then deposited onto substrates to form VG. Prior to the fabrication of VG, the substrates were cleaned by cycles of cleaning with acetone, isopropanol and deionized water. Then, these substrates were loaded into the PECVD chamber and placed side-by-side at the growth-region (i.e., hot region as shown in Figure 1) of the

PECVD chamber. After that, the PECVD chamber was pumped to a low pressure of 0.1 Pa before the growth region was heated-up to 300–1000 °C in 30 min with the constant dosage of gaseous Ar with flow rate of 50 sccm. Then, the VG growth stage began by introducing methane with flow rate 10 sccm and simultaneously tuning-on the radio frequency generator of a power of 300 W. The duration time for the growth stage was changed from sample to sample, and it was usually varied from a few minutes to a few hours depending on the thickness of VG. When the growth stage is over, radio frequency generator was shut off and dosing of methane was stopped. Finally, the CVD chamber was cooled down to room temperature before the VG sample was removed out of the CVD chamber.

Zeiss sigma300 scanning electron microscope was employed to measure the morphology and the aligning nature of the VG films. High-resolution transmission electron microscopy (HRTEM) of JEM-2100F was used to investigate the thickness and crystallinity of the as-fabricated VG. Horiba HR evolution Raman spectrometer (LabRAM.HR Evolution) with a wavelength of 532 nm was employed to analyze the bonding structure and characteristics of the PECVD prepared VG.

3. RESULTS AND DISCUSSION

In Figure 2, we show an example of VG after growth with the PECVD method for 120 min with methane partial pressure of

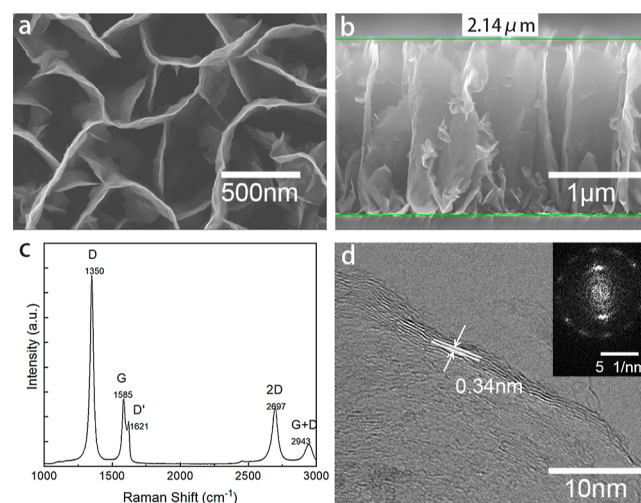


Figure 2. Scanning electron microscopy (SEM) top-view (a) and sectional (b) images of vertical graphene, which are deposited at 550 °C. (c) Raman spectrum of VG. (d) TEM images of the edges of the VG which is less than 10 layers. The inserted figure is the fast Fourier transform (FFT) of the graphene sheet.

200 Pa and substrate temperature of 550 °C. The top image of SEM in Figure 2a exhibits a petal-like graphene sheet with lateral extension from a few hundred nanometers to a few micrometers. Figure 2b shows the cross-section image of the VG film grown on the SiO_2 substrate. The single piece of VG can be grown in direction perpendicular to substrate surface as high as 2.14 μm without branching. The Raman spectrum was employed to analyze the quality of graphene sheet. The typical Raman peaks of VG are shown in Figure 2c. Characteristic Raman peaks of graphene, i.e., G $\sim 1585\text{ cm}^{-1}$ and 2D at $\sim 2697\text{ cm}^{-1}$ are clearly observed.³² The slightly offset of G peaks from the classical values of 1581 cm^{-1} bands of

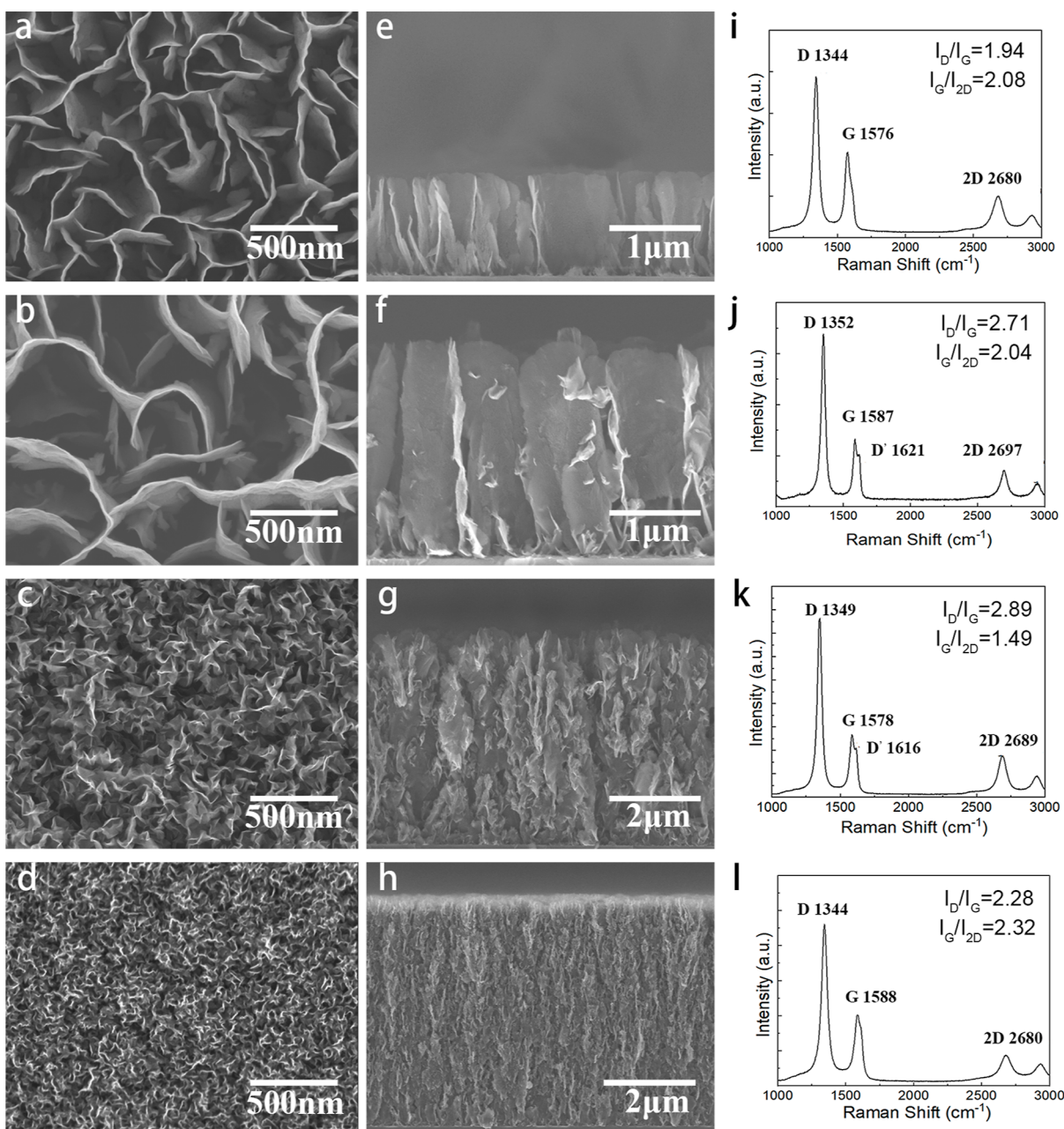


Figure 3. SEM top-view (a–d) and sectional (e–h) images of VG which are deposited at 400 °C (a,e), 550 °C (b,f), 600 °C (c,g), and 700 °C (d,h), respectively. (i–l) Raman spectra of VG at corresponding temperatures of 400 (i), 550 (j), 600 (k), and 700 °C (l), respectively.

freestanding single layer graphene may be attributed to doping effect due to abundant defects of graphene which were identified by the abnormally strong D peak located at 1350 cm^{-1} , and the D' peak located at 1621 cm^{-1} .³³ TEM measurements were also carried out to reveal the layer number of VG. Typical HRTEM image of a VG sheet is shown in Figure 2d. The measured layer separation is 0.34 nm which is quite good assistant with the reported value of multilayer graphene.²² It also shows the typical thickness of the VG sheets, which is less than 10 layers. The inset of Figure 2d is a FFT image of the graphene sheet which indicates the crystal structure of VG. All of the measurements mentioned above demonstrated high quality of the as-fabricated VG samples.

It is well-known that for a molecular beam deposition (MBD) process where gas-to-solid phase transition is governed by thermodynamic laws, the morphology and even the

structure of thin film is highly sensitive to the growth temperature, i.e., substrate temperature in MBD cases during the growth stage. By contrast, the CVD process of VG fabrication also contains a gas-to-solid phase transition, implying that the morphology of VG may also be influenced by the growth temperature, i.e., chamber temperature in CVD cases during the growth stage. To date, there is still a lack of detailed knowledge about how the morphology of the VG is varied with respect to the growth temperatures. In this section, we scrutinize the variation of growth manner of VG as a function of substrate temperatures. In Figure 3, we show the SEM morphology of the VG grown SiO_2 substrate with the substrate temperature varied from 400 to 700 °C. It was observed that the VG appears as petal-like patterns with large-sized VG sheet aligned in the direction normal to the substrate surface under the growth temperature lower than 600 °C. The

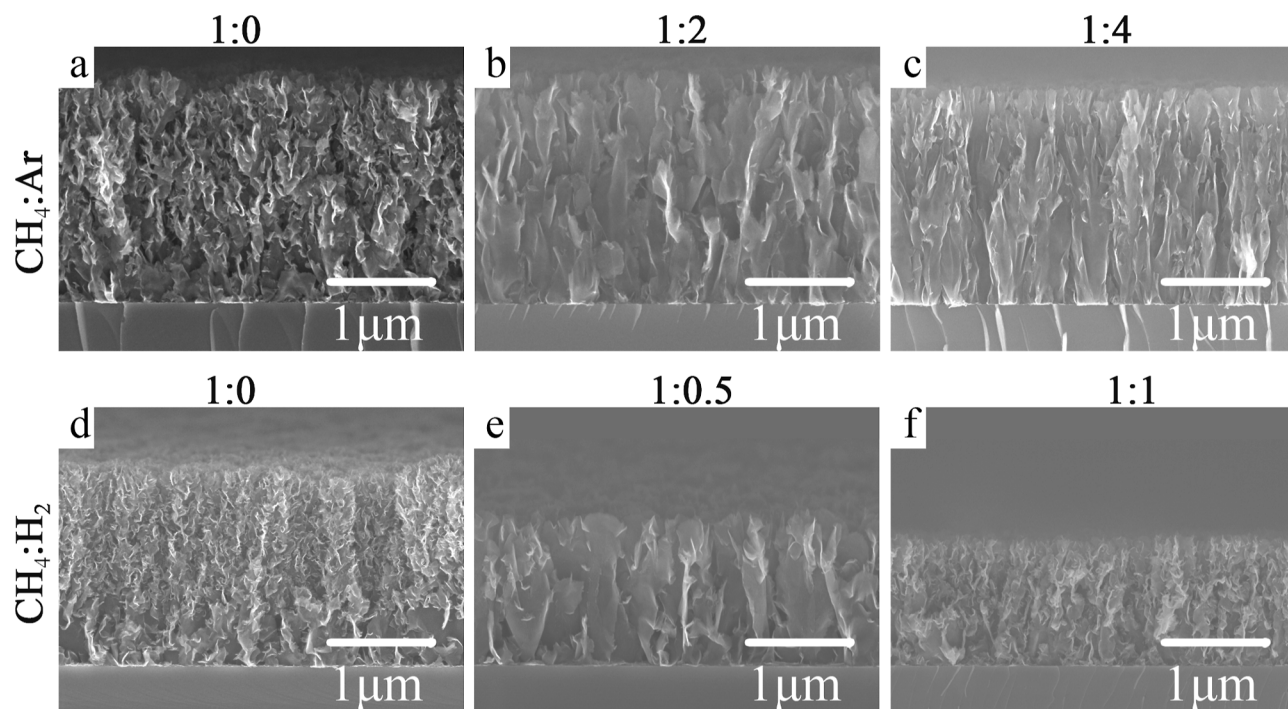


Figure 4. SEM sectional images of VG prepared at 600 °C but with different proportions of mixed gas. (a–c) The proportions of CH₄ and Ar are 1:0, 1:2, and 1:4, respectively. (d–f) The proportions of CH₄ and H₂ are 1:0, 1:0.5, and 1:1, respectively.

size of VG sheet is increased when the growth temperature was increased from 400 °C up to 550 °C since the deformation of carbon precursors are more active at higher growth temperature. As a result, the growth speed of the VG sheet is increased in both lateral and vertical directions (see Figure 3a,b,e,f), leading to a VG sheet with a size much larger than that of VG sheet fabricated at lower growth temperatures. However, the size of VG sheets does not always increase with the increment of growth temperature. Figure 3c,d shows the SEM images of VG samples fabricated at growth temperature of 600 and 700 °C, respectively. It was obviously observed that, compared with that of VG fabricated at 550 °C, the grain size of the VG sheet fabricated at 600 °C is indeed dramatically decreased rather than increasing. In addition, branches on VG sheets begin to show up under growth temperatures higher than 600 °C, which degrades the vertical growth nature of VG sheets. The brunching is more vigorous when the growth temperature was raised to 700 °C, and the VG grains are highly intersected with each other, leading to a much-densely packed geographical structure of VG than the ones fabricated at lower growth temperatures. This phenomenon emphasizes the importance of growth temperature for the fabrication of VG with desired morphologies and geographical structures. The quality of VG was evaluated by measuring the Raman spectrum as a function of growth temperature (Figure 3i–l). All of the Raman spectra manifest defect-rich graphene indicated by the dominant D peak at $\sim 1350\text{ cm}^{-1}$. It was verified that the ratio of the intensity of D band and G band (I_D/I_G) of Raman spectra can be used to evaluate the quality of graphene, while the ratio of the intensity of G band and 2D band (I_G/I_{2D}) contain the info of graphene thickness.^{32,34} In Figure 3i–l, it was shown that I_D/I_G slightly increased with the increment of growth temperature. So, it seems that VG fabricated at lower temperatures has better quality than VG prepared at higher temperatures. By contrast, the thickness of the graphene was

less influenced by the growth temperature since the I_G/I_{2D} values do not change remarkably with the variation of growth temperature. Although the increment of growth temperature speeded up the deformation rate of carbon precursor which would increase the partial pressure of carbon, the extra-high growth temperature seems to degrade the quality of VG, which was indicated by the reduction of the 2D band in Raman spectra of graphene sample fabricated at a higher growth temperature. In addition, the growth of VG grains along lateral direction rather than vertical direction was enhanced with the increment of growth temperature, e.g., the thickness of VG film was not obviously increased with the increment of growth temperature. This indicates that the growth of VG was influenced by factors more than growth temperature.

It has been reported that the ratio of methane versus other gases such as argon and hydrogen can highly influence the growth manner of 2D graphene on metal substrates.⁹ So, it is rational to ask, would and how would the ratio of methane with other gaseous species influence the growth of VG? To answer this question, we investigate the variation of the growth manner of VG as a function of the methane ratio with argon and hydrogen. Figure 4 shows the SEM images of VG samples fabricated under the same conditions except for the flow rates of argon and hydrogen. The flow rate of methane was fixed at 10 sccm for all controlled experiments mentioned here, while the flow rate of argon (hydrogen) was variable from case to case. No hydrogen was used for controlled experiments of methane vs argon, and likewise no argon was employed in the case of controlled experiments of methane vs hydrogen. Figure 4a–c shows the cross-section SEM images of the VG sample prepared at different methane-to-argon ratio. It was observed that the growth VG grains gradually varied from a branch-dominated mode to vertical-sheet-dominated mode with the increment of argon content ratio in the mixed gas during PECVD growth of VG. It is noted that the increment of Ar

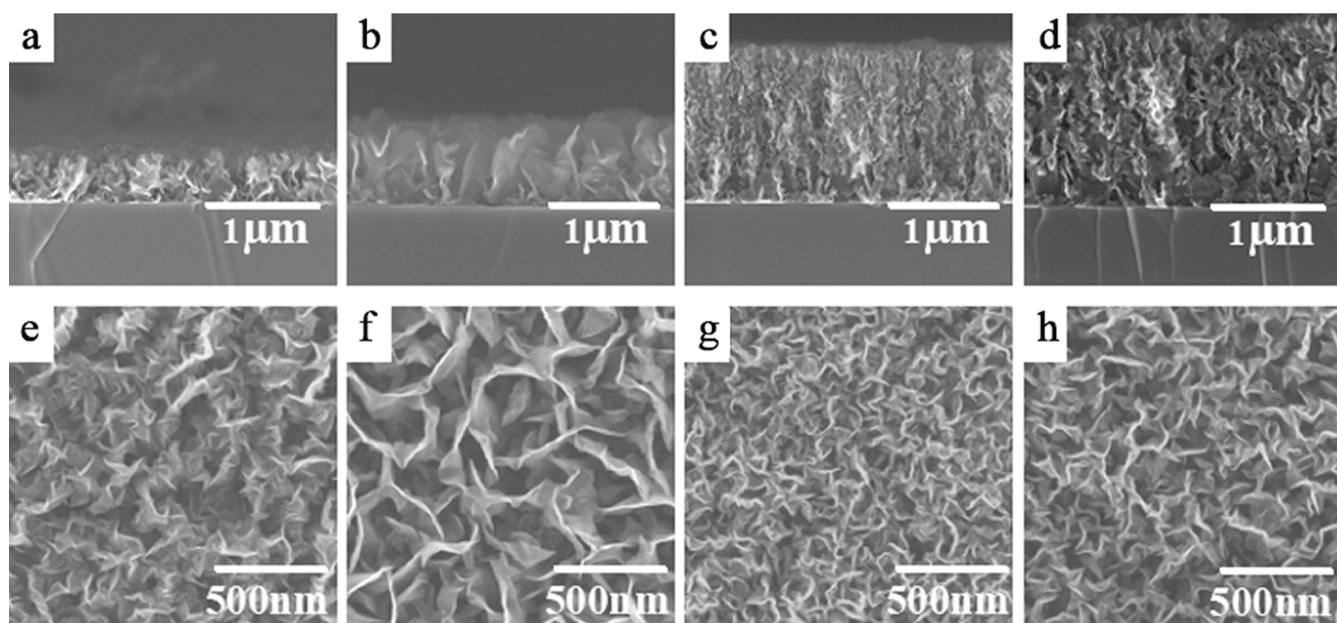


Figure 5. SEM sectional (a–d) and top-view (e–h) images of VG which are deposited at 600 °C but with different plasma powers, i.e., 100 (a,e), 200 (b,f), 300 (c,g), and 400 W (d,h), respectively.

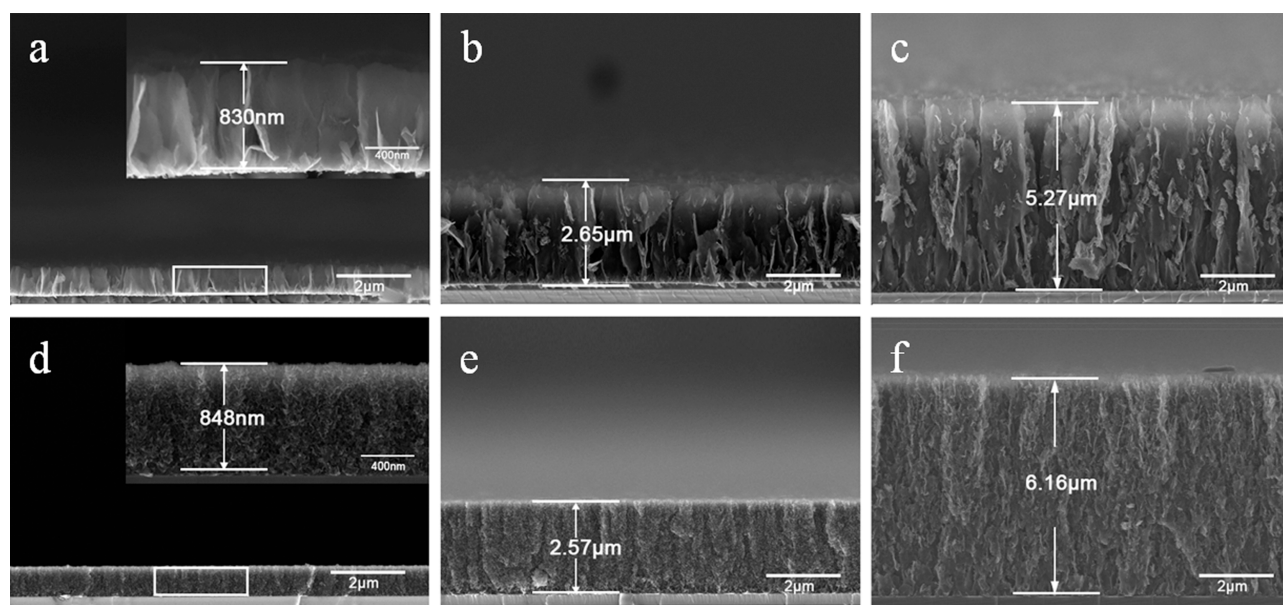


Figure 6. SEM sectional images of vertical graphene show the difference in growth manners at different growth stage. The samples shown in (a–c) were fabricated at a growth temperature of 500 °C, the duration times for the growth stage are 40 (a), 120 (b), and 240 min (c), respectively; samples shown in (d–e) were fabricated at a growth temperature of 700 °C, the duration times for the growth stage are 20 (a), 50 (b), and 120 min (c).

diluted CH_4 in the mixed gas, therefore slowing down the growth rate of VG. As a result, the branching of VG grain was substantially suppressed, which is conducive to the growth of graphene in the direction vertical to substrate surface. Similar phenomena were also observed for the case of hydrogen (Figure 4d–f). The vertical growth of VG was enhanced when the content ratio of hydrogen was increased.

Then, the role of H_2 in the growth of VG is studied with the same method. Only CH_4 and H_2 were introduced during the deposition of VG. Figure 4d–f shows the cross-sectional view of the VG grown under different gas ratios. It should be noted that the flow rate of methane was unchanged for the previously

mentioned controlled experiments. So, the effect of the density of the carbon precursor on the growth behavior of VG can be ruled out. In addition, the fact that the growth of VG is sensitivity to the total pressure of mixed gas, i.e., the total flow rate of mixed gas rather than the gaseous species, reminds us that the electric field normal to substrate surface (E_n) produced by the plasma may be responsible for the vertical growth of graphene. To verify this suspicion, we investigated the growth manners of VG as a function of RF power. Figure 5a–d shows SEM images of VG as RF power increased from 100 to 400 watt. The growth of VG is inactive when RF power is 100 W, which is a result of weak electric field along normal

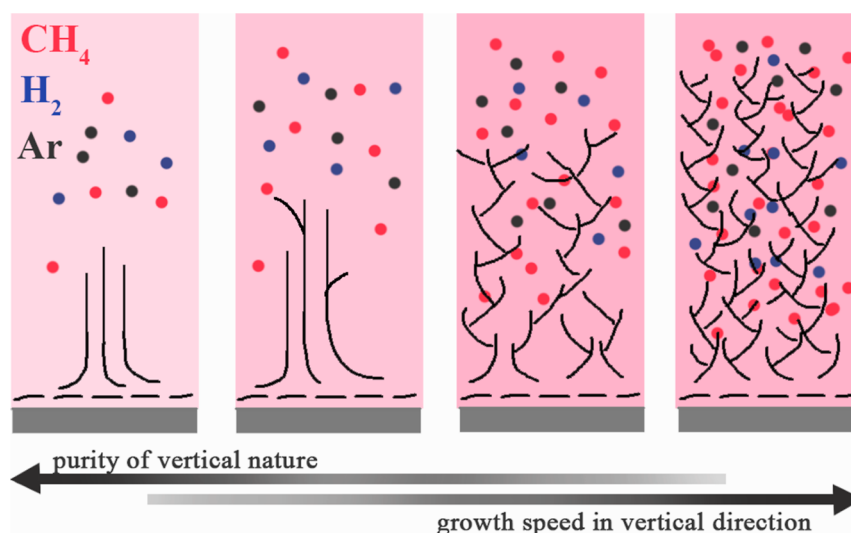


Figure 7. Schematic sketch shows the difference in the growth behavior of VG under different plasma densities.

direction of substrate due to small RF power (see Figure 5a). In contrast, the growth of VG is highly enhanced when the RF power is increased since the electric field along normal direction of substrate surface was spontaneously increased with the enhancement of RF powder. This emphasizes the importance of E_n on the growth of VG. This finding confirmed the electric field-based growth mechanism of VG.³⁵

We also investigated the variation of the growth manner of VG as a function of film thickness. Figure 6 shows the SEM results of side-view of VG samples which were fabricated under two different growth-temperatures but with different durations for VG growth. For VG grown at low temperature, e.g., 500 °C, a pure vertical growth nature was clearly evidenced by the SEM image at the initial growth stage, and no obvious branching growth was found even when the thickness of VG was increased to a few micrometers (Figure 6c). By contrast, branching growth dominates the VG samples prepared at a high growth temperature, e.g., 700 °C, as shown in Figure 6d–f. Branching growth begins even at initial growth stage (Figure 6d), and the branching growth becomes more profound with the increment of thickness of VG. It is clear that compared with high temperature growth, low temperature conditions are more conducive to the growth of VG. However, higher growth temperature is conducive to rapid growth of VG.

The above-mentioned results clearly indicated that moderate growth temperature is preferable for the growth of VG with a pure vertical growth nature. The relation between growth behavior of VG and the growth parameters mentioned in this study is summarized in Figure 7. Although growing at high temperatures can greatly increase the growth rate, it leads to significant lateral growth phenomena, namely, branching behavior. It is known that a high-temperature environment is more conducive to methane decomposition, producing more precursors, which is conducive to the rapid growth of VG. However, a higher growth temperature leads to larger defects, which may bring chance to the lateral growth, resulting in branching behavior. It was also shown that the branching behavior of VG at high growth temperature can be suppressed by moderately improving the dosage of mixed gas or the power of the plasma generator. It is worth noting that both approaches can improve the density of plasma, resulting in a stronger vertical electric field along the normal direction of the

substrate, which is helpful for the enhancement of vertical growth of graphene rather than along the lateral direction. This observation strongly indicates that the growth of VG is governed by the interfacial vertical electric field between the substrate and plasma field. Fast growth of pure VG can be achieved by optimizing the growth parameters such as temperature, dosage of mixed gas, and power of plasma generator. It is worth to note that other factors such as chamber pressure, the distance between the plasma source and the substrate are also important for the fabrication of VG because these parameters are closely related with the distribution of the plasma field.^{36–43} These parameters are preoptimized for the experiments reported in this work.

4. CONCLUSIONS

For summary, we studied the growth manners of VG tuned by parameters such as growth temperature, ratio between methane and carrier gases, and plasma intensity. It is found that the VG morphology is sensitive to temperature. Its morphology gradually changed from petal-like patterns with large VG sheets and loose packing density at moderate temperature to a shrubby-like appearance with small VG pieces and dense packing density at a higher temperature. Beside the growth temperature, other growth parameters such as the ratio of the mixed gas and power of the RF generator influence the branching behavior and growth speed of VG sheets. These observations indicate that the vertical growth of graphene sheets is actually governed by the interfacial electric field between the plasma field of mixed gases and substrate. Moderate conditions are vital for the growth of high-quality VG films. Furthermore, remote PECVD is surprisingly manifested as an efficient way to fabricate VG although the samples are placed outside the intensive electric field area.

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Notes

The authors declare no competing financial interest.

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