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RESEARCH ARTICLE

Analysis of the Effect of Growth Parameters on Graphene Synthesized by Chemical Vapor Deposition

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Chemical vapor deposition (CVD) has emerged as an important method for the preparation and production of graphene for various applications. This study analyzes previous work on various parameters that affect the properties of graphene synthesized through the CVD method. These parameters include the growth temperature, the growth time, and the flow rate of the carbon precursor. The characteristics of graphene synthesized under different conditions are compared in terms of the number of layers and the defect concentration, as determined by Raman spectroscopy and scanning electron microscopy (SEM). This comparison reveals that graphene grown on copper with a relatively low flow rate of precursor, a short growth time, and a high growth temperature exhibits the best quality. The optimum parameters required to produce graphene with high quality and with a low concentration of defects, both of which are essential in the development of graphene as a sensing material, are ascertained in this review.

Keywords: Graphene, Chemical Vapor Deposition, Growth Parameters, Raman Spectroscopy.

1. INTRODUCTION

In recent years, the synthesis and development of graphene have been a major focus in the field of nanotechnology. The interest in graphene by the research community can be attributed to its extraordinary properties, thus showing great potential for use in the semiconductor industry as a sensing element,[1] field-effect transistor,[2] memory device,[3] photovoltaic device,[6] or solar cell.[10]

Graphene, which is a one-atom-thick layer of graphite, was discovered by Novoselov and Geim, who shared the Nobel Prize in Physics in 2010 for their work.[1] Since the discovery of the one-atom-thick graphene, several researchers have made extensive efforts to improve the synthesis of graphene as a functional nanomaterial, with the goal of making the material suitable for use in semiconductor devices, sensors, and transducers. In the initial method demonstrated by Novoselov and Geim, exfoliated graphene was produced through repeated peeling of graphite via the Scotch-tape repeated peeling process.[12] Although effective, this method is not readily applicable because controlling the quality and density of the extracted graphene is impossible. After 2010, further efforts were focused on the synthesis of high-quality graphene on large areas.[14] The properties of graphene that have been previously reported are summarized in Table I.[12–15, 20, 21, 32–35]

Balandin et al.[27] has reported that the thermal conductivity of single layer graphene is up to $(5.30 \pm 0.48) \times 10^3$ W/mK. The experiment that they have been done is using noncontact optical-based technique. In addition, graphene's electrons can travel large distances without being scattered, making it a promising component for fast electronic products. The electrons can travel up to 25,000 cm^2/Vs, which is only 300 times less than the speed of light reported by Nika et al.[28] In contrast with other massless, Dirac fermions, graphene's electrons carry one unit of electric charge and therefore, they can be controlled using electromagnetic fields. Because electron manipulation is an important part in modern electronics, the different behavior of graphene's electrons may allow scientists to branch out of silicon-based semiconductor technology as shows in the experiment done by Nika et al.[29] Ghosh et al.[30] demonstrates that adding another atomic plane to few-layer graphene (FLG) leads to an increase in the Raman intensity which shows more power has been dissipated in FLG. Novoselov et al.[31] reported that the carrier mobility, for FLG is between 3000 and 10,000 cm^2/Vs. They also observed even higher mobilities, up to ~15,000 cm^2/Vs at 300 K and ~60,000 cm^2/Vs at 4 K for multilayer graphene.

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Table I. Properties of graphene.

Properties	Authors
Strength (Strongest material measured, σ = 42 N/m, E = 1.0 TPa)	Havener et al., Shao et al., Basu et al., Zhu et al., Huang et al., Lindvall et al.
Thickness (Thinnest material, largest area, one atomic layer, 2630 m^2/g)	Shao et al., Li et al., Zhu et al.
Flexibility (Very flexible for use in flexible and wearable devices)	Shao et al., Li et al., Ren et al.
Optical (97% transmission, transparent)	Havener et al., Li et al., Zhu et al., Huang et al., Lindvall et al.
Thermal (At 27 °C, thermal conductivity is 5000 W/mK)	Shao et al., Basu et al., Huang et al.
Electron mobility (High electron mobility, 200,000 cm^2/Vs at room temperature)	Havener et al., Basu et al., Zhu et al., Chen et al., Yang et al., Ren et al., Huang et al.

Practical methods for producing graphene include physical exfoliation,[7] the epitaxial method,[8] the use of graphite silicon carbide (SiC)[9] or reduced graphene oxide (RGO), and chemical vapor deposition (CVD).[10] Mechanical exfoliation produces the cleanest graphene; however, the size and quantity are limited and the number of layers is extremely difficult to control. Epitaxial graphene formed on SiC is very difficult to transfer to other substrates for device fabrication. CVD has been widely adopted and has shown promising results for the growth of graphene on large areas, such as on a wafer-level substrate.[16] Graphene produced via CVD has the best potential to be used in semiconductor or sensor applications. CVD has thus emerged as an important method for the preparation and production of graphene for various applications.

To the best of our knowledge, no study has reviewed the growth parameters of graphene. In view of the aforementioned developments in the field of graphene research, this study seeks to contribute an in-depth analysis of the parameters that affect the growth of graphene, particularly through the CVD method. The optimum parameters as well as the challenges facing the CVD-based production of graphene will also be discussed.

2. GRAPHENE SYNTHESIS VIA CVD

The growth of graphene via CVD typically requires a metal catalyst, as reported by numerous researchers, including Flores et al.[4] and Regan et al.,[18] the process starts with a thin film of the metal catalyst being subjected to heat treatment under vacuum at 1000 °C Kim et al.,[8] however, varied the temperature between 750 and 950 °C to investigate the effect of temperature on graphene growth. Methane and hydrogen gases are then flowed through the furnace.

Argon gas is used as a carrier gas during synthesis to dilute the carbon precursor gas (methane). Hydrogen catalyzes a reaction between the carbon precursor gas and the surface of the metal substrate, which consequently leads to the carbon atoms from methane being deposited onto the surface of the metal through chemical adsorption.

The metal thin film utilized for this process is chosen on the basis of its carbon solubility, which affects the growth mechanism, whereas low carbon concentrations are required for one or-more layers of graphene to be grown in a controlled manner. If the deposited carbon exhibits significant solubility at the defined growth temperature, it will most likely diffuse to form the bulk graphite material.[20] One way of mitigating this problem is by limiting the amount of carbon dissolved in the metal through the use of a thinner metal film or through the use of metals with very low bulk carbon solubilities. Copper is currently the most popular metal catalyst for the growth of graphene.[20] The low carbon solubility of copper facilitates graphene growth by surface adsorption rather than by dissolution, segregation, or precipitation. Figure 1 illustrates a typical setup of a CVD system for graphene synthesis.

Raman spectroscopy has been widely employed to characterize graphene because of its ability to distinguish the quality and type of synthesized graphene. The Raman spectrum of pristine graphene as noted by Guermoune et al.[5] generally exhibits Raman shifts in the regions of 1350 cm^{-1} (D peak), ~1580 cm^{-1} (G peak), and ~2700 cm^{-1} (2D peak). Liu et al.[11] have reported that the D peak corresponds to the concentration of defects in the crystalline layers of graphene. The intensity of the D band is directly proportional to the concentration of defects in the sample. The spectrum of pristine graphene does not show a D peak, thus indicating that it is free of defects.

Meanwhile, Suk et al.[19] found that the 2D band is always a strong peak in Raman spectra of graphene and that the intensity of this band indicates the number of graphene layers. For a single layer of graphene, the 2D peak is more intense than the G peak; in this case, the density of graphene is high. The G peak reflects the layer properties and indicates the thickness of the graphene layer. Ferrari et al.[24] also show that graphene's electronic

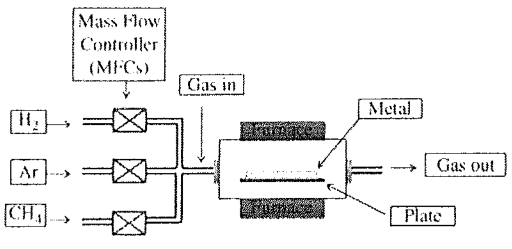

Fig. 1. Complete apparatus setup for graphene synthesis on metal via CVD.

structure is captured in its Raman spectrum that clearly evolves with the number of layers. The D peak second order changes in shape, width, and position for an increasing number of layers, reflecting the change in the electron bands via a double resonant Raman process.

3. COMPARISON OF GRAPHENE SYNTHESIZED UNDER DIFFERENT CVD GROWTH CONDITIONS

Most researchers distinguish the quality of graphene by the number of layers and defects. Based on previous work, the three most critical parameters affecting graphene growth are the flow rate of the precursor gas, the growth temperature, and the growth time. These parameters have been explored to optimize the conditions for graphene growth. Here, we analyze the effects of these parameters on graphene growth and investigate the characteristics of graphene produced via CVD.

3.1. Effect of Growth Temperature on Graphene

Flores et al.[4] and Regan et al.[18] set the growth temperature at 1000 °C for CVD-grown graphene. Other researchers have utilized other temperatures for graphene growth.

An example is the work of Regmi et al.,[17] who conducted experiments in which they varied the growth temperature between 600 °C and 1000 °C; results of their Raman measurements are given in Table II. The percentage (%) of intensity represents the presence of graphene growth on specified temperature. Based on the Table II, 2D peak, G peak and D peak values are consistent and the intensity value is directly proportional to the temperatures. The higher the temperature, the higher graphene growth showed by percent of intensity.

Figure 2 shows the ratio of the D and G peak intensities (I_D/I_G), which is widely used as a measure of defect density, and the ratio of the G and 2D peak intensities (I_G/I_{2D}), which is used to track the number of layers. After an initial decrease, the I_D/I_G decreases slowly above 900 °C (Fig. 2), which suggests a slow reduction in defect density with increasing temperature. SEM imaging and the low value of the I_G/I_{2D} ratio reveal that graphene growth exhibits a strong tendency for single-layer termination at temperatures greater than 900 °C.

Table II. Raman spectra values for graphene growth under various temperatures.

Temperature (°C)	Intensity (%)	2D peak (cm⁻¹)	G peak (cm⁻¹)	D peak (cm⁻¹)
600–800	0	2700	1580	1350
850	20	2700	1580	1350
900	40	2700	1580	1350
950	65	2700	1580	1350
1000	100	2700	1580	1350

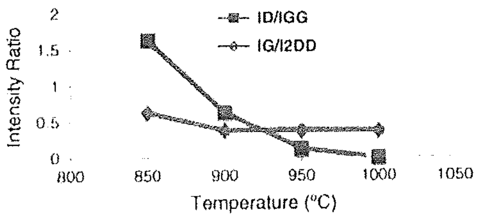

Fig. 2. Average values of I_D/I_G and I_G/I_{2D} from different measurements.

In another approach to observing the effect of temperature on the quality of graphene, Kim et al.[8] employed temperatures between 750 and 950 °C, as shown in Table III. This approach is similar to those used by Regmi et al.[17] As evident from the results in Table III, the intensities of the peaks increase proportionally with increasing growth temperature as shown in intensity (%). The value of other peaks are consistent as the different temperature affected only to the intensity peak. Although different temperatures have been employed for graphene growth, the most effective temperatures for graphene synthesis are those ranging from 900 to 1000 °C.

The growth of graphene within this temperature range guarantees the successful synthesis of graphene with few defects. The defects could be edges, dislocations, cracks, or vacancies in the sample. As illustrated in Figure 3, high temperatures yield graphene with high quality and a stable structure; the domain size also increases, and the occurrence of multilayer flakes is dramatically reduced.

The synthesis of graphene at low temperatures is not easy because the peak exhibits several defects and low density under this setting. Bi- or few-layered graphene with defects, such as grain boundaries and cracks, can be synthesized with a short growth period; in this case, the D peak will appear in the Raman spectrum. Future developments in temperature variation should lead to improved control over the thickness of graphene layers and to large-scale graphene production, even at low temperatures.

3.2. Effect of the Flow Rate of the Precursor Gas (Methane) on Graphene Growth

Several researchers as highlighted by the works of Kim et al.[8] and Regmi et al.,[17] have used various flow rates of the precursor gas to analyze the effects of the flow rate

Table III. Raman spectroscopy results for graphene grown at different temperatures.

Methane flux (sccm)	Intensity (%)	2D peak (cm⁻¹)	G peak (cm⁻¹)	D peak (cm⁻¹)
0.4	20	2700	1580	1350
1.0	40	2700	1580	1350
2.0	60	2700	1580	1350
5.0	80	2700	1580	1350
15.0	100	2700	1580	1350

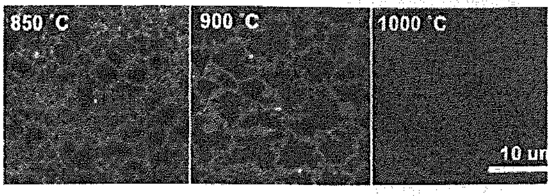

Fig. 3. Representative SEM images of graphene grown on Cu for 30 min.

on the defects in graphene, Wang et al.[23] varied the flux of methane from 0.4 sccm to 15 sccm. Methane flux is observed in sccm, an abbreviation for standard cubic centimeter per minute.

The results of their work are illustrated in Table IV in terms of Raman peak locations and intensities. The peaks increase in intensity (%) when the methane flux is increased (Table IV). Table V shows that, when the methane flux is increased, each graphene peak shifts to a lower wavenumber, possibly because of the effect of the substrate. Thus, the thickness of the layer increases. With this increase, the band positions shift to lower energies, representing a slight softening of the bonds. Meanwhile, the integrated peak intensity ratio between the intensities of the G and 2D peaks increases.

Reduction of the flow rate of methane to a very low value does not result in uniform graphene coverage. Continuous graphene coverage is observed for methane flow rates from 5 to 10 sccm. A low flow rate of precursor gas is an important parameter for decreasing the number of layers formed during the growth step and for improving the quality of the resulting graphene by reducing the number of defects. Similar investigations have been reported by Regmi et al.[17] and Regan et al.[18] to observe graphene growth at different methane fluxes.

Raman spectra reveals that methane flux influences the thickness and structural defects of graphene. Moreover, the G and 2D peaks of the Raman spectra shift to lower wavenumbers with increasing methane flux and then broaden; low-quality graphene is subsequently generated. Different flow rates of the carbon precursor have been explored for graphene growth. Graphene synthesis is best conducted at methane flow rates between 5 sccm and 10 sccm to guarantee successful growth with few defects. In future research, high-quality graphene could be achieved even at high values of methane flux.

Table IV. Raman spectroscopy results for graphene prepared using various methane fluxes.

Methane flux (sccm)	Intensity (%)	2D peak (cm^{-1})	G peak (cm^{-1})
0.4	50	2700	1580
1.0	50	2690	1579
2.0	50	2680	1578
5.0	50	2670	1577
15.0	50	2660	1576

Table V. G and 2D peak band positions for graphene.

Temperature (°C)	Intensity (%)	2D peak (cm^{-1})	G peak (cm^{-1})	D peak (cm^{-1})
750–800	0	2700	1580	1350
850	25	2700	1580	1350
900	50	2700	1580	1350
950	100	2700	1580	1350

3.3. Effect of the Growth Time of Graphene

Growth time influences the quality of graphene and its defects, as demonstrated by several studies. To observe the effect of growth time on graphene growth, Regan et al.[18] adjusted the growth time to range between 10 s and 1 min. Raman measurements presented in Table VI show that, at 10 s, bi-or few-layered graphene with defects, such as grain boundaries and cracks, can be synthesized, and the D peak can be observed in the Raman spectrum. At a growth time of 1 min, the upper layer is covered by a defective section and the intensity of the D peak is reduced. The result that has been reported by Calizo et al.[26] also support that high temperatures will produce high quality of graphene in terms of D-peak and 2D-peak. The number of layer can be determine by calculate the ratio between IG and 2D peak (I_G/I_{2D}) according to Balandin et al.[25]

In another experiment, researchers adjusted the growth time to range between 1 min and 30 min to investigate the effects of various growth times on graphene.[17] The experiment in Figure 4 shows similar results; a growth time between 1 min and 2 min causes the number of layers to decrease during the growth step, thus improving graphene quality in terms of defect density.

Graphene synthesis should be performed with a growth time between 1 min and 2 min to guarantee the successful growth of graphene with few defects. At a particular growth time, the synthesis of graphene with a stable structure and high quality is achieved. Moreover, the domain size increases, and the occurrence of multilayer flakes is dramatically reduced. With long growth times, bi-or few-layered graphene with defects, such as grain boundaries and cracks, can be synthesized, and the D peak can be observed in the Raman spectrum. Future developments in growth times should lead to improved control over the thickness of graphene layers and to large-scale graphene production at long growth times.

Table VI. Raman peak of graphene prepared under different growth conditions.

Time	Intensity (%)	2D peak (cm^{-1})	G peak (cm^{-1})	D peak (cm^{-1})
10 s	100	2700	1580	1350
30 s	50	2700	1580	1345
1 min	25	2700	1580	1340

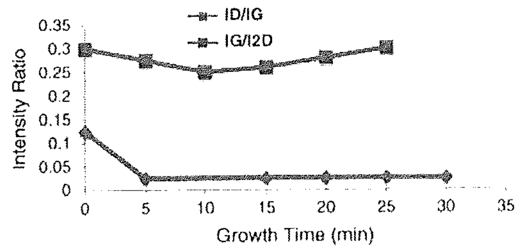

Fig. 4. Average values of I_D/I_G and I_G/I_{2D} from different measurements.

4. ISSUES AND CHALLENGES

Researchers have successfully grown graphene using almost all types of metals via the CVD method. However, the effect of different metals on the physical, chemical, electronic, optical, and magnetic properties of synthesized graphene is unclear. If any correlation is established between the type of metal used and the properties of graphene grown, then graphene with select properties can be grown. Copper, in particular, is the most widely used metal in graphene synthesis. Future research must therefore be conducted to grow high-quality graphene with few defects.

Researchers have succeeded in growing stable and high-quality graphene at high temperatures. The synthesis of graphene at low temperatures is difficult; the Raman spectra of graphene grown at low temperatures indicate that the resulting graphene has a low density and contains numerous defects. Future developments in temperature variation should lead to improved control over the thickness of graphene layers and to large-scale graphene production, even at low temperatures.

A low flow rate of methane gas guarantees successful graphene production. With further research, the preparation of high-quality grapheme, even at relatively high values of methane flux, should be possible. Graphene synthesis is best conducted with short growth times to guarantee the successful growth of graphene with few defects. Future developments in growth times should lead to improved control of the thickness of graphene layers and to large-scale graphene production at long growth times. In addition to the growth-related challenges previously discussed, many related issues beyond the scope of this review can be explored. Graphene synthesis will undoubtedly be a very important topic of research for many years to come.

5. CONCLUSION

The effects of various parameters, such as the growth temperature, the growth time, and the flow rate of the carbon precursor, on graphene synthesis via CVD were compared. Optimization of these parameters is important to produce high-quality graphene for various applications. Through this comparison, graphene growth on copper with a relatively low flow rate of the precursor, a short growth time, and a high growth temperature were found to result in the best-quality graphene. Copper is the preferred substrate for graphene synthesis because of its low carbon solubility, which is important for controlling the number of graphene layers. The most suitable temperatures are from 900 to 1000 °C; temperatures within this range guarantee the successful growth of graphene with few defects. The required growth time, ranging from 1 to 2 min, ensures the synthesis of high-quality graphene. The optimal methane flux was found to range between 5 and 10 sccm. Raman spectroscopy results show that control of the temperature, methane flux, and growth-time parameters influences the thickness of graphene and its structural defects. Raman spectroscopy and SEM were used to characterize graphene, and the results can be used to distinguish the number of layers in a given sample.

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