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Research Progress on the Preparation of Graphene Films through Carbonization of Polymers in Stacked Structures

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Abstract: *Graphene has garnered significant attention owing to its atomic layer thickness and unique electronic structure, rendering it widely employed in conventional silicon-based chips and flexible electronics. The utilization of polymer carbonization for graphene synthesis confers several advantages, including the ease of polymer deposition on various substrate surfaces and its widespread availability, cost-effectiveness, and safety. This paper presents a comprehensive review of the research progress in preparing graphene films through the polymer carbonization method, with a particular focus on the changes observed in the resulting products and the influencing factors associated with the stacked structure carbonization. The insights provided herein serve as a valuable reference for future researchers seeking to harness polymers in graphene preparation.*

Keywords: *Polymers; Carbonization; Stacked structure*

1. Introduction

In 2004, Andre and Konstantin successfully prepared graphene through tape mechanical exfoliation, igniting a wave of research on two-dimensional materials [1]. Graphene's single-atom thickness and unique electronic structure bestow it with outstanding properties. Recent studies have revealed that graphene surpasses other materials in terms of strength, electrical conductivity, thermal conduction, and optical performance, making it highly promising for applications in sensors [2], energy storage devices [3], field-effect transistors [4], biomedical fields [2], and more. Currently, the main methods for graphene preparation involve chemical vapor deposition (CVD) and SiC epitaxial growth on substrates. The main preparation methods and applications of graphene are shown in Figure 1. However, the preparation of high-quality graphene still faces challenges such as high costs, complex transfer processes, and safety concerns, thus necessitating further exploration [1].

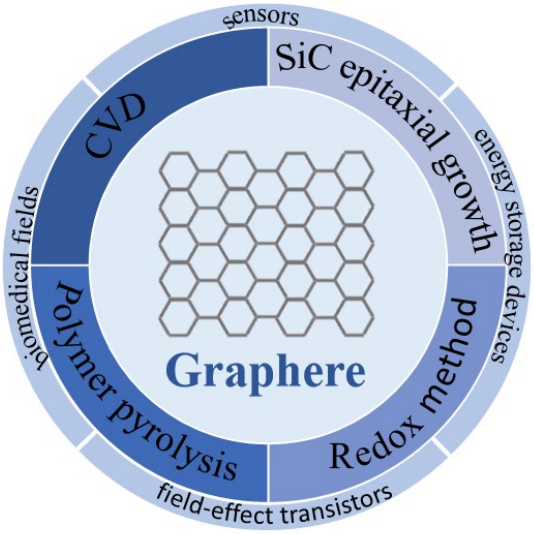

Figure 1: Preparation method and application of graphene.

Compared to the widely used explosive precursors in the current CVD process, polymers offer advantages such as stable properties, increased safety, widespread availability, and low cost. Using polymers as solid carbon sources for graphene synthesis allows for easier deposition on various surfaces, avoiding potential damage to the graphene film during subsequent transfer processes. This is beneficial for fabricating diverse electronic devices, leading researchers to increasingly focus on employing polymers to prepare graphene. This paper will introduce the process of utilizing polymers as solid carbon sources for graphene synthesis and compare the quality differences of graphene prepared with different structures. Additionally, it will analyze the influencing factors in graphene growth and the growth mechanism with metal catalysis.

2. Structural and Property Differences between Aliphatic and Aromatic Polymers

Utilizing polymers for graphene preparation typically involves high-temperature carbonization methods, but the choice of polymer types can vary significantly among different researchers. Notably, aliphatic and aromatic polymers exhibit considerable differences in the quality of the resulting graphene during the carbonization process.

2.1. Aliphatic Polymers

As carbon sources for graphene synthesis, polymers require their main chains to consist entirely of carbon atoms. Aliphatic polymers refer to open-chain hydrocarbons, which are distinctly different from aromatic compounds possessing benzene ring structures. Byun et al. [5] suggested that the use of hybrid carbon bonds formed by aliphatic C-C single bonds is preferable for graphene preparation, as their bond dissociation energies (284-368 kJ/mol) are lower than C═C (615 kJ/mol), C≡C (812 kJ/mol), and aromatic/heterocyclic C-C bonds (410 kJ/mol). This favors the recombination and production of graphene upon reaching the polymer's thermal decomposition temperature. On the other hand, Shin et al. [6] compared the quality differences in graphene prepared from aliphatic and aromatic polymers under the same conditions. They observed various forms of graphene layers with pores and islands from aliphatic carbonization products, while the aromatic carbonization products yielded uniformly layered graphene without pores.

2.2. Aromatic Polymers

Aromatic polymers possess benzene ring structures akin to graphene, and the benzene rings formed after high-temperature dehydrogenation can directly serve as constituent units for graphene. This characteristic significantly reduces the synthesis energy required for graphene and demonstrates vast opportunities and potential. Xue et al. [7] successfully prepared N-doped graphene using pyridine as a carbon source at a low temperature of 300 ℃. Zhuo et al. [8] synthesized graphene directly on a dielectric substrate using polycyclic aromatic hydrocarbons (PAHs) at temperatures as low as 600 ℃. Wang et al. [9] used polycyclic aromatic hydrocarbons as carbon precursors and dopants to directly synthesize doped graphene on a dielectric substrate at 1000 ℃. Currently, it is widely recognized that aromatic polymers hold a distinct advantage over aliphatic polymers as precursors for graphene preparation.

3. Stacked Structures and Catalytic Mechanisms

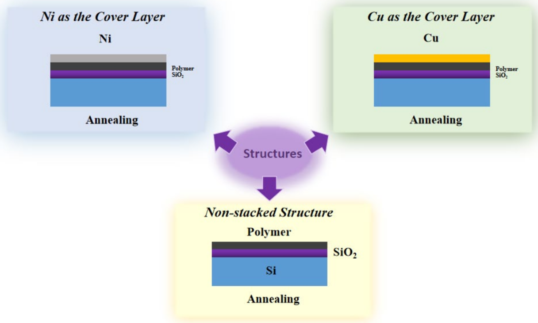

Figure 2: Preparation of graphene with different stacking structures.

The adoption of different stacked structures during polymer-based graphene preparation significantly impacts the quality of the resulting product. Additionally, in the process of metal-catalyzed graphene growth, metals like Ni and Cu may follow different growth mechanisms due to differences in their carbon solubility. Preparation of graphene using different stacking structures are shown in Figure 2.

3.1. Non-stacked Structure

When a non-stacked structure is used, the quality of graphene produced through direct polymer carbonization is relatively low, with most products being graphite or amorphous carbon. In certain cases, high-temperature conditions may lead to precursor evaporation, resulting in the absence of carbonization products. Li et al. [10] observed distinct G and D peaks on both SiO_2/Si and Cu foil substrates when using polydopamine as the carbon source for transparent electrodes. Jiang et al. [11] obtained typical mixtures of amorphous carbon and nanocrystalline graphite during the carbonization of self-assembled PDA films on Si-H surfaces at 550 °C. Tiwari et al. [12] deposited PMMA on Ni foil and carbonized it at 750 °C, but no peaks were observed in the Raman spectra.

3.2. Stacked Structures

3.2.1. Ni as the Cover Layer

Most studies using Ni as the cover layer demonstrate effective catalytic properties. Tiwari et al. [12] achieved monolayer graphene films on Ni foil through the application of pressure using stainless steel screws during thermal decomposition at 750 °C for 10 minutes. Seo et al. [13] spin-coated coal tar pitch (CTP) films on SiO_2/Si substrates and deposited a 200nm thick Ni layer on the film, resulting in almost no surface defects. Shin et al. [6] obtained few-layer graphene directly on a dielectric substrate through thermal decomposition and squeezing between catalytic metal and the substrate, without the need for transfer. Peng et al. [14] demonstrated the easy synthesis of bilayer graphene directly on SiO_2 by placing the carbon source on top of nickel, leading to bilayer graphene formation between the insulating substrate and the nickel layer due to carbon diffusion.

3.2.2. Cu as the Cover Layer

When using Cu as the cover layer, the quality of carbonized products varies significantly among different studies, and there is an ongoing debate about the catalytic effects of Cu cover layers. Seo et al. [13] investigated the role of Cu in catalyzing graphene growth and found no significant catalytic effect under the same experimental conditions. Peng et al. [14] also compared the catalytic effect of Cu and observed almost no graphitization structures on SiO_2 under the same conditions. However, Wang et al. [9] successfully synthesized high-quality doped graphene on a dielectric substrate using a thin copper layer as the top catalyst and polycyclic aromatic hydrocarbons as the carbon source. Wan et al. [15] also synthesized graphene on copper foil using defect-free polycyclic aromatic hydrocarbons (PAHs) via self-assembly in a hydrogen-free high vacuum (HV) chamber.

3.3. Catalytic Mechanisms

3.3.1. Ni-Catalyzed Graphene Growth Mechanism

The growth of graphene in the polymer/Ni system follows a solid solution-precipitation mechanism. Carbon atoms dissolve in the metal at high temperatures and precipitate upon cooling, leading to graphene growth.

3.3.2. Cu-Catalyzed Graphene Growth Mechanism

The growth of graphene in the polymer/Cu system may involve the surface-mediated nucleation of Cu-catalyzed dehydrogenation of polycyclic aromatic hydrocarbons, rather than the segregation or precipitation of small precursor molecules during precursor decomposition [7,8]. The copper catalyst promotes the nucleation of polycyclic aromatic hydrocarbon molecules on its surface, forming graphene precursors. This process is facilitated by active sites provided by the copper catalyst on its surface. These sites can adsorb polycyclic aromatic hydrocarbon molecules and promote chemical reactions between them, leading to the formation of larger molecules. This process is known as the "surface-mediated nucleation process."

4. Factors Affecting Stacked Structures Carbonization

In the preparation of graphene using carbonized polymers with stacked structures, many factors including polymer thickness, metal layer thickness, annealing temperature, etc. significantly affect the quality of the carbonized product, so it is important to determine the optimal set of parameters during the experimental process. The different factors affecting the carbonization of graphene are shown in Figure 3.

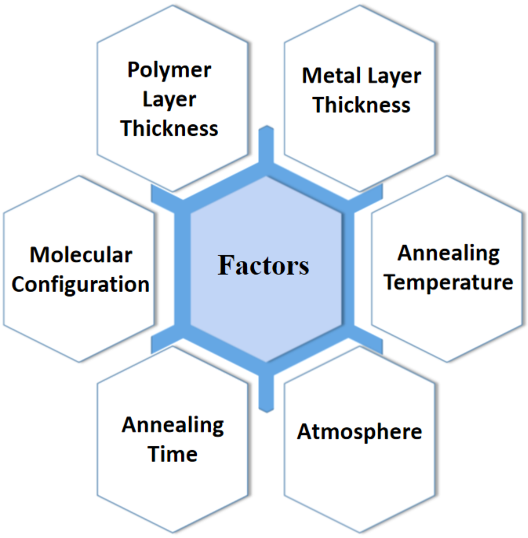

Figure 3: Different factors affecting graphene carbonization.

4.1. Polymer Layer Thickness

The thickness of the polymer layer significantly impacts the quality of carbonization products. When the polymer layer is too thin, the lack of a sufficient carbon source during annealing results in discontinuous graphene films. On the other hand, excessively thick layers may lead to the formation of higher-quality graphene near the metal layer and lower-quality graphene, including some amorphous carbon, near the substrate. Thus, finding the appropriate polymer layer thickness is crucial. Zhuo et al. [8] demonstrated that 5-10 nm thick polycyclic aromatic hydrocarbons provided better-quality graphene, whereas thicker layers resulted in more amorphous carbon. Byun et al. [6] observed that reducing the film thickness from 100 nm to 10 nm increased the intensity of the D-band, indicating that thinner films improved graphene quality. Seo et al. [13] determined through Raman spectroscopy that the optimal concentration was 8 wt% (corresponding to a 20 nm thick CTP film).

4.2. Metal Layer Thickness

The thickness of the metal layer is another critical factor influencing the quality of carbonization products. When the metal layer is too thin, it tends to agglomerate and partially evaporate from the substrate during the annealing process, leading to the formation of discontinuous doped graphene. On the other hand, for Ni, an excessively thick layer prevents complete carbon diffusion into the thick Ni layer during pyrolysis, hindering carbon precipitation on the surface upon cooling. For Cu, a thicker layer does not significantly affect graphene quality, but it is not economical and increases the time required for later etching of the Cu layer. Byun et al. [6] found that the optimal Ni layer thickness on SiO_2 substrates, using PAN as the carbon source, was approximately 50 nm. Seo et al. [13] spin-coated CTP on SiO_2 substrates and determined that the optimal Ni layer thickness was around 200 nm. Zhuo et al. [8] used polycyclic aromatic hydrocarbons as the carbon source on glass and found that the optimal Cu layer thickness exceeded 100 nm. Wang et al. [9] used polycyclic aromatic hydrocarbons as the carbon source on SiO_2 substrates and obtained relatively high-quality doped graphene when the Cu layer thickness was increased to 1000 nm.

4.3. Annealing Temperature

During high-temperature processes, the polymer is initially transformed into amorphous carbon. As the temperature increases, the graphitization process of carbon atoms improves, reducing the intensity of the D-band in the Raman spectrum, enhancing the crystallinity of the graphene layer, and eventually leading to the formation of graphene. Zhuo et al. [8] found that the growth method using polycyclic aromatic hydrocarbons as the carbon source significantly reduced the growth temperature, enabling graphene formation even at 600 ℃. Tiwari et al. [12] observed that PMMA formed a high-quality monolayer graphene film on the metal surface after pyrolysis at 800 ℃. Seo et al. [13] found that using CTP as the carbon source, the D peak was minimized at an annealing temperature of 1100 ℃.

4.4. Other Factors

In addition to the mentioned factors, there are other experimental variables that influence the quality of carbonization products, such as the presence of hydrogen in the carbonization atmosphere, annealing time, and molecular configuration. Seo et al. [13] found that hydrogen content is a critical factor affecting the quality of synthesized graphene. H_2 gas aids in removing defects (such as dangling bonds) from carbon. Zhuo et al. [8] observed that excessively short annealing times led to incomplete reaction between the carbon source and catalyst, while overly long times caused the catalyst to volatilize, hindering graphene synthesis. They also suggested that the molecular configuration of polycyclic aromatic hydrocarbons might be a key factor in graphene growth, with planar aromatic hydrocarbons yielding graphene with lower defect levels.

5. Conclusion

This paper provides a comprehensive introduction to the technique and method of synthesizing graphene using stacked structures carbonization with polymers as precursors. By employing polymers as precursors, we can directly synthesize graphene on dielectric substrates, thereby avoiding potential damages and contaminations that may occur during the later transfer process. Moreover, aromatic polymers containing benzene rings exhibit structural similarities to graphene, which aids in lowering the reaction temperature and improving the efficiency of the carbonization process. On the other hand, by introducing a covering layer, we not only reduce the phenomenon of evaporation but also catalyze the formation of graphene. Hence, the adoption of stacked structures significantly enhances the quality of the carbonization product.

The paper comprehensively summarizes and analyzes the influencing factors during the carbonization process, providing valuable insights and references for future researchers utilizing polymers to prepare graphene.

In conclusion, utilizing polymers as precursors and employing stacked structures for carbonization is a feasible and effective approach. This technique optimizes the graphene synthesis process by leveraging the structural characteristics of aromatic polymers and the application of covering layers, resulting in higher-quality products.

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