Study on Controllable growth of graphene prepared by CVD

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Abstract. Graphene is a two-dimensional honeycomb crystal of monoatomic thickness composed of hexagonal sp2 hybrid carbon atoms. Since the mechanical separation of Andre Gamm and Konstantin Novoselov in 2004 to obtain a single layer of graphene, this unique two-dimensional structure makes graphene excellent physical, chemical, mechanical, electrical and other properties. It has become the focus of much research in recent years. These properties include exceptionally high charge, high mechanical strength and elasticity, optical clarity and a variety of possible chemical modifications that make graphene promising in micro-nanoelectronics, photodetection and conversion materials, structural and functionally enhanced composites and storage. It can be applied in a wide range of fields, but graphene is different from graphite in nature, and its size is small and the yield is low. So how to prepare high quality graphene is the key to study its application prospects. The emergence of chemical vapor deposition (CVD) technology solves these problems and has evolved into an important method for preparing large-area, large-size, multi-purpose graphene. Large-sized graphite thin single crystals can be obtained on a substrate by controlling the growth mode and different treatments for the substrate. Due to the strong interaction between carbon atoms and the substrate, there are still many difficulties and challenges in directly growing graphite on the insulating substrate. This topic aims to prepare graphene by chemical vapor deposition (CVD) and prepare it. The method is improved to obtain graphene with excellent performance, which provides more feasibility for the practical application of graphite thinning in semiconductor devices.

Keywords: graphene, chemical vapor deposition, method control, substrate.

1. Graphene overview and characteristics
Graphene, also known as "single-layer graphite sheet", refers to a layer of dense carbon atoms encased in a honeycomb crystal lattice. The carbon atoms are arranged in a two-dimensional structure similar to the graphite monoatomic layer. A new carbon material with a two-dimensional honeycomb lattice structure tightly wrapped by carbon atoms, which can be stacked to form three layers of graphite, which can be crimped to form one-dimensional carbon nanotubes or decomposed into zero-dimensional fullerenes. Early studies have shown that this single-layer atom cannot achieve thermodynamic stability. However, in 2004, the experimental team led by Novoslov, Manchester University, UK, used a simple tape to highly exfoliate graphite, which was used to experiment. The independent two-dimensional graphene crystals studied and won the Nobel Prize in Physics in 2010. This achievement set off a wave
of scholars to study graphene, and various valuable properties of graphene have been discovered successively. Graphene materials have gradually entered the field of industrial production.

2. Preparation method of graphene

The first condition for studying graphite thinning is to prepare raw materials. At present, the methods for preparing graphene are mainly divided into physical methods and chemical methods. The physical method refers to a method for preparing graphene using low-cost graphite as a raw material, including a mechanical stripping method, a liquid phase or vapor phase stripping method, an orientation epitaxy method, and the like. Chemical methods include chemical vapor deposition, redox, epitaxial growth, and the like. The chemical method has the advantage of being able to be applied to production on a large scale, and is the main method for preparing graphene so far.

3. The research content, methods and means of selection

Although graphene has excellent performance, its performance is often not maximized due to limitations in preparation methods and practical conditions. Even though the specific surface area of graphene is large, chemical conversion graphene (CCG) is liable to be closely stacked due to the π-π bond interaction, and the specific surface area is lost. The main research content of this paper is the controllable preparation of the small layer of graphene material, and some properties of it are simply studied. The micro-mechanical stripping method is used to strip high-oriented pyrolytic graphite into high-quality graphene, even single-layer graphene, and in order to make the produced graphene larger, the silicon wafer is heated in this experiment. Thereafter, the number of layers and the area of the produced graphene were initially judged by an optical microscope, and the number of layers of graphene and some properties were further determined according to Raman spectroscopy. In addition, a series of studies and characterization of graphene strain properties have been carried out.

4. Experiment

4.1. Experimental instruments and equipment

Ultrasonic cleaning machine, CVD tube furnace, optical microscope (OM), Raman spectrometer, small ion sputtering instrument.

4.1.1. Preparation of graphene. Cut 25μm thick copper foil into 2cm×2cm, then flatten the copper foil in half, and roll it around. At this time, pay attention to the middle part, do not compact it, put the folded copper foil into the quartz boat, and then use the hook to push the boat. Push into the quartz tube and place it in the center of the furnace. At this time, do not stop the argon gas process and seal the furnace. Open the vacuum pump switch and heating switch, open the angle valve, and run the heating program when the vacuum is reduced to 1-2Pa (1 step, heating time 40 minutes, temperature 1030, hydrogen 10sccm, 2 steps 30 minutes, 1030 degrees, methane 10 scm, hydrogen 10 sccm, 3 steps, 0 degrees, methane 10 scm, hydrogen 10 sccm). Sampling after cooling, pay attention to vacuum and then argon. The angle valve is closed, the argon gas is 1000sccm, and the vacuum should be heard at 1.13, and the sample should be heard.

4.1.2. Transfer of graphene. After the copper foil sample was taken out, it was carefully spread out, flattened with a glass slide (pad paper towel), and then cut into small pieces of 5 × 5 mm. Spin coating was carried out with a PMMA solution (PMMA 40K or more, 30 g, 500 ml of anisole/toluene/chlorobenzene). Heat on the heating table at 150 degrees for 1 min, remove and mark (or dry in the air for 10 min). Then, the inner layer of the sample was placed in the ammonium persulfate solution upwards, and after 10 minutes, the back surface was rinsed with deionized water, and then placed in an ammonium persulfate solution, and rinsed again after 10 minutes, three times until the copper was completely etched, using a slide. The pmma membrane was transferred to deionized water for 30 min. Then use the cleaned silicon wafer to salvage the pmma membrane and control the moisture.
Here you can use a paper towel to absorb the moisture around the membrane. After the silicon wafer was naturally dried, it was placed in a vacuum drying oven at 150 degrees for 1 hour (30 minutes). Or placed on a heating station 150 degrees for 1-2 minutes. After the sample is taken out, it is placed in acetone, and after 10 minutes, the acetone is exchanged, so that after 3 consecutive times, it is immersed for 1-2 days for a long time. After the sample is taken out, it is immersed in absolute ethanol for 10 minutes, rinsed once with deionized water and then taken out. The transfer flow chart is shown in Figure 1:

![Transfer process of graphene prepared by CVD](image)

**Figure 1.** Transfer process of graphene prepared by CVD

4.1.3. Effect of preparation methods on graphene. In this experiment, a graphene sample was prepared according to a conventional method, and the number of sample layers obtained was large. Through many experiments, the method of heating the silicon wafer was finally selected to realize the controllable preparation of graphene. In the process of preparing graphene, the peeling of graphite was repeated several times at the beginning, and the peeling method was also improved, and the thin graphite was better adhered to the tape by the pressing of the ruler at the time of peeling. The treated silicon wafer was then placed in a box furnace at a temperature controlled at 100 °C for 2-5 minutes. After the heating was completed, the silicon wafer was taken out and cooled to room temperature, and then the silicon wafer was stuck on a tape with graphene, and the obtained graphene was as shown in Fig. 2. It can be seen from the figure that the graphene produced by this method is not only controlled in the number of layers, but also the area is secured.

![Photograph of graphene obtained after heat treatment of silicon wafer](image)

**Figure 2.** Photograph of graphene obtained after heat treatment of silicon wafer

4.2. graphene characterization results

4.2.1. Optical microscope (OM) characterization results. An OM photograph of graphene prepared under a silicon wafer substrate is shown in Fig. 3.
By observing the results of optical microscopy characterization, we can know that the preparation method used in this experiment can successfully transfer graphene to the silicon wafer substrate. Among them, 3.5(a) is a single-layer graphene, and its color is very close to that of the silicon substrate, indicating that the transmittance of single-layer graphene is very high. In other graphene samples, as the number of layers increases, the graphene sheets are more and more different from the substrate color. It shows that we can preliminarily discern the number of layers of graphene based on the contrast between the obtained graphene and the substrate color.

4.2.2. Raman spectrometer (RS) characterization results.

During the test, the laser was focused onto the graphene sample with a scan range of 1200 cm$^{-1}$ - 3500 cm$^{-1}$. It can be seen from Figure 4 that under the existing experimental conditions, we can prepare a few layers or even a single layer of graphene. Figure 3 (b) is a Raman spectrum measured at different layers of graphene based on Figure 4 (a). From Raman spectroscopy, we can know that the number of layers of graphene is different. The Raman spectrum shows different intensity and peak shape, but the common point is that there are two characteristic peaks, namely G peak and 2D peak. As the number of graphene layers increases, the G peak does not shift, and the 2D peak undergoes a Raman shift, which gradually moves toward the long wave direction, that is, a blue shift occurs. Because single-layer graphene does not have interlayer coupling, its 2D peak intensity is very high, but when the number of layers is gradually increased, the interlayer coupling between the layers is manifested. As the number of layers increases, the 2D peak intensity decreases. And the peak shape is widened. The graphene G peaks of different layers have different intensities. As the number of layers increases, the intensity of the G peaks gradually increases, showing a linear law. Therefore, in the Raman spectrum, the single-layer graphene has a lower G-intensity than the other two-layer graphene, and the other layers have a higher G-intensity than the 2D peak, so it can be clearly seen from other The spectra of the samples are resolved, but the 2D peaks of the 2-4 layers are very similar. Based on this, we can distinguish whether the produced graphene is a single layer.
4.3. Graphene strain test sample preparation
First step: In this sample preparation, the pretreatment of the silicon wafer was consistent with the previous method, and was shaken for 15 minutes in deionized water, propanol, absolute ethanol, and deionized water, respectively.

Step 2: The treated silicon wafer is plated with a gold film in a small ion sputtering apparatus with a time setting of 200 s and a current of 20 mA.

The third step: the gold film-coated silicon wafer is placed in a vacuum drying oven for annealing, the temperature is set at 300 °C, and after heating for 15 minutes, it is cooled with the furnace.

Step 4: Transfer the pre-teared graphene to a gold-plated, annealed silicon wafer.

4.4. Graphene strain characterization
In this experiment, the processed samples were mainly subjected to optical microscopy and Raman spectroscopy.

4.4.1. Optical microscope (OM) characterization results. As shown in Fig. 5, the area 1 (a) and the area 1 (b) are unsprayed silicon wafers, and the regions (a) and 2 (b) are gold-plated silicon wafers. We can see that after the annealing treatment (a), the original layered gold film becomes granular compared to the previous (b).

![Figure 5](image)

Figure 5. (a) Photograph of silicon wafer OM after annealing (b) Photograph of silicon wafer OM before annealing

As shown in Figure 3.8, it is a photomicrograph of graphene after gold annealing of silicon wafer. From the figure, we can see that the small layer of graphene has been transferred to the gold-plated, annealed silicon wafer, and there are obvious grooves at the pick-up point, and the groove width is about 1 μm.

![Figure 6](image)

Figure 6. Photograph of graphene OM after silicon wafer annealing
4.4.2. **Raman spectroscopy (RS) characterization results.** During the test, the laser is focused to the groove in Figure 3.8, in order to compare the change in the strain of the sprayed gold or not. The scanning range is 1200cm\(^{-1}\)-3500cm\(^{-1}\).

![Raman spectroscopy](image)

**Figure 7.** Raman spectroscopy of silicon wafers with graphene after gold plating and annealing

In the figure, no D peak was observed, indicating that no defects were found in the graphene-prepared graphene, which proved that graphene may have good performance. The G peak shifted by 2 cm\(^{-1}\) in the long-wave direction, and the long-wave direction of the 2D peak shifted by 39 cm\(^{-1}\), and both of them shifted red, indicating that the strain of graphene changed. However, there are inconsistencies in the references. It is possible that the stress of graphene is different because the peak position of the Raman spectrum is related to the tensile force or tension it receives. Further research on this process can be carried out in future research and study.

5. **Conclusion**

The highly oriented pyrolytic graphite can be peeled off into a single layer or even a small layer of graphene by mechanical stripping method. However, in the course of this experiment, the processing of the silicon wafer is different from the conventional method. In this experiment, the temperature of the silicon wafer is at 100 °C for a period of time. After 2-5 minutes of heat treatment, the obtained graphene has not only a small number of layers but also an area of several hundred micrometers, indicating that the results of graphene production are affected by temperature and heating time. In this paper, the controllable preparation of graphene is realized. Among them, optical microscope and Raman spectroscopy show that single-layer graphene has different properties from other graphenes. The single-layer graphene has better light transmittance than other graphenes. Many, and as the number of layers increases, the G and 2D peaks in the Raman spectrum exhibit different intensities and peak shapes.

In addition, in the study of the strain characteristics of graphene, it was found that after the gold film was sprayed and annealed, the gold film was changed into a granular shape, and the graphene attached thereto did strain, and the Raman peak occurred. Displacement. In this experiment, the controllable preparation of graphene was studied. Finally, single layer and few layers of graphene were successfully prepared. The single layer, double layer, three layer and four layer graphene were distinguished by characterization method. The true development of graphene has been more than a decade, but its excellent performance has made it a lot of applications, and its related research has also developed rapidly. Although this experiment has gained, there are some shortcomings. I hope that later scholars will improve and improve.

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