Investigation in double layer graphene superlattice and its electronic properties

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Abstract. This paper mainly discussed the graphene and other 2D materials, as well as their electronic properties. The history and theory prediction of graphene, and production of graphene (mechanical exfoliation and CVD method) are discussed. Graphene hBN superlattice and bilayer graphene superlattice are presented, with following discussion of the superconductivity of the magic angle. Finally, characterization methods such as AFM and SEM are presented.

Keywords. Monolayer materials, Bilayer graphene, Superlattice.

1. Introduction
Graphene, the name of a special carbon who is only one atom thick, is now continuously attracting more attention in scientific community. Because of the combination of great mechanical strength, unique thermal and electrical conductivities and a plenty of impressive properties, this supreme two-dimensional material has swiftly become one of the cut-edge technologies in the area of inorganic materials.

Only graphite, a kind of carbon which stretches in three directions could be commonly found in nature world. However, graphene is more widely being used for scientists describing the structure of most carbon materials. For example, graphite is considered as a stack of graphene on a single direction, which probably explains why electrical conductivity of it is much better than expected. For 0D material like fullerenes and 1D material like nanotube, by wrapping up or rolling into the material we need, graphene is also regarded as a “building block” of them. On this basis, generally, the material composed of atomic layers below 10 layers is called graphene, more than 10 layers is called 3D film, and higher layers become graphite. Graphene is usually subdivided into three categories: single layer, double layer, and 3-10 layers. The first two show some unique properties and have attracted more attention from academia. They have become potential substitutes for many existing cutting-edge materials [1].

About 70 years ago, graphene is firstly pointed out in theory as a basic fundament of many carbon materials. Unfortunately, within ten years, the existence of it had not been proved. Landau and Peierls announced that graphene could not exist because of the bad thermodynamical stability. Studies done later confirmed that atomic monolayer is an integral part of a bigger 3D structure, grows with the crystal lattice it matches, and cannot be separated independently. This shows that although the monolayer cannot be separated alone, it is completely possible to manufacture or separate graphene on a certain substrate. In 2004, two scientists Andre Geim and Konstatin Novselov obtained a single-layer graphite sheet by mechanical stripping, which proved that even two-dimensional substances considered impossible in thermodynamics can be manufactured under certain conditions. At present, single-layer
graphene can be operated alone to obtain the relevant information required by the research through the change of angle and number of layers. This is a major progress in the research of carbon materials [2].

2. Mechanical exfoliation of graphene

The mechanical stripping of graphite was mentioned earlier. Up to now, this method is still a common preparation method of graphene. In this process, we usually face two challenges, one is how to peel off graphene layer by layer, and the other is how to observe graphene as a single atomic layer. We will introduce them one by one.

In the process of separating each layer of graphene, the main force to be overcome is the van der Waals interaction between adjacent layers, which is why scientists prefer to use mechanical ways. There are two stripping methods that can be referred to, one using normal force and the other using lateral force. Usually, normal force stripping is carried out with the help of a special tape, which is also the method used by the two scientists who first isolated graphene in 2004. They used HOPG (highly oriented pyrolytic graphite) obtained after high-temperature treatment of graphite as raw material. This kind of graphite is close to natural single crystal graphite, so it is easier to separate the perfect graphene raw material. A thinner graphite layer can be obtained by bonding the special tape mentioned above and then applying the normal force. After repeated many times, a single-layer graphene material can be obtained. This method is relatively simple, and is conducive to the integrity of graphene as a whole. It can prepare very large area 2D materials. But at the same time, this method also has its disadvantages, that is, it takes too long and needs people to operate continuously, so it is impossible to carry out large-scale production without leaving the laboratory [3].

As can be seen from Figure 1, special adhesive tape is used for pasting, and then it is pasted on a specific substrate. After repeated operation, a single layer of graphene is obtained.

Fig.1. The operation principle of mechanical stripping method.

Lateral force stripping takes advantage of the small radial force between graphene layers, and promotes the sliding between graphite layers by applying the force in this direction, so as to "push" the graphene monolayer from the surface of graphite. Since it is almost impossible for manual operation to achieve such high accuracy, the method uses mechanical operation throughout the process. Even so, because the crushing of raw materials is inevitable in the process of applying force, this method can not prepare graphene with large area. Therefore, the larger HOPG is often trimmed into small pieces in advance and broken with special tools (such as single crystal diamond knife) before operation, so as to improve the separation efficiency and reduce the separation loss, and obtain the final product with predictable shape.
After the mechanical method is successfully used to obtain monolayer graphene, observation is also needed to determine its existence. Taking normal stripping as an example, after it is considered that the graphite material attached to the tape is already a graphene monatomic layer, it is pasted on the prepared silica wafer. This wafer with special thickness (usually 300nm, only about 5% thickness difference will invalidate the detection method mentioned below) will produce slight optical interference with graphene. By comparing with the empty wafer, we can see whether the expected product is obtained, and this difference can be identified by optical microscope. This subtle difference is a key factor in the discovery of graphene in 2004. At present, the detection methods using electron microscopy provide researchers with more information. For example, the edge of single-layer graphene often presents sawtooth shape, which also makes whether the edge of graphene has properties such as special magnetism or 1D transport capacity become one of the research topics of interest in the academic community [4-5].

3. CVD growing graphene
However, it is unrealistic to prepare graphene with larger area only by mechanical stripping method. Chemical vapor deposition, or CVD for short, is the most commonly used method for the preparation of large-area graphene. This method usually generates graphene molecular layer directly on the metal surface, so it needs to invest higher cost than mechanical stripping method.
As early as 1970, CVD method has been considered as a feasible method. At first, scientists succeeded on the surface of nickel single crystal, and found that copper is an ideal material in the exploration of transition metal materials. These two materials are now used to manufacture single-layer graphene and controlled multilayer graphene, respectively. Today, the manufacturing method of silicon carbide crystal, which is also very common, is very different from the beginning. At first, it sublimates the silicon atoms in the crystal at high temperature and high vacuum (about 1200 °C), leaving only a layer of carbon. However, the obvious problem of this method is that it is difficult to produce large-area uniform graphene. At the same time, the connection between graphene and substrate is too strong to peel off graphene at all. This problem was solved after a layer of germanium was grown on the silicon carbide substrate. Graphene which is easier to peel was obtained by reducing the temperature and connecting ability. Nowadays, this growth law is more complex. For example, hexagonal boron nitride is used to build a sacrificial layer for fine regulation, which is also a method to manufacture magic angle graphene [6].

**Fig.4.** (a)-(d) are the growth of hexagonal graphene on copper substrate at different time lengths detected by Atomic Force Microscope, which are 20, 40, 60 and 80 minutes respectively. (e) is the change of particle size with time (From: Muñoz, R. & Gómez-Aleixandre, C. Review of CVD synthesis of graphene).

Today's CVD method uses lower temperature and methane hydrogen feed gas to deposit the carbon atoms in the gas phase after methane cracking on the surface for nucleation and growth of the next layer of carbon atoms, so as to obtain graphene with different layers. Usually, this regulation is achieved by regulating the copper nickel ratio of the substrate. If the proportion of nickel is high, the number of layers becomes more. The start and stop of reflection are controlled by temperature and hydrogen ratio, which is very mature on the whole.
The CVD method on the surface of silicon carbide crystal is a new method. This method does not need to build a sacrificial layer or sublimate silicon atoms, but uses carbon atom deposition to manufacture graphene as the CVD method on the metal surface. This method requires lower temperature to prevent silicon atoms from diffusing into graphene monolayer, but it is still an immature method [7].

Fig.5. (a) Schematic diagram of graphene production on copper foil. The method is divided into carrier adhesion, copper etching, drying and transfer printing. (b) The copper foil is wrapped in a 7.5-inch quartz tube and inserted into an 8-inch quartz tube for CVD reaction. The raw materials are methane and hydrogen. (c) Transfer of large area graphene film on PET sheet (From: Plutnar, J., Pumera, M. & Sofer, Z. The chemistry of CVD graphene).

4. Magic angle of graphene superlattice
Magic angle graphene is a kind of multilayer graphene with special twist angle, usually two layers. The different angles between the two layers will bring many different special properties to graphene materials. The changing patterns with different twist angles are called moiré superlattices by the scientific community. Similar to the hexagonal carbon structure of single-layer graphene, the moiré superlattice is also hexagonal, but its size is much larger, usually up to 13 nm, between the crystal superconductor and the optical lattices. At the same time, it has a unique periodicity that neither the upper nor lower layers have, and has a far-reaching impact on the electronic activity and transfer in the whole structure.

At the beginning of its discovery, this wonderful structure received considerable attention. It was first found in the graphene layer based on hexagonal boron nitride. This material is to minimize the damage to graphene in the manufacturing process. It is found that under the action of interlayer van der Waals force, there is a certain angle distortion between them. Because graphite and boron nitride are very similar in structure, it is approximately considered that they are degenerate, and the pattern shape can be deduced into two identical graphene monolayers, which is also one of the inspiration sources of magic angle graphene material, shown in Fig 7.
Fig. 6. Characterization of hexagonal graphene. (a) Optical image of graphene on copper surface after CVD and oxidation. (b) SEM image. (c) Optical microscope image. (d) Raman spectra of four randomly selected positions in Fig. (c). (From: Plutnar, J., Pumera, M. & Sofer, Z. The chemistry of CVD graphene)

Fig. 7. Graphene hBN superlattice
Subsequent studies found that the style of the moiré superlattice will directly affect the electron distribution between the interlayer and its energy band structure and spin state, which is the result of the periodic change caused by the change of angle [8].

Two layers of graphene materials will naturally have a similar phenomenon. If stacked according to the traditional AA or AB, the interlayer interaction will lead to the change of the lower energy band. If there is a twist angle between layers, a superlattice will be generated, which will have a greater impact on the energy band.

Generally, magic angle graphene is the product of a specific angle. When the interlayer twist angle is small, the interlayer coupling is strong, the energy band structure is sensitive to the angle, and the electron motion slows down under the action of Coulomb repulsion. When the kinetic energy of the electron is less than the Coulomb repulsion, that is, when the twist angle comes near \(1.1^\circ\), the electron is almost localized in the moiré superlattice, the energy band is almost completely flattened and folded into the mini Brillouin region (MBZ), bringing a series of properties such as superconductivity and unique magnetism [9].

At present, fully encapsulated TBG devices are usually used to study twisted graphene. As shown in Figure 8 (a), a graphene sheet attached to the boron nitride substrate is installed at the top and bottom of the device respectively. Through the device, the twist angle can be accurately controlled at about \(1.1^\circ\) and can be accurately adjusted within the range of \(0.1^\circ\). Several metal gates of the device can be applied with voltage to change the carrier density of magic angle graphene, tune the whole system and increase the angle and temperature range of superconductivity. The effect of twist angle on superconductivity can be seen from (b). Although the twist angle graphene is superconducting in a certain range at both angles, the maximum temperature at \(1.05^\circ\) can reach 1.7k, which is closer to the traditional copper oxide superconducting materials. The current voltage curve shown in figure 9 (E) shows the effect of temperature on the superconducting ability of twisted graphene. It can be seen that it roughly fits the law of \(V_{xx} \propto I^3\) and still follows the typical properties of two-dimensional superconductors.

The generation principle of a series of special properties of twisted graphene is a complex physical process, especially a great challenge to the traditional superconductor theory. How to improve the use environment and expand the range of twist angle is also one of the important directions of magic angle graphene research in the future. In addition to carrier regulation, the use of pressure regulation of interlayer action is also a feasible method. Efforts to improve properties will make magic angle graphene more used in a variety of potential electronic components and become an ideal substitute for many existing materials [10-11].

![Fig.8. (a) Device schematic demonstration (b) Temperature vs. resistivity curve.](image)
5. Characterisation of superlattice
After the manufacture of graphene is the detection process. Whether qualified graphene has been manufactured shall be detected by atomic force microscope (AFM) and scanning electron microscope (SEM). AFM can not only accurately image the surface, but also measure the interfacial force and displacement, shown in Figure 10.

![AFM scanning area](image1)

![Force distance curve](image2)

Fig.9. Voltage vs. current curves in one of the superconductivity devices

Fig.10. (a) AFM scanning area (b) Force distance curve

The working principle of AFM is to contact and scan the material through the probe (the tip is silica material with a radius of 405.4nm). Through the pressure felt by the probe on the material surface, the height information of the object surface can be obtained, and then the specific surface morphology can be restored. This method is relatively simple, but because it is in direct contact with the material surface, it will cause material damage, so we should be very careful when using it. At the same time, slow
working speed is another major disadvantage. Therefore, in scientific research, we will also use SEM for relevant detection. In SEM detection, through the dispersion mechanism of secondary electron intensity distribution, we can see some regions with different contrast in the image, and these regions represent graphene structures with different thickness. In this way, we can also get the basic morphological characteristics of graphene surface [12-13].

6. Conclusion
This paper presented the graphene and other 2D materials producing methods and electronic properties. The superconductivity of the bi-layer graphene superlattice provide a breakthrough result and this is studied and discussed in this paper. Finally, this paper provides a meaningful parts of characterization methods (AFM and SEM), these could be a useful method in future study of 2D materials topographic properties.

Reference
[1] Geim, A. K. & Novoselov, K. S. The rise of graphene. www.nature.com/naturematerials.
[2] Novoselov, K. S. et al. A roadmap for graphene. Nature vol. 490 192–200 (2012).
[3] Novoselov, K. S. & Castro Neto, A. H. Two-dimensional crystals-based heterostructures: Materials with tailored properties. Physica Scripta (2012) doi:10.1088/0031-8949/2012/T146/014006.
[4] Yi, M. & Shen, Z. A review on mechanical exfoliation for the scalable production of graphene. Journal of Materials Chemistry A vol. 3 11700–11715 (2015).
[5] Technical Data Sheet ACS Material Mechanically Exfoliated Single Crystal Graphene On SiO2/Si (SiO2: 300nm Thick). www.acsmaterial.com.
[6] Plutnar, J., Pumera, M. & Sofer, Z. The chemistry of CVD graphene. Journal of Materials Chemistry C vol. 6 6082–6101 (2018).
[7] Muñoz, R. & Gómez-Aleixandre, C. Review of CVD synthesis of graphene. Chemical Vapor Deposition vol. 19 297–322 (2013).
[8] Ponomarenko, L. A. et al. Cloning of Dirac fermions in graphene superlattices. Nature 497, 594–597 (2013).
[9] Woods, C. R. et al. Commensurate-incommensurate transition in graphene on hexagonal boron nitride. Nature Physics 10, 451–456 (2014).
[10] Cao, Y. et al. Unconventional superconductivity in magic-angle graphene superlattices. Nature 556, 43–50 (2018).
[11] Castro Neto, A. H., Guinea, F., Peres, N. M. R., Novoselov, K. S. & Geim, A. K. The electronic properties of graphene. Reviews of Modern Physics 81, 109–162 (2009).
[12] Jiang, T. & Zhu, Y. Measuring graphene adhesion using atomic force microscopy with a microsphere tip. Nanoscale 7, 10760–10766 (2015).
[13] Park, M. H., Kim, T. H. & Yang, C. W. Thickness contrast of few-layered graphene in SEM. in Surface and Interface Analysis vol. 44 1538–1541 (John Wiley and Sons Ltd, 2012).