Progress in Graphene and Magic-angle Graphene Superlattice in the Aspect of Superconductivity

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Abstract: Graphene, a relevant new material first defined in 1986, is gathering more and more interest in the circle of science and engineering especially material and electrical fields. It exhibit excellent mechanical features, extraordinary electrical and thermal properties due to its single atomic layer thickness and honeycomb bonding structure. Graphene is used as an advanced alternative to many traditional materials in a wide range of applications. There are two main synthesis methods, the top-down and the bottom-up, with many branches. The current research state cannot fulfill the urgent demands from the application. Therefore, sub-subjects of graphene are created by splitting or restructuring such as graphene quantum dot and graphene nanotube. In 2018, Yuan Cao et al. have reported a newest research about twisted multilayer graphene. This derivative of graphene showed tunable superconductivity, which also inherited the mechanical structure and thermodynamic properties of graphene. The twisted graphene holds great promise and is likely to be a milestone in superconductivity. Therefore, in this work, the progress in graphene and magic-angle graphene superlattice in the aspect of superconductivity were introduced.

Keywords: Graphene, Magic-angle, Twisted Bilayer Graphene, Twisted Multilayer Graphene.

1. Introduction

Carbon, the fundamental of life and organic chemistry, can form various different physical structures. Graphene as one of these structures is stripped from graphite and attracting more worldwide attention nowadays. Due to its outstanding properties in the aspects of physical, chemistry and especially electrical, graphene has become a top priority in materials science research. Graphene is the basic material which can build all other graphitic structures. As more resources are devoted to research in this area, graphene-related materials appear ranging from multilayer graphene to graphene quantum dot, graphene nanotube, and graphene nanoribbon. The recent research made by Yuan Cao and his team [1-2] revealed a new direction for graphene. By stacking multiple monolayer graphene in a specific angle named magic angle, the material's electrical conductivity will be greatly enhanced. Superconductivity has been shown in the material.

2. About graphene

2.1 History of graphene

The earliest theory of the possibility of graphene's existence can be chased back to the 1940s. It predicted if the layers in graphite can be isolated or split into a single layer, it will exhibit unexpected characteristics in electronics. When it came to 1986, Boehm and his team [3-4] first gave an accurate definition of graphene in science, the carbon monolayer of the graphitic structure. And it was formally defined by IUPAC after 11 years in 1997 [5].

In contrast to the theoretical definition, research related to graphene emerged as early as 1840 but has mainly centered around graphite oxides, graphene oxides and graphite intercalation compounds. The name given to graphene was “reduced graphene oxide” [6]. Schafhaeutl, a German scientist, gave the first report about preparing graphite oxides by using acids. This method was improved by British scientist Brodie in 1859 which makes exfoliating the oxidized layers easier under certain circumstances [7]. In 1962, the same team which first defined the concept of graphene confirms the assumption of graphene exists by producing lamellar carbon [8]. The monolayer carbon flakes which

are consistent with the structure of graphene and multilayer carbon material were found by van Bommel et al. in 1975 [9]. This is the earliest report on using of chemical synthesis methods for graphene. The first mechanical exfoliation of graphene occurred in 1999, but this method only produced thin sheets of graphene in stacks [10]. The mature method of mechanically exfoliating graphene appeared in 2004 and was completed by the team of Geim and Novoselov [11].

2.2 Properties of graphene

Graphene is the 2D hexagonal lattice constructed by carbon atoms in a single layer. It is the foundation for all graphitic materials such as graphene quantum dots and graphene nanotubes. The lamellar structure brings significant electronic and mechanical properties. Graphene is an extremely thin and strong material. The breaking strength of it is 42 newton per meter. With unique surface architecture that allows a high water flux, it can be used for desalination. In addition, graphene has excellent electrical and thermal conductivity. The electron mobility of it is 200 cm^2/Vs which is similar to copper but the density is only a quarter of the same unit of copper. Thus, graphene is an excellent alternative to copper in electrical engineering. These properties make graphene a good material for energy storage devices such as supercapacitors and batteries. Compare to traditional materials especially graphite, graphene has more stable chemistry properties, higher surface area and electrical conductivity. It also has good optical performance. 97% transparency ensures graphene can be used as transparent electrodes which have many optical and optoelectronic applications.

However, graphene is a zero-gap semiconductor material which means it cannot be used as a switch. The toxicity exhibited by graphene and the functional damage it can cause to cells under certain circumstances also poses a challenge to its application [12-13].

2.3 Fabricating processes of graphene

There are two directions to manufacturing graphene, top-down and bottom-up. The front one is to exfoliate a thin layer from the stacked graphene layers of graphite. The bottom-up method is let carbon atoms grow under specific conditions to form graphene spontaneously.

The major exfoliations are the mechanical method and chemical method. Graphite is the assemblies of stacked single-layer graphene which are bonded together by the week van der Waals force. Theoretically, bonds between these layers can be broken to release graphene from high-purity graphite. Novoselov et al. found the first workable mechanical exfoliation process to produce graphene in 2004 [11, 14]. They placed a pyrolytic graphite sheet which is highly oriented in the oxygen plasma to dry etching to get 5μm deep mesas. Then put these on the photoresist and peeled the baked mesas with scotch tape to get few-layer or single-layer graphene sheets. In 2005, Stankovich's team provided a new direction of exfoliation, aqueous exfoliation [15]. And two years later, he refined this method by chemical reduction of peeled graphite oxide [16]. However, graphite oxide has different properties from graphene. It is an insulator that leaves a number of defects in the finished product. Compare to theoretical-needed graphene, these products' electronic properties will be significantly compromised. The improvement was made by Hernandez et al. in 2008. They used solution-phase exfoliation to produce high-quality, unoxidized graphene by relatively less-defects graphite in certain organic solvents(N-methyl-pyrrolidone) [17]. This liquid-based graphene-producing process is promising for scaling up graphene production. However, it still has the limitation of the number of defects and poor electronic properties of graphene.

Thermal chemical vapor deposition or the CVD is a large branch method of the bottom-up method[18]. As the name suggests, this method uses a high-temperature carbon-containing gas on a transition metal substrate material at a specific flow rate to synthesize few-layer graphene. Nature raw materials such as the mixture of methane and hydrogen gases will be first evaporated in a low-temperature chamber and pyrolyzed at the high-temperature condition around 700-850 degrees Celsius. Then Ni or Cu foils as the substrate will be exposed to the product curried by argon gas to construct a solid solution. Due to carbon's low solubility in metal at a low temperature, it will diffuse out from the substrate and form graphene with fewer layers. The method gives better results on metals with a lower affinity for carbon such as copper [19]. CVD can produce graphene with fewer structural

and electronic defects than exfoliation, but the high expenditure on substrate materials, the tiny size of graphene growth and the difficulty of controlling the number of graphene layers in the product limit scale of its production.

3. Current electronic research directions for graphene

3.1 Graphene quantum dot

Graphene quantum dots or GODs are graphene fragments in the size range of less than 20 nm which can cause quantum size effect and exciton confinement[20]. The synthesis directions of GQD are similar to the fabrication of graphene, the top-down and bottom-down. Top-down is a major one with various branch methods. The basic idea is to 'cut' these fragments mechanically or chemically from graphene as the raw material. These dots retain the electronic properties of graphene, and a size small enough to trigger quantum size effects further extends the material's advantages. In addition, graphene quantum dot as a low-toxicity carbon material shows the properties of high soluble in a wide variety of solvents and is abundantly available. Multiple functional groups can be equipped at the edges of dots, making this material more desirable for various functions compared to other inorganic semiconductor quantum dots.

The applications of GQD are most about its exciton confinement. By doping GQDs, the structure of the doped material will become porous with a higher electron transfer rate. These active sites can capture photons efficiently which makes these dots have a high incident-light absorption percentage. Therefore, GQDs are an ideal material to construct photovoltaics and photodetectors. The high electron mobility can also benefit organic light-emitting diodes. It effectively reduces the starting voltage of the diode and enhances the performance of white light LEDs.

3.2 Graphene nanotube

Graphene nanotube (GNT) or single-wall carbon nanotube can be seen as graphene rolled into tubes at the nanoscale [21]. Due to the limitation of layers, "rolling" a nanotube by graphene is impossible. CVD is one of the synthesis methods of GNT. Compare to the production of graphene, an extra step will be applied after using CVD method to synthesize graphene. Metal nanoparticles will be "planted" as the "seed" of the nanotube on the surface of graphene surrounded by an alumina buffer layer. When comes to the growth stage, the buffer layer will be lifted up and nanotubes grow up from the graphene layer. The electronic properties of the nanotube are similar to graphene. By adjusting the gap at the Fermi level, the graphene nanotube can become metal (no gap) or semiconductor (the gap near the Fermi level) [22].

3.3 Magic-angle of twisted multilayer graphene

Research on graphene takes a step up when it comes to the angle that occurs between layers of graphene. The magic angle alters the graphene layer's energy band structure and brings it close to zero Fermi energy [1-2]. By using this property, the superconductor could be achieved.

3.3.1 Twisted bilayer graphene

All the related research began in 2018 when Yuan Cao et al. found the magic angle and superconductivity in twisted bilayer graphene and defined the material as the purely flat superconductor based on carbon [1]. Twisted bilayer graphene or the TBG is the double layer graphene that has slightly-rotated superlattices concerning each other. When the angle between two layers is around 1.1 degrees, Fermi velocity decreases to zero and the flat band occurs which has an energy scale of about 5-10 meV. At this point, the device shows zero resistivity at the lowest experiment temperature around 70 mK. One advantage of TBG compared to other known two-dimensional superconductors is the small gate voltage required. In a high-mobility system, a gate-tunable superconductor is shown without extra conditions such as chemical doping. TBG also has an attractive property, its magnetic-filed response. Its conductivity varies with the magnetic field and its doping

density. When the magnetic field is less than about 70 mT, two similar domes appear on either side of the semi-doped area. In addition, the presence of a Mott-like insulating zone between the peaks of domes indicates that the insulating and superconducting properties of the material can be regulated.

Furthermore, Yankowitz et al. proved the superconductivity of twisted bilayer graphene can be achieved at higher angles and temperatures [23]. The width of the flat band in TBG is determined by the interplay spacing and the interplay of twist angle [24]. They used hydrostatic pressure to vary the space between interlayers which means superconductivity can be induced at a twist angle greater than 1.1 degrees. This method greatly relaxes the harsh angle conditions of TBG and reduces the difficulty of adjusting accuracy.

The synthesis of TBG is neither a top-down nor bottom-up method. It is a reconstructing process of general bilayer graphene named modified dry-transfer technique. The exfoliated graphene is placed on a substrate (hexagonal boron nitride) and then removed at 90ºC to tear the graphene by van der Waals forces. The graphene is then manually twisted at an angle around 1.2 to 1.3 degrees and stacked back. After being packed by another flake, the device is shaped by lithography and etching, then made the electronic connection by chromium or gold. A CVD method using copper is presented by Cho et al. in 2020 [25]. They used atomic-stepped materials, Cu (311) and Cu (110), to produce the TBG with 3-5 degrees angle. A nucleation point is shared by two layers, which will grow in the order of the upper layer before the bottom layer.

3.3.2 Twisted trilayer graphene

The structure of twisted trilayer graphene (TTG) is like an imperfect sandwich that has a twisted sliced cheese between two bread. The angle between the top layer and the middle shares the same absolute value (about 1.6°) as the one between the middle and bottom layers. The synthesis of it is similar to TBG but has an extra layer that needs to be added on. Compare to the bilayer graphene, TTG exhibits superconductivity which may not be affected by magnetic fields and has better performance in electronic properties because of the richer phase diagram and greater electronic-filed tunability. By reconfiguration of the moiré superlattice, the twisted angular disorder in twisted trilayer graphene forms electronic particles, resulting in an intrinsically controllable moiré disorder. And this result could redefine the fundamental recognition and applications for the strongly coupled superconductor.

4. Conclusions

In the past few hundred years, graphene, the derivative of graphite, has had significant developments in the area of material science. With the gradual development of its research and the gradual improvement of its synthesis, the superior properties of graphene, especially its electronic properties, have provided great progress in semiconductors. If the discovery of graphene opened a gate to modern material, the development of twisted multi-layer graphene is definitely paving the way to superconductivity. More and more researches show that its tunable superconductivity could lead to a huge influx of research and related applications. This would be a huge step towards a tunable superconductor.

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