The development of graphene and its use in flexible electronics

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Abstract. In recent years, graphene has been deeply studied by scholars, and has attracted high attention in the field of flexible electronics. In order to better understand the properties and application of graphene, this article systematically summarized and analyzed the applications in the field of flexible electronics from multiple angles to better display its characteristics. It mainly introduces the development, preparation method, classification, and application of graphene. Since its discovery in 2004, it has become a special and useful nanomaterial. Graphene has been widely used in the field of flexible electronics in the past few years due to its excellent mechanical properties, electrical conductivity, and transparency. Moreover, we specifically show the development trends and application characteristics of graphene in flexible solar cells, field-effect transistors, nanogenerators. In addition, the problems facing graphene are also mentioned. Finally, the development prospects of graphene-based flexible electronics are presented and suggested for further studies.

Keywords: Graphene, flexible electronic, flexible solar cells, field-effect transistors, nanogenerators

1. Introduction

Carbon can be said to be one of the most widespread elements in the world, with lots of forms of existence. Since the rise of nanomaterials, carbon nanomaterials have been the focus of scientists' research. Due to the special structure of graphene, it produces a great deal of excellent properties, among which flexible electronics is a big application area. In 2004, graphene was discovered[1]. After that, it was found that graphene can be divided into three types according to their structure which are monolayer graphene, bilayer graphene and multilayer graphene[2]. This article explains the properties of three types of graphene. There are usually three main methods to prepare graphene. The most common method is CVD. The advantages and disadvantages of the three methods are discussed in this paper. Graphene has a wide range of applications in flexible electronics. This paper mainly introduces three representative applications which are flexible solar cells with graphene, field-effect transistors and nanogenerators[3]. In addition, this paper introduces the future prospects of graphene. The development of graphene and its application in the field of flexible electronics are of great significance. The specific properties of graphene have attracted extensive concern, driving product development in both advanced technology and downstream fields, expanding the application of graphene-related products and promoting the development of the entire material field.

2. Development status

2.1 The development of graphene

In 1859, it was reported that the graphene oxide and reduced graphene oxide were synthesized[4]. Graphite chemistry came into view of the whole world. In 1918, V. Kohlschutter and P. Haenni described the characteristic physical and chemical properties of graphite oxide paper in detail. After

a long time of that, in 1948, the micrograms of single-layer graphene oxide flakes was observed. In 2004, Geim and Novoselov, physicists at the University of Manchester, successfully isolated atomically stable, independent carbon nanosheets from graphite with scotch tape. Because graphene is considered as the final polycyclic aromatic hydrocarbon, the name ‘graphene’ came out[5].

Since the discovery of graphene, it has gained attention and made breakthroughs in plenty of fields. From 2004 to 2019, the three main disciplines of graphene research are materials science multidisciplinary, chemistry physical and physics applied[6]. So far, graphene has been mainly applied in four categories[7], the first one is sensors, which are thousands of times more sensitive to light than the imaging sensors used in video cameras. The second application is energy storage and new displays, a display with graphene can bend. The third application is semiconductor materials, which have better electrical conductivity. And the last application is biomedicine, which can offer greater biocompatibility. As far as the current situation is concerned, the electrical, thermodynamic and mechanical properties of graphene have irreplaceable advantages. Graphene's applicability has also led to its development in various fields. The future of graphene is bright.

2.2 The Main method of producing graphene

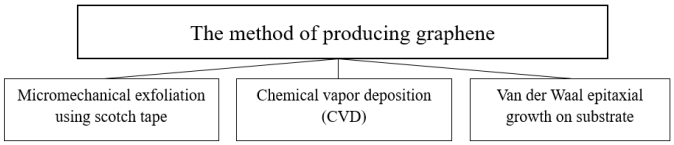


Figure 1. Three main methods of producing graphene

2.3 Micromechanical exfoliation using scotch tape

Micromechanical exfoliation with scotch tape is simple, rapid and economical, and can be used to obtain thick sheets of two-dimensional layered non-polar materials from the perspective of atoms[8]. The method is to rub the material on tape on the surface of the photoresist. As the van der Waals force decreases, the material becomes thinner and thinner with repeated rubbing. The monolayer is then transferred to an oxidized silicon wafer with acetone. Graphene made by this method is alwasys with smoother surface, fewer defects and its mobility is more excellent than other methods. This technique has some disadvantages at the same time. First, the production rate is very low, so this method can't be used in mass production, only in experiments[9]. Second, because this method relies on physical methods, the structure is easy to destroy.

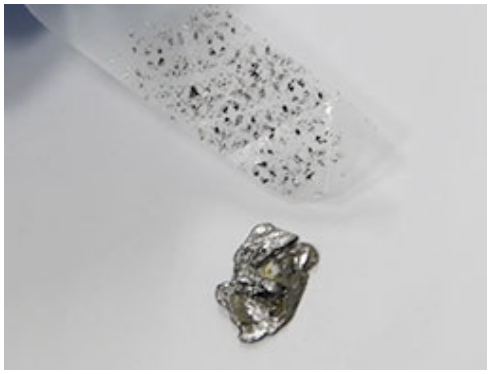


Figure 2. Macroscopic morphology of graphene after micromechanical exfoliation with scotch tape

2.4 Chemical vapor deposition (CVD)

Chemical vapor deposition involves the epitaxial growth of single and multilayer graphene with processes of carbon segregation and precipitation on a metal substrate[10]. Graphene with few layers are always produced on Ni films in CVD[11]. Generally, Ni films are annealed at high temperature and then exposed to H_2/CH_4 gas mixture. In this process, carbon atoms dissolve in the Ni films after hydrocarbon atoms decomposing. Finally, samples are cooled down on the substrate. In the terms of

single-layer graphene , Cu films are usually used us the substrate[12]. First of all, set Cu foils in atmosphere with hydrogen and high temperature about 1000℃. Then next step is introducing the H_2/CH4. When graphene films are formed continuously, the system cools down.

To fabricate graphene which meets the requirements of nano-devices or optoelectronics applications, it is necessary to detach catalytic metal substrates from graphene and then transfer graphene onto arbitrary substrates[13], like glass, Si/SiO_2 substrates and polyethylene terephthalate films.

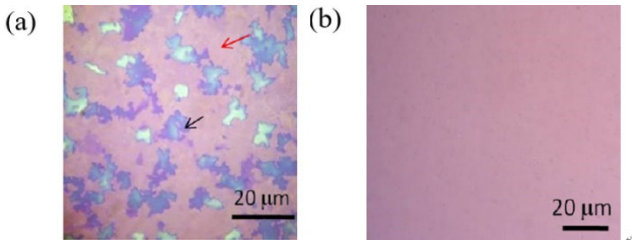


Figure 3. Optical images of graphene transferred to SiO2/Si substrates form Ni (a) and Cu (b)[14].

2.5 Van der Waal epitaxial growth on substrate

Van der Waal epitaxial is another kind of CVD method. As mentioned before, CVD uses substrate surface as a catalyst. In contrast, substrate surface is often a seed crystal in this method by which materials with thick atom and large aspect ratio are fabricated[10]. However, there are several disadvantages about this approach, such as high cost, strict temperature requirement and harsh ambient atmosphere, which really limit the wide spread use of it.

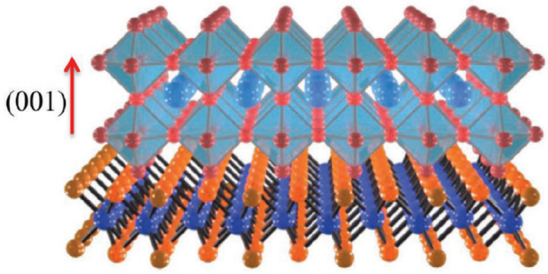


Figure 4. Schematic image of the epitaxial growth of perovskite film on the WS2 substrate [15].

2.6 Classification and properties

According to the structure of the graphene, it can be separated into different groups including monolayer graphene, bilayer graphene and multilayer graphene. In general, although the structure of bilayer graphene and multilayer is similar to that of monolayer graphene, the mechanical properties of them are quite different.

The mechanical properties of monolayer graphene can be probed by compressing the center of each flake with an AFM. Due to the phenomenon that stress-strain response curves over the lowest points, researches shows that the elastic response of monolayer graphene is nonlinear[16].

Bilayer graphene owns a special characteristic called the interlayer shear interaction which increases natural frequencies according to some researches. Wang et al. first gauged the interlayer shear pressure (40KPa) of the zone outside the bubble edge of bilayer graphene with pressurized microscale bubble loading devices, which is a useful tool to measure the properties of the interaction[17]. Additionally, there are some sp3 bonds appearing in bilayer graphene. These bonds connect 2 carbon atoms from different layers and reduce Young's modulus and tensile strength through Molecular dynamic simulation. Meanwhile they also build up interlayer modulus and load transfer rate to make graphene sheets stabler. In terms of elastic properties, the Young's modulus of bilayer graphene at room temperature is 0.2 Tpa smaller than that of monolayer graphene[17]. This value will fluctuate when the temperature begins to change.

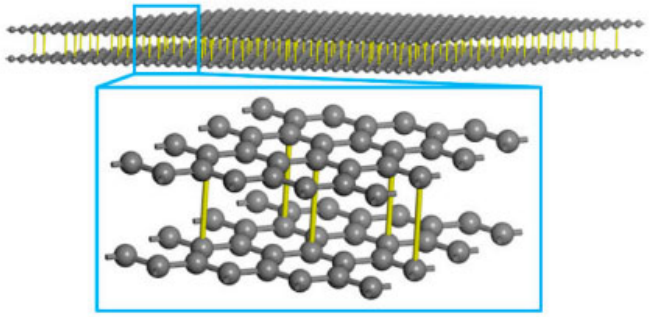


Figure 5. Sp3 bonds randomly distributed (shown in yellow) between bilayer graphene sheets [17].

In terms of the multilayer graphene, twisting, friction and mechanical properties are more attractive. The friction coefficient of it reduces when it is under tensile strain while increases under compressive strain. That may because the decreasing number of contacting atoms leads to the decline of the friction coefficient during the changes of strain. Through the study from Lu et al.[18], the vibrational frequency of multilayer graphene sheet depend on total tension mostly and a formula is derived for natural frequencies under tension loads. The modes of vibration can be effected by residual stress at the same time.

3. Applications of graphene

3.1 Flexible solar cells with graphene

Organic solar cells (OCSs) now use solar energy to harvest electricity and are promising and effective owing to their flexibility, light wight, low fabrication cost and most importantly, the high-power conversion efficiency (PCEs) [19]. Over past few years, Indium tin oxide (ITO) and carbon nanotubes (CNTs) have been commonly used as the transparent electrode of OCSs. However, ITO has poor mechanical and CNTs have rough surface and need polymer binders. As a result, it is quite difficult to utilize them as the electrode of OCSs [19]. Nowadays graphene is employed as the suitable alternative in the terms of transparent conductive electrodes due to its advantages of flexibility and high PCEs [20].

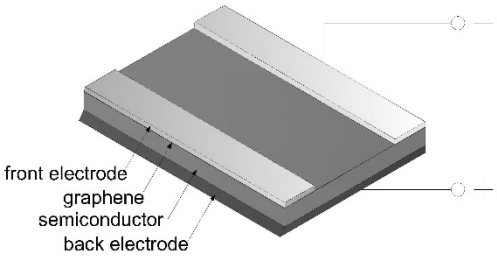


Figure 6. Graphene Schottky junction solar cell structure

Recently, several science communities develop reduced graphene oxide (rGO) and CVD-grown graphene. After doing some researches, CVD-grown graphene is confirmed to have lower sheet resistance values than those of rGO , high quality with low density of defects and high electrical conductivity[9].

There are two difficulties when using graphene as the electrodes: i) graphene is hydrophobic, while a hole extraction layer (HEL) is traditionally use hydrophilic material (poly(3,4-ethylenedioxythiphene): poly (styrenesulfonate) (PEDOT: PSS) [19], so it is a little challenging to coat HEL on top of graphene. ii) graphene will not be stable as before if it is doped with wet chemical dopants which are employed to surmount the low electrical conductivity of graphene. There are several

ways to solve these problems. First method is adding layers to improve the wettability of PEDOT: PSS. Another approach is that use GraHEL solution that contains the less-hydrophilic perfluorocarbon-based ionomer in order to attach PEDOT onto the graphene surface[9].

3.2 Field-effect transistors

Recently, graphene shows the ability to be assembled onto other flexible substrates to create field-effect transistors (FETs) that are thin-film incorporating a top -gate structure. In FETs, there is a semiconducting channel set onto a dielectric layer surface which relates to the gate, source and drain gate electrically [9].

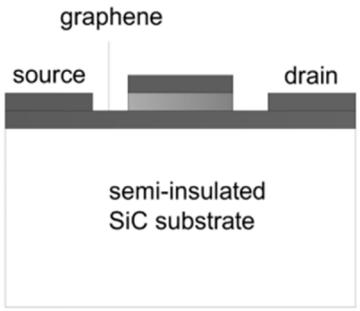


Figure 7. Field effect transistor, top gate structure

Owing to its outstanding mechanical properties and great electrical conductivity, graphene can be the component of either channel or electrode in FETs. Meanwhile, both holes and electrons in graphene have high μ values [9] at any temperature which means it can work in switching and logic devices. In general, graphene is such a promising material as a stretchable channel in FETs at high speed. Nevertheless, pristine graphene has a zero bandgap as a channel, as a result FETs are hard to switch off. It is necessary that inducing bandgap in graphene with some methods, such like hydrogenation, using nanoribbons of graphene or bilayer graphene [21].

3.3 Nanogenerators

Nanogenerators (NGs) have been developed based on nanoscale piezoelectric materials [22] which can easily convert mechanical energy from other kinds of energy. Among these materials, some one-dimensional piezoelectric semiconductor materials with wurtzite structure (ZnO[23], CdS, and GaN) and materials with electromechanical coupling (PbZr0.52Ti0.48O3 and vinlyidene flfluoride) have been exhibited in some electrical devices[19]. However, there is a disadvantage that all these piezoelectric materials have short life time. That because poor mechanical properties of limit the practical use. To solve this problem, materials with excellent mechanical properties and transparency such as carbon nanotubes and graphene films have been used in the NGs. These NGs behave better optical transmittance, more excellent mechanical properties and have longer life time than before [22].

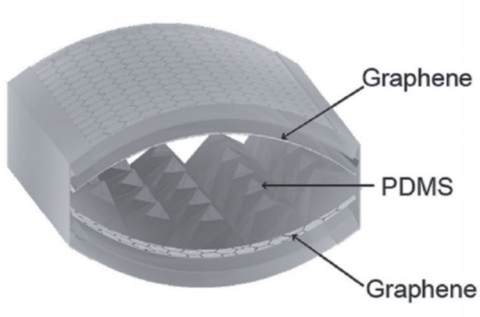


Figure 8. Schematic illustration of graphene/EVA/PET-based triboelectric nanogenerators [19].

3.4 Prospect of graphene

Graphene is valued because of its excellent thin-film properties and flexibility, and it has gradually become a hot spot in the research field of flexible electronic devices[24]. With the deeply research, graphene will be employed in Flexible solar cells with graphene, Field-effect transistors, Nanogenerators, etc. gradually enter people's daily life. In order to functionalize and productize graphene, the overlapping development of multiple fields may become the development direction of flexible electronics. How to conduct multi-field cross-cooperation is the basis of graphene moving towards functionalization and productization. However, there is a lack of product research in graphene at present, but with the development of technology, such as cross-integration with solar conversion, energy storage, display, and motion control system, it may promote product functional research, optimize performance and enrich functions as soon as possible. In addition, the preparation of flexible extensible films is of positive significance to improve the competitiveness in the field of flexible electronic devices in China. The development of excellent flexible thin films with rich resources, low cost, electrical conductivity, ductility, and mechanical properties is the future development trend of the flexible electronics industry. In addition, other study shows that when the two-dimensional plane structure of the graphene itself increases its size, the area is multiplied and the folds appear. The forces prevent sliding at the interface between layers and graphene and substrate. Therefore, it is a very important topic to explore new models, such as the composite structure of metal thin film and conductive polymer material thin film, metal thin film and conductive polymer material thin film and graphene thin film, and to study its film formation mechanism and key manufacturing technology [25].

4. Conclusion

As the materials industries developing so rapidly today, materials with more extraordinary properties is really necessary. Then the analysis of internal structure of the graphene makes scholars realize that graphene has many excellent properties such as flexibility, transparency, electrical conductivity and great mechanical properties which are really helpful in flexible electronics and stretchable devices. Recently, lots of researches have shown the promising development future in materials and many other areas. Graphite and graphene-related materials are widely used in battery electrode materials, semiconductor devices, transparent displays, sensors, capacitors, transistors and other aspects. In view of the excellent properties and potential application value of graphene materials, a series of important progress has been made in chemistry, materials, physics, biology, environment, energy and many other disciplines. However, there are still challenges that need to be overcomed in real-world application. For instance, lower cost, better properties and larger spread of use are all the ambition we pursuit. To deal with problems, graphene with uniformity and high electrical conductivity should be generated in the future. In conclusion, the application of graphene has a positive significance in the electronics field, but there is still a long way to go to overcome the difficulties.

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