Graphene and the Applications in Graphene-Based Flexible Sensors

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Abstract. The combination of biomedicine and intelligent technology has promoted the development of flexible sensors. This type of sensor requires highly flexible materials for modification, achieving the goal of improving wearability and performance. Carbon material is the most commonly used functional material in the world. Graphene, as a material composed of carbon elements, has excellent flexibility and conductivity. The discovery of graphene augmented the family of carbon materials. Graphene, as a two-dimensional material, completed a dimensional hierarchy of carbon material family. As graphene is high flexible with outstanding in-plane conductivity, graphene can be applied in the flexible sensors. Skin is the largest organ in the human body. It is stretchable and flexible. Meanwhile, the skin can perceive external signals. Wearable smart sensors, which exhibit high flexibility, can mimic the tactile sensing capabilities of human skin to detect various stimuli, such as pressure, strain, temperature, and humidity. This work focuses on graphene and graphene based flexible sensors. Its working mechanism and application are discussed. This work will contribute to the development of flexible wearable sensors.

Keywords: Graphene; Sensor; Application; Flexible.

1. Introduction

With the development of intelligent technology, flexible sensors have become a research hotspot in the medical and healthcare fields. The flexible sensor refers to the sensor which is made of flexible materials. This kind of sensor has good flexibility, ductility, and can even be bent freely. The structure of this sensor is flexible and diverse. It can be arranged arbitrarily according to the requirements of the measurement conditions. Therefore, flexible sensors can adapt to complex measurement environments [1-3].

Wearable sensors play a critical role in enabling personalized medicine, as they can continuously collect data on the body. It can enable timely detection of meaningful changes in health status for proactive interventions. Wearable sensors can advance the medical technology.

Graphene is one of the strongest materials in the world. It has very excellent flexibility. Graphene is a two-dimensional (2D) carbon nanomaterial which is composed of carbon atoms with sp^2 hybrid orbitals and a hexagonal honeycomb lattice. There are many different shapes of graphene such as graphene sheets and three-dimensional (3D) porous graphene. It has been extensively studied in the field of materials [4].

When It is combined with graphene, the flexible sensors can obtain an enhancement in the strength of the flexible sensors. In addition, it can be more suitable for different shapes on the human body. Therefore, the graphene-based flexible sensor is strong and suitable for every part of the human body. Till now, a lot of works have been carried out around graphene-based flexible sensors. This flexible sensor which is made by graphene can detect the heart rate. It can also detect the temperature, humidity and chemical substance concentration [5].

Therefore, in this work, graphene-based flexible sensors are studied. Graphene materials and their applications in flexible sensors are discussed.

2. Preparation of Graphene

Graphene can be prepared by the mechanical stripping method. The first graphene in the world is stripped by a sellotape in 2004 [1]. The graphite is stripped into a single atomic plane. It is referred to as a scotch-tape technique. The method is mainly to use an oxygen plasma beam to etch a groove surface of 20 microns to 2 mm wide and 5 microns deep on the surface of high-orientation pyrolytic graphite. After that, it is pressed on a SiO_2/Si substrate with a photoresist. After roasting, the excess graphite flakes are repeatedly peeled off with scotch tape. The remaining graphite flakes are then soaked on the Si wafer in acetone. Afterwards, it is ultrasonic cleaned by using a large amount of water and propanol to remove most of the thicker flakes. In this way, a flake with a thickness of less than 10 nanometers can be obtained. The thin flakes are mainly tightly bound to SiO_2 by van der Waals force or capillary force. Finally, the graphene flakes with a thickness of only a few single atomic layers are selected under atomic force microscopy. This method can obtain graphene sheets with a width of up to micron size, but it is not easy to obtain graphene with independent monoatomic layer thickness. In addition, the low yield is also a limitation of this preparation method.

The oxide reduction method is a preparation method which is often used to obatin graphene. By chemically oxidizing graphite, graphite oxides with carboxyl and hydroxyl groups at the edges are produced. Besides, graphite oxides with epoxy and carbonyl groups between the layers can also be prepared by this method. This process can increase the gap between graphite layers from 0.34 nm to approximately 0.78 nm. Graphene oxides with single-atomic layer thickness are then exfoliated by external force. The three primary techniques for oxidizing graphite are the Hummers, Brodie, and Staudenmaier procedures. In each case, inorganic strong protic acid is used to treat the initial graphite layer, followed by the introduction of tiny strong acid molecules and oxidation using strong oxidants. This method of manufacturing graphene has a high yield and it is frequently used.

Besides, chemical vapor deposition (CVD) is an effective method for the controlled synthesis of graphene. Unlike the case for carbon nanotubes (CNTs), catalyst nanoparticles are not required in the CVD process for graphene synthesis. Instead, a flat substrate is placed in a high-temperature atmosphere of a volatile precursor, leading to the deposition of carbon atoms on the substrate surface to form graphene upon high-temperature annealing. Finally, the metal substrate is removed using a chemical etching process, yielding isolated graphene sheets. This method has been able to successfully prepare single or multilayer graphene with an area of up to square centimeters. The biggest advantage of this method is that it can make large-area graphene [2].

3. Graphene-Based Flexible Sensors

There are lots of types of graphene-based flexible sensors such as pressure sensors, temperature sensors, humidity sensors and gas sensors [5-7]. These four sensors exhibit widely applications.

For pressure sensors, it can be installed in the car wheels. The sensors can detect the pressure in the car wheels to prevent explosion once the air pressure in the car wheels is too high. It can greatly increase the safety of the drivers. Moreover, the flexible sensors made by graphene have good flexibility that it can fit different types of car wheels.

For the temperature sensors, it can detect the temperature outside, and it can tell people the corresponding information. Besides, the flexible sensors produced by graphene can be applied in more scenes. For example, the flexible temperature sensors can be used on the human body. The sensors can detect the temperature of the human skin and judge if the human has disease. This sensors made by graphene can be fitted to the human body very well. It can make the human more comfortable. The humidity sensors can detect the humidity in the air. It is mostly used in the whether prediction. The humidity sensors produced by the graphene can also be fitted in different scenes. The graphene endows humidity sensors with more functions.

For the gas sensors, they are used in the factories or some machines. The sensors can detect the danger gas to make sure the workers are safe. The flexible gas sensors made by graphene can make the sensors more durable.

3.1. Working Mechanisms of Flexible Sensors

There are four working mechanisms of flexible sensors.

Piezoresistive sensors are very sensitive, with a vast detecting range. They are easy to prepare, and they can respond quickly. They can transform changes in material resistance brought on by external stimuli into electrical signal output. They have also been extensively explored. Changes in the shape of the sensitive components, modifications to the energy level structure of semiconductors, variations in the particle spacing of composite material, and changes in the contact resistance between the two materials are the main factors affecting the resistance change of piezoresistive sensors [3].

The function of this sensor is similar to capacitors. They alter the capacitance in response to an object approaching the sensor, which modifies the oscillator circuit and enables object detection. Miniature, cylindrical, high-temperature, and analog capacitive sensors are among the sensor types that are often utilized in many applications. They can be applied in realms including proximity, level, position, and humidity measurement. Most capacitive sensors have a dielectric layer sandwiched between two electrodes, which changes capacitance between the plates when subjected to pressure or strain due to their deformation. However, since the change in capacitance of a parallel-plate capacitor is relatively small, these sensors tend to have low sensitivity.

The piezoelectric effect refers to the generation of voltage in a material in response to external mechanical stimulation. The anisotropic crystals develop a dipole moment when subjected to external pressure, resulting in a macroscopic potential within the crystal. Piezoelectric sensors convert dynamic pressure changes into measurable currents, which are utilized in wearable sensing applications to detect sound vibrations or pulse beats. It can offer advantages of high sensitivity and fast response. Graphene, which is more flexible than other piezoelectric materials, displays broader applications in flexible piezoelectric sensing.

Compared to resistive and capacitive sensors, transistor-based sensors have benefits including low crosstalk, high-throughput sensing, and downsizing. It can make them especially well suited for flexible sensing applications. A typical field-effect transistor (FET) consists of source, drain, gate, semiconductor layer, and dielectric layer. The unique current amplification property of transistors enables FET sensors to distinguish complex signals, making them an ideal choice for sensing weak signals. Furthermore, each component of an FET, including the gate electrode, dielectric layer, semiconductor layer, and drain-source electrodes, can potentially serve as the active sensing layer, thereby providing more possibilities for integrating multiple sensing functions.

3.2. Applications of Graphene-Based Flexible Sensors

The ideal graphene consists of a single layer of carbon atoms, with each carbon atom in it serving as an active site for sensing stimuli. Graphene possesses numerous properties that make it suitable for sensing applications. Firstly, it has a large surface area, high electron mobility, and good conductivity, enabling it to detect various stimuli. Secondly, graphene is the thinnest two-dimensional material, with a low mass, excellent mechanical flexibility, facile processability, and good compatibility with large-area flexible solid substrates, making it ideal for fabricating flexible sensors. Finally, graphene may be combined with other functional materials to produce flexibility and stretchability. Improve sensitivity and selectivity towards particular analytes, and enable the development of multifunctional graphene-based sensors.

3.2.1 Graphene-based flexible pressure sensors

Graphene-based piezoresistive sensors are the most widely studied pressure sensors. The deformation of the sensitive layer under pressure leads to changes in graphene resistance. A fast shift in the contact resistance of the material surface is essential to obtain excellent perceptual performance, since resistance changes can be caused by both the deformation of individual graphene sheets and the contact between them. Constructing porous structures can improve the performance of piezoresistive pressure sensors. It is evidenced by the good pressure sensing capabilities of three-dimensional porous graphene structures such as foam, sponge, aerogel, and hydrogel.

3.2.2 Graphene-based flexible temperature sensors

Skin can detect mechanical stimuli and temperature changes. In addition to identifying illnesses like fever, heatstroke, and infections, wearable sensing systems must also continually track variations in body temperature to represent physiological states [4]. Temperature sensors can be fabricated using thermistors, thermoelectric effects, or optical means, among which thermistors are the most common. Thermistors can be classified as positive temperature coefficient (PTC) or negative temperature coefficient (NTC) based on whether resistance increases or decreases with temperature rise. Graphene possesses a positive temperature coefficient, with resistance increasing as temperature rises. Trung et al. reported a flexible field-effect transistor temperature sensor,which was fabricated on a polymer substrate by reducing graphene oxide. The sensor exhibits high temperature sensitivity within a temperature range of 30^{o}C to 80^{o}C and it is capable of detecting small temperature changes as low as 0.1^{o}C.

3.2.3 Graphene-based flexible humidity sensors

Humidity sensing is the conversion of the number of water molecules in the environment into a measurable signal for detection purposes. Electrostatic doping of the graphene layer due to the interaction between the polar moment of water and the charge impurities in the substrate accounts for the high humidity sensitivity of resistive graphene humidity sensors. When graphene is exposed to a humid environment, its bandgap increases with the increase in the number of adsorbed water molecules, leading to an increase in its resistivity [7]. The resistance change is also affected by the different locations of water molecules adsorbed on graphene defects.

3.2.4 Graphene-based flexible gas sensors

Ideal graphene has a strong gas adsorption capacity. The mechanically stripped graphene can even sense the adsorption of individual gas molecules. Structural design and optimization of graphene can lead to better gas adsorption and detection sensitivity [6]. Theoretical studies have shown that the adsorption of different gas molecules on the surface of graphene will introduce doping states. Common gas molecules such as ammonia, carbon monoxide and ethyl alcohol act as electron donors for graphene, while others such as nitrogen dioxide, water, oxygen and iodine act as electron acceptors. If the remaining oxygen-containing groups on the surface of graphene are electron-sucking, the adsorption of reducing gas will lead to the depletion of holes in the valence band, thereby reducing the conductivity of graphene. Conversely, the adsorption of oxidizing gases leads to an increase in the hole concentration and conductivity of graphene.

4. Conclusion

In summary, significant advancements in the study of graphene have been achieved. It has drawn a great deal of interest in the domains of chemical power supply, optoelectronic devices, and heterogeneous catalysis. Nonetheless, the large-scale, inexpensive, and controlled synthesis and processing of graphene is essential to its study and use. Future research should focus on preparing high-quality graphene materials in large quantities and at low cost. It is evident that the mechanical stripping method will not be able to meet the demands of future industrialization. Graphite oxide reduction can produce a large amount of graphene at a relatively low cost. But strong oxidants seriously damage the electronic structure and crystal integrity of graphene, which affects its electronic properties and limits its application in microelectronic devices to some extent. Chemical deposition can produce graphene with a large area and excellent performance. However, the immaturity of the current process and the high cost limit its large-scale application. The functionalization of graphene has advanced significantly in recent years. However, in order to fully utilize its excellent properties and broaden its application fields, new functionalization techniques must be developed and improved. These techniques include ways to control the number of functionalized sites and groups. The ways to develop functionalization techniques that preserve the good intrinsic properties of graphene as much as possible during the functionalization process are also worthy of exploring.

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