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# Research of Graphene Electronics and its Applications

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## Abstract:

Imagine a material as thin as a single atom, yet stronger than steel and more conductive than copper. This is graphene, a two-dimensional wonder material with a unique monolayer hexagonal honeycomb lattice structure. Its exceptional electrical properties, particularly its high carrier mobility, have sparked widespread interest in the scientific community for potential applications in electronics.However, because its conduction and valence bands intersect at the Dirac point, it behaves as a zero-bandgap semimetal, limiting its use in electronic devices. Therefore, opening a bandgap has become a focal research task in the scientific community. This paper explains the inherent conductivity of intrinsic graphene and summarizes how doping can theoretically further enhance its conductivity. Through further research on the development of graphene doping methods, this article primarily introduces how adsorption doping and lattice doping techniques can open the bandgap of graphene. It analyzes the stability of different doping types to achieve their application in nano-electronic devices.

**Keywords:** Graphene; Bandgap; Doping.

## 1. Introduction

Graphene's exceptional properties, particularly its high electronic mobility and excellent electrical conductivity, have made it a focal point of scientific research. Its potential to replace existing materials in various applications promises to usher in a new era of technological breakthroughs across multiple fields. In a breakthrough that would later earn them the Nobel Prize, Kostya Novoselov, Andre Geim, and their team successfully isolated graphene in 2004. Their method was surprisingly simple yet ingenious: they used adhesive tape to repeatedly peel off layers from high-quality graphite, eventually achieving samples just a few atoms thick [1].

This groundbreaking discovery unveiled graphene's exceptional electrical properties, particularly its high carrier mobility. Under optimal conditions, such as low temperatures, graphene's carrier mobility can reach an astonishing 250,000 cm²/(V*s), far surpassing conventional materials. This property makes graphene extremely promising for electronic applications. However, a significant challenge emerged: pristine graphene is a zero-bandgap semimetal, which limits its direct use in many electronic devices. As a result, creating a bandgap in graphene became a critical research focus. A significant breakthrough came when Taisuke Ohta and his team demonstrated an electronic switch using graphene just two atoms thick. Their innovative approach involved potassium doping, which proved to be an effective method for bandgap engineering [2]. This article will explain the inherent conductivity of graphene, selecting doping methods as the primary research approach. It summarizes how doping methods can enhance the inherent conductivity of graphene and primarily discusses the principles and effects of two types of doping formed by two doping methods on opening the bandgap of graphene.

## 2. Result and Discussion

### 2.1 Methodology

Based on the conductivity formula $\sigma = ne\mu$, the conductivity of graphene can be calculated [3-5]. However, since conductivity is affected by factors such as temperature, the calculation of conductivity should involve derivations using two available graphene conductivity models, the Kubo formula, and the QFT-b model, and comparisons are made between them by Pablo Rodríguez-López and Pablo Rodríguez-López [6][7]. Through the conductivity formula σ=neμ, it can be understood that conductivity is jointly controlled by the electron mobility (μ) and carrier concentration (n). Although the electron mobility value of graphene is 250,000 cm²/(V·s), which is far higher than copper's 23 cm²/(V·s), its carrier concentration is much lower than that of copper. The use of doping methods can increase the carrier concentration in graphene. In addition to this, doping methods not only enhance the conductivity of graphene for practical applications, but also open the bandgap of graphene. The doping method of graphene is similar to the doping effect of semiconductors, which can be generally categorized into adsorption doping and lattice doping, and each doping method is also categorized into two types: n-type and p-type [8].

## 2.2 Advancements in Enhancing the Conductivity of Graphene

Intrinsic conductivity is nothing short of remarkable. At room temperature, it can reach an astonishing $6\times10^6$ S/m, and under optimal conditions, it can even soar to $10^7$ S/m. When K. S. Novoselov and his team first unveiled graphene to the world, they reported its extraordinary ambipolar electric field effect. They found that graphene could achieve a carrier concentration as high as $10^{13}$ per square centimeter, coupled with a room-temperature mobility approaching 10,000 square centimeters per volt-second [1]. In their research on graphene conductivity modeling, Pablo Rodríguez-López and his team made an interesting discovery. They found that two different models - the Kubo formula and the QFT-b model - produced almost identical results for longitudinal conductivity. The slight differences observed could be attributed to the use of different regularization parameters [7]. This consistency across different models reinforces this paper understanding of graphene's conductivity properties. In using doping methods to increase the applied values of theoretical and practical conductivity of graphene, research by Liuyan Zhao and others has found that the impact of a single nitrogen dopant on the electronic structure of graphene is strongly altered only within a few lattice spacings of the nitrogen doping site. This result indicates that chemical doping methods not only ensure the quality of graphene but also increase its carrier concentration [9]. As this paper increase the concentration of carriers in graphene, a fascinating phenomenon occurs. The interactions between these carriers become more intense, which leads to enhanced scattering effects. This scattering slows down electron motion, resulting in a decrease in electron mobility. However, counterintuitively, this doesn't negatively impact graphene's overall performance. In a network structure, despite the reduced mobility, the increased carrier concentration actually enhances graphene's conductivity.

## 2.3 Zero-bandgap

As a zero-bandgap semimetal, the valence and conduction bands of graphene intersect at the K(K') point in the Brillouin zone. This zero-bandgap structure is susceptible to surface adsorption and lattice doping, which causes the Fermi surface of graphene to move up and down at the Dirac point (Fig. 1). The bandgap is then introduced.

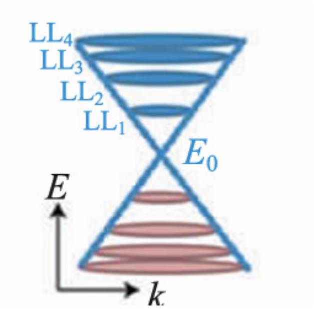

**Fig. 1 Electronic structure of graphene with quantized Landau energy levels, conduction and valence bands conically distributed, intersecting at the Dirac point [10].**

## 2.4 Two Doping Solutions

### 2.4.1 Adsorption doping method

The adsorption doping method primarily involves charge transfer between graphene and the dopant. The direction of charge transfer depends on the relative position of graphene's Fermi energy level to the dopant's lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). P-type doping occurs when the dopant's LUMO is lower than graphene's Fermi level, causing electrons to move from graphene to the dopant. Conversely, n-type doping happens when the dopant's HOMO is higher than graphene's Fermi level, resulting in electron transfer from the dopant to graphene.

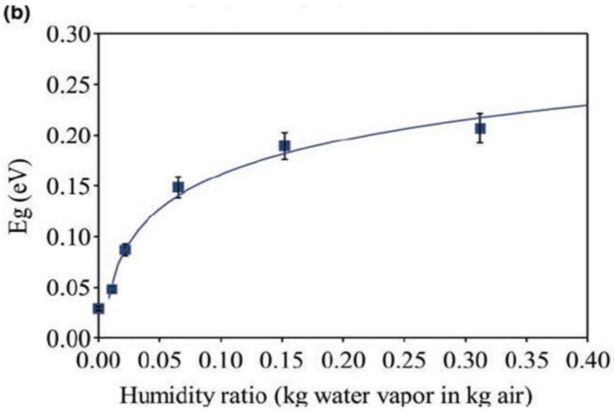

**Fig. 2 Absolute humidity versus bandgap curve [11].**

The atmosphere contains molecules of $O_2$ and $H_2O$. These molecules possess a strong electron-withdrawing effect, which enables them to perform p-type doping on graphene [12]. This method is adsorptive doping. Yavari and colleagues found that a bandgap can also be introduced on the surface of graphene under certain humidity conditions [11]. With the increase in absolute humidity (the mass of water contained in each kilogram of dry air), the bandgap also increases until it stabilizes, with a maximum bandgap reaching 0.206 eV (Fig. 2). The adsorption process is typically reversible because it primarily involves physical electron transfer. This means that when graphene is placed in a vacuum, the bandgap reverts to its initial value of 0.029 eV. This reversibility is a key characteristic of adsorption doping, distinguishing it from other doping methods. However, AC Crowther et al. found that, adsorption of the strongly oxidizing molecule $NO_2$ on the surface of 1□10 layers of graphene can lead to strong electron transfer, where electrons are transferred from graphene to $NO_2$, doping the graphene layer with holes that can move away from the domains, forming a p-type doping that is more stable compared to the adsorption of other weak oxidants [13].

Interestingly, adsorptive doping in graphene tends to favor p-type characteristics. This preference stems from graphene's inherent reductive chemical nature, which makes it somewhat of an electron 'donor'. In other words, graphene is more inclined to give up its electrons, naturally leading to p-type doping. The real challenge lies in reversing this trend - coaxing electrons to move from the dopant to graphene, which is crucial for achieving n-type doping [14]. The quest for n-type doped graphene had its first breakthrough with graphene grown on silicon carbide (SiC) substrates. This method, known as SiC epitaxy, unexpectedly resulted in n-type doped graphene. The mechanism behind this was quite fascinating: a small fraction of electrons from the SiC substrate migrated into the graphene layer, effectively creating an n-type doping effect [15]. This discovery opened up new avenues for exploring n-type doping in graphene. However, it is not infeasible to transfer electrons from the dopant to graphene, and some strong electron donors can successfully transfer electrons to graphene to form n-type adsorptive doping. For example, Wei et al. found that 2-(2-methoxyphenyl)-1, 3-dimethyl-2, 3-dihydro-1H-benzimidazole (o-MeO-DMBI) is a strong electron donor, which can apply its own electrons to graphene surface when adsorbed on the surface of graphene to cause n-type doping [16]. According to Fig. 3, the Fermi energy level of graphene rises with the increase of o-MeO-DMBI adsorption concentration. When o-MeO-DMBI is 0 mg/mL, graphene does not maintain its zero bandgap but seems to be p-type doped, probably because gases such as $O_2$ in the air, as mentioned earlier in this paper, can seize electrons in graphene, and this phenomenon occurs at any time. The doping effect of o-MeO-DMBI exhibits a concentration-dependent behavior. At low concentrations (0.01-0.1 mg/mL), it merely compensates for the electrons lost to atmospheric gases, resulting in no net doping. However, when the concentration exceeds 1 mg/mL, o-MeO-DMBI provides excess electrons, leading to observable n-type doping. This concentration threshold demonstrates the delicate balance required for effective n-type doping in graphene.

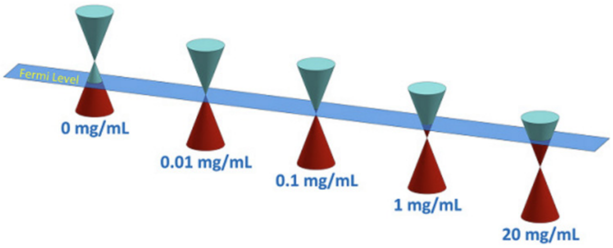

**Fig. 3 Graphene Fermi surface shifts upward with increasing o-MeO-DMBI molecule concentration [17].**

### 2.4.2 Lattice doping method

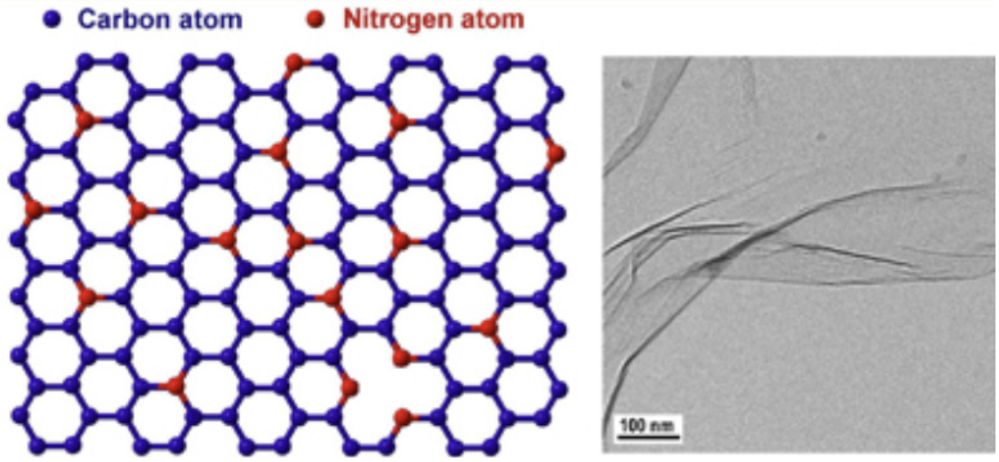

**Fig. 4 Schematic diagram of nitrogen-doped graphene and its scanning electron micrographs [18].**

Lattice doping in graphene is akin to a molecular-level game of musical chairs. The basic idea is to swap out some of the carbon atoms in graphene's honeycomb structure with other elements. This process is most effective when the graphene structure is still in its formative stages, allowing foreign atoms to slip into the lattice more easily. The result? A graphene sheet with strategically placed 'impurities' that fundamentally alter its electronic properties. Generally speaking, it is easy to form n-type doping with group V atoms and p-type doping with group III atoms. As the doping concentration increases, the bandgap of graphene increases. Preparation of nitrogen-doped graphene by CVD method for the first time by Dacheng Wei [17]. However, the method tends to form a few layers of graphene, and monolayers are occasionally found. Moreover, its sites are not controllable for selective doping. Zhang et al. inlaid a nitrogen source and a carbon source on a metal and grew nitrogen-doped graphene by a separation method, which was doped at the same time as the carbon species were separated, so that C could be replaced by N [18]. Nitrogen-doped graphene is shown in Fig. 4. This method achieves controllable doping concentration and doping position, making the bandgap of graphene tunable. Some et al. found that in addition to n-type doping of graphene by nitrogen atoms, phosphorus atoms can also n-type dope graphene and show greater stability in oxygen environments [19].

Compared to n-type lattice doping, the development of p-type lattice doping has been slower. Initially, p-type doping was mainly based on boron atoms of the third main group as dopant. Zhu et al. prepared boron-doped graphene using CVD with ethanol and boron powder as precursors [20]. However, this method is still difficult to control due to the fact that the rate of thermal decomposition of ethanol and boron powder does not coincide with the rate of synthesis of boron doped graphene. Wang et al. used $C_6H_7BO_2$ as a stand-alone precursor molecule and provided both carbon and boron sources to prepare large-area, high-quality boron-doped graphene [21].

In the realm of lattice doping, n-type doping often takes center stage. There are two key reasons for this preference. Firstly, n-type dopants, being multi-electron entities, generously donate electrons to graphene. Secondly, these donated electrons move more swiftly through the graphene lattice compared to the 'holes' created by p-type doping. The result? A significant boost in electron mobility, which is a crucial factor in enhancing graphene's electronic performance.

## 3. Conclusion

Numerous studies have unveiled graphene's astonishing conductivity, which can soar to a remarkable $6\times10^6$ S/m. This figure places graphene in a league of its own among conductive materials. Even more intriguing is the potential to push this boundary further through strategic doping techniques, hinting at possibilities that could redefine this paper understanding of material conductivity. However, the high conductivity of intrinsic graphene is difficult to apply in practical electronics. The zero bandgap of graphene leads to large currents even at the charge neutrality point, limiting the switching ratio. The key to unlocking graphene's potential in electronics lies in modifying its energy band structure. By introducing a bandgap, this paper can transform this wonder material into a practical semiconductor. Doping emerges as the most straightforward approach to achieve this transformation. This process involves tweaking graphene's natural lattice structure or electronic properties, which in turn shifts its Fermi level. Depending on how this paper manipulate this level, this paper can achieve either P-type or N-type doping, opening up a world of possibilities for graphene in semiconductor applications. The world of graphene doping is diverse and complex. Different dopant molecules can steer graphene towards different doping types, each with its unique properties. However, not all doping methods are created equal when it comes to stability. Some doping processes occur spontaneously but lack longevity, while others offer more enduring effects. This variability has led researchers to focus intensively on developing doping methods that are both stable and controllable - a crucial step towards realizing graphene's full potential in practical applications.

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