

Study on Physical Properties of Graphene Doping Based on First Principles

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ABSTRACT: Because of its unique two-dimensional structure and excellent physical and chemical properties, graphene has become a research hotspot of nanometer material science since it has been discovered. In order to have a deeper understanding of graphene's electronic properties and thus to have an effective regulation on their electronic structure, this study analyzes several different kinds of electronic properties of little doping graphene, and gets some meaningful results. Through first principles density functional calculations this paper mainly gets the nickel atoms doping band structure (or electronic structure) and dielectric properties of double-layer and three-layer graphene. Firstly, this paper systematically reviews the research status of graphene, including the discovery and preparation, morphology, physical properties and potential applications. And on this basis, this paper selects the appropriate research method --first-principles method based on density functional theory to build a reasonable structure model for depth study on doping effect of the electronic properties of graphene, investigates its electronic band structure and charge distribution characteristics, and gives a physical mechanism.

KEYWORDS: Graphene; First-principles method; Doping; Dielectric properties; Density functional theory.

INTRODUCTION

In recent years, the successful preparation of graphene added carbon family a new two-dimensional member. The research on graphene was firstly began in 1947 in Canada, a theoretical physicist P.R. Wallace firstly studied the electronic structure of graphite and graphene in theory, but Lev Davidovich Landau and Peierls believed that the theory of strict two-dimensional quantum system would be of instability for the thermodynamic fluctuation and 30 years after the Mermin's judgment about the interaction between atoms would destroy the long-range order of system does not support the existence of strict two-dimensional quantum system in theory, and supported by experimental results of the system. Until 2004, Novoselov and Geim from the University of Manchester, who used mechanical peeling method, obtained a stable presence of graphene structure, led to the research boom of this new type of two-dimensional carbon material. Therefore, 2010 Nobel Prize in Physics was awarded to the two physicists Prof. Andre Geim and Prof. Konstantin Novoselov from University of Manchester in England [1].

Graphene is defined as carbon atom single layer or graphite single layer. Before graphene was discovered, structure based on carbon such as graphite, research on Carbon Nanotube and Fullerene has been extensive in theory and experiments. Graphene is considered to be structural unit that all based on carbon system, curly and cluster of two-dimensional graphene may form one-dimensional carbon nanotubes and zero-dimensional fullerenes, and its multi-layer stacking may constitute graphite [2]. The reason graphene can exist stably at room temperature rather than theory predicts instability to decomposition is that outside three-dimension about 1nm on graphene exist the Ripple structure. Observed in this experiment, the elastic potential energy produced by curved structure may suppress thermal dynamic vibration within the system, so in finite temperatures the system can still maintain internal stability. Graphene has been unexpectedly discovered under experimental conditions, and with its subsequently extensive carried out of theoretical and experimental work, it enriches the study content of modern physics and adds new vitality.

Graphene is a two-dimensional regular hexagonal honeycomb lattice structure consisting of single-layer sp² hybridized carbon atoms, it can curl into a zero-dimensional fullerene, one-dimensional carbon nanotubes or stack into three-dimensional graphite, therefore graphene is rich and fresh physical phenomena existed in basic unit graphite refining that may build other dimensions carbonaceous material, which has important theoretical research value and

wide range of applications [3]. Graphene has a high mechanical strength, what is more peculiar is its unique electronic structure and high carrier mobility characteristics. The valence band and conduction band of graphene will be intersected at the top corner of the hexagonal Brillouin zone, which is a semiconductor of zero energy gap, electrons and holes in the vicinity of the top exhibit linear dispersion relation, and the motion equations are similar with Dirac equation satisfied by effective quality zero fermions. This phenomenon leads graphite refining has the emergence of quantum Hall effect, minimum quantum conductivity, quantum interference effects and other fresh electrical properties. Through radiation, ion implantation, doping and other means to generate vacancies, replace atoms, absorb atoms and other defect structures in graphite refining to make graphene generate a very strong magnetic. In addition to be used to design the magnetism and spin electronics devices in nanometer level, the graphene can be processed into strips, triangles and other certain shapes by candle carved and other methods. In short, the excellent mechanical, electrical and magnetic properties make graphene exhibit many excellent performances in composite materials, field emission materials, bio-materials, sensor materials, high performance nano-devices, energy storage, catalyst carrier, and many other fields, which has broad application prospects. Firstly, this paper systematically reviews the research status of graphene, including the discovery and preparation, morphology, physical properties and application prospect. And on this basis, this paper selects the appropriate research method -- first-principles method based on density functional theory to build a reasonable structure model for depth study on doping effect of the electronic properties of graphene, investigates its electronic band structure and charge distribution characteristics, and gives a physical mechanism [4].

FIRST-PRINCIPLES THEORETICAL BASIS

The so-called first-principles calculation refers to the basic principle of ab initio calculation, solving the Schrödinger equation for many-particle system. In calculation process, without the use of any empirical parameters, but only need the help of five fundamental physical constants -- electron charge e , electron mass m_0 , the speed of light c , Planck's constant h and the Boltzmann constant k_B , then the physical property and condition of Micro System can be get.

Expression of the Schrödinger equation for many-particle system is:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + U(r_1, r_2 \dots r_N) \Psi$$

When there is no relation between potential field U of the system and time, the solution to the equations described above can be simplified by method of separation of variables, which can be drawn:

$$\left[-\sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + U(r_1, r_2 \dots r_N) \right] \Psi = E \Psi$$

Density Functional Theory (DFT)

DFT = Density Functional Theory: a new theory that uses the electron density distribution $n(\mathbf{r})$ as the basic variable to study ground state properties of multi-particle system. It provides the calculation frame of first-principles or ab initio. In this framework a wide range of energy band calculation can be developed. In condensed matter physics, such as: material electronic structure and geometry, phase transition in solid and liquid metals, and so on, all these methods can be developed into molecular dynamics methods that accurately calculated by quantum mechanics. DFT adapted to the number of different types of applications: (1) the relationship between the electronic ground state energy and atomic (nuclear) positions can be used to determine the structure of molecules or crystals; (2) when the atom is not in its equilibrium position, DFT can give the force on atomic (nuclear) position. Therefore, DFT can resolve many problems in atomic and molecular physics, such as (1) the calculation of ionization potentials, (2) the study of vibration spectra, (3) chemical reaction problems, (4) structure of biomolecule and characteristics of catalytic active position, (5) dimensionality reduction.

Hohenberg Kohntheorem

P. Hohenberg Kohn and W. Kohn put forward density functional theory in 1964. The next year, Kohn and Sham deduced Kohn-Sham equation, which makes the density functional theory has been widely used in practice. Thereafter, the density functional theory has been developing rapidly. This theory not only established many theoretical basis that simplify electron problem to single electron equation, but also provided theoretical foundation for how to calculate the single electron effective potential, so it is a powerful tool to calculate the total energy of molecular and solid and electronic structure.

Hohenberg-Kohn theorem: for a common external potential $v(r)$, all of the ground state properties of interacting many-particle system are uniquely determined by the (non-degenerate) ground state electron density distribution $n(r)$. Or: For non-degenerate ground state, particle density distribution $n(r)$ is the basic variables of the system.

Consider a multi-particle system (electronic system, any number of particles), in the external potential and interaction effect Coulomb potential, Hamiltonian is as follows:

$$\hat{H} = \hat{T} + \hat{V} + \hat{U}$$

$$\hat{T} = \frac{1}{2} \int \nabla \Psi^+(r) \nabla \Psi(r) dr$$

Hartree Unit

$$\hat{V} = \int v(r) \Psi^+(r) \Psi(r) dr$$

External Potential

$$\hat{U} = \frac{1}{2} \int \frac{1}{|r-r'|} \Psi^+(r) \Psi^+(r') \Psi(r') \Psi(r) dr dr'$$

Electron density distribution $n(r)$ is:

$$n(r) = \left(\Psi, \hat{n}(r) \Psi \right)$$

External potential $v(r)$ is the only functional of $n(r)$. That is it is only determined by $n(r)$. In other words, if there is another $v'(r)$, it is not possible to produce the same $n(r)$. T and U are also the only functional of $n(r)$. Define:

$$F[n(r)] = \left(\Psi, (T + U) \Psi \right)$$

This is a universal function, and is suitable for any particle system and any external potential. So the ground state energy functional of the entire system can be written as:

$$E[n(r)] = \int v(r) n(r) dr + F[n(r)]$$

Second, if $n(r)$ is the correct density distribution in the system, the $E[n(r)]$ is the lowest energy, that is the ground state energy of the system.

There is a solution using the properties of functional extremum to solve gross energy problem. While the Kohn-Sham equation proposed by Kohn and Sham makes density functional theory have been widely used in practice. Kohn-Sham equation written F as the sum of two parts of functional, energy functional can also be written as:

$$E[n'] = T_s[n'] + \int v(r) n(r) dr + \frac{1}{2} \int \frac{n(r) n(r')}{|r-r'|} dr dr' + \int n(r) \varepsilon_{xc}[n'(r)] dr$$

Compared with the real energy functional, the above formula still has some errors, so an unknown form functional term is introduced for error correction. Therefore, the final gross energy functional is expressed as:

$$E[n'] = \sum_{i=1}^N \varepsilon_i' - \int v(r) n'(r) dr + \int v(r) n'(r) dr + \frac{1}{2} \int \frac{n(r) n(r')}{|r-r'|} dr dr' + E_{xc}[n']$$

Electron density distribution $n(r)$ is as the basic variable to study then ew theory of multi-particle ground state properties.

PHYSICAL PROPERTIES OF GRAPHENE DOPED WITH NICKEL

Model Building

The reason to carry out a nickel-doped with double layer grapheme is that since the (111) (001) (111) and (111) plane spacing of transition metal nickel (face-centered cubic structure) are respectively 2.48Å, 2.51Å, 2.49Å, 2.62Å, so the lattice constants are equivalent with graphene (2.46Å), at the same time, because of the metallicity of intrinsic monolayer and double layer graphene, a mixed system (that is doping system) will not significantly change the structure of acceptor system for different atomic species, which is considered from structural equivalence’s point of view. Second, because of the inter lamellar Van Der Waals interaction of double layer intrinsic graphene itself so that two energy band around Fermi level are separated, then if the strong coupling between non-similar atoms of the closed lattice constant is taking into consideration, without the situation of significantly changing the system structure, it is expected that the introduced external atoms will have an impact on the dispersion relation near the Fermi level, which is considered from the perspective of the interlayer interaction. Do pin gone nickel atom into a one to four double layer graphene cells (interlayer). Through a simple calculation to get the most stable position of a single nickel atom in a graphene cell, and through simple calculation to get corresponding system gross energy that the nickel atoms above inter laminar carbon atoms, above inter laminar carbo cycle center and above two carbon atoms center to give nickel atoms a stable position between double layers that tend to above two carbon atoms center in a single layer. So any of the below doping concentration will fix the most stable position (Top Site) of nickel atoms. A double layer primitive cell doped with nickel atoms is shown as Figure 1.

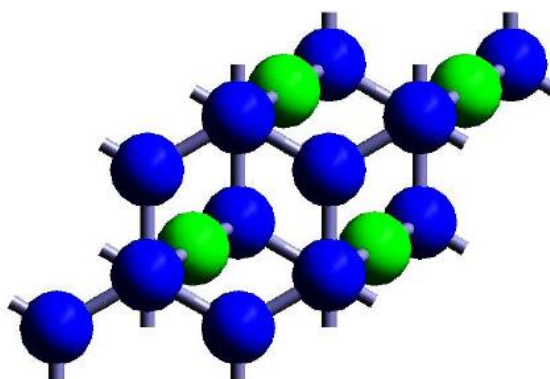


Figure 1. A double layer primitive cell doped with nickel atoms.

Calculation Results

System band structure and density states by calculation are shown in Figure 2, for convenience and intuition, the system Fermi energy level has been selected as the zero point (because of potential relativity). The top filled band below Fermi energy level is the valence band, the lowest empty tape is conduction band. System density is shown on the left in Figure 2, noted that near the Fermi energy level within a certain energy interval corresponds to the density is zero, which is coincide with the system band diagram. In this figure, the lowest point of conduction band and the highest point of valence band can read out an indirect energy gap of the doping system at this time is about 0.3eV, therefore the doped system exhibits semiconductor properties. The Single primitive cell doped with double layer graphene of a nickel atom near the Dirac point level is shown as Figure 3.

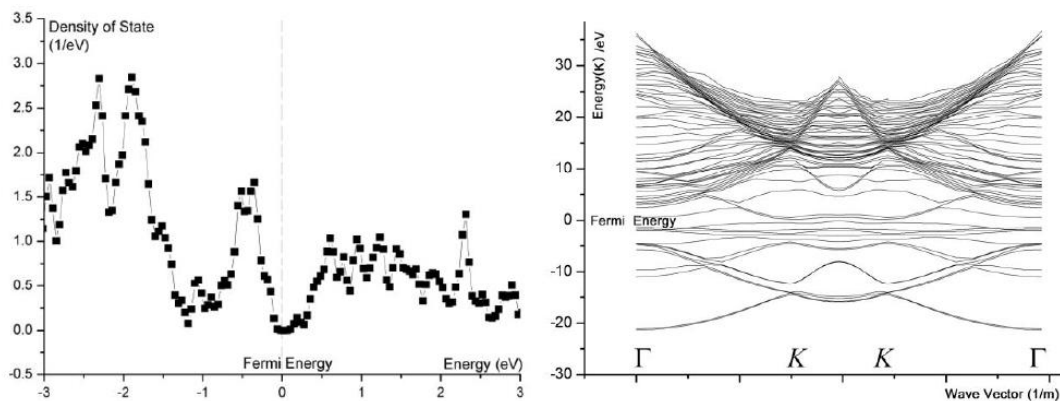


Figure 2. Left one is system energy density states, Fermi level is indicated by a dotted line, right one is the energy band structure.

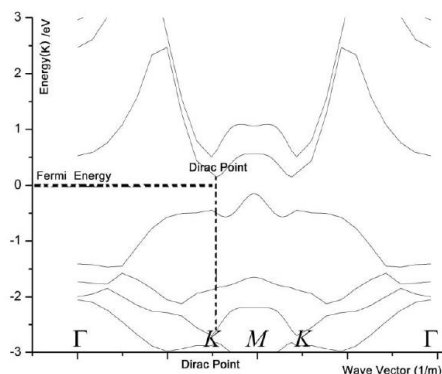


Figure 3. Single primitive cell doped with double layer graphene of a nickel atom near the Dirac point level.

PHYSICAL PROPERTIES OF GRAPHENE DOPED WITH CL

Model Building

Replace hydrogen atom in graphene with Cl atom, using the same method to establish a new graphene-based derivatives.

Calculation Results

In Figure 4, in Fermi level, the bottom of conduction band of intrinsic graphene and valence band top intersected, and in the vicinity of the point K, the energy band structure is approximately in linear distribution, but also get that its band gap is zero. Fermi energy level doped with Cl graphene into the conduction band and the energy band structure is no longer approximately in linear distribution at the K point is for the incorporation of Cl will make C atom sp² hybrid orbital in graphene change.

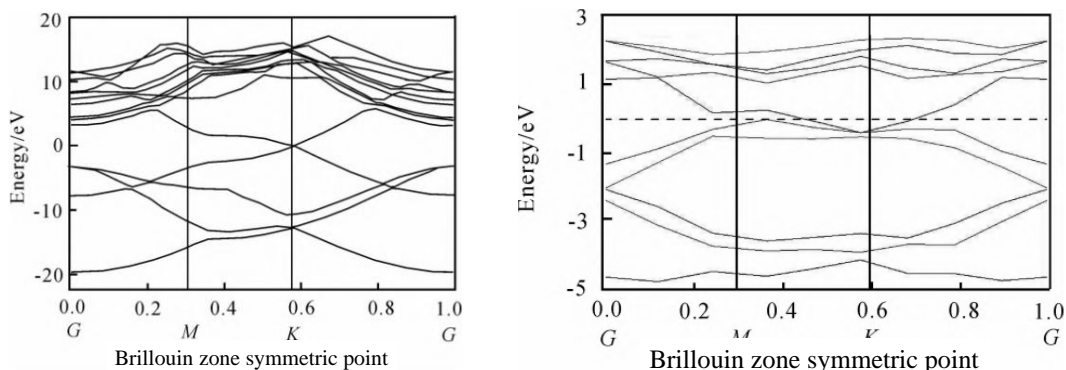


Figure 4. Left one is the intrinsic graphene energy band structure, right one is energy band structure doped with Cl graphene.

In Figure 5, at the Fermi energy level, the gross density of the intrinsic graphene approximately presented 0eV, on both sides of the Fermi energy level, the gross density gradually increased. At Fermi energy level doped with Cl grapheme, density of states appears a peak of about 3.04eV. Thus it can be seen, the doped Cl can cause changes of graphene in the gross density of states distribution.

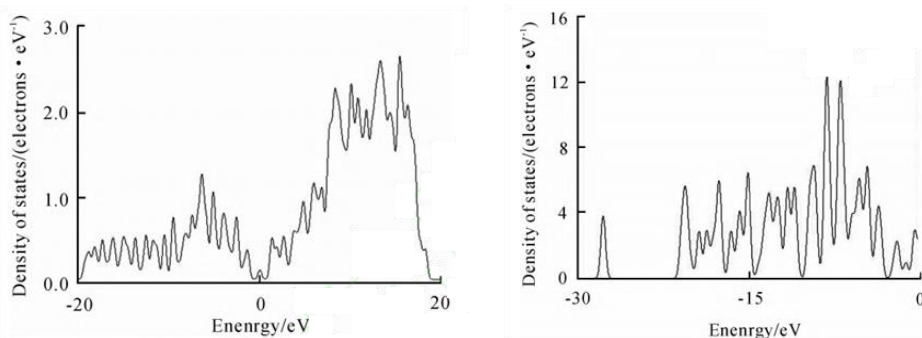


Figure 5. Left one is the gross density of intrinsic graphene, right one is the gross density doped with Cl graphene.

In Figure 6, it can be known by data analyzing that the doped Cl would change the conductivity of graphene, so that the electrical conductivity of graphene may in an enhancement in certain degree.

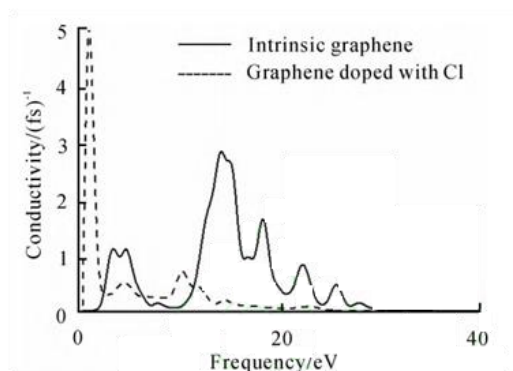


Figure 6. Conductivity.

CONCLUSION

- 1) Doped nickel systems exhibit semiconductor properties.
- 2) Doped Cl changes the conductivity of graphene, so that the electrical conductivity of graphene may in an enhancement in certain degree.

Although only there are only a few years since graphene nanoribbon was found, it has shown an important application potential in many fields: graphene nanoribbon has good conductivity, and in nanoelectronics, it is expected to become a new kind of basic material of the next semiconductor generation.

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