Study on Vacancy Defect Concentration and Hybrid Potential of Metal-based Epitaxial Graphene with Temperature

J H Gao, W Liu[*], X X Ren and R L Zheng

Engineering Research Center of New Energy Storage Devices and Applications, Chongqing Chongqing University of Arts and Sciences, Chongqing 402160, P. R.China

Corresponding author and e-mail: W Liu, liuwei127@126.com

Abstract. This paper investigates the variation of the vacancy defect concentration and hybrid potential of copper and nickel - based epitaxial graphene with temperature by considering the existence of vacancy defects. Moreover, we discuss the impact of atomic non-harmonic vibration on the metal - based epitaxial graphene. First, the concentration of vacancy defects increases nonlinearly with increasing temperature, and the changing rate of the vacancy defect concentration of the metal-based epitaxial graphene with temperature is smaller than that of graphene; Second, the hybrid potential increases with increasing temperature, but not much; Third, the hybrid potential is independent of temperature without considering the atomic non-harmonic vibration which has an important influence on the vacancy defect concentration and the hybrid potential. The higher the temperature is, the more significant the non-harmonic effects are.

1. Introduction

Epitaxial graphene has attracted the attention of researchers worldwide for its application prospect [1-4]. Conductivity is one of the most widely used and most important properties. Beside the experimental research, many literatures have studied the conductivity of epitaxial graphene. In 2013, Z Z Alisultanov studied the electrical conductivity of electron gas on metal-based and semiconductor-based epitaxial graphene in Ref. [5]. In 2015, the variation of electrical conductivity with temperature and thickness of little layer graphene and graphene nanosheets were studied, indicating that the electrical conductivity gradually decreased with increasing temperature in Ref. [6]. However, these studies did not consider the existence of defects such as vacancies. In 2015, Davydov made some discussions about the effect of epitaxial graphene vacancy defects on the density of graphene in Ref. [7], nevertheless, neither the state density of epitaxial graphene on the specific substrate, nor the relationship between the vacancy defect concentration and the temperature are studied. At the same time, the physical model is established without taking the non-harmonic vibration of the atom into account. Therefore, the hybrid potential of graphene is used as a constant which is irrelevant to the temperature, and the experimental results of the electrical conductivity of the epitaxial graphene with temperature cannot be explained well. Because of the preparation

194

conditions and the thermal fluctuations of atoms, there are many defects in the epitaxial graphene, such as vacancies, and the atoms are bound to undergo non-harmonic vibration at the equilibrium position due to the thermal motion of microscopic particles. It is important to theoretically study the properties of epitaxial graphene, such as density of state and conductivity, and investigate the temperature dependent variation of vacancy defects and hybrid potential of epitaxial graphene. However, the reports about the analytical formula with temperature changing have not yet been seen so far.

Therefore, in this paper, by using the solid state physics theory and methods, the variation of the hybrid potential and concentration of vacancy defects in epitaxial graphene with temperature as well as the effects of non-harmonic vibrations on the variation are studied and compared with graphene. This study has theoretical significance for revealing the properties of electronic energy states of materials, and is important for improving material properties and preparing high-performance electronic materials in practical applications.

2. Physical model and harmonic coefficients and non-harmonic coefficients

The system we studied consists of a single layer of grapheme, which has a hexagonal structure by adsorbing N carbon atoms on a planar substrate of metal or semiconductor. The area is $L \times L$, its top and side views are shown in Figure 1. Take any plane of carbon atoms as the origin of coordinates, the monolayer graphene plane is the OXY plane, and the Z-axis vertical up to the graphene plane.
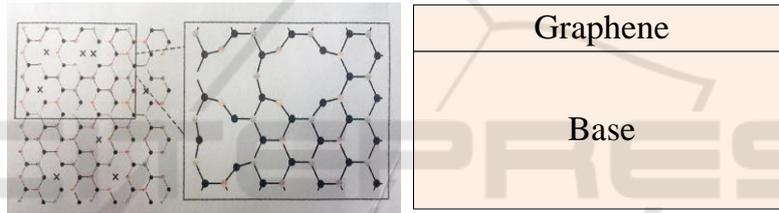
Figure 1. Top view and side view of epitaxial grapheme.

It is supposed that the ions in the metal substrate are stationary and the electrons are in motion. Graphene has N carbon atoms, there are n_0 atoms from the normal position to form vacancies due to the thermal excitation, the vacancy defect concentration is $\alpha = n_0/N$. Since the graphene carbon atoms interacting with each other, S.Yu.Davydov [8] gives the interaction between carbon atoms in graphene $\varphi(d)$

$$\varphi(d) = -V_2[1 + \frac{9R}{V_2 d^{12}} + 5\beta_2(\frac{V_1}{V_2})^2]$$ (1)

Where V_2 is the covalent energy of the sp^2-bond σ bond between two atoms, which is inversely proportional to the square of the bond length (distance between atoms) d: $V_2 = 3.26\hbar^2/md^2 = B/d^2$, where m is the mass of free electrons; V_1 is the metallization energy, $R = 0.154 \times 10^4 (\hbar^2/2m)a_0^{10}$, a0 is the Bohr radius, $\beta_2 = 2/3$, which is a two-dimensional structure constant.

Due to the thermal motion, the graphene atoms perform non-harmonic vibration in the plane. $\varphi(d)$ is expand near the equilibrium position of d_0 and the deviation $\delta = d - d_0$ is very small, there is

$$\varphi(\delta) = \varphi(d_0) + \frac{1}{2}\varepsilon_0\delta^2 + \varepsilon_1\delta^3 + \varepsilon_2\delta^4 + \cdots$$ (2)

where $\varepsilon_2 = \dfrac{20V_2}{3d_0^4}[1 - \dfrac{1}{3}(\dfrac{V_1}{V_2})^2]$ are the harmonic coefficients, the first and second non-harmonic coefficients of graphene carbon atom vibration. According to equation (1):

$$\varepsilon_0 = \frac{4}{d_0^2}V_2[1 - \frac{10}{3}(\frac{V_1}{V_2})^2], \varepsilon_1 = -\frac{16V_2}{3d_0^3}[1 - \frac{5}{3}(\frac{V_1}{V_2})^2], \varepsilon_2 = \frac{20V_2}{3d_0^4}[1 - \frac{1}{3}(\frac{V_1}{V_2})^2] \qquad (3)$$

3. Variations of vacancy defect concentration in epitaxial graphene with temperature

Due to the thermal movement, the carbon atoms of graphene leave the original position to form vacancy defects. If the metal-based epitaxial graphene is to form a vacancy defect, it is necessary to overcome the effect of the metal atoms of the base (set the required energy to be u_2) and overcome the effect of other carbon atoms (set the required energy to be u_1). Therefore, the energy u required to form a vacancy defect can be considered as the sum of the two, that is, $u = u_1 + u_2$, the experimental value $u_1 = 7.0 \pm 0.5 eV$ [9] for the formation of a vacancy defect in graphene has been given, and u_2 can be considered as equal to the bonding energy W of the graphene carbon atoms to the metal atoms of the base, that is, $u_2 = W$. the change in the density of states of the graphene system due to adsorption, the analytical formula W obtained is [10]:

$$W = W_m + W_i \qquad (4)$$

where W_m and W_i are the metal components and ionization components of the adsorption energy.

$$W_m = -\varepsilon_a + (1 + 2\ln 3)\rho_m V_m^2 \{\frac{\varepsilon_a}{\Delta}[\ln\frac{\Delta + 2\varepsilon_a}{2\varepsilon_a} - \frac{\Delta}{2 + 2\varepsilon_a} - \frac{4\Delta + 2\varepsilon_a}{3(\Delta + 2\varepsilon_a)(3 + 2\varepsilon_a/\Delta)}] - (1 + \frac{4\varepsilon_a}{\Delta}\ln\left|\frac{2\varepsilon_a}{\Delta + 2\varepsilon_a}\right|)\}$$

$$W_i = -\frac{1}{4\pi\varepsilon_0}\frac{Z^2 e^2}{4a} \qquad (5)$$

Where $\Delta/2$ is called the half-width of the "pseudogap"[11], $\Delta = 4.76 eV$; $\varepsilon_a = \phi_g - (1/4\pi\varepsilon_0)e^2/4a$, which is the atomic energy level, ϕ_g is the work function of graphene carbon atom, $\phi_g = 5.11 eV$ [11], a is the length of the adsorption bond, which is approximately equal to the sum of the radius r_a of the adsorption atom and the radius r_c of the carbon atom, that is, $a = r_a + r_C$; Z is the charge that the adsorbed atom had before it is adsorbed, $\rho_m = 4/(1 + 2\ln 3)\Delta$; V_m is the interaction energy of the graphene s orbital with the σ bond of the adatom atom p orbital, for graphene-transition metal, $V_m = \eta_{sp\sigma}r_a^{3/2}\hbar^2/m(r_a + r_C)^{7/2}$, the coefficient $\eta_{sp\sigma} = 2.95$, ε_0 is the vacuum dielectric constant.

Graphene forms n vacancy defects, causing the system entropy to increase, the increased amount is $\Delta S = k_B \ln[(N + n)!/N!n!]$, which causes the free energy of the system to change from F_0 to $F = F_0 + nw - T\Delta S$. When the system reaches equilibrium, the free energy is minimal, considering that both N and n are large and N $\gg$ n, the relationship between vacancy defect concentration α=n/N and temperature T is obtained as following:

$$\alpha = \exp(-\frac{w}{k_B T}) \qquad (6)$$

4. Variation of epitaxial graphene hybrid potential with temperature

According to the theory of solid physics[12], the hybrid potential is the average interaction energy of electrons in the hybrid orbital, and it is proportional to the size of the overlapping region of the two-atom hybrid orbitals. The largest direction of the electron cloud of the carbon four-hybrid orbit points to the four corners of the tetrahedron (see Figure 2 a).

Supposed that the electron cloud of a hybrid orbital of carbon atom points to the positive x direction and the maximum direction of a hybrid orbital electron cloud of carbon atom B to the negative x direction, the hybrid orbits of the two atoms almost completely coincide in the direction at equilibrium (see Figure 2 (b)). According to Ref. [4], the hybrid potential $V = \eta \hbar^2 / md^2$, where η is the undetermined parameter which can be obtained from the hybrid potential of graphene given in the literature. In equilibrium, the distance between atoms A and B is d_0. Because of the non-harmonic vibration of atoms, the distance between atoms at any temperature is $d(T) = d_0[1 + \alpha_l T]$, where α_l is the linear expansion coefficient at temperature T. When the temperature is moderate, it is determined by the following formula[13]:

$$\alpha_l = \frac{1}{d_0}[\frac{3\varepsilon_1 k_B}{\varepsilon_0^2 - 3\varepsilon_2 k_B T} - \frac{9\varepsilon_1 \varepsilon_2 k_B^2 T}{(\varepsilon_0^2 - 3\varepsilon_2 k_B T)^2}] \tag{7}$$
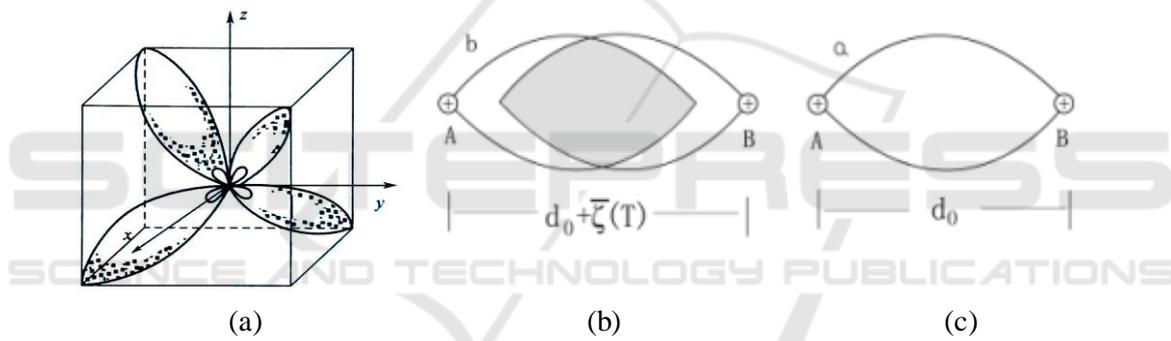
Figure 2. Variation of electron clouds caused by non-harmonic vibration. The hybrid orbital distribution of Carbon sp^3 hybrid orbital distribution (a), direction equilibrium (b) and vibrational (c).

Due to the change in the distance between atoms, the overlap region of the electron clouds in the x-direction hybrid orbitals of the two atoms changes (see Figure 2(c)), causing a change in the hybridization potential. Since the hybridization potential is inversely proportional to the square of the atomic distance, the hybrid potential at any temperature is:

$$V'(T) = \frac{\eta \hbar^2}{md_0^2([1 + \alpha_l T]^2} = \frac{V_0}{(1 + \alpha_l T)^2} \tag{8}$$

From equations (7) and (8), we can see that the non-harmonic vibration of atoms has an important influence on the hybridization potential.

5. Effect of atomic non-harmonic vibration on the variation of vacancy defect concentration and hybrid potential with temperature

The lattice constants $a_{Cu} = 3.61 \times 10^{-10} m$ and $a_{Ni} = 3.61 \times 10^{-10} m$ of copper and nickel are given in Ref. [14], and the atomic radii $r_{Cu} = 1.27 \times 10^{-10} m$ and $r_{Ni} = 1.2445 \times 10^{-10} m$ and the radius of carbon $r_C = 0.77 \times 10^{-10} m$ are obtained from the crystal structure. The interaction energy V_m between graphene and the substrate is obtained. Substituting the data of $\Delta = 4.76 eV$ and $\phi_g = 5.11 eV$ given in Ref. [11] into formula (5), we can get W_m, W_i and $u_2 = W_m + W_i$ for copper and nickel substrates, respectively. Then, the experimental value $u_1 = 7.0 \pm 0.5 eV$ of graphene forming a vacancy defect is given by Ref. [9], and the energy u required to form a vacancy defect is obtained. For copper base $u_{Cu} = 9.6526 eV$; for nickel base $u_{Ni} = 9.6768 eV$. Substituting it with $k_B = 1.38 \times 10^{-23} J.K^{-1}$ into equation (6), the variation curve of vacancy defect concentration α versus temperature for copper and nickel-based epitaxial graphene is obtained, as shown in Figure 3(b) and Figure 3(c) and Table 1. For comparison, Table 1 and Figure 3(a) also show the change of the concentration α of vacancy defect in graphene with temperature.

Table 1. Variation of vacancy defect concentration of graphene, copper - based and nickel - based epitaxial graphene with temperature.

	T/K	700	800	900	1000	1100	1200	1300
α	Graphene($\times 10^{-28}$)	0	0	0	0	0	0.004	7.706
	Copper-base($\times 10^{-38}$)	0	0	0	0	0	0.003	4.120
	Nickel-base($\times 10^{-38}$)	0	0	0	0	0	0.002	3.302

As can be seen from Table 1 and Figure 3, first, the concentration of vacancy defects increases with temperature nonlinearly for both graphene and epitaxial graphene. At T<1200 K, the concentration of vacancy defects almost reaches 0. However, when the temperature is higher than 1200 K, the vacancy defect concentration sharply increases with increasing temperature. Second, At the same temperature, the concentration of vacancies in graphene is much greater than that in epitaxial graphene, and its variation with temperature is much greater. In other words, the graphene is more likely to form vacancy defects and is more readily be affected by temperature.

The equilibrium bond length of graphene carbon atom $d_0 = 1.42 \times 10^{-10} m$, $V_2 = 12.32 eV$, $V_1 = 20.08 m$, R=10.08$eV.(10^{-10}m)^{12}$ are given by Ref. [15], and the simple harmonic coefficient and the first and second non-harmonic coefficients of the graphene atom vibration are obtained from equation (3): $\varepsilon_0 = 3.5388 \times 10^2 J.m^{-2}$, $\varepsilon_1 = -3.4973 \times 10^{12} J.m^{-3}$, $\varepsilon_2 = 3.2014 \times 10^{22} J.m^{-4}$. Ref. [5] also gives the hybrid potential $V_0 = 2.0 eV$ of epitaxial graphene at zero temperature. From equations (7) and (8), the hybrid potential of epitaxial graphene varies with temperature as shown in Figure 4, where lines 0, 1 and line 2 are the results of simple harmonic approximation, only the first non-harmonic term, and the first and second non-harmonic terms, respectively.

(a)

(b)

(c)
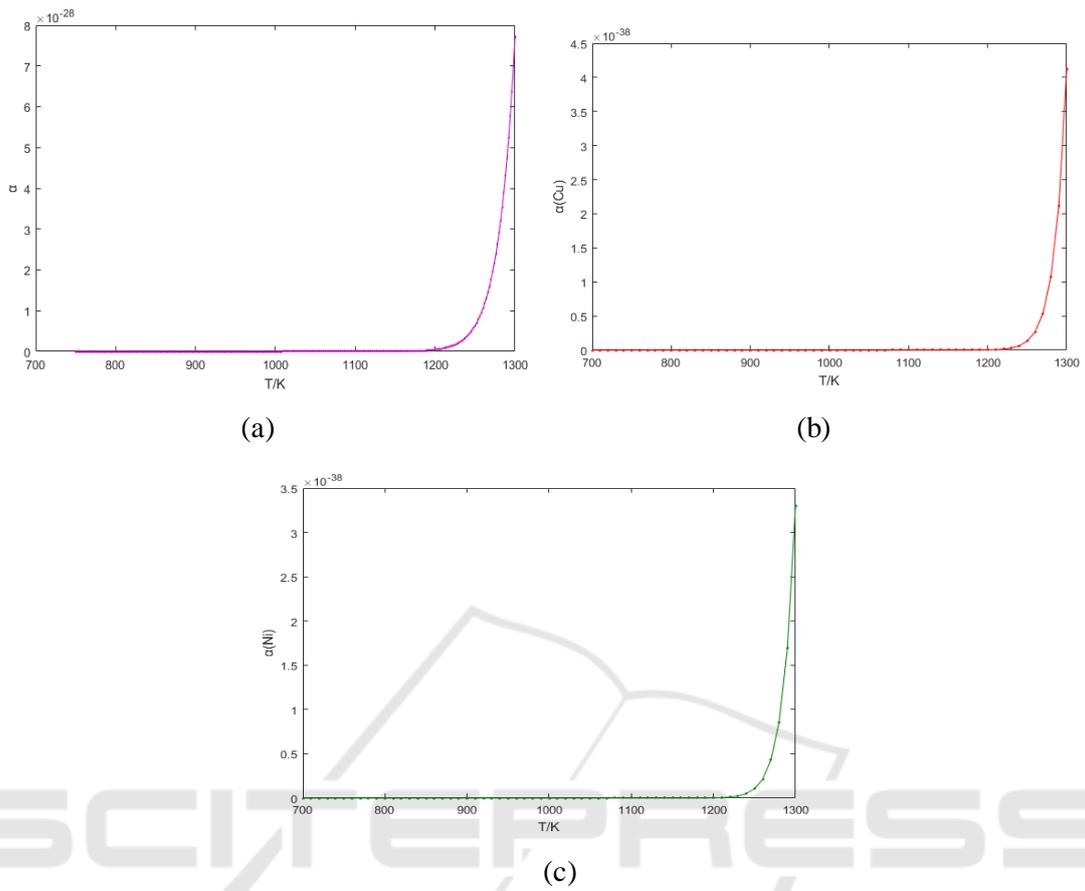
Figure 3. Variation of vacancy defect concentration of graphene (a), copper - based (b) and nickel - based epitaxial graphene (c) with temperature.

Table 2. Variation of Silicon (Si) Based Epitaxial Graphene Hybrid Potential with Temperature.

T(K)	300K	500K	700K	800K	1000K	1100K	1300K
V1(ev)	2.009811	2.016391	2.023003	2.026321	2.032982	2.036324	2.043032
V1,2(ev)	2.009811	2.016391	2.023005	2.026323	2.032986	2.036329	2.043040
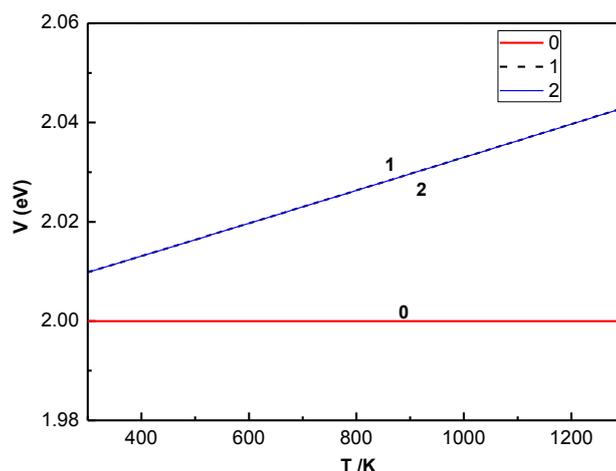
Figure 4. Variation of Silicon (Si) Based Epitaxial Graphene Hybrid Potential with Temperature.

It can be seen from Table 2 and Figure 4 that in the case of harmonic approximation, the hybrid potential of epitaxial graphene does not change with temperature. However, if taking into account the non-harmonic vibration of the atoms, the hybrid potential increases with the increase of temperature, but the change is not significant. When the temperature rises, the hybrid potential increases by only 1.65%. Also, it is noticed that the higher the temperature is, the greater the difference between the values of the non-harmonic and harmonic approximations is, that is, the non-harmonic effects become more significant.

6. Conclusions

In summary, the variation of the concentration and the hybrid potential of metal-based epitaxial graphene with temperature are studied. First, the concentration of vacancy defects in both graphene and metal-based epitaxial graphene increases nonlinearly with increasing temperature. The vacancy defect concentration of epitaxial graphene and its change rate with temperature are more significant than that of graphene. Second, the hybrid potential increases with the increase of temperature, but the change is not great. Third, the atomic non-harmonic vibration has an important influence on the variation of the hybrid potential with temperature. The higher the temperature is, the more significant the change is, and the more significant the non-harmonic effect is.

References

[1]   Castro A H, Guinea F, Peres N M R, Novoselov K S, Geinm A K 2008 *Rev. Mod. Phys.* 81 109
[2]   Haas J, De Heer W A, and Conrad E H 2008 *J. Phys. C: Condens. Matter* 20 323202
[3]   Wu Y H, Yu T, Shen Z X 2010 *J. Appl. Phys.* T108 071301
[4]   Das Sarma S, Adam S, Hwang E H, Rossi E 2011 *Rev. Mod. Phys.* 83 40
[5]   Alisultanov Z Z 2013 *Tachnical Physics Letter* 39 17 8-16
[6]   Fang X Y, Yu X X, Zheng H M, Hai B J and et al 2015 *Physics Letters A* 379 37 2245-2251
[7]   Davydov S Y 2015 *Semiconductors* **49(8)** 1095-1103
[8]   Davydov S Y 2014 *Physics of the Solid State* **56(4)** 849-853
[9]   Thrower P A, Wayer R M 1978 Point defects and self-diffusion in graphite *Phys. Stat. Sol.* (a). 47 11-37
[10]   Davydov S Y 2011 Adsorption atoms and bond energy of monolayer graphene *Physics of the Solid State* 53 12 2412-2423

[11] Davydov S Y and Subinovu G I 2011 *Physics of the Solid State* 53 3 608-616

[12] Huang K and Han R Q 2013 *Solid state physics* (Beijing: Higher Education Press) 552-555

[13] Cheng Z F and Zheng R L 2016 *Acta Phys. Sin.* 65 104701

[14] Kittle C (translated by Yang S H) 1979 *Introduction to Solid State Physics* (Beijing: Science Press) 45

[15] Davydov S Y 2011 *Technical Physics Letters* 37 42