First-Principles Electronic-Structure Calculations of Functional Materials

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July 2014

Abstract

1 Importance of Study Device

Nowadays, electronic products, such as computers, mobile phones, televisions, and so on, are necessary in our daily life. In these products, the semiconductor devices are commonly used. The function of semiconductors is developing because of down sizing to several nano-meters, and we need to control devices on the atomic level. One of the problems in device function is remarkable effects (the conductivity, stability and getting) of the defects and impurities. Thus, control of defects and impurities is necessary. The experimental methods are considered to be not so sufficient to observe the atomic phenomenon. However, the computational methods are expected to study these problems much efficiently.

On the other hand, spintronics develops rapidly in recent years which are also considered to be suitable for nano device application in the future. Many materials such as ferromagnetic material, half-metal, and so on, are considered to have applications with spintronics on nano-devices. As an important parameter, it is essential to know the spin-polarization of these materials. However, the methods for analysing it are still rare.

The First-Principles methods allow us to get information on electrons in materials which leads us to understand the atomic phenomenons of the objects. It contributes to development of material science if there is some progress on the understanding of defects in semiconductors or on the investigating some possible tools for analysing magnetic momentum of materials on spintronics.

2 Scope of This Study

In this study, we carry out quantum mechanic simulation which gives useful information on device application. We choose two topics. One is the control of defect in graphene; the other is spin-polarization in ferromagnetic materials.

2.1 Adatom-vacancy Pair in Graphene

Control of defects are very important to the semiconductor devices. First, we would like to introduce the background of our study related to the understanding of the defects in the semiconductors.

Among various defects, adatom related defects were observed at low temperatures. Recently low-energy electron irradiation on single-walled carbon nanotubes (SWCNTs) was performed[1]. The observation of I-V characteristic shows that some defects having some band gaps are created at low temperature by irradiation. Scanning tunneling microscope (STM) with the bias of 4.5 V at low temperature (95 K) also induces some unknown defects having band gaps[2, 3]. These defects are expected to be related to adatoms which can be created by electron irradiation or STM. Then, a hydrogen thermal desorption spectroscopy treat the defects induced by low-energy electron irradiation in SWCNTs. And it shows that some defects are healed at 44-70 K[4]. It is expected that the observed defect was the adatom-vacancy pair. It is emerge to have a theoretical study to understand this kind of defect better.

Graphene, as a SWCNT with infinite radius, is a good sample to be investigate for the defect details. A previous calculation of graphene found that the energy barrier was 0.47 eV for migration of one adatom[5]. A past study based on first-principles calculation clarified the energy barrier (0.49 eV) for migration of one adatom[6].

The purpose of this study is to make sure if the defect induced by low-energy electron irradiation is the adatom-vacancy pair by performing the numerical healing barrier calculations, and also to make sure if the adatom tends to return to the vacant site or to immigrate to other position. The results of the energetic stable structures and the healing barriers of adatom-vacancy

pairs will be described.

2.2 Positron Annihilation Study on Ferromagnetic Metals

Detecting the spin-polarization in magnetic material on spintronics is necessary. Here, we would like to introduce the background of our study related to the understanding of the possible analysing tool for magnetic momentum on spintronics.

Recently, spin-polarized positron experiment attracts scientific attention because of application to the study of electron spin phenomena.[7, 8] Low-energy spin-polarized positron beams enable us to study magnetism at surfaces, interfaces and in thin films. Positrons are trapped by vacancy defects, so spin-polarized positron annihilation spectroscopy (SP-PAS) is expected to be an useful tool to study vacancy induced magnetism [9]. Ferromagnet is one of fundamental spin polarization materials. Therefore, to detect spin-polarization in ferromagnet by using SP-PAS is scientifically important.

The 3γ spin-polarized positron experiment on ferromagnetic materials was first carried out by S.Berko in 1971[10]. Later, two-dimensional two-photon angular correlation of the spin-polarized positron annihilation radiation in Ni[11, 12, 13] and Co[14], and the Doppler broadening of annihilation radiation[7, 8] were measured. These experiments allow us to get information in ferromagnetic materials. However, it is still unknown what kind of useful information we can get from these experiment. There are still few theoretical studies on spin-polarized positron. We would like to investigate the positron annihilation calculations on ferromagnetic materials by using first-principles calculations base on electron-positron density functional theory.

3 Results and Discussion

We first study adatom-vacancy pairs in graphenes by using first-principles calculations based on density functional theory (DFT). We find that when the adatom is bonded to a nearest atom of the vacant site (shown this geometry A in Fig. **??**), the healing barrier is very small (0.06 eV). Therefore, this defect is easily healed. On the other hand, the healing energy becomes

high (0.24-0.32 eV), when the adatom (geometries from B to E) is located 4.26-5.54 far from the vacant site(shown the formation energies in Fig. **??**). However, these barriers are lower than that of adatom diffusion. Thus, it is expected that these adatom-vacancy pair defects are healed in low temperature range where the adatom does not diffuse.

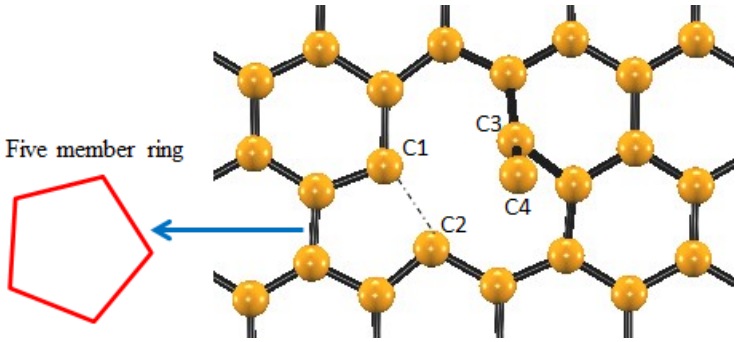

Figure 1: Adatom-vacancy pair when the adatom is bonded to a nearest site of the vacancy in the graphene.

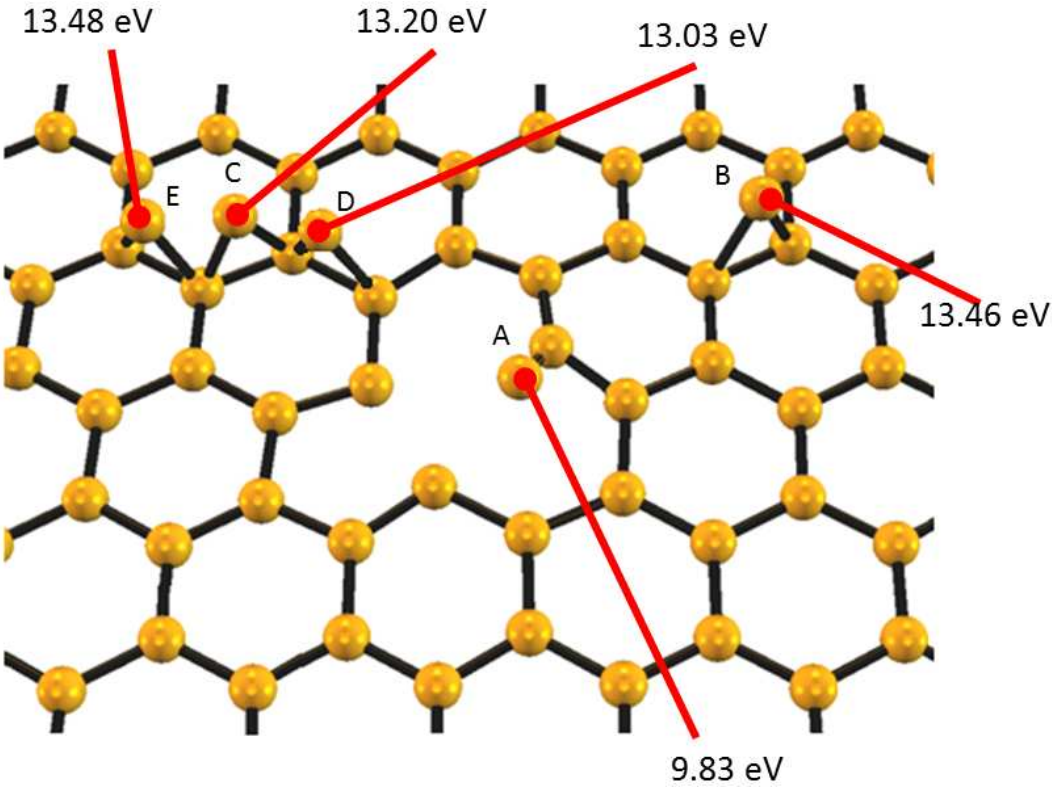

Figure 2: Formation energies of the adatom-vacancy pairs in the graphene.

Table 1: Spin-polarized positron lifetimes for the bulk Fe (bcc), Co (hcp), Ni (fcc), and Gd (hcp). We also show the spin moments ($\mu B/atom$).

elements	spin moment(μB/atom)			lifetime(ps)		
	majority spin	minority spin	total magnetic moment	$\tau^{\uparrow}$	$\tau^{\downarrow}$	$\tau^{\downarrow} - \tau^{\uparrow}$
Fe	5.156	2.844	2.311	95.159	107.008	-11.849
Co	5.319	3.681	1.637	94.493	98.245	-3.752
Ni	5.473	4.527	0.945	101.129	96.764	4.365
Gd	12.837	5.164	7.673	175.694	255.049	-79.355

We next study spin-polarization of ferromagnetic materials. The spin-polarized positron lifetime calculations are carried out by using electron-positron DFT. We investigate the ferromagnetic metals Fe, Co, Ni, and Gd, and find that the difference between the positron lifetimes for minority and majority spins (-) are 11.85 ps, 3.75ps, -4.37 ps, and 79.34 ps, respectively(details in Table.**??**). The negative sign of Ni is expected to originate from the delocalized distribution of minority electrons.

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平成 26 年8 月 7 日

学位論文審査報告書（甲）

1．学位論文題目（外国語の場合は和訳を付けること。）

First-Principles Electronic-Structure Calculations of Functional Materials

（機能性材料の第一原理電子構造計算）

2．論文提出者 (1) 所　　属　数物科学　　専攻

(2) 氏（ふり）　名（がな）　林（りん）　建波（じぇんぼー）

3．審査結果の要旨（600～650 字）

7月17日に主査、副査が参加して予備審査を行い、8月6日に学位論文公聴会を行った。公聴会の直後に、主査と副査4名が協議し、合格と判断した。デバイス向け機能性材料開発において、原子レベルの現象を量子力学に基づくシミュレーションによって解析する事が重要である。林氏は、はじめに、新しいデバイス材料の候補であるグラフェンに着目し、電気伝導に影響を与えると予想される吸着原子―空孔対のシミュレーションを行った。この欠陥の消滅に対する活性化エネルギーは、0.3eV 以下である事を明らかにした。このことは、この欠陥が低温で消滅することを意味し、既存の実験結果と矛盾しない事が明らかになった。つぎに、スピントロニクス材料の評価において今後重要なスピン偏極陽電子実験の結果を解析するため、強磁性体における対消滅速度を求めた。計算は、電子・陽電子密度汎関数法に基づき行った。とくに、Ni においては、少数スピン電子の消滅速度が、多数スピン電子の消滅速度よりも大きい事を明らかにした。この結果は、3光子対消滅実験の結果と矛盾しないことを示し、シミュレーションの信頼性を確立した。さらに、少数スピン密度が広がった分布を持つ事により、陽電子密度と大きな重なりを持ち、その事が少数スピン電子の消滅速度の大きい原因である事を明らかにした。以上述べた様に、林氏の研究は、今後のデバイス向け材料の開発に有益な知見をもたらす基礎研究であると判断し、合格と結論する。

4．審査結果　(1) 判　　定（いずれかに○印）（合　格）・　不合格

(2) 授与学位　　博　士（理学）