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Nitrogen-induced local spin polarization in graphene on cobalt

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ABSTRACT

Using first principles calculations, we demonstrate an effective method to tailor the local spin configuration of graphene on Co(0 0 1) surface through nitrogen doping. Two different site occupancies of the N impurities are discussed with the focus on structural, electronic and magnetic properties. N induces opposite local spin polarization at the two sites through π - d Zener exchange-type hybridization with Co substrate. In addition, the induced spin polarization is energy dependent and controllable by electric field. Consequently, this structure can be applied as a spin injection source in graphene based spintronics.

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1. Introduction

Since its first experimental discovery [1], graphene has become of considerable interest to scientists in many areas due to its intriguing physical properties [2,3]. Being comprised of light element C with weak spin-orbit coupling, graphene enjoys a large spin relaxation length (about $2\ \mu\text{m}$) at room temperature [4], which makes it an exceptional spin transport medium and advantageous over conventional semiconductors in spin electronics (spintronics) application [5]. One crucial issue for the achievement of grapheme-based spintronics is how spin-polarized electrons can be effectively injected into nonmagnetic grapheme [6,7]. Ferromagnetic (FM) contact is among the most popular spin injection methods applied in graphene spin valve devices [8–10]. Combining graphene and FM metals [11], such as Co and Ni, has been studied with the focus on interfacial structural and electronic properties [12–20], and predicted to have promising applications [21]. Nevertheless, experimental results have shown that magnetoresistance (MR) ratios in such spin valves are fairly low [8,22]. Namely, the spin injection efficiency at the graphene/FM-metal interfaces is rather limited. Therefore, it is of particular significance to find other efficient ways to inject spin into graphene.

In this report, we theoretically propose one highly efficient spin injection method by implanting N impurity into a graphene sheet that is grown on Co(0 0 1) surface. Recently, the individual

nitrogen dopants in monolayer graphene grown on a copper substrate was characterized, which strongly modified the electronic structure of nitrogen-doped grapheme [23]. So far, there have been several experimental approaches for doping nitrogen in graphene, including chemical vapor deposition [24,25], ion implantation [26] and plasma processing [27]. Simultaneously, nitrogen impurities in graphene have been studied theoretically as well [28–31]. These results have shown that nitrogen in graphene layers are almost nonmagnetic namely not spin-polarized [28,30], except some edge doping situations [30,31]. Here, by employing Co substrate, we are able to turn N impurity to highly spin-polarized states and thus create highly efficient spin injection sources in graphene. Furthermore, the spin polarization induced by N is localized, so that it can contribute to point spin injection source in nanospintronics and spin quantum bit in quantum computation. Hereby, our method is a prototype and will inspire new approaches for tailoring the local spin configuration of graphene through point defects with the help of magnetic substrates.

2. Computational details

Our theoretical study is based on first principles calculations at the level of spin-polarized density functional theory (DFT) [32,33], using projector augmented wave (PAW) formalism [34] as implemented in VASP code [35]. General gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange–correlation function [36] is employed together with a plane wave cutoff of 400 eV. Brillouin zone integration is performed on a Γ centered $6 \times 6 \times 1$ grid using Monkhorst–Pack scheme [37]. The structural models are

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constructed by substituting one C atom of a 3×3 graphene supercell with one N atom and covering the graphene sheet over a Co(0001) substrate of five Co layers. The in-plane lattice constant a is fixed to 7.518 Å, the same as Co(0001) lattice, and the vacuum slabs are set to more than 10 Å above the graphene sheets. Atoms in the graphene sheet as well as the upper most two Co layers are free to move during atomic relaxation, which is conducted by conjugate gradient method [38], and the structures are optimized when the force on each atom is less than 0.01 eV/Å.

3. Results and discussion

First the characteristics of pure graphene adsorbed on a Co surface are briefly reviewed.¹ The lattice mismatch between graphene and Co(0001) plane is so small (1.8%) [39], that the graphene sheet is in registry with the Co surface and suffers only a very little tensile. Above the Co(0001) surface, there are three sites marked A, B and C in Fig. 1(a). Two of them may be occupied by Graphene C atoms, resulting in three on-top registry configurations named Gr^{AB} , Gr^{AC} and Gr^{BC} . Our results show that Gr^{AC} is the most stable one with graphene–Co separation $d_0 = 2.12$ Å.

A possible reason for the low spin injection efficiency at the interfaces in the spin valves, could be understood from the projected density of states (PDOS) of C atoms in Gr^{AC} , as presented in Fig. 1(b). All s , p_x and p_y components are symmetric and only p_z component is asymmetric with respect to the two spins. This indicates π - d hybridization between out-of-plane π (p_z) states of graphene and d band of Co substrate. Because of their different site occupancies, the two C atoms present different p_z PDOS features. C^{A} , sitting above a surface Co, presents positive spin peaks within $[-2.8, -2.2]$ eV, $[0.1, 1.2]$ eV intervals, and negative spin peaks within $[-1.7, -1.0]$ eV, $[1.4, 2.2]$ eV intervals. In comparison, C^{C} presents a strong positive peak within $[-1.0, -0.2]$ eV, a strong negative peak and a weak positive peak within $[0.6, 1.4]$ eV. It is noteworthy that PDOS of both C^{A} and C^{C} diminish at the Fermi level (E_{F}). Therefore the graphene is not spin-polarized [40] at E_{F} , and the resistance across the interface is large.

Next, we study the effects of N impurity in Gr^{AC} . By substituting one C^{A} or C^{C} with N dopant, we create two situations $\text{Gr}^{\text{AC}}\text{N}^{\text{A}}$ and $\text{Gr}^{\text{AC}}\text{N}^{\text{C}}$ as shown in Fig. 2(a) and (b), respectively. Superscript of the notation in each pane denotes the site occupancy. Subscripts (1, 2 and 3) of the C notations denote the first, second and third nearest neighbors.

We calculated the binding energy $\Delta E = E_{\text{tot}} - E_{\text{GrN}} - E_{\text{Co}}$. Here, E_{tot} , E_{GrN} and E_{Co} are energies of total structure, graphene with N impurity and Co substrate, respectively. ΔE of Gr^{AC} , $\text{Gr}^{\text{AC}}\text{N}^{\text{A}}$ and $\text{Gr}^{\text{AC}}\text{N}^{\text{C}}$ are -0.93 eV, -0.89 eV and -0.97 eV. N^{A} impurity decreases the stability of graphene adsorption while N^{C} impurity improves the stability. Furthermore, $\text{Gr}^{\text{AC}}\text{N}^{\text{C}}$ is more stable than $\text{Gr}^{\text{AC}}\text{N}^{\text{A}}$ which has a relative high total energy about 0.075 eV per unit cell with one N atom. It indicates that experimentally the N impurity prefers to form at C site instead of at A site in the growth of graphene on the Co substrate with the CVD method. Some other data determining their properties are presented in Table 1. In either case, N is located above the graphene layer with the distance d_1 larger than d_0 .

The PDOS of these N impurities is spin asymmetry, especially around E_{F} . For $\text{Gr}^{\text{AC}}\text{N}^{\text{A}}$ presented in Fig. 2(c), the out-of-plane p_z component becomes spin asymmetric above -5 eV. For instance, there is only a positive PDOS peak at E_{F} , while in the negative spin channel the PDOS is almost zero at E_{F} . A sharp positive peak and a sharp negative peak are also presented at -2.8 eV and -1.8 eV,

respectively. Similarly, N^{C} displays spin asymmetric p_z PDOS as well [see Fig. 2(d)], but the characteristics are completely different from N^{A} . In the vicinity of E_{F} , the N^{A} positive peak vanishes in N^{C} PDOS. Instead, a broad negative peak appears within $[-0.6, 0.1]$ eV. A strong positive peak is presented within $[-1.6, -0.8]$ eV and two other positive peaks are located around 0.3 eV and 1.6 eV.

The π - d Zener exchange mechanism [41] can be employed to explain the spin asymmetry of p_z states of these N impurities. In diluted magnetic semiconductors, the p band of semiconductor is mixed with the d states of the transition metal impurity ions and thereby broadened and shifted with different variations in the two spin channels around E_{F} . In the cases discussed here, Co substrates play the roles of transition metal impurity and N act as the semiconductor. Specifically, in $\text{Gr}^{\text{AC}}\text{N}^{\text{A}}$, strong hybridization is apparent as exhibited in Fig. 2(c): the positive peak at -2.8 eV and the negative peak at 1.2 eV are present both in the p_z PDOS of on-top N^{A} and the d_{xz} , d_{yz} and d_{z^2} PDOS of surface Co^{A} . While in $\text{Gr}^{\text{AC}}\text{N}^{\text{C}}$, the N^{C} negative peak around E_{F} is the result of strong π - d hybridization with d_{xz} and d_{yz} states of the nearest Co (Co^{A}) [See Fig. 2(d)]. The positive peak, as well as the negative states, within $[-1.6, -0.8]$ eV also hybridize with $\text{Co}d_{xz}$ and d_{yz} states in the same energy interval. Below -5.5 eV in Fig. 2(c) and (d), where Co PDOS drops to zero, both N^{A} and N^{C} display spin symmetric p_z PDOS because of the absence of π - d mixing.

It is interesting that N^{A} and N^{C} have opposite local spin polarizations at E_{F} . Actually, the N^{A} and N^{C} dopants on Co substrate have different adjacent atoms. N^{A} on the top of Co^{A} has a strong direct interaction with Co^{A} atom of 2.25 Å N^{A} - Co^{A} bond through the π - d Zener exchange mechanism. Meanwhile, N^{C} interacts directly only with three bonded C atoms, and has indirect π - d interaction with surface Co atoms. Furthermore, it was found that N^{A} will gain more electrons about 0.44 e than N^{C} from the bader population analysis. So, the difference of PDOS structure and local charge doping induced by different interaction with adjacent atoms, will lead to the opposite local spin polarizations of N impurity.

It may be assumed that the N impurity will introduce some changes to its neighboring graphene C and substrate Co. In fact, this is true only when N takes the place of on-site C^{A} in $\text{Gr}^{\text{AC}}\text{N}^{\text{A}}$. N^{A} hybridizes substantially with its neighboring C in the conjugate loops and causes considerable changes to their PDOS [see Fig. 2(c)]. Most apparently, all C_1^{C} , C_2^{C} and C_3^{C} present the strong positive peaks at E_{F} as N^{A} does, which is not found in undoped Gr^{AC} . Also the positive peak around -2.8 eV and the negative peak around -1.8 eV exist in N^{A} PDOS due to the hybridization between N^{A} and C_2^{A} that are both on-top of Co^{A} . N^{A} brings some changes to the Co^{A} beneath it too. Especially for the d_{z^2} PDOS, in Fig. 2(c) the positive peak within $[-1.5, -0.4]$ eV and the negative peak within $[0.2, 1.5]$ eV are both broadened and lifted compared to the Co^{A} in $\text{Gr}^{\text{AC}}\text{N}^{\text{C}}$ as shown in Fig. 2(d). Nevertheless, in the more stable $\text{Gr}^{\text{AC}}\text{N}^{\text{C}}$, the PDOS characteristics of neighboring C and Co are hardly altered. For example, the first (third) nearest neighbor C_1^{C} (C_3^{C}) of N^{C} is characterized by two positive PDOS peaks within $[-2.8, -2.2]$ eV, $[0.1, 1.2]$ eV and two negative peaks within $[-1.8, -1.0]$ eV, $[1.3, 2.2]$ eV [see Fig. 2(d)], which is the hallmark of C^{A} in pure Gr^{AC} on Co. The second nearest neighbor C_2^{C} presents similar PDOS as the C^{C} shown in Fig. 1 too. The π - d hybridization features of undoped Gr^{AC} with Co substrate (not shown here) are also retained, such as the positive (negative) hybridization between Co^{A} and C_1^{A} within $[-2.8, -2.2]$ eV ($[-1.8, -1.0]$ eV), and the positive hybridization between Co^{A} and C_2^{A} around -0.5 eV [see Fig. 2(d)].

Under the influence of Co substrate, N impurity introduces high spin polarization [40] around E_{F} to the graphene layer and thus substantially increases the initially diminishing density of states around E_{F} in one spin channel. [Note that the vertical scales of N PDOS are twice the scale of C in Fig. 2(c) and (d)] So that the

¹ See supplemental material for more details about pure graphene on Co.

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