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Effects of uniaxial strains on the magnetic properties and the electronic structures of Fe/graphene system: An *ab initio* study

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Using *ab initio* calculations, we investigated the changes of the magnetic moment and electronic structures of Fe adatoms on strained graphene sheets. By the uniaxial tensile strains in armchair and zig-zag directions on graphene sheets, the amounts of charge transfers from graphene $2p_z$ orbital to Fe adatom $3d$ orbitals were linearly increased. The magnetic moments of Fe, however, show the tendency of linear decrements with the uniaxial tensile strains. The increased Fe magnetic moments by uniaxial graphene compressions resulted from the shifting of spin-minority states of electrons while the decreased Fe magnetic moments were due to the reduction in the spin-majority states of $3d_{xy}$ -orbitals of the Fe adatom. © 2012 American Institute of Physics. [doi:10.1063/1.3672870]

I. INTRODUCTION

Graphene based materials have demonstrated their potential applications in a wide range of technology.^{1–3} Since its discovery, graphene has been understood as a promising candidate for several technological applications.^{4,5}

Especially, transition-metal/graphene structures are extraordinarily expected to be used in various technical applications, such as next generation magnetic recording media, hydrogen storage materials, gas sensor or catalysts.^{4–7} Among the transition-metal/graphene systems, Fe/graphene system is one of the most strongly studied systems due to the sensitive changes of the magnetic moments and chemical properties by the change of characteristics of bonding of Fe with supporting graphene sheets.^{8,9} The magnetic properties and chemical reactivity of Fe/graphene are determined by the electronic structure changes, which are originated from the charge transfer and the hybridization aspects between Fe $3d$ -orbitals and C $2p_z$ -orbitals. Hence, there have been a number of efforts to tailor the properties. For instance, the magnetic moments of the Fe adatom and carbon atoms in graphene bonded to Fe are controllable with the atomic configurations of underlying substrate materials,¹⁰ the bonding with $5d$ metal atoms and the number of atoms in Fe islands.⁴ Among various trials to control the electronic structures and chemical properties of graphene based materials, strains on graphene sheets were reported to efficiently tune the graphene electronic structures.^{5,6,11–13} The altered electronic structure change of graphene sheets by strains also affects the charge transfer amounts and reactivity of the graphene. Since the magnetic and chemical properties of Fe adatom or thin films are sensitively affected by the underlying substrates, the effects of graphene strain on the chemistry and magnetism of Fe/graphene are worth studying.

In this study, using the density functional theory (DFT) calculations, we investigated how the strains on graphene change the magnetic properties of Fe single atoms.

II. CALCULATION METHOD

DFT calculations¹⁴ were performed using the Vienna *ab initio* simulation package (VASP) code.¹⁵ The plane-wave basis set was expanded to a cutoff energy of 500.00 eV. All of the self-consistent loops were iterated until the total energy difference of the systems between the adjacent iterating steps became less than 10^{-6} eV. The projector-augmented waves (PAW) (Ref. 16) were used to describe the ion cores and the exchange-correlation of the Fe/graphene systems were expressed with generalized gradient approximation (GGA).¹⁷ The Gaussian broadening scheme of the width was set to be 0.1 eV. Ionic relaxation was done using the conjugate gradient method. The k-point grids for structural relaxations and electronic structures were set to be $8 \times 8 \times 1$ and $14 \times 14 \times 1$, which were generated by the Monkhorst-Pack scheme.¹⁸ The effective range of the cutoff energy and the validity of the mesh density used in this calculation were determined by a convergence test using the theoretically estimated lattice constants of pristine graphene, 2.464 Å.

The supercell of the 2×2 single layer graphene in this study consists of 16 carbon atoms and the most stable adsorption site of a single Fe atom was on the center of a hexagonal carbon ring. The constituent atoms in Fe/graphene systems were fully relaxed until the maximum Hellmann-Feynman forces were in the range of ± 0.01 eV/Å. The constructed supercells were periodically repeated with a 15 Å vacuum spacer lying along the vertical direction.

III. RESULTS AND DISCUSSION

Through the adsorption energy comparison, the most stable adsorption sites of the Fe atom on a graphene sheet were found to be the center of the carbon hexagon of the graphene surface. The distance of Fe adatoms from the graphene sheet, which was calculated with GGA method, was 1.614 Å. Figure 1 shows the changes of distances between Fe and graphene sheet (Fig. 1(a)) and the adsorption energy of Fe on graphene (Fig. 1(b)) with strains in armchair (AC)

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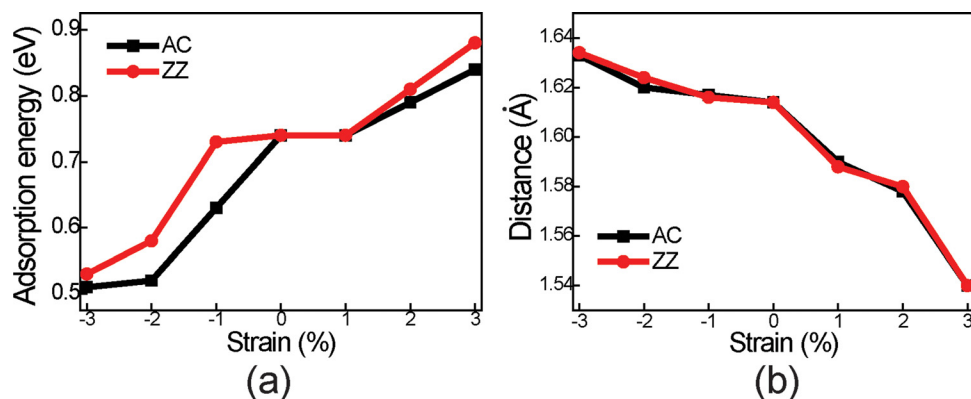


FIG. 1. (Color online) The plots of (a) distances between Fe and graphene sheets and (b) adsorption energy of Fe on graphene with the armchair and zig-zag strains on graphene.

and zig-zag (ZZ) directions. The Fe-graphene distance is increased with the compressive strains noticeably, while the tensile strain makes the bonding length shorter. The reduced bond length between the graphene sheet and Fe with the increased lattice enhanced the adsorption energy of Fe on graphene as can be seen in Fig. 1(b). The adsorption energies E_{ad} were calculated using the equation,

$$E_{ad} = -[E_{total}(Fe \text{ on graphene}) - E_{graphene} - E_{Fe}]. \quad (1)$$

As can be seen in Fig. 2, the charge transfer amounts are increased as the graphene sheet is stretched in AC or ZZ directions. In the previous comparative study on Ti and Fe adsorption on graphene,⁸ the larger charge transfer amount to Ti was related with the higher binding energy of Ti adatom on graphene than that of Fe. In this study, we could see that adsorption energy and the amount of charge transfer from graphene sheet to Fe adsorbate can be controlled with the uniaxial strains. We obtained the decomposed 3d-orbital density of states (DOS) of the Fe adatom, in order to see find the origin of the charge transfer amount variation with the strains (Fig. 3). The reduced charge transfer to Fe by AC and ZZ compression were mainly originated from the reduction in the electron states of the $3d_{yz}$ -orbital. The shifting of the spin-minority states toward the higher energy states is related with the lower adsorption energy of Fe graphene sheets in the range of the graphene compressions. With the Fe adsorption, on the other hand, the energy state distribution in graphene carbon atoms became broader and significant amount of charge in carbon was shifted above

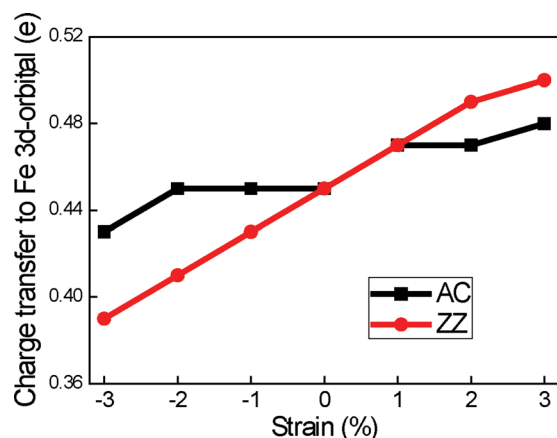


FIG. 2. (Color online) The amounts of charge transfer from graphene to Fe 3d-orbital.

Fermi level. Since the lower bond strength and smaller charge transfer amount to transition metal on graphene induces greater reactivity with gas molecules,^{4,8} the controls of bond strength and charge transfer are expected to give various technological advantages such as sensitivity of gas sensor or hydrogen energy storage/release, too. From the calculated charge transfer amount change by uniaxial strains, we can infer that the ZZ strain is more efficient to control the amount of charge transfer.

We calculated the magnetic moments of the adsorbed Fe adatoms on strained graphene sheets (Fig. 4). From both the ZZ and AC strains, the magnetic moments of Fe are decreased gradually over the ranges of compressive and tensile strains. It is noticeable that the amount of electron

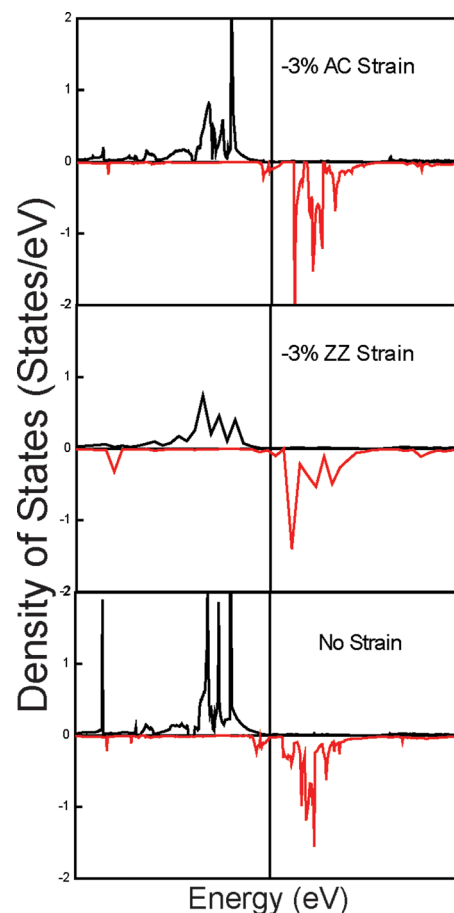


FIG. 3. (Color online) The decomposed density of states of Fe (a) $3d_{xy}$ -orbital with -3% AC strain on graphene and (b) $3d_{yz}$ - and $3d_{xz}$ - orbitals of Fe with -3% ZZ strains on graphene.

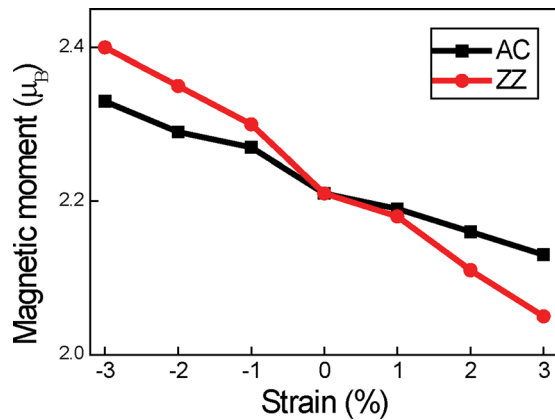


FIG. 4. (Color online) Magnetic moments of Fe on the strained graphene.

transfers from graphene to Fe are increased with lattice stretches both in the ZZ and AC directions (Fig. 3) even with the decreasing magnetic moment of the Fe adatom.

The electron DOS of Fe on the strain-free graphene sheet is similar with the bulk Fe (Ref. 19) (Fig. 5(a)). In the Fe adatoms on the uniaxially compressed graphene sheets, the spin-minority states were shifted (circles) to higher energy states (Fig. 5(b)). Accordingly, the net magnetic moments of Fe on compressed graphene were increased (Fig. 4), in spite of the reduced amounts of charge transfer from the graphene sheet (Fig. 3). On the contrary, as the graphene sheet is elongated in the AC and ZZ directions, the spin-minority DOS peak in the Fe adatom below Fermi level becomes larger (Fig. 5(c)). To be interesting, the larger

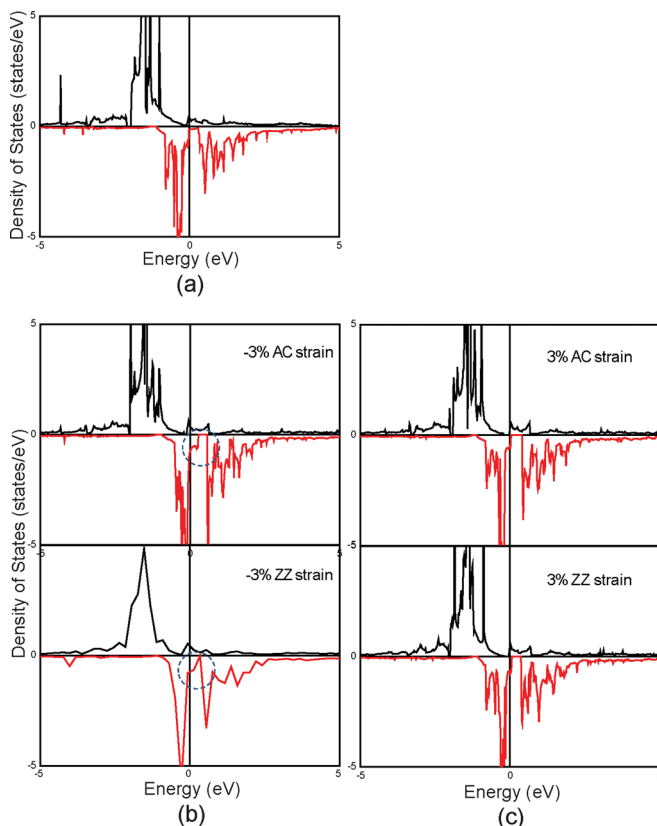


FIG. 5. (Color online) The density of states of Fe on (a) strain-free, uniaxially (b) compressed with -3% strain, and (c) 3% elongated graphene sheets.

reduction in the Fe magnetic moment on graphene under ZZ tensile strain (Fig. 4) is due to the noticeably reduced spin-majority electron states of the $3d_{yz}$ orbital. The reduction of electron states by the ZZ strains is for the increased lateral distance between Fe and C atoms in the ZZ(y-) direction.

Overall, the controllability of the magnetic moment of the Fe adatom on graphene with uniaxial strains is due to the changed aspects of charge transfers between Fe and graphene carbon atoms. The increased charge transfer from graphene to Fe with uniaxial strains is consistent well with the previous theoretical results,¹¹ which predicted the increasing work function of strained graphene.

IV. CONCLUSION

In this study, using *ab initio* calculations, we investigated the electronic structures and magnetic properties of Fe/graphene under uniaxial strains. As the dimensions of the graphene sheet are increased, both in the AC and ZZ directions, the adsorption energy and charge transfer amount in Fe were increased. As a result, the bond lengths between Fe and carbon atoms were decreased. The increased charge transfer and the reduced magnetic moments of Fe on stretched graphene were found to result from the variations of selective filling of the Fe $3d$ -orbitals. In summary, from the systematic *ab initio* study of the present work, the chemical reactivity and magnetism of Fe/graphene heterostructures are found to be controllable with uniaxial strains.

ACKNOWLEDGMENTS

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