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Tunable Magnetic Properties of Rhombohedral Graphite Thin Films

Nguyen Thanh Cuong[1,3], Minoru Otani[1,3] and Susumu Okada[2,3]

[1] AIST
AIST Central 2, 1-1-1 Umezono, Tsukuba 305-8568, Japan
Phone: +81-29-861-6067 E-mail: cuong-nguyen@aist.go.jp
[2] Univ. of Tsukuba
1-1-1 Tennodai, Tsukuba 305-8571, Japan
[3] JST-CREST
5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

1. Introduction

Ever since the fabrication of single and few layers graphene, the thin films of graphite have been attracting so much attention in the field not only of low-dimensional sciences but also of nano-scale technologies due to their perfect two-dimensional network. One of fascinating issues in this carbon allotrope is the intrinsic magnetism that is inherent in their topological properties. We have demonstrated that the surfaces of few-layer graphite with rhombohedral stacking arrangement exhibit ferrimagnetic spin ordering induced by flat dispersion band associated with the peculiar surface localized electron states classified as the "edge state" [1]. In this work, we systematically investigate how the electronic and magnetic properties of the rhombohedral graphite thin films depend on the interlayer spacing and number of layers using first-principles total-energy calculations in the framework of density functional theory.

2. Methods

All theoretical calculations have been performed based on the density functional theory with local spin density approximation and plane wave basis set. We considered thin films of graphite with rhombohedral (ABCABC…) stacking comprising three to thirteen graphene layers. For each thin film, the interlayer spacing between graphene layers is varied from 2.7 to 3.4 Å. In the repeated slab model, each thin film is separated from its periodic image by a 12-Å vacuum region. In the lateral directions, we used 1x1 periodicity with two C atoms in each graphene layer.

3. Results and Discussion

Figure 1 shows the contour plots of the electron spin density of rhombohedral graphite thin films with eight atomic layers at various interlayer spacings. We find that the spin density of the topmost or bottom most surfaces exhibits ferrimagnetic ordering. At the equilibrium interlayer spacing of 3.35 Å, the spins between the two surfaces are coupled in an antiparallel spin configuration, resulting a zero net spin moments of the thin film. However, upon further decrease in the interlayer spacing about of 3 Å, the spin density drastically changes its distribution: the polarized spins on tthe topmost and bottommost surfaces become coupled in parallel, leading to finite net spin moment for the thin film. Thus, by applying the uniaxial pressure on the films, a modulation in the magnetic properties can be detectable. We also estimated that the critical uniaxial pressure of 7.5 GPa could cause such a magnetic phase transition.

Our detail analyses on energy band and wave functions have clarified that the mechanism of the magnetism modulation of the rhombohedral graphite thin films on the interlayer spacing: The magnetism is induced by the delicate balance among the π-electrons along the interlayer direction of graphite thin films [2]. In the case of compressed thin film, the wave functions overlap between orthogonalized degenerate states results in the high spin state to

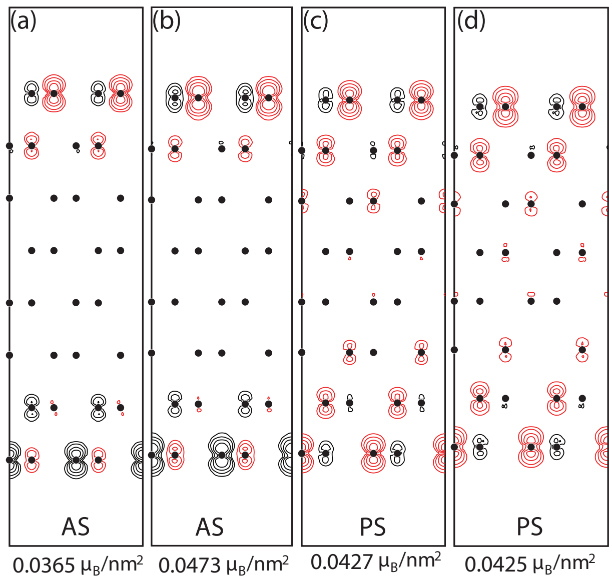

Fig. 1 Contour plots of spin density and surface magnetic moment of eight atomic layer rhombohedral graphite slabs at various interlayer spacing: (a) 3.35 Å, (b) 3.1 Å, (c) 3.0 Å and (d) 2.8 Å. The solid circles denote the positions of C atoms. Positive and negative values of spin density are shown by red and back lines. AS and PS symbols denote antiparallel and parallel coupling spin states.

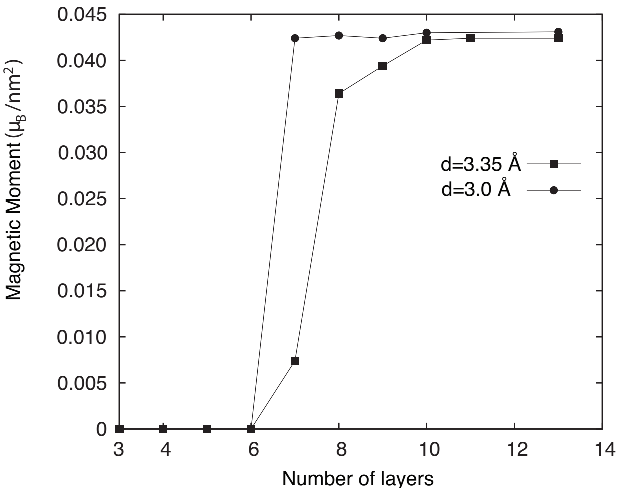

Fig. 2 Surface magnetic moment of the rhombohedral graphite slab with interlayer spacing 3.35 Å (solid square) and 3.0 Å (solid circles) as a function of the number of graphene layers.

exclude the double occupancy of the π-states of each C atomic site (in a similar way as for Hund's rule for the d-orbitals in transition metal magnets). This electron-electron repulsion results in a parallel spin ordering in the rhombohedral graphite thin films.

The magnetic properties of thin films of rhombohedral graphite depend not only on the interlayer spacing but also on the film thickness. Figure 2 shows the surface magnetic moments of thin films of rhombohedral graphite as a function of the number of layers. Graphite thin films with six or less atomic layers are metallic, without any magnetic ordering. Increase of the number of layers to seven or more leads to films that possess magnetic ordering. Furthermore, the surface magnetic moment gradually increases with increasing the number of graphene layers, and saturates at ten atomic layers with the surface moment of 0.04 μ_B/nm^2.

The substrates or mediums are essential to apply the pressure on the graphite thin films. Therefore, we investigated the effect of substrate on the magnetic properties of graphite thin film under the uniaxial compression. We considered the model in which the graphite thin film is sandwiched by two hexagonal boron-nitride (h-BN) sheets simulating the insulating substrate or pressure mediums. We chose 2 Å spacing between h-BN and the topmost/bottommost graphene layer to simulate the strong coupling limit between substrate and graphite. Figure 3 shows the contour plot of polarized electron spin density of the ten atomic layer rhombohedral graphite thin film with 3.0 Å interlayer spacing sandwiched by two h-BN layers. We find that the electron spin density dismisses at the topmost and the bottommost graphene layers situated at interface with substrate due to the strong interaction. However, we still observe the polarized electron spins on the sub-layers of graphite thin film. The polarized spins on these surfaces are coupled in parallel. The calculated surface magnetic moment is found to be 0.045 μ_B/nm^2. The results corroborate

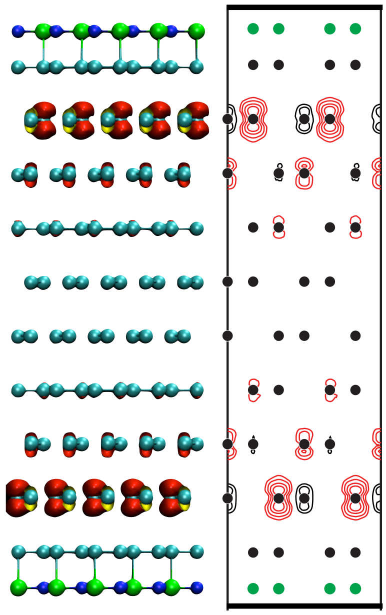

Fig. 3 Spin density of ten atomic layer rhombohedral graphite thin film sandwich by two h-BN layers with graphene interlayer spacing 3.0 Å.

that the magnetic properties of graphite thin film are certainly tunable by the external pressure.

4. Conclusions

Based on first-principles total energy calculations, we studied the magnetic properties of thin films of graphite with the rhombohedral stacking arrangement in terms of the interlayer spacing and film thickness. Our calculations show that the magnetic ordering of the thin films depends on the interlayer spacing. Thin films under compression normal to the layers possess finite magnetic moments caused by the parallel spin coupling between the two surfaces. We also find that thin graphite films with seven or more atomic layers exhibit magnetic ordering while films with six or less atomic layers are metallic without any magnetic ordering. In addition, we find that the substrate suppresses the magnetism on the topmost and the bottommost layers of graphite. However, we still observe the polarized electron spins on the second sublayers of graphite. These results indicate that the thin films of the rhombohedral graphite is applicable for the magnetic devices of which magnetic properties are tunable by controlling the external pressure or its thickness.

References

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