Antiferromagnetic ordering in one-dimensional dangling-bond wires on a hydrogen-terminated C(001) surface: A density-functional study

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We predict the existence of antiferromagnetic ordering in the one-dimensional dangling-bond wires fabricated on a hydrogen-terminated C(001) surface. Our spin-polarized density-functional theory calculations show that the antiferromagntic configuration, where the spins of adjacent dangling bonds point in opposite directions, is favored over the ferromagnetic one. Using the broken symmetry method, we estimate an exchange coupling constant of ~31 meV between adjacent spins. It is thus shown that unpaired electrons in sp^3-bonded diamond yield magnetic moments which interact antiferromagnetically with each other.

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Recent observations of magnetism in polymerized fullerenes[1] and proton-irradiated graphites[2–4] have ignited intensive research[5] for the magnetic orderings in various carbon-based materials such as nanometer-scale graphene ribbons[6–11] and carbon nanofoams with hyperbolically curved graphite sheets.[12,13] Although the detailed mechanism of "carbon magnetism" is yet to be understood, it is likely that different forms of carbon-based materials may have different origins of the magnetism. A recent density-functional theory (DFT) calculation[14] for proton-irradiated graphites showed that hydrogen adsorption on the irradiation-induced carbon vacancy gives rise to a magnetic moment. According to an electron spin resonance experiment,[15] the origin of irradiation-induced ferromagnetism in graphites is associated with direct interaction between the localized spins produced by proton irradiation. On the other hand, the magnetic orderings in graphene nanoribbons have been explained in terms of itinerant ferromagnetism resulting from strong electron-electron interactions.[7–9] In the case of zigzag graphene nanoribbon (ZGNR) which consists of a single graphite layer terminated by zigzag edges on both sides, localized edge states decaying exponentially into the center of the ribbon[9,10] induce ferromagnetically ordered spins at each side but with an opposite spin orientation between the edges.

Despite numerous reports of carbon magnetism in the above mentioned sp^2-bonded nanostructures,[1–15] there are very few reports of magnetism in the sp^3-bonded diamond.[16] Osipov *et al.*[16] reported magnetism in nanometer-scale diamond (ND) particles. Using hydrothermal treatment, they generated dangling bonds (i.e., unpaired electrons) from the H-terminated ND particles by desorbing H atoms, which give rise to magnetic moments on the surface of NDs. The magnetic susceptibility versus temperature data[16] for the ND samples containing different concentrations of dangling bonds showed the presence of antiferromagnetic interaction between the spins, where the exchange coupling constant was estimated to be between 7 and 17 meV.

In this paper, we predict the antiferromagnetic ordering in the one-dimensional carbon dangling-bond (DB) wire (see Fig. 1) which can be fabricated by the selective removal of H atoms from a H-terminated C(001) surface along the edge of a carbon dimer row.[17–19] We employ the spin-polarized DFT calculations to investigate the electronic and magnetic properties of the infinite-length DB wire as well as the short-length DB wires containing up to five dangling bonds. We find that antiferromagnetically aligned spins in the DB wires are more energetically favored over their ferromagnetic alignment. The mechanism for such an antiferromagnetic ordering in the DB wires may be related with relatively less-localized dangling-bond wave functions in sp^3-bonded diamond, contrasting with sp^2-bonded ZGNRs where the ferromagnetic ordering takes place at each side. Using the broken symmetry method,[20] we estimate the exchange coupling constant between adjacent spins in the DB wires as about 31 meV, somewhat larger than the above experimental[16] values measured from unpaired electrons on the surfaces of H-terminated NDs. Thus, the present prediction together with a recent experiment[16] for NDs manifest that unpaired electrons in sp^3-bonded diamond are antiferromagnetically coupled with each other.

The total-energy and force calculations were performed using density-functional theory[21] within the generalized-gradient approximation.[22] The norm-conserving pseudopotential of the H atom was constructed by the scheme of Troullier and Martins.[23] For the C atom whose 2*s* and 2*p* valence orbitals are strongly localized, we used Vanderbilt ultrasoft pseudopotentials.[24] A periodic slab geometry was employed with 12 C atomic layers and terminated H atoms on both sides of the slab. The vacuum spacing between these slabs is about 10 Å. The electronic wave functions were ex-

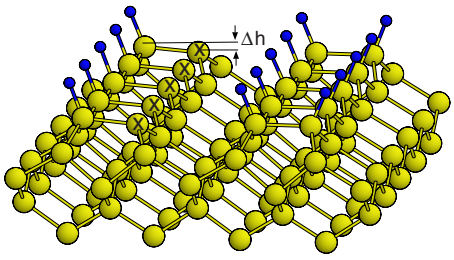

FIG. 1. (Color online) Optimized structure of the infinite-length DB wire on H-terminated C(001) surface. The large and small circles represent C and H atoms, respectively. For distinction, the C atoms composing the DB wire are marked X.

TABLE I. Calculated magnetic moment and magnetic energy of the infinite-length DB wire and the short-length DB wires containing up to five dangling bonds. $\Delta E_{\text{NM-FM}}$ ($\Delta E_{\text{NM-AFM}}$) represents the energy difference per dangling bond between the NM and FM (AFM) configurations.

DB wire	FM M (μ_B/unit cell)	$\Delta E_{\text{NM-FM}}$ (meV/DB)	AFM M (μ_B/unit cell)	$\Delta E_{\text{NM-AFM}}$ (meV/DB)
1	1	393	···	···
2	2	128	0	146
3	3	173	1	194
4	4	119	0	142
5	5	144	1	168
Infinite	1	102	0	133

panded in a plane-wave basis set with a cutoff of 25 Ry. The **k**-space integration was done with 16 and 8 points in the surface Brillouin zone of the 4×1 and 4×2 unit cells, respectively. All the atoms except the two central C layers were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr. Our calculation scheme has been successfully applied for the adsorption of molecules on the C(001) surface.[25]

We first optimize the atomic structure of the infinite-length DB wire on the H-terminated C(001) surface. Here, we consider the nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) configurations by employing the 4×1 or 4×2 (for the calculations of AFM) unit cell where the DB wires are separated, perpendicular to the C dimer row, by an additional H-terminated C dimer row. The optimized structure of the NM configuration is shown in Fig. 1. We find that the position of the surface C atoms composing the DB wire is lowered by $\Delta h=0.10$ Å compared to that of the H-bonded C atoms. However, for the FM and AFM configurations, Δh decreases to 0.08 Å, indicating that the presence of magnetism gives rise to an outward displacement of the surface C atoms composing the DB wire. The calculated energetics and magnetic moments of the FM and AFM configurations are listed in Table I, together with the results for the short-length DB wires containing 2, 3, 4, and 5 dangling bonds (hereafter designated as DB-2, DB-3, DB-4, and DB-5, respectively). We find that the AFM (FM) configuration is more stable than the NM one by 133 (102) meV per dangling bond, indicating that the ground state of the infinite-length DB wire is antiferromagnetic. Here, the total spin of the AFM configuration is zero, while that of the FM configuration is $1\mu_B$ per dangling bond.

Figure 2 shows the calculated band structures for the NM, FM, and AFM configurations of the infinite-length DB wire. In the NM configuration, the dangling-bond state crosses the Fermi level at the midpoint of the ΓX line (along the direction of the DB wire). The resulting Fermi surface with a nested vector $2k_F=\pi/a_0$ (a_0 is the lattice constant along the DB wire) may induce a charge-density wave coupled to a lattice vibration of wavelength $2a_0$, leading to a Peierls instability.[26] However, the present C DB wire does not show any lattice distortion within a 4×2 unit cell, contrasting with the Si DB wire[27,28] on the H-terminated Si(001) surface which exhibits a Peierls instability. This absence of a Peierls distortion in the C DB wire can be traced to the strong C-C bonding between the substrate and the wire, caused by more localized C $2p$ orbitals due to the absence of core p orbitals. As a result, the electronic energy gain in the C DB wire which can be obtained by a Peierls distortion cannot prevail over the larger elastic energy cost.[29] On the other hand, if the spin degrees of freedom are not restricted within DFT calculations, the electronic energy gain caused by spin polarization stabilizes the FM and AFM configurations over the NM

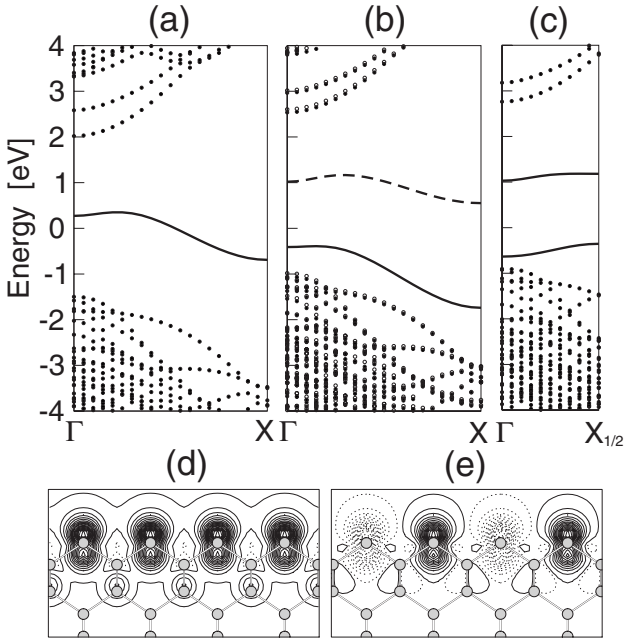

FIG. 2. Surface band structure for the (a) NM, (b) FM, and (c) AFM configurations of the infinite-length DB wire on H-terminated C(001) surface. The energy zero represents the Fermi level. The direction of the ΓX line is along the DB wire. The solid line represents the dangling-bond state. In (b), the solid (dashed) line represents the dangling-bond state of majority (minority) spin, while the filled (open) circles represent the majority(minority-) spin eigenvalues obtained from the slab calculations. The spin density, ρ_{up}-ρ_{down}, of the (d) FM and (e) AFM configurations are also displayed. The plots are drawn in the vertical plane containing the C atoms of the DB wire. In (d) and (e), the first solid (dashed) line is at 0.001 (−0.001) electron/bohr^3 with spacings of 0.005 (−0.005) electron/bohr^3.

one. Thus, we can say that the stability of the C DB wire is realized not by a Peierls-like lattice distortion but by generating spontaneous spin polarization. As shown in Fig. 2(b), the band structure of the FM configuration shows the split of the majority- and minority-spin bands, yielding a band-gap opening. For the AFM configuration, we find a band-gap opening of 1.66 (1.54) eV at the Γ ($X_{1/2}$) point [see Fig. 2(c)], thereby being a semiconductor.

In Fig. 2(a), the dangling-bond state in the NM configuration does not have a flat-band-like character, differing from the case of ZGNR[9,10] where a twofold degenerate flat band is formed at the Fermi energy in a part of the Brillouin zone away from the zone center. This implies that the dangling-bond state in the DB wire would be relatively less localized compared to the edge states in ZGNR. This different feature of electronic states between the DB wire and ZGNR possibly results in the different magnetic orderings for the two systems: the former has an antiferromagnetic ground state, while the latter gives rise to a ferromagnetic ordering for the dangling bonds at each zigzag edge. Note that the spin density ρ_{up}-ρ_{down} (defined by the difference of majority- and minority-spin densities) of the FM configuration [see Fig. 2(d)] not only overlaps between adjacent C atoms along the DB wire but also persists down to the third-layer C atoms. Consequently, the FM configuration may become less stable than the AFM one because of a weakened Hund coupling of dangling bonds while with a relatively more favorable antiferromagnetic interaction. However, the detailed mechanism for the AFM ordering should be disclosed in future. It is notable that ferromagnetic and antiferromagnetic orderings in high-temperature superconducting cuprates are competed depending on the extent of wave-function overlap between neighboring atoms. For example, in the $(La\text{-}Nd)_4Ba_2Cu_2O_{10}$ system, the ferromagnetic interaction becomes antiferromagnetic with increasing overlap between the wave functions of oxygen and La (Nd) ions.[30,31]

In order to examine how the magnetic properties of the DB wire change with respect to its length, we study the NM, FM, and AFM configurations for the short-length DB wires containing up to five dangling bonds. Here, we used a 4×6 unit cell for modeling the short-length DB wires. For an isolated dangling bond, the FM configuration is more stable than the NM one by 393 meV per dangling bond. This energy difference per dangling bond $\Delta E_{NM\text{-}FM}$ between the NM and FM configurations is significantly reduced to 128 meV at the DB-2 wire. We find that $\Delta E_{NM\text{-}FM}$ oscillates with increasing the length of the DB wire (see Fig. 3), showing that $\Delta E_{NM\text{-}FM}$ of the odd DB wires (i.e., 173 and 144 meV for DB-3 and DB-5, respectively) are larger than those of the even DB wires (128 and 119 meV for DB-2 and DB-4). This oscillatory behavior of $\Delta E_{NM\text{-}FM}$ indicates that the NM configurations of the odd DB wires, which have a half-filled uppermost energy level, are relatively less stable compared to those of the even DB wires, which have a doubly paired uppermost energy level. For each DB wire, the AFM configuration is further stabilized compared to the FM one. The calculated energy difference $\Delta E_{NM\text{-}AFM}$ between the NM and AFM configurations is given in Table I, also showing an oscillatory behavior of $E_{NM\text{-}FM}$ (see Fig. 3). An opposite spin orientation between adjacent dangling bonds in the AFM

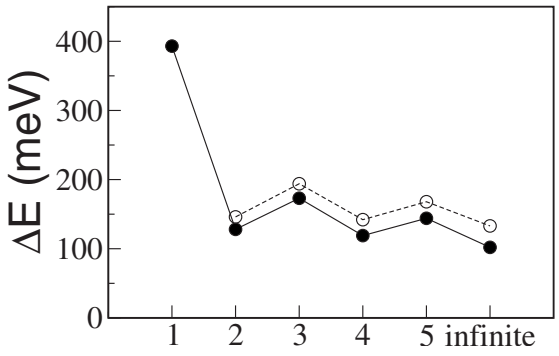

FIG. 3. Calculated energy difference per dangling bond between the NM and FM (or AFM) configurations as a function of the length of the DB wire. The filled (open) circles represent $\Delta E_{NM\text{-}FM}$ ($\Delta E_{NM\text{-}AFM}$) between the NM and FM (AFM) configurations.

configuration is illustrated in Fig. 4. Therefore, the total spin of the finite-length DB wire containing odd (even) dangling bonds is $1\mu_B$ ($0\mu_B$) (see Table I).

On the basis of our DFT calculations, we estimate the exchange coupling constant J between two spins (S_1 and S_2) in the DB-2 wire, which is defined through the Heisenberg spin Hamiltonian $\hat{H}=J\hat{S}_1\hat{S}_2$. Here, J is expressed in terms of the energy difference between the triplet (which has the total spin $\hat{S}_{tot}=1$) and singlet ($\hat{S}_{tot}=0$) states,

$$J = E_{triplet} - E_{singlet}. \quad (1)$$

According to the broken symmetry method,[20,32] even though our calculated AFM configuration corresponds to a mixed spin state with a combination of singlet and triplet states, the energy of the AFM configuration is approximated to $E_{singlet}$. Therefore, J can be obtained by the energy difference between the FM and AFM configurations. For the DB-2 wire, we obtain $J=36$ meV (see Table II), which is smaller than

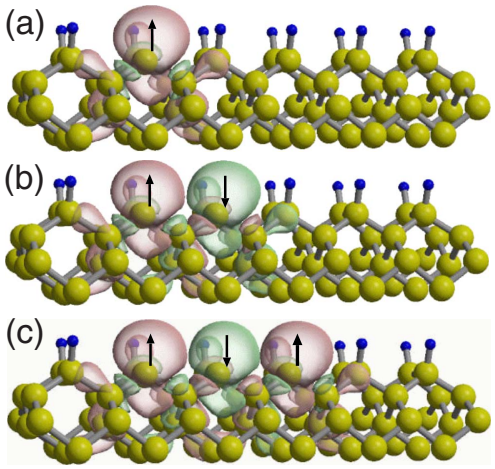

FIG. 4. (Color online) Calculated spin density ρ_{up}-ρ_{down} for the ground states of (a) isolated dangling bond, (b) DB-2, and (c) DB-3 wires. The positive (negative) spin density is displayed with an isosurface of 0.001 (−0.001) electron/bohr^3.

TABLE II. Calculated energy difference per unit cell between the FM and AFM configurations for the infinite-length DB wire and the short-length DB wires. The calculated exchange coupling constants between adjacent spins are also given.

DB wire	E_{FM}-E_{AFM} (meV/unit cell)	J (meV)
2	36	36
3	63	32
4	92	31
5	120	30
Infinite	31	31

the observed[16] values (ranging from 7 to 14 meV) from dangling bonds generated on the surfaces of H-terminated NDs. If we assume only the existence of the nearest neighbor interactions in the DB-3, DB-4, DB-5, and infinite-length DB wires, we can express the energy difference between the FM and AFM configurations as a sum of pairwise interactions between the nearest neighbors. Hence, J in each DB-n wire is given by $J=\frac{1}{n-1}(E_{FM}-E_{AFM})$. For the DB-3, DB-4, and DB-5 wires, we obtain $E_{FM}-E_{AFM}=63$, 92, and 120 meV, thereby yielding $J=32$, 31, and 30 meV, respectively (see Table II). In the same way, we obtain $J=31$ meV for the infinite-length DB wire. Therefore, the exchange coupling constant between adjacent spins in the DB wires converges to ~31 meV.

In summary, we have performed a first-principles DFT study for the magnetism of one-dimensional dangling-bond wires on a H-terminated C(001) surface. Our study showed that unpaired electrons on the C(001) surface yield magnetic moments which are coupled antiferromagnetically. Thus, the existence of carbon magnetism can be extended to sp^3-bonded diamond.

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[29] In order to examine the substrate-wire interaction in the C DB wire, we calculated the total energy of the C DB wire with respect to the lattice distortion. Similar to the Si DB wire, we allowed an alternating vertical displacement (i.e., up and down) of the surface C atoms composing the DB wire on C(001). We found that the total energy of the distorted C DB wire relative to that of the undistorted one monotonically increases with increasing the height difference (Δz) between the up and down atoms. This energy difference between the distorted and undistorted DB wires is calculated to be 0.013, 0.055, 0.125, and 0.235 eV/DB for $\Delta z=0.12$, 0.24, 0.36, and 0.48 Å. For comparison, in the

silicon case, the distorted DB wire (where Δz is 0.76 Å) is more stable than the undistorted one by 0.043 eV/DB. Thus, we can say that the Peierls instability costs more elastic energy in diamond than in silicon.

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