Tunable half-metallicity in substitutionally-doped boronitrene

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Abstract. First principles calculations are performed within density functional theory to investigate the effect of dopant clusters on the physical properties of boronitrene. We show that the electronic structure in boronitrene can be tuned to give full spin-polarized currents by embedding self-assembled substitutional complexes of carbon, boron or nitrogen atoms. We find that doping the layer with a hexagonal ring cluster of boron, nitrogen or a star-shaped cluster of carbon atoms induces spontaneous magnetic moments in the layer. Our results show that the geometry of the embedded cluster, the in-plane strain, and the charge state of the layer are relevant means for engineering the electronic degrees of freedom. The hybridization states of both the itinerant and localised defect states are investigated to unravel the origin of the spontaneous magnetic moments.

1. Introduction

Recent developments in magnetoelectronics have aroused renewed interests in half-metallics. These are materials with only one type of conduction electrons - spin up or spin down. Their electronic structure presents a gap only in the minority band. The dominance of metallic transport in one spin channel, and either insulating or semiconducting behavior in the opposite spin channel makes them useful as spin filters, and for enhancing the performance of spin-dependent devices, among many other applications [1]. This arises because their Fermi-level electrons are 100% spin polarized. In nanoscale spintronics however, it is desirable to use materials with tunable spin magnetic moments. Because only *s* and *p* electrons are involved in the magnetism of carbon-only materials [2-6], it is potentially possible to overcome the limitations of current technologies that rely on half-metallic materials, such as dilute magnetic semiconductors (DMS), Heusler alloys and perovskites, whose magnetism originates from *d*- and *f*- electrons [7]. Moreover, the search for spintronic effects in intrinsically nonmagnetic semiconductors is of current interests [8-11], because of promising new functionalities [12] for nanoscale magnetic applications. This paper shows that half-metallic electronic structure is induced in boronitrene, a one-atom thick plane of hexagonal boron nitride, when self-assembled clusters of boron, carbon or nitrogen are embedded in the layer. We predict, based on results of first-principles calculations, that the electronic structure is tunable to full spin-polarized currents by microstructural engineering, application of compressive biaxial strain or charge injection.

2. Computational details

Spin-polarised and nonmagnetic electronic structure calculations were performed based on density functional theory as implemented in Vienna *ab initio* simulation package (VASP) [13–16]. The exchange-correlation potential was described in the generalized gradient approximation, using the parameterization of Perdew, Burke, and Ernzerhof (PBE) [17]. The projector-augmented wave (PAW) method [18,19] was used to describe ionic interaction. Cut off limits of 500 eV and 10^{-7} eV were set for the plane wave expansion set and electronic energy convergence. The Monkhorst-Pack scheme [20] was used to sample the Brillouin zone using a grid of density 10×10×1. A vacuum region of height 15 Å was used to separate periodic images of the monolayers to avoid spurious layer-layer interactions. Self-assembled substitutional complexes of carbon, boron or nitrogen atoms, were constructed in each case, using a 5×5 supercell. Electronic states were populated in the Methfessel-Paxton scheme [21], with a smearing parameter of 0.2 eV. Atomic positions were relaxed until the average forces reduced to less than 0.01 $eVÅ^{-1}$.

3. Results and Discussion

Figure 1 shows fully-relaxed local defect structure and the corresponding spin-resolved difference charge density distribution for spin-up (top panels) and spin-down (bottom panels) electrons. The difference charge density, in this case, is the difference between the charge density in the defective monolayer and the free atom charge density of constituents. These indicate that spin-up electrons are predominantly strong localised along bond axes, except along the hexagonal nitrogen ring cluster. Spin down electron localise mainly at hollow sites and on boron atoms. These suggest that the hybridization states of both the itinerant and localised defect states are important in determining the resulting magneto-electronic properties of the doped monolayers. The observed trend in majority carrier density localisation agrees with *a priori* expectations for the ionicity of B-N bonds because of electronegativity differences between B and N. There are significant distortions in the charge density distribution to show depletion zones in the vicinity of the substitutional defects. Within the hexagonal rings, the bond relaxations are similar (to 3 sig. Figs.). Mean lengths of 1.42 Å (C_{3B}+C_{3N}), 1.43 Å (N_{3B}) and 1.53 Å (B_{3N}) complexes for C-C, N-N and B-B bonds, in each case. These suggest that locally, i.e. along bonds within the embedded ring, there is no build-up of strain, and by extension, no frozen-in local structural disorder.

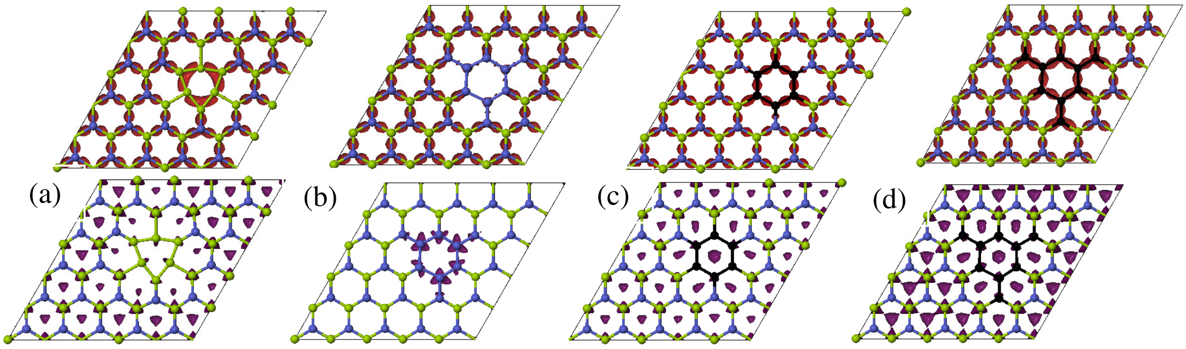

Figure 1. Local structure and difference charge density distribution showing spin-up (top panels) and spin-down (bottom panels) electron localisation in self-assembled clusters: B_{3N} (a), N_{3B} (b), C_{3B}+C_{3N} (c), and C_{3B}+C_{6N} (d) complexes in boronitrene.

Heteroatom substitutional complexes of hexagonal symmetry yield defect complexes that are both stoichiometric (C_{3B} +C_{3N}) and nonstoichiometric (B_{3N}, N_{3B} and C_{3B}+C_{6N}). The ground state of the stoichiometric C_{3B} +C_{3N} complex is nonmagnetic because an imposed spin polarisation does not change the total energy of their ground state and results in zero macroscopic magnetic moment. On the other hand, the magnetically-ordered state of the nonstoichiometric N_{3B} complex is only 2×10^{-6} eV more stable than the corresponding nonmagnetic state. The macroscopic magnetic moment vanishes in to give antiferromagnetically-ordered ground state in the N_{3B} complex because of mutual cancellation of the ordered electron spins. In the nonstoichiometric B_{3N} complexes however, the magnetoelectronic properties of the monolayer is significantly different. We find that the magnetic ground state of the B_{3N} complex is favoured over the nonmagnetic state by 0.207 eV. This results in a spontaneous macroscopic magnetic moment of 2.00 μ_B in the layer. For carbon complexes that maintain triangular symmetry, we note that the smallest size, designated as star-shaped cluster, is obtained when the number of carbon N_C that substitutes boron and nitrogen is four. Triangular ring cluster (TRC) geometries are obtainable from the star-shaped cluster when $N_C > 4$. We find that both boron-terminated (C_{1B}+C_{3N}) and nitrogen-terminated (C_{1N}+C_{3B}) star-shaped carbon complexes present the same total energy of -437.17 eV under spin-polarisation. However, their nonmagnetic state is relatively less stable because its total energy is higher than the corresponding spin-polarised state by 0.336 eV.

Because the energy of formation of the B_{3N} (9.84 eV), N_{3B} (15.09 eV) and C_{3B}+C_{3N} (24.82 eV) complexes are significantly higher relative to C_{1B}+C_{3N} complex (-0.09 eV), we conclude that their formation is not spontaneous and therefore will require external energy to activate. For complexes formed through substitutions with carbon, we find that the energy penalty required for formation of boron-terminated complexes from free boron, nitrogen and carbon atoms at their standard reference states (P = 1 atm and T=273 K) is lower than that of the nitrogen-terminated. For instance, the formation of the C_{1B}+C_{3N} complex [see Fig. 1(a)] is energetically more favourable than formation of the C_{1N}+C_{3B} complex by 137.3 kJmol^{-1}. The same trend is observed in larger carbon clusters of triangular geometry. Similarly, although the number of carbon N_C is 16 in each case, the boron-terminated cluster requires a smaller energy penalty of -3398.93 kJmol^{-1} compared to -3362.88 kJmol^{-1} for the nitrogen-terminated analogue. We will therefore only show boron-terminated carbon clusters because of their high relative stability, and will limit the discussion to the carbon TRC for which N_C = 9 (i.e. C_{3B}+C_{6N} complex).

Figure 2 shows the corresponding spin-polarised DOS. Both commensurate and non-commensurate electron states are present in both spin channels. This gives zero (or non-zero) spin polarizations because the degree of spin polarization $P = [n\uparrow(E_F) - n\downarrow(E_F)]/(n\uparrow(E_F) + n\downarrow(E_F))$, where $n\uparrow(E_F)$ and $n\downarrow(E_F)$ denote the DOS of majority (spin up) and minority (spin down) carriers. Fig. 2 shows that HRCs of boron, nitrogen and carbon induce magnetic moments that are aligned parallel (ferromagnetism) anti-parallel (antiferromagnetism) due to the sign of the charge densities. Carbon TRCs give rise to half-metallic ferromagnetic (HMFM) ground states because their DOS shows non-zero DOS at the Fermi level independent of the cluster size. At zero-bias voltage, the DOS of the hybrid HMFMs clearly favour spin polarised currents, thus making them attractive for spin-based electronics. There is a resulting spontaneous transition from the nonmagnetic (NM) ground state of pristine boronitrene to HMFM ground state when TRCs of carbon are embedded in the layer. We also tested, and confirmed, the presence of non-zero DOS at E_F in both B- and N-terminations of larger sizes (i.e. N_C = 9 and 16) of the same defect cluster geometry.

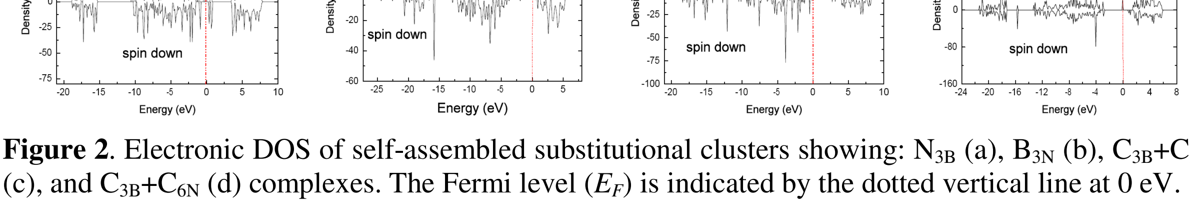

Figure 2. Electronic DOS of self-assembled substitutional clusters showing: N_{3B} (a), B_{3N} (b), C_{3B}+C_{3N} (c), and C_{3B}+C_{6N} (d) complexes. The Fermi level (E_F) is indicated by the dotted vertical line at 0 eV.

Because B-terminated (i.e. C_{1B}+C_{3N}) or N-terminated (i.e. C_{1N}+C_{3B}) star-shaped carbon cluster consistently gives the HMFM ground state, we conclude that half-metallicity is independent on edge-termination of embedded cluster. Thus, the HM character of the spin-up channel coupled with the large spin magnetic moment makes the resulting hybrid BCN layer suitable in spin-filtering applications [22]. However, when the shape of the embedded carbon cluster is changed from triangular geometry to hexagonal ring geometry, we obtain the antiferromagnet (AFM) ground state. We ascribe the nonmagnetic ground state in the C_{3B}+C_{3N} complex to the stoichiometry. More importantly, because HRCs of boron (i.e. B_{3N}) also give rise to HMFM behaviour, albeit with comparably smaller magnetic moment, we conclude that the electronic structure of a hybrid BCN monolayer is tunable using the cluster geometry as a degree of freedom.

Consider that defect-free h-BN monolayer is intrinsically nonmagnetic because an imposed spin polarisation does not affect the ground state total energy. Similarly, the uncharged state of the N_{3B} complex, though magnetically-ordered with zero net magnetic moment, is not half-metallic. Figure 3 shows that finite magnetic moment is induced in these materials by strain engineering and by charge injection. Fig. 3(a) shows the magnitude of the induced magnetic moments due to applied biaxial strain. In this case, positive (+) and negative (-) strain denote the external application of uniform stretching or compression along the plane of the monolayer, in each case. This shows that application of more than 3% compressive strain induces finite magnetic moments in pristine h-BN monolayer. Uniform stretching, on the other hand, does not alter the nomagnetic ground state of thre pristine layer. Similarly, we find that the AFM-ordered ground state in the N_{3B} complex, and the nonmagnetic B_{3B}+B_{3N} complex exhibit spontaneous magnetic moments when subjected to > 1% in-plane compression. The strain-induced magnetic moments increases with increased compression, and the carbon HRC gives substantially larger magnetic moment compoared to nitrogen HRC.

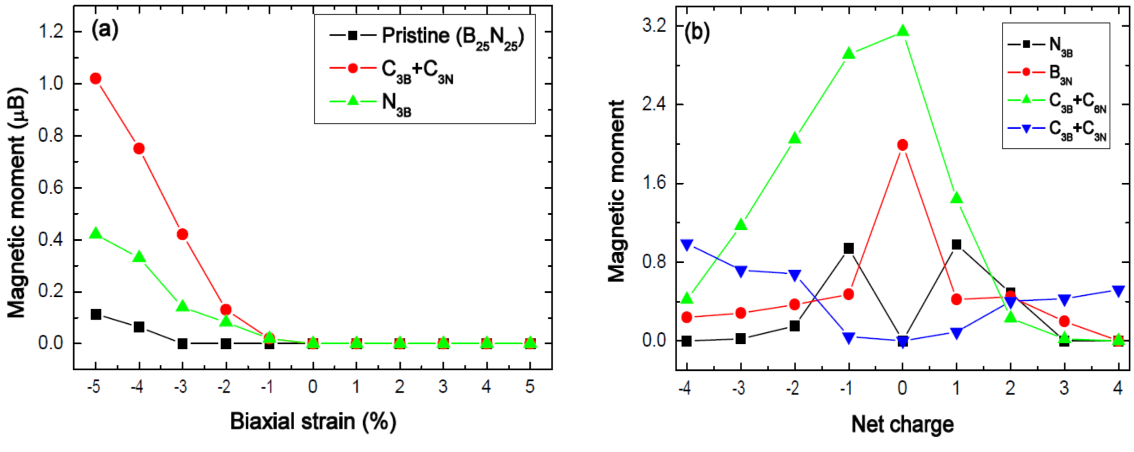

Figure 3. Tunability of magnetic moment by strain engineering (a), and charge injection (b), in hybrid BCN monolayers

Similarly, Figure 3(b) shows the tunability of the defect-induced magnetic moments in typical *h*-BN monolayer by charge injection. This shows that the magnetic moment due to the HM ferromagnetism of the uncharged C_{3B}+C_{6N} complex [see Fig. 2(d)] decreases to give HM ferrimagnetism when electrons (i.e. up to -4), and holes (i.e. up to +2), are injected into the layer. For the half-metallic B_{3N} complex, the same trend is obtained. However, the magnetic moment is only quenched when the injected charge q = +4. Consider that the electronic DOS at the Fermi level must only vanish in one spin channel to obtain the HM magnetic ground state. The observed variation in magnetic moments of HMFMs shows that the half-metallic electronic structre is tunable.

Thus far, it is clear that the uncharged state of the both N_{3B} and C_{3B}+C_{3N} complexes have zero magnetic moment. Finite magnetic moments are induced when charges are injected into the hybrid BCN layers that contain these complexes. In the N_{3B} complex for instance, doping by a single electron gives rise to magnetic moment of 0.98 μ_B, and a single hole injection also induces magnetic moment of the same magnitude. We attribute this trend to stoichiometry of the C_{3B}+C_{3N} complex. The nonstoichiometric N_{3B} complex shows a similar general trend, but between -1 → -2, and +1 → +2 charge states, we find that the two complexes show opposing characteristics [see Fig. 3(b)]. Nevertheless, further electron (or hole) doping beyond -3 (or +3) charge states results in no magnetic moments. Taken together, we conclude that the site ordering and the geometry of the embedded complexes determine the magnetic transitions, which are tunable, or charge injection.

Figure 4 shows the electronic band structure of the half-metallic C_{3B}+C_{6N} complex under variable charge injection levels. In its uncharged state, the valence band is filled – up to the Fermi level. Here the Fermi level is indicated by the red horizontal line at 0 eV. However, the complex introduces a defect which forms an *s*-resonance with the Fermi level. Because of the Fermi-level resonant state is dispersive – showing strong dependence on Brillouin zone direction – it localises as non-zero DOS under spin polarisation [see Fig. 2(d)]. The electronic structure of the HM ferromagnetic C_{3B}+C_{6N} complex changes significantly under the influenec of electron and hole doping. For instance, under electron doping, the Fermi level is found to shift deeper into the conduction band as more electrons are injected. On the other hand, the Fermi level shifts slightly deeper into the valence band when more holes are injected into the layer. It is therefore expected that the extra electrons are mainly delocalised, and therefore contribute itinerant electron states that cancels the local spin magnetic moment. By contrast, we conclude that hole states are localised because the position of the Fermi level shifts to lower energies with progressive hole-injection. It is therefore not unexpected for hole states to modify the bonding states. It is therefore plausible that the effect of the resulting hybridization with localised hole states should justify the progressive cancelation of the local spin magnetic moment (see Fig. 3(d)]. Since the observed changes in magnetic moments with charge state do not alter the half-metallic character of the layer, we assert that the electronic structure is tunable to half-metallic ferrimagnetism in a manner similar to hole doping in carbides and nitrides of main group elements [23,24].

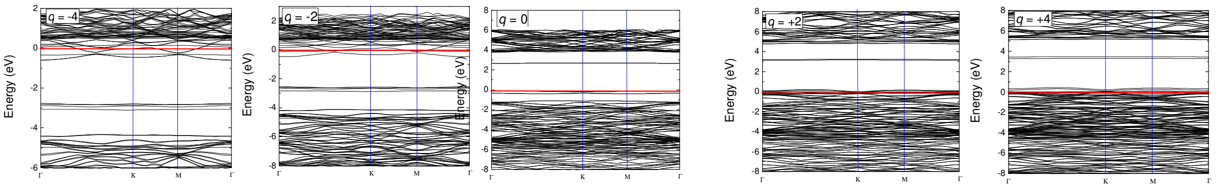

Figure 4. Electronic band structure in half-metallic C_{3B}+C_{6N} complex under variable charge injection.

4. Conclusion

We have performed first principles calculations to investigate the effect of dopant clusters on the physical properties of boronitrene. Our results show that half-metallic electronic structure is induced in boronitrene when self-assembled hexagonal cluster of boron or triangular cluster of carbon is embedded in the layer. We have shown that finite magnetic moments are induced in nonmagnetic hybrid layers by application of compressive biaxial strain and charge injection. Our results suggest that the half-metallic electronic structure originates from the competition between itinerant and localised electron states when a hexagonal ring cluster (HRC) of boron or triangular ring cluster (TRC) carbon is embedded. By contrast, we find that embedding the HRC of carbon does not alter the nonmagnetic state of the layer.

Acknowledgments

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