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Half-metallicity in armchair boron nitride nanoribbons: A first-principles study

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ABSTRACT

Using density functional theory, we predict half-metallicity in edge hydrogenated armchair boron nitride nanoribbons (ABNNRs). The predicted spin polarization is analyzed in detail by calculating electronic and magnetic properties of these hydrogenated ABNNRs by means of first-principles calculations within the local spin-density approximation (LSDA). ABNNRs with only edge B atoms passivated by H atoms are found to be half-metallic (regardless of their width) with a half-metal gap of 0.26 eV. Upto 100% spin polarized charge transport is predicted across the Fermi level owing to the giant spin splitting. Transmission spectrum analysis also confirms the separation of spin up and spindown electronic channels. It is revealed that H-passivation of only edge N atoms transforms non-magnetic bare ribbons into energetically stable magnetic semiconductors whereas hydrogenation of both the edges does not affect the electronic and magnetic state of bare ribbons significantly. The results are promising towards the realization of inorganic spintronic devices.

1. Introduction

Half-metallicity is the key property for spin transport based electronic devices. It has been widely studied and predicted in different nanoscale materials [1–5] accompanied with other compounds like double layer perovskites, [6,7] alloys (including ternary and quaternary Heusler alloys) [8–10], transition metal pnictides, and chalcogenides in zinc blende phase [11–13]. Recently, an exceptionally large room temperature spin polarization of $(93^{+8}_{-11})\%$ has been directly evidenced in an epitaxial thin film of Co_2MnSi [14]. Present article predicts half-metallicity/spin polarization in armchair boron nitride nanoribbons (ABNNRs) via edge hydrogenation. Quasi-one 1-D thin strips carved out of hexagonal boron nitride (h-BN) sheet(s), [5,15–17] properly known as BNNRs, are of high research interest because, as compared to their parent counterpart(s), they also exhibit excellent structural stability and distinct electronic properties due to the quantum confinement effects [5]. Synthesis of hollow BNNRs using B–N–O–Fe as precursor has already been reported by Chen et al. [18]. Similar to their organic counterparts, Graphene Nanoribbons (GNRs), BNNRs can also be fabricated from a single h-BN layer via lithographic patterning [19]. Depending on the definite shape of edges BNNRs are of two type – armchair boron nitride nanoribbons (ABNNRs) and zigzag boron nitride nanoribbons (ZBNNRs). It has been already proven that BNNRs exhibit very fascinating electronic properties similar to that of GNRs, [20,21] which are very important from the application point of view. The band gap (E_g) of BNNRs whose armchair edges are passivated by hydrogen oscillates periodically with increasing width [22] whereas the band gap of ZBNNRs decreases monotonically when both the edges are H-passivated [23,24]. It has been already shown through first principles calculations that spin-polarization may be realized also in BNNRs either with the application of an external in-plane electric field [25] or by chemically functionalizing zigzag edges with different groups such as H and F [26,27]. In our previous study on ZBNNRs, [23] we predicted that one-edge (only B-edge) H-termination makes the ribbons 'semi-metallic' in nature unlike 'half metallic' as predicted by Zheng et al. [26] but for spin polarized transport both of these results are in agreement with each other. Furthermore, half-metallicity has also been revealed theoretically in ZBNNRs through structural modifications (e.g., by making stirrup, boat, twist-boat, etc.) [28] and percentage hydrogenation [29]. In case of ribbons with armchair edges, spin polarization has been predicted in

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hybrid armchair BCN- nanoribbons [30]. However, any systematic and detailed study for analyzing the effect of edge hydrogenation on electronic, magnetic and transport properties of ABNNRs has not been reported so far.

Here, we predict half-metallicity in ABNNRs, induced due to the H-passivation of only edge B atoms. In addition, this article presents detailed and systematic analysis of electronic, magnetic and transport properties for edge hydrogenated (i.e. ribbon edges are passivated partially/fully with H atoms) ABNNRs of different widths. Present analysis reveals that H-passivation of only edge N atoms ($ABNNR_{HN}$) transforms bare ribbons into energetically stable 'magnetic semiconductors' unlike 'nonmagnetic semiconductors' as predicted by Ding et al. [31] On the other side, H-termination of only edge B atoms ($ABNNR_{HB}$), regardless of ribbon width, converts bare ABNNRs into ferromagnetic/anti ferromagnetic half-metals.

1.1. Computational details

The first-principles calculations were performed with Atomistix Tool Kit-Virtual NanoLab (ATK-VNL). [32,33] We employed ATK-VNL simulation package which is based on density functional theory (DFT) coupled with non-equilibrium Green's function (NEGF) formalism. The exchange correlation energy was approximated by local spin density approximation (LSDA) as proposed by Perdew and Zunger [34]. The reason for selecting LDA is that the generalized gradient approximation underestimates the surface–impurity interactions. [35] The ABNNRs were modeled with periodic boundary conditions along z-axis, whereas the other two dimensions were confined. The energy cutoff value of 100 Rydberg was selected for the expansion of plane waves. We implemented double ζ plus polarized basis set for all the calculations. The k-point sampling was set to $1 \times 1 \times 100$. In order to avoid artificial inter-ribbon interactions, ribbons were separated using a cell padding vacuum region of 10 Å. All the atoms, in the considered geometries, are relaxed and optimization of atomic positions and lattice parameters has been continued until the forces on each constituent atom reduced upto 0.05 eV/Å. We represent the ribbon-width by a width parameter N_a, defined as the number of B/N atoms along the ribbon width as depicted in Fig. 1, therefore, ABNNR with n B/N atoms across the ribbon is named as n-ABNNR.

2. Results and discussion

For present calculations we have considered ABNNRs with – (i) fully H-passivated edges ($ABNNR_{HBN}$) and (ii) half H-passivated edges. Furthermore, the ABNNRs belonging to later category are divided into two subgroups i.e., $ABNNR_{HB}$ and $ABNNR_{HN}$ depending upon whether only B or only N edge atoms are passivated by H-atoms respectively. The electronic and magnetic properties of bare ABNNRs have also been investigated and said ribbons were found to be nonmagnetic semiconductors in consistent with Ding et al. [31]. In order to take size effects into considerations, we investigate ABNNRs having widths N_a=6–10. Since the findings are qualitatively similar for symmetric ribbons (Odd N_a), we displayed the figures only for ABNNRs with N_a=9. Fig. 1 schematically represents optimized geometry of 9-ABNNR in all considered ribbon configurations with N_a=9 as representative case. The corresponding convention of super cell, used for simulation, is also depicted for various ribbon structures.

The calculated electronic band structures with corresponding density of states (DOS) for 9-$ABNNR_{HB}$ and 9-$ABNNR_{HN}$ are illustrated in Figs. 2 and 3 respectively. A significant difference in the form of giant splitting of spin states can be clearly observed in, both, band structure as well as DOS profile. For 9-$ABNNR_{HB}$, the spindown channels [Fig. 2(a)] are metallic as (shown with red lines), α [valence band maximum (VBM)] and β [conduction band minimum (CBM)] crossing the Fermi level. On the other hand, due to the presence of a larger band gap (4.64 eV) the spin-up (blue) bands exhibit insulating behavior as shown in Fig. 2(b). This half-metallic behavior is qualitatively independent of width and is observed for all investigated $ABNNR_{HB}$ structures. We predict that the charge transport across the Fermi level through all $ABNNR_{HB}$ structures should be dominated by the spin-down electrons. The same behavior is also reflecting in the corresponding DOS profile [Fig. 2(c)] where the crossing of Fermi level by spindown states is observed. The transmission spectrum (TS), [20] plotted as transmission coefficient (TC) versus energy graph in the

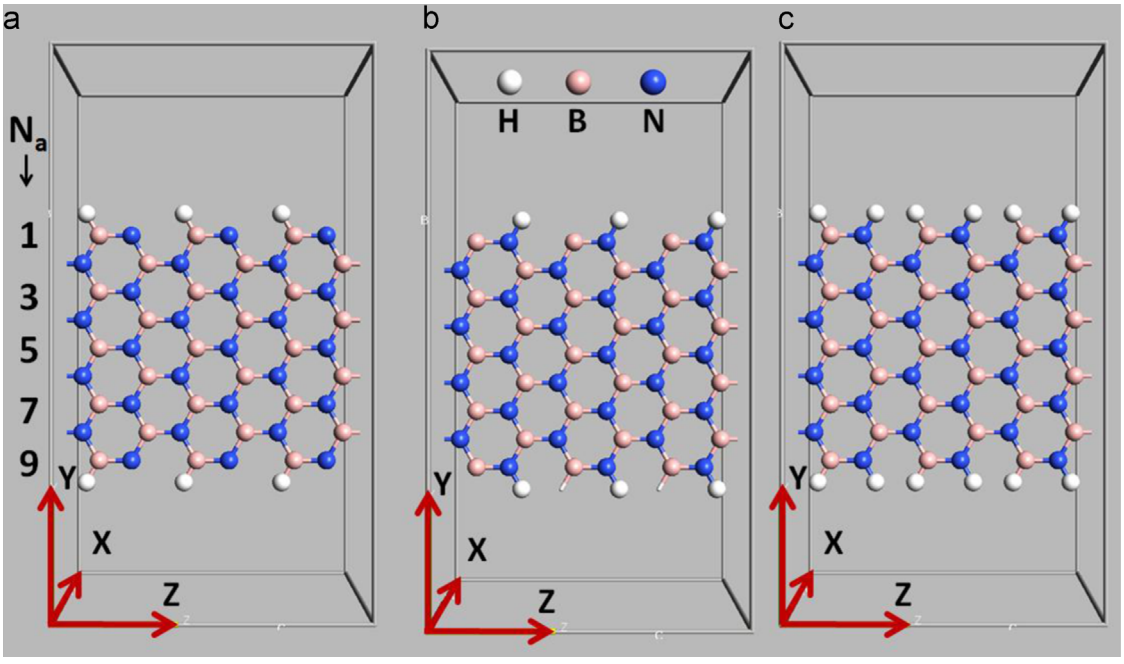

Fig. 1. (Color online) Convention of ribbon width and the supercell units (N_a=9) for (a) $ABNNR_{HB}$, (b) $ABNNR_{HN}$ and (c) $ABNNR_{HBN}$. The ABNNRs are modeled with periodic boundary conditions along z-axis whereas x and y directions are confined.