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Strain engineering effect on surprising magnetic semiconducting behavior in zigzag arsenene nanoribbons

M. Abid [a,*], Anwer Shoaib [b], Imran Aslam [c], Muhammad Asim Farid [d]

[a] School of Physics, Beijing Institute of Technology, Beijing 100081, China
[b] Beijing Key Laboratory of Construction-Tailorable Advanced Functional Materials and Green Applications, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China
[c] Department of Physics, Riphah Institute of Computing and Applied Sciences (RICAS), Riphah International University, Lahore, Pakistan
[d] Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, China

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ABSTRACT

The enduring goal in condensed matter physics is to search for controlled magnetism in semiconducting materials. Based on first principles DFT calculations, we systematically investigate the electronic and magnetic properties of zigzag arsenene nanoribbons (ZAsNRs). We find that metallic edge states originate in the middle of bulk band gap for different widths of ZAsNRs due to electronic instability. Besides, edge magnetism for different magnetic configurations of ZAsNRs, have been investigated to remove these instabilities. There occurs a transition from non-magnetic to magnetic and metallic to semi-conducting edge states and as a result an intra-edge antiferromagnetic (AFM) semiconducting ground state has been found. In order to tune the edge states, strain engineering is employed on magnetic ground state and found that at critical value of compressive strains (−6%), there happens a transition from magnetic to nonmagnetic (NM) and semiconductor to metal. We expect that these semiconducting properties can be controlled by edge magnetism and strain engineering and make ZAsNRs a best semiconducting material which can be used as promising candidate for device applications in semiconducting industry.

1. Introduction

Graphene, a monolayer of carbon atoms with honeycomb structure, is the most attractive material with wonderful properties like high mobility [1], mechanical strength and heat conductance [2,3]. But the absence of intrinsic band gap make graphene difficult to use in electronics applications. The discovery of this novel material develop the interest of researchers to find other (two-dimensional) 2D materials with intrinsic band gap and scientific community continue the search to find perfect superconducting materials. Recently 2D materials of carbon group: silicene, germanene and stanene with honeycomb structures have attracted much attention due to their optical, electronic and magnetic properties [4–6] with intrinsic gaps [7]. Their band gaps can be controlled by applying perpendicular electric field [8–10] and these are the topological insulators with spin-orbit interactions [11]. Black phosphorene (BP), a monolayer of phosphorus atoms with puckered structure, owing exceptional properties like mechanical, optical, thermoelectric and electronic properties [12–16], was obtained by mechanical exfoliation [17,18], plasma-assisted exfoliation [19] and liquid exfoliation [20,21]. Because of the chemical and structural similarity of elements belonging to the same group-V of periodic table, arsenene and antimonene (As/Sb), monolayers of As/Sb atoms with different phases are under experimental investigations [22–25]. The orthorhombic arsenene own extraordinary properties like high carrier mobility and solid anisotropy [26] which makes it favourable candidate for device applications and solar cell. In a theoretical study, it has been reported that puckered arsenene is a 2D topological material with ultra-high mechanical stretch-ability [27].

By getting motivation from the work on phosphorene and orthorhombic arsenene, we systematically studied the electronic and magnetic properties of the edge atoms for the black phosphorene type structure of zigzag arsenene nanoribbons (ZAsNRs). Carefully examining the electronic band structures for different widths of ZAsNRs, we have observed that the width of 8-ZAsNRs gives the sharp, well defined edge states which cross the fermi level exactly at $\pi/2a$ and make the ZAsNRs metal. It has already been reported that monolayer arsenene has an indirect band gap

* Corresponding author.
E-mail address: abid629@yahoo.com (M. Abid).

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[23]. Herein we employee the edge magnetism by considering different magnetic configurations at the edge of 8-ZAsNRs. Our results unexpectedly show an AFM semiconducting ground state (AFM-3) with intrinsic direct band gap.

It has also been known that strain engineering is an efficient mechanism for tuning electronic and magnetic properties of 2D materials. Recently, for 2D materials like phosphorene and arsenene, strain engineering assist as a practical way for controlling electronic, optical, magnetic and thermodynamic properties [12,15,28–30]. Finally, we apply the strain-engineering in order to check whether it affects the magnetic properties or edge states. From our results, it is found that a compressive strains of critical value (−6%) will make the edge states crossing the fermi level twice which results a transition from magnetic to nonmagnetic and semiconductor to metal. These stable electronic and magnetic properties make this ZAsNRs a promising potential candidate for nanoelectronic devices.

2. Computational details

We employ the first principle calculations based on density functional theory (DFT) as implemented in the Vienna ab initio simulation package [31]. The electron exchange-correlation functional was treated within the generalized-gradient approximation (GGA) in the form suggested by Perdew, Burke, and Ernzerhof (PBE) [32–34]. The cutoff energy of 400 eV is employed for the plane wave basis set. The atoms are fully relaxed until the energy and force convergence standard are set to 10^{-5} eV per atom and 10^{-2} eV/Å for each atom. The relaxed lattice parameters for [1]monolayer arsenene are **a = 3.688** and **b = 4.756** as shown in Fig. 1(e). The electronic wave functions are described using a plane wave basis set. We also use a vacuum distance of 20 Å in order to avoid an artificial interaction from neighboring unit cell during the whole calculations. Different k-mesh scheme of 9×1×1 and 15×1×1 are adopted for ZNRs and it is found that 9×1×1 is suitable which is used during the whole self-consistent calculations. The valance electrons from $4s^2 4p^3$ orbitals of As (arsenene) are explicitly included. While doing edge magnetism calculations, we fix the As atoms in the nanoribbon while we only relax the edge atoms during edge magnetism. This process allows us to keep the high symmetry of the bulk locally and to do better comparison of the desired features of edge states.

3. Results and discussion

3.1. Influence of ribbon width on band splitting of edge states

We have performed the non-spin polarized calculations to check the electronic band structure of ZAsNRs. The schematic diagram for 8-ZAsNRs are shown in Fig. 1. The outermost edge atoms are bonded with just two nearest neighbor edge atoms while have different situation with internal atoms as shown in Fig. 1(e). In order to explore the influence of nanoribbon width on the electronic properties, we have considered different width of ZAsNRs. The band structure calculations for widths of 4, 6 and 8 ZAsNRs are shown in Fig. 1(a–c) respectively. It can be observed that there are two bands crossing the fermi level shown by red line in Fig. 1 (a–c). The bands are quite separated from the bulk band gap and can be seen as pure edge states. The edge states come from different edges of the ZAsNRs. On one hand, it can be noticed that as the width of ZAsNRs increases in Fig. 1(a–c), the band splitting at Γ point decreases and these edge states vanish for small width of nanoribbons. While on the other hand as the width increases from 12-ZAsNRs, the interactions between the edge atoms become weaker which leads to decrease the edge state splitting at Γ point. Herein we notice that the width of 8-ZAsNRs shows well shaped edge states so we take 8-ZAsNRs in all our calculations. For the width of 8-ZAsNRs in Fig. 1(c), the edge states are one dimensional and exactly half-filled because of one dangling bond per edge atom. These edge states are nearly degenerate in more than half of the brillion zone and cross the fermi level exactly at $\pi/2a$ make the ZAsNRs to be metal. The density of states have also been shown in Fig. 1(d), which confirms the metallic edge state behavior for 8-ZAsNRs.

3.2. Strain effect on electronic band structure of ZAsNRs

As mentioned above that the edge states for 8-ZAsNRs are well shaped and cross the fermi level exactly at $\pi/2a$, so it is natural to guess that electronic band structure can change affectedly if one can tune the edge states. It is very well known that edge sates are very sensitive to strain [35], doping, external field effect and passivation [36]. Herein we are taking into account the effect of strain on the edge states. The band structure for strained system of 8-ZARNs are calculated in Fig. 2. When the compressive strain is applied, we observed that the edge states move a little away from the fermi level up to −4%. The main influence of compressive strain is that it increase the band splitting at Γ point as compared to strain free arsenene nanoribbons. The band splitting of edge states continue to increase and at a critical value of −6%, it cross the fermi level at Γ point. It is noticeable that the edge states cross the fermi level twice at critical compressive strain (−6%), so the system behaves as metal. On the other hand, when extensive strain is implied, it gives the same result. But for extensive strain, the edge states at Γ point cross the fermi level at critical value of 10%.

3.3. Ground state for ZAsNRs with edge magnetic configurations

In former discussion, it has been confirmed that for 1D metallic edge states, the electronic band is exactly the half-filled of the brillion zone. Herein we want to demonstrate that a unique edge magnetism at the edge atoms shows some unexpected magnetic properties. Spin-polarized calculations have been performed with relaxed structure of 8-ZAsNRs. In order to find the ground state, we select four different magnetic configurations: ferromagnetic (FM), intra-edge FM and inter edge AFM (AFM-1), intra-edge AFM and inter-edge FM (AFM-2), intra-edge AFM and inter-edge AFM (AFM-3), as shown in Fig. 3.

Firstly, we performed the spin-polarized calculations for 8-ZAsNRs with structure relaxation. Initially magnetic moments based on magnetic arrangement were assigned to all the magnetic configurations shown in Fig. 3. The band structure calculations for NM case and all four magnetic configurations (Fig. 3) are shown in Fig. 4(a). For NM, FM and AFM-1 cases in Fig. 4(a), it can be noticed that edge states from valance band maximum (VBM) and conduction band minimum (CBM) meet at Y point which were crossing the fermi level exactly half of the brillion zone in previous section of without magnetism. This happen because of the reason that for magnetic configurations in Fig. 3, we have to make the unit cell double and as we make the unit cell double, the brillion zone becomes half so the edge states which were crossing the fermi line exactly at half of brillion zone in previous case, now meet at Y point. In order to find the magnetic ground state from all these configurations, we make a comparison of their total energy. It has been found that for relaxed structure of 8-ZAsNRs, FM and AFM-1 magnetic configurations are unstable and always converge to NM energy state lastly. The energy difference between FM and AFM-1 is zero which implies that these are degenerated states. From Fig. 4(a), we also observed that size of the semiconducting

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.