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Hydrogenated and halogenated *M*B (*M*=As, Sb and Bi) monolayers: Structural, electronic, optical and topological properties by first principles calculations

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ABSTRACT

The electronic and optical properties of the functionalization of *M*B (*M* = As, Sb and Bi) by hydrogen and halogen atoms, namely MBX_2 are investigated by first principles calculations. The analysis of the phonon spectra show that all the structures are dynamically stable. The electronic structures indicate that $AsBH_2$ and $SbBH_2$ are suitable catalyst for water splitting, while, $BiBI_2$ and $BiBBr_2$ are intrinsic 2D topological insulators with a large gap of 0.43 eV. Interestingly, $BiBCl_2$, $BiBH_2$, $SbBBr_2$, $AsBBr_2$, $SbBCl_2$ and $AsBCl_2$ monolayers can transform trivial to nontrivial phases under the tensile strain of 2, 10, 10, 12, 14 and 18%, respectively. This work indicates that the functionalized groups can effectively broaden the applications of MBX_2 for water splitting and good topological insulators by tuning the band gaps and the band edges under tensile strains.

1. Introduction

Two-dimensional (2D) materials such as graphene [1,2], silicone [3], stanene [4], germanene [5], borophenes [6], hafnium ene [7], phosphorene [8], transition metal dichalcogenides (TMDs) [9–11], arsenene and antimonene [12] have been rapidly attracted considerable interest for novel and useful electronic, optical or topological properties and have potential application in next-generation semiconductors, electronic and photoelectric devices [13–15]. As one of the effective strategies, the compounds formed by different groups have been broadened significantly the 2D material families and their potential applications. Compounds between different main groups of IV(X = C, Si, Ge, Sn) and VI(Y=O, S, Se, Te), are extensively discussed [16]. Recently, the 2D hexagonal structure of group III-IV binary monolayers of MX (M = B, Al, Ga, In and X = O, S, Se, Te) [17] and the group III-V binary compounds of MX (M = Al, Ga, In and X = N, P, As, Sb) [18] are systematically investigated for high-performance device applications in nanoelectronics and optics. Sahin et al. [19] investigated the III-V binary compounds and found that several monolayers are stable structures. Among those monolayers, the compounds based on arsenic, antimony and bismuth have potential perspectives for the reason that antimony and bismuth are ideal topological insulators (TIs) [20–30] candidates for the strong spin–orbit coupling (SOC).

Furthermore, in order to broaden the potential applications of 2D materials, several techniques can be achieved by introducing defects, external strain engineering and chemical functionalization [31–47]. For example, Xu et al. [40] have determined functionalization with different chemical groups (H, F, Cl Br, I and OH^-) can result in topologically distinct phases of stanene. Very recently, Jin et al. [41] realized the quantum spin Hall (QSH) and quantum anomalous Hall (QAH) phase through chemically modification and nitrogen deposit on Bi or Sb bilayers. Freitas [48] and Li et al. [49] theoretically predicted a promising topological insulator with large gaps by chemical functionalization III-Bi with halogen elements. Therefore, application of chemical functionalization can effectively modify the electronic properties of 2D materials. Motivated by the mentioned above, we will concentrate on exploring the application of functionalized group III-V binary monolayers of *M* (*M* = As, Sb and Bi) boron.

In this paper, the binary monolayers of *M* (*M* = As, Sb and Bi) boron and MBX_2 (*X* = H, Cl, Br and I) are investigated by the first principles calculations. The phonon dispersions calculation results indicate that MBX_2 monolayers are dynamically stable, except for that of $AsBI_2$ and $SbBI_2$. The electronic properties show that $AsBH_2$ and $SbBH_2$ are suitable and efficient catalysts for water splitting

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under the biaxial tensile strain of 0–14% and 0–6%, respectively. Meanwhile, the calculations of edge states and topological invariant Z_2 of halogenation *M*B monolayers reveal that $BiBI_2$ and $BiBBr_2$ are topological insulators with large band gaps, and $BiBCl_2$, $BiBH_2$, $SbBBr_2$, $AsBBr_2$, $SbBCl_2$ and $AsBCl_2$ monolayers can transform trivial to nontrivial phases under the tensile strain of 2, 10, 10, 12, 14 and 18%, respectively.

2. Computational details

All the calculations are performed by using the Vienna ab initio simulation package (VASP) [50,51] based on the density functional theory (DFT). The exchange correlation potential is approximated by generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [52,53]. The vacuum region is set to 20 Å to avoid the interlayer effects of the *c*-axis. The energy cutoff of the basis function is set at 500 eV, and the $19 \times 19 \times 1$ Γ-centered Monkhorst-Pack *k*-points [54] is employed to integrate in the Brillouin-zone for electronic properties. The atomic positions is completely relaxed and the Hellmann-Feynman force between each atom is less than 0.02 eV/Å for the structural optimization, and the convergence criteria of 10^{-6} eV per atom is applied to self-consistent. Considering that the standard PBE functional always underestimate the band gap values, we also apply the HSE06 [55] functional to calculate the band structures. There are heavy atoms in our calculations, the spin-orbit coupling (SOC) effect is considered in calculations. Meanwhile, we use the PHONOPY code [56] with VASP through the density functional perturbation theory (DFPT) [57,58] for phonon dispersions calculations to confirm the stabilities. Herein, the WANNIER90 code is used to construct the maximally localized Wannier functions (MLWFs) [59,60]. Based on the MLWFs, the surface Green's function of the semi-infinite system are then obtained for the edge states calculations.

3. Results and discussion

3.1. Structural optimization

The relaxed monolayers *M*B and MBX_2 (*M* = As, Sb, Bi; *X* = H, Cl, Br, I) crystallizes are shown in Fig. 1, which in the hexagonal structure with space group $P3m1$ (C_{3V}^{-1}). Fig. 1(a) shows the monolayer structure of AsB and SbB, which are graphene-like structures with the lattice constants of 3.39 Å and 3.74 Å, respectively. While, the structure of BiB is nonplanar as shown in Fig. 1(b), and the lattice constant and the buckling distance is 3.89 Å, 0.51 Å, respectively, which are in good agreement with previous results [19,61]. All the relaxed structural parameters of *M*B monolayers can be seen in Table S1 (Supporting Information). Fig. 1(c) shows the top views (left) and side views (right) of hydrogenated and halogenation *M*B monolayers. The relaxed lattice constants (*a*), buckling distances (Δ), bond angles (θ) of B-*M*-B, bond lengths (*l*) are displaying in Table 1. The buckling distances and bond angles are about 0.6–0.7 Å and 111.4–112.7°, respectively. As is seen, the lattice constants and the buckling distances for MBH_2, $MBCl_2$ and $MBBr_2$ increase with the atomic number.

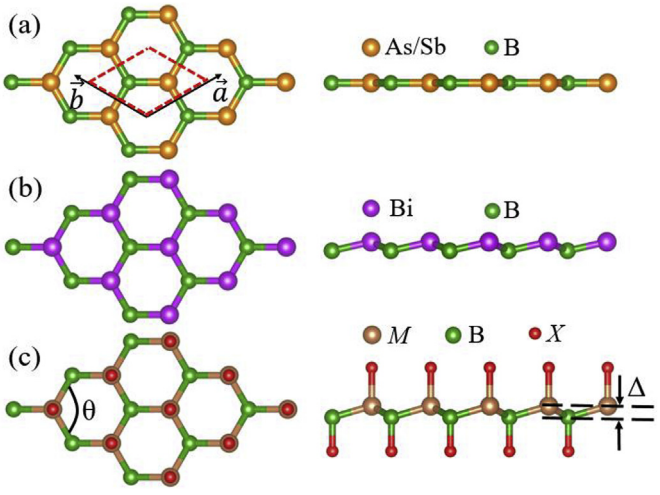

Fig. 1. Top views (left) and side views (right) of the relaxed structure (a) As/SbB, (b) BiB and (c) MBX_2 (*M* = As, Sb, Bi and *X* = H, Cl, Br, I) monolayer. The red dashed box represents the unit cell and the primitive (black dashed arrows) lattice vectors of *M*B and MBX_2 monolayers. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Considering the successful fabrication techniques in the experiments of few-layer materials (Sb, BiIn and TiBi) [62–66], such as mechanical exfoliation, Van der Waals epitaxy, molecular beam epitaxy and chemical vapor deposition, and the *M*B (*M* = As, Sb and Bi) monolayers are expected to be synthesized in experiment. Moreover, previous studies discussed that modification can be realized utilizing electron irradiation or scanning tunneling microscope (STM) technologies [30,67], therefore, hydrogenated and halogenated *M*B (*M* = As, Sb and Bi) monolayers can be achieved in the near future in experiment. And in the following we mainly focus on the optical and topological properties.

3.2. Electronic and optical properties of MB monolayers

The electronic band structures of *M*B monolayers are calculated (see Table S1 and Fig. S1). The results indicate that AsB, SbB and BiB monolayers are all semiconductors with direct band gaps of 0.76 eV, 0.32 eV, 0.51 eV at K (−1/3, 2/3, 0) point, respectively. Meanwhile, HSE06 functional were also applied for comparison and the SOC effect are considered. We can see that the band gaps are a little larger than that of the PBE functional calculations.

In order to explore the applications of AsB, SbB and BiB monolayers, we then investigated the optical properties of *M*B monolayers in the range of the visible light. The calculated optical absorption coefficients are shown in Fig. 2 by PBE, HSE06, PBE+SOC and HSE06 + SOC functionals. Our results indicate that AsB, SbB and BiB monolayers have efficient absorption coefficients around $6 \times 10^4\ cm^{-1}$, which is remarkably larger than that of pure BN [68,69] and alkaline earth metal atom doped-BN monolayers [70] in the range of visible light. In addition, the isotropic phenomenon along *a* and *b* axises is clear. The absorption performances suggest that the *M*B monolayers is promising materials for optoelectronic devices.

3.3. Stabilities and electronic properties of MBX_2 monolayers

To investigate the stabilities of the MBX_2 monolayers, the phonon dispersions are calculated using DFPT method, as is shown in Fig. 3. Fig. 3(a)–(j) represent the $AsBH_2$, $SbBH_2$, $BiBH_2$, $AsBCl_2$, $SbBCl_2$, $BiBCl_2$, $AsBBr_2$, $SbBBr_2$, $BiBBr_2$ and $BiBI_2$ monolayers, respectively. Obviously, there is no imaginary frequency in the whole Brillouin zone, indicating all the structures are stable. However, for $AsBI_2$ and $SbBI_2$ monolayers, there are some visible imaginary frequencies near the Γ point. Therefore, we only discuss the properties of $AsBH_2$, $SbBH_2$, $BiBH_2$, $AsBCl_2$, $SbBCl_2$, $BiBCl_2$, $AsBBr_2$, $SbBBr_2$, $BiBBr_2$ and $BiBI_2$ monolayers in the following work.

Fig. 4 shows the band structures of MBX_2 monolayers by PBE functional. It can be clearly seen that all the MBX_2 monolayers are direct band gap semiconductors with the bandgaps of 3.37, 2.59, 1.27, 1.64, 1.25, 1.06, 1.08, 0.30, 0.06 and 0 eV, respectively, while,