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Research article

Electronic and adsorption properties of halogen molecule X_2 (X=F, Cl) adsorbed arsenene: First-principles study

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ABSTRACT

The geometry, electronic structure, and adsorption properties of halogen molecule X_2($X = F$, Cl) on arsenene were investigated using first-principles calculations. The adsorption of molecules was considered at various sites and in various orientations on the pristine arsenene (p-As) surface. Both molecules show chemisorption and the crystal orbital Hamiltonian population (COHP) analysis reveals the formation of strong X-As bonds. In particular, the adsorbed molecules spontaneously dissociate into atomic halogen atoms, with a diffusion barrier of 1.91 (1.72) eV for F_2(Cl_2). The adsorbed X_2 molecules induced distortions in the local geometry due to strong interaction with arsenene. Importantly, the formation of X-As bonding remarkably changed the electronic properties, evidenced by the decrease of the actual band gap due to the emergence of defect states within the band gap. For instance, the F_2 adsorbed arsenene system (F_2-As) exhibited an average band gap of 1.17 eV, and Cl_2 adsorbed arsenene (Cl_2-As) showed an average band gap of 0.83 eV. In particular, indirect to direct band gap transition was observed for some adsorption configurations. The reduction in band gap resulted in the enhancement of electrical conductivity. These findings suggest that the electronic properties of arsenene can be tuned by halogen decoration.

1. Introduction

In recent years, driven by unique physical properties and applications, two-dimensional (2D) materials have received great attention in the scientific community [1,2]. A monolayer of arsenic, known as arsenene, was first predicted theoretically in 2015 and

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later on, realized experimentally in 2020, has earned particular attention in the research community due to its stable structure and intrinsic semiconducting nature [3–5]. The remarkable electronic properties owned by arsenene make it a promising candidate for a variety of electronic and optoelectronic applications [6–8]. In its buckled structure (β-arsenene), it is found to be an indirect band gap semiconductor with a theoretical band gap of 1.59 eV [9]. To fully explore the technical scope, different strategies have been employed to modulate the intrinsic properties of arsenene. For example, a direct band gap can be achieved in arsenene with strain [9]. Similarly, direct band gap was also observed for cutting arsenene sheets into nanoribbons with zigzag edges [10].

In a buckled arsenene (hereafter arsenene) lattice, arsenic (As) atoms are alternatively located in two planes forming a honeycomb lattice with a certain buckling height. In this structure, each As-atom is bonded to three neighboring As-atoms through covalent bonds, while, each As-atom has a lone pair on it [11]. The presence of these extra electrons makes the arsenene an active material for capturing the gas molecules. In particular, molecules of high electronegative elements (halogens) could strongly interact with arsenene and alter the actual properties. There have been numerous theoretical studies on the investigation of the adsorption of toxic gas molecules on arsenene. For instance, using first-principles calculations, Liu et al. observed a moderate interaction strength between gas molecules (CO, CO_2, N_2, NO, NO_2 and NH_3) and arsenene, where the adsorption of NO and NO_2 turned non-magnetic arsenene into magnetic giving a magnetic moment of 1 μ_B [12]. It was reported that NO molecule could be chemically adsorbed on arsenene doped with non-magnetic elements (Al, B, Si) [13]. Chen et al. investigated the adsorption properties of SO_2 and NO_2 on arsenene (p-As), B-doped arsenene (B-As) and N-doped arsenene (N-As) using first-principles calculations and observed that SO_2 and NO_2 are physically adsorbed on p-As and N-As, whereas, chemically adsorbed on B-As [14]. Furthermore, arsenene exhibits weak sensitivity toward H_2S and CH_4 molecules, however, in the presence of NO and SO_2 molecules, the optical response of arsenene is significantly modified, which could be used in optical sensors [15]. In addition, the HCN molecule exhibited physisorption on both p-As and defected arsenene, which turned into chemisorption upon transition metal dopants (Ti, V, Cr and Ni) [16]. Interestingly, the O and B doped arsenene showed improved catalytic activity for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [17]. These studied depict the potential scope of arsenene as gas sensor sensing toxic gases and chemicals.

In 2D materials, the electronic properties are tailored in various ways including external strain, vacancy defects, or doping with external atoms. In particular, owing to large surface area and carrying abundant adsorption sites, decorating 2D materials with small molecules has a great potential to tune the electronic band gap, electrical transport, magnetism, and other properties of the materials as evidenced by the recent studies on the adsorption of molecules on 2D materials [18–24]. Given the high electronegativity and strong bonding environment, halogenation (decorating with fluorine, chlorine, and iodine) serves as a versatile route for the chemical modification of materials to achieve the desired properties [25,26]. The Cl and Br-decorated phosphorene shows improved H_2O and CO_2 adsorption [27]. Halogenated graphene can exhibit extended properties of graphene [28]. The adsorption of diatomic halogen molecules (F_2, Cl_2, Br_2) on two-dimensional materials has been investigated on graphene [29], grapehene-MoS_2 heterostructure [30], and borophene [31]. These findings prove the great potential of halogens to achieve tunable properties. In this study, to address how halogen molecules interact with arsenene and alter its electronic properties, we perform density functional theory (DFT) calculations to investigate the adsorption of halogen molecules X_2 (X = F, Cl) on pristine arsenene (p-As). The results show that both molecules strongly interact with arsenene and dissociate into atomic halogens. The halogen-arsenene systems can exhibit a direct band gap and magnetism, which can broaden the applications of arsenene in various fields.

2. Computational methods and detail

We obtained simulations results by executing total energy (TE) calculations with Vienna Ab-initio Simulation Package (VASP), being known as an efficient and most reliable code for density functional theory calculations [32]. The exchange-correlation part of the TE was incorporated in generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) formalism [33]. The gas capturing capability of 2D arsenic was examined on a 5 × 5 × 1 supercell slab with a sufficient vacuum (15 Å) across the adjacent layers. The lattice vectors and atomic positions were allowed to fully relax with the energy difference between two consecutive iterations of 10^{-4} eV. The ground state charge density was calculated using 8 × 8 × 1 k-points mesh, and the density of states was computed with 12 × 12 × 1 k-mesh. The plane wave basis set was expanded with an energy cut-off of 500 eV. In addition, the effect of van-der-Waal (vdW) forces was respected in the Grimme scheme (DFT-D3) [34]. The binding of molecules on the adsorbent was measured with adsorption energy E_a defined as

$$E_a = E_{X_2/arsenene} - E_{arsenene} - E_{X_2} \tag{1}$$

where $E_{X2/arsenene}$, $E_{arsenene}$ and E_{X2} are the energy of molecule adsorbed As, the energy of p-As without molecule, and energy of isolated X2 (X = F, Cl) molecule, respectively. The net charge exchanged between substrate (arsenene) and gas molecule ΔQ was computed using $\Delta Q = \sum Q_i$ where Q_i is the net charge on the i-atom of the gas molecule. For example, in the case of X_2 (X = F or Cl) molecule, $\sum Q_i = Q_{X1} + Q_{X2}$, where Q_{X1} (Q_{X2}) is the net charge on the first(second) halogen atom of the molecule. To explore the chemical bonding, the Crystal Orbital Hamiltonian Population (COHP) calculations are performed using LOBSTER code [35].

3. Results and discussion

The adsorption of halogen molecules can significantly modify the physical and chemical properties of arsenene. In our previous study on the adsorption of CO molecule on SiX (X = Be, Al, S, N) dual doped arsenene was investigated onto 5 × 5 × 1 supercell [36]. The same supercell size and computational parameters were used in the present study. The relaxed geometry, electronic band

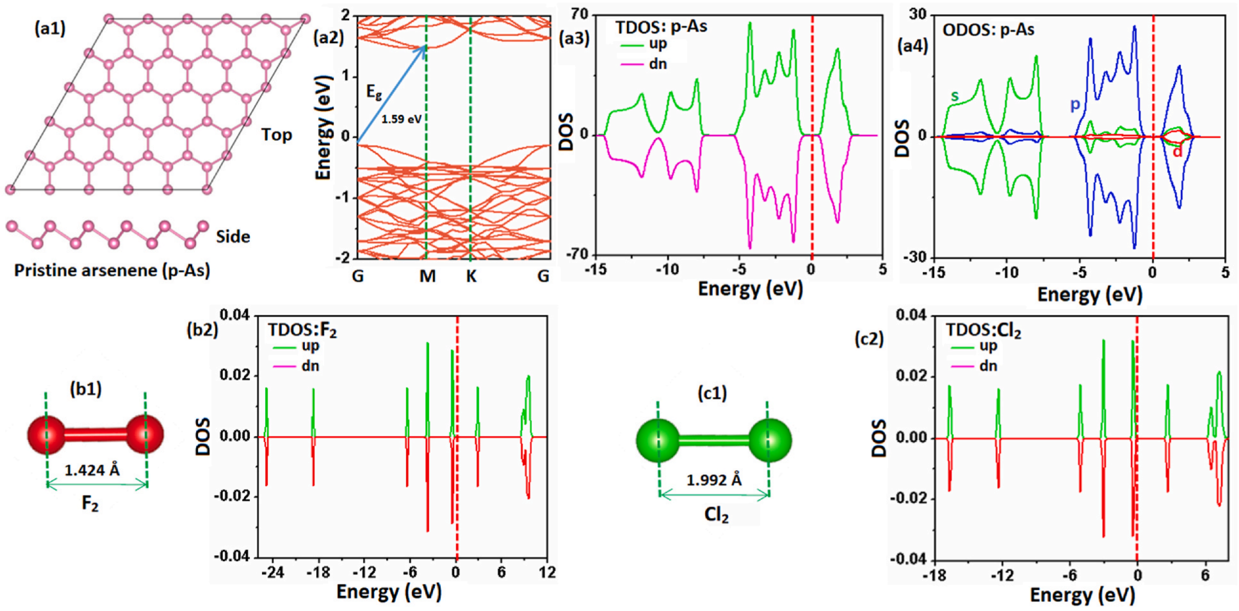

Fig. 1. Geometry and electronic properties of pristine arsenene (a1-a4), geometry and density of states of isolated F_2 molecule (b1, b2), geometry and density of states of isolated Cl_2 molecule (c1, c2).

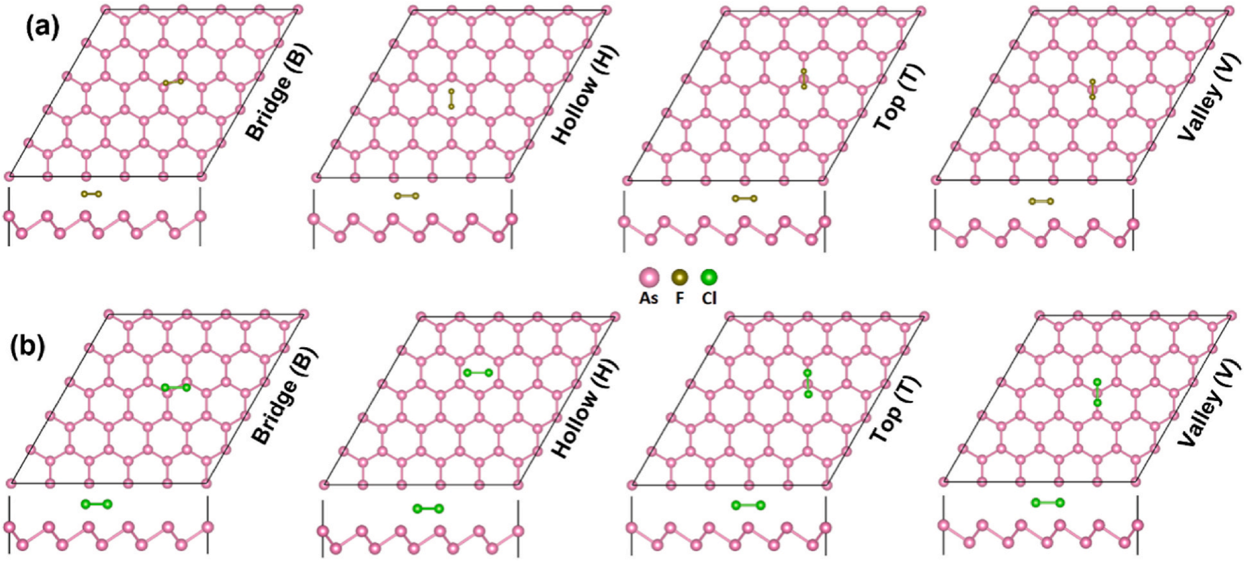

Fig. 2. Initial configuration of X_2 (X = F, Cl) molecule on pristine arsenene p-As.

structure, and density of states or p-As are shown in Fig. 1(a1, a2, a3, and a4). 2D-As has a graphene-like honeycomb lattice formed by the As-atoms. From the side view, it is obvious that it has a buckled structure formed by the AB staking of two atomic planes of As-atoms. This relaxed structure has lattice constant a of 3.608 Å, buckling height of 1.399 Å, bond length d(As) of 2.50 Å, and bond angle of 91.95°. The band structure (Fig. 1-a2) reveals p-As as an indirect bandgap semiconductor, where the valence band top is at the high symmetric gamma-point and the conduction band bottom is located between the gamma and M-point in the Brillouin zone, with a band gap of 1.59 eV. The symmetric distribution of the total density of states TDOS (Fig. 1-a3) in majority and minority electronic states confirms the non-magnetic nature of the material. The analysis of orbital-resolved DOS (ODOS) demonstrates that band edges are mainly formed by the p-orbital electrons. Such results are in agreement with the literature [9,11] and thus ensure the reliability and validity of the proposed computational method. The optimized geometry of the isolated F_2 and Cl_2 is shown in Fig. 1(b1) and Fig. 1(c1), respectively. The ground state F-F interatomic distance d(F-F) is 1.424 Å, and for Cl2, the d(Cl-Cl) is 1.992 Å. The larger interatomic distance in Cl_2 molecule is attributed to the larger size of the Cl-atoms. The TDOS plot for F_2 shown in Fig. 1(b2) shows a symmetric

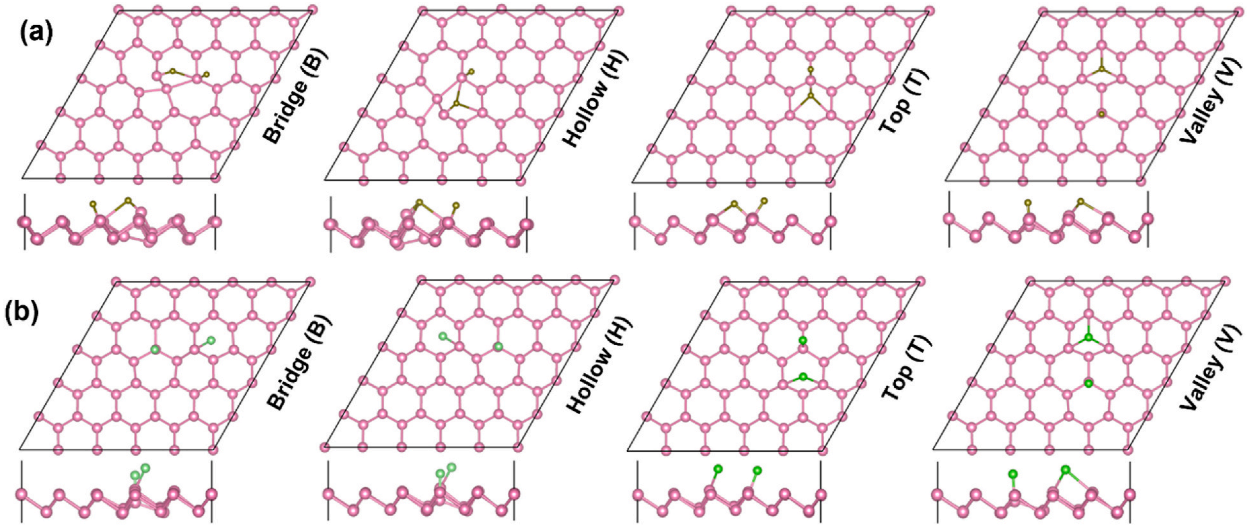

Fig. 3. Relaxed configurations of $X_2(X = F, Cl)$ molecule on pristine arsenene p-As.

Table 1
Adsorption energy E_a in electron-volt (eV), the distance between arsenic (As) atom and X-atom d(X-As) in angstrom (Å), the distance between two X-atoms d(X-X) in Å, and total magnetic moment M in μ_B.

System	site	E_a	d(X-As)	d(X-X)	M
F_2@Arsenene	B	−4.42	1.83	3.18	0
	H	−4.42	1.83	3.24	0
	T	−4.47	1.81	2.39	0
	V	−4.10	1.79	4.16	0
Cl_2@Arsenene	B	−1.37	2.23	5.33	0
	H	−1.37	2.23	5.32	0
	T	−1.09	2.22	3.35	0
	V	−1.26	2.20	4.28	0

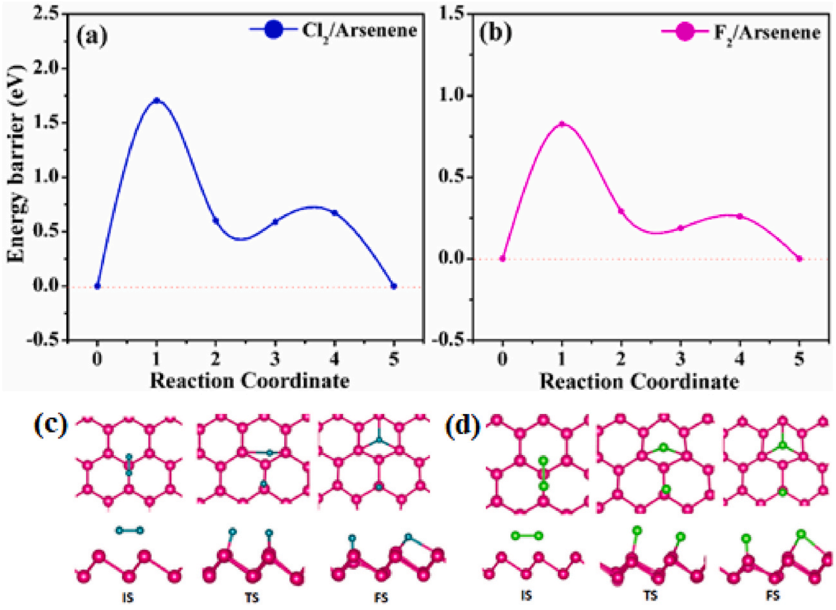

Fig. 4. Diffusion energy barrier as a function of diffusion coordinate for (a) F_2 molecule and (b) Cl_2 molecule. The initial state (IS), transition state (TS), and final state (FS) configurations of F_2 and Cl_2 on arsenene are shown in panels (c) and (d), respectively.

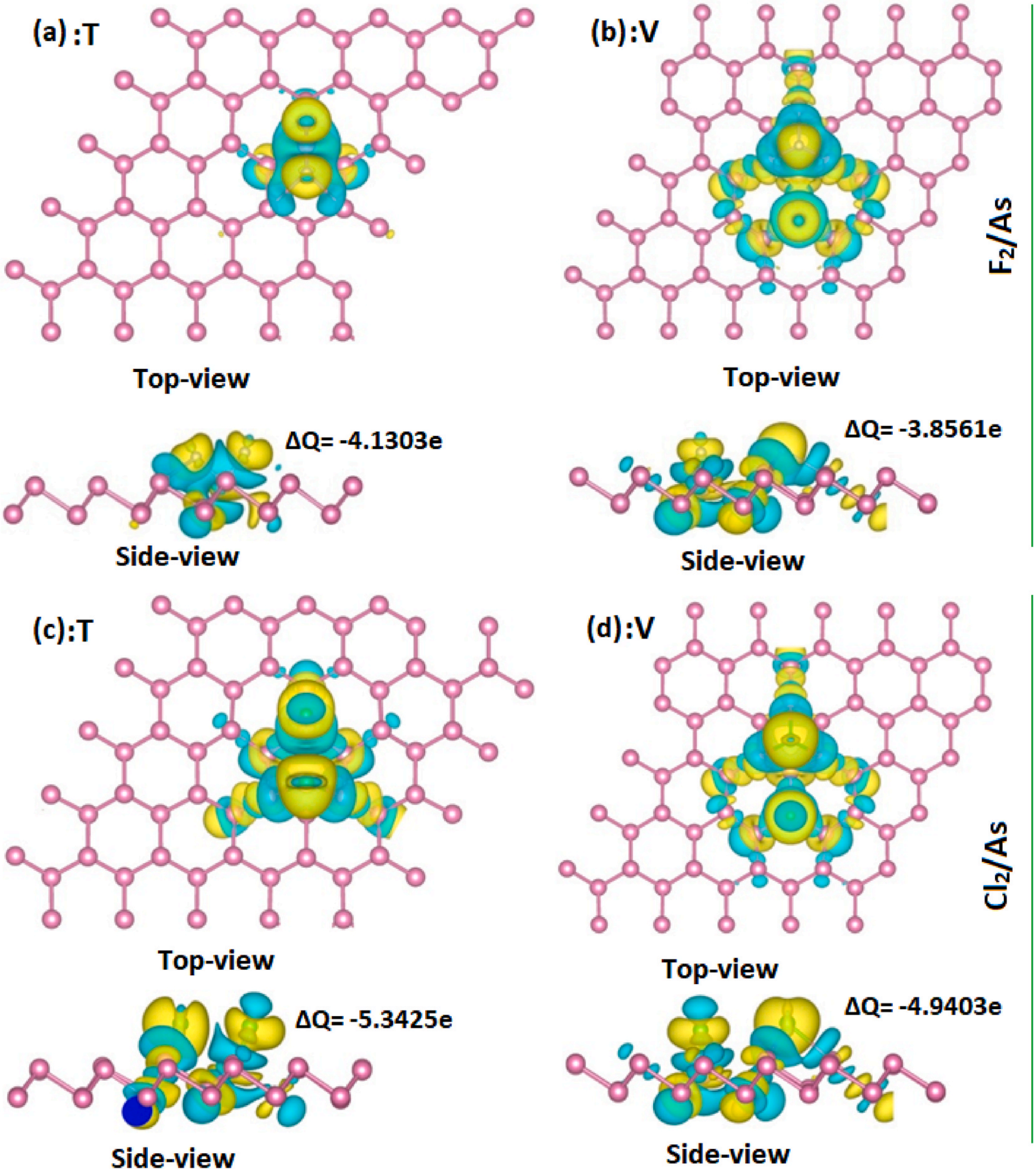

Fig. 5. Charge density difference (CDD) and net charge exchange (ΔQ) for F_2 adsorbed at top-site T and valley-site V (a, b), Cl_2 adsorbed at top-site T and valley-site V (c, d). The yellow (cyan) color represents charge accumulation (depletion) region. The isosurface value is 1.0×10^{-3} e/Å^3. The negative sign of ΔQ shows transfer of charge from arsenene to adsorbed species.

distribution of electronic states in two spin channels, manifesting a non-magnetic nature of the molecule. In addition, the energy states are localized as they appear only at specific energy values. Similarly, the TDOS of Cl_2 shown in Fig. 1(c2) also presents a symmetric and well-localized distribution of electronic states for majority and minority electrons, indicating that Cl_2 has a non-magnetic character.

Four sites were considered for the adsorption of X_2 molecules shown in Fig. 2. The bridge site B lies in the middle of the As-As bond length, the hollow site H lies in the middle of the hexagonal ring of As atoms, the top site T lies on the top of As atom of the upper plane of arsenene, and valley site V lies on the top of As atom of the lower plane of As atoms. On each site, the halogen molecule is placed horizontally at a certain distance of about 1.5 Å from the surface of arsenene. The relaxed geometries after adsorption are depicted in Fig. 3. Our results indicate that for all adsorption sites, the X_2 molecules undergo chemical adsorption and spontaneously dissociate into atomic halogen atoms. To account for the deformation in the local geometry at adsorption sites, calculated bond lengths are shown in Table 1. In F_2 adsorption at the B-site, the F1 atom binds to As1 atom, and F2 binds to As4. The bond length between F1 and As1 atom d(F1, As1) is 1.83 Å, d(F2, As4) is 1.81 Å, and the distance between F1 and F2 atom d(F1, F2) is 3.18 Å, evidencing formation of chemical bonds between F and As atoms. In H-site, d(F1, As1) is 1.83 Å, d(F2, As4) is 2.50 Å and d(F1, F2) is 3.24 Å. Interestingly, when F2 is initially placed at T-site, after adsorption the F1 atom is adsorbed at the off-center position of the hexagonal ring, and F2 occupies

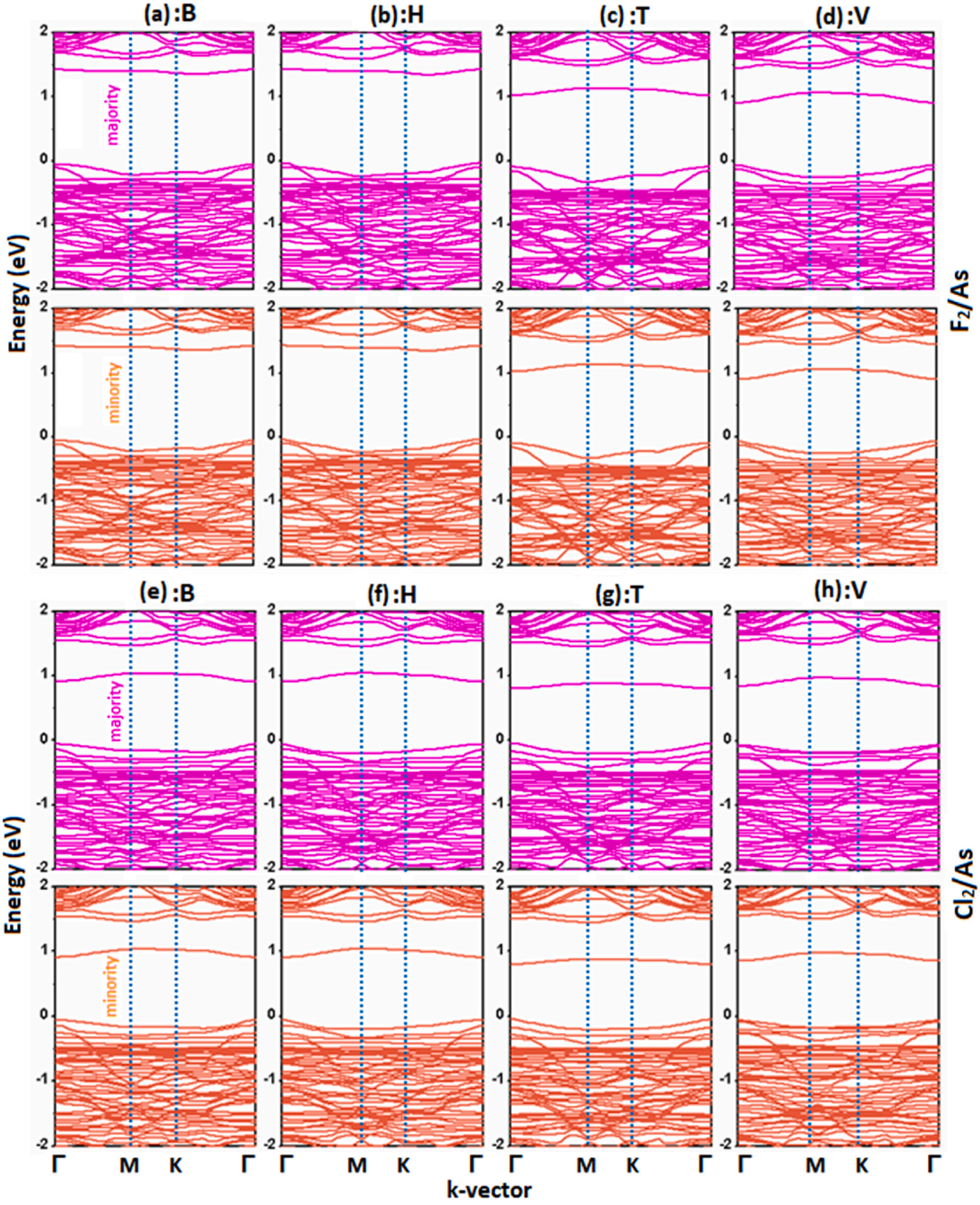

Fig. 6. Electronic band structure for arsenene after the adsorption of F_2 and Cl_2.

the position exactly in the middle of As4 and As5 atoms. The F1 atom binds to As4 with d(F1, As4) of 1.87 Å, and F2 also binds to As4 with d(F2, As4) of 1.83 Å. The two F atoms are at a separation of 2.39 Å. In the V-site, the F1 and F2 atoms stick at regular positions, F1 being on the top of V-site atom with d(F1, As1) = 1.79 Å, and F2 is exactly on the top of the middle of the hexagon with d(F2, As4) =

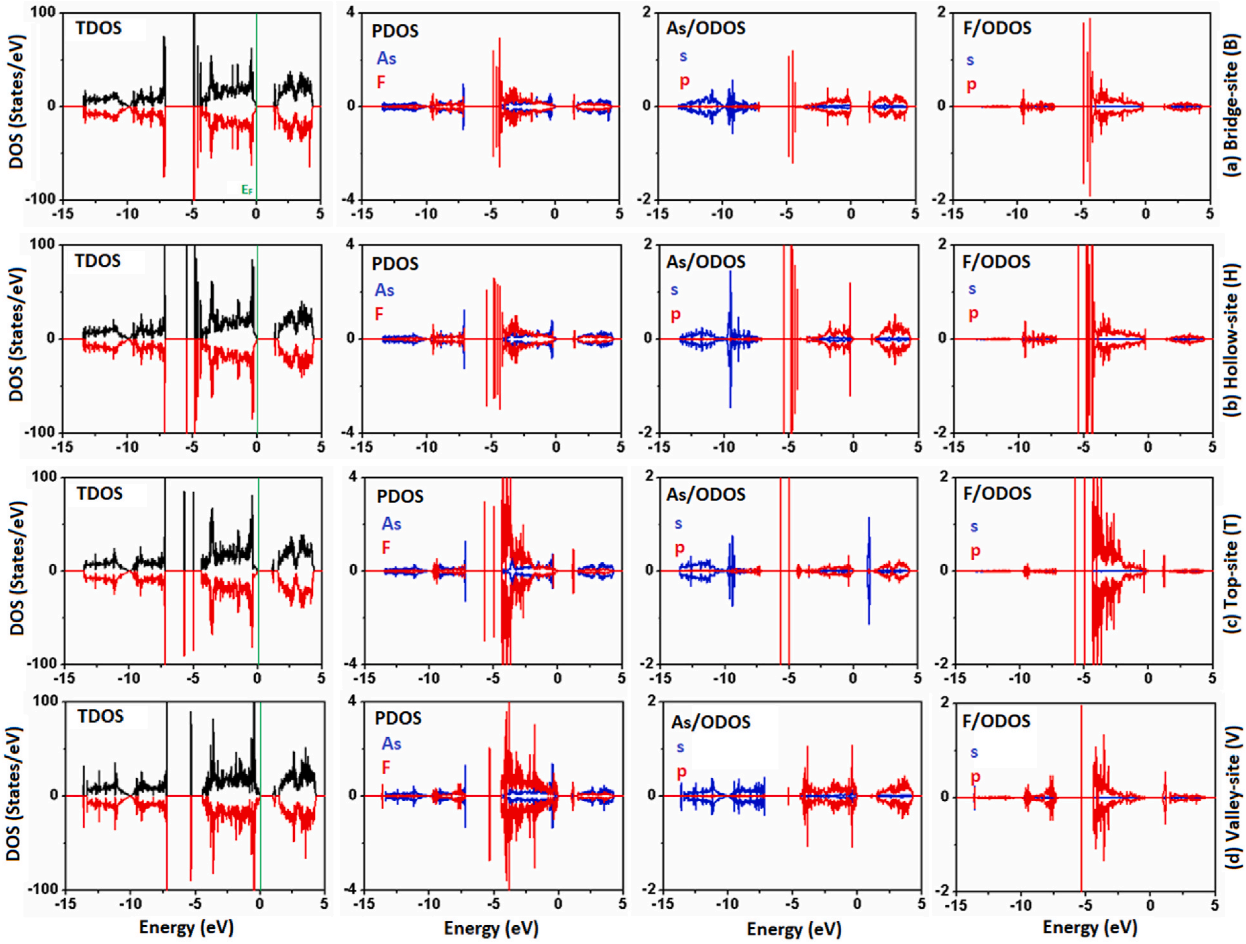

Fig. 7. Density of states (DOS) plots for F_2 adsorbed at B, H, T and V site of arsenene.

2.35 Å, and two F atoms have a large separation of 4.16 Å. On comparing Fig. 3(a–d), it is noticed that adsorption at B-site and H-site induces local strain in the structure, which splits the hexagons into irregular pentagons and octagons. To balance the effect of strain, the neighboring As-atoms move from the actual positions, inducing substantial deformation in the local geometry of the arsenene, while T-site and V-site have almost no typical deformation in the geometry and original geometry is said to be preserved. In Cl_2 adsorption, a distinct feature is observed that is, no hexagon rings have no splitting except the deviation from its regular shape, caused by the slight displacement of the As-atoms from the perfect positions. Similar to F_2, the Cl_2 molecule also dissociates into atomic Cl. The separation between two Cl atoms d(Cl1, Cl2) is 5.33 Å, 5.32 Å, 3.35 Å and 4.28 Å, respectively, for B-, H-, T-, and V-site. These atom Cl atoms are found to be occupied at regular positions above the arsenene. For example, in B-site adsorption, the Cl1 is above V-site and Cl_2 is above H-site. In H-site adsorption, Cl1 is above H-site and Cl2 is at T-site. The average bond length between Cl1 and As1 d(Cl1, As1) is 2.51 Å, and d(Cl2, As2) is 2.35 Å. On comparing the adsorption of two molecules, it is obvious that F atoms have a profound impact on the local geometry, while Cl atoms bring negligible deformation in the structure of arsenene. The formation of chemical bonds between F/Cl and As-atoms is further evidenced by the large value of $|E_a|$. The F_2/As system has E_a of −4.24, −4.23, −4.47, and −4.10 eV for B-, H-, T-, and V-site, respectively. Accordingly, the E_a for Cl_2 adsorption at B-, H-, T-, and V-site is −1.37, −1.37, −1.09, and −1.27 eV. The larger E_a value for F_2 molecule is attributed to the smaller size and electronegativity of F atoms than that of Cl ones. Lamichhane and co-workers investigated the adsorption of halogen molecules (F_2, Cl_2, Br_2 and I_2) on graphene-MoS_2 hetero-structure using first-principles calculations and reported that F_2 molecule shows chemisorption and dissociates into F-atoms with an adsorption energy of −1.82 eV, whereas other halogen molecules show weak interaction and possess very small adsorption energy (Cl_2: 0.158 eV, Br_2: 0.238 eV, I_2: 0.387) [37]. Owing to the large adsorption energy of X_2 (F, Cl) on arsenene, one can predict that arsenene has a great capability to capture halogen molecules. In another study, the adsorption of F_2 molecules on a graphene nanosheet was investigated theoretically [38]. It was reported that F_2 molecule could be chemically adsorbed (with adsorption energy of −1.81 eV, −1.65 eV, −1.03 eV or −1.16 eV) as well as physically adsorbed (−0.40 eV). Thus, in comparison with pristine graphene and graphene-MoS_2 system, the adsorption energy for F_2 on arsenene is much higher.

The negative E_a shows that the adsorption of halogen molecules lowers the energy of the system due to the formation of X-As bonds. To examine how the reactants are converted into products, the diffusion barrier height for the F_2 and Cl_2 molecule has been calculated

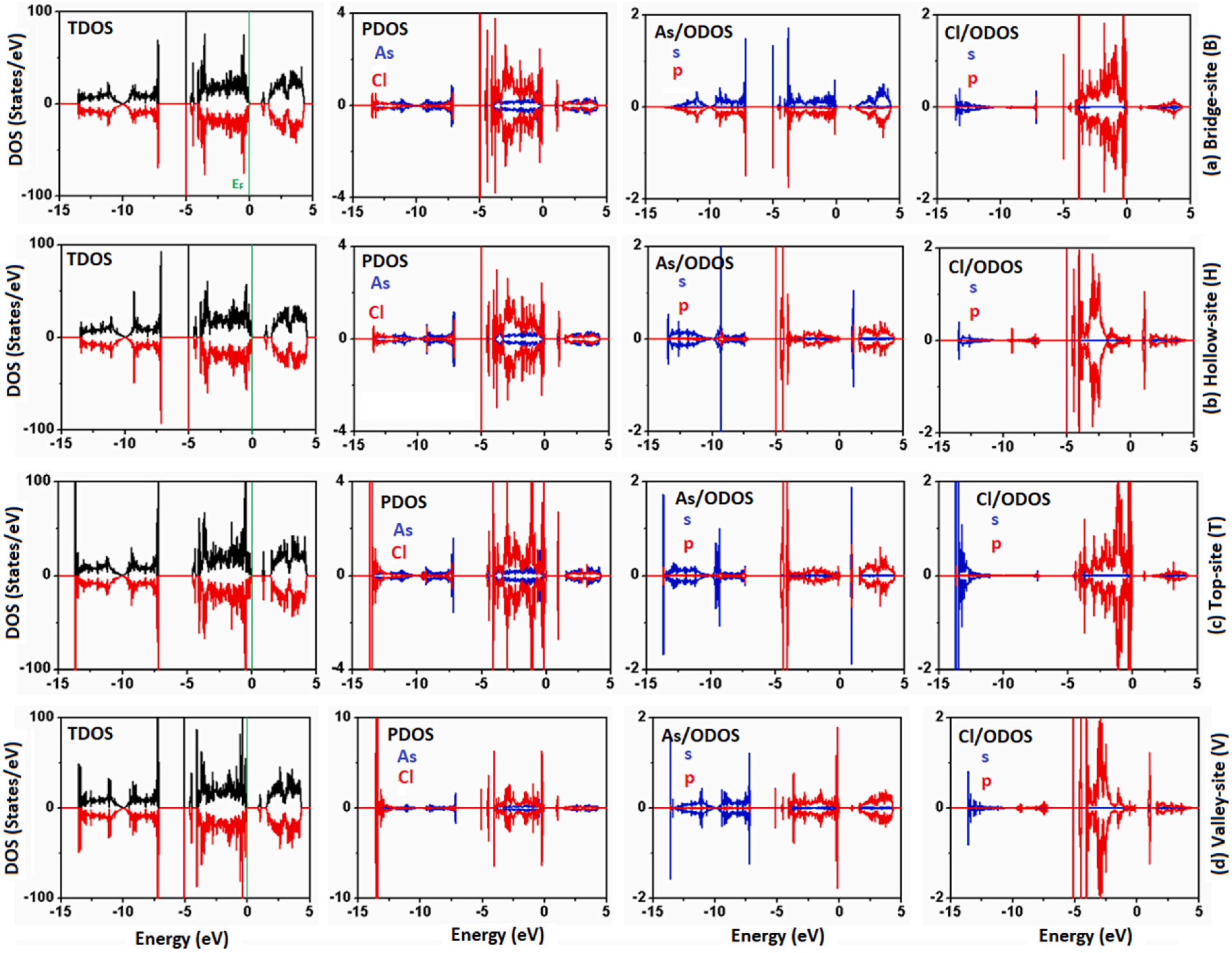

Fig. 8. Density of states (DOS) plots for Cl_2 adsorbed at B, H, T, and V sites of arsenene.

using the nudge elastic band method (NEB) [39], shown in Fig. 4. The initial state (IS), transition state (TS), and final state (FS) configuration of the reactants and products are shown in Fig. 4(c) for F_2, and in Fig. 4(d) for Cl_2 respectively. The results showed that for F_2 (Cl_2) molecule a barrier height of 1.91 (1.72) eV must be crossed for the dissociation of the molecule into individual atoms. The slightly larger barrier height of the F_2 molecule might be attributed to its more compact bonding due to the shorter interatomic bond length.

To better understand the effect of molecule adsorption on the net charge distribution of the substrate, electronic charge density difference (CDD) plots are computed, shown in Fig. 5. The yellow color represents the charge accumulation region and the cyan color represents the charge depletion region. It is indicated in the figure that significant charge redistribution occurs around the molecule adsorption site. The charge depletion region lies within the arsenene surface and the charge accumulation region is located around halogen atoms. Thus, the charge is transferred from the arsenene atoms to the connected halogen atom, in other words, arsenene acts as a charge donor and halogen molecules act as charge acceptors. Due to the formation of new bonds, the electronic structure of the arsenene is believed to be changed as seen in Fig. 6. The new energy states that emerged within the actual band gap are associated with the formation of X-As bonds, leading to the decrease in the band gap width. The transfer of charge between substrate and gas molecule can be explored with DOS plots shown in Figs. 7 and 8. Careful observation of the distribution and shape of orbital DOS plots of As and F atoms reveals that As-p orbitals have a strong overlapping (hybridization) with F-p orbitals, particularly in the region −5 eV to E_F, which causes exchange of charge between the two species.

Spontaneous dissociation of X_2 molecules accompanied by large adsorption energy and charge exchange might bring new features in the electronic structure by redistributing the charge density in arsenene. The dissociative adsorption of gas molecules after adsorption on the 2D surface has been investigated in numerous studies [40–42]. For instance, the adsorption of small molecules F_2, Cl_2, Br_2 and I_2 on graphene-MoS_2 hetero-system was investigated with first-principles calculations [37]. It was observed that, after adsorption, the F_2 molecule dissociates into atomic components, while other molecules keep their isolated geometry. In another work, it was reported that on Si(001) surface Cl_2 and Br_2 molecules spontaneously dissociate into atomic Cl and Br [43].

Next, we examine the electronic properties of arsenene monolayer adsorbed with X_2 (X = F, Cl) molecules. The spin-resolved band

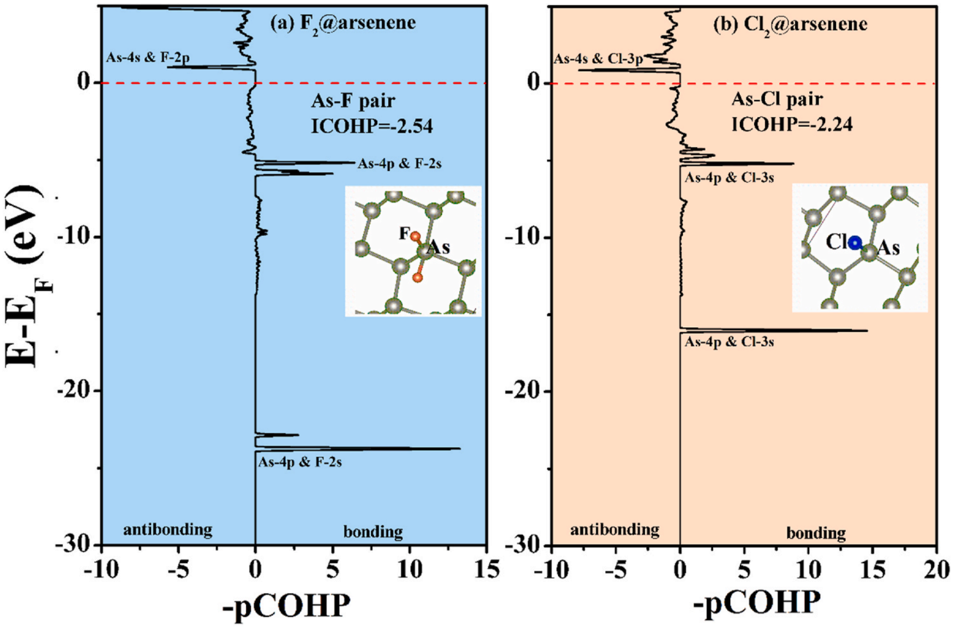

Fig. 9. Crystal Orbital Hamiltonian Population (COHP) analysis for (a) F_2@arsenene, and (b) Cl_2@arsenene.

structure after adsorption is presented in Fig. 6. It is found that the band structure is significantly altered molecules are adsorbed. The E_g is reduced due to the impurity states induced by the molecules. Interestingly, the band structure is identically in both spins, which shows that arsenene adsorbed X_2 (X = F, Cl) system is non-magnetic. The computed E_g is 1.34, 1.34. 1.02 and 0.93 eV for F_2 adsorbed at B-, H-, T- and V-site. Accordingly, the E_g is 0.93, 0.93, 0.73, and 0.73 eV for Cl_2 systems. In particular, indirect-to-direct band gap transition is noticed for i) F_2 adsorbed at T- and V-site, ii) all configurations of Cl_2 adsorption. This change in band structure promises the effectiveness of tailoring the electronic properties of arsenene decorated with halogen molecules and offers new functionalities of the arsenene for optoelectronic applications where a direct band gap is desirable.

The partial density of states (PDOS) and orbital density of states (ODOS) shown in Figs. 7 and 8 indicate that valence band maxima and conduction band minima are mainly attributed to p-state electrons of As and X atom, while the s-state electrons of As atoms contribute mainly to deep energy levels of the bands (around −10 eV below the E_F). In addition, the occupied As-p and X-p states show a strong hybridization in the valence band, indicating a strong bond between them. In contrast, the As-s and X-s states have almost no inter-atomic overlap, thus, we can predict that halogen molecules interact with arsenene through p-p hybridization, leading to the formation of strong chemical bonding between arsenene and halogen molecules.

To analyze the chemical bonding between As-atoms and X-atoms, we have calculated COHP curves for As-F and As-Cl bonds, shown in Fig. 9. The positive value of -pCOHP represents bonding states and nonbonding states correspond to the negative value of -pCOHP. The bonding states stabilize the material whereas antibonding states destabilize the bonding interactions. We find that for both materials, below the Fermi level, the bonding states dominate and are localized. Such a behavior of COHP shows strong bonding between the As-atoms and connected X-atoms. The magnitude of the integrated COHP written as ICOHP is a measure of the strength of bonding. The ICOHP value of the As-F bond (−2.45) is slightly greater than that of As-Cl (−2.24), indicating the As-F bond is stronger which is in agreement with the small size of the F-atom.

The change in electrical conductivity (σ) of the gas sensor after gas molecule adsorption has been analyzed using $\sigma \propto \exp\left(\frac{-E_g}{2k_BT}\right)$, where E_g is band gap, T is thermodynamic temperature and k_B is Boltzmann constant [44]. The electrical conductivity of the gas sensor depends on the E_g of the base material. Our calculations demonstrated that E_g value decreases from the actual value of 1.59 eV–1.13 eV (0.71 eV) for F_2 (Cl_2) molecule adsorption. The corresponding electrical conductivity of the arsenene-based gas sensor increases on halogen molecule adsorption, which can be used as a signal for the detection of the gas molecules.

4. Conclusion

We have investigated the interaction between halogen molecules X_2 (X = F, Cl) and perfect arsenene (p-As) with DFT + D3 method. The horizontal orientation of the molecules was found more stable than the vertical one. Both halogen molecules are chemically adsorbed on p-As and undergo spontaneous dissociation into atomic halogen atoms. The strong binding of X atoms with substrate induces local deformation due to the displacement of the As-atoms at the adsorption site. The formation of new X-As bonds cause reduction in the band gap due to the emergence of defect states inside the band gap. In particular, depending on the adsorption site, the intrinsic indirect bandgap of arsenene can be turned into direct one. The reduction in bandgap increases the electrical conductivity of arsenene. These findings suggest a novel way to modulate the functionality of 2D-As for selective sensing of toxic halogen gases.

CRediT authorship contribution statement

Muhammad Mateen: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Muhammad Mushtaq:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Abdelazim M. Mebed:** Visualization, Validation, Investigation, Conceptualization. **Hanan A. Althobaiti:** Visualization, Validation, Investigation, Conceptualization. **Amel Laref:** Visualization, Validation, Resources, Methodology, Conceptualization. **Niaz Ali Khan:** Visualization, Validation, Methodology, Data curation, Conceptualization. **Sidra Tul Muntaha:** Visualization, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Samah Al-Qaisi:** Methodology, Formal analysis, Data curation, Conceptualization. **Ghulam Abbas Ashraf:** Writing – review & editing, Visualization, Project administration, Conceptualization.

Declaration of competing interest

The authors have no conflicts of interest to declare.

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