DFT study of adsorption and diffusion of Mg, K, Ca over monolayer antimonene

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Abstract. Density Functional theory (DFT) based calculations are carried out to investigate adsorption and diffusion properties of Magnesium (Mg), Potassium (K) and Calcium (Ca) over single layer antimony (Sb) i.e. antimonene. Ca has highest value of absolute adsorption energy followed by K and Mg respectively. Charge transfer is greater in case of K adsorbed antimonene as compared to both of the other metals. This affects the electronic properties such as bandstructure and density of states. Antimonene is semiconducting in its pristine form. The adsorption of K leads to a shift to metallic nature, whereas Mg and Ca adsorption still maintain the semiconducting nature after reducing the bandgap. Diffusion of these metals shows that K can easily diffuse through the antimonene surface as compared to the Mg and Ca. The value of diffusion barrier for Mg, K and Ca is 0.30, 0.12 and 0.43 eV respectively. The effective adsorption and charge transfer along with low values of diffusion barrier suggests that phosphorene can be explored further as potential candidate for metal-ion batteries.

1. Introduction
The Two-dimensional (2D) materials are being constantly researched due to their manifestation of novel properties at nano level. These properties emerge due to the quantum confinement imposed over them in two-dimensions [1,2]. Phosphorene, derived from black phosphorus [3,4] was the first 2D material and it led to synthesis and analysis of many others too, such as silicene [5], germanene [6], borophene [7], arsenene, antimonene, bismuthene [8,9], Transition Metal Dichalcogenides (TMDs) [10,11] 2D tellurium [12] and nitrides [13,14]. Antimonene, the monolayer of antimony (Sb) [15,16] is the material of interest in this work. Among the four allotropes of antimonene [17] β-antimonene is the most stable and thus, it has been used in this research work. Various methods have been developed for its synthesis such as epitaxial growth on Ag (1 1 1) substrate [18], germanene substrate [19] and on various other substrates [20], liquid phase exfoliation [21,22] and mechanical exfoliation [23]. The 2D pnictogens due to their semiconducting nature provide an advantage over graphene which is semimetal with a zero bandgap. The bandgap of these materials can be tamed easily via doping, defects, multi layers or by presence of any foreign element in their vicinity due to which they find place in numerous applications [2,8,17]. Here, we investigated adsorption and diffusion of Magnesium (Mg), Potassium (K) and Calcium (Ca) atoms (metal (M)-atoms) over antimonene monolayer surface. Due to the bigger atomic radius of Sb and buckled structure of antimonene, these large metal atoms can conveniently react over...
its surface without much disturbing the lattice which may not be the case with graphene [24]. The obtained results related to adsorption energy ($E_{\text{ads}}$), activation energy ($E_a$), charge transfer and band structure analysis indicate that adsorption of M-atoms shift the semiconducting antimonene towards metallic properties providing better conductivity and ease of diffusion. This opens up its prospects in applications such as electronic/optical sensors, batteries and smart switching.

2. Computational Details

The visualization and simulation of adsorption and diffusion of metal atoms on antimonene have been done using Density Functional Theory (DFT) [25,26] based Atomistic -Virtual Nanolab (ATK-VNL)[27] simulator. All of the structural relaxations and the calculations incorporate the use of Generalized Gradient Approximation (GGA)[28] functional with Perdew–Burke–Ernzerhof (PBE) exchange correlation and a k-point sampling of 10×10×1 points [29]. During optimization the maximum force of convergence was 0.05 eV/Å. To calculate van der Waals (vdW) effect, Grimme DFT-D2[30] correction has been applied and the density mesh cut-off energy used was 150 Ryd. A vacuum padding of 24 Å in z-axis has been used to neglect the effect of interaction with other layers.

3. Results and Calculations

3.1 Adsorption of Mg, K and Ca over Antimonene and the Associated Properties.

Mg, K and Ca are adsorbed over antimonene individually at different sites as shown in the Figure 1. These sites are named H-site, HEX-site, B1-site, B2-site and T-site for reference. Single atom of these metals was placed above the antimonene surface and the structure was allowed to relax. It results in rearrangements of these sites which are site and metal specific. The lattice parameters of antimonene are $a = b = 4.3$ Å and $\Delta c = 1.59$ Å [31]. The lattice structure remains undisturbed and these parameters remain same after the successful adsorption of M-atoms. However, the adjacent Sb-Sb bonds in supercell were affected a little in some cases which can be traced back successfully after desorption. The $E_{\text{ads}}$ (eV) is calculated using equation,[32]

$$E_{\text{ads}} = E_{\text{(Sb+M)}} - E_{\text{Sb}} - E_{\text{M}}$$

(1)

Where, $E_{\text{Sb+M}}$ is the total energy of M-atom adsorbed antimonene, $E_{\text{Sb}}$ is total energy of pristine antimonene and $E_{\text{M}}$ is total energy of M-atom in molecular configuration. Values of $E_{\text{ads}}$ in each and every case come out to be a negative value as listed in table 1. This infers that all the adsorptions done are exothermic and energetically favourable.

When K is adsorbed, H-site comes out to be the most stable adsorption site since it has highest absolute value of adsorption energy. For Mg and Ca adsorption, Hex-site is the most energetically stable site. In case of Mg, B1 and B2 site converted to Hex-site while all the other sites were retained. For Ca adsorption, only H- and Hex-sites were retained and rest were converted to Hex-site after optimization. However, in case of K adsorption, all the sites were retained after optimization. The height after optimization ($\Delta h_{\text{opt}}$) (Å) and charge transferred ($\Delta Q_M|e|$) between M-atoms and antimonene is mentioned in table 1 for each case. These results confirm that, for each particular atom lowest $h_{\text{opt}}$ and maximum $\Delta Q_M|e|$ obtained corresponds to the most stable site reported.
Figure 1. (colour): Front and cross sectional view of adsorption sites for M-atoms; (a, b) H-site; (c, d) Hex-site; (e, f) B1-site; (g, h) B2-site; (i, j) T-site, (k, l) axis system. Where blue colour represents Sb atoms and pink colour represents M-atoms.

Table 1. Adsorption energy ($E_{ads}$), vertical height of M from antimonene surface after optimization ($\Delta h_{opt}$), M-antimonene bond distance ($\Delta d$) (the numbers in bracket represent number of bonds with same values) and total absolute charge transferred between M and antimonene ($\Delta Q_{M|e|$}) for all the identified adsorption sites.

| Site | H  | HEX | B1  | B2  | T   |
|------|----|-----|-----|-----|-----|
| $E_{ads}$(eV) | Mg | -0.92 | -1.15 | -1.11 | -1.12 | -0.36 |
|       | K  | -1.78 | -1.77 | -1.70 | -1.70 | -1.30 |
|       | Ca | -2.17 | -2.78 | -2.73 | -2.73 | -2.62 |
| $\Delta h_{opt}$ (Å) | Mg | 2.10 | 1.59 | 1.43 | 1.50 | 3.40 |
|       | K  | 2.20 | 2.36 | 2.53 | 2.53 | 2.28 |
|       | Ca | 1.40 | 1.01 | 1.20 | 1.50 | 1.20 |
| $\Delta d$(Å) | Mg | 3.32(3) | 3.03(3) | 2.98(2), 2.99 | 2.98(3) | 3.40 |
|       | K  | 3.45(3) | 3.44(3) | 3.37(2) | 3.37(2) | 3.29 |
|       | Ca | 3.08(3) | 3.01(3) | 3.01(2), 3.02 | 3.01(2), 3.02 | 3.02(2), 3.00 |
| $\Delta Q_{M|e|$} | Mg | 0.03 | 0.09 | 0.09 | 0.09 | 0.02 |
|       | K  | 0.12 | 0.14 | 0.14 | 0.14 | 0.23 |
|       | Ca | 0.02 | 0.04 | 0.01 | 0.01 | 0.01 |
Figure 2. (colour): (a) adsorption energy ($E_{\text{ads}}$), (b) Charge transferred between M-atom and antimonene ($\Delta Q_{M}|e|$) and (c) vertical height of M from antimonene surface after optimization ($\Delta h_{\text{opt}}$) when the M-atom has been placed at varying heights over antimonene for adsorption and the structure is then relaxed. Values shown in black refer to Mg, red to K and blue to Ca related properties.

For better understanding of adsorption phenomena, we tried analysing adsorption when the M-atom was placed at different heights. The resulting graphs are shown in figure 2. At lower heights, the adsorption took place successfully but after a specific height (6 Å for Mg and 7 Å for K and Ca) the atom stops interacting with the antimonene. That is why $E_{\text{ads}}$ and $\Delta Q_{M}|e|$ tends to become zero with increasing distance in figure 2(a) and figure 2(b) respectively. The corresponding $h_{\text{opt}}$ eventually becomes equivalent to the distance at which atom was placed initially in figure 2(c). Mg stops interacting at smaller height due to the smaller size of Mg atom compared to the other two atoms. For every atom, values of $h_{\text{opt}}$ remain almost constant at whatever distance it would have been placed. The average $h_{\text{opt}}$ is 1.3 Å for Mg and Ca and 2.5 Å for K which can be attributed to the larger atomic radii of K. Similarly, the average bond length for Mg and Ca is 3.0 Å and for K, it is 3.3 Å. The number of bonds in each case of adsorption for each atom varies after optimization and it has been given in table 1 for perusal.
Antimonene, in pristine condition is a semiconductor with 1.1 eV energy bandgap [31]. When a single M-atom is adsorbed over it, the bandstructure experiences some shifts as can be seen from the plots given in figure 3(a). The bandgap of the structure experiences a reduction after the adsorption of Mg and Ca atoms. The value of the new bandgap observed is approximately 0.4 eV. K adsorption, however, changes the electronic property of antimonene altogether. We can see from the graph that K adsorption induces metallic properties and the antimonene is no longer a semiconductor. As seen from the bandstructure graph, fermi energy level is moving towards the conduction band in all cases. This, alongwith the reduced bandgap (or conversion to metallicity) indicates that M-atom adsorption leads to higher conductivity in antimonene. The DOS analysis shown in figure 3(b) is also in coordination to what we found out in bandstructure diagram. The reduced bandgap is clearly visible in case of Mg and Ca adsorption. In case of K adsorption, some bands occupy and cross the fermi level. This eletronic behavioural shift can be backed up with the charge transfer analysis as given in table 1. Charge transferred between K and antimonene is higher in comparison to other two adsorbents. This gives us a clear picture that why K adsorption leads to metallic antimonene while Mg and Ca adsorbed antimonene still remains semiconducting in nature.

3.2 Diffusion of Mg, K and Ca over Antimonene.

Movement of M-atoms over antimonene is analyzed using Climbing Image Nudged Elastic Band (CI-NEB) method [33,34]. Three diffusion paths (path I, II, III) were identified over the antimonene surface
as shown in figure 4. Since, Hex-site was most suitable for Mg and Ca, so the initial and final images taken in these cases were of Hex-sites (set B in figure 4) while for K atom, H-sites were used for the same (set A in figure 4). When an atom moves over the substrate surface, it faces energy barrier throughout that path which resists its diffusion. This energy barrier is known as activation energy ($E_a$). For each identified path, graph can be plotted between the diffusion coordinates and the $E_a$ as shown in figure 5. The highest value of $E_a$ at peak in graph decides whether the path is preferred by atom or not. While diffusing, the adsorbent prefers the path of lowest $E_a$, i.e. minimum energy paths.

Figure 4. (colour): Front view of various diffusion paths (path I, II, III) for each M-atom over antimonene layer. (set A) H-site to H-site paths for K-diffusion. (set B) Hex-site to Hex-site paths for Mg- and Ca- Diffusion. Where blue colour represents Sb atoms and pink colour represents M-atoms.

Among all of the three paths, path III has highest $E_a$ for all three atoms because in path III, the M-atom has to cross one Sb atom which requires a lot of energy. For path I and II, the graph looks identical due to the similar placement of saddle points and Sb-Sb bonds in both of these paths. Saddle point is an intermediate stable adsorption site which lies near the defined path. Since the site is stable, relaxation of nearby image of atom during CI-NEB relaxation tends to bring it to that site. This introduces a trough between the energy peaks as can be seen in figure 5(a,b). For Hex sites, H site is the intermediate site and vice-versa. The only exception is when Ca moves along path I or II. Saddle point is absent in both of these plots because Ca does not move to the stable intermediate site, instead it goes rather straight affecting some Sb-Sb bonds. The lowest $E_a$ is 0.3 eV for Mg, 0.12 eV for K and 0.43 eV for Ca. The exact values of energies at saddle points and secondary peaks along with the lowest $E_a$ values are given in table 2 for each atom on each path. We have discussed in earlier section that K adsorption increases conductivity of antimonene more compared to the other two atoms. As a consequence of this, here we see that K diffuses rather easily than the other two atoms. K is followed by Mg and Ca respectively in ease of diffusion. The peak and saddle point in case of K-diffusion for path I and II is very small because the adsorption energies of Hex- and H-site was approximately same as mentioned in table 1.
Figure 5. (colour): Diffusion path vs $E_a$ plot at all the three paths, path I (black), path II (red) and path III (blue) for metal atoms diffusion over antimonene.

Table 2. Diffusion parameters i.e. Activation Energy ($E_a$) (eV), Energy at saddle point (eV) and Energy barrier at Secondary Peak (eV) of antimonene across each path for each M-atom.

| Parameter                              | Path | Mg  | K   | Ca  |
|----------------------------------------|------|-----|-----|-----|
| Activation Energy ($E_a$) (eV)         | I    | 0.30| 0.12| 0.43|
|                                        | II   | 0.30| 0.12| 0.43|
|                                        | III  | 0.75| 0.49| 0.86|
|                                        | I    | 0.22| 0.09|--  |
| Energy at saddle point (eV)            | II   | 0.22| 0.09|--  |
|                                        | III  | 0.29| 0.01| 0.43|
|                                        | I    | --  | --  | --  |
| Energy barrier at Secondary Peak (eV)  | II   | --  | --  | --  |
|                                        | III  | 0.36| 0.10| 0.72|
4. Conclusion

The adsorption and diffusion of M-atoms (Mg, K and Ca) over antimonene monolayer has been studied thoroughly and their properties have been analyzed. The M-atoms can interact with antimonene from a distance as large as 6 Å. The adsorption process is exothermic in nature and the bond formation depends upon at which site the atom resides over surface. The charge transfer is greater between K and antimonene and thus, antimonene starts behaving metallic. In case of Mg and Ca, charge transfer is insignificant but they incorporate in reducing the bandgap of antimonene. As a result of these phenomena, K diffuses easily over the antimonene surface compared to that of Mg or Ca, making the structure more conducting in nature.

Hence, it can be emphasized that M-atoms can be successfully adsorbed over antimonene surface and K-adsorption provides better diffusivity and conductivity to antimonene than Mg and Ca.

References

[1] Geim A K and Grigorieva I V 2013 Nature 499 419
[2] Ersan F, Keçik D, Özçelik V O, Kadioglu Y, Aktürk O Ü, Durgun E, Aktürk E and Ciraci S 2019 Applied Physics Reviews 6 021308
[3] Carvalho A, Wang M, Zhu X, Rodin A S, Su H and Castro Neto A H 2016 Nat. Rev. Mater. 1
[4] Bagheri S, Mansouri N and Aghaie E 2016 Int. J. Hydrogen Energy 41 4085
[5] Vogt P, De Padova P, Quaresima C, Avila J, Frantzeskakis E, Asensio M C, Resta A, Ealet B and Le Lay G 2012 Phys. Rev. Lett. 108 155501
[6] Bianco E, Butler S, Jiang S, Rodil A S, Su H and Castro Neto A H 2016 Nat. Rev. Mater. 1
[7] Alducin D, Myers B D, Liu X and Fisher B L 2013 Research | Reports 16 151
[8] Pumera M and Sofer Z 2017 2D Adv. Mater. 29 1605299
[9] Zhang S, Guo S, Chen Z, Wang Y, Gao H, Gómez-Herrero J, Ares P, Zamora F, Zhu Z and Zeng H 2018 Chem. Soc. Rev. 47 982
[10] Hu Z, Wu Z, Han C, He J, Ni Z and Chen W 2018 Chem. Soc. Rev. 47 3100
[11] Manzeli S, Ovchinnikov D, Pasquier D, Yazhev O V and Kis A 2017 Nat. Rev. Mater. 2 17033
[12] Xie Z, Xing C, Huang W, Fan T, Li Z, Zhao J, Xiang Y, Guo Z, Li J, Yang Z, Dong B, Qu J, Fan D and Zhang H 2018 Adv. Funct. Mater. 28 1705833
[13] Song L, Ci L, Lu H, Sorokin P B, Jin C, Ni J, Kvasnin A G, Kvasnin D G, Lou J, Yakobson B I and Ajayan P M 2010 Nano Lett. 10 3209
[14] Mahmood J, Lee E K, Jung M, Shin D, Choi H, Seo J, Jung S M, Kim D, Li F, Lah M S, Park N, Shin H-J, Oh J H and Baek J-B 2016 Proc. Natl. Acad. Sci. 113 7414
[15] Ares P, Palacios J J, Abellán G, Gómez-Herrero J and Zamora F 2018 Adv. Mater. 30 1
[16] Wang X, Song J and Qu J 2019 Angew. Chemie - Int. Ed. 58 1574
[17] Wang G, Pandey R and Karma S P 2015 ACS Appl. Mater. Interfaces 7 11490
[18] Shao Y, Liu Z L, Cheng C, Wu X, Liu H, Liu C, Wang J O, Zhu S Y, Wang Y Q, Shi D X, Ibrahim K, Sun J T, Wang Y L and Gao H J 2018 Nano Lett. 18 2133
[19] Fortin-Deschénes M, Waller O, Menteş T O, Locatelli A, Mukherjee S, Genuzio F, Levesque P L, Hébert A, Martel R and Moutanabbir O 2017 Nano Lett. 17 4970
[20] Ji J, Song X, Liu J, Yan Z, Huo C, Zhang S, Su M, Liao L, Wang W, Ni Z, Hao Y and Zeng H 2016 Nat. Commun. 7 1
[21] Gibaja C, Rodriguez-San-Miguel D, Ares P, Gómez-Herrero J, Varela M, Gillen R, Maultzsch J, Hauke F, Hirsch A, Abellán G and Zamora F 2016 Angew. Chemie - Int. Ed. 55 14345
[22] Hsu C, Yan Z, Song X and Zeng H 2015 Sci. Bull. 60 1994
[23] Ares P, Aguilar-Galindo F, Rodríguez-San-Miguel D, Aldave D A, Díaz-Tendero S, Alcamí M, Martín F, Gómez-Herrero J and Zamora F 2016 Adv. Mater. 28 6332
[24] Wang Y X, Chou S L, Liu H K and Dou S X 2013 Carbon N. Y. 57 202
[25] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[26] Hohenberg, P., Kohn W 1964 Phys. Rev. B 136 864
[27] Anon Atomistix ToolKit Virtual NanoLab (ATK-VNL) QuantumWise Simulator.
[28] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[29] Monkhorst H J and Pack J D 1976 Phys. Rev. B. 13 5188
[30] Grimme S 2006 J. Comput. Chem. 27 1787
[31] Upadhyay S and Srivastava P 2020 Mater. Chem. Phys. 241 122381
[32] Srivastava P, Abhishek, Sharma V and Jaiswal N K 2020 Appl. Phys. A Mater. Sci. Process. 126 1
[33] Henkelman G and Jónsson H 2000 J. Chem. Phys. 113 9978
[34] Henkelman, G., Uberuaga, B. P., Jónsson H 2000 J. Chem. Phys 113 9901