

Contents lists available at ScienceDirect

Chinese Journal of Structural Chemistry

journal homepage: www.journals.elsevier.com/chinese-journal-of-structural-chemistry

Short Communication

Defective structures and oxidation resistance of Janus AsP from first-principles prediction



Hao Zhang^a, Wenwen Wang^a, Shaojuan Li^b, Lu Wang^{a,*}, Youyong Li^{a,c,**}

^a Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu, 215123, China

^b State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130033,

China

^c Macao Institute of Materials Science and Engineering, Macau University of Science and Technology, Taipa, 999078, Macau SAR, China

1. Text

Black phosphorus (BP) has sparked immense interests among twodimensional (2D) nanomaterials since its first mechanical exfoliation from bulk BP in 2014 [1]. The atoms in BP are not distributed in the same plane, where the lone pair electrons of P atoms are highly reactive, and the structural anisotropy leads to many distinctive physical properties [2, 3], like highly anisotropic effective masses and tunable electronic properties [4]. Particularly, it possesses thickness-dependent direct bandgap values from 0.3 eV (bulk) to 1.5 eV (monolayer) [5]. Owing to its unique structural and electronic properties, BP shows potential applications in electronic or optoelectronic devices [6–8]. However, BP is reported to be unstable and easy to decompose in ambient conditions, which hinders its wide applications [9]. Layered BP can rapidly transform into oxides, and further degrade into acids or salts within hours [10]. Therefore, it is necessary to take some measures to inhibit the degradation of BP.

Since the electronegativity and atomic radii of As and P are very close, 2D AsP binary materials have gained great interests [11,12], and it is expected to have better oxidation resistance than BP. Recently, a stable single-layer Janus AsP has been theoretically predicted, which has a puckered lattice consisting of two different atomic layers, showing stronger in-plane anisotropy in Poisson ratio [12]. To further explore the unique properties of this novel Janus structure, in this communication, we have investigated the defective structures and oxidation properties of Janus AsP based on the first-principles calculations. Our work finds a new strategy to improve the oxidation resistance in phosphorus-related materials and provides them potential applications in photoelectric devices.

Similar to BP, which is prone to produce vacancies during the synthesis or transfer process [13], the Janus AsP could also possess defective

structures. Since it is composed of two types of atoms, P and As, as shown in Fig. 1a, there are more possibilities of defective structures than BP. We have systematically investigated the possible point defect structures in Janus AsP, including the Stone-Wales (SW) defect, single vacancy (SV), and double vacancies (DVs).

As shown in Fig. 1b, a SW-I defect is formed by rotating an As–P bond. The As–P bonds are rotated by 90° to produce a 5577 structure. The top five-membered ring consists of two P and three As atoms, while another five-membered ring contains three P and two As atoms. The As–P bond changes to 2.339 Å after rotation, which is shared by two seven-membered rings. Similarly, we could also rotate the P–P or As–As bond to obtain the SW-II and SW-III structures, respectively, which are shown in Fig. 1c and d. Among these three SW defects, the formation energies of SW-II and SW-III are 1.677 and 1.343 eV, respectively, and SW-I possesses the smallest formation energy of only 0.103 eV, which is the easiest to form.

There are five possible SV structures, formed by removing one P or As atom. The SV-59-I and SV-5566-I structures are created by removing a P atom. As shown in Fig. 1e, the five-membered ring shares an As–P bond with a nine-membered ring. As the As–P distance decreases from 4.08 to 2.77 Å, the SV-59-I transforms into SV-5566-I (Fig. 1g). Similarly, removing an As atom leads to three defective structures of SV-59-II, SV-5566-II and SV-5566-III (Fig. 1f, h and i). The SV-59-I and SV-59-II possess very close formation energies (1.239 and 1.218 eV) due to the similar structures. SV-5566-II possesses a unique structure of five As atoms at the top atomic layer connecting with the bottom P atoms to form two five- and two six-membered rings. It is found that the SV-59-II defect could easily transform into SV-5566-II by overcoming a small barrier of 0.51 eV.

https://doi.org/10.1016/j.cjsc.2023.100103

Received 6 April 2023; Received in revised form 12 May 2023; Accepted 21 May 2023 Available online 23 May 2023 0254-5861/© 2023 Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

^{*} Corresponding author.

^{**} Corresponding author. Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu, 215123, China.

E-mail addresses: lwang22@suda.edu.cn (L. Wang), yyli@suda.edu.cn (Y. Li).



Fig. 1. Optimized structures for perfect and defective Janus AsP with SW and SV defects. The P and As atoms are labeled by purple and green balls, respectively. (a) Perfect. (b) SW-I. (c) SW-II. (d) SW-JII. (e) SV-59-I. (f) SV-59-II. (g) SV-5566-II. (h) SV-5566-II and (i) SV-5566-III structures.

The DV defects are formed by removing two atoms. There are nine kinds of DV defects in Janus AsP. The DV-585-I and DV-585-II are produced by removing two P or two As atoms, respectively. The DV-585-III and DV-585-IV are formed by removing one As and one P atoms. These four DV-585 structures (Fig. 2a–d) are very similar, and the major difference is the number of As and P atoms contained in the defect. The DV-5775 and DV-4104 are formed by removing one As and one P atoms. As shown in Fig. 2e–f, the DV-4104 has a symmetric structure, consisting of two four- and one ten-membered rings. The DV-555777-II and DV-555777-III are constructed by removing two As, two P or one As and one P atoms, respectively, as shown in Fig. 2g–i. Among these nine DVs structures, DV-555777 structures possess relatively high formation energies more than 2 eV, which are relatively difficult to form. The DV-4104 defect possesses the smallest formation energy, which is calculated to be 0.90 eV, relatively easy to form on the Janus AsP surface.

We have further investigated the influence of these defects on the electronic properties of Janus AsP, which is crucial for the future applications in electronic devices. The band gaps are summarized in Table S1 and the band structures are plotted in Fig. S1. Under the computational level of PBE functional, the band gap of perfect Janus AsP is calculated to be 0.80 eV. By introducing the defects, the band gaps are modulated with a small range. The Janus AsP with SW defects are all indirect band-gap semiconductors with the band gaps of

0.84, 0.73 and 0.80 eV, respectively. By introducing the DV-585-I, DV-4104 and DV-555777-II defects, the Janus AsP still remains direct bandgap property with the band gaps of 0.78, 0.87 and 0.68 eV, respectively. Compared with BP [14], the defects formation in Janus AsP has less impact on the electronic structures, especially for SW and DV defects. However, the SV induces the defect states around the Fermi level.

Considering the electric device applications, the existence of defect states will make the carriers recombined, and then affect its performance. It is necessary for us to adopt some strategies to avoid this. Previous studies have shown that two SVs are energetically favored to coalesce to form a DV defect in BP [15], so here we also considered the coalescing of two SV defects to eliminate the defect states. As shown in Fig. S2, the initial state is two SV-59-I defects, and the final state is a DV-5775 defect. It is found that these two SV defects are easy to transform into a DV by overcoming a small barrier of 0.82 eV, which could efficiently eliminate the defect states produced by SV defect in Janus AsP.

The BP is prone to be oxidized in air condition, leading to the performance degradation of the devices based on BP. Here we propose the Janus AsP could enhance the oxidation resistance and prevent the surface oxidation of P atoms in AsP under the condition of air. To prove this, we have considered the O_2 adsorption and dissociation processes on defective AsP surface, and calculated the O_2 dissociation barriers. Once O_2 is adsorbed on the BP surface, it spontaneously dissociates into two O atoms



Fig. 2. Optimized structures for DVs. (a) DV-585-I. (b) DV-585-II. (c) DV-585-III. (d) DV-585-IV. (e) DV-5775. (f) DV-4104. (g) DV-555777-I. (h) DV-555777-II and (i) DV-555777-III.



Fig. 3. The O₂ dissociated process and barriers on different defective structures of Janus AsP.

without any barrier, so the surface P atoms are easily to be oxidized. However, as we expected, the O₂ on Janus AsP surface does not dissociate spontaneously. Taking the defective SV-5566-I structure as an example, initially, O₂ adsorbs on the defective structure with the adsorption distance of 2.85 Å, and then it goes closer to the P atoms on the AsP surface and dissociates into two O atoms bonded with P atoms by overcoming a barrier of 0.93 eV, which indicates that it is relatively difficult for O₂ to dissociate on the AsP surface. We have calculated and examined nine different defective structures, obtaining the same conclusion (see Fig. 3). Among these defective structures, the SW-I defect exhibits the highest barrier of 0.98 eV and the DV-5775 defect has the lowest barrier of 0.57 eV. Therefore, compared to BP, the Janus AsP exhibits distinctive oxidation resistance in air condition, even though the defects exist on the AsP surface.

2. Conclusion

We have performed DFT calculations to explore the defective structures and oxidation properties of Janus AsP. By comparing the structural stabilities of these defective structures, the SW-I possesses the smallest formation energy of only 0.103 eV, which is easy to form on the Janus AsP surface, while DV-555777 defects have relatively high formation energies due to the larger structural distortion. The SV defects induce the electronic defect states near the Fermi level, but SW and DVs defects do not. Different from BP, where the O₂ molecule will dissociate spontaneously on its surface, the dissociation of O₂ molecule on Janus AsP needs to overcome a large barrier, i.e., 0.98 eV for SW-I and 0.93 eV for SV-5566-I. Our work has indicated that the Janus AsP possesses better oxidation resistance than BP, and even with surface defects, they provide wide applications in electronic and optical devices.

Conflict of interest

The authors declare no competing interests.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21973067, 22173067, 62022081 and 61974099), the Natural Science Foundation of Jiangsu Province (BZ2020011), the Science and Technology Development Fund, Macau SAR (FDCT No. 0052/2021/A). This project was also supported by the Fund for Collaborative Innovation Center of Suzhou Nano Science & Technology, the Priority Academic Program Development of Jiangsu Higher Education Institutions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.cjsc.2023.100103.

References

- L. Li, Y. Yu, G.J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X.H. Chen, Y. Zhang, Black phosphorus field-effect transistors, Nat. Nanotechnol. 9 (2014) 372–377.
- [2] A. Avsar, I.J. Vera-Marun, J.Y. Tan, K. Watanabe, T. Taniguchi, A.H.C. Neto, B. Özyilmaz, Air-stable transport in graphene-contacted, fully encapsulated ultrathin black phosphorus-based field-effect transistors, ACS Nano 9 (2015) 4138–4145.
- [3] X. Chen, Y. Wu, Z. Wu, Y. Han, S. Xu, L. Wang, W. Ye, T. Han, Y. He, Y. Cai, N. Wang, High-quality sandwiched black phosphorus heterostructure and its quantum oscillations, Nat. Commun. 6 (2015) 7315.
- [4] L. Zeng, X. Zhang, Y. Liu, X. Yang, J. Wang, Q. Liu, Q. Luo, C. Jing, X.-F. Yu, G. Qu, P.K. Chu, G. Jiang, Surface and interface control of black phosphorus, Chem 8 (2022) 632–662.
- [5] H. Liu, A.T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, P.D. Ye, Phosphorene: an unexplored 2d semiconductor with a high hole mobility, ACS Nano 8 (2014) 4033–4041.
- [6] S.P. Koenig, R.A. Doganov, H. Schmidt, A.H.C. Neto, B. Özyilmaz, Electric field effect in ultrathin black phosphorus, Appl. Phys. Lett. 104 (2014) 103106.
- [7] C. Lin, R. Grassi, T. Low, A.S. Helmy, Multilayer black phosphorus as a versatile mid-infrared electro-optic, Nano Lett. 16 (2016) 1683–1689.
- [8] M. Buscema, D.J. Groenendijk, G.A. Steele, H.S.J. van der Zant, A. Castellanos-Gomez, Photovoltaic effect in few-layer black phosphorus PN junctions defined by local electrostatic gating, Nat. Commun. 5 (2014) 4651.
- [9] R.A. Doganov, E.C.T. O'Farrell, S.P. Koenig, Y. Yeo, A. Ziletti, A. Carvalho, D.K. Campbell, D.F. Coker, K. Watanabe, T. Taniguchi, A.H.C. Neto, B. Özyilmaz, Transport properties of pristine few-layer black phosphorus by van der waals passivation in an inert atmosphere, Nat. Commun. 6 (2015) 6647.
- [10] Y. Zhao, H. Wang, H. Huang, Q. Xiao, Y. Xu, Z. Guo, H. Xie, J. Shao, Z. Sun, W. Han, X.F. Yu, P. Li, P.K. Chu, Surface coordination of black phosphorus for robust air and water stability, Angew Chem. Int. Ed. 55 (2016) 5003–5007.
- [11] S. Guo, Y. Zhang, Y. Ge, S. Zhang, H. Zeng, H. Zhang, 2d V–V binary materials: status and challenges, Adv. Mater. 31 (2019) 1902352.
- [12] L.L. Li, C. Bacaksiz, M. Nakhaee, R. Pentcheva, F.M. Peeters, M. Yagmurcukardes, Single-layer janus black arsenic-phosphorus (b-AsP): optical dichroism, anisotropic vibrational, thermal, and elastic properties, Phys. Rev. B 101 (2020) 134102.
- [13] R. Zhang, X. Wu, J. Yang, Blockage of ultrafast and directional diffusion of Li atoms on phosphorene with intrinsic defects, Nanoscale 8 (2016) 4001–4006.
- [14] W. Hu, J. Yang, Defects in phosphorene, J. Phys. Chem. C 119 (2015) 20474–20480.
- [15] Y. Cai, Q. Ke, G. Zhang, B.I. Yakobson, Y.-W. Zhang, Highly itinerant atomic vacancies in phosphorene, J. Am. Chem. Soc. 138 (2016) 10199–10206.