Group 15 Monolayers

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Semiconducting Group 15 Monolayers: A Broad Range of Band Gaps and High Carrier Mobilities

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Abstract: *Optoelectronic applications require materials both responsive to objective photons and able to transfer carriers, so new two-dimensional (2D) semiconductors with appropriate band gaps and high mobilities are highly desired. A broad range of band gaps and high mobilities of a 2D semiconductor family, composed of monolayer of Group 15 elements (phosphorene, arsenene, antimonene, bismuthene) is presented. The calculated binding energies and phonon band dispersions of 2D Group 15 allotropes exhibit thermodynamic stability. The energy band gaps of 2D semiconducting Group 15 monolayers cover a wide range from 0.36 to 2.62 eV, which are crucial for broadband photoresponse. Significantly, phosphorene, arsenene, and bismuthene possess carrier mobilities as high as several thousand* $cm^2 V^{-1} s^{-1}$*. Combining such broad band gaps and superior carrier mobilities, 2D Group 15 monolayers are promising candidates for nanoelectronics and optoelectronics.*

In the past decade, two-dimensional (2D) crystals have emerged as intriguing materials for photonic and optoelectronic applications.[1] Compared with conventional 3D materials, 2D crystals are ultrathin, transparent, and flexible. Although being atomically thin, 2D crystals have strong interactions with lights, and the quantum confinement in the vertical direction gives rise to many unique electronic and optical properties. Furthermore, it is possible to construct van der Waals heterostructures with different 2D crystals, which can avoid the lattice mismatch issue of conventional heterostructures,[2] bringing unanticipated flexibilities in device design.

Many fascinating optical and optoelectronic properties of different 2D crystals have been explored, as well as related device applications. Graphene, as a semimetal with high carrier mobility, interacts with light strongly from microwave to ultraviolet wavelengths, enabling various applications such as transparent conductive thin films, ultrafast photodetectors, broadband optical modulators, and touch screens.[3] However, the zero band gap prevents graphene-based light emitting devices. In contrast, monolayer transition-metal dichalcogenides (TMDCs), such as molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2), are direct band gap semiconductors with promising light emitting properties. However, 2D TMDCs also have limitations for optoelectronic applications. First, the electronic band gaps of TMDCs are smaller than 2 eV, and thus light emitting is limited in the near-infrared or red wavelength range. For flexible display applications, 2D semiconductors with larger band gaps which enable green light and blue light emitting are desired. Second, the carrier mobilities of 2D TMDCs are several orders of magnitude lower than graphene, resulting in the rather low speed of TMDC-based electronic and optoelectronic devices.[4] Therefore, new 2D materials with proper electronic band gaps and higher carrier mobilities are still desired for novel electronic and optoelectronic applications.

Recently, following theoretical predictions,[5] Li et al. successfully fabricated field effect transistors based on few-layer black phosphorus.[6] Phosphorene possesses a band gap of about 2.0 eV and a high carrier mobility of about 10^3–10^4 $cm^2 V^{-1} S^{-1}$.[7] These studies have brought Group 15 elements (P, As, Sb, Bi) into the family of 2D crystals and inspired research interest on other single-layer allotropes.[8–10] Very recently, we predicted that the most stable arsenene and antimonene have buckled structures, and their electronic band structures transit from semimetal in the bulk form into semiconductor in the single-layer form.[9] However, for future optoelectronic applications, crucial broad range of band gaps and high carrier transfer abilities are still absent up to now.

Herein, by means of comprehensive density functional theory (DFT) computations, we report on the attractive wide range of band gap and high mobility of a 2D semiconductor family, composed of monolayer of Group 15 elements. In contrast to graphene, silicene, germanene and stanene in Group 14, Group 15 monolayers possess a broad range of band gaps, which are very helpful for broadband photoresponse. Among the different allotropes of Group 15 monolayers, α-phosphorene, α-bismuthene, and β-bismuthene are direct band-gap semiconductors with band gaps of 1.83, 0.36, and 0.99 eV, respectively, while α-arsenene and α-antimonene show quasidirect band gaps of 1.68 and 1.43 eV at the Γ point. More importantly, Group 15 monolayers such as puckered phosphorene, arsenene, and buckled bismuthene

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possess carrier mobilities as high as several thousand $cm^2 V^{-1} s^{-1}$. Furthermore, the various conduction band minimum (CBM) and valence band maximum (VBM) energy levels of Group 15 monolayers might facilitate the designing of 2D crystals based van der Waals heterostructures, which are also very promising for optoelectronic applications.

Herein, we report a class of monolayer Group 15 (that is, phosphorene, arsenene, antimonene, and bismuthene) allotropes with five typical honeycomb (α, β, γ, δ, ε) and four non-honeycomb (ζ, η, θ, ι) structures, as shown in Figure 1. Detailed descriptions about Group 15 monolayers are given in the Supporting Information, Figure S1 and Table S1.

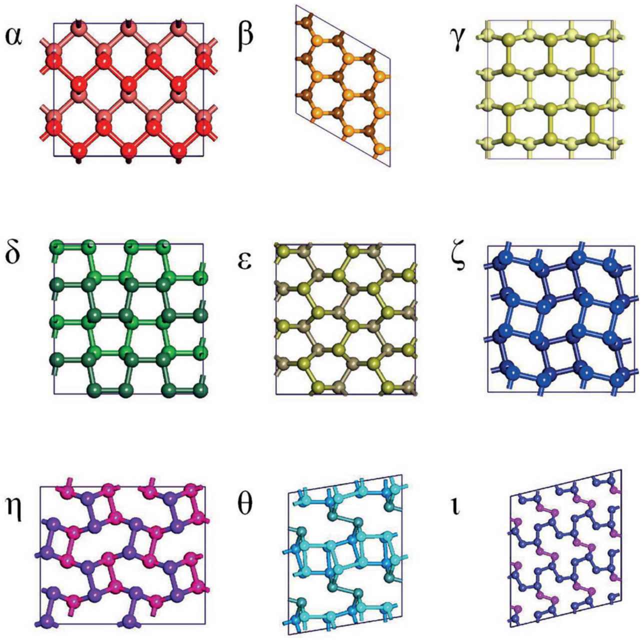

Figure 1. Top views of the relaxed Group 15 monolayer allotropes with five typical honeycomb structures (α, β, γ, δ, ε) and four non-honeycomb structures (ζ, η, θ, ι). All side views from *x* and *y* horizontal directions are shown in the Supporting Information, Figure S1.

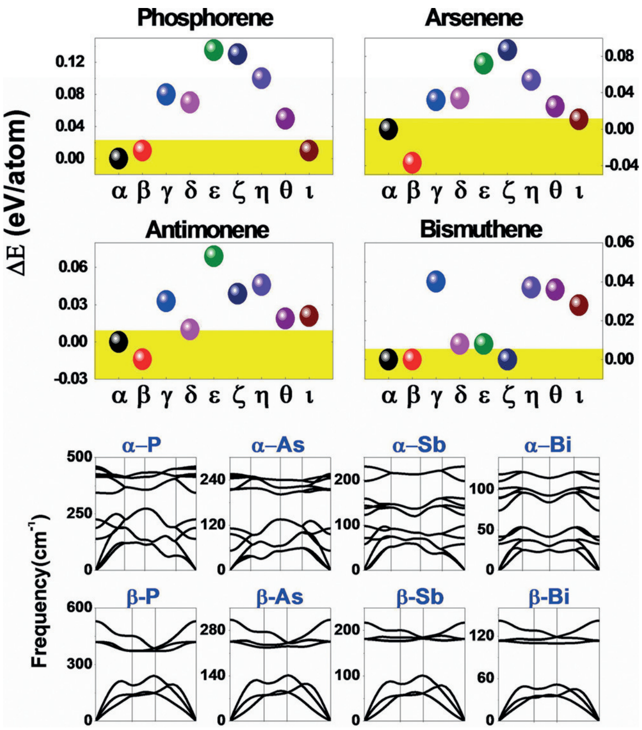

Figure 2. a) Calculated average binding energies of all Group 15 monolayer allotropes, which show energetic stability for α and β phases of Group 15 monolayers. b) Phonon band dispersions of all Group 15 monolayers, which exhibit thermodynamic stability.

First, we performed the binding energy calculations for all possible Group 15 monolayer configurations (Figure 2a). For phosphorene, among the honeycomb α, β, γ, δ, ε nanosheets and non-honeycomb ζ, η, θ, ι nanosheets, α-phosphorene with a puckered structure is the lowest-energy configuration, in agreement with previous studies.[8] However, among the possible arsenene, antimonene, and bismuthene allotropes, their β phases with buckled forms are the most stable structures, which are different from the lowest-energy configuration of phosphorene. Note that three phases of bismuthene, namely α, β, and ζ, have similar average binding energy at the same theoretical level (PBE). In fact, the counterpart bulk material of α-phosphorene monolayer is black phosphorus (α-P) with the space group *Cmca*, which is the most stable form of the allotropic modifications (white, red, and black phosphorus and some amorphous forms[11]) under standard conditions. In contrast, the counterpart bulk materials of β-arsenene, β-antimonene, and β-bismuthene are rhombohedral layered gray arsenic, gray antimony, and β-type bismuth (β-bismuth has the same crystal structure as gray arsenic) under normal conditions with the same space group ($R\bar{3}m$). To sum up, till now two types of layered phases experimentally exist in the Group 15 phases, namely, the bulk α-P, α-As, β-As, β-Sb, and β-Bi.[12] Considering the energetic stability and possible successful fabrication in the experiment, in the following we mainly focus on α and β phases of Group 15 monolayers. Other metastable Group 15 monolayer configurations can be found in the Supporting Information, Figure S1 and Table S1.

Then, we calculated the phonon spectra of these free-standing Group 15 monolayers, which serve as a criterion to judge the thermodynamic stability.[13] As shown in Figure 2b, no appreciable imaginary phonon modes are available for Group 15 monolayers, indicating that these free-standing Group 15 monolayers are thermodynamically stable. Because of the weak interlayer interactions, α- and β- P, As, Sb, and Bi layered bulk crystals are expected to be exfoliated easily to form 2D Group 15 monolayer structures. For example, α-phosphorene has been successfully exfoliated from bulk α-P.[14] Encouragingly, β-bismuthene as thin as a monolayer has been grown on different substrates.[15] Considering the rapid development of experimental techniques for fabricating 2D materials in recent years, we are optimistic that other members of the Group 15 monolayers can be fabricated experimentally in the near future.

To examine electronic properties, we calculated band structures and energy levels of free-standing α and β phases of

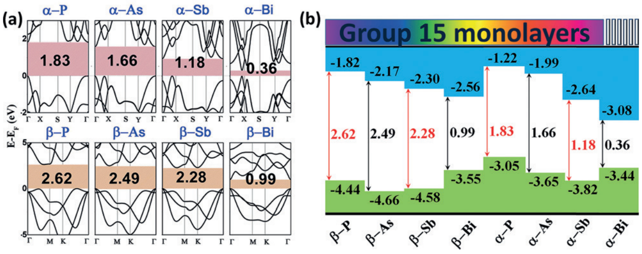

Figure 3. a) Electronic band structures of Group 15 monolayers at the HSE06 level of theory. b) Energy levels of Group 15 monolayers calculated also at the HSE06 level of theory, which indicate that Group 15 monolayers can have a broadband photoresponse.

Group 15 monolayers at the HSE06 level, as shown in Figure 3. Clearly, the energy band gaps of α-phosphorene, α-arsenene, α-antimonene, and α-bismuthene are smaller than those of β-phosphorene, β-arsenene, β-antimonene, and β-bismuthene, respectively. Among Group 15 monolayers, α-phosphorene, α-bismuthene, and β-bismuthene are direct band-gap semiconductors with band gaps of 1.83, 0.36, and 0.99 eV, respectively. Besides, α-arsenene and α-antimonene show quasi-direct band gaps of 1.68 and 1.43 eV at the Γ point, as shown in Figure 3a. The others are indirect band-gap semiconductors. Meanwhile, the optimized structure parameters are shown in the Supporting Information, Tables S2 and S3. Furthermore, we also computed the overlap populations (Table S2) and charge density (Figure S2). These results indicate a natural consequence, that is, the covalent characteristics would gradually be weakened for heavier VA atoms. The subtle structure difference between α-P and other α phases of Group 15 monolayers could result in different electronic properties.

The energy band gaps of 2D materials are of great importance for potential electronic and optoelectronic applications. Our calculation results indicate that the electronic band gaps of Group 15 monolayers cover a wide range from 0.36 eV to 2.62 eV. The 2.62 eV band gap already corresponds to a photon wavelength in the blue light range. We also calculated the optical absorption coefficients of Group 15 monolayers (Supporting Information, Figure S3). The wide range of energy band gaps and high absorption coefficients are crucial for optical and optoelectronic applications that require broadband photoresponse. Furthermore, the VBM and CBM energy levels of Group 15 monolayers are also provided in Figure 3b, which are important for designing heterostructure based electronic and optoelectronic devices.

To further study the electronic properties, we map out the respective density profiles of the electron at VBM and CBM for all Group 15 monolayers (Supporting Information, Figure S4). These β phases of Group 15 monolayers are structurally similar to silicene, germanene, and stanene.[16] However, their electronic properties differ significantly. In gapless silicene, germanene, and stanene, the electron densities of VBM and CBM consist of π-type bonding states. In contrast, in β phases of Group 15 monolayers there are three σ-bonding orbitals and a lone pair of electrons, which decline to form p-type bonding states. This is probably the underlying reason for the different electronic properties between Group 14 silicene, germanene, and stanene and Group 15 β monolayer phases.

Besides electronic band gaps, the electronic properties and applications of 2D semiconductors are governed to a large extent by the carrier mobilities. Thus, we further estimate the room temperature carrier mobilities of Group 14 monolayers based on the so-called acoustic phonon limited approach.[17] As described in the method, the carrier mobilities of 2D Group 14 monolayers are not completely determined by the effective mass. The other two properties, the deformation potential and the 2D elastic modulus are also involved. The deformation potential is derived from linear fits to the respective energies of the VBM and CBM as functions of the lattice dilation or compression of 2D Group 15 monolayers (See the band structures in the Supporting Information, Figure S5). Figure 4 shows the room temperature carrier mobilities of Group 15 monolayers. Our calculated mobility of α-phosphorene agrees well with the available report,[17] indicating that our computational methods and sets are reliable and accurate enough. In Figure 4, we summarize the calculated room temperature carrier mobilities of Group 15 monolayers, which are also compared with the experimentally reported mobilities of organic pentacene, polysilicon (Poly-Si), single-layer transition-metal dichalcogenide (S-TMD), graphene, and Group 13/15 (III-V) semiconductors.[1] Significantly, we find that α phases of Group 15 monolayers (we also concern directional anisotropy of electron and hole mobilities) can afford higher carrier mobilities than the corresponding β phases of Group 15 monolayers and polysilicon. Moreover, of particular interest is that α-arsenene owns a higher mobility up to 10^4 cm^2 V^{-1} s^{-1} than III-V semiconducting materials. The high mobility in α-arsenene not only benefits from a small effective mass of electron of 0.21, but also benefits from a very small

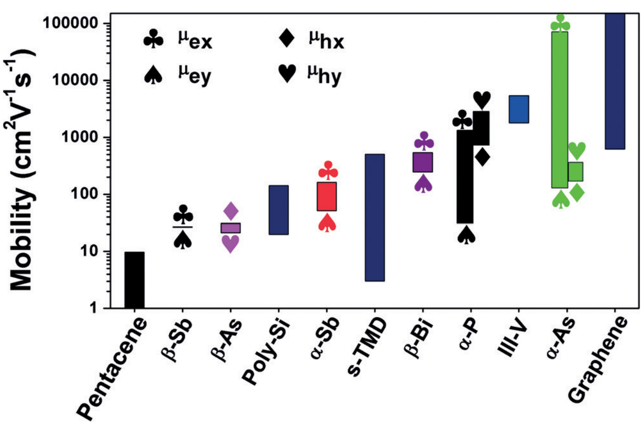

Figure 4. The room-temperature carrier mobilities of Group 15 monolayers, which are compared with experimentally reported mobilities of pentacene, polysilicon (Poly-Si), single-layer transition-metal dichalcogenide (s-TMD), and III-V semiconductors. The club and spade symbols represent the electron mobility along *x* (μ_{ex}) and *y* (μ_{ey}) of α phases of Group 15 monolayers, and the diamond and heart symbols represent the hole mobility along *x* (μ_{hx}) and *y* (μ_{hy}) of α phases of Group 15 monolayers.

deformation potential of 0.65 eV. Intriguingly, α-phosphorene has a high hole mobility, but is smaller than the electron mobility of α-arsenene. Although α-phosphorene has a small deformation constant of the valence-band minimum for holes (0.21 eV), it has a heavy electron carrier (6.40; Supporting Information, Figure S6). Note that the subtle structure difference between α-P and other α phases of Group 15 monolayers could result in different electronic properties (See the Structural Analysis in the Supporting Information, Tables S1–S3). Anyhow, α-phosphorene and α-arsenene possess a high intrinsic mobility, which will play a crucial role in the performance of nanoelectronic and optoelectronic devices.

In conclusion, we systematically investigated a family of 2D mono-elemental semiconductors, Group 15 monolayers. We find that Group 15 monolayers cover a broad range of band gaps, which can be helpful for broadband photoresponse. More importantly, Group 15 monolayers such as phosphorene, arsenene, and bismuthene possess carrier mobilities as high as several thousand square centimeters per volt-second. Combining such superior carrier mobilities and varied band gaps, 2D Group 15 monolayers can be promising candidates for novel applications in nanoelectronics and optoelectronics. Quite recently, we have synthesized few-layer β-antimonene experimentally by vapor transport method in our laboratory, and the results will be reported elsewhere. We believe that the present investigations on the electronic band structures and transport properties of 2D Group 15 monolayers are significant because these results can extend the whole family of semiconductor materials into Group 15 elemental materials.

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[1] a) F. N. Xia, H. Wang, D. Xiao, M. Dubey, A. Ramasubraaniam, *Nat. Photonics* **2014**, *8*, 899; b) D. J. Akinwande, N. Petrone, J. Hone, *Nat. Commun.* **2014**, *5*, 5678.
[2] a) A. K. Geim, I. V. Grigorieva, *Nature* **2013**, *499*, 419; b) H. Wang, F. C. Liu, W. Fu, Z. Y. Fang, W. Zhou, Z. Liu, *Nanoscale* **2014**, *6*, 12250.
[3] a) F. Bonaccorso, Z. Sun, T. Hasan, A. C. Ferrari, *Nat. Photonics* **2010**, *4*, 611; b) Q. L. Bao, K. P. Loh, *ACS Nano* **2012**, *6*, 3677.
[4] Y. Yoon, K. Ganapathi, S. Salahuddin, *Nano Lett.* **2011**, *11*, 3768.
[5] a) Y. Takao, A. Morita, *Physica B+C* **1981**, *105*, 93; b) H. Asahina, K. M. Shindo, *J. Phys. Soc. Jpn.* **1982**, *51*, 1193.
[6] L. K. Li, Y. J. Yu, G. J. Ye, Q. Q. Ge, X. D. Ou, H. Wu, D. L. Feng, X. H. Chen, Y. B. Zhang, *Nat. Nanotechnol.* **2014**, *9*, 372.
[7] a) L. Z. Kou, T. Frauenheim, C. F. Chen, *J. Phys. Chem. Lett.* **2014**, *5*, 2675; b) R. Fei, L. Yang, *Nano Lett.* **2014**, *14*, 2884; c) J.-W. Jiang, H. S. Park, *Nat. Commun.* **2014**, *5*, 4727; d) Q. Liu, X. Zhang, L. B. Bdalla, A. Fazzio, A. Zunger, *Nano Lett.* **2015**, *15*, 1222.
[8] a) C. Kamal, M. Ezawa, *Phys. Rev. B* **2015**, *91*, 085423; b) Z. Zhu, J. Guan, D. Tománek, *Phys. Rev. B* **2015**, *91*, 161404; c) Z. Zhu, J. Guan, D. Tománek, *Phys. Rev. Lett.* **2014**, *112*, 176802; d) M. H. Wu, H. H. Fu, L. Zhou, K. L. Yao, X. C. Zeng, *Nano Lett.* **2015**, *15*, 3557; e) G. X. Wang, R. Pandey, S. P. Karna, *ACS Appl. Mater. Interfaces* **2015**, *7*, 11490.
[9] a) S. L. Zhang, Z. Yan, Y. F. Li, Z. Chen, H. B. Zeng, *Angew. Chem. Int. Ed.* **2015**, *54*, 3112; *Angew. Chem.* **2015**, *127*, 3155; b) S. L. Zhang, Y. H. Zhang, Z. Y. Hu, B. Cai, H. B. Zeng, *Appl. Phys. Lett.* **2015**, *107*, 022102.
[10] J. Y. Wang, S. B. Deng, Z. F. Liu, Z. R. Liu, *Natl. Sci. Rev.* **2015**, *2*, 22.
[11] a) R. Hultgren, N. S. Gingrich, B. E. Warren, *J. Chem. Phys.* **1935**, *3*, 351; b) H. Thurn, H. Kerbs, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 1047; *Angew. Chem.* **1966**, *78*, 1101.
[12] a) N. C. Norman, *Chemistry of Arsenic, Antimony and Bismuth*, Academic Press, Springer, Dordrecht, **1998**; b) J. H. Xu, E. G. Wang, C. S. Ting, W. P. Su, *Phys. Rev. B* **1993**, *48*, 17271; c) H. Krebs, W. Holz, K. H. Worms, *Chem. Ber.* **1957**, *90*, 1031.
[13] a) J. Dai, X. C. Zeng, *Angew. Chem. Int. Ed.* **2015**, *54*, 7572; *Angew. Chem.* **2015**, *127*, 7682; b) Y. F. Li, Y. L. Liao, Z. F. Chen, *Angew. Chem. Int. Ed.* **2014**, *53*, 7248; *Angew. Chem.* **2014**, *126*, 7376; c) P. Miró, M. Ghorbani-Asl, T. Heine, *Angew. Chem. Int. Ed.* **2014**, *53*, 3015; *Angew. Chem.* **2014**, *126*, 3059.
[14] a) E. S. Reich, *Nature* **2014**, *506*, 19; b) P. Yasaei, B. Kumar, T. Foroozan, C. H. Wang, M. Asadi, D. Tuschel, J. E. Indacochea, R. F. Klie, A, Salehi-Khojin, *Adv. Mater.* **2015**, *27*, 1887.
[15] a) J. T. Sun, H. Huang, S. L. Wong, H.-J. Gao, Y. P. Feng, A. T. S. Wee, *Phys. Rev. Lett.* **2012**, *109*, 246804; b) Y. H. Lu, W. T. Xu, M. G. Zeng, G. G. Yao, L. Shen, M. Yang, Z. Y. Luo, F. Pan, K. Wu, T. Das, P. He, J. Z. Jiang, J. Martin, Y. P. Feng, H. Lin, X. Wang, *Nano Lett.* **2015**, *15*, 80.
[16] S. Balendhran, S. Walia, H. Nili, S. Srira, M. Bhaskaran, *Small* **2015**, *11*, 640.
[17] J. S. Qiao, X. H. Kong, Z. X. Hu, F. Yang, W. Ji, *Nat. Commun.* **2014**, *5*, 4475.

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