A Promising Two-dimensional Solar Cell Donor: Black Arsenic–phosphorus Monolayer with 1.54 eV Direct Bandgap and Mobility Exceeding $14,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

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Abstract: Excitonic solar cells (XSCs) have attracted tremendous attentions due to their high solar-to-electric power conversion efficiency (PCE). However, to further improve the PCE of XSC, finding an efficient donor material with both suitable direct bandgap and high carrier mobility is still a great challenge. Here, we report a black arsenic–phosphorus monolayer as highly efficient donor for XSCs based on first-principle calculations. Firstly, monolayer arsenic-phosphorus polymorphs with α , β , γ , δ , and ε phases were built, among which α -AsP and β -AsP have been verified to be thermodynamically stable. Significantly, monolayer α -AsP possesses a direct bandgap with energy of 1.54 eV, which covers the main energy of solar spectrum. Moreover, its electronic mobility is as high as $14,380 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is much higher than silicon. These two crucial merits made it a promising candidate as donor materials for XSC device and the theoretical simulations demonstrate a maximum PCE of 22.1% for the primarily designed α -AsP/GaN XSC. Interestingly, the suitable electronic structure of α -AsP enables a formation of perfect type-II semiconductor heterojunction with GaN, which will boost the separation and transport of photogenerated carriers with the assistance of built-in field and high mobility. Particularly, α phase few-layer material of arsenic-phosphorus alloy has been experimentally synthesized recently, which paves the way for experimental realization of black arsenic–phosphorus monolayer donor.

Keywords: Excitonic solar cells, Power conversion efficiency, Black arsenic–phosphorus monolayer, First-principle calculations, Type-II semiconductor heterojunction

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The maximum PCE of monolayer α -AsP/GaN-based excitonic solar cell (XSC) could achieve 22.1%, which is competitive with the best to date in 2D thin-film solar cells.

1. Introduction

Solar cell devices converting sunlight directly into electricity is of great importance for energy production related applications. According to the form of photogenerated free carrier (electron-hole pairs) solar cells are typically divided into two groups: I: those based on bulk inorganic semiconductors like Si, GaAs, CdTe, [1] where no coulomb interaction is present between the photogenerated electrons and holes, II: those based on conjugated polymers [2,3] or other materials in which the exciton (electron and hole pairs with coulomb interaction) form with a excitonic binding energy typically surpassing kT (26 meV). For the former type, silicon-based (Si) solar cells, due to its stability and enrichment of raw materials have been most widely used. Despite of the above merits, silicon-based solar cells also have obvious disadvantages due to the inherent materials properties of silicon. For example, as an indirect bandgap (1.1 eV) material [4] silicon absorbs light quite weakly in the solar spectrum. Moreover, a relatively low carrier mobility ($\sim 1,400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) also limits the efficient charge extraction in Si solar cell. Such two limitations lead to both low photocurrent and power conversion efficient (PCE) of silicon-based solar cells. Thus, the high performance solar cells are urgently needed in the current photovoltaic market.

To exploit solar radiation more effectively, we consider the latter type of solar cells, that is excitonic solar cells (XSCs). [5] In XSCs, the free carrier will be generated by separating bounded excitons at semiconductor heterojunction interfaces, due to discontinuities of the ionization potential and electron affinity across the interface. However, a high-quality XSC device require the active materials to have direct bandgap of $\sim 1.2\text{--}1.6 \text{ eV}$ [6] and a high electron mobility to promote efficient electron transport. Therefore, the selective of electron-donor and electron-acceptor semiconducting materials for the XSCs are extremely important. [7] Typical two-dimensional (2D) semiconductors, [8-19] especially phosphorene and arsenene, have been recognized as promising materials in device applications recent years. However, finding an efficient donor 2D semiconductor with both suitable direct

bandgap and high carrier mobility to further improve PCE of XSC is still a great challenge.

Here, we report a black arsenic–phosphorus monolayer as highly efficient donor for XSCs. Based on the density functional theory (DFT), 2D arsenic-phosphorus polymorphs (compound of phosphorene and arsenene) with different configurations (α , β , γ , δ , and ϵ) are investigated. Among them, α and β phases have been confirmed to be thermodynamically stable according to phonon spectra and cohesive energy. Our calculated results show that monolayer α -AsP has a direct band gap of 1.54 eV, which falls exactly into the optimum value range according to XSCs requirement. Furthermore, high carrier mobility ($14,380 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) is also achieved in α -AsP, which is one order of magnitude higher than that of Si. These two merits enable α -AsP to be promising candidate as highly performance efficient donor material for XSCs. The theoretical simulations do indicate a considerably high PCE of 22.1% of our designed α -AsP/GaN XSC. Such high PCE is due to the appropriate band alignment which results in a type-II semiconductor heterojunction between α -AsP and GaN, promoting the separation of bounded carriers as well as high electron mobility which ensures fast and efficient carrier transport. Moreover, α phase few-layer material of arsenic-phosphorus alloy has been experimentally synthesized very recently, [20] which would expedite the experimental realization of black arsenic–phosphorus monolayer donor.

2. Computational methods

For the monolayer AsP polymorphs (α , β , γ , δ , and ϵ), our calculations were employed within ab initio DFT as carrying out Vienna Ab initio Simulation Package (VASP) [21,22]. Projector-augmented-wave (PAW) methods [23] using the norm-conserving pseudopotentials [24] for P and As atoms were treated to understand the electrostatic interactions between valence and core electrons. For distinct atomic species, the valence electrons included in this study for pseudo-atoms are P $3s^23p^3$, As

4s²4p³. The Generalized gradient approximation (GGA) [25] of Perdew-Wang 1991 (PW91) [26] functional were depicted during geometry optimizations and electronic structure calculations. To correct the underestimated bandgaps in PW91, electronic band structures are calculated by Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) [27,28]. All models were relaxed until none of the forces exceeded 0.005 eV/Å. The Brillouin zone integration was exploited by 13×13×1 and 7×7×1 Monkhorst Pack k-point mesh in PW91 and HSE06 levels, respectively. A bigger vacuum layer of 20 Å was taken on to exclude the artificial interlayer interaction. The plane-wave cutoff energy for wave function was adopted as 500 eV. Moreover, because of the interaction between monolayer α-AsP and monolayer GaN, the dispersion correction should be adopted in the α-AsP/GaN heterojunction. Phonon spectra, as well as Raman spectra and Scanning Tunneling Microscopy (STM) were implemented by using Cambridge Sequential Total Energy Package (CASTEP) [29], where 8×8×2 and 13×13×1 k meshes were applied, respectively.

In inorganic semiconductors, the coherent wavelength of thermally activated electrons or holes at room temperature is much longer than the lattice constant and is close to the acoustic phonon wavelength. [30] The electron-acoustic phonon coupling, leading to scattering in the low energy region [31,32], can be attained based on deformation potential (DP) theory, which is first proposed by Bardeen and Shockley [33]. By means of the effective mass approximation, the DP theory has been widely used to investigate carrier mobility μ in 2D [34-36] materials:

$$\mu_{2D} = \frac{e\hbar^3 C_{2D}}{k_B T m_e^* m_d (E_I^I)^2}, \quad (1)$$

where, m_e^* is the effective mass in the transport direction; m_d is the average effective mass determined by $m_d = (m_x^* m_y^*)^{1/2}$. T is the temperature. E_I is the DP constant which characterizes the shift of the band edges (the bottom of conduction band for electrons and the top of valence for holes) induced by the strain and is defined as $E_{Ii} = \Delta E_i / (\Delta l / l_0)$. C_{2D} is the elastic modulus of x (zigzag) and y (armchair) uniformly

deformed crystal for emulating the lattice distortion activated by the strain. For the 2D models the in-plane stiffness can be determined as $C_{2D} = [\partial^2 E / \partial \delta^2] / S_0$, here E is the total energy of the supercell, δ is the applied uniaxial strain, and S_0 is the area of the equilibrium supercell.

Fig. 1. Atomic structure and thermodynamic stability of monolayer AsP polymorphs. (a) Optimized structures of five monolayer AsP polymorphs in both top and side views. The primitive unit cell is highlighted by shadows. Meanwhile, calculated cohesive energy (b) and phonon band dispersions (c) of AsP monolayers are displayed.

3. Results and discussion

3.1 Structures of AsP monolayers

The atomic structures of 2D AsP polymorphs (α , β , γ , δ , and ϵ) are presented in Fig. 1a, in which all of them have honeycomb types. Such structural shapes are similar to graphene, phosphorene, arsenene, and phosphorus allotropes, i.e., γ , δ , and θ -P [37,38]. Here, our AsP polymorphs can be obtained by replacing neighboring P atom with As atom. Among all of the polymorphs, α and β phases agree well with previous

report [39]. None of the layers are perfectly flat, which is different from graphene with planar structure and sp^2 orbital. Actually, the non-planar configurations guarantee their stability, owing to the formation sp^2 and sp^3 -hybridized chemical bonds. The details about the configurations are listed Fig. S1, Table S1, and Table S2. In addition, in order to identify the typical honeycomb configurations, we have introduced two simulations methods, i.e., Raman spectra and Scanning Tunneling Microscope (STM), as presented in top of Fig. S9.

3.2 Stabilities of AsP monolayers

Stability is a prerequisite of practical applications of the theoretical designed 2D materials. The thermodynamic stabilities of AsP polymorphs are confirmed by phonon spectra and cohesive energy. The cohesive energy of AsP monolayers is calculated as: $E_{coh}(AsP) = (E_{AsnPn} - nE_{As} - nE_P)/n$, where E_{AsnPn} , E_{As} , and E_P stand for the energies of AsP monolayers, a single As atom, and a single P atom, respectively. Among five AsP phases, β phase has the lowest-energy, as listed in Table S1 and Fig. 1b. However, the cohesive-energy difference between α and β phases is small, indicating that both phases are almost equally thermodynamic stable. The coexistence of both stable α and β phases might be attributed to the fact that phosphorene, monolayer black phosphorus, i.e., α -P, is the phase with the lowest energy, while arsenene, monolayer grey arsenic, the so-called β -As, is the most stable phase.

We then calculate the phonon spectra to examine the kinetic stability (see Fig. 1c). No soft modes are present, indicating a great structural stabilities. The highest phonon frequencies of the AsP monolayers (α , β , γ , δ , and ϵ) are about 372, 424, 384, 339, and 364 cm^{-1} , respectively. What's more, the phonon spectra, to be quite resembling in AsP polymorphs, mirror a much analogous bonding feature. Meanwhile, we find the optical and acoustic modes are well deviated in all five 2D layer materials. Significantly, Zhou *et al.* [20] successfully synthesized the few-layer black arsenic-phosphorus (α phase) by performing a mineralizer-assisted short way

chemical transport reaction recently. We are quite optimistic about the experimental realization of monolayer α -AsP donor in the near future.

3.3 Electronic properties of AsP monolayers

For the application of 2D semiconductors in photovoltaic devices, the bandgap is a critical influential factor because it directly determines the light absorption and PCE as well. Fig. 2 presents the electronic band structures for AsP polymorphs with both PW91 and HSE06 calculations. The bandgaps of different phases about these two methods are listed in Table S1. Within PW91, our results show that both α (0.90 eV) and δ -AsP (0.75 eV) are direct bandgap semiconductors, while others have indirect bandgaps (details shown in Fig. S2). Among them, β -AsP has a largest bandgap of 1.79 eV. Since DFT-PW91 often underestimates the bandgaps, we have also calculated the band gaps at the HSE06 level for comparison (Fig. 2f). Despite of the slight discrepancy in the bandgaps of AsP polymorphs, we note that these two methods provide almost the same band shapes near the Fermi level. While for PBE level, δ -AsP possesses indirect band-gaps since the VBM and CBM are not at the same k points shown in Figs. S3-S5, which is not consistent with HSE level. Thus, we only utilize PW91 level band structure to calculate the carrier mobility of AsP polymorphs.

Fig. 2. Electronic band structures of monolayer (a) α -AsP, (b) β -AsP, (c) γ -AsP, (d) δ -AsP, and (e) ϵ -AsP; the lime lines base on PW91 level while the navyblue ones are for HSE level. The VBM and CBM of PW91 level are highlighted by diamond and circle shapes. (f) Energy band gaps of such AsP monolayers are examined at the HSE06 calculation.

As shown in Fig. 2a and d, both α and δ -AsP are direct band-gap phases since valence band maximum (VBM) and conduction band minimum (CBM) are at the same Γ point in the Brillouin zone. All other phases have indirect band gaps, where the VBM and CBM are not at the same k points. For β and ϵ -AsP, only VBM locates at the high symmetry Γ point, while the CBM are along the Γ -M (Fig. 2b) and the Γ -X (Fig. 2e) direction. In case of γ -AsP, neither VBM nor CBM locates at the high

symmetry points (the VBM and CBM are all along the Γ -Y direction). But within HSE06 level, the VBM is at the high symmetry Γ point.

Notably, the direct bandgap of the stable α -AsP is 1.54 eV by HSE06 level, which falls perfectly into the optimum range for XSCs requirement (~ 1.2 -1.6 eV). Such direct bandgap structure which is in favor of solar cell applications is due to the quantum confinement along c-axis when the material becomes 2D while its bulk counterpart has an indirect bandgap. [40] Therefore, if one can find suitable acceptor material with good band alignment to form type-II semiconductor heterojunction, it is very possible to realize a α -AsP monolayer-based photovoltaic device with high efficiency.

Before searching such electron-acceptor material, we should get a comprehensive understanding of the contributed orbital of the electronic states first. Fig. 3 plots the computations of partial density of states (PDOS) for such configurations. The PDOS analysis reveals that the VBM and CBM of monolayer AsP systems are all mainly contributed by P-3p and As-4p orbitals. The contributions from the s orbitals to the total DOS are negligible. Actually, as the sp^2 -like bonds form a non-planar system, the p orbitals are predominant, which is a common trait of monolayer honeycomb systems like phosphorene and silicene. It is clear that contributions of P-3p and As-4p orbitals below or above the Fermi level are almost equivalent. It might be attributed to the almost equal electronegativities of P and As. More details about p orbitals contribution are explained as follows. From the orbital decomposition in Fig. 3, the VBMs of both As and P are mainly contributed by p_z orbital except δ -AsP, in which VBM for As stemmed from p_z orbital, while for P atom is p_y orbital. The CBMs of α and ϵ -AsP, as well as β and γ -AsP are principally derived from p_y and p_x orbital, respectively. For δ -AsP, CBM for As atom is originated from p_x orbital, while for P atom is mainly from p_z orbital. Furthermore, we also calculated the partial charge densities corresponding to the VBM and CBM of AsP monolayers (in the inset of Fig.

3). The VBM and CBM all correspond to the p-bonding between P and As atoms, which is consistent with the above PDOS analysis.

Fig. 3. PDOS of As (up) and P (down) atoms in monolayer AsP polymorphs. Meanwhile, the electronic profiles for CBM (up) and VBM (down) of AsP monolayers are inseted in the PDOS.

3.4 Carrier mobilities in α and β -AsP monolayers

As described above, besides the requirement of bandgap, carrier mobility is also an important factor for the XSCs. Considering the thermodynamic stability and probability of successful experimental fabrication, we would mainly focus on α and β -AsP from now on. By performing first-principles calculations and DP theory, we examine the carrier mobilities of α and β phases in both zigzag and armchair directions. Because of the rhombus primitive cell of β phase and the necessity to calculate the effective mass in both zigzag (x or a_1) and armchair (y or b_1) directions, we give the band structures of β phase in rectangular supercell, as shown in Fig. S6. Three most principal influential factors that affect the carrier mobilities of α and β -AsP are effective mass m^* , DP constant E_{li} , and elastic modulus C_{2D} along the transport directions, as shown in Table 1. Among them, the DP constant E_{li} is calculated by linearly fitting the data through compressing or stretching the lattice parameters along zigzag and armchair directions, as shown in Figs. S7 and S8.

With Eq. (1) and the obtained E_{li} , C_{2D} , and m_e^* , the carrier mobilities at room

temperature (300 K) are computed in Table 1. We find that the electron mobilities of monolayer α and β -AsP are higher than that of holes along both zigzag and armchair directions. For α -AsP, the electron mobility along zigzag ($\sim 14,380 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) is almost 28 times larger than that along armchair ($\sim 510 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). More importantly, the electron mobility of α -AsP is an order of magnitude higher than that of Si ($\sim 1,400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), which is in well consistency with Fazel *et al.* [41]. Similar with α -AsP, the calculated carrier mobility of β phase exhibits strong anisotropy for both electrons and holes. The electron mobility along armchair direction is $3,390 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and is about 2-3 times larger than that of Si. It should be noted that since α -AsP has a shaper band structure near Fermi level than β -AsP, the intrinsic mobility of α phase is, in general, higher than that of β phase, especially for electron mobility along zigzag direction ($14,380$ vs $220 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

Table 1

Effective mass m_i^*/m_0 , deformation potential E_{Li} , elastic constant C_{2D} , and carrier mobility μ , at 300 K for electrons and holes in monolayer α and β -AsP. (x=zigzag, y=armchair)

Carrier type	m_x^*/m_0 Γ -X	m_y^*/m_0 Γ -Y	E_{Lx} (eV)	E_{Ly} (eV)	$C_{x/2D}$ (Jm ⁻²)	$C_{y/2D}$ (Jm ⁻²)	$\mu_{x/2D}$ (10 ³ cm ² V ⁻¹ s ⁻¹)	$\mu_{y/2D}$ (10 ³ cm ² V ⁻¹ s ⁻¹)
$\pm$-AsP								
e	0.17	1.23	0.60	2.43	19.33	78.94	14.38	0.51
h	0.15	2.04	4.87	3.28	19.33	78.94	0.21	0.14
2-AsP								
e	0.15	0.56	10.88	1.40	49.70	49.76	0.22	3.39
h	1.27	0.03	15.46	13.12	49.70	49.76	0.02	0.97

3.5 Power conversion efficient of α -AsP

Given the direct bandgap around 1.54 eV and high electron mobility of 14,380

$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, monolayer α -AsP seems to be a very promising solar cell donor materials. Following the CBM (-2.09 eV) and VBM (-3.63 eV) levels of α -AsP illustrated in Fig. 2f, we find that monolayer GaN with CBM (-2.10 eV) and VBM (-5.32 eV) as suitable acceptor materials meeting the requirement for type-II band alignment with α -AsP. Moreover, there is appreciable 0.3 |e| charge transfer from monolayer α -AsP to monolayer GaN, which confirms donor role of monolayer α -AsP in α -AsP/GaN heterojunction. Thus, we can design an α -AsP-based photovoltaic system as shown in Fig. 4a, b. Meanwhile, the band structure of α -AsP/GaN heterojunction is presented in Fig. S10. According to Scharber et al., [7] the power conversion efficiency PCE (η) of such a α -AsP and GaN device described as

$$\eta = \frac{J_{sc}V_{oc}\beta_{FF}}{P_{solar}} = \frac{0.65(E_g^d - \Delta E_c - 0.3) \int_{E_g^d}^{\infty} P(\hbar\omega) d(\hbar\omega)}{\int_0^{\infty} P(\hbar\omega) d(\hbar\omega)}, \quad (2)$$

where 0.65 is the fill factor (β_{FF}), $P(\hbar\omega)$ is the AM1.5 solar energy flux (stated in $\text{Wm}^{-2}\text{eV}^{-1}$) at the photon energy ($\hbar\omega$), and E_g^d is the band gap of the donor (α -AsP). ΔE_c is the CB offset between donor (α -AsP) and acceptor (GaN). The $(E_g^d - \Delta E_c - 0.3)$ term is an estimation of the maximum open circuit voltage (V_{oc} , here in eV units). The integral in the numerator is the short circuit current (J_{sc}) performed applying the limit external quantum efficiency (EQE) of 100%, and the integral in the denominator is the incident solar radiation ($P_{solar} = 1000 \text{ Wm}^{-2}$).

From Eq. (2), V_{oc} is determined by the energy difference between VBM of α -AsP and CBM of GaN. A larger energy difference results in larger V_{oc} and further leads to higher PCE in solar cells. With these two key elements in mind, GaN (as acceptor) just fulfill our requirements to fabricate high-quality α -AsP/GaN bilayer XSCs. Actually, ΔE_c between monolayer α -AsP and monolayer GaN is 0.01 eV (Figure 4b), which is in favor of high PCE according to Fig. 4c. The practical upper limit of PCE

(η) for α -AsP/GaN bilayer XSCs can be up to 22.1% as highlighted with lime in Fig. 4c. This efficiency is competitive with that of existing devices (Table 2), such as phosphorene/MoS₂ trilayer system (16–18%), [42] PCBM/CBN heterojunctions (10–20%), [43] g-SiC₂ based systems (12–20%) [44] and phosphorene nanoflake heterojunctions (20%) [40], and much higher than single-bulk-heterojunction solar cell (10%) [7] and nanocarbon-based photovoltaics (9–13%). [45] Although our monolayer α -AsP-based photovoltaic device is just two atomic layers thick, thicker multilayer stacking in a heterojunction manner should also be achievable. Moreover, few-layer black arsenic-phosphorus alloy has been experimentally fabricated, which paves the way for successful synthesis of α -AsP monolayer donor.

Fig. 4. α -AsP/GaN type-II semiconductor heterojunction. (a) Schematic drawing of type-II donor-acceptor band alignments between α -AsP and GaN according to HSE06 level. (b) Contour

plot showing the power conversion efficient versus the donor band gap and the conduction band offset.

Table 2

Confirmed existing XSC devices and the PCE measured under the global AM1.5 spectrum (1000 Wm^{-2}).

Classification	PCE (%)	Refences	Years
α-AsP/GaN bilayer XSCs	22.1%		
Edge-modified phosphorene nanoflakes	20%	Ref 40	2016
g-SiC ₂ nanotube/ZnO monolayer XSC	12-20%	Ref 44	2013
PCBM/CBN heterojunctions	10-20%	Ref 46	2012
AA-/AB-stacked bilayer phosphorene/monolayer MoS ₂	18/16%	Ref 42	2014
Monolayer MoS ₂ /monolayer phosphorene	17.5%	Ref 47	2014
g-SiC ₂ /GaN bilayer XSC	14.2%	Ref 44	2013
Nanocarbon-based photovoltaics	9-13%	Ref 45	2012
Single-bulk-heterojunction solar cell	10%	Ref 7	2006
Nanoparticle-aided polymer solar cell	8.92%	Ref 48	2013
Tandem polymer solar cells	8.62%	Ref 49	2012

4. Summary

In conclusion, we have studied five monolayer AsP polymorphs (α , β , γ , δ and ϵ) by DFT computations. All the five phases are thermodynamically stable with α and β -AsP being the two most stable ones. The results suggest that α -AsP possesses a direct bandgap of 1.54 eV and high electron mobility of $\sim 14,380 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which are the key factors for it to be electron donor materials in XSCs. Moreover, we also theoretically designed α -AsP/GaN XSC showing a maximum PCE of 22.1%. As far as we know, this PCE is competitive with the reported PCE to date for 2D thin-film solar cells. Interestingly, under the HSE06-based calculations, α -AsP/GaN bilayer XSCs with type-II type interfaces will induce the separation of photogenerated

carriers and high electron mobility will ensure the fast carrier transport. The high stability, unique electronic structures, high electron mobility, and appropriate interface band alignment, make α -AsP/GaN bilayer XSCs be of significant for next-generation flexible optoelectronic devices. This work reveals that monolayer α -AsP can become the next material widening the applications of photovoltaic devices.

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