Induced out-of-plane piezoelectricity and giant Rashba spin splitting in Janus WSiZ$_3$H (Z = N, P, As) monolayers toward next-generation electronic devices

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Induced out-of-plane piezoelectricity and giant Rashba spin splitting in Janus WSiZ3H (Z = N, P, As) monolayers toward next-generation electronic devices

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ABSTRACT

Two-dimensional (2D) piezoelectric nanomaterials have widely been studied recently due to their promise for various applications in technology. Investigation of vertical piezoelectricity will contribute to a deeper understanding of the intrinsic mechanism of piezoelectric effects in the 2D structures. In this paper, we report a first-principle study for the structural, electronic, piezoelectric, and transport properties of new-designed Janus WSiZ3H (Z = N, P, and As) monolayers. The structural stability of WSiZ3H is theoretically confirmed based on the energetic, phonon dispersion, and also elastic analyses. At the ground state, while WSiN3H is an indirect semiconductor, both WSiP3H and WSiAs3H are predicted to be direct semiconductors with smaller bandgaps. When the spin-orbit coupling effects are taken into account, a large valley spin splitting is observed at the K point of WSiZ3H materials. Interestingly, a giant Rashba spin splitting is found in WSiP3H and WSiAs3H with Rashba constant αR up to 770.91 meV Å. Additionally, our first-principles study indicates that Janus WSiZ3H monolayers are piezoelectric semiconductors with high out-of-plane piezoelectric coefficient j_{31}, up to 0.15 pm/V, due to the broken mirror symmetry. Besides, with high electron mobilities and also possessing direct band gaps, WSiP3H and WSiAs3H monolayers are favorable for applications in optoelectronics.

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I. INTRODUCTION

Controlling the mechanical and electrical characteristics of nanoscale devices dynamically is one of the biggest obstacles to fully using the power of nanotechnology. The unique aspect of two-dimensional (2D) piezoelectric nanomaterials lies in their ability to convert mechanical strain into electrical energy and vice versa, even at the nanoscale.1 Piezoelectricity is essential to many different kinds of applications, ranging from sensors and actuators to energy harvesting devices.2,3 The thin and flexible nature of the 2D structures makes them particularly attractive for integration into nanoelectronic devices and wearable technologies.4,5 Scientists are presently delving into and manipulating diverse 2D materials to unlock their full potential in the realm of piezoelectricity. The studies of 2D piezoelectric structures not only help us to understand their physical characteristics but also open up new avenues for innovative technologies with enhanced performance and adaptability.6

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Recent studies have shown that 2D materials can have many advantages in piezoelectric characteristics. The piezoelectricity has been experimentally reported in a free-standing MoS2 monolayer. The in-plane piezoelectric coefficient \( d_{31} \) of the MoTe2 material was found to be 9.13 pm/V by the density functional theory (DFT) calculations, much larger than that of the traditional bulk form of \( \alpha \)-quartz (2.3 pm/V). Particularly 2D group IV monochalcogenides exhibit an outstanding piezoelectric effect with \( d_{31} \) ranging from 75.43 to 212.13 pm/V. Such positive initial results are worthy of continuing studies on the piezoelectric effect in 2D materials.

Since 2D Janus materials have been reported experimentally, these asymmetric structures have been of particular interest because they possess many rich physical characteristics with many technological application prospects. Many novel characteristics of Janus structures have been found, which do not exist in their corresponding symmetric materials. Recently, Janus \( X\text{MoSi}_2\text{N}_4 \) \((X = S, Se, Te)\) has been designed from the MoSi2N4 monolayer. The Rashba spin splitting does not often appear in the vertically symmetrical structure. However, the mirror symmetry breaking in Janus materials can give rise to the Rashba spin splitting effects. This is explained by the presence of a perpendicularly internal electric field because of the difference in electronegativity between layers of atoms in the Janus material, such as in the 2D Janus structures based on transition metal dichalcogenides. Furthermore, the lack of vertical mirror symmetry may induce the out-of-plane piezoelectric effect in the 2D Janus materials. The out-of-plane piezoelectric coefficient \( d_{31} \) for Janus \( \gamma \)-SnS2Te and \( \text{Sb}_2\text{Te}_2\text{Se} \) monolayers has theoretically been predicted to be 1.02 \( \pm 0.72 \) and 1.72 pm/V, respectively, which are suitable for piezoelectric devices. In this paper, we theoretically design the novel Janus WSiZ3H monolayers and systematically examine their structural, electronic, piezoelectric, and transport features based on a first-principles approach.

II. COMPUTATIONAL METHODS

First-principle calculations were carried out with the projector augmented wave (PAW) method as performed in the Vienna \textit{Ab initio} Simulation Package. We used the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) to treat the electron exchange-correlation functional. The hybrid functional suggested by Heyd, Scuseria, and Ernzerhof (HSE06) was also adopted to get a better examination of the electronic bandgap. The semimetal DFT-D3 method was used to consider the weak van der Waals forces. The spin-orbit coupling (SOC) effect was included in the self-consistent calculations. An energy of 650 eV was adopted as the energy cutoff of the plane wave basis set, and the Brillouin zone integration was sampled by a 12 \( \times \) 12 \( \times \) 1 k-point mesh grid. The threshold for energy convergence was chosen to be 10\(^{-6}\) eV, and the positions of atoms in the studied structures were fully relaxed until the maximum force on each atom was smaller than 10\(^{-3}\) eV/Å. A vacuum space of 40 Å was inserted to the vertical direction. Phonon spectra were calculated by the frozen-phonon technique as implemented in the PHONOPY code. The \textit{Ab initio} molecular dynamics (AIMD) simulation with the canonical ensemble was performed at 300 K to examine the thermal stability. The dipole correction was included to correct the dipole moment induced in the asymmetric structures. The strain–stress relationship and density functional perturbation theory (DFPT) were used to calculate the elastic and piezoelectric coefficients. We adopted the deformation potential (DP) method to examine the mobility of the carriers.

III. RESULTS AND DISCUSSION

We show the crystal structures of 2D Janus WSiZ3H \((Z = N, P, \text{and As})\) monolayers in Fig. 1(a). At equilibrium, Janus WSiZ3H belongs to the \( P3m1 \) (No. 156) space symmetry group. Our calculations indicate that the optimized lattice constants of WSiN3H, WSiP3H, and WSiAs3H are 2.91, 3.42, and 3.57 Å, respectively. These values are very close to those of WSiN4 (2.91 Å), WSiN4 (3.46 Å), and WSiN4 (3.61 Å). The obtained structural parameters of Janus WSiZ3H are presented in Table I.

We next evaluate the chemical bonding strength in the studied compound through the calculations for the cohesive energy \( E_{\text{coh}} \), as follows:

\[
E_{\text{coh}} = \frac{E_{\text{tot}} - (N_W E_W + N_S E_S + N_Z E_Z + N_{\text{H}} E_{\text{H}})}{N_W + N_S + N_Z + N_{\text{H}}},
\]

where \( E_{\text{tot}} \) and \( E_\eta \) \((\eta = W, S, Z, \text{and H})\) are the total energy of WSiZ3H, and energy of the isolated \( \eta \) element, respectively. \( N_\eta \) are the numbers of the \( \eta \) atom in the unit cell.

The electron localization function (ELF) of Janus WSiZ3H is depicted in Fig. 1(b) to analyze the spatial charge distribution and the unique bonding characteristics in their structures. We can see that the electron in Janus WSiZ3H monolayers is mainly located around the hydrogen and Z atoms. Meanwhile, the charge density around the W and Si atoms is very low. This suggests that there is an electron transfer from W and Si atoms to H/Z atoms. We show the results of the Bader analysis for Janus WSiZ3H monolayers in Table I.

The calculated \( E_{\text{coh}} \) for Janus WSiZ3H compounds are also listed in Table I. Based on Eq. (1), the material exhibits a stable structure in energy since its cohesive energy is negative. The more energetically stable the structure, the more negative the cohesive energy is. As listed in Table I, the calculated \( E_{\text{coh}} \) for all three compounds is negative, suggesting that their structure is energetically stable. The most energetically stable structure is indicated to be WSiN3H with \( E_{\text{coh}} = -8.23 \) eV/atom. The most energetically stable structure of WSiN4 is due to their shorter chemical bond lengths in comparison with other compounds. In addition, the Bader charge analysis is also carried out to quantitatively study the distribution and variations in the effective electrons in the studied compounds. As shown in Table I, the hydrogen atoms in WSiP3H and WSiAs3H monolayers accumulated additional charge, while a small amount of charge on the hydrogen atom in the WSiN4 monolayer was lost. This is also clearly shown in the ELF image in Fig. 1(c). The calculated results also indicated that the Si atoms lose charge. However, there are large differences in the amount of charge loss of Si in different monolayers. The atomic charges for Si atoms in WSiN3H, WSiP3H, and WSiAs3H monolayers are \(-2.086[e], -0.310[e], \) and \(-0.001[e], \) respectively, as reported in Table I.
Furthermore, charge polarization in the vertical direction will result from the asymmetry in the vertical charge distributions in each structure. Consequently, Janus WSi$_Z$H materials have the out-of-plane piezoelectricity.

To evaluate the structural stability, we carry out the phonon spectra of Janus WSi$_Z$H monolayers as depicted in Fig. 2. Since the unit cell of Janus WSi$_Z$H contains six atoms, its phonon dispersions have 18 phonon modes. We recognize that, as presented in Fig. 2, there is a vibrational region where both acoustic and optical phonons co-exist. This induces the robust acoustic-optical scattering in the Janus WSi$_Z$H. Importantly, there are no negative vibrational frequencies in the phonon dispersion relations of all three investigated structures. This demonstrates that the dynamical stability of Janus WSi$_Z$H monolayers is confirmed. Furthermore, we also evaluate the thermal stability of WSi$_Z$H based on the AIMD simulations. The total energy fluctuations to simulation time at 300 K within 10 ps by the AIMD simulation for WSi$_Z$H monolayers are depicted in Fig. S1 in the supplementary material. It is found that the crystal structures of WSi$_Z$H monolayers remain robust after 10 ps of AIMD simulation. There is no structural transition nor the breaking of chemical bonds. This demonstrates that WSi$_Z$H monolayers are thermally stable at room temperature.

We next examine the electronic properties of WSi$_Z$H based on the analysis of their electronic band diagrams as shown in Fig. 3. Our calculated results for the band structures indicate that all three configurations of WSi$_Z$H are semiconductors. However, while WSiN$_3$H exhibits indirect semiconducting characteristics.

**TABLE I.** The lattice constant $a$ (Å), bond length $d$ (Å), thickness of monolayer $\Delta h$ (Å), cohesive energy $E_{\text{coh}}$ (eV), and Bader charge $q$ (|e|) of atoms for WSi$_Z$H monolayers. The sub-indexes Z(1), Z(2), and Z(3) denote the Z atom located in the bottom, middle, and topmost of the monolayer as shown in Fig. 1(a), respectively.

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
<th>$d_4$</th>
<th>$d_5$</th>
<th>$\Delta h$</th>
<th>$E_{\text{coh}}$</th>
<th>$q_W$</th>
<th>$q_Si$</th>
<th>$q_{Z(1)}$</th>
<th>$q_{Z(2)}$</th>
<th>$q_{Z(3)}$</th>
<th>$q_H$</th>
</tr>
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<tbody>
<tr>
<td>WSiN$_3$H</td>
<td>2.91</td>
<td>1.76</td>
<td>1.74</td>
<td>2.10</td>
<td>2.08</td>
<td>1.02</td>
<td>5.75</td>
<td>$-$8.23</td>
<td>$-$1.374</td>
<td>$-$2.086</td>
<td>1.446</td>
<td>1.347</td>
<td>0.741</td>
<td>$-$0.075</td>
</tr>
<tr>
<td>WSiP$_3$H</td>
<td>3.42</td>
<td>2.23</td>
<td>2.22</td>
<td>2.44</td>
<td>2.43</td>
<td>1.42</td>
<td>7.53</td>
<td>$-$6.25</td>
<td>$-$0.553</td>
<td>$-$0.310</td>
<td>0.157</td>
<td>0.377</td>
<td>$-$0.183</td>
<td>0.512</td>
</tr>
<tr>
<td>WSiAs$_3$H</td>
<td>3.57</td>
<td>2.35</td>
<td>2.34</td>
<td>2.55</td>
<td>2.54</td>
<td>1.53</td>
<td>7.99</td>
<td>$-$5.64</td>
<td>$-$0.094</td>
<td>$-$0.001</td>
<td>$-$0.065</td>
<td>0.071</td>
<td>$-$0.487</td>
<td>0.576</td>
</tr>
</tbody>
</table>
with the valence band maximum (VBM) located at the K point and conduction band minimum (CBM) found at the Γ point as revealed in Fig. 3(a), both WSiP\(_3\)H and WSiAs\(_3\)H monolayers possess the small direct bandgaps opening at the K point. At the PBE level, the bandgaps of WSiN\(_3\)H, WSiP\(_3\)H, and WSiAs\(_3\)H are predicted to be 2.06, 0.65, and 0.58 eV, respectively. Notably, the band structure characteristics of Janus WSi\(_Z\)\(_3\)H are similar to those of WSi\(_Z\)\(_4\) monolayers; for example, WSi\(_2\)N\(_4\) exhibits the indirect semiconducting characteristics with energy gap of 2.08 eV,\(^{40}\) which is similar to its corresponding Janus WSi\(_Z\)\(_3\)H. To correct the bandgap, we carry out the band structures of Janus WSi\(_Z\)\(_3\)H monolayers calculated by the HSE06 method as illustrated in Fig. 3. The HSE06 calculations give a larger bandgap of the examined materials of 2.63, 0.92, and 0.83 eV for WSiN\(_3\)H, WSiP\(_3\)H, and WSiAs\(_3\)H, respectively, as presented in Table II.

Figure 4 shows the band structures of WSi\(_Z\)\(_3\)H calculated by the PBE+SOC approach. When including the SOC effect, the band structures of Janus WSi\(_Z\)\(_3\)H are significantly changing and the SOC effect slightly reduces the bandgap of the studied materials as listed in Table III. In addition, the spin degeneracy is eliminated when the SOC effect is taken into account. A valley spin splitting \(\lambda_Z\) is found at the K point in the valence band of all three Janus WSi\(_Z\)\(_3\)H materials as shown in Fig. 4. The \(\lambda_Z\) value for WSiN\(_3\)H, WSiP\(_3\)H, and WSiAs\(_3\)H is observed to be 0.42, 0.45, and 0.51 eV, respectively. Furthermore, we also observe the obvious Rashba splitting near the Γ point in the valence band of the Janus WSiP\(_3\)H and WSiAs\(_3\)H monolayers as shown in Figs. 4(b) and 4(c). We can describe the strength of the Rashba SOC splitting via three Rashba parameters: Rashba energy \(E_R\), the \(k\)-space shift or momentum offset \(k_R\), and Rashba constant \(\alpha_R\). Here, we can get the values of \(E_R\) and \(k_R\) from the band structures\(^{41}\) and the Rashba constant \(\alpha_R\) is obtained via the expression as \(\alpha_R = 2E_R/k_R\)\(^{41}\) with the schematic description of the Rashba-type spin splitting at the Γ point illustrated in Fig. 4(d). The calculated Rashba parameters of Janus WSiP\(_3\)H and WSiAs\(_3\)H monolayers are presented in Table II. It can be seen that there are differences in the Rashba energy in the Γ–K \(E^K_R\) and Γ–M \(E^M_R\) directions. However, this difference is small. The values of Rashba energy \(E^K_R\) for WSiP\(_3\)H and WSiAs\(_3\)H monolayers are calculated to be 55.9 and 47.3 meV, respectively, which are slightly higher than those in the Γ–M direction. We found the values of \(E^M_R\) for WSiP\(_3\)H and WSiAs\(_3\)H monolayers to be 49.9 and 47.3 meV, respectively. In addition, the momentum offset \(k^R_K\) is also quite close to that \(k^R_K\) for both two studied systems. From Table II, we can see that the Rashba constants in the Γ–K/Γ–M directions \(\alpha^K_R/\alpha^M_R\) for WSiP\(_3\)H and WSiAs\(_3\)H monolayers are 621.1/623.7 and 674.7/730.9 meV Å, respectively. The obtained \(\alpha_R\) for WSi\(_Z\)\(_3\)H is comparable with that of Janus MoSeTe (524 meV Å)\(^{26}\) but much higher than that of WSiGe\(_4\) (111 meV Å).\(^{42}\) It is clear that while the dependence of the Rashba parameters of WSiP\(_3\)H on the investigated directions in their Brillouin zone is weak, the WSiAs\(_3\)H monolayer exhibits slightly anisotropic Rashba spin splitting. The Rashba constants \(\alpha_R\) for WSiAs\(_3\)H are higher than those for WSiP\(_3\)H because the SOC effect in As is larger than that in P.
Another important electronic feature of materials is work function $\Phi$, which can be calculated based on the Fermi level $F_l$ and vacuum level $V_l$ as $\Phi = V_l - F_l$. The values of $F_l$ and $V_l$ can be found by the analysis of the electrostatic potential as shown in Fig. S2 in the supplementary material. Due to the asymmetric structure, WSi$_3$H monolayers possess an intrinsic built-in electric field. Therefore, we include the dipole corrections in the calculations for Janus structures. From Fig. S1 in the supplementary material, we can see that there is a distinct vacuum level difference for Janus structures. From Fig. S1 in the supplementary material, we can see that there is a distinct vacuum level difference $\Delta \Phi$ existing on the two different sides of Janus WSi$_3$H monolayers. Consequently, there is a difference in the work function on the two sides $\Phi_H$ and $\Phi_M$ as listed in Table II. The calculated results for the work functions show that the value of $\Phi_H$ is always higher than $\Phi_M$ on all three materials, demonstrating that the electrons escape more easily from the H side than the Z side. Differences in the electrostatic potential at the surfaces of WSi$_3$H not only affect the work function but also affect their other chemical properties, including photocatalytic characteristics.

Piezoelectric materials are strongly restricted by their crystal symmetry, and the necessary condition for piezoelectric material is the lack of central symmetry. Since WSi$_3$H materials are semiconductors with non-centrosymmetric structure, we can consider them as piezoelectric materials. The piezoelectric properties are the ground state features; therefore, the DFT approach is a suitable methodology as Duerloo et al.\textsuperscript{12} in order to investigate the piezoelectric characteristics of Janus WSi$_3$H monolayers.

To examine the piezoelectricity, we first calculate the planar elastic stiffness coefficients $C_{ij}$ by fitting the strain-dependent unit-cell energy.\textsuperscript{12} In the strained unit cell, the positions of atoms are allowed to be fully relaxed and the obtained corresponding coefficients in this model are so-called relaxed-ion stiffness coefficients. The relaxed-ion stiffness coefficients, which represent the piezoelectricity from contribution of both electronic and ionic components, are considered to be in better agreement with experimental measurements than the clamped-ion model.\textsuperscript{14,44} For the strain energy calculations, small uniaxial strains from $-1.5\%$ to $1.5\%$ (in increments of 0.5\%) are applied. For Janus WSi$_3$H monolayers, only two independent coefficients $C_{11}$ and $C_{12}$ should be carried out [$C_{22} = C_{11}$ and $C_{66} = (C_{11} - C_{12})/2$]. The calculated relaxed-ion $C_{ij}$ and also corresponding Young’s modulus $Y_{2D} = (C_{11} - C_{12})/C_{11}$ and Poisson’s ratio $\nu = C_{12}/C_{11}$ are listed in Table III. Due to hexagonal symmetry, Janus WSi$_3$H monolayers are mechanically isotropic. We can see that the in-plane elastic coefficients of WSi$_3$H materials are positive and they satisfy Born’s mechanical stability criteria for 2D hexagonal crystal,\textsuperscript{16} namely, $C_{11} > 0$ and $C_{66} > 0$. This demonstrates that the mechanical stability of Janus WSi$_3$H monolayers is confirmed. Furthermore, WSi$_3$H monolayers, particular Janus WSi$_3$H, exhibit high Young’s modulus $Y_{2D}$. The value of $Y_{2D}$ for WSi$_3$H, WSi$_3$H, and WSiAs$_3$H is calculated to be 373.83, 153.47, and 124.80 N/m,

Table II. The PBE/HSE06/PBE+SOC bandgap $E_g$ (eV), vacuum level difference $\Delta \Phi$ (eV), valley spin splitting energy $\lambda$ (eV), Rashba energy $E_R$ (meV), momentum offset $k_0$ (Å\textsuperscript{-1}), Rashba constant $\alpha_R$ (meV Å), and work function $\Phi$ of WSi$_3$H (Z = N, P, As) monolayers. Indexes $K$ and $M$ indicate the Rashba parameters calculated in the $\Gamma$-K and $\Gamma$-M directions, respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_g$ PBE</th>
<th>$E_g$ HSE06</th>
<th>$E_g$ PBE+SOC</th>
<th>$\lambda_K$</th>
<th>$\lambda_M$</th>
<th>$\Phi_K$</th>
<th>$\Phi_M$</th>
<th>$\Delta \Phi$</th>
<th>$\Phi_Z$</th>
<th>$\Phi_H$</th>
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<tbody>
<tr>
<td>WSi$_3$H</td>
<td>2.06</td>
<td>2.63</td>
<td>1.85</td>
<td>0.42</td>
<td>...</td>
<td>...</td>
<td>2.85</td>
<td>5.06</td>
<td>2.21</td>
<td></td>
</tr>
<tr>
<td>WSiP$_3$H</td>
<td>0.65</td>
<td>0.92</td>
<td>0.40</td>
<td>0.45</td>
<td>55.9</td>
<td>49.9</td>
<td>0.18</td>
<td>0.16</td>
<td>621.11</td>
<td>623.75</td>
</tr>
<tr>
<td>WSiAs$_3$H</td>
<td>0.58</td>
<td>0.83</td>
<td>0.30</td>
<td>0.51</td>
<td>47.3</td>
<td>42.4</td>
<td>0.14</td>
<td>0.11</td>
<td>675.71</td>
<td>770.91</td>
</tr>
</tbody>
</table>

![Diagram](image-url)
respectively. The Young modulus of WSiN$_3$H is comparable with that of graphene (340 N/m)$^{46}$ and much higher than that of MoS$_2$ (130 N/m)$^{57}$ and Janus MoSSe (113 N/m).$^{48}$ This suggests that the Janus WSiN$_3$H monolayer is a very mechanically hard material.

The polarization of the noncentrosymmetric systems can be changed by uniaxial strain. We examine the linear piezoelectric coefficients based on evaluating the polarization change under the applied uniaxial strains within the framework of the modern theory of polarization.$^{49}$ The linear piezoelectric effect in 2D structures can be described through the third-rank piezoelectric tensors $e_{ijk}$ and $d_{ijk}$, which depend on the relationship between the surface polarization $p_i$ and strain $\varepsilon_{jk}$ or stress $\sigma_{jk}$ as$^5$

$$e_{ijk} = \frac{\partial p_i}{\partial \varepsilon_{jk}},$$

$$d_{ijk} = \frac{\partial p_i}{\partial \sigma_{jk}},$$

where indices $i, j, k \in \{1, 2, 3\}$ with 1, 2, and 3 correspond to $x$, $y$, and $z$, respectively.

In the case of Janus WSiZ$_3$H monolayers, due to the break of the vertical symmetry, both in-plane $e_{11}$ and out-of-plane $e_{31}$ piezoelectric coefficients are available when the uniaxial strain is introduced. The piezoelectric coefficients can be obtained by using the density functional perturbation theory (DFPT) and we then derive the coefficients $d_{ij}$ using the relations with the previously obtained $e_{ij}$ and elastic coefficients $C_{ij}$ as$^8$

$$d_{11} = \frac{e_{11}}{C_{11} - C_{12}},$$

$$d_{31} = \frac{e_{31}}{C_{11} + C_{12}}.$$

We apply the uniaxial strains along the $x$ and $y$ directions of the orthorhombic supercell to calculate the coefficients $e_{11}$ and $e_{31}$. The obtained $e_{11}$ and $e_{31}$ and corresponding $d_{11}$ and $d_{31}$ for Janus WSiZ$_3$H are listed in Table III. We can see that $e_{11}$ for WSiN$_3$H, WSiP$_3$H, and WSiAs$_3$H is $2.90 \times 10^{-10}$, $5.92 \times 10^{-10}$, and $6.36 \times 10^{-10}$ C/m, respectively. The obtained $e_{31}$ for Janus WSiZ$_3$H monolayers is comparable to that of Janus MoS$_2$ (3.70 $\times 10^{-10}$)$^{51}$ Janus MoSSe (4.55 $\times 10^{-10}$)$^{52}$ or Janus $\gamma$-S$_2$Te (4.26 $\times 10^{-10}$)$^{27}$ Our calculations indicate that the Janus WSiN$_3$H monolayer has the smallest piezoelectric response with $d_{11} = 0.99$ pm/V and $d_{31} = -0.02$ pm/V, as presented in Table III. Interestingly, the piezoelectric effect is enhanced by the moving upward of the $Z$ element from N to As. The magnitude of piezoelectric coefficients for WSiAs$_3$H is the highest, being $d_{31} = 6.57$ pm/V and $d_{11} = -0.15$ pm/V. This tendency to vary the piezoelectric effect with atomic size has also been found in transition metal dichalcogenides$^{32}$ or group IV monochalcogenides.$^{44}$ We can see that the in-plane piezoelectric coefficient $d_{11}$ for WSiN$_3$H (0.99 pm/V) and WSiP$_3$H (4.86 pm/V) is higher than that of their corresponding symmetric structures WSi$_2$N$_4$ (0.25 pm/V) and WSi$_2$P$_4$ (1.65 pm/V).$^{53}$ It is worth noting that the out-of-plane piezoelectric effect in Janus WSiZ$_3$H monolayers due to the breaking of mirror symmetry is significant, and the value of $d_{31}$ ranges from $-0.02$ to $-0.15$ pm/V. This amplitude of $d_{31}$ is comparable to that of other 2D sandwiched structures, including GaAs (0.125 pm/V).$^{39}$ Janus MoSiGeN$_4$ ($-0.014$ pm/V)$^{52}$ or Janus group III monochalcogenides (0.07-0.46 pm/V).$^{50}$ However, the out-of-plane piezoelectric effect in Janus WSiZ$_3$H monolayers is significantly weaker than that in Janus MoSTe ($d_{31} = 0.40$ pm/V) or Janus $\gamma$-S$_2$Te ($d_{31} = 1.02$ pm/V).$^{27}$

In the last part, we investigate the transport characteristics of WSiZ$_3$H monolayers. The carrier mobility of semiconductors can be examined by using Bardeen–Shockley deformation potential (DP) theory.$^{39}$ The mobility of carrier for the 2D structures $\mu_{2D}$ is given by$^{42}$

$$\mu_{2D} = \frac{e\hbar C_{2D}}{k_B T m^* E_d^2},$$

where $T$ is the temperature; $m^*$ is the effective mass; and $m' = \sqrt{m'' m^*}$ indicates the average effective mass. $C_{2D}$ and $E_d$ are the 2D elastic modulus and DP constant, respectively. In the calculations for the carrier mobility, we adopt $T = 300$ K.

In Table IV, we show the calculated results for the carrier effective masses along the $x$ and $y$ axes $m_x$ and $m_y$. It is demonstrated that, except for the WSiN$_3$H monolayer, the effective masses of both the electron and hole in WSiP$_3$H and WSiAs$_3$H monolayers are quite small. This is consistent with their energy band structures displayed in Fig. 3. The difference in the mass between electrons and holes in WSiP$_3$H and WSiAs$_3$H monolayers is small. However, the effective masses of both electron and hole exhibit slightly directional anisotropic along the $x$ and $y$ axes as revealed in Table IV. The transport parameters $C_{2D}$ and $E_d$, which can be obtained by fitting the uniaxial-strain-dependent total energy and band edges as shown in Fig. S3 in the supplementary material, and the corresponding carrier mobilities $\mu$ are displayed in Table IV in the supplementary material. It is indicated that the WSiN$_3$H monolayer possesses very low-electron mobility, about

<table>
<thead>
<tr>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{66}$</th>
<th>$Y_{2D}$</th>
<th>$\nu$</th>
<th>$e_{11}$</th>
<th>$e_{31}$</th>
<th>$d_{11}$</th>
<th>$d_{31}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSiN$_3$H</td>
<td>402.86</td>
<td>108.15</td>
<td>147.35</td>
<td>373.83</td>
<td>0.27</td>
<td>2.90</td>
<td>-0.08</td>
<td>0.99</td>
</tr>
<tr>
<td>WSiP$_3$H</td>
<td>162.88</td>
<td>41.17</td>
<td>60.85</td>
<td>152.47</td>
<td>0.25</td>
<td>5.92</td>
<td>-0.16</td>
<td>4.86</td>
</tr>
<tr>
<td>WSiAs$_3$H</td>
<td>136.13</td>
<td>39.27</td>
<td>48.43</td>
<td>124.80</td>
<td>0.29</td>
<td>6.36</td>
<td>-0.26</td>
<td>6.57</td>
</tr>
</tbody>
</table>
only 10 cm² V⁻¹ s⁻¹, due to its large effective mass. The carrier mobility in all three structures exhibits slightly directional anisotropies along the two examined directions. The Janus WSiP₃H monolayer has the highest electron mobility, up to 610.61 cm² V⁻¹ s⁻¹ along the y axis. The electron mobilities μₓ and μᵧ of the WSiAs₃H monolayer are found to be 209.91 and 327.11 cm² V⁻¹ s⁻¹, respectively. In addition, the hole mobilities of WSiS₃H monolayers are high, ranging from 426.42 (μₓ of WSiN₃H) to 882.08 cm² V⁻¹ s⁻¹ (μᵧ of WSiP₃H).

IV. CONCLUSION

In conclusions, we have examined the electronic, piezoelectric, and transport properties of novel Janus WSiZ₃H monolayers. We have identified the structural stability of novel Janus WSi materials. Our first-principles simulations reveal that WSi monolayers are semiconductors with large valley spin splitting energy when the Z and transport properties of novel Janus WSi materials. Our first-principles simulations reveal that WSi monolayers are high, ranging from 10 to 5×10⁷ cm² V⁻¹ s⁻¹. The electron mobilities μₓ of the WSiAs₃H monolayer are predicted to be piezoelectric materials with large in-plane piezoelectric coefficients d₁₁ up to 6.57 pm/V. Moreover, the breaking of mirror symmetry in Janus structures induces an out-of-plane piezoelectricity with d₃₃ from 0.02 to 0.15 pm/V (absolute value). Our calculations also indicate that both WSiP₃H and WSiAs₃H monolayers are the direct bandgap semiconductors with very high electron mobility, indicating that they are more favorable than WSiN₃H for applications in optoelectronic devices.

SUPPLEMENTARY MATERIAL

See the supplementary material for the calculated results for the AIMD simulations, average plane electrostatic potentials, and uniaxial strain-dependence of the total energy and band edge positions of Janus WSiZ₃H (Z = N, P, As) monolayers.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tuan V. Vu: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal). Bui D. Hoi: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Validation (equal). A. I. Kartamyshev: Conceptualization (equal); Investigation (equal); Software (equal); Validation (equal). Nguyen N. Hieu: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

REFERENCES