




## Article

# Novel Two-Dimensional Layered $\text{MoSi}_2\text{Z}_4$ ( $\text{Z} = \text{P}, \text{As}$ ): New Promising Optoelectronic Materials

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**Abstract:** Very recently, two new two-dimensional (2D) layered semi-conducting materials  $\text{MoSi}_2\text{N}_4$  and  $\text{WSi}_2\text{N}_4$  were successfully synthesized in experiments, and a large family of these two 2D materials, namely  $\text{MA}_2\text{Z}_4$ , was also predicted theoretically (Science, 369, 670 (2020)). Motivated by this exciting family, in this work, we systematically investigate the mechanical, electronic and optical properties of monolayer and bilayer  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$  by using the first-principles calculation method. Numerical results indicate that both monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  ( $\text{Z} = \text{P}, \text{As}$ ) present good structural stability, isotropic mechanical parameters, moderate bandgap, favorable carrier mobilities, remarkable optical absorption, superior photon responsivity and external quantum efficiency. Especially, due to the wave-functions of band edges dominated by  $d$  orbital of the middle-layer Mo atoms are screened effectively, the bandgap and optical absorption hardly depend on the number of layers, providing an added convenience in the experimental fabrication of few-layer  $\text{MoSi}_2\text{Z}_4$ -based electronic and optoelectronic devices. We also build a monolayer  $\text{MoSi}_2\text{Z}_4$ -based 2D optoelectronic device, and quantitatively evaluate the photocurrent as a function of energy and polarization angle of the incident light. Our investigation verifies the excellent performance of a few-layer  $\text{MoSi}_2\text{Z}_4$  and expands their potential application in nanoscale electronic and optoelectronic devices.

**Keywords:** DFT; remarkable optical absorption; superior external quantum efficiency; optoelectronic devices



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## 1. Introduction

Two-dimensional (2D) materials have attracted extensive attention due to their distinctive physical and material properties and the potential application on account of monolayer limit [1–9]. As a typical representative, graphene has been widely expected to be a proper material for the preparation of a new generation of nanoelectronic devices due to remarkable high carrier mobility, but its zero bandgap reminds us that it may not be an effective solution [1,10,11]. Transition metal dichalcogenides (TMDCs) possess tunable bandgap, but its comparatively low carrier mobilities is a not neglectable obstacle for practical applications [3,12–14]. For example, the carrier mobility of  $\text{MoS}_2$  is roughly  $72 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for electron and  $200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for hole, which are roughly four to six orders of magnitude smaller than graphene and even much lower than those of low-doped Si ( $1350 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for electron and  $480 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for hole). Beyond TMDCs, a large 2D family of transition metal carbides and carbonitrides, called MXenes, has been discovered in recent years [15–17]. MXenes are produced by the etching out of the A layers from MAX phases of  $\text{M}_{n+1}\text{AX}_n$ , where M is a transition metal, A is mainly a group IIIA or IVA element, and

X is C or N with  $n = 1, 2, 3$ . So far, more than 60 different pure MXenes have been explored. Their electronic properties, such as band-gap and magnetism, can be tuned by changing the MXene elemental composition and the surface terminations.

Very recently, a new kind of hexagonal 2D MXene,  $\text{MoSi}_2\text{N}_4$  and  $\text{WSi}_2\text{N}_4$ , was successfully synthesized by chemical vapor deposition method with large size up to  $15 \text{ mm} \times 15 \text{ mm}$  [18]. They show good environmental stability, and even have no structural deformation within six months. Monolayer  $\text{MoSi}_2\text{N}_4$  is septuple-atomic-layer structure of N-Si-N-Mo-N-Si-N, which can be view as a  $\text{MoN}_2$  layer sandwiched by two SiN layers. It exhibits indirect bandgap semiconducting behavior with band-gap roughly equal to 1.94 eV. The elastic modulus is four times that of monolayer  $\text{MoS}_2$ , and electron/hole mobility is also roughly four-to-six times larger than that of monolayer  $\text{MoS}_2$ . In addition, a large family of  $\text{MA}_2\text{Z}_4$  is predicted by first-principles calculation, where M represents the elements of IVB, VB, or VIB groups, A represents Si or Ge, and Z represents the elements of VA group. The nanosheets in this family are expected to have wide tunable bandgap and magnetic properties, meaning potential application in electronics, optoelectronics and spintronics.

Motivated by the exciting properties of  $\text{MoSi}_2\text{N}_4$  and  $\text{WSi}_2\text{N}_4$ , some theoretical works have been carried out to further explore the mechanical and physical properties of their family by using the first-principles calculation method [19,20]. The lattice thermal conductivity, piezoelectric and flexoelectric response, and photocatalytic and electronic feature of monolayer  $\text{MA}_2\text{Z}_4$  (M = Cr, Mo, W; A = Si, Ge; Z = N, P) were systematically calculated. They show diverse electronic properties from antiferromagnetic metal to half metal and semiconductor with band gaps ranging from 0.31 to 2.57 eV. Monolayer  $\text{MoSi}_2\text{N}_4$  and  $\text{WSi}_2\text{N}_4$  were predicted to show outstandingly high lattice thermal conductivity of 440 and 500 W/mK, respectively [19]. The piezoelectricity property was calculated for six different configurations of  $\text{MSi}_2\text{N}_4$  (M = Mo, W) which are built through translation, mirror and rotation operations. The maximum piezoelectric strain and stress coefficients is 3.53 pm/V and  $13.95 \times 10^{-10} \text{ C/m}$  for  $\text{MoSi}_2\text{N}_4$ , and 2.91 pm/V and  $12.17 \times 10^{-10} \text{ C/m}$  for  $\text{WSi}_2\text{N}_4$ , respectively, which are much larger than those of 2D TMD, metal oxides, III-V semiconductor and Janus TMD [20]. By tuning biaxial in-plane strain to monolayer  $\text{VSi}_2\text{P}_4$ , a continuous phase transition can be occurred from a ferromagnetic metal to a spin-gapless semiconductor to a ferromagnetic semiconductor to spin-gapless semiconductor to a ferromagnetic half-metal. At the ferromagnetic semiconductor phase, ferromagnetism and piezoelectricity can exist together due to broken inversion symmetry [21]. The van der Waals hetero-structures composed of  $\text{MoSi}_2\text{N}_4$  contacted by graphene and  $\text{NbS}_2$  monolayers were predicted to exhibit ultra-low Schottky barrier height, which can be modulated via the interlayer distance or external electric field [22]. Due to the intrinsic inversion symmetry breaking and strong spin-orbital coupling, remarkable spin-valley coupling in the inequivalent valleys at  $K$  and  $K'$  points can be found for  $\text{MoSi}_2\text{X}_4$  (X = N, P, As). It induces spin-valley coupled optical selection properties, which can be tuned by in-plane strain [23]. Beyond traditional two-level valleys, monolayer  $\text{MoSi}_2\text{N}_4$  shows multiple folded valleys, implying an additional intrinsic degree of freedom. The valley-contrasting properties in monolayer  $\text{MoSi}_2\text{N}_4$  were discussed by using a three-band low-power Hamiltonian, where each valley and energy band can be selectively controlled [24].

In this paper, we systematically investigate the structural, electronic, optoelectronic and quantum transport properties of monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  (Z = P, As). All these 2D materials possess stable configuration, moderate direct band-gap, high and anisotropic carrier mobilities, large optical absorption coefficient, superior photon responsivity and external quantum efficiency in the visible light region. An optoelectronic device based on monolayer  $\text{MoSi}_2\text{Z}_4$  is also built to model the adjustable photocurrent. Our investigation further expands the application prospect of few-layer  $\text{MoSi}_2\text{Z}_4$  in nanoelectronics and optoelectronics.

The rest of this paper is organized as follows. In Section 2, the computational methods are briefly introduced. In Section 3, the numerical results of the structural, electronic

and optoelectronic properties are presented. In addition, the photocurrent of monolayer  $\text{MoSi}_2\text{Z}_4$ -based nanodevice is also calculated. In Section 4, a brief summary is presented.

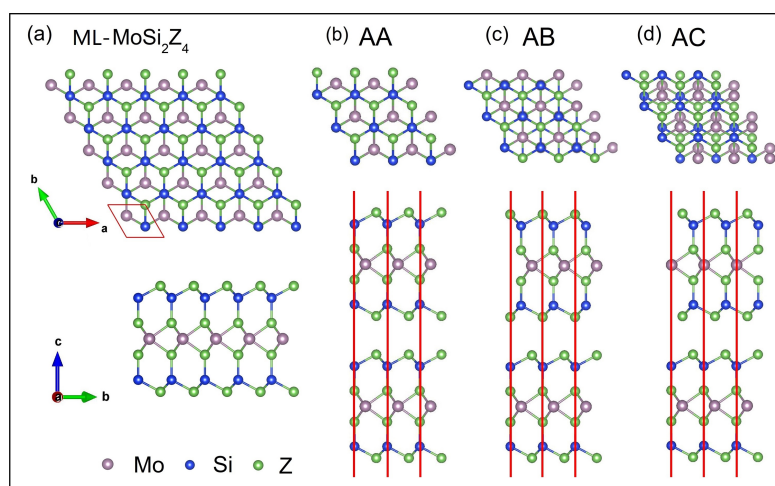
## 2. Numerical Methods

A first-principles calculation is performed by using the Vienna *ab initio* simulation package [25,26] based on the density functional theory (DFT). Both the generalized gradient approximation with a PBE form [27] and the Heyd-Scuseria-Ernzerhof (HSE06) [28] hybrid functional is adopted to calculate the band structures and optical-electronic properties. The energy cutoff and reciprocal k-points are chosen as 500 eV and  $16 \times 16 \times 1$  in structure relaxation and electronic calculation. A vacuum space of 20 Å perpendicular to the 2D plane is applied to separate the periodic images. The weak vdW interaction between adjacent layers is described by the DFT-D2 functional with Grimme correction [29]. The convergence criteria of force and energy are set to 0.01 eV/Å and  $10^{-5}$  eV. To examine the stability of all the structures, PHONOPY code is used to calculate the phonon dispersion curves [30], and *ab initio* molecular dynamics (AIMD) simulation [31] is carried out to examine the total energy evolution at high temperature. To calculate the photocurrent of 2D layered  $\text{MoSi}_2\text{Z}_4$  based nanodevice, Nanodcal software is evaluated which is developed based on the combination of DFT and non-equilibrium Green's function (NEGF-DFT) [32]. In the calculation, norm-conserving pseudopotential, double-zeta polarization basis set and exchange-correlation functional at PBE level are employed.

## 3. Results and Discussion

### 3.1. Structural and Mechanical Properties of Few-Layer $\text{MoSi}_2\text{Z}_4$ ( $Z = \text{P, As}$ )

Figure 1 shows the optimized schematic structures of monolayer (a) and bilayer (b–d)  $\text{MoSi}_2\text{Z}_4$  from top view and side view, where  $Z = \text{P, As}$ . Monolayer  $\text{MoSi}_2\text{Z}_4$  is constructed from septuple atomic layers of  $Z\text{-Si-Z-Mo-Z-Si-Z}$ , which can be viewed as a  $\text{MoZ}_2$  layer sandwiched by two  $\text{SiZ}$  layers. It presents A–B stacked hexagonal lattice from the top view, and its primitive cell includes one Mo atom, two Si atoms and four Z atoms as labeled by the parallelogram in Figure 1a. The lattice parameters  $a = b = 3.470$  Å and 3.620 Å for  $Z = \text{P}$  and  $\text{As}$ , respectively, which are well coincident with those predicted in previous work [18]. Figure 1b–d present three most likely stacking patterns of bilayer  $\text{MoSi}_2\text{Z}_4$ , namely AA, AB and AC, where the Si atoms in the lower layer are aligned with the Si, Z, and Mo atoms in the upper layer, respectively. The relaxed lattice parameters  $a$  and interlayer distances  $d$  are listed in Table 1 for each stacking pattern and two kinds of Z atoms. We find that the interlayer distance of AB stacking is the smallest compared to the other two stacking patterns for both  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$ .



**Figure 1.** (a) Schematic structure of monolayer  $\text{MoSi}_2\text{Z}_4$  ( $Z = \text{P, As}$ ) from top view and side view. The parallelogram indicates its primitive cell. (b) AA, (c) AB, (d) AC stacking patterns of bilayer  $\text{MoSi}_2\text{Z}_4$ .

**Table 1.** Lattice constants  $a$ , interlayer distance  $d$ , cohesive energy  $E_c$ , binding energy  $E_b$  and band gap of few-layer  $\text{MoSi}_2\text{Z}_4$  ( $Z = \text{P}, \text{As}$ ).

System Patterns	Monolayer	Bilayer $\text{MoSi}_2\text{P}_4$			Monolayer	Bilayer $\text{MoSi}_2\text{As}_4$		
	$\text{MoSi}_2\text{P}_4$	AA	AB	AC	$\text{MoSi}_2\text{As}_4$	AA	AB	AC
$a(\text{\AA})$	3.470	3.449	3.450	3.450	3.620	3.581	3.583	3.583
$d(\text{\AA})$	—	3.850	3.075	3.081	—	3.825	3.108	3.112
$E_c(\text{eV})$	−6.089	—	—	—	−5.475	—	—	—
$E_b(\text{eV})$	—	−3.536	−3.614	−3.613	—	−4.272	−4.385	−4.384
Bandgap(eV)	1.015	0.994	1.019	1.021	0.891	0.888	0.894	0.894

Firstly, we check the stability of monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  before further studying their physical properties. For monolayer  $\text{MoSi}_2\text{Z}_4$ , the cohesive energy is calculated by

$$E_c = (E_{\text{Mo}} + 2E_{\text{Si}} + 4E_{\text{Z}} - E_{\text{MoSi}_2\text{Z}_4})/7, \quad (1)$$

where  $E_{\text{Mo}}$ ,  $E_{\text{Si}}$ ,  $E_{\text{Z}}$  and  $E_{\text{MoSi}_2\text{Z}_4}$  are total energies of isolated Mo atom, Si atom, Z atom and a primitive cell of  $\text{MoSi}_2\text{Z}_4$ . The calculated cohesive energies are 6.089 eV/atom for  $\text{MoSi}_2\text{P}_4$  and 5.475 eV/atom for  $\text{MoSi}_2\text{As}_4$ . They are smaller than that of graphene (7.46 eV/atom), while larger than those of  $\text{MoS}_2$  (4.98 eV/atom) and phosphorene (3.30 eV/atom) [33–35] indicating proper stability. For bilayer  $\text{MoSi}_2\text{Z}_4$ , the stability is generally measured by the binding energy defined as

$$E_b = E_{\text{BL}} - 2E_{\text{ML}}, \quad (2)$$

where  $E_{\text{BL}}$  and  $E_{\text{ML}}$  stand for total energies of bilayer and monolayer  $\text{MoSi}_2\text{Z}_4$ , respectively. As listed in Table 1, the binding energies are negative for all the bilayer  $\text{MoSi}_2\text{Z}_4$ , and the AB stacking has the smallest value indicating the most stable stacking pattern. Thus, we only focus on the AB stacking pattern for the bilayer  $\text{MoSi}_2\text{Z}_4$  in the rest of this paper.

Next, the phonon dispersion spectrums of monolayer  $\text{MoSi}_2\text{Z}_4$  are calculated to examine their dynamic stability. Figure 2a presents the phonon dispersion spectrum of monolayer  $\text{MoSi}_2\text{P}_4$ . The low-frequency band near  $\Gamma$  point is roughly linear and there is no imaginary modes in the Brillouin zone, which indicates monolayer  $\text{MoSi}_2\text{P}_4$  is dynamically stable. An AIMD simulation is performed at 300 K to further examine the thermal stability of the structure by employing a  $4 \times 4$  supercell. As shown in Figure 2b, the total energy of monolayer  $\text{MoSi}_2\text{P}_4$  oscillates slightly in the vicinity of  $-720$  eV for a long time without decay. Neither bond-breaking nor geometry reconstruction appears in the structure at 10 fs indicating thermal stability of monolayer  $\text{MoSi}_2\text{P}_4$  at room temperature. Similar phonon dispersion spectrums and total energy evaluations are also obtained for all the other monolayer and bilayer structures, as shown in Figure 3.

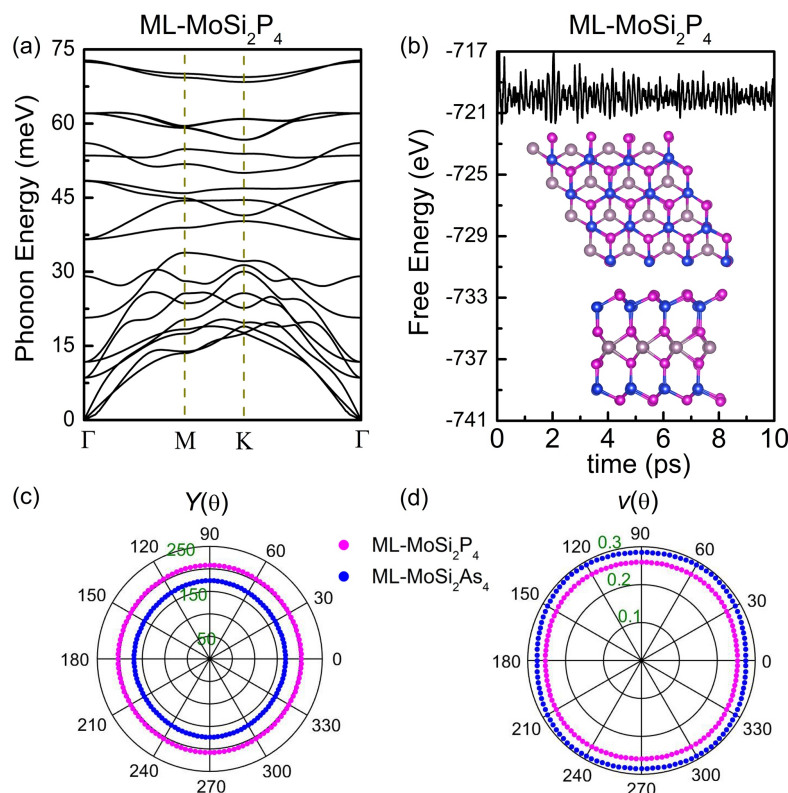
Finally, we examine the mechanical properties of all the structures under external force by calculating elastic constants  $C_{ij}$ . As listed in Table 2, the Born criteria  $C_{11}C_{22} - C_{12}^2 > 0$  and  $C_{66} > 0$  are both satisfied for the monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  meaning their mechanical stability [36]. Based on  $C_{i,j}$ , Young's modulus  $Y(\theta)$  and the Poisson's ratio  $\nu(\theta)$  along the in-plane angle  $\theta$  and the layer modulus  $\gamma$  are also calculated.  $Y(\theta)$  indicates the reciprocal of the response of strain to stress along a specific direction along  $\theta$  in the 2D plane.  $\nu(\theta)$  is the ratio of the absolute value of transverse normal strain to axial normal strain.  $\gamma$  represents the resistance of the 2D surface to stretching, and thus is independent of  $\theta$ . These physical quantities can be calculated by the following formulas [37]

$$Y(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11} \sin^4 \theta + A \sin^2 \theta \cos^2 \theta + C_{22} \cos^4 \theta},$$

$$\nu(\theta) = \frac{C_{12} \sin^4 \theta - B \sin^2 \theta \cos^2 \theta + C_{12} \cos^4 \theta}{C_{11} \sin^4 \theta + A \sin^2 \theta \cos^2 \theta + C_{22} \cos^4 \theta},$$

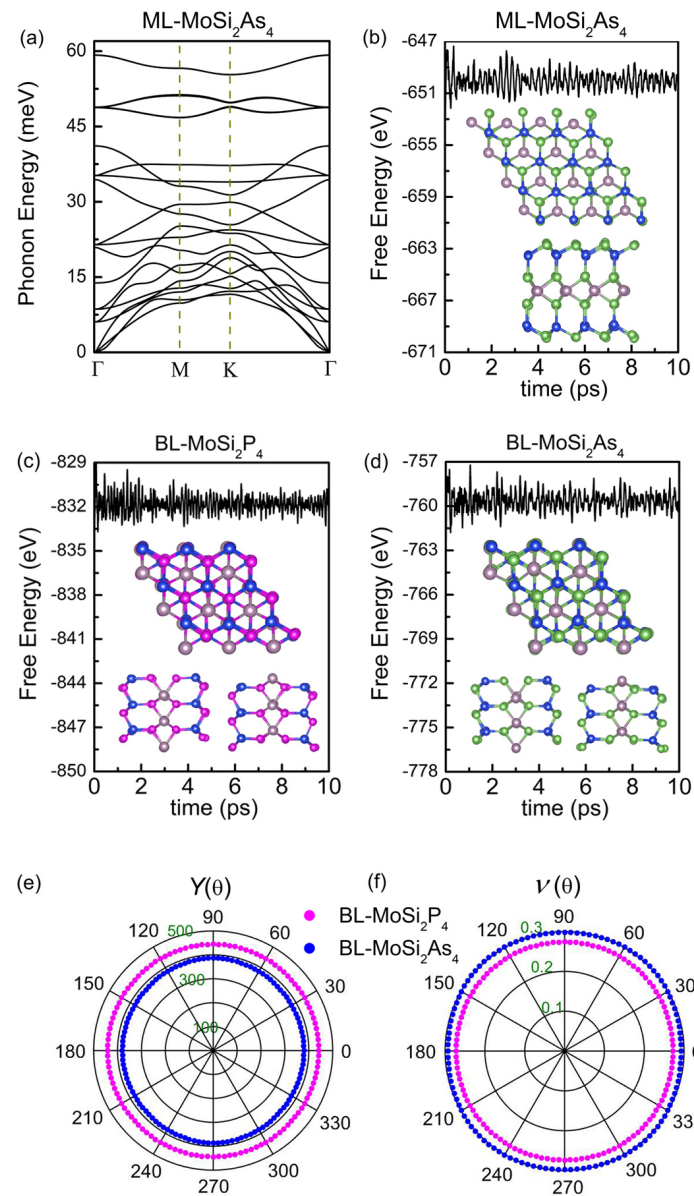
$$\gamma = \frac{1}{4}(C_{11} + C_{22} + 2C_{12}),$$

in which  $A = (C_{11}C_{22} - C_{12}^2)/C_{66} - 2C_{12}$  and  $B = C_{11} + C_{22} - (C_{11}C_{22} - C_{12}^2)/C_{66}$ . Figure 2c,d show the  $Y(\theta)$  and  $\nu(\theta)$  of monolayer  $\text{MoSi}_2\text{Z}_4$ .  $Y(\theta)$  is isotropic and  $\nu(\theta)$  is roughly isotropic for both monolayers.  $Y(\theta)$  of  $\text{MoSi}_2\text{P}_4$  is larger than that of  $\text{MoSi}_2\text{As}_4$ , while  $\nu(\theta)$  of the former is smaller than that of the latter. This means monolayer  $\text{MoSi}_2\text{As}_4$  is easier to deform under in plane external force than monolayer  $\text{MoSi}_2\text{P}_4$ . It is reasonable because the As–Mo and As–Si bonds are longer and deformable than the P–Mo and P–Si bonds. Similarly,  $\gamma$  of  $\text{MoSi}_2\text{P}_4$  is larger than that of  $\text{MoSi}_2\text{As}_4$ .  $Y$  and  $\gamma$  of monolayer  $\text{MoSi}_2\text{Z}_4$  are slightly smaller than that of monolayer graphene (340 N/m and 215.9 N/m) and BN (318 N/m and 177.0 N/m) [38], while comparable to those of SiC (179.7 N/m and 116.5 N/m) [38] and monolayer  $\text{PC}_3$  (180.4 N/m and 102.1 N/m) [39] implying their similar mechanical response. In terms of bilayer  $\text{MoSi}_2\text{Z}_4$ , both  $Y(\theta)$  and  $\gamma$  are nearly two times as those of monolayer  $\text{MoSi}_2\text{Z}_4$  (see Table 2 and Figure 3). Such behavior is physically reasonable and in good accordance with that of multilayer graphene [38] and  $\text{PC}_3$  [39]. The calculated moduli indicate that few-layered  $\text{MoSi}_2\text{Z}_4$  are stretchable and flexible as most of the other common 2D materials, indicating potential application in flexible electronic devices.



**Figure 2.** (a) Phonon dispersion curves and (b) total energy variation at 300 K of monolayer  $\text{MoSi}_2\text{P}_4$ . Inset in (b) shows the top view and side view of a snapshot at 10 ps. (c) Young's modulus  $Y(\theta)$  and (d) Poisson's ratio  $\nu(\theta)$  of monolayer  $\text{MoSi}_2\text{P}_4$  (purple curve) and  $\text{MoSi}_2\text{As}_4$  (blue curve) along arbitrary in-plane directions.





**Figure 3.** (a) Phonon band dispersion curves of the monolayer  $\text{MoSi}_2\text{As}_4$ . Variations of total energy at 300 K as functions of time for (b) monolayer  $\text{MoSi}_2\text{As}_4$ , (c) bilayer  $\text{MoSi}_2\text{P}_4$ , (d) bilayer  $\text{MoSi}_2\text{As}_4$ . (e) Young's modulus  $Y(\theta)$  and (f) Poisson's ratio  $\nu(\theta)$  of bilayer  $\text{MoSi}_2\text{P}_4$  (purple curve) and  $\text{MoSi}_2\text{As}_4$  (blue curve) along arbitrary in-plane directions.

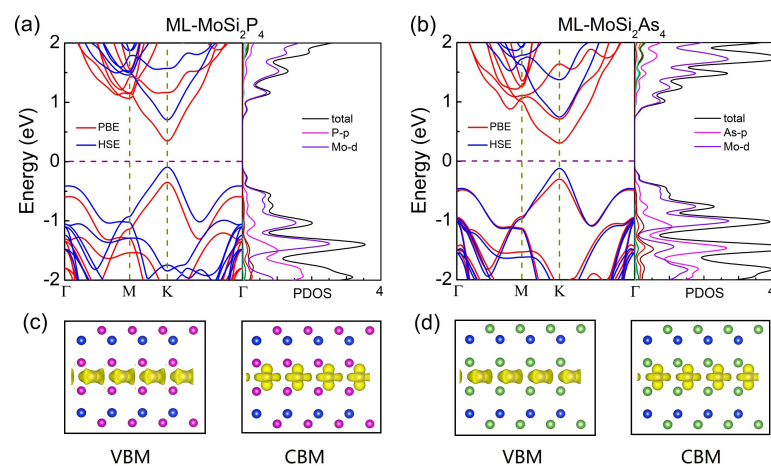
**Table 2.** The calculated elastic constants  $C_{ij}$ , Young's modulus  $Y$  and Poisson's ratio  $\nu$  along the  $x$  ( $\theta = 0$ ) and  $y$  ( $\theta = \pi/2$ ) directions, layer modulus  $\gamma$  for monolayer (ML-) and bilayer (BL-)  $\text{MoSi}_2\text{Z}_4$  ( $Z = \text{P, As}$ ).

Type	$C_{11}(\text{N/m})$	$C_{22}(\text{N/m})$	$C_{12}(\text{N/m})$	$C_{66}(\text{N/m})$	$Y_x(\text{N/m})$	$Y_y(\text{N/m})$	$\nu_x$	$\nu_y$	$\gamma(\text{N/m})$
ML- $\text{MoSi}_2\text{P}_4$	217.70	222.65	56.35	80.67	203.43	208.06	0.253	0.259	138.26
BL- $\text{MoSi}_2\text{P}_4$	476.59	479.76	130.42	173.09	441.14	444.07	0.272	0.274	304.30
ML- $\text{MoSi}_2\text{As}_4$	182.38	188.67	52.01	65.18	168.04	173.84	0.276	0.285	118.77
BL- $\text{MoSi}_2\text{As}_4$	415.86	423.43	124.00	145.93	379.54	386.45	0.293	0.298	271.82

### 3.2. Electronic Properties of Few-Layer $\text{MoSi}_2\text{Z}_4$

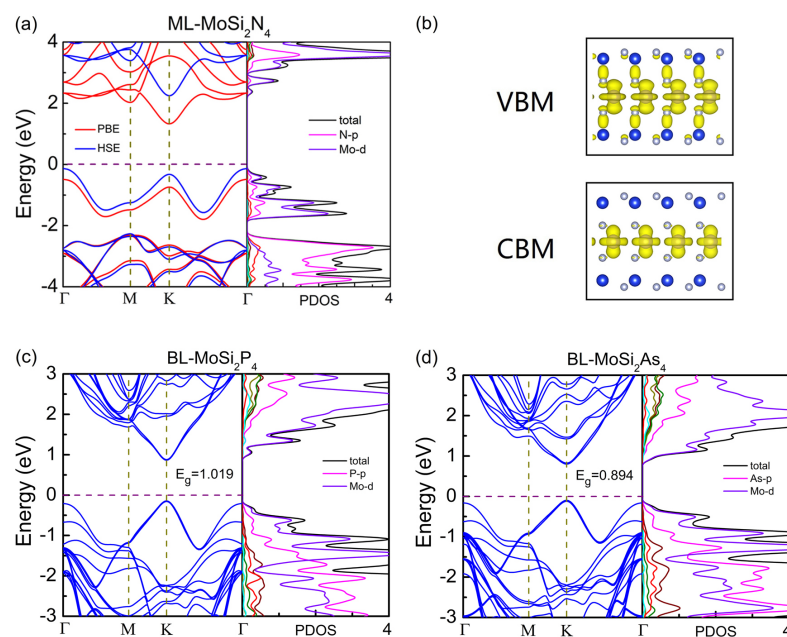
Figure 4a,b show the band structure and projected density of states (PDOS) of monolayer  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$  based on PBE and HSE06 exchange-correlation functionals.

For each configuration, the band structure based on the PBE exchange-correlation functional is similar to that based on the HSE06 functional except the smaller bandgap. Both structures show a direct bandgap, and both conduction band minimum (CBM) and valence band maximum (VBM) locate at K point. This is different from monolayer  $\text{MoSi}_2\text{N}_4$ , whose CBM sits K point while VBM locates at  $\Gamma$  point, presenting indirect band-gap semiconducting behavior (Ref. [18], also see Figure 5a). To get more insight into this difference, PDOS and charge distribution at VBM and CBM are plotted in Figure 5c,d. For monolayer  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$ , both CBMs and VBMs are mainly originated from the  $d$  orbitals of Mo atoms which locate in the middle layer of the structures. While, for monolayer  $\text{MoSi}_2\text{N}_4$ , VBM is dominated by both  $d$  orbital of Mo atoms and  $p$  orbital of Z atom (see Figure 5b). Due to the orbital hybridization, an obvious extension of VBM from the middle Mo atoms to beside the Z atoms occurs, which is much different from the charge distribution of VBMs in  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$ . This is reasonable because the N–Mo bonds are shorter than the P–Mo and As–Mo bonds, and thus the orbital hybridization is more likely to happen in  $\text{MoSi}_2\text{N}_4$ .



**Figure 4.** The electronic band structure and projected density of states (PDOS) of monolayer (a)  $\text{MoSi}_2\text{P}_4$  and (b)  $\text{MoSi}_2\text{As}_4$ . (c,d): Corresponding charge distribution at valence band maximum (VBM) and conduction band minimum (CBM) dominated by the  $d$  orbital of Mo atoms in the middle layer.

In terms of bilayer  $\text{MoSi}_2\text{Z}_4$ , similar direct bandgap semiconducting behavior to monolayer  $\text{MoSi}_2\text{Z}_4$  are obtained, where both CBM and VBM locate at K points (see Figure 5c,d). The bandgap of bilayer  $\text{MoSi}_2\text{Z}_4$  changes very little in comparison to that of monolayer  $\text{MoSi}_2\text{Z}_4$  (see Table 1). The independence of bandgap with the number of layers can be attributed to the orbital shield. Because the states at CBM and VBM are dominated by the  $d$  orbital of Mo atoms, they are effectively screened inside the monolayer  $\text{MoSi}_2\text{Z}_4$  because the Mo atoms located in the middle layer of seven atomic layers. For bilayer  $\text{MoSi}_2\text{Z}_4$ , the rather weak interlayer vdW interaction makes the Mo atoms at the up layer and those at the down layer have nothing to do with each other, and thus the band gap is very close to that of the monolayer. Similar layer number independent bandgap behavior has also been found in layered 2D  $\text{KAgSe}$  [40]. The layer number independent electronic properties provide enormous convenience and less difficulty in experimental fabrication of finite layer  $\text{MoSi}_2\text{Z}_4$ -based electronic devices.



**Figure 5.** (a) The electronic band structure and PDOS of monolayer  $\text{MoSi}_2\text{N}_4$ , (b) Corresponding charge distribution at VBM and CBM of monolayer  $\text{MoSi}_2\text{N}_4$ . The electronic band structure and PDOS of bilayer (c)  $\text{MoSi}_2\text{P}_4$  and (d)  $\text{MoSi}_2\text{As}_4$ .

### 3.3. Carrier Mobilities of Few-Layer $\text{MoSi}_2\text{Z}_4$

Carrier mobility is an important factor to describe the transport ability of electronic and optoelectronic materials, which can be evaluated by using the deformation potential method as follows [41,42],

$$\mu = \frac{e\hbar C}{k_B T m^* m_d E_{DP}^2}, \quad (3)$$

where  $T$  is the temperature and equal to 300 K in this calculation;  $m^* = \pm \hbar^2 (d^2 E_k / dk^2)$  is the effective mass of electrons and holes depending on the change of energy with wave vector  $k$  along different transport directions;  $m_d$  is the averaged effective mass defined as  $m_d = \sqrt{m_x^* m_y^*}$ ;  $C = (\partial^2 E / \partial^2 \epsilon) / S_0$  is the elastic modulus related to the change of total energy with strain along different directions;  $E_{DP} = dE_{edge} / d\epsilon$  is the deformation potential constant given by the change rate of band edges with strain. The calculated carrier mobilities and corresponding parameters of layered  $\text{MoSi}_2\text{Z}_4$  are summarized in Table 3.

Three pieces of information can be obtained from Table 3. Firstly, the carrier mobility of holes is roughly three to four times larger than that of electrons for both monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  along with both  $x$  and  $y$  directions, which mainly attributes to the smaller deformation potential constant  $E_{DP}$  of holes. This difference of carrier mobilities can effectively facilitate the spatial separation of electrons and holes, which reduces the recombination probability of photo-excited carriers and suggests satisfactory performances for nanoscale electronic and optoelectronic devices. Secondly, the carrier mobilities of bilayer  $\text{MoSi}_2\text{Z}_4$  are largely improved in contrast to those of monolayer  $\text{MoSi}_2\text{Z}_4$  due to the roughly doubled elastic modulus  $C$ . Similar properties were also found for MXs [43]. Thirdly, the carrier mobilities of  $\text{MoSi}_2\text{P}_4$  are slightly higher than that of  $\text{MoSi}_2\text{As}_4$  for both monolayer and bilayer structures, which are also independent of carrier types and directions. Especially, these carrier mobilities are relatively high, which are much larger than those of  $\text{MoS}_2$  ( $200\text{--}500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) [44] and even comparable to those of black phosphorene [42] indicating potential application in 2D electronic devices.



**Table 3.** The effective mass  $m^*$ , elastic modulus  $C_{2D}$ , deformation potential constant  $E_{DP}$ , and carrier mobility  $\mu$  along x and y directions for monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  at 300 K.

System	Carrier Type	$m^*/m_0$	$C_{2D}$ ( $\text{Nm}^{-1}$ )	$E_{DP}$ (eV)	$\mu$ ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )
ML- $\text{MoSi}_2\text{P}_4$	e (x)	0.325	214.88	6.82	828.76
	e (y)	0.415	218.74	6.28	778.90
	h (x)	0.339	214.88	3.43	3171.83
	h (y)	0.430	218.74	3.65	2131.78
BL- $\text{MoSi}_2\text{P}_4$	e (x)	0.313	481.13	6.94	1919.84
	e (y)	0.403	484.88	6.40	1759.76
	h (x)	0.344	481.13	2.99	8652.25
	h (y)	0.435	481.88	3.55	4860.34
ML- $\text{MoSi}_2\text{As}_4$	e (x)	0.499	178.40	4.05	823.19
	e (y)	0.640	178.37	3.76	743.11
	h (x)	0.419	178.40	3.04	2093.38
	h (y)	0.524	178.37	3.16	1552.98
BL- $\text{MoSi}_2\text{As}_4$	e (x)	0.496	432.14	4.19	1855.52
	e (y)	0.659	432.12	3.88	1629.69
	h (x)	0.425	432.14	2.79	5905.10
	h (y)	0.528	432.12	2.77	4819.97

### 3.4. Optical Absorption Spectrums of Layered $\text{MoSi}_2\text{Z}_4$

Monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  with direct band gaps about 0.85–1.0 eV exhibit potential application for visible–light solar harvesting/utilizing techniques or making narrow-gap semiconductor devices. Recent studies revealed that such narrow band gap materials are good candidates of infrared photodetectors, such as phosphorus carbides and black arsenic phosphorus [6,45,46]. Thus, we further investigate the optoelectronic performance of few-layer  $\text{MoSi}_2\text{Z}_4$  by calculating the absorption coefficient as follows [47,48]

$$\alpha(\omega) = \sqrt{2}\omega \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)}, \quad (4)$$

where  $c$ ,  $\omega$ ,  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  stands for the light velocity, frequency of incident light, real part and imaginary part of the frequency-dependent dielectric function, respectively.  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  can be calculated by using the Kramers–Kronig relation and summing all the empty states in the Brillouin zone.

Figure 6 shows the optical absorption coefficients of monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  based on PBE and HSE06 calculations, where the polarization direction of incident light is parallel to the 2D plane. All the few-layer  $\text{MoSi}_2\text{Z}_4$  display very similar and remarkably high absorption coefficients ( $\sim 10^5 \text{ cm}^{-1}$ ) in the visible-ultraviolet light region, which agrees well with their similar band gaps as shown in Figure 4. The large absorption is even comparable to that of graphene, phosphorene and  $\text{MoS}_2$  [6]. The strong optical absorption and broad absorption ranges make layered  $\text{MoSi}_2\text{Z}_4$  promising materials for photovoltaic solar cells and optoelectronic devices. Especially, the layer number independence to the bandgap and optical absorption makes the experimental fabrication more convenient of few-layer  $\text{MoSi}_2\text{Z}_4$ -based 2D optoelectronic devices.

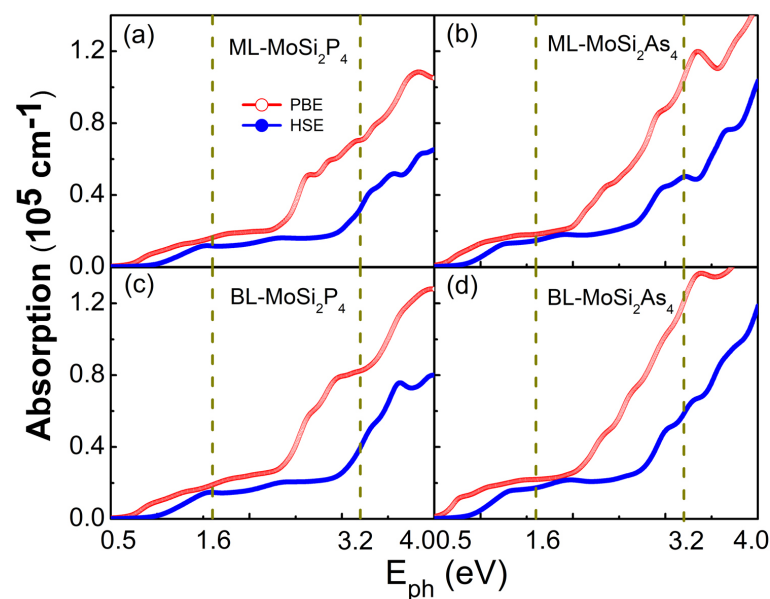
### 3.5. Photocurrent in Monolayer $\text{MoSi}_2\text{Z}_4$ Nanodevice

On account of the similar and excellent optical absorption performance of layered  $\text{MoSi}_2\text{Z}_4$ , we build a monolayer  $\text{MoSi}_2\text{Z}_4$ -based two-probe 2D optoelectronic device as shown in Figure 7 and evaluate its photoinduced current. To solve the quantum transport problem in this identical system, the device can be separated into three parts theoretically including a central scattering region and two semi-infinite electrodes. When the incident light energy in the scattering region is larger than the bandgap, the electrons at the valence band can be excited to the conduction band by absorbing photons. When a tiny external

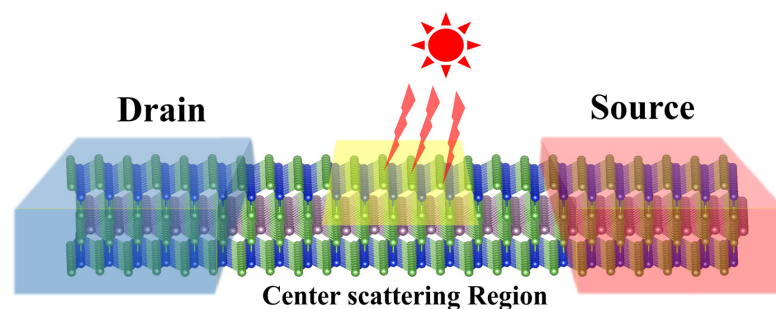
bias is applied between the source and the drain, the excited electrons can be driven to produce photocurrent in the system. Note that the potential difference between the left and the right leads should be much smaller than the bandgap of the system to ensure that the detected current in the electrode is completely generated by the light but not bias. The photocurrent flowing into the left probe can be expressed in terms of the NEGF as follows [49–51],

$$J_L^{ph} = \frac{ie}{h} \int \text{Tr} \left[ \Gamma_L \{ G^{<(ph)} + f_L(E)(G^{>(ph)} - G^{<(ph)}) \} \right] dE, \quad (5)$$

where  $f_L$ ,  $\Gamma_L$  and  $G^{</>(ph)}$  denotes the Fermi distribution function, line-width function and greater/lesser Green's function of the two-probe system including electron-photon interaction, respectively.



**Figure 6.** Optical absorption coefficients versus the energy of incident light for 2D (a) monolayer  $\text{MoSi}_2\text{P}_4$ , (b) monolayer  $\text{MoSi}_2\text{As}_4$ , (c) bilayer  $\text{MoSi}_2\text{P}_4$  and (d) bilayer  $\text{MoSi}_2\text{As}_4$  based on PBE and HSE06 functionals. For each panel, the polarization vector of incident light is set parallel to the plane, and the two vertical dashed lines indicate the region of visible light.



**Figure 7.** Schematic structure of monolayer  $\text{MoSi}_2\text{Z}_4$ -based 2D optoelectronic device. The yellow zone in the center scattering region stands for the lighting area. The left blue region and right red region represent the drain and source, respectively.

In this calculation, the incident light is perpendicular to the 2D plane, and the angle between polarization direction and transport direction is labeled as  $\theta$ . Figure 8a,c show the photocurrent versus energy of the linearly polarized light with power density equal to  $10^3 \mu\text{W}/\text{mm}^2$  and  $\theta$  equal to  $0^\circ$  and  $90^\circ$ . When energy is smaller than 0.5 eV, photocurrent

is equal to zero for both  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$  because the energy is smaller than their band gaps. With further increase of energy, photocurrent appears and oscillates with the energy for both  $\theta = 0^\circ$  and  $90^\circ$  depending on the detailed behavior of band structures. Photocurrent reaches local maximum in the visible region at  $\theta = 0^\circ$ , and in the ultraviolet region at  $\theta = 90^\circ$ . To further explore the influence of incident polarization angle  $\theta$ , photocurrent as a function of  $\theta$  under different photon energy in the visible light region are evaluated as shown in Figure 6b,d. For both  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$ , the photocurrent is roughly symmetrical with respect to  $\theta = 90^\circ$ , and reaches maximums at  $\theta = 0^\circ$  and  $\theta = 180^\circ$ . Similar symmetrical distribution of photocurrent with polarization angle was also reported for monolayer KAgSe-based 2D optoelectronic device [40].

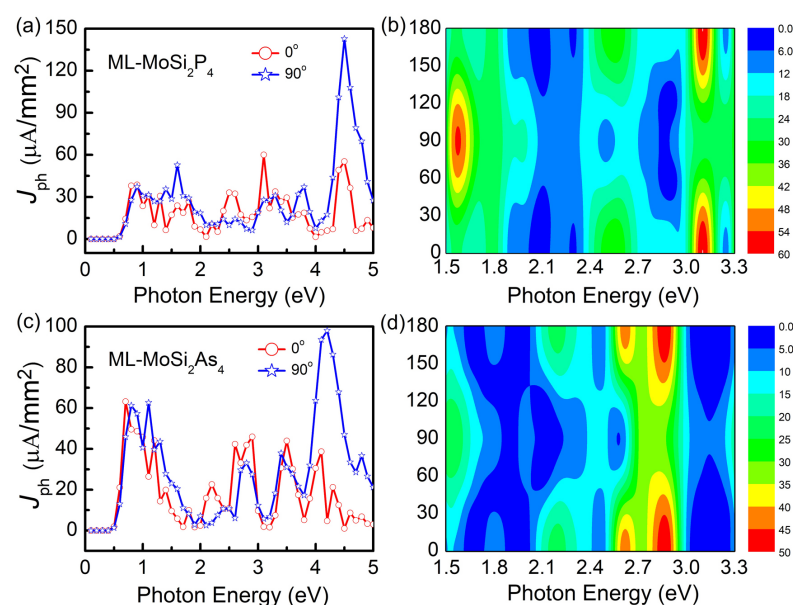
The responsivity  $R_{ph}$  and external quantum efficiency  $\tau_{eqe}$  are generally used to measure the photovoltaic performances, which are defined as

$$R_{ph} = \frac{J_L^{ph}}{eF_{ph}} \quad (6)$$

and

$$\tau_{eqe} = R_{ph} \frac{hc}{e\lambda}, \quad (7)$$

in which the photon flux  $F_{ph}$  stands for the number of incident photons in unit area and unit time.  $R_{ph}$  of monolayer  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$  in the visible light region are  $0.060 \text{ AW}^{-1}$  and  $0.046 \text{ AW}^{-1}$ , respectively, which are the same order as those of  $\text{MoS}_2$  ( $0.016 \text{ AW}^{-1}$ ) and monolayer chalcogenides ( $0.035 \text{ AW}^{-1}$  for GeS and  $0.075 \text{ AW}^{-1}$  for SnS), while two orders higher than that of graphene ( $5 \times 10^{-4} \text{ AW}^{-1}$ ) [52].  $\tau_{eqe}$  of monolayer  $\text{MoSi}_2\text{P}_4$  and  $\text{MoSi}_2\text{As}_4$  in the visible light region can reach 18.60% and 13.33%, respectively, which are comparable to those of KAgSe (17.92%) [40] and monolayer chalcogenides (10.27% for GeS and 22.01% for SnS) [53]. In addition,  $R_{ph}$  and  $\tau_{eqe}$  of monolayer  $\text{MoSi}_2\text{Z}_4$  are greatly increased within the whole light region, ie,  $0.143 \text{ AW}^{-1}$  and 64.26% for  $\text{MoSi}_2\text{P}_4$ ,  $0.098 \text{ AW}^{-1}$  and 41.16% for  $\text{MoSi}_2\text{As}_4$ . Here, it is worth mentioning that the above values of photon responsivity  $R_{ph}$  and external quantum efficiency  $\tau_{eqe}$  are all calculated theoretically based on the computational models. It is hoping that there will be more experimental results to support in the future. Once again, these ideal performances of  $\text{MoSi}_2\text{Z}_4$  suggest their powerful potential application in optoelectronic and photovoltaic devices.



**Figure 8.** Photocurrent as a function of photon energy with polarization angle  $\theta$  of the incident light equal to  $0^\circ$  and  $90^\circ$  for monolayer (a)  $\text{MoSi}_2\text{P}_4$  and (c)  $\text{MoSi}_2\text{As}_4$  nanodevice. (c,d) show the photocurrent versus photon energy and  $\theta$  for monolayer (b)  $\text{MoSi}_2\text{P}_4$  and (d)  $\text{MoSi}_2\text{As}_4$  nanodevice.

#### 4. Conclusions

Recently synthesized 2D semiconductors  $\text{MoSi}_2\text{N}_4$  and  $\text{WSi}_2\text{N}_4$  exhibit prominent material and physical properties, including remarkable stability, high strength and large carrier mobility, which also inspires increasing theoretical researches to further explore the physical properties of their family  $\text{MA}_2\text{Z}_4$ . First principle calculations indicate that  $\text{MA}_2\text{Z}_4$  materials possess wide tunable band gaps, magnetic properties and valley-contrasting properties, indicating potential applications in electronics, optoelectronics, spintronics and valleytronics. In this case, we investigated the electronic and photoelectrical properties of monolayer and bilayer 2D  $\text{MoSi}_2\text{Z}_4$  ( $Z = \text{P, As}$ ) by using the first-principles calculation method. Firstly, the structural, dynamic, thermal and mechanical stabilities of the few-layer  $\text{MoSi}_2\text{Z}_4$  were numerically verified. Secondly, both monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  show direct bandgap semiconducting behavior, which is different from  $\text{MoSi}_2\text{N}_4$  with indirect bandgap. Moreover, the band gaps of layered  $\text{MoSi}_2\text{Z}_4$  are roughly independent of the number of layers due to effective screening to the atomic orbital of Mo atoms. Thirdly, monolayer and bilayer  $\text{MoSi}_2\text{Z}_4$  show high carrier mobilities and remarkable optical absorption coefficients. Monolayer  $\text{MoSi}_2\text{Z}_4$ -based optoelectronic device displays large photon responsivity and external quantum efficiency. All these appealing properties make  $\text{MoSi}_2\text{Z}_4$  promising candidates for application in electronic and optoelectronic devices.

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