Rui qi,‡ Rui qi, † Yingjie Jiang, † Cuicui Sun, † Guiling Zhang, † Yangyang Hu, †‡ Zhao-Di Yang, † and Weiqi Li †‡

†School of Materials Science and Engineering, Harbin University of Science and Technology, Harbin 150080, China
‡Department of Physics, Harbin Institute of Technology, Harbin 150001, China

ABSTRACT: The transport and photoelectric properties of four two-dimensional (2D) silicene/MX₂ (M = Mo, W; X = S, Se) heterostructures have been investigated by employing density functional theory, nonequilibrium Green’s function, and Keldysh nonequilibrium Green’s function methods. The stabilities of silicene (SiE) are obviously improved after being placed on the MX₂ (M = Mo, W; X = S, Se) substrates. In particular, the conductivities of SiE/MX₂ are enhanced compared with free-standing SiE and MX₂. Moreover, the conductivities are increased with the group number of X, i.e., in the order of SiE < SiE/MX₂ < SiE/MX₂. An evident current oscillation phenomenon is observed in the SiE/WX₂ heterostructures. When a linear light illumination is applied, SiE/MX₂ shows a stronger photoresponse than SiE/MX₂. The maximum photoresponse with a value of 9.0e²/photons was obtained for SiE/MX₂. More importantly, SiE/MX₂ (M = Mo, W) heterostructures are good candidates for application in designing solar cells owing to the spatial separation of the charge carriers. This work provides some clues for further exploring 2D SiE/MX₂ heterostructures involving tailored photoelectric properties.

1. INTRODUCTION

In recent years, tremendous attention has been focused on two-dimensional (2D) group-IV monolayers because of their unique physical properties and potential applications in the electronic industry.1–4 As the most representative 2D material, graphene, a sp²-hybridized carbon monolayer, has attracted wide interest due to its peculiar electronic properties which allow electrons to move freely in its surface with high speed.5,6 However, it lacks an intrinsic band gap, which makes electronic applications of graphene difficult for electronic devices.7,8 Two-dimensional silicene (SiE),9–13 another well-known sp²–sp³ hybridized group-IV monolayer, has most similar remarkable electronic properties to graphene.14 Differently, free-standing SiE is estimated to be the subject to a slight buckling5,16 with the height of approximately 0.44 Å due to sp²–sp³ hybridization.17–19 Therefore, despite in the same group, SiE is not atomically flat as graphene, suggesting that SiE may be superior to graphene in many aspects, such as having an enhanced quantum Hall effect,20–22 electrically tunable band gap,23 and better surface reactivity.18 Another obvious advantage of SiE is the better compatibility with current silicon-based technologies.24 Thus, SiE has been fabricated successfully on metal or other 2D material substrates, which is of fundamental importance to enable a wide range of nanoelectronic devices.25–27 Several experimental groups have reported the epitaxial growth of SiE on metallic substrates such as MgX₂(0001) (X = Cl, Br, I),28,29 Ir(111),30,31 Al(111),32 and Ag(111),33–41 and found, however, that the Dirac cone of SiE can be destroyed since the Si-π bands strongly hybridize with the substrates.41–46 Many nonmetallic 2D materials as substrates, including graphite,47 graphene,48 silicon,49,50 SiC,51,52 PtSe₂,53 MoS₂,54 and ZrC,55 have also been proposed and investigated theoretically. Recently, high-buckled 2D Si nanosheets have been fabricated by molecular beam epitaxial growth on the bulk MoS₂ surface.56 Zhao et al.57 have reported density functional theory (DFT) analysis of SiE/MoS₂ and addressed that silicene/MoS₂ can be formed by SiE adsorbing on the MoS₂ substrate via van der Waals (vdW) interactions, and the transport behavior of SiE/MoS₂ is tuned by the interface between SiE and MoS₂ substrates. The substrate under the SiE not only serves as a mechanical support for SiE but also modulates the band gap of SiE.58,59 In particular, vdW interaction between the SiE and the substrate makes the sublattice symmetry break, which opens the band gap.60–62 Additionally, the high carrier mobility of 2D materials can be retained from vdW interactions, since it does not destroy the bonding properties between intralayer atoms. The interlayer coupling between the two vdW-stacked 2D layers can result in novel physical properties. For example, owing to the tunable band alignments and strong light–matter interactions, the vdW is beneficial for light harvesting and detecting.63–66 In contrast to other layer materials, considering the tunable band gaps of

© 2018 American Chemical Society

DOI: 10.1021/acsomega.8b01282
ACS Omega 2018, 3, 13251−13262
SiE and easy integration into the modern Si-based device technologies, studying the transport and photoelectric properties for a series of SiE/MX₂ (M = Mo, W; X = S, Se), thus, becomes a valuable research topic.

In the present paper, calculations were performed using DFT and nonequilibrium Green’s function (NEGF) methods for four SiE/MX₂ heterostructures (M = Mo, W; X = S, Se) to explore the electronic structures, transport properties, and the photoresponses of SiE supported on MX₂ (M = Mo, W; X = S, Se). Previous investigation indicated that the band gap depends on the rotation angle and stacking pattern, whereas the formation energy did not. In the present work, a series of SiE/MX₂ (M = Mo, W; X = S, Se) heterostructures with a 30° rotational angle between the base vectors of the two lattices have been investigated since such layer stacking orientation makes a good match for modeling periodic supercells to calculation. Moreover, due to the opened band gaps of these structured SiE/MX₂ (M = Mo, W; X = S, Se), they can be applied as candidates of optoelectronic materials. We found that SiE attached to different MX₂ (M = Mo, W; X = S, Se) substrates could introduce different intriguing transport and photoelectric properties, which offer clues for designing novel 2D nanoscaled electronic and optoelectronic devices.

2. RESULTS AND DISCUSSION
The stability of SiE/MX₂ (M = Mo, W; X = S, Se) heterostructures can be demonstrated by computing the binding energy (ΔEₘ) per supercell (Figure 1) for the total equation [MX₂ + SiE → SiE/MX₂ − ΔEₘ], as listed in Table 1. Here, the values of ΔEₘ are negative for all the considered heterostructures, indicating that the process is exothermic and the heterostructures tend to be more stable, and hence, SiE and MX₂ (M = Mo, W; X = S, Se) nanosheets yearn for stacking each other. The M–X bond lengths (Lₘ−X) in SiE/MX₂ are 2.475–2.589 Å, close to that of 2.38–2.55 Å in pure SiE and MX₂. The electron density difference for SiE/MX₂ (M = Mo, W; X = S, Se), and the isosurface value is ±0.005 e/Å³.

| species        | ΔEₘ/eV | Lₘ−X/Å | R₁/Å  |
|----------------|--------|--------|-------|
| SiE/MoS₂       | −19.145| 2.775  | 2.630 |
| SiE/MoSe₂      | −18.495| 2.889  | 2.743 |
| SiE/WS₂        | −17.866| 2.805  | 2.656 |
| SiE/WSe₂       | −16.743| 2.851  | 2.794 |

Figure 1. Supercells and two-probe devices of SiE/MX₂ (M = Mo, W; X = S, Se) for electronic and transport property computations.
MX$_2$,\textsuperscript{70–74} moreover, the Si–Si bond lengths in SiE/MX$_2$ are 2.265 Å, consistent with previous reported values of 2.25–2.27 Å for pure SiE.\textsuperscript{75–77} The balance distances between SiE and MX$_2$ ($R_{\text{SiE/MX}_2}$) are in the range of 2.630–2.794 Å (cf. Table 1), in line with the experimental data for SiE on the bulk MoS$_2$ surface ($R_{\text{SiE/MoS}_2} = 3$ Å)\textsuperscript{56} and other theoretical report ($R_{\text{SiE/MoS}_2} = 2.93$ Å).\textsuperscript{78} Such separations are longer than the typical covalent Si–S and Si–Se bond lengths of 2.019–2.345 Å,\textsuperscript{79,80} indicating a vdW interaction between SiE and MX$_2$.

In the following sections, the results of electronic structures of SiE/MX$_2$ (M = Mo, W; X = S, Se) are displayed, followed by discussing the transport properties, and finally the photoelectric properties under linear light illumination are analyzed.
2.1. Electronic Structures. Figure 2 shows the electron difference densities for SiE/MX₂. Clearly, SiE sheet transfers electrons to the MX₂ layer, indicating coupling between SiE and MX₂, which may result in the changing of the SiE band structure by placing on the MX₂ substrates. Figures 3 and 4 show the band structures and the average projected density of states (PDOS) of per element for SiE/MX₂ (M = Mo, W; X = S, Se) as well as the corresponding Kohn–Sham orbitals near the Fermi level (E_f). For comparison, the calculated results of free-standing SiE are also presented in Figure 3. For the SiE
sheet, linear band dispersion behavior around the Dirac point at the Γ point in the Brillouin zone can be seen from Figure 3. The valence band and conduction band primarily derived from the Si 3p orbital cross at E₀ leading to massless Dirac Fermion behavior of electrons and holds. It opens merely a trivial band gap (E₀) about 1.8 meV.

From Figures 3 and 4, it is notable that the band gaps are increased to 0.261, 0.208, 0.212, and 0.183 eV for SiE/MoS₂, SiE/MoSe₂, SiE/WS₂, and SiE/WSe₂, respectively, meaning that all the four MoX₂ (X = S, Se) substrates enable to stabilize the SiE nanosheet. Evidently, the band gap of SiE/MX₂ decreases with the group number of M, namely, SiE/MoS₂ > SiE/WS₂ and SiE/MoSe₂ > SiE/WSe₂. What’s more, a decrease trend is also found as the group number of X, that is, SiE/WS₂ > SiE/WSe₂ and SiE/MoS₂ > SiE/MoSe₂. Therefore, the stability of SiE could be much more increased by placing on MoX₂ surfaces compared to WS₂ and MoSe₂, respectively. This anisotropic feature was also observed for SiE/graphene by Zhou et al. using first-principles. Interestingly, SiE exhibits a distinctive feature of negative differential resistance (NDR) near ±0.8 V in the x direction. Generally, the electric-field induced change in resistivity causes so-called NDR effects, where the voltage appearing on both ends of the scatter region decreases with the increasing current. Namely, the slope of the I−V curve is negative. To gain more insight into this striking NDR feature, we compute the transmission spectra T(E) and the density of states (DOS) of SiE at the bias of 0.6, 0.8, and 1.0 V, respectively.

![Figure 6](image)

Figure 6. (a) Transmission spectra T(E) and (b) the density of states (DOS) of SiE at the bias of 0.6, 0.8, and 1.0 V, respectively.

hybridization between the M d state and the Si 3p state at the band edges, which is responsible for increasing the band gaps to 0.208 and 0.183 eV for SiE/MoSe₂ and SiE/WSe₂, respectively. Different from X = S, both valence and conduction bands in SiE/MSe₂ are mainly originated from the Si 3p orbitals. Therefore, the SiE/MSe₂ gives a type-I heterostructure. Moreover, the stability of SiE is improved after being fabricated to the MX₂ (M = Mo, W; X = S, Se) surfaces by increasing the band gaps, rendering the SiE/MX₂ (M = Mo, W; X = S, Se) heterostructures to be semiconductors. Considering the component of band edges, it is found that the electrons in SiE/MX₂ (M = Mo, W) mainly undertake an indirect hopping transport mechanism from SiE to MS₂ (M = Mo, W), while those in SiE/MSe₂ (M = Mo, W) mainly carry out a direct transport mechanism within the SiE layer.

2.2. Transport Properties. To move forward to study the quantitative transport properties of the SiE/MX₂ (M = Mo, W; X = S, Se) nanostructures, two-probe devices were established by sandwiching a supercell of considered nanostructures between the two Au electrodes, as shown in Figure 1. It is well-known that the transport properties in a certain direction is closely related to its topological structure. Owing to the anisotropic structures in different directions of SiE/MX₂ (M = Mo, W; X = S, Se), in this work, transport properties along the x and z directions are both considered. The calculated current−voltage (I−V) curves for the two-probe systems of SiE/MX₂ (M = Mo, W; X = S, Se) are given in Figure 5 together with those of pristine SiE for comparison.

As expected from the different topological structures, the conductivities of SiE and SiE/MX₂ show an anisotropic character in the x and z directions. Although the pure SiE shows a negligible band gap, it behaves as an insulated material in the z direction as can be seen from the nearly zero current, in contrast, it shows a semiconductivity character along the x direction with the current value smaller than 70 μA in the considered bias region. This anisotropic feature was also observed for SiE/graphene by Zhou et al. using first-principles. Interestingly, SiE exhibits a distinctive feature of negative differential resistance (NDR) near ±0.8 V in the x direction. Generally, the electric-field induced change in resistivity causes so-called NDR effects, where the voltage appearing on both ends of the scatter region decreases with the increasing current. Namely, the slope of the I−V curve is negative. To gain more insight into this striking NDR feature, we compute the transmission spectra T(E) and the density of states (DOS) of SiE at the bias of 0.6, 0.8, and 1.0 V, respectively (Figure 6). It can be seen that the carriers transport easily through the scatter region at the low bias of 0.6 V, owing to the large T(E) and DOS at the E₀. When the bias rises to 0.8 V, the T(E) and DOS peaks are lowered altogether at the E₀ leading to a drop in the current. It is noteworthy that the channel can also be opened if the bias increases to 1.0 V. As such, the current rises rapidly at higher biases. The striking NDR behavior of the SiE complex may find some applications in molecular electronics, which shows behavior similar to previous studies.

Attaching SiE to the MX₂ (M = Mo, W; X = S, Se) surfaces gives rise to significant changes in the transport properties. On one hand, the conductivities of the SiE/MX₂ (M = Mo, W; X = S, Se) heterostructures are increased either in the x direction or in the z direction comparing with SiE. It is worth noting that for both directions, the conductivities are ranked in the increasing order of the group number X: SiE < SiE/MoS₂ <
SiE/MoSe₂ and SiE < SiE/WS₂ < SiE/WSe₂. This is in agreement with the band gap predication mentioned above (Figures 3 and 4). In SiE/MoSe₂ and SiE/WSe₂, the electron transport is mainly through a direct transport mechanism by tunneling within the SiE framework. However, in SiE/MoS₂ and SiE/WS₂, the electron transport is, by a large extent, via an indirect path by hopping from the SiE component to the MS₂ (M = Mo, W) substrates. This is maybe the major reason for the lower conductivity of SiE/MS₂ (M = Mo, W) comparing with SiE/MSe₂ (M = Mo, W). On the other hand, the MX₂ (M = Mo, W; X = S, Se) substrates also influence the NDR behavior of SiE. When MoSe₂ or MoS₂ is placed on SiE, the NDR feature in the pure SiE vanishes and the currents of SiE/MX₂ (X = S, Se) substrates take the Ohm’s law regardless of the transmission direction. This evidently attributes to the major contribution of the M d bands to the conduction band. Similar to SiE, the x direction of SiE/MX₂ (X = S, Se) shows a higher conductivity than the z direction. At 1.0 V bias voltage, the currents of SiE/MoS₂ and SiE/MoSe₂ in the x direction are up to 99.5 and 102.7 μA, respectively, while those in the z direction reach only 40.9 and 54.7 μA, respectively. Notably, a significant current oscillation phenomenon can be observed after attaching SiE to WX₂ (X = S, Se), especially in the z direction (Figure 5). Moreover, the amplitude of the oscillation increases with the imposed voltage. Previous literature studies have addressed that NDR is one of the key factors for obtaining current oscillation. As we know, transport channels in SiE/WX₂ (X = S, Se) are still dominated by the SiE sheet. The WX₂ (X = S, Se) substrates enhance the NDR effect of SiE, and as a result, multiple NDR peaks appear continuously leading to the current oscillation. Such character is an important issue for the design of oscillation devices, e.g., thyristors.

2.3. Photoelectric Properties. Figure 1 schematically shows the structures of our devices of SiE/MX₂ (M = Mo, W; X = S, Se) for calculating photoelectric properties along the x and z directions. To this end, the scattering region was irradiated by linearly polarized light which propagates along the y direction. Light polarized in the x−z plane has polarization forming an angle θ with respect to the y direction. The photocurrents in the x and z directions were determined at different θ for photoenergies ranging from 0.1 to 1.0 eV with an interval of 0.2 eV.

The photocurrents of SiE/MX₂ (M = Mo, W; X = S, Se) under linearly polarized light illumination are given in Figures 7−10. As known for the linearly polarized light, the photocurrent is determined by three terms which are \( \sin^2 \theta \), \( \cos^2 \theta \), and \( \sin 2 \theta \) components, respectively. Therefore, the photoresponse curves in Figures 7−10 take the sine or cosine shapes with θ, which are decided by complicated factors such as the geometric symmetry and the full band structures of the material. Note that different MX₂ (M = Mo, W; X = S, Se) substrates induce different photocurrent responses. The sign of the photocurrent varies with θ and photon energies, as
indicated in Figures 7–10. This is due to the fact that the sign of the photocurrent is determined by the summation of all activated electrons with different velocity distributions. For SiE/MoS2, the x and z directions show similar photoresponses. The largest photocurrent is found to be 1.5 a0^2/photon within the considered situation (Figure 7). As for SiE/MoSe2, an anisotropy is observed in the photoresponse between the x and z directions. The amplitude of the photoresponse curves in the z direction is greater than that in the x direction (Figure 8). The maximum photocurrent in SiE/MoSe2 is up to 3.0 and 5.5 a0^2/photon for the x and z directions, respectively, 2 and 3 times larger than that in SiE/MoS2. Similar to SiE/MoSe2, SiE/WS2 shows a similar magnitude of photocurrent in the x and z directions (Figure 9). The maximum value of photocurrent in SiE/WS2 is about 2.0 a0^2/photon at the photon energy of 1.0 eV, larger than that of SiE/MoS2 (1.5 a0^2/photon). The photoresponse in SiE/WS2 is not obvious until the applied photon energy reaches a threshold value of 0.7 eV, beyond which the photoresponse is very sensitive to the photon energy. Clearly, at 0.7–1.0 eV photon energies, the amplitudes of the photoresponse are much higher in the z direction compared to the x direction. As for SiE/WSe2, two very high response peaks with values of about 7.0 and 9.0 a0^2/photon are found for the z direction, located at the photon energies of 0.2 and 0.5 eV, respectively (Figure 10). These values are also much higher than other reported 2D materials such as S-doped monolayer black phosphorus (1.8 a0^2/photon) and N- or B-doped graphene (2.2 a0^2/photon). Overall, the anisotropy of the photoresponse in the x and z directions is not obvious in the case of X = S, while it is evident when X = Se. The z direction gives a stronger photoresponse than the x direction in SiE/MSe2. The response properties are enhanced when SiE/MS2 changed to SiE/MSe2 (M = Mo, W). The SiE/WSe2 exhibits the strongest photoresponse when compared with other three heterostructures, SiE/MoS2, SiE/MoSe2, and SiE/WS2.

Different photoresponse mechanisms are found between SiE/MS2 and SiE/MSe2 (M = Mo, W) by analyzing the band structures and PDOS as shown in Figures 3 and 4. It can be seen that the valence and conduction bands of the SiE/MSe2 (M = Mo, W) nanocomposites are both dominated by SiE. Thus, these heterostructures show type-I band alignment. The photoinduced electron transfer mainly occurs within the SiE planes. In contrast, SiE/MS2 (M = Mo, W) shows type-II band alignment, where the valence band comes from SiE and the conduction band from MS2 (M = Mo, W), clearly indicating the possibility of a charge separation between the SiE and MS2 (M = Mo, W) layers. So, the photoinduced electron transfer could be expected from SiE donors to noncovalently bound MS2 (M = Mo, W) acceptors. Therefore, SiE/MSe2 (M = Mo, W) shows a stronger photoresponse than SiE/MS2 (M = Mo, W).

According to convention, for solar energy conversion, the type-II band alignment between the complexes is a required condition. In this regard, SiE/MS2 (M = Mo, W) heterostructures are good candidates for designing solar...
devices. In addition, the Kohn−Sham orbitals of the conduction and the valence band in Figures 3 and 4 clearly indicate that the valence band is localized on SiE and the valence band is localized on MS₂ (M = Mo, W). According to the semiclassical model of Marcus electron-transfer theory, the electron−hole recombination rate largely depends on the electronic coupling between the initial and final states, which in turn depends on the overlap of the valence band and conduction band wave functions of the composite system, the value of which depends on the overlap densities of the valence band and the conduction band. For SiE/MS₂ (M = Mo, W), the electron and hole wave functions are spatially well separated as shown in Figures 3 and 4, indicating that electron−hole overlap can be ignored. Thus, a conclusion can be at least drawn, the rate of electron−hole recombination between the SiE/MS₂ (M = Mo, W) heterostructures is quite low, and therefore suitable for designing solar cell devices.

3. CONCLUSIONS

Transport properties and photoelectric effects of four two-dimensional (2D) silicene/MX₂ (M = Mo, W; X = S, Se) heterostructures have been investigated by employing DFT and NEGF methods. From the results, it can be concluded that attaching SiE onto different MX₂ (M = Mo, W; X = S, Se) substrates is energetically favorable. Importantly, the substrates could stabilize the SiE by increasing the band gap. In particular, conductivities of SiE/MX₂ (M = Mo, W; X = S, Se) are enhanced compared with free-standing SiE and MX₂ (M = Mo, W; X = S, Se). Moreover, the conductivities are increased with the group number of X, i.e., in the order of SiE < SiE/MS₂ < SiE/MSe₂. An evident current oscillation phenomenon is observed in the SiE/WX₂ (X = S, Se) heterostructures. Otherwise, having investigated the optical properties of SiE/MX₂ (M = Mo, W; X = S, Se), we found that SiE/MSe₂ (M = Mo, W) shows a stronger photoresponse than SiE/MS₂ (M = Mo, W). The maximum photoresponse with a value of 9.0 a₀²/ photon was found for SiE/WSe₂. More importantly, SiE/MS₂ (M = Mo, W) heterostructures are good candidates for the use in designing solar cells owing to the well spatial separation of the charge carriers. In addition, an anisotropy is observed in both transport properties and photoresponse between the x and z directions of the heterostructures. Their transport properties and photoresponse correlate well with the electronic structures. This work provides some clues for further exploring 2D SiE/MX₂ (M = Mo, W; X = S, Se) heterostructures involving tailored photoelectric properties.

4. MODELS AND COMPUTATIONAL METHODS

The SiE was selected as the prototype host layers by placing on four monolayer substrates of MX₂ (M = Mo, W; X = S, Se). The infinite 2D heterostructures of SiE/MX₂ (M = Mo, W; X = S, Se) were modeled under the periodic conditions in the x and z axial directions to obtain the electronic structures. For a relative comparison, supercells with the same atom numbers are required, so the supercells of SiE/MX₂ were all set by planes containing 96 Si atoms, 64 M (Mo, W) atoms, and 128...
X (S, Se) atoms (Figure 1). The lattice parameters are 22.800 Å × 26.327 Å, 22.780 Å × 26.304 Å, 21.846 Å × 25.227 Å, and 22.794 Å × 26.320 Å for SiE/MoS2, SiE/MoSe2, SiE/WS2, and SiE/WSe2 respectively. The heterostructures were separated by a vacuum of 16 Å in the y direction to overlook the SiE/MX2-to-SiE/MX2 interactions. All the periodic systems were fully optimized until the maximum absolute force was less than 0.02 eV/Å.

The two-probe devices were constructed to compute the transport properties. In these devices, the optimized supercells of SiE/MX2 (M = Mo, W; X = S, Se) were selected as the central scatter region sandwiched between the two Au (111)-(9 × 5) electrodes (Figure 1). Generally, interactions between the two electrodes can be eliminated if their separation is over a distance of 10 times the radius of the electrode atom. The lengths of the supercell along the transport direction are 22.8 Å in the z direction and 26.3 Å in the x direction, much larger than 10 times of the maximum interaction radius of Au (16.6 Å). Therefore, the central scatter regions in the SiE/MX2 two-probe devices are long enough to ignore the influence of electrode-to-electrode interactions. Transport properties along the two topological structures of the nanosheet were considered: one along the x direction, and another along the z direction (as shown in Figure 1). The transport current was computed by changing the applied bias voltage in the step of 0.2 V in the range of −1.0 to 1.0 V.

All the computations for the electronic and transport properties were performed using the Atomistix ToolKit (ATK) based on the combination of DFT and NEGF methods.97–100 A generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) formalism was applied to depict the exchange correlations between electrons. A double-ζ basis with polarization (DZP) was adopted for all atoms. K-point in the string Brillouin zone was set to be 15 × 1 × 15, and 150 Ry cutoff energy was employed to describe the periodic wave function.

To gain an insight into the photoelectric properties of SiE/MX2 (M = Mo, W; X = S, Se), we irradiated the scatter region SiE/MX2 of the abovementioned two-probe systems in the y direction with linearly polarized light (Figure 1). The polarized angle θ was assigned to that between the y direction and the irradiation direction. The photocurrents were calculated under the photoenergy ranging from 0.1 to 1.0 eV. We also calculated the photocurrent varying with θ from 0 to 180° in a photoenergy interval of 0.2 eV.

The photocurrents of SiE/MX2 (M = Mo, W; X = S, Se) were computed using the Nanodcal package which carried out DFT within the Keldysh nonequilibrium Green’s functions (KNEGF).101–103 Standard norm-conserving nonlocal pseudopotentials were adopted to define the atomic cores, and a s, p, d single-ζ plus polarization (SZP) linear combination of atomic orbital basis set was used to expand physical quantities. The exchange–correlation potential was treated at the generalized gradient approximation (GGA) level with Perdew–Burke–Ernzerhof (PBE).
**AUTHOR INFORMATION**

*E-mail: guiling-002@163.com. Tel: +86-451-86392705. Fax: +86-451-86392708 (G.Z.).
*E-mail: 937972827@qq.com (Y.H.).
*E-mail: tcllwzqi@hit.edu.cn (W.L.).

**ORCID**

Yuxiu Wang: 0000-0001-5120-1927

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (Grant No. 51473042, 11574062), the Natural Science Foundation of Heilongjiang Province of China (Grant No. B2018007), Harbin foundation for leaders of disciplines (Grant No. 2017RAXX(002)), and the Fundamental Research Funds for the Central Universities and Program for Innovation Research of Science in Harbin Institute of Technology (PIRS OF HIT 201620).

**REFERENCES**

1. Gao, N.; Liu, H.; Zhou, S.; Bai, Y.; Zhao, J. Interaction between Post-Graphene Group-IV Honeycomb Monolayers and Metal Substrates: Implication for Synthesis and Structure Control. J. Phys. Chem. C 2017, 121, S123–S129.
2. Zhang, Y.; Rubio, A.; Le Lay, G. Emergent elemental two-dimensional materials beyond graphene. J. Phys. D: Appl. Phys. 2017, 50, No. 053004.
3. Li, W.; Walther, C. F.; Xu, A.; Heine, T. Density functional theory and beyond for band-gap screening: Performance for transition-metal oxides and dichalcogenides. J. Chem. Theory Comput. 2013, 9, 2950–2958.
4. Cheng, A. Q.; He, Z.; Zhao, J.; Zeng, H.; Chen, R. S. Monolayered Silicon and Germanium Monopnictide Semiconductors: Excellent Stability, High Absorbance, and Strain Engineering of Electronic Properties. ACS Appl. Mater. Interfaces 2018, 10, 5133–5139.
5. Leven, I.; Maaravi, T.; Azuri, I.; Kronik, L.; Hod, O. Interlayer potential for graphene/h-BN heterostructures. J. Chem. Theory Comput. 2016, 12, 2806–2905.
6. Durr, R. A.; Haberer, D.; Lee, Y. L.; Blackwell, R.; Kalayjian, A. M.; Marangoni, T.; Ihm, J.; Louie, S. G.; Fischer, F. R. Orbitally Matched Edge-Doping in Graphene Nanoribbons. J. Am. Chem. Soc. 2018, 140, 807–813.
7. He, M.; Quan, C.; He, C.; Huang, Y.; Zhu, L.; Yao, Z.; Zhang, S.; Bai, J.; Xu, X. Enhanced Nonlinear Saturable Absorption of MoS2/Graphene Nanocomposite Films. J. Phys. Chem. C 2017, 121, 27147–27153.
8. Cheng, H.; Huang, Y.; Shi, G.; Jiang, L.; Qu, L. Graphene-based functional architectures: sheets regulation and macrostructure construction toward actuators and power generators. Acc. Chem. Res. 2017, 50, 1663–1671.
9. Huang, L.; Zhang, Y. F.; Zhang, Y. Y.; Xu, W.; Que, Y.; Li, E.; Pan, J.; Wang, Y.; Liu, Y.; Du, S.; Pantelides, S. T.; Gao, H. Sequence of Silicon Monolayer Structures Grown on a Ru Surface: from a Herringbone Structure to Silicene. Nano Lett. 2017, 17, 1161–1166.
10. Luo, W.; Ma, Y.; Gong, X.; Xiang, H. Prediction of silicon-based layered structures for optoelectronic applications. J. Am. Chem. Soc. 2014, 136, 15992–15997.
11. Zhao, J.; Liu, H.; Yu, Z.; Qiu, R.; Zhou, S.; Wang, Y.; Liu, C.; Zhong, H.; Han, N.; Lu, J.; Yao, Y.; Wu, K. Rise of silicene: A competitive 2D material. Prog. Mater. Sci. 2016, 83, 24–151.
12. Vogt, P.; De Padova, P.; Quaresima, C.; Avila, J.; Frantzeskakis, E.; Asensio, M. C.; Resta, A.; Eale, B.; Le Lay, G. Silicene: compelling experimental evidence for graphene like two-dimensional silicon. Phys. Rev. Lett. 2012, 108, No. 155501.
13. Drummond, N. D.; Zolyomi, V.; Fal`Ko, V. I. Electrically tunable band gap in silicene. Phys. Rev. B 2012, 85, No. 075423.
14. Wang, Y. P.; Ji, W. X.; Zhang, C. W.; Li, S. S.; Li, F.; Li, P.; Ren, M. J.; Chen, X. L.; Yuan, P.; Wang, P. J. Enhanced band gap opening in germanene by organic molecule adsorption. Mater. Chem. Phys. 2016, 173, 379–384.
15. Gao, J.; Zhao, J. Initial geometries, interaction mechanism and high stability of silicene on Ag(111) surface. Sci. Rep. 2012, 2, No. 8561.
16. Ding, Y.; Ni, J. Electronic structures of silicon nanoribbons. Appl. Phys. Lett. 2009, 95, No. 083115.
17. Houssa, M.; Pourtois, G.; Afanas’ev, V. V.; Stensmans, A. Can silicene behave like graphene? A first-principles study. Phys. Rev. Lett. 2010, 97, No. 112406.
18. Peng, B.; Zhang, H.; Shao, H.; Xu, Y.; Zhang, R.; Lu, H.; Zhang, D. W.; Zhu, H. First-Principles Prediction of Ultralow Lattice Thermal Conductivity of Dumbbell Silicene: A Comparison with Low-Buckled Silicene. ACS Appl. Mater. Interfaces 2016, 8, 20977–20985.
19. Yang, Y.; Mosquera, M. A.; Skinner, K.; Becerra, A. E.; Shamamian, V.; Schätz, G. C.; Ratner, M. A.; Marks, T. J. Electronic Structure and Potential Reactivity of Silicene Molecular. J. Phys. Chem. A 2016, 120, 9476–9488.
20. Tahir, M.; Schwingenschlögl, U. Valley polarized quantum Hall effect and topological insulator phase transitions in silicene. Sci. Rep. 2013, 3, No. 1075.
21. Le Lay, G.; Salomon, E.; Angot, T. Silicene: silicon conquers the 2D world. Europhys. News 2016, 47, 17–21.
22. Zhang, L. Z.; Zhai, F.; Jin, K. H.; Cui, B.; Huang, B.; Wang, Z.; Lu, J. Q.; Liu, F. Quantum Spin Hall Effect and Tunable Spin Transport in As-Graphane. Nano Lett. 2017, 17, 4359–4364.
23. Jose, D.; Datta, A. Structures and chemical properties of silicene: unlike graphene. Acc. Chem. Res. 2014, 47, 593–602.
24. Li, X.; Zou, D.; Cui, B.; Fang, C.; Zhao, J.; Li, D.; Li, D. Edge hydrogenation-induced spin-filtering and negative differential resistance effects in zigzag silicene nanoribbons with line defects. RSC Adv. 2017, 7, 25244–25252.
25. Scalse, E.; Iordanidou, K.; Afanas’ev, V. V.; Stensmans, A.; Houssa, M. Silicene on non-metallic substrates: Recent theoretical and experimental advances. Nano Res. 2018, 11, 1169–1182.
26. Li, S.; Wu, Y.; Liu, W.; Zhao, Y. Control of band structure of van der Waals heterostructures: Silicene on ultrathin silicon nanosheets. Chem. Phys. Lett. 2014, 609, 161–166.
27. Yang, G.; Xu, Q.; Fan, X.; Zheng, W. Quantum Capacitance of Silicene-Based Electrodes from First Principles Calculations. J. Phys. Chem. C 2018, 122, 1903–1912.
28. Zhu, J.; Schwingenschlögl, U. Band gap opening in silicene on MgBr2(0001) induced by Li and Na. ACS Appl. Mater. Interfaces 2014, 6, 19242–19246.
29. Zhu, J.; Schwingenschlögl, U. Structural and Electronic Properties of Silicene on MgBr2(X = Cl, Br, and I). ACS Appl. Mater. Interfaces 2014, 6, 11675–11681.
30. Lei, M.; Ye-Liang, W.; Li-Zhi, Z.; Shi-Xuan, D.; Hong-Jun, G. Fabrication and properties of silicon and silicene–graphene layered structures on Ir(111). Chin. Phys. B 2015, 24, No. 086803.
31. Wei, W.; Dai, Y.; Huang, B.; Wangbo, M. H.; Jacob, T. Loss of linear band dispersion and trigonal structure in silicene on Ir(111). J. Phys. Chem. Lett. 2015, 6, 1065–1070.
32. Morishita, T.; Spencer, M. J.; Kawamoto, S.; Snook, I. K. A New Surface and Structure for Silicene: Polygonal Silicene Formation on the Al(111) Surface. J. Phys. Chem. C 2013, 117, 22142–22148.
33. Du, Y.; Zhuang, J.; Liu, H.; Xu, X.; Eliers, S.; Wu, K.; Cheng, P.; Zhao, J.; Pi, X.; See, K. W.; Peleckis, G.; Wang, X.; Dou, S. X. Tuning the Band Gap in Silicene by Oxidation. ACS Nano 2014, 8, 10019–10025.
(54) Friák, M.; Holec, D.; Šob, M. An ab initio study of mechanical and dynamical stability of MoSi₂. J. Alloys Compd. 2018, 746, 720–728.

(55) Aizawa, T.; Suehara, S.; Otani, S. Silicene on Zirconium Carbide(111). J. Phys. Chem. C 2014, 118, 23049–23057.

(56) Chiappe, D.; Scalise, E.; Cinquanta, E.; Grazianetti, C.; van den Broek, B.; Fanciulli, M.; Houssa, M.; Molle, A. Two-Dimensional Si Nanosheets with Local Hexagonal Structure on a MoS₂ Surface. Adv. Mater. 2014, 26, 2096–2101.

(57) Li, L.; Zhao, M. Structures, Energetics, and Electronic Properties of Multifarious Stacking Patterns for High-Buckled and Low-Buckled Silicene on the MoS₂ Substrate. J. Phys. Chem. C 2014, 118, 19129–19138.

(58) Gao, N.; Li, J. C.; Jiang, Q. Bandgap opening in silicene: Effect of substrates. Chem. Phys. Lett. 2014, 592, 222–226.

(59) Zhang, H.; Wang, H.; Xiong, S.; Han, H.; Volz, S.; Ni, Y. Multiscale Modeling of Heat Dissipation in 2D Transistors Based on Phosphorene and Silicene. J. Phys. Chem. C 2018, 122, 2641–2647.

(60) Jin, C.; Dai, Y.; Wei, W.; Sun, Q.; Li, X.; Huang, B. Modulation of silicene properties by AsSb with van der Waals interaction. RSC Adv. 2016, 6, 5827–5835.

(61) Gao, N.; Lu, G. Y.; Wen, Z.; Jiang, Q. Electronic structure of silicene: effects of the organic molecular adsorption and substrate. J. Mater. Chem. C 2017, 5, 627–633.

(62) Lin, C. L.; Arafune, R.; Kawahara, K.; Kanno, M.; Tsukahara, N.; Minamitani, E.; Kim, Y.; Kawai, M.; Takagi, N. Substrate-induced symmetry breaking in silicene. Phys. Rev. Lett. 2013, 110, 076801.

(63) Xu, L.; Huang, W. Q.; Hu, W.; Yang, K.; Zhou, B. X.; Pan, A.; Huang, G. F. Two-dimensional MoS₂-graphene-based multilayer van der Waals heterostructures: enhanced charge transfer and optical absorption, and electric-field tunable Dirac point and band gap. Chem. Mater. 2017, 29, 5504–5512.

(64) Aggoune, W.; Cocchi, C.; Nabok, D.; Rezouali, K.; Akli Belkhir, M.; Drazil, C. Enhanced Light-Matter Interaction in Graphene/h-BN Bilayer van der Waals Heterostructures. J. Phys. Chem. Lett. 2017, 8, 1464–1471.

(65) Miller, O. D.; Ilic, O.; Christensen, T.; Reid, M. H.; Atwater, H. A.; Joannopoulos, J. D.; Soljačić, M.; Johnson, S. G. Limits to the Optical Response of Graphene and Two-Dimensional Materials. Nano Lett. 2017, 17, 5408–5415.

(66) Zhou, X.; Hu, X.; Yu, J.; Liu, S.; Shu, Z.; Zhang, Q.; Li, H.; Ma, Y.; Xu, H.; Zhai, T. 2D Layered Material-Based van der Waals Heterostructures for Optoelectronics. Adv. Funct. Mater. 2018, No. 1706587.

(67) Hong, J.; Wang, C.; Liu, H.; Ren, X.; Chen, J.; Wang, G.; Jia, J.; Xie, M.; Jin, C.; Ji, W.; Yuan, J.; Zhang, Z. Inversion Domain Boundary Induced Stacking and Bandstructure Diversity in Bilayer MoSe₂. Nano Lett. 2017, 17, 6653–6660.

(68) Ji, Z.; Hong, H.; Zhang, J.; Zhang, Q.; Huang, W.; Cao, T.; Qiao, R.; Liu, C.; Liang, J.; Jin, C.; Jiao, L.; Shi, K.; Meng, S.; Liu, K. Robust Stacking-Independent Ultrafast Charge Transfer in MoS₂/WSe₂ Bilayers. ACS Nano 2017, 11, 12020–12026.

(69) Nayak, P. K.; Horbatenko, Y.; Ahn, S.; Kim, G.; Lee, J. U.; Ma, K. Y.; Jang, A. R.; Lim, H.; Kim, D.; Ryu, S.; Cheong, H.; Park, N.; Shin, H. S. Probing Evolution of Twist-Angle-Dependent Interlayer Excitons in MoSe₂/WSe₂ van der Waals Heterostructures. ACS Nano 2017, 11, 4041–4050.

(70) Ding, Y.; Wang, Y.; Ni, J.; Shi, L.; Shi, S.; Tang, W. First-principles study of structural, vibrational and electronic properties of graphene-like MX₂ (M = Mo, Nb, W; T = S, Se, Te) monolayers. Phys. B 2011, 406, 2254–2260.

(71) Apte, A.; Kochhal, V.; Rajak, P.; Krishnamoorthi, A.; Manimunda, P.; Hachtel, J. A.; Idrobo, J. C.; Amarnath, S. A.; Vashistha, P.; Nakano, A.; Kalia, R. K.; Tiwary, C. S.; Ajayan, P. M. Structural Phase Transformation in Strained Monolayer MoWSe₂ Alloy. ACS Nano 2018, 12, 3468–3476.

(72) Wang, Y.; Tseng, L. T.; Murmu, P. P.; Bao, N.; Kennedy, J.; Ionescu, M.; Ding, J.; Suzuki, K.; Li, S.; Yi, J. Defects engineering
induced room temperature ferromagnetism in transition metal doped MoSe₂, Mater. Des. 2017, 121, 77–84.

(73) Li, N.; Liu, Z.; Hu, S.; Wang, H. Structural and electronic properties of effective p-type doping WS₂ monolayers: A computational study. Solid State Commun. 2018, 269, 58–63.

(74) Cui, P.; Choi, J. H.; Chen, W.; Zeng, J.; Shih, C. K.; Li, Z.; Zhang, Z. Contrasting structural reconstructions, electronic properties, and magnetic orderings along different edges of zigzag transition metal dichalcogenide nanoribbons. Nano Lett. 2017, 17, 1097–1101.

(75) Cahangirov, S.; Topsakal, M.; Akırtık, E.; Şahin, H.; Ciraci, S. Two- and One-Dimensional Honeycomb Structures of Silicon and Germanium. Phys. Rev. Lett. 2009, 102, No. 236804.

(76) Marjaoui, A.; Stephan, R.; Hanf, M. C.; Diani, M.; Sonnet, P. Using strain to control molecule chemisorption on silicene. J. Chem. Phys. 2017, 147, No. 044705.

(77) Liu, H.; Gao, J.; Zhao, J. Silicene on Substrates: A Way To Preserve or Tune Its Electronic Properties. J. Phys. Chem. C 2013, 117, 10353–10359.

(78) Gao, N.; Li, J. C.; Jiang, Q. Tunable band gaps in silicene-MoS₂ heterobilayers. Phys. Chem. Chem. Phys. 2014, 16, 11673–11678.

(79) Junöld, K.; Baus, J. A.; Burschka, C.; Auerhammer, D.; Tacke, R. Stabile Five-Coordinate Silicon (IV) Complexes with Si₉N₂X Skeletons (X = S, Se, Te) and Si = X Double Bonds. Chem. - Eur. J. 2012, 18, 16288–16291.

(80) Kauffmann, S.; Schäfer, S.; Gamer, M. T.; Roessky, P. W. Reactivity studies of silylene [PhC(NtBu)₂(C₅Me₅)]Si reactions with [M(COD)Cl]₂ (M = Rh (I), Ir (I)), S, Se, Te, and BH₃. J. Am. Chem. Soc. 2007, 129, 11708–11719.

(81) Lee, Y.; Hwang, Y.; Chung, Y. C. Achieving type I, II, and III heterojunctions using functionalized MXenes. ACS Appl. Mater. Interfaces 2015, 7, 7163–7169.

(82) Zhou, R.; Lew Yan Voon, L. C.; Zhuang, Y. Properties of two-dimensional silicon grown on graphene substrate. J. Phys. Appl. Phys. 2013, 114, No. 093711.

(83) Kumai, R.; Okimoto, Y.; Tokura, Y. Current-induced insulator-metal transition and pattern formation in an organic charge-transfer complex. Science 1999, 284, 1645–1647.

(84) Iwasa, Y.; Koda, T.; Koshihara, S.; Tokura, Y.; Iwasawa, N.; Saito, G. Intrinsic negative-resistance effect in mixed-stack charge-transfer crystals. Phys. Rev. B 1989, 39, No. 10441(R).

(85) Okamoto, K.; Tanaka, T.; Fujita, W.; Awaga, K.; Inabe, T. Charge ordering and nonlinear electrical transport in quasi-one-dimensional organic chains with strong electrostatic interchain interactions. Phys. Rev. B 2007, 76, No. 075328.

(86) Kishida, H.; Ito, T.; Nakamura, A.; Takashi, S.; Yamashita, M. Current oscillation originating from negative differential resistance in one-dimensional halogen-bridged nickel compounds. J. Appl. Phys. 2009, 106, No. 016106.

(87) Iimori, T.; Ohta, N.; Naito, T. Molecular-based light-activated thyristor. Appl. Phys. Lett. 2007, 90, No. 262103.

(88) Zhang, G.; Zhou, R.; Gao, Y.; Zeng, X. C. Silicon-containing multidecker organometallic complexes and nanowires: a density functional theory study. J. Phys. Chem. Lett. 2012, 3, 151–156.

(89) Sawano, F.; Terasaki, I.; Mori, H.; Mori, T.; Watanabe, M.; Ikeda, N.; Nogami, Y.; Noda, Y. An organic thyristor. Nature 2005, 437, 522.

(90) Mori, T.; Bando, Y.; Kawanoto, T.; Terasaki, I.; Takimiya, K.; Otsubo, T. Giant nonlinear conductivity and spontaneous current oscillation in an incommensurate organic superconductor. Phys. Rev. Lett. 2008, 100, No. 037001.

(91) Hu, J.; Li, L. S.; Yang, W.; Manna, L.; Wang, L. W.; Alivisatos, A. P. Linearly polarized emission from colloidal semiconductor quantum rods. Science 2001, 292, 2060–2063.