1. Introduction

Solar-to-electricity conversion offers a promising clean energy source to power a more sustainable technology landscape in the future. Despite the widespread deployment of conventional silicon-based solar cell, the continual improvement of the solar-to-electricity conversion efficiency remains a formidable challenge. Conventional crystalline silicon pn junction solar cell is plagued by nonradiative recombination of photogenerated electron–hole pairs,[1] which severely limits its solar-to-electricity conversion efficiency. [2] Silicon solar cells also entail the use of thicker layers to achieve longer optical path for better light absorption, which fundamentally limits their deployment in ultracompact and low-mass solar cell design.[3] The search for novel nanomaterials and device architectures beyond the conventional silicon pn junction remain an open research challenge that urgently needs to be addressed.

2D materials van der Waals heterostructures (vdWHs) provide a revolutionary route toward high-performance solar energy conversion devices beyond the conventional silicon-based pn junction solar cells. Despite tremendous research progress accomplished in recent years, the searches of vdWHs with exceptional excitonic solar cell conversion efficiency and optical properties remain an open theoretical and experimental quest. Here, this study shows that the vdWH family composed of MoSi$_2$N$_4$ and WSi$_2$N$_4$ monolayers provides a compelling material platform for developing high-performance ultrathin excitonic solar cells and photonics devices. Using first-principle calculations, 51 types of MoSi$_2$N$_4$ and WSi$_2$N$_4$-based [(Mo,W)Si$_2$N$_4$] vdWHs composed of various metallic, semimetallic, semiconducting, insulating, and topological 2D materials are constructed and classified. Intriguingly, MoSi$_2$N$_4$/[InSe, WSe$_2$] are identified as Type II vdWHs with exceptional excitonic solar cell power conversion efficiency reaching well over 20%, which are competitive to state-of-the-art silicon solar cells. The (Mo,W)Si$_2$N$_4$ vdWH family exhibits strong optical absorption in both the visible and UV regimes. Exceedingly large peak UV absorptions over 40%, approaching the maximum absorption limit of a freestanding 2D material, can be achieved in (Mo,W)Si$_2$N$_4$/α$_2$-(Mo,W)Ge$_2$P$_4$ vdWHs. The findings unravel the enormous potential of (Mo,W)Si$_2$N$_4$ vdWHs in designing ultimately compact excitonic solar cell device technology.
Excitonic solar cell has recently emerged as a compelling candidate for high-efficiency solar-to-electricity conversion. In contrast to conventional semiconductor-based pn junction solar cell where light-to-electricity conversion occurs exclusively within the same bulk material, excitonic solar energy conversion is an interfacial effect that arises from the band discontinuity across a heterojunction. Unlike the pn junction solar cell in which a built-in potential is needed to separate the photogenerated electron–hole pairs in the bulk, electrons and holes are spontaneously dissociated onto the two sides of the interface in an excitonic solar cell. The interfacial band alignment thus provides an exothermic pathway for exciton dissociation even though they do not possess sufficient energy to dissociate in the bulk. The huge chemical potential gradient created across the interface significantly increases the open-circuit voltage beyond the built-in potential.

Recent advances of 2D materials and their van der Waals heterostructures (vdWHs) unravel an exciting route toward advanced excitonic solar cell technology. The vertical coupling of different 2D materials via weak van der Waals (vdW) forces results in “designer” heterostructures with physical properties not easily found in the nature, thus enabling myriads of high-performance nanoelectronics, optoelectronics, photonics, and neuromorphic devices to be realized.[4,5,12-23] The optical absorption, band alignment, and bandgap of vdWHs can be custom made with ease. Together with the long exciton lifetime and the capability of efficient charge harvesting at ultrafast timescales,[11-15] vdWH has become a compelling and potentially disruptive platform for the development of ultimately compact excitonic solar cell technology.[5,24,25] Designing high-performance excitonic solar cell is, however, a complex technological challenge both theoretically and experimentally. Computational, the design space of vdWHs is enormously large due to nearly unlimited material combinations and the continual discovery of new 2D materials. The maximum power conversion efficiency (PCE) of vdWH is predicted to lie within the range of 10%-20%, with only a minority of vdWHs[20,21,23] (e.g., GaAs/InAs, HfSe2/GeO2, and BAs/BP) capable of achieving large PCE over 20%. Experimentally the PCE of fabricated devices are only a small fraction of the theoretical limit[10] due to material defects and carrier recombination losses.[5] Furthermore, the experimentally realizable material combinations of vdWHs are constrained by the material synthesis and assembly processes.[26,27] The limited availability of high-PCE vdWHs and the formidable challenges of fabricating high-quality vdWHs highlight the urgency and importance of continual computationally searching for high-PCE vdWH to further expand the ground for the experimental realization of high-performance excitonic solar cell technology.

The discovery of MoSi2N4 and WSi2N4 opens an exciting avenue toward the development of novel 2D material device technology.[28] Monolayer MoSi2N4 and WSi2N4 are synthetic 2D semiconductors with exceptional electrical mobilities that outperform the widely studied MoS2 monolayer, holding great promises in nanoelectronics and sub-10-nm transistor applications.[29-31] Structurally, MoSi2N4 is a septuple-layered material composed of a transition metal nitride sub-monolayer (Mo-N) intercalated between two silicon-nitride (SiN) sub-monolayers. Such intercalated architecture gives rise to a large family of six-membered ring monolayers with septuple-atomic-layer structure, known as the MA2Z4 monolayer family.[32] Intriguingly, the band edge states of MoSi2N4 are localized around the inner Mo-N sublayer and are protected by the outer Si-N sublayer[33,34] from external influences. Such unusual built-in atomic-layer protection mechanism renders MoSi2N4 as exceptional robust against environmental coupling effects and enables the formation of highly energy-efficient Ohmic contact without severe degradation of its electronic properties.[31] Recent studies have unraveled myriads of exceptional behaviors in MoSi2N4 including strong exciton–phonon coupling at room temperature,[19] strain-tunable optical response,[46] tunable electronic properties via molecular doping,[47] field-induced metal–semiconductor transition,[48] large piezoelectric coefficient,[49] sizable thermoelectric figure of merit,[50] strained enhanced solar energy absorption,[51] and ultras high thermal conductivities.[52] Beyond MoSi2N4 and WSi2N4 monolayers, the family of MA2Z4 monolayers also exhibit unusually rich physical and chemical behaviors, including nontrivial topological phases,[32] valley-contrasting physics,[45-48] non-linear optical response,[49] hydrogen (oxygen) evolution catalytic performance,[50,51] and superior electrocatalytic activity for energy storage application.[52]

Driven by the success of vdWH material engineering, MoSi2N4-based vdWHs have also been intensively studied recently. For example, MoSi2N4 interfaced with InSe,[53] blue phosphorus,[54] C2N,[55] CrCl3,[56] C3N4,[57] MoS2,[58] graphene,[59] NbSe2,[60] GaN,[60] ZnO,[60] MoSe2,[61] C60,[62] MoGe2N4,[63] MoGeSiN4,[64] and MoSH[65] have been computationally predicted to exhibit efficient photocatalytic water splitting[53-55] strain-tunable valley splitting effect,[56] strongly optical absorption in the visible light regime with strain, and field-effect tunable band structures.[57-66] Nonetheless, a catalogue of (Mo,W)Si2N4-based vdWHs constructed with representative monolayers remains largely incomplete thus far.

In this work, we show that the vdWH family composed of septuple-layered MoSi2N4 and WSi2N4 monolayers[28]—the recently discovered archetypes of the emerging MA2Z4 monolayer family—offers a versatile material platform toward high-efficiency solar energy harvesting, optoelectronics, and photonics applications. Using first-principle density functional theory (DFT) simulations, we constructed 51 types of (Mo,W)Si2N4-based vdWHs and characterized their electronic and optical properties. The vdWHs are systematically classified according to their contact types and band alignments.[67] Remarkably, we found that MoSi2N4/(ZnO, WGe2N4) and...
MoSi$_2$N$_4$/InSe, WSe$_2$) are Type II vdWHs with PCE reaching well over 15% and 20%, respectively, which are comparable to many state-of-the-art solar cells composed of silicon and perovskite as well as vdWHs.\textsuperscript{[20,21]} Furthermore, majority of the 51 types of vdWHs exhibit substantial optical absorption in the visible and ultraviolet (UV) spectrum. Nearly all vdWHs exhibit peak optical absorption in the UV regime, thus suggesting their potential in UV photonics applications. Our work unravels the enormous potential of (Mo,W)Si$_2$N$_4$ based vdWHs in UV photonics, optoelectronics, and solar energy harvesting applications, and call for a comprehensive computational and experimental search for vdWHs with exceptional physical properties in the expansive MA$_2$Z$_4$ material family.

2. Computational Methods

QuantumATK\textsuperscript{[69]} is used to construct the heterostructures with the strain induced by lattice mismatch to be less than 5\%\textsuperscript{[70,71]} between monolayers using supercell structure and applying the appropriate rotation. We distribute the strain equally among both layers as implemented in QuantumATK in which an intermediate supercell is created for both monolayers, such that the strain acting on each monolayer is equal in magnitude with opposite sign after mapping onto the intermediate supercell. Based on this approach, the resultant strain induced by lattice mismatch for 49 of our constructed vdWHs are typically about or less than 3\% (see Table S1, Supporting Information). These values of strain are less than or comparable to those obtained in existing literatures for the (Mo,W)Si$_2$N$_4$ based vdWHs (see Table S2, Supporting Information, for a comparison of our vdWHs and several similar vdWHs reported elsewhere).\textsuperscript{[33,53,67,72,73]} A vacuum layer of thickness $\approx 25$ Å is inserted between adjacent bilayer unit cell to eliminate the interactions from periodic images. We used the Vienna Ab initio Simulation Package (VASP)\textsuperscript{[74]} for structural optimization, energy and charge calculation, and VASPKit\textsuperscript{[75]} for optical properties calculation. For structural optimization and self-consistent field calculations, a Gamma-centered Brillouin zone k-point sampling grid of $11 \times 11 \times 1$ with Monkhorst–Pack method is used. In the structural optimization step, the supercell volume is kept constant while the ion positions are allowed to change. The break condition for each ionic relaxation loop is set to $10^{-3}$ eV Å$^{-1}$ such that the forces acting on the unit cell after convergence is less than this value and the break condition for each electronic relaxation loop is set to $10^{-6}$ eV. To take into account the weak van der Waals interactions between the monolayers, we adopted the DFT-D3 method with the Becke–Johnson damping scheme. To assess the importance of van der Waals correction, we perform test simulations using two representative vdWHs of MoSi$_2$N$_4$/InSe and MoSi$_2$N$_4$/WSe$_2$, without the van der Waals correction. A comparison of the fully relaxed lattice structures with and without van der Waals corrections (see Figure S1, Supporting Information) shows that the interlayer distance, obtained without including van der Waals correction, becomes noticeably larger after structural relaxation, thus suggesting that van der Waals correction is indispensable in the calculation.

We standardized using generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) form for the exchange correlation functional in the calculations for all our heterostructures. Although the Heyd–Scuseria–Ernzerhof hybrid functional form (HSE06) provides more accurate prediction for most bandgap calculations, the reduced computational cost of the PBE is more appropriate for the large-scale study performed in this work which covers multiple vdWHs with large number of atoms. PBE has also been used in multiple previous literatures to study vdWHs,\textsuperscript{[33,59,60,67,76–79]} and the bandgap obtained via PBE for MoSi$_2$N$_4$ (1.73 and 1.78 eV)\textsuperscript{[33,59]} is closer to the experimental value of 1.94 eV\textsuperscript{[28]} as compared to 2.30 eV\textsuperscript{[28]} produced by HSE06. More importantly, the band alignment types—a key quantity that directly influence the classification of contact types and subclasses—predicted using PBE is in good agreement with that obtained using HSE06.\textsuperscript{[67]} We thus expect PBE calculations to capture the general trends and features of the vdWHs studied. The supercells of the vdWHs are shown in Figures S2–S6 (Supporting Information). The electronic band structures, plane-averaged electrostatic potential profiles, plane-averaged differential charge density profiles, dielectric constants, optical absorption spectra, and the general calculation data of all 51 types of vdWHs are compiled and systematically presented in Figures S7–S15, S16–S21, S22–S27, S28–S33, Tables S1–S5 (Supporting Information), respectively.

3. Results and Discussion

As summarized in Figure 1, 51 types of (Mo,W)Si$_2$N$_4$ based vdWHs are constructed in this work, which are composed of (Mo,W)Si$_2$N$_4$ monolayers in contact with seven classes of 2D materials (see Figure 1A): i) semiconducting transition metal dichalcogenides (TMDC), such as MoS$_2$ and WSe$_2$; ii) Janus semiconducting TMDC, such as MoSSe and WSeSe; iii) metallic TMDC, such as NbS$_2$ and iT-MoS$_2$; iv) honeycomb monolayers, such as the semimetallic graphene and insulating hBN; v) Group III–IV monolayer of InSe; vi) ultrathin topological Dirac semimetal of Na$_3$Bi monolayer; and vii) other members from the MA$_2$Z$_4$ family, such as Al$_2$MO$_6$P$_4$, MoGe$_3$N$_6$, as well as the vdWH formed by the mutual stack of MoSi$_2$N$_4$/WSi$_2$N$_4$. In Figure 1B, the 51 vdWHs are systematically categorized into six subtypes, namely: i) metal/semiconductor (MS) Ohmic contact (four species); ii) MS Schottky contact (six species); and semiconductor/semiconductor (SS) contact with iii) Type I (19 species); iv) Type II (15 species); v) Type III (two species); and vi) unconventional hybridized-type (five species) band alignments (see Figure 1C for schematic drawings of the band diagram of different contact types). The band alignment diagrams of the 25 types of 2D monolayers considered in this work are shown in Figure 2A which provides a qualitative understanding on the contact type and band alignment formation via Anderson rule (AR) which does not include any interface interaction effect.\textsuperscript{[80]} Due to the finite interaction between the two constituent monolayers,\textsuperscript{[81]} AR may no longer be valid in vdWHs with sizable interlayer coupling and interface dipole.\textsuperscript{[82,83]} As shown in Figure 2B, AR remains valid for most of the metallic TMDC, graphene, InSe, hBN, and MA$_2$Z$_4$ family due to their weak coupling nature. In contrast, the disagreement between AR and direct DFT calculations is rather
severe for semiconducting and Janus TMDC monolayers as well as the honeycomb semiconducting monolayers of GaN, BP, and ZnO. This disagreement highlights the importance of including interfacial interaction effects via direct DFT calculations for contact type and band alignment determination.

3.1. Metal/Semiconductor (MS) Contacts

We first consider (Mo,W)Si$_2$N$_4$-based vdWHs of MS contact type. In this case, either Ohmic or Schottky contacts can be formed at the interface. For an Ohmic contact, the absence of a...
Schottky barrier greatly facilitates charge injection across an MS contact and is much sought after for creating energy-efficient electrical contacts. MS vdWH contacts are particularly attractive due to the strong suppression of the Fermi level pinning effect, a detrimental effect that severely impedes the engineering of energy-efficient electrical contacts. Here, we identify four species of p-type Ohmic contacts formed by MoSi$_2$N$_4$ and WSi$_2$N$_4$ in contact with NbS$_2$ and NbSe$_2$ (see Figure 3A–D). The formation of these p-type Ohmic vdWHs can be readily understood from the band alignment diagram in Figure 2A, where the relatively larger work functions of NbS$_2$ (6.06 eV) and NbSe$_2$ (5.35 eV) align with the valence band maximum (VBM) energies of MoSi$_2$N$_4$ (5.30 eV) and WSi$_2$N$_4$ (5.14 eV) to yield p-type Ohmic contact by virtue of AR. We note that the MoSi$_2$N$_4$/NbS$_2$ contact is predicted to be a p-type Schottky contact with ultralow Schottky barrier height (SBH) where the strain arising from lattice mismatch upon forming the vdWH is entirely distributed on the NbS$_2$ monolayer only. In contrary, strain is distributed evenly between the two monolayers in our calculations, which yields a p-type Ohmic contact instead.

For a bilayer vdWH made up of monolayer A and monolayer B, the plane-averaged differential charge density ($\Delta \rho$) is calculated as, $\Delta \rho = \rho_{AB} - \rho_A - \rho_B$, where $\rho_{AB}$ is the charge density of the heterostructure AB, $\rho_A$ is the charge density of monolayer A, and $\rho_B$ is the charge density of monolayer B. The charge redistribution of MoSi$_2$N$_4$ and WSi$_2$N$_4$ contacted by NbS$_2$ and NbSe$_2$ is examined from the $\Delta \rho$ plots in the upper panel of Figure 3E–H. Significant electrons redistribution from the (Mo,W)Si$_2$N$_4$ monolayer toward the Nb(S$_2$,Se$_2$) monolayer occurs due to the higher VBM energies of the semiconducting monolayers when compared to the Fermi levels of the metallic monolayers. Such electron migration causes the p-doped characteristics of the (Mo,W)Si$_2$N$_4$ sub-monolayers upon contact formation. We further note that the interface charge redistribution occurs universally for all vdWHs as evident from the differential charge density plots in Figures S22–S27 (Supporting Information). The interface charge redistribution creates an interface dipole potential ($\Delta \Phi$) that manifests as an electrostatic potential energy difference between the two sides of the vdWHs. The $\Delta \Phi$ are marked directly in the plane-averaged electrostatic profile plots in Figures S16–S21 (Supporting Information) for all vdWHs studied in this work.

Although SBH is absent in Ohmic vdWH contact, a van der Waals gap is present between the two contacting monolayers that may impede charge ejection efficiency. The tunneling potential barrier ($\Phi_{TB}$) and the barrier width ($d_{TB}$) can be extracted from the plane-averaged electrostatic potential plots with reference to the Fermi level (see bottom panel of Figure 3E–H). For MoSi$_2$N$_4$/NbS$_2$, MoSi$_2$N$_4$/NbSe$_2$, WSi$_2$N$_4$/NbS$_2$, and
Figure 3. Electronic band structures, differential charge densities, and electrostatic potential profiles of (Mo,W)Si$_2$N$_4$ Ohmic vdWHs. A–D) Electronic band structures of MoSi$_2$N$_4$/NbS$_2$, MoSi$_2$N$_4$/NbSe$_2$, WSi$_2$N$_4$/NbS$_2$, and WSi$_2$N$_4$/NbSe$_2$, respectively. E–H) Plane-averaged differential charge density (upper and middle panels) and the electrostatic potential profile (bottom panel) of the Ohmic contact of (A)–(D), respectively. The yellow (cyan)-shaded region represents electron accumulation (depletion).
WSi2N4/NbSe2, the tunneling potential barriers are 5.14, 4.70, 5.04, and 4.60 eV, respectively, and the barrier widths are 1.88, 1.86, 1.85, and 1.84 Å, respectively. Accordingly, the charge injection efficiency across the van der Waals gap can then be characterized by the tunneling-specific resistivity (ρ) and the tunneling probability (T) using Simmons formula:

$$\rho = \frac{8\pi^2\hbar^2d_{12}}{3e^2\sqrt{2m}\Phi_{12}}T^{-1}$$  \hspace{1cm} (1)

$$T = \exp\left(-\frac{2d_{12}\sqrt{2m}\Phi_{12}}{h}\right)$$  \hspace{1cm} (2)

where $\hbar$, $e$, and $m_{12}$ are the reduced Planck’s constant, charge magnitude, and mass of the free electron, respectively. Here, T is an important figure of merit describing the charge injection efficiency as the ballistic tunneling current across the MS contact is directly proportional to T based on the Landauer model.[90] The calculated values of ρ and T are tabulated in Figure 4A, which shows that ρ lies in the order of 10−9 which are comparable to those of metal/MoS2N4 and metal/WSi2N4 contacts (i.e., from 0.1 × 10−9 to 3.85 × 10−9 Ω cm²).[91] and that in the semimetal contact of Bi/MoS2 contact (1.81 × 10−9 Ω cm²).[92] Finally, when (Mo,W)Si2N4 monolayers are interfaced with (Mo,W)Si2N4-based vdWHs, we examine the "S parameters" (S) which can be extracted from the slope of ΦSBH,p against the work function of the isolated metals (ΦM), i.e., $S = \partial\Phi_{SBH,p}/\partial W_M$ (see Figure 4B).[93] The p-type SBH can be generally expressed as

$$\Phi_{SBH,p} = E_{IP} - SW_M + \epsilon$$  \hspace{1cm} (3)

where $E_{IP}$ is absolute value of the VBM energy and ΦSBH,p < 0 will represent an Ohmic contact. The conditions of $S = 1$ and $\epsilon = 0$ represent the ideal noninteracting MS contact as described by the Schottky–Mott rule. Deviation from such ideal case is reflected as $S < 1$ and $\epsilon \neq 0$. Here, $\epsilon$ represents nonidealities arising from the MS material interface interaction upon contacting, and can be dependent on several physical quantities, such as charge-neutrality level, the band edge energies and/or the interface dipole potential.[94] For 2D MS vdWHs contacts composed of MoSi2N4 and WSi2N4, we obtained $S_{MoSi2N4} = 0.62$ and $S_{WSi2N4} = 0.48$, which are, respectively, less than the reported values of 0.69 and 0.76 for their bulk metal contact counterparts.[95] It should be noted that such nonideal S-parameters are not caused by band hybridization or metal-induced gap states as in the case of 3D metal contacts. In 2D/2D MS contact, charge redistribution upon forming the contact inevitably leads to a dipole potential difference $\Delta\Phi$ establishing across the contact, that is dependent on the metal’s work function.[96] By adding $\Delta\Phi$ which can be extracted from the plane-averaged electrostatic potential profile plot (e.g., see Figure 3E–H) into the p-type SBH as a correction factor (i.e., taking $b = -\Delta\Phi$), $S_{MoSi2N4}$ ($WSi2N4$) = 1.14(1.13) is obtained for MoSi2N4($WSi2N4$). We further note that as W atom is less electronegative than Mo atom, more electrons are transferred to the metallic monolayers [e.g., see Figure S22, Supporting Information, for MS contacts composed of Nb(S,Se)2], thus resulting in the modification of $S_{WSi2N4}$ by a larger extent (i.e., from 0.48 to 1.13) compared to $S_{MoSi2N4}$ (i.e., from 0.62 to 1.14). We trace the unusual S-parameter of $S > 1$ to be originating from the strain on the monolayers induced by lattice mismatch upon constructing the vdWHs, which modifies the bandgap and band edge energies of the monolayers. To verify such strain-related origin of $S > 1$, we calculate the p-type Schottky barrier height by including correction factors corresponding to both interface dipole potential and strain that are present ($\Phi_{SBH,p}^{(S)}$)

$$\Phi_{SBH,p}^{(S)} = \Phi_{SBH,p} + \Delta\Phi + \Delta E_{VBM} + \Delta W_M$$  \hspace{1cm} (4)

with

$$\Delta E_{VBM} = E_{IP}^{pristine} - E_{IP}^{strain}$$  \hspace{1cm} (5)

$$\Delta W_M = W_M^{pristine} - W_M^{strain}$$  \hspace{1cm} (6)

where $E_{IP}^{pristine}$ and $E_{IP}^{strain}$ are the absolute value of the VBM energy of the pristine and strained semiconductor, respectively, $W_M^{pristine}$ and $W_M^{strain}$ are the work function of the strained and pristine metal, respectively. Equations (5) and (6) account for the dipole potential as well as the VBM and metal work function offset, respectively (see Table S3, Supporting Information, for tabulated values). These corrections together with the dipole potential, when added to the p-type Schottky barrier heights extracted from the electronic band structures recover the ideal Schottky–Mott rule of $S = 1$ (see Figure 4C), thus revealing the important roles of both interface dipole potential and strain in the Fermi level pinning effect of (Mo,W)Si2N4-based MS contacts. The interface dipole and any resultant strain upon forming vdWHs are thus important factors to consider when selecting an appropriate 2D metal (e.g., metallic TMDC and graphene) for Ohmic or Schottky contact applications.

### 3.2. Semiconductor/Semiconductor (SS) Contacts

We classify all SS vdWHs according to the relative location of the conduction band minimum (CBM) and VBM in the energy space, i.e., the three conventional band alignment types:[94–96]

i) Type I straddling gap band alignment where the CBM and VBM arise dominantly from only one of the constituent monolayers; ii) Type II staggered gap band alignment where the CBM
Figure 4. Tunneling-specific resistivity and probability of Ohmic MS contacts, Schottky barrier heights of Schottky MS contacts, and slope parameter of (Mo,W)Si₂N₄. A) The tunneling-specific resistivity (probability) for four types of Ohmic MS vdWHs are colored in red (blue). B) p-type Schottky barrier heights of the MS vdWHs that form Schottky contact. C) (i) p-type Schottky slope parameter of MoSi₂N₄ (dark blue) and WSi₂N₄ (light blue) in contact with 2D metals. Also plotted are the slope parameters after accounting for the interface dipole potential, of MoSi₂N₄ (dark green) and WSi₂N₄ (light green). Diagonal black lines are the ideal Schottky–Mott slope of MoSi₂N₄ (upper) and WSi₂N₄ (lower). (ii) Slope parameters of MoSi₂N₄ (red) and WSi₂N₄ (orange) after further including the semiconductor valence band and metal work function offset. D–I) The electronic band structures of the p-type Schottky vdWHs.
and VBM reside dominantly in different sub-monolayers; and iii) Type III broken gap band alignment where the CBM of one sub-monolayer overlaps with the VBM of another sub-monolayer. Unconventional band alignment types can also occur in vdWH in which the CBM and VBM energies cannot be straightforwardly classified according to these conventional band/or alignment types (denoted as Type H in this work).[97] In this section, the 41 types of SS (Mo,W)Si₂N₄-based vdWHs are classified according to their band alignment types (see Figure 5A).

The electronic band structures of representative Type I, II, III, and H vdWHs are shown in Figure 5B–E, respectively.
Type I vdWHs—a band alignment type that is useful for photoluminescence applications, such as light-emitting diodes and lasers, due to the localization of CBM and VBM states within the same sub-monolayer. Among these Type I vdWHs, 15 species possess direct bandgap that is highly beneficial for engineering efficient excited electron–hole pair recombination.\[98\] The electronic band structure of a representative Type I vdWH, MoSi2N4/hBN is shown in Figure 5B. We note that the MoSi2N4/MoS2 calculated using PBE (HSE06) here shows a direct bandgap of 0.60 eV (1.06 eV) at the Γ point which is in stark contrast to the 1.26 eV (1.84 eV) reported in a previous work.\[38\] We attribute this difference to the stacking orientation of the vdWH construction. The biaxial strain arising from lattice mismatch of the supercell considered in this work is only 2.7% (i.e., 30° rotation between the two monolayers), as compared to the substantially larger biaxial strain of 78% in the previous work.\[38\]

For Type II band alignment, 15 species of vdWHs are identified. Figure 5C shows the electronic band structure of MoSi2N4/WSi2N4, a Type II vdWH compose entirely of MA2Z4 monolayers. The type II band alignment and the indirect nature of MoSi2N4/WSi2N4 are in good agreement with a recent DFT calculation of the same vdWH but under different stacking configuration.\[99\] Type II vdWHs are potential candidates for excimeric solar cell application. The maximum PCE calculated for each Type II vdWHs are presented in Figure 6A,B below. Finally, we note that (Mo,W)Si2N4/Na3Bi are the only Type III vdWHs. Such band alignment arises from the ultralow work function\[100\] and the narrow bandgap\[30\] nature of Na3Bi monolayer (see Figure 2A). The VBM of Na3Bi overlaps strongly with the CBM of (Mo,W)Si2N4, thus leading to the formation of Type III SS contacts. Figure 5D shows the electronic band structure of WSi2N4/Na3Bi as an illustrative example.

Beyond the conventional band alignment types discussed above, we further observed five vdWHs with unconventional band alignments, namely, the (Mo,W)Si2N4/MoS2, MoSi2N4/SMoSe, MoSi2N4/2H-WSe2, WSe2/Pd, and WSe2/SWSe (see Figure 5E for the electronic band structure of a representative vdWH, WSe2/SWSe). As the VBM electronic states are delocalized and distributed rather evenly among the two sub-monolayers, the conventional Type (I, II, III) classification scheme is no longer applicable, and we denote these vdWHs as the hybridized type (denoted as Type H), which are intermediate between Type I and Type II vdWHs due to the spatial distribution of VBM states in both sub-monolayers. The Type H contacts are also observed in vdWHs composed of TMDC monolayers\[67,101\] and binary semiconducting monolayers composed of group IV–V elements\[97\] which arise due to the orbital hybridization of the out-of-plane p\text{z}-states. As the VBM states are distributed among the two sub-monolayers in Type H contacts, some of the excited electron–hole pairs can recombine within the same sub-monolayers, thus rendering charge separation much less effective and may impede the potential of Type H vdWHs for optoelectronics applications. We further note that to verify these unusual band structures, we use the HSE06 exchange correlation functional in the electronic band structure calculations of these heterostructures. The Gamma-centered Brillouin zone k-point sampling grid of 6×6×1 is used due to computational resources constraint. Interestingly, the VBM hybridization is removed in MoSi2N4/2H-MoS2 and MoSi2N4/α2-WGe2P4 under the HSE06 calculations (see Figure S13, Supporting Information).

3.2.2. Excitonic Solar Cell Maximum Conversion Efficiency of Type II vdWHs

Optically excited electron–hole pairs are spatially well-separated in Type II vdWHs, which enables the efficient dissociation of these carriers to form conduction current. Such vdWHs are thus practically useful for applications where long-live and/or delocalized electron–hole pairs are needed, such as photodetector, excitonic solar cell, and photocatalytic water splitting.\[95\] We calculated the maximum solar cell PCE of these Type II vdWHs, which represents the theoretical upper limit of solar-to-electricity conversion in a heterostructure device. The PCE is calculated as

\[\eta = \frac{0.65(E_s^d - \Delta E_c - 0.3) \int_{E_0}^{E_g} \left( \frac{P(h\omega)}{h\omega} - \Delta \right) \omega d\omega}{\int_0^{E_g} P(h\omega) d\omega} \tag{7}\]

where \(E_s^d\) is the bandgap of the donor monolayer, \(\Delta E_c\) is the conduction band offset (CBO) between the two monolayers, \(P(h\omega)\) is the solar spectral irradiance as a function of photon frequency \(\omega\) and the 0.3 eV term in Equation (7) is an empirical parameter to account for the energy loss during the conversion process.\[100\] The AM1.5G standard solar spectrum is used for the solar spectral irradiance \(P(h\omega)\), which yields an integrated solar intensity of \(P_{int} = \int_0^{E_g} P(h\omega) d\omega = 1000\) W m\(^{-2}\). A representative value of 0.65 is assumed for the electrical fill factor of the solar cell\[103\] which corresponds to the typical situation where ~60% of the excited electron–hole pair are dissociated to form the short-circuit current as observed experimentally.\[104\] To achieve high PCE, the donor monolayer bandgap should be within the desirable range of 1.0–1.7 eV, while the CBO should be as small as possible to suppress the energy loss. Equation (7) reveals the ultimate conversion efficiency of a material by assuming that the incoming light is fully absorbed, thus enabling a unifying comparison across different nanomaterials. The light absorption of 2D materials can be tuned externally, such as using substrate engineering, optical cavity, and nanoparticles.\[105,106\]

The calculated PCEs are listed in Figure 6A,B for MoSi2N4- and WSi2N4-based Type II vdWHs, except for WSi2N4/MoGe2N4 in which the overly small bandgap of \(E_s - \Delta E_c < 0.3\) is unsuitable for solar cell application. In general, MoSi2N4-based Type II SS contacts exhibit higher overall PCE when compared to the WSi2N4-based Type II vdWHs. In our work, the PCE of MoSi2N4/InSe and MoSi2N4/WSe2 vdWHs reaches 20.5% and 22.0%, respectively, which are comparable to several vdWHs in recent high-throughput screenings to uncover potential vdWHs candidates for solar cell applications, such as: i) the screening of 581 Type II vdWHs based on Anderson rule which uncovered 17 candidates with the highest being HfSe2/GeO2 (22.6%);\[21\] ii) the screening on 15 Group III–V vdWHs with 24 different configurations with the highest being GaSb/InSb (22.9%);\[20\] and iii) the incorporation of machine learning model on Group III–VI Janus
vdWHs which uncovered 71 candidates with the highest being In$_2$STe/Al$_2$SSe (21.4%). An exceedingly high PCE of 23.2% has been very recently reported from Sc$_2$CCl$_2$/SiS$_2$ vdWH. The MoSi$_2$N$_4$/InSe and MoSi$_2$N$_4$/WSe$_2$ vdWHs predicted here are thus among the some of the exceptional high-efficiency solar cells, which outperforms many other vdWHs.

Figure 6. Solar cell maximum power conversion efficiency (PCE) of Type II SS vdWHs. A, B) The calculated PCE ($\eta$) for MoSi$_2$N$_4$ and WSi$_2$N$_4$ vdWHs, respectively. C) Energy fluctuation of MoSi$_2$N$_4$/WSe$_2$ under AIMD simulation at temperature 300 K for 3 ps. Insets show the top and side views of the structure before and after the simulation. D) PCE of MoSi$_2$N$_4$/WSe$_2$ under varying electric field (blue) and interlayer displacement (green). The dielectric constants and the optical absorption spectra of Type II SS vdWHs with PCE higher than 15% are shown in: E) MoSi$_2$N$_4$/InSe, F) MoSi$_2$N$_4$/WGe$_2$N$_4$, G) MoSi$_2$N$_4$/ZnO, and H) MoSi$_2$N$_4$/WSe$_2$. I, J) The dielectric constant and optical absorption spectra of isolated (Mo,W)Si$_2$N$_4$, respectively.
such as (Mo,W)S$_2$-based vdWHs,\textsuperscript{[109–113]} N-doped Ga(S,Se)/SnS$_2$,\textsuperscript{[114]} h-BP/h-BAs,\textsuperscript{[115]} and Group IIIA monochalcogenide bilayers.\textsuperscript{[116]} The large PCE of MoSi$_2$N$_4$/InSe and MoSi$_2$N$_4$/WSe$_2$ can be attributed to the small CBO of 0.03 and 0.05 eV, respectively. Furthermore, MoSi$_2$N$_4$/InSe and MoSi$_2$N$_4$/WSe$_2$ are indirect bandgap Type II heterostructures in which the recombination of excitons is expected to be less effective due to the need of phonon-assisted process to compensate the momentum mismatch between CBM and the VBM states.\textsuperscript{[117]} MoSi$_2$N$_4$/InSe and MoSi$_2$N$_4$/WSe$_2$ are thus expected to host long-lived interlayer exciton that are highly beneficial for highly efficient light-to-electricity conversion. We further note that the band structure of MoSi$_2$N$_4$/WSe$_2$ is also similar to a recent study with different stacking order.\textsuperscript{[72]}

For the four MoSi$_2$N$_4$-based Type II vdWHs with PCE over 15%, we calculated the real and imaginary parts of their dielectric function as well as the optical absorption spectra (see Figure 6E–H). All four heterostructures exhibit substantial optical absorption of >10% in the visible light regime (denoted by dashed vertical lines in Figure 6E–H). Particularly, the vdWH with the highest PCE, i.e., MoSi$_2$N$_4$/WSe$_2$ exhibits a strong optical absorption shoulder (>20%) in the visible light regime of energies 2.5 eV and above. To assess the thermal stability of MoSi$_2$N$_4$/WSe$_2$, ab initio molecular dynamics (AIMD) simulation using an expanded $2 \times 2 \times 1$ supercell of the vdWH are performed under a temperature of 300 K for time duration of 3 ps. The lattice structure of MoSi$_2$N$_4$/WSe$_2$ is well maintained with small energy fluctuation over a small range (≈0.02 eV), thus demonstrating that the thermal stability of MoSi$_2$N$_4$/WSe$_2$ (see Figure 6C). As the band alignment of the vdWH is sensitively influenced by the interaction between the two constituent monolayers, we further investigate how external electric field and interlayer distance can be used to tune the PCE of MoSi$_2$N$_4$/WSe$_2$. We consider two tuning mechanisms: i) an external out-of-plane electric field (positive electric field pointing from WSe$_2$ to MoSi$_2$N$_4$) from $-1.0$ to $1.0$ V nm$^{-1}$ in steps of $0.2$ V nm$^{-1}$ which can be achieved by electrostatic gating; and ii) variation of the interlayer distance from $-0.8$ Å to 0.8 Å (tensile) in steps of 0.2 Å, which can be achieved via experimental means like nanomechanical pressure,\textsuperscript{[118]} thermal annealing in vacuum,\textsuperscript{[119] or inserting a layer of dielectric between monolayers.\textsuperscript{[120] The gradual increment in electric field and interlayer separation (see Table S5, Supporting Information, for tabulated values) is found to be able to tune the transition from Type II indirect to Type I direct bandgap, with an enhancement of PCE before such transition (see Figure 6D), thus suggesting that electric field and interlayer separation can be used as an external knob to engineer the excitonic solar cell performance of MoSi$_2$N$_4$/WSe$_2$.

The optical absorption spectra of the studied Type II vdWHs and tunable band alignment of MoSi$_2$N$_4$/WSe$_2$ suggest that (Mo,W)Si$_2$N$_4$-based vdWHs have strong potential for solar energy absorption and photodetection applications.\textsuperscript{[121–123]} Comparing to the isolated MoSi$_2$N$_4$ and WSi$_2$N$_4$ monolayers (see Figure 61,J), the overall optical absorption in the visible light regime is significantly enhanced upon forming the vdWHs, thus establishing the importance of vdW engineering in boosting the solar energy conversion capability of MoSi$_2$N$_4$ and WSi$_2$N$_4$.

3.3. Optical Properties

The optical properties of the 51 vdWHs are calculated based on quantum mechanical interband transition process from the valence bands to the conduction bands. The macroscopic frequency-dependent complex dielectric function $\varepsilon(\omega)$ is calculated based on the random phase approximation formalism (RPA).\textsuperscript{[75]} The optical absorbance ($\alpha$) of a freestanding 2D monolayer under normal illumination can then be calculated as\textsuperscript{[105]}

$$\alpha = \frac{\text{Re}(\sigma(\omega))}{\text{Im}(\sigma(\omega))+i}$$

where $\sigma(\omega) = \sigma_{2D}(\omega)/\varepsilon_0c$, $\sigma_{2D}(\omega) = i\varepsilon_0\omega L$, $\varepsilon_0$ is the vacuum permittivity, $L$ is the length of the in-plane lattice constant, and $c$ is the speed of light in vacuum. Equation (8) yields a maximum absorbance of $\alpha_{max} = 0.5$ when $\text{Re}(\sigma(\omega)) = 2$ and $\text{Im}(\sigma(\omega)) = 0$, which represents the theoretical absorption limit of a freestanding monolayer.\textsuperscript{[105]}

The complex dielectric function and optical absorbance of the 51 types of vdWHs are calculated and presented in Figures S28–S33 (Supporting Information). In general, the (Mo,W)Si$_2$N$_4$ vdWH family exhibits sizable optical absorption in the visible regime with optical absorbance up to 25%. We compiled the peak absorbance for photon energies up to 5 eV for all vdWHs as shown in Figure 7. Intriguingly, almost all vdWHs exhibit peak absorbance in the UV regime, except for MoSi$_2$N$_4$/2H-WSe$_2$ vdWH which has a peak absorbance at the visible photon energy of 3.2 eV. The peak absorbance of the isolated MoSi$_2$N$_4$ and WSi$_2$N$_4$ monolayers (see Figure 61,J for the optical absorption spectra of MoSi$_2$N$_4$ and WSi$_2$N$_4$ monolayers) is 20% at 4.0 eV and 17% at 4.4 eV, respectively, which are comparable to some of the strongest mid-UV-absorbing 2D materials (e.g., SnS$_2$ and SnSe$_2$).\textsuperscript{[105]} More importantly, the peak absorbance is significantly enhanced upon forming the vdWHs, with many vdWHs reaching a peak absorbance of over 30% in the UV regime. In general, the WSi$_2$N$_4$ vdWHs exhibit peak absorbance at higher photon energies as compared to that of MoSi$_2$N$_4$ counterpart in the energy range being studied, owing to the slightly higher peak absorbance photon energies of 4.4 eV of the WSi$_2$N$_4$ monolayer, as compared to that of monolayer MoSi$_2$N$_4$ at 4.0 eV (see Figure 61,J). We grouped the vdWHs into the subgroups of near-UV (3.5–4.0 eV), mid-UV (4.1–4.4 eV), and deep-UV (≥4.5 eV) according to the peak absorbance photon energies. Intriguingly, for the vdWHs composed of entirely MA$_2$Z$_2$ (i.e., (Mo,W)Si$_2$N$_4$/α$_2$-(Mo,W)Ge$_2$P$_2$) the vdWHs exhibit exceptionally strong UV absorption of over 40%, which approaches the optical absorption limit of a freestanding monolayer, and a broadband strong absorption shoulder between 3 and 5 eV (see Figures S31 and S33, Supporting Information). These findings suggest the potential strength of MA$_2$Z$_2$-based vdWHs in photonics device applications.

4. Conclusion

In summary, we investigated 51 types of MoSi$_2$N$_4$ and WSi$_2$N$_4$ vdWHs and categorized these heterostructures based on their
contact and band alignment types. For MS Ohmic contacts, the tunneling-specific resistivities are comparable or lower than many of the previously reported 2D semiconductor electrical contacts, while in MS Schottky contacts we have shown that both strain and interface dipole potential lead to the deviation from the Schottky–Mott rule. Multiple Type II heterostructures had been identified, particularly MoSi2N4/InSe and MoSi2N4/WSe2 exhibit excellent solar cell energy conversion efficiency greater than 20% and substantial optical absorption in the visible light regime, making them potential candidates for photovoltaic applications. In terms of optical absorption, the family of (Mo,W)Si2N4-based bilayer van der Waals heterostructures generally exhibits much enhanced UV optical absorption when compared to their isolated counterparts. The (Mo,W)Si2N4/ (α2-MoGe2P4,α2-WGe2P4) heterostructures have an exceedingly high UV peak absorbance of over 40% that approaches the theoretical maximum absorption limit of a freestanding monolayer, thus revealing their strength in UV photonics applications. Our findings reveal the promising role of (Mo,W)Si2N4-based van der Waals heterostructures as a versatile platform for designing novel optoelectronics and photonics applications, and call for a more comprehensive screening of the expansive MA2Z4 vdWH family to fully unlock their potential as building blocks of high-performance nanodevice technology.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.
