Tunable Electronic Properties and Band Alignments of MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO van der Waals Heterostructures

Jin Quan Ng, Qingyun Wu, L. K. Ang, and Yee Sin Ang

1Science, Mathematics and Technology, Singapore University of Technology and Design (SUTD), 8 Somapah Road, Singapore 487372, Singapore

Van de Waals heterostructures (VDWH) is an emerging strategy to engineer the electronic properties of two-dimensional (2D) material systems. Motivated by the recent discovery of MoSi$_2$N$_4$ - a synthetic septuple-layered 2D semiconductor with exceptional mechanical and electronic properties, we investigate the synergy of MoSi$_2$N$_4$ with wide band gap (WBG) 2D monolayers of GaN and ZnO using first-principle calculations. We find that MoSi$_2$N$_4$/GaN is a direct band gap Type-I VDWH while MoSi$_2$N$_4$/ZnO is an indirect band gap Type-II VDWH. Intriguingly, by applying an electric field or mechanical strain along the out-of-plane direction, the band structures of MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO can be substantially modified, exhibiting rich transitional behaviors, such as the Type-I-to-Type-II band alignment and the direct-to-indirect band gap transitions. These findings reveal the potentials of MoSi$_2$N$_4$-based WBG VDWH as a tunable hybrid materials with enormous design flexibility in ultracompact optoelectronic applications.

In recent years, van der Waals heterostructures (VDWHs) have been widely employed for engineering the electronic, optical and photocatalytic properties of two-dimensional (2D) materials [1]. With an appropriate selection of 2D monolayers and stacking order, VDWHs can give rise to myriads of interesting physics, such as strongly interacting artificial heavy fermions [2], and excitonic Bose-Einstein Condensates [3]. VDWHs also offer an avenue to engineer high-quality electrical contacts [4, 5] with exceptionally low contact resistance and significantly suppressed Fermi level pinning effect, thus playing a pivotal role towards the development of practical 2D semiconductor device technology [6, 7].

As such, VDWHs have the ability to enable applications in new devices not available with currently available materials or enhance current devices with new characteristics. One example of which are tunnelling transistors which operate by tunnelling current [8]. Such devices made using VDWHs promise to have subthreshold swings below traditional MOSFET limits and hence have lower off currents and standby power dissipation, thus better suited for low power applications [9]. Another example are better photodetectors with fast switching speed [10] due to narrow channel width, higher responsivity due to tunnelling current [8] and the extended light range [18] among many other properties, which provide many potential applications in electronics and photonics.

The recent discovery of MoSi$_2$N$_4$ and the extended MA$_2$Z$_4$ monolayer family reveals an exciting material platform for designing novel 2D material devices. MoSi$_2$N$_4$ monolayer is a synthetic 2D semiconductor without 3D parent structure and has been synthesized experimentally by passivating MoN$_2$ monolayer with Si to create a septuple-layered nanosheet composed of a MoN$_2$ inner layer sandwiched by two Si-N outer layers [12]. Interestingly, the Conduction Band Minimum (CBM) and the Valence Band Maximum (VBM) are concentrated within the MoN$_2$ core-layer and the outer Si-N atomic sublayer, hence serving as a built-in protective layer to preserve the conduction channels from the external perturbations [6, 13] and to strongly suppress the adverse Fermi level pinning effect. Quantum transport simulations have also suggested MoSi$_2$N$_4$ monolayer to be an exceptional 2D channel material for field-effect transistor applications [14–16]. Beyond pristine monolayer, MoSi$_2$N$_4$ has been predicted to be half metallic with N or Si vacancies [17] and excellent optical absorption in visible light range [18] among many other properties, which provide many potential applications in electronics and photonics.

MA$_2$Z$_4$-based VDWHs is an emerging area, recent studies include MoSi$_2$N$_4$/TMDC [19, 20] and Janus MA$_2$Z$_4$-based VDWHs [21, 22]. Unusual properties, such as electric-field and strain tunable Ohmic-to-contact transition, semiconductor-to-metal transition [23], Type-I-to-Type-II band alignment transition and excellent optical absorption around the visible light regime [21], have been predicted in various MA$_2$Z$_4$-based VDWHs. Nonetheless, the synergy of MA$_2$Z$_4$ monolayer with wide band gap (WBG) semiconductors, such as GaN and ZnO honeycomb monolayer remains largely unexplored thus far. Due to quantum confinement, WBG monolayers are expected to exhibit a larger band gap than the bulk counterparts [24, 25]. WBG semiconductors have been widely explored for optical [26–28] and electronic device applications [29, 30]. WBG semiconductor typically have a band gap of $>2$ eV [31], making them excellent for optoelectronic applications [32] due to higher excitonic binding energy that is robust against thermal fluctuations. The wider band gap is also beneficial for devices operating at higher temperatures and higher voltage operation [33–36]. In particular, 2D ZnO has been experimentally synthesised [37] and investigated for photocatalytic [38] and photodetector capabilities [39]. On the other hand, low-cost and easy growing of high quality, transferable 2D GaN is challenging due to the parent compound being

* Authors to whom correspondence should be addressed: ricky_ang@sutd.edu.sg and yeesin_ang@sutd.edu.sg
a non-layered, non-exfoliatable compound. Thus, ongoing research dominantly focuses on the growth of high-quality GaN monolayers [24, 40]. Nevertheless, novel applications, such as flexible electronics [41], light-emitting diodes [42] and piezoelectric strain-gated logic gates [43], have been demonstrated recently, thus suggesting the potential of 2D GaN in electronics and optoelectronics applications. Beyond GaN, other 2D WBG semiconductors, such as GaSe, GaS and SnS2, have been also been fabricated. These monolayers exhibit fast response times and high photoresponsivity [44, 45], good compatibility in flexible device applications [45], and can be incorporated for logic gates applications with large on-off ratios [46].

Motivated by the potentials of MA$_2$Z$_4$ based WBG semiconductors, we perform first-principle calculations on the electronic and structural properties of MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO VDWHs by using density functional theory (DFT). We find that MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO are Type-I direct band gap and Type-II indirect band gap VDWHs, respectively. Interestingly, an external electric fields perpendicular to the plane of the VDWHs can be used to drive a transition between direct and indirect band gaps, thus indicating a field-effect tunable optoelectronic properties of
FIG. 2. (a) Band structure of MoSi$_2$N$_4$/GaN when subjected to external electric fields, with corresponding external electric field values at the top. (b) Band structure of MoSi$_2$N$_4$/ZnO when subjected to external electric fields, with corresponding external electric field values at the top.

MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO VDWHs. Additionally, the electronic properties, band alignment and the direct/indirect band gap nature of MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO can be further controlled under mechanical compression and strain. These results suggest the potentials of MoSi$_2$N$_4$/WBG-2D-semiconductor VDWHs. Additionally, the electronic properties, band alignment and the direct/indirect band gap nature of MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO can be further controlled under mechanical compression and strain. These results suggest the potentials of MoSi$_2$N$_4$/WBG-2D-semiconductor VDWHs.

All simulations are carried out using DFT implemented in the Vienna *Ab initio* Simulation Package [47–50]. PAW pseudopotentials [51] are used to simulate the ion electron bonding and the layers are relaxed using GGA PBE [52] with Grimme DFT-D3 vdW [53] interactions between the monolayers. It is known that PBE underestimates the band gaps and that HSE06 will produce better band gaps for 2D GaN and ZnO [24, 54]. Using PBE allows the effect of strain and external electric fields to be studied without the high computational costs of HSE06 and has been used before in previous literature [55, 56], so PBE results are used and presented here. Crucially, the general trend of the band structure and band alignment are expected to be sufficiently captured by PBE. We thus expect our key findings to be qualitatively accurate using PBE calculations. All materials were sampled using a gamma-centred Brillouin zone at $11 \times 11 \times 1$ using the Monkhorst-Pack grid [57]. Ionic force convergence was set to 0.01 V/Å and electronic convergence was set to $10^{-8}$ eV. A vacuum layer of 20 Å was used to prevent interactions between periodic layers. The energy cutoff at 500 eV was made to allow comparisons between materials and different electric field and strain settings. Dipole corrections are enabled in all calculations for consistency. Spin orbit coupling was not considered in this paper, since MoSi$_2$N$_4$ [12], GaN and ZnO are nonmagnetic semiconductors. Thus, spin is unlikely to play a major role in the properties of the studied VDWH, with spin-orbit coupling showing only small differences [58–61]. However, we note that the magnetic properties of VDWH can be altered by means of doping [62], hydrogen adsorption [63] or proximity effects to magnetic materials [64], thus suggesting further avenues for magnetic and spintronic properties engineering of MoSi$_2$N$_4$-based VDWH.

MoSi$_2$N$_4$, GaN and ZnO layers are constructed using previously reported experimental and computational lattice parameters [12, 17, 24, 28]. The bond lengths of the fully relaxed monolayers are 2.087 Å for Mo-N, 1.858 Å for Ga-N and 1.906 Å for Zn-O, which are in agreement with those previously reported. Several stacking configurations were built using QuantumATK, with strain distributed among the GaN and ZnO layer. The binding energy is calculated as follows: $E_b = (E_{vdW} - E_{MoSi_2N_4} - E_{\mu})/34$, where $\mu$ is GaN or ZnO. The binding energy of all configurations was found to be negative, suggesting their energetic stability. The binding energy was all VDWHs very similar to within 0.0001 eV per atom, hence the slightly lower energy was chosen. The final stacking configuration has a binding energy of -0.0158 eV/atom for MoSi$_2$N$_4$/GaN and -0.0202 eV/atom for MoSi$_2$N$_4$/ZnO. The overall lattice strain for MoSi$_2$N$_4$/GaN is 2.68 % and 0.92 % for MoSi$_2$N$_4$/ZnO.

The chosen VDWHs consist of $2 \times 2$ unit cells of MoSi$_2$N$_4$ and $\sqrt{3} \times \sqrt{3}$ unit cells of GaN or ZnO. The $2 \times 2$ supercells are shown in Figs. 1(a) and (b). The fully relaxed MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO have an interlayer distance of 3.44 Å and 3.15 Å, respectively, which are well above the vdW radius of 2.05 Å (gallium) [65], 1.55 Å (nitrogen) [65] and 1.52 Å (oxygen) [65]. The electronic band structures of the isolated MoSi$_2$N$_4$/GaN and ZnO monolayers exhibit the band gaps of 1.796 eV,
2.118 eV, and 1.648 eV, respectively. The work function is calculated for the monolayers and VDWHs as \( W = E_{\text{vacuum}} - E_{\text{Fermi}} \), where \( E_{\text{vacuum}} \) is the vacuum energy and \( E_{\text{Fermi}} \) is the Fermi level. The calculated \( E_{\text{vacuum}} \) are 4.6 eV, 0.91 eV and 0.54 eV for MoSi\(_2\)N\(_4\), GaN and ZnO respectively. Correspondingly, the work functions of MoSi\(_2\)N\(_4\), GaN and ZnO are calculated as 5.25 eV, 5.23 eV and 5.36 eV, respectively.

The electronic band structures of the modified monolayers based on the structural parameters taken from the VDWHs are plotted in in Supplementary Materials Figure S1. Compared to the free-standing monolayers, the band gaps are modified to 1.952 eV, 1.482 eV and 1.648 eV for MoSi\(_2\)N\(_4\), GaN and ZnO, respectively. The overall MoSi\(_2\)N\(_4\), GaN and ZnO band structures are preserved in forming the VDWHs. However, the conduction band of GaN and ZnO at \( \Gamma \) is split from a single continuous band into avoided crossings across multiple MoSi\(_2\)N\(_4\) conduction bands. The MoSi\(_2\)N\(_4\)/GaN has a Type-I direct band gap of 1.56 eV at \( \Gamma \)-point, with both VBM and CBM contributed by the GaN. In contrast, MoSi\(_2\)N\(_4\)/ZnO has a Type-II indirect band gap of 1.60 eV between the VBM at the \( \Gamma \)-point as contributed by ZnO, and the CBM at the \( K \)-point as contributed by MoSi\(_2\)N\(_4\) CBM.

We now examine the electron transfer in Figs. 1(e) and 1(f) for MoSi\(_2\)N\(_4\)/GaN and MoSi\(_2\)N\(_4\)/ZnO, respectively. In general, MoSi\(_2\)N\(_4\)/GaN has a net transfer of electrons from MoSi\(_2\)N\(_4\) to GaN, while MoSi\(_2\)N\(_4\)/ZnO has a net transfer of electrons in the opposite direction from ZnO towards MoSi\(_2\)N\(_4\). In Fig. 1(e), the electron distributions of the MoSi\(_2\)N\(_4\)/GaN are shown at the cross-sectional and the top views. The electrons accumulate at the contact interface and generally spread out along the interface. In contrast, the electron charge accumulation and depletion in concentric shells around each atom in ZnO for the MoSi\(_2\)N\(_4\)/ZnO as shown in Fig. 1(f).

The differential charge charge densities are calculated via \( \Delta \rho = \rho_{vdW} - \rho_{MoSi_2N_4} - \rho_{\mu} \), where \( \mu \) is GaN or ZnO, \( \rho_{vdW} \) is the charge density of the VDWH and \( \rho_{\mu} \) is the charge density of the individual monolayer. Comparing the differential charge density plots in Figs. 1(e) and (f), it is seen that the peak magnitude of the charge transfer in MoSi\(_2\)N\(_4\)/GaN is 40 times smaller than that of MoSi\(_2\)N\(_4\)/ZnO, due to the smaller work function difference between GaN and MoSi\(_2\)N\(_4\) versus that of ZnO and MoSi\(_2\)N\(_4\). The sharp peaks in the differential charge density plot also reveals a significant electron redistribution within the ZnO monolayer but not the MoSi\(_2\)N\(_4\), which is in strong contrast to the case of MoSi\(_2\)N\(_4\)/ZnO VDWH where the electron distributions occur with comparable strength in both MoSi\(_2\)N\(_4\) and GaN.

We next examine the heterostructures response to external electric fields. An external electric field was added in a self-consistent manner on relaxed heterostructures in steps of 0.2V/Å in Fig. 2. To illustrate the effect of an external electric field on the VDWHs, the differences in charge density are calculated as: \( \Delta \rho(E) = \rho(E) - \rho_{\text{initial}} \) where \( E \) is the external electric field, \( \rho(E) \) and \( \rho_{\text{initial}} \) are the charge density of the VDWHs with and without electric field, respectively. The external electric field induces electron depletion on GaN or ZnO, and electron accumulation on MoSi\(_2\)N\(_4\) due to the electrostatic-induced charge redistributions (see Supplementary Materials for the charge density difference and plane-averaged electrostatic potential plots). Thus, at increasing positive electric field the energy of MoSi\(_2\)N\(_4\) bands are raised relative to GaN and ZnO, while the GaN and ZnO bands are lowered relative to MoSi\(_2\)N\(_4\) [see Figs. 2(a) and 2(b) for MoSi\(_2\)N\(_4\)/GaN and MoSi\(_2\)N\(_4\)/ZnO, respectively]. Correspondingly, the CBM of both GaN and ZnO at the \( \Gamma \)-point decreases in energy. Both VDWHs thus undergo a transformation into the Type-II direct band gap VDWHs, featuring the CBM from GaN and ZnO and VBM from MoSi\(_2\)N\(_4\).

Under a negative electric field, electron accumulation is induced on GaN and ZnO heterostructure interface and
FIG. 4. (a) Band gap plots of MoSi$_2$N$_4$/GaN under external electric field. (b) Band gap plots of MoSi$_2$N$_4$/ZnO under external electric field. (c) Band gap plots of MoSi$_2$N$_4$/GaN under strain and compression. (d) Band gap plots of MoSi$_2$N$_4$/ZnO under strain and compression

depleted on MoSi$_2$N$_4$. In this case, the GaN and ZnO energy is raised relative to MoSi$_2$N$_4$, shifting the band structure of GaN and ZnO upwards generally. This results in the CBM of MoSi$_2$N$_4$ at $K$-point being lower in energy than the $\Gamma$-point CBM of GaN and ZnO, turning both VDWHs into an indirect band gap Type-II VDWHs [see Figs. 2(a) and 2(b) for MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO, respectively].

Experimentally, the interlayer distance can be tuned by several methods during material fabrication stage, such as insertion of hBN buffer layer [66] or via nanomechanical pressure [67]. We thus investigate how mechanical strain or compression applied perpendicularly to the VDWHs influences the electronic band structures by changing the interlayer spacing in steps of 0.3 Å [see Figs. 3(a) and 3(b) for MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO, respectively]. For compression, we decrease the bond lengths of Mo-N from 2.080 Å and 2.088 Å from the initial MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO VDWHs, respectively, to 2.062 Å and 2.068 Å in MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO VDWHs, respectively. When the VDWHs are compressed [see Figs. 3(a) and (b)], MoSi$_2$N$_4$ is observed to decrease in energy with respect to GaN and ZnO in general. These changes are similar to those observed when the VDWHs are subject to an external electric field in the positive $z$-direction. Furthermore, the width of the vacuum tunneling potential barrier between the monolayers decreases under compression (see the plane-averaged electrostatic potential profile plots in the SM), which leads to easier tunneling of electrons from GaN and ZnO to MoSi$_2$N$_4$. The GaN or ZnO sublayer increases in energy with increasing compression, with bands shifting higher relative to MoSi$_2$N$_4$. For MoSi$_2$N$_4$/GaN, the CBM of GaN at the $\Gamma$-point retracts into the higher energies, resulting in the transformation from direct band gap Type-I into indirect band gap Type-II band alignment. For MoSi$_2$N$_4$/ZnO, an indirect band gap Type-II band alignment is similarly observed at large compression.

For tensile strain, the bond lengths of Mo-N increases from 2.080 Å and 2.088 Å in initial MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO VDWH to 2.083 Å and 2.090 Å in the strained VDWHs at maximum strain. GaN and ZnO is observed to decrease in energy with the band structure shifting downwards relatively to MoSi$_2$N$_4$. However, the increasing width of the potential barrier between the monolayers as the interlayer distance is increased (see SM) severely limits the ability of electrons
to tunnel across and reduces the coupling between the two materials. Thus, the changes in the band structure less dramatic as compared to the case of compression. For MoSi$_2$N$_4$/GaN, the band structure remains a direct band gap Type-I band alignment under increasing strain with decreasing change in direct band gap energy. For MoSi$_2$N$_4$/ZnO, the band structure changes from indirect band gap Type-II to direct band gap Type-I band alignment as the ZnO CBM energy decreases relative to MoSi$_2$N$_4$ CBM.

The properties of the band gap and the heterostructure types are summarized in Fig. 4, with blue-shaded regions representing Type-II alignment and red-shaded regions representing Type-I alignment. The VDWHs retain the Type-II band alignment under external electric fields in both directions as shown in Figs. 4(a) and 4(b) for MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO, respectively. However, the heterostructures changes between direct and indirect band gap when the electric fields are varied in the range of 0.0 V/Å to -0.6 V/Å for MoSi$_2$N$_4$/GaN and +0.2V/Å to -0.6 V/Å for MoSi$_2$N$_4$/ZnO. This is in contrast to the case of compression and strain, as shown in Figs. 4(c) and 4(d) for MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO, respectively. Under compression, MoSi$_2$N$_4$/GaN changes from direct band gap Type-I to indirect band gap Type-II band alignment, while MoSi$_2$N$_4$/ZnO changes from indirect band gap Type-I to indirect band gap Type-II band alignments. Under strain, MoSi$_2$N$_4$/GaN remains unchanged while MoSi$_2$N$_4$/ZnO changes from Type-I indirect band gap to Type-I direct band gap under strain.

In summary, the electronic properties of MoSi$_2$N$_4$-based wide band gap semiconductor van der Waals heterostructures are studied using density functional theory simulations. The MoSi$_2$N$_4$/GaN and MoSi$_2$N$_4$/ZnO heterostructures are in direct band gap Type-I and indirect band gap Type-II band alignment, respectively. Differential charge density analysis suggests that the electron redistribution upon forming the contact heterostructure is much stronger in MoSi$_2$N$_4$/ZnO than that in MoSi$_2$N$_4$/GaN. Furthermore, we show that the application of an external perpendicular electric field or mechanical strain effectively alter the band gap type and the band alignment type of the heterostructures, thus offering a tuning knob for engineering the electronic and optoelectronic properties of the heterostructures. These findings reveal the potentials of MoSi$_2$N$_4$-based wide band gap van der Waals heterostructures as a versatile platform for designing novel tunable optoelectronics.

**SUPPLEMENTARY MATERIAL**

See supplementary material for the electronic band structures of isolated monolayers, and the plane-averaged differential charge and electrostatic potential profiles of the MoSi$_2$N$_4$/ZnO and MoSi$_2$N$_4$/GaN heterostructures.

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**AUTHOR DECLARATIONS**

Conflict of Interest

The authors declare that there are no conflicts of interest.

Author Contributions

J.Q.N. performed the simulations and data analysis. Q.W., L.K.A. and Y.S.A. supervised the project. All authors contributed to the writing and the revision to this work.

DATA AVAILABILITY

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

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