

Article

Interface Properties of MoS₂ van der Waals Heterojunctions with GaN

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Abstract: The combination of the unique physical properties of molybdenum disulfide (MoS₂) with those of gallium nitride (GaN) and related group-III nitride semiconductors have recently attracted increasing scientific interest for the realization of innovative electronic and optoelectronic devices. A deep understanding of MoS₂/GaN interface properties represents the key to properly tailor the electronic and optical behavior of devices based on this heterostructure. In this study, monolayer (1L) MoS₂ was grown on GaN-on-sapphire substrates by chemical vapor deposition (CVD) at 700 °C. The structural, chemical, vibrational, and light emission properties of the MoS₂/GaN heterostructure were investigated in detail by the combination of microscopic/spectroscopic techniques and ab initio calculations. XPS analyses on as-grown samples showed the formation of stoichiometric MoS₂. According to micro-Raman spectroscopy, monolayer MoS₂ domains on GaN exhibit an average *n*-type doping of $(0.11 \pm 0.12) \times 10^{13} \text{ cm}^{-2}$ and a small tensile strain ($\epsilon \approx 0.25\%$), whereas an intense light emission at 1.87 eV was revealed by PL analyses. Furthermore, a gap at the interface was shown by cross-sectional TEM analysis, confirming the van der Waals (vdW) bond between MoS₂ and GaN. Finally, density functional theory (DFT) calculations of the heterostructure were carried out, considering three different configurations of the interface, i.e., (i) an ideal Ga-terminated GaN surface, (ii) the passivation of Ga surface by a monolayer of oxygen (O), and (iii) the presence of an ultrathin Ga₂O₃ layer. This latter model predicts the formation of a vdW interface and a strong *n*-type doping of MoS₂, in closer agreement with the experimental observations.

Keywords: MoS₂; GaN; interface; DFT; vdW heterostructures; wide-band gap

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1. Introduction

In the last decade, molybdenum disulfide (2H-MoS₂) emerged as the most investigated two-dimensional (2D) semiconductor material of the transition metal dichalcogenides (TMDs) family, due to its unique physical properties, combined to a good chemical stability and its abundance in nature [1]. MoS₂ crystals (and in general all TMDs) are characterized by strong in-plane bonds between the chalcogen (X) and the transition metal (M) atoms and weak van der Waals (vdW) interactions between the stacked layers [2–5]. In particular, the 2H-MoS₂ polytype exhibits a tunable bandgap as a function of the thickness, i.e., an indirect bandgap of 1.2 eV in the bulk form and a direct bandgap of 1.8–1.9 eV for a monolayer (1L) MoS₂ [6,7]. One layer and few-layers MoS₂ have been employed

as channel materials in field-effect transistors (FET), showing very promising performances in terms of the on/off state current ratio ($\geq 10^8$) and decent mobility values (up to ~ 200 cm²/Vs under proper conditions) [1]. These properties make MoS₂ one of the potential replacements of Si for the continuation of the Moore scaling law in digital electronics [8]. Furthermore, 2H-MoS₂ is very appealing for a wide range of More-than-Moore applications [1,9–12], including sensing [13,14], photocatalysis [15,16], photovoltaics [17,18], and photonics [19,20] until reaching the more exotic spin-valley physics [21–23].

In this context, the dangling bonds-free MoS₂ surface allows the creation of several vdW heterostructures by the combination of various 2D materials (2D/2D vdW heterostructures) [24–27], by integration of MoS₂ with semiconductor nanowires (1D core-shell heterostructures) and with bulk semiconductors (2D/3D vdW heterostructures) [1,28–32]. In particular, increasing research efforts have been directed in the last years to the integration of MoS₂ with wide-bandgap (WBG) semiconductors, including silicon carbide (SiC), gallium nitride (GaN), and related group-III nitrides (AlN and AlGaN alloys). The combination of the unique physical properties of MoS₂ with the robust properties of highly mature WBG semiconductors (such as high breakdown field and electron saturation velocity [33,34]) set the basis for the realization of new heterojunction diodes that exploit the vertical current at the MoS₂/WBG interface [35–37] and of advanced photodetectors covering both the UV and the visible spectral range [38–40].

2H-MoS₂ exhibits a very low lattice constant mismatch with the basal planes of 4H-SiC ($\sim 2.9\%$) [41] and 2H-GaN ($< 1\%$) [42] crystals, which represents a favorable condition for highly oriented epitaxial growth of MoS₂ on these hexagonal substrates [43]. Furthermore, the small difference between the thermal coefficient expansion of the MoS₂/GaN heterostructure ($\alpha_{\text{MoS}_2} - \alpha_{\text{GaN}} \approx 0.97 \times 10^{-6} \text{ K}^{-1}$ [40,44,45]) permits the reduction of the residual strain induced by the cooling of the system from the higher growth conditions to the room temperature [40]. The promising performances of devices obtained by the integration of MoS₂ on GaN have been demonstrated by several research groups [46,47]. As an example, innovative heteroepitaxial devices have been recently reported, such as vertical heterojunction devices [48], Esaki tunnel diodes obtained by the combination of degenerate p⁺-MoS₂ on n⁺-GaN/Si [49], self-powered broadband (UV–vis–NIR) photodetectors [50–54], light emitting diodes [55], and photovoltaics applications [56].

Nevertheless, understanding and controlling the interface properties of the MoS₂/GaN heterostructures represent the key steps to optimize the performances of demonstrated devices and, eventually, to demonstrate new ones. In fact, the interface of such vdW systems plays a crucial role in terms of electronic transport and carrier transfer. As an example, Poudel et al. reported an increase in photoluminescence (PL) emission from MoS₂ and a consequent decrease from GaN, which was attributed to electron–phonon coupling and energy transfer at the MoS₂/GaN interface [57]. Furthermore, angle-resolved photoemission spectroscopy (ARPES) measurements performed on *n*-MoS₂ flakes transferred on *p*-doped GaN displayed a modification of the band structure caused by the formation of an interface dipole of 0.2 eV [58]. Recently, Zhang et al. [59] performed a nitridation of the GaN surface by N₂ plasma treatment before transferring MoS₂ on top of GaN. A modification of the MoS₂/GaN band structure with respect to a not-nitridated surface and a corresponding enhancement of photo-catalytic properties of the heterojunction were demonstrated, which can be exploited for hydrogen generation.

Besides experimental studies, several theoretical investigations based on the density functional theory (DFT) approach have been performed during the last few years to predict the interfacial properties and energy band-alignment in MoS₂/GaN heterostructures. Most of these simulation studies considered an ideal lattice-matched interface between monolayer MoS₂ and the Ga-terminated GaN(0001) surface, which resulted in the prediction of a covalent-like bond at the interface [57,59]. These theoretical results contradict the experimental evidence of a van der Waals (vdW) bond between MoS₂ and GaN, reported by different authors [36,37,42]. Clearly, studies combining experimental investigations

and more refined modeling of the interface are necessary to better understand the properties of this heterostructure.

In this paper, we combined experimental characterizations and DFT calculations to provide a detailed evaluation of the MoS₂/GaN interface structure and the strain, doping, and the optical emission properties of MoS₂ domains grown by CVD on GaN. X-ray photoelectron spectroscopy (XPS) displayed the formation of stoichiometric MoS₂ ([S]/[Mo] \approx 2) without the presence of Mo-oxide (MoO_x) components. Raman mapping showed that the MoS₂ domains mainly consisted of monolayers, with a small bilayer fraction, consistently with the intense light emission peak revealed by micro-photoluminescence (μ -PL) mapping. Furthermore, an average *n*-type doping of $(0.1\text{--}0.2) \times 10^{13} \text{ cm}^{-2}$ and a very low tensile strain of $\sim 0.25\%$ was evaluated by the correlative plot of the E' and A'1 Raman peaks. The obtained strain was in perfect agreement with the one derived by the exciton peak positions obtained by μ -PL spectra. Cross-sectional scanning transmission electron microscopy (STEM) measurements confirmed both the monolayer MoS₂ thickness, the presence of a van der Waals (vdW) gap at the interface with GaN, and a modification of the topmost GaN layers with respect to the bulk crystal. Finally, we employed DFT calculations to better understand the structural and electronic properties of the interface between 1L of MoS₂ and GaN. In particular, three configurations of the GaN surface were considered within this heterostructure: (i) an ideal Ga-terminated GaN(0001) surface, (ii) the passivation of Ga terminations with a monolayer coverage of oxygen (O) atoms, and (iii) the presence of an ultrathin Ga₂O₃ film on the GaN surface. The first two configurations resulted in a strong covalent bond at the interface, very different from the experimentally observed vdW interaction. On the other hand, the formation of a vdW gap of 3.05 Å and a significant *n*-type doping of 1L of MoS₂ was predicted in the presence of an ultrathin Ga₂O₃ film at the MoS₂/GaN interface, which is in close agreement with the experimental results.

2. Materials and Methods

The starting material for these experiments was an unintentionally doped GaN(0001) template grown on a c-sapphire substrate. The pristine GaN surface showed a low root mean square (RMS) roughness of $\sim 0.3 \text{ nm}$, evaluated from the AFM image in Figure S1 of the Supporting Information.

MoS₂ was grown on a GaN/c-sapphire substrate by single step CVD at a temperature of 700 °C for 10 min at atmospheric pressure. The process was carried out in a quartz tube furnace with two-heating zones, the first employed for the evaporation of the sulfur powders (7–10 mg) at 150 °C, and the second for the evaporation of the MoO₃ powders (2–3 mg) at 700 °C. The GaN substrate was placed in the second zone of the furnace above the MoO₃ crucible. The reaction between the S vapors (transported by an Ar flux of 100 sccm) and MoO₃ vapors occurred in the gas phase close to the GaN surface, resulting in the nucleation and growth of MoS₂ domains.

The MoS₂ domain coverage on GaN was evaluated by scanning electron microscopy (SEM) using a ThermoFisher Scios 2 dual-beam microscope. X-ray photoelectron spectroscopy (XPS) analysis was carried out by using Escalab Xi+ equipment by Thermo Fisher (Waltham, MA, USA), with a monochromatic Al K X-ray source (energy = 1486.6 eV). The spectra were collected at a take-off angle of 90° relative to the sample surface and pass energy of 20 eV. The instrument resolution was 0.45 eV (FWHM of the Ag 3d5/2 peak). The spectra were aligned using C1s (285 eV) as a reference.

High-resolution transmission electron microscopy (HR-TEM) and high-angle annular dark field scanning transmission microscopy (HAADF-STEM) were carried out with an aberration-corrected Titans Themis 200 microscope by Thermo Fisher. For the cross-sectional analysis, a focused ion beam (FIB) was used to prepare lamellas from the sample.

Micro-Raman (μ -Raman) spectra were acquired employing both WiTec Alpha equipment by WiTec (Ulhm, Germany) and a Horiba Raman system with a confocal microscope (100 \times) and with a laser excitation wavelength of 532 nm. The second Raman setup was

also employed to acquire the micro-photoluminescence (μ -PL) spectra changing the grating from 1800 l/mm to 600 l/mm. In all the configurations, the laser power was filtered with a neutral density (ND) filter at 1%.

Calculations of the MoS₂/GaN(0001) interface were performed within the density functional theory (DFT). We used the plane-wave Quantum Espresso code [60] with Hamada's van der Waals exchange-correlation functional [61] and standard solid-state pseudopotentials [62,63]. The latter was based on the Perdew–Burke–Ernzerhof functional [64]. To have a broader comparison with the experiment, monolayer MoS₂ interfaces with ideal Ga-terminated GaN surfaces and with oxidized GaN surfaces were considered. A slab model comprising 16 bilayers of Ga-N, whose bottom termination was passivated with hydrogen, was used to model the GaN substrate. On the top termination instead, the Ga-terminated GaN(0001) surface interacted with the MoS₂ layer. The quasi-commensurate lattice constants of MoS₂ with respect to the surface vectors of GaN(0001) allowed for the construction of an interface model with unit-cell periodicity. This (1 × 1) interface model resulted in a small tensile strain for the MoS₂ layer (1.7%), whereas the GaN substrate was unstrained. The plane-wave cut-off kinetic energy was set to 50 Ry and the augmented charge density cut-off was set to 400 Ry, respectively. A (12 × 12 × 1) Monkhorst-Pack grid [65] was used for the sampling of the Brillouin zone. To avoid spurious interactions between the periodic replicas of the system perpendicular to the interface, a vacuum space of 20 Å was inserted in the simulation supercell.

3. Results

The nucleation and growth of MoS₂ on the GaN surface was preliminarily investigated by SEM images collected immediately after the deposition of the samples on different areas. Figure 1 shows a representative image on a 6 μ m × 6 μ m area, which demonstrates a very dense coverage with MoS₂ domains (dark contrast). The insert of Figure 1 allows us to better distinguish the domain's size and coverage, with typical sizes ranging from 50 to 150 nm and an estimated surface coverage ~35%. Furthermore, the typical triangular shape of these domains can be deduced clearly by a plan view TEM image, as reported in Figure S2 of the Supporting Information.

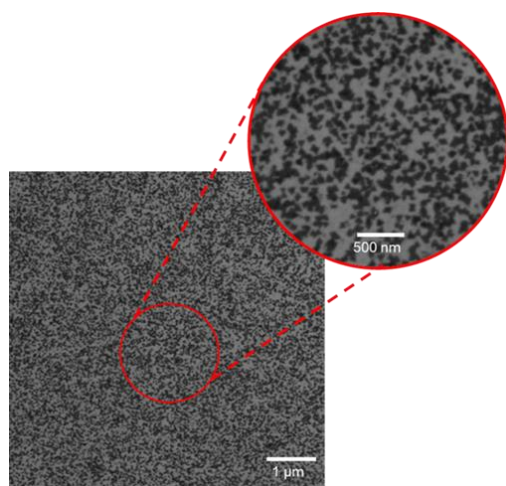


Figure 1. Overview SEM image and magnification (insert) of CVD-grown MoS₂ domains on GaN.

XPS analyses provided surface-sensitive chemical information on the stoichiometry of MoS₂ domains. A near-stoichiometric [S]/[Mo] \approx 2 ratio was deduced by a preliminary elemental analysis. To obtain more detailed information on the Mo oxidation state and Mo-S bonding, the Mo 3d_{5/2}, Mo 3d_{3/2}, and S 2s core-level spectra (located at 229.3, 232.5, and 226.5 eV, respectively) were collected, as reported in Figure 2. In particular, the Mo 3d spectrum confirms that Mo atoms exhibit only the Mo⁴⁺ oxidation state associated with

the 2H-MoS₂ [66], without any contribution at higher oxidation states correlated with the presence of MoO₃ [67].

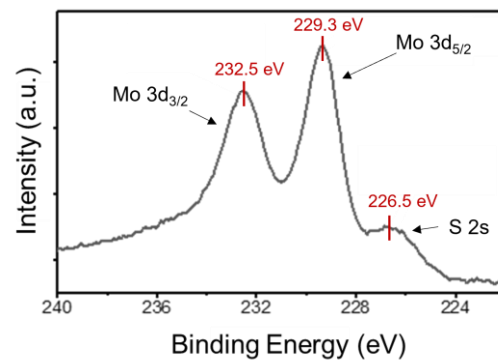


Figure 2. XPS spectra of Mo 3d and S 2s core levels were collected on the as-grown MoS₂ on GaN. The binding energies of the S 2s peak (226.5 eV), Mo3d_{3/2} (232.5 eV), and Mo3d_{5/2} (229.3 eV) peaks associated with Mo atoms with Mo⁴⁺ oxidation are indicated.

Subsequently, Raman spectroscopy was exploited to evaluate the vibrational features of the MoS₂/GaN heterostructure. In particular, the characteristic Raman peaks of GaN, i.e., E₂ low-high energy and A₁(LO), and of MoS₂, i.e., E_{2g} and A_{1g}, can be observed in the wavenumber range between 100 and 1000 cm⁻¹, as shown by the blue and red lines in Figure 3a. The very narrow and intense A₁(LO) peak is consistent with the low *n*-type doping (~10¹⁶ cm⁻³) of the GaN substrate [36]. Focusing on the wavenumber region between 365 and 425 cm⁻¹ reported in Figure 3b, a baseline subtraction and a normalization of the A_{1g} peak were applied with the purpose of extrapolating detailed information on the crystal quality of the CVD-grown MoS₂ flakes. Despite a low-medium A_{1g}/E_{2g} intensity ratio (~0.5), the two main Raman modes could be fitted by narrow single Gaussian peaks. In addition, the deconvolution analysis revealed the presence of a small LO(M) component near the E_{2g} mode, associated with defects or with the domain boundaries [68].

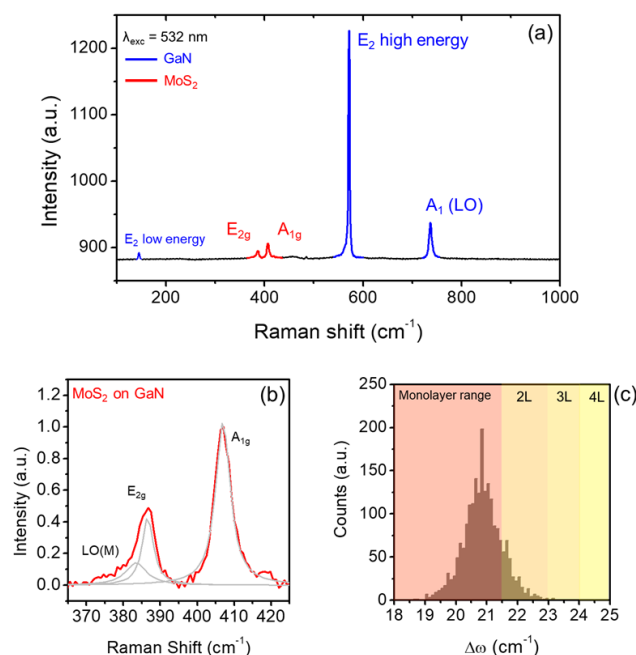


Figure 3. (a) Raman spectrum of the 2D/3D van der Waals heterostructures, showing the GaN and MoS₂ vibrational modes by blue and red lines, respectively. (b) Detail on the MoS₂ peaks after a

deconvolution analysis, which pointed out the presence of a further LO(M) peak at lower wavenumbers. (c) Histogram of the difference between the two peaks ($\Delta\omega = \omega_{A_{1g}} - \omega_{E_{2g}}$).

To obtain statistically relevant information, a wide number of Raman spectra were collected in a $10\ \mu\text{m} \times 10\ \mu\text{m}$ sample. From this array of spectra, we evaluated the homogeneity of the MoS₂ number of layers, by extracting the wavenumber difference of the A_{1g} and E_{2g} Raman modes ($\Delta\omega = \omega_{A_{1g}} - \omega_{E_{2g}}$), which is known to be dependent on MoS₂ thickness [69]. In particular, the statistical distribution of the MoS₂ thickness was obtained from the $\Delta\omega$ histogram in Figure 3c, which shows a mean value of $\Delta\omega = 20.9\ \text{cm}^{-1}$ with a standard deviation of $0.9\ \text{cm}^{-1}$. This distribution shows that the MoS₂ mainly consisted of monolayers, with a small percentage of bilayers.

In addition to the thickness assessment, the A_{1g} and E_{2g} Raman peak positions provide information on the strain and doping of the thin MoS₂ domains, according to the procedure discussed in several recent papers [9,35,70,71]. These doping and strain effects can be due to the CVD growth conditions and to the interaction with the GaN substrate. Figure 4a shows a correlative E_{2g} vs. A_{1g} plot, where the graph is separated in four quadrants by the intersection of the ideal strain (red) and doping (black) lines. The intersection point represented by the light blue square corresponds to the ideal (E_{2g}, A_{1g}) Raman modes of unstrained and undoped monolayer MoS₂. To this aim, the literature values of the (E_{2g}, A_{1g}) peak positions ($\omega_{E_{2g}} = 385\ \text{cm}^{-1}$; $\omega_{A_{1g}} = 405\ \text{cm}^{-1}$) for suspended MoS₂ flakes [5,72] were taken as the best approximation to this ideal condition, since the effects of the interaction with substrate are excluded in that case.

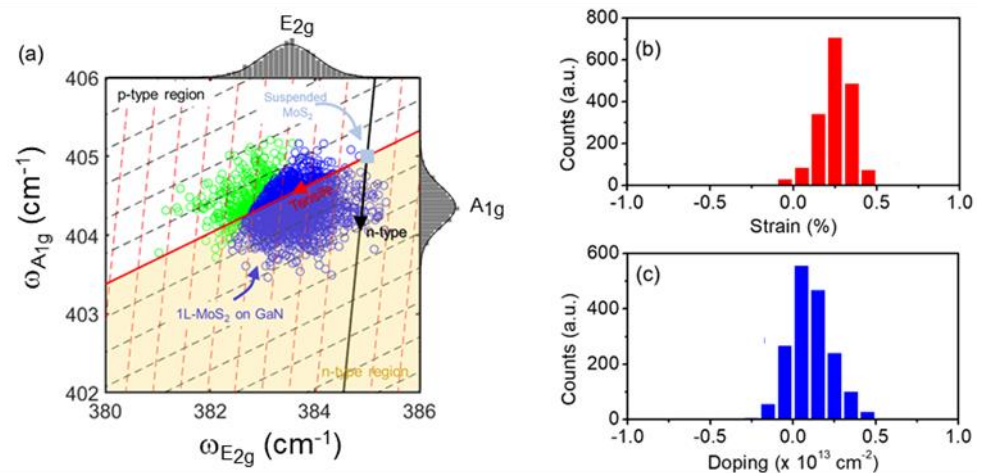


Figure 4. (a) Correlative E_{2g} vs. A_{1g} plot to evaluate the strain and doping effects induced on the MoS₂ flakes by the growth conditions and the interaction with GaN substrate. Blue and green points in panel (a) correspond to the peak positions obtained in the 1L and multilayers regions, respectively. Evaluated strain (b,c) doping distributions for 1L of MoS₂.

The red and black arrows indicate the directions of tensile strain and *n*-type doping regions, respectively, while the opposite side of the red and black lines correspond the compressive strain and *p*-type doping. The *n*-type doping region was indicated by the yellow area to better distinguish it from the *p*-type region (white) in the upper-side of the graph. The experimental values of the peak positions from the same array of Raman spectra used in Figure 3 are reported by the empty circles in the graph of Figure 4a. The corresponding histograms of the E_{2g} and A_{1g} peak values are also reported on the upper-side and right-side of the graph (grey bars). In Figure 4a, the blue and green points correspond to the peaks' positions obtained in the 1L and 2L (or multilayer) regions, respectively, as determined in the histogram of Figure 3c. For 1L of MoS₂, an average tensile strain of around 0.2% and light *n*-type doping ($<0.1 \times 10^{13}\ \text{cm}^{-2}$) is deduced from the correlative plot in Figure 4a. A more precise evaluation was obtained by evaluating the strain and doping

for each data point of 1L-MoS₂ and by building the histograms of the strain and doping distribution, as reported in Figure 4b,c. A tensile strain of $0.25 \pm 0.10\%$ and a *n*-type doping of $(0.11 \pm 0.12) \times 10^{13} \text{ cm}^{-2}$ were deduced from the mean value and the standard deviation of these two distributions. Notably, nearly unstrained monolayer MoS₂ on GaN has been recently reported also under different CVD growth conditions, resulting in the formation of micrometer size triangular domains [42] or continuous monolayer MoS₂ films [36,42]. These observations confirm the key role played by the low mismatch of the in-plane lattice constants (<1%) and of thermal expansion coefficients between MoS₂ and GaN. Furthermore, the low *n*-type doping is consistent with the typically reported unintentional *n*-type doping of MoS₂ obtained by exfoliation from bulk crystals, probably induced by the presence of native defects (such as sulfur vacancies) [73,74]. On the other hand, *n*- or *p*-type doping behavior has been reported for MoS₂ grown by CVD approaches, depending on several factors, such as the content of MoO₃ residues in the films (typically responsible for *p*-type doping) or the peculiar interaction with the underlying substrate. In this regard, the average *n*-type doping of the CVD-grown MoS₂ on GaN in the present work is consistent with the absence of MoO₃ residues, as indicated by XPS analyses in Figure 2.

Figure 5a shows a representative PL spectrum of the MoS₂/GaN obtained with a laser excitation wavelength of 532 nm. The intense PL emission is a further confirmation of the good MoS₂ crystal quality achieved by CVD. In fact, a high density of defects in MoS₂ films would involve non-radiative recombination of excitons, causing PL quenching [75,76].

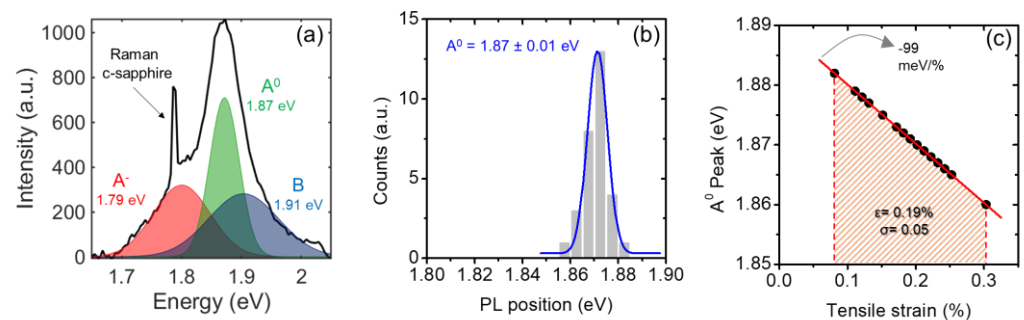


Figure 5. (a) Photoluminescence spectrum of MoS₂ on GaN, where the two excitons (A⁰ and B) and trion (A⁻) components were extracted after deconvolution analysis. (b) Distribution of the A⁰ exciton peak positions evaluated at different points of the sample. (c) A⁰ peak positions as a function of the tensile strain.

In detail, a deconvolution analysis performed on the spectrum of Figure 5a revealed the coexistence of three components. The A⁰ and B peaks located at 1.87 eV and 1.91 eV correspond to the excitonic emissions due to the spin-orbit coupling splitting of the MoS₂ valence band [77]. Differently, the red-area convoluted peak at lower energy (1.79 eV) is related to the trion (also known as charged exciton) contribution, consisting of the bound state between an electron (or hole) and an exciton [78,79]. This deconvolution analysis confirms the absence of the defect-related peak X_D, typically located at lower energy with respect to the trionic component. After a statistical analysis of different MoS₂/GaN areas, we built a histogram of the excitonic peak energy A⁰, as reported in Figure 5b. This distribution showed a standard deviation of 10 meV around a mean value of 1.87 eV, indicating a spatially uniform PL emission from the sample surface. The energy of the main PL peak (A⁰) has been shown in the literature to be dependent on the strain of MoS₂, with a red shift of the peak at increasing strain with a rate of $-99 \text{ meV}/\%$ [72]. By applying this linear relation, the values of the tensile strain were calculated from the experimental values of the A⁰ peak energy, as reported in Figure 5c. From this analysis, strain values in the range between 0.08 and 0.3% were deduced, with a mean value of $\epsilon = 0.19 \pm 0.05\%$, in good agreement with the previous estimation by Raman measurements.

The interface properties of the 2D/3D vdW heterostructure were characterized by cross-sectional transmission electron microscopy analyses. Figure 6a is an overview HR-TEM image, showing a monolayer MoS₂ conformal to the crystalline GaN substrate, similarly to other reports for MoS₂ grown by CVD approaches on GaN or other crystalline hexagonal substrates [36,37,80,81]. Furthermore, the presence of a vdW gap between the single layer of MoS₂ and GaN surface is clearly demonstrated by the high-resolution HAADF-STEM image in Figure 6b. This is a direct indication of a weak bond between MoS₂ and the underlying GaN crystal. Notably, this high-resolution STEM analysis reveals a different structure of the first crystalline planes of GaN with respect to the underlying bulk crystal. As reported in previous structural investigations of CVD MoS₂/GaN heterostructures [37], such differences can be attributed to partial oxidation of the GaN surface during the MoS₂ growth process or some form of surface reconstruction.

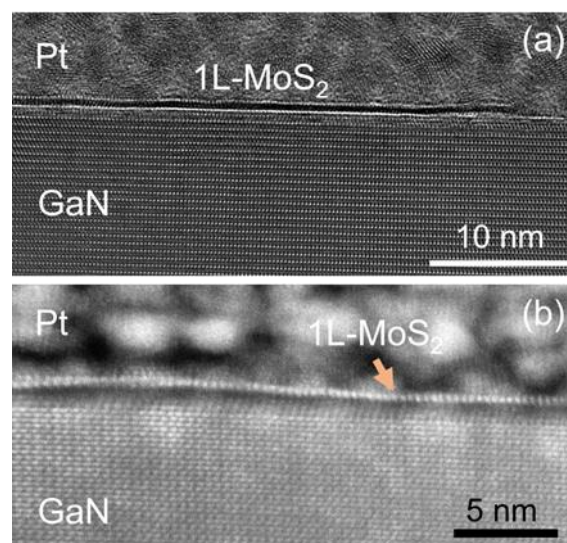


Figure 6. (a) Overview the HR-TEM image showing 1L of MoS₂ conformal to the (0001) basal plane of GaN. (b) Atomic resolution STEM image showing the presence of a van der Waals gap between 1L of MoS₂ and the underlying GaN surface.

In the last section of this paper, DFT calculations have been performed to obtain a deeper physical understanding of the type of interaction and electronic properties of the MoS₂/GaN interface. In this context, it is worth mentioning that DFT calculations of this kind of heterostructure have been recently reported in the literature [57,59]. A S-Ga equilibrium distance of 0.232 nm in Ref. [57] and 0.237 nm in Ref. [59] was evaluated for the ideal case of a lattice-matched interface between MoS₂ and Ga-terminated GaN, indicating the formation of a covalent-like bond at the interface. Clearly, those calculation results do not match with the results of atomic resolution TEM analyses of the MoS₂/GaN heterostructure obtained in the present work and with those recently reported by different research groups [37,47], which showed the presence of a larger vdW gap separating S from Ga atoms.

As a matter of fact, under real experimental conditions, the GaN(0001) surface can be subjected to reconstructions or to oxidations. Hence, to provide a more complete description of the MoS₂/GaN system, we performed DFT calculations of the heterostructure considering three different model configurations of the GaN surface (see Figure S3 of the Supporting Information): (i) the ideal Ga-terminated GaN, analogous to the one reported in the literature; (ii) the passivation of the Ga termination with an oxygen coverage of one monolayer; and (iii) the formation of an ultra-thin crystalline Ga₂O₃ oxide. The analysis of the DFT predictions for these three configurations has been compared with the experimental results for our system.

Figure 7a shows the most stable configuration obtained by DFT calculations of the ideal Ga-terminated GaN surface, where a Ga-S equilibrium distance of 0.241 nm was

estimated, in close agreement with recent literature reports [57,59]. Furthermore, the calculated band structure for this system (reported in Figure 7b) shows a high n -type doping of MoS₂ and strong perturbation of its energy bands. As a matter of fact, this ideal configuration of the MoS₂/GaN(0001) interface does not provide a real representation of the system. For this reason, we performed DFT calculations considering the presence of O atoms bonded to the GaN(0001) surface.

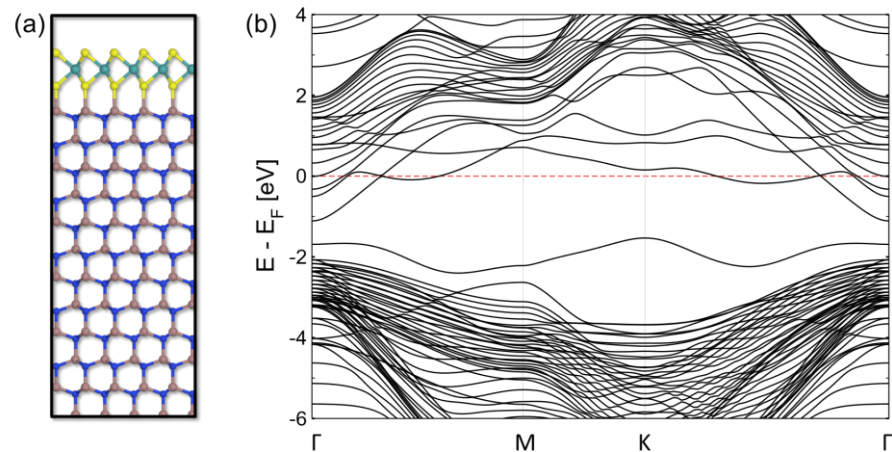


Figure 7. (a) Structure of the interface between Ga-terminated GaN and monolayer MoS₂ seen from the (11 $\bar{2}$ 0) plane and (b) the energy band structure of this heterostructure. E_F refers to the calculated Fermi level of the system.

Figure 8a,b shows the results for oxygen-passivated Ga terminations with one monolayer O surface coverage. Also in this case, a covalent interface interaction was obtained, which again deviates from the experimental evidence of a weak van der Waals bonding. The theoretically calculated strong interface coupling had a structural impact only on the topmost Ga layer of the substrate and perturbed the MoS₂ bands with respect to those of a freestanding MoS₂ layer (see Figure S4 of the Supporting Information).

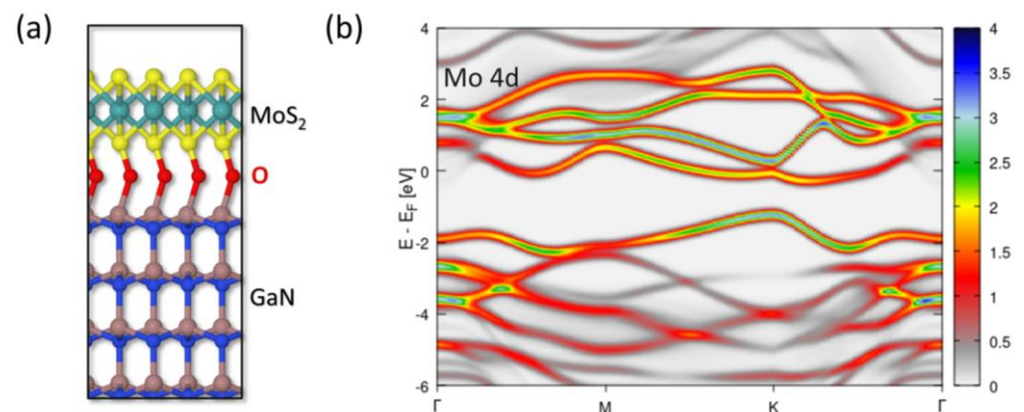


Figure 8. (a) Structure of the MoS₂/GaN interface with oxygen passivation of Ga terminations with monolayer O surface coverage, seen from the (1 $\bar{1}$ 00) plane. (b) Electronic contributions of Mo d orbitals in the wavevector-resolved projected density of states along the Γ -M-K- Γ Brillouin zone path. E_F refers to the calculated Fermi level of the system.

We thereon considered the formation of an ultra-thin layer of surface native oxide Ga_2O_3 , which significantly reduces the surface energy of $\text{GaN}(0001)$ as compared to other oxidized reconstructions [82]. This layer is characterized by an O–Ga–O trilayer which inverts the polarization of the GaN layer along the $[0001]$ direction, followed by a Ga–O bilayer that terminates the oxidized surface (Figure 9a). The interaction of this Ga_2O_3 -terminated GaN surface with MoS_2 gave rise to a van der Waals interface with an oxygen-sulfur interface distance of 3.05 Å. This distance is significantly larger than the one reported in the literature for the ideal $\text{MoS}_2/\text{GaN}(0001)$ system [57,59] and it is in better agreement with the experimental observations of a vdW gap at the interface. Figure 9b–e shows the total and partial electronic contributions (Mo d and Ga s orbitals) in the density of states of the heterosystem, plotted at the close Γ -M-K- Γ path of the Brillouin zone. The pristine bands of MoS_2 are clearly preserved in this case, showing a direct band gap of 1.7 eV at the K point of the Brillouin zone. We note that such an interface induces a significant *n*-type doping for the MoS_2 sheet, due to a shift of surface Ga s states deriving from the oxide layer towards lower energies (because of Ga–O bonding). Such a shift brings the Fermi level of the system close to the conduction band of the MoS_2 layer. Overall, the theoretical calculations indicate that a van der Waals interface at the $\text{MoS}_2/\text{GaN}(0001)$ heterosystem is expected when an ultra-thin Ga_2O_3 native oxide forms at the substrate's surface, whereas it is rather improbable for low surface oxygen coverages.

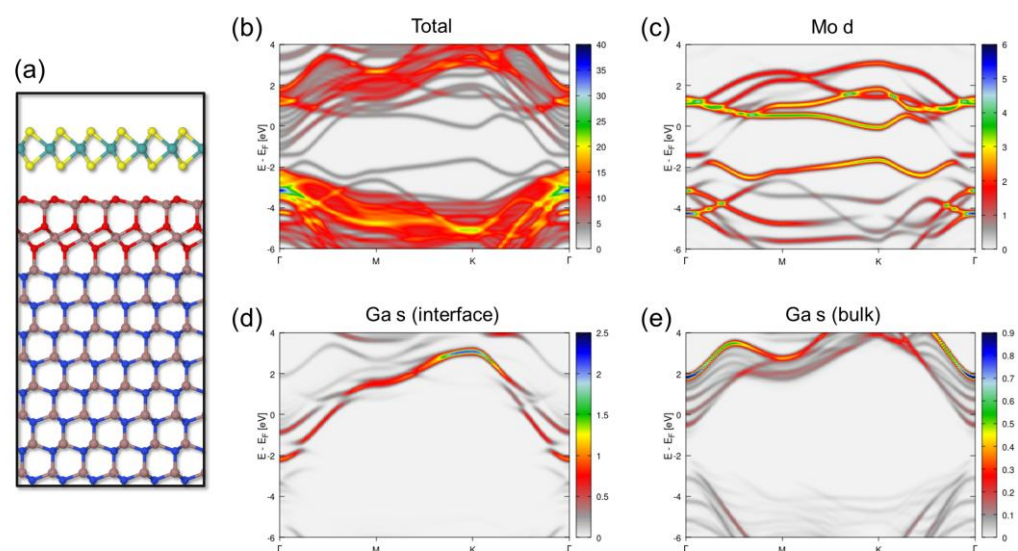


Figure 9. (a) Structure of the oxidized $\text{MoS}_2/\text{GaN}(0001)$ interface, showing the formation of an ultra-thin layer of native oxide Ga_2O_3 , seen from the $(11\bar{2}0)$ plane. Wavevector-resolved projected density of states along the Γ -M-K- Γ Brillouin zone path for (b) all electronic states, (c) contributions of Mo d orbitals, (d) contributions of surface Ga s orbitals, and (e) contributions of bulk Ga s orbitals. E_F refers to the calculated Fermi level of the system.

4. Conclusions

The structural, chemical, vibrational, and light emission properties of the CVD-grown MoS_2 heterostructure with GaN have been investigated in detail by several microscopic and spectroscopic techniques and by DFT calculations. XPS analyses on as-grown samples showed the formation of stoichiometric MoS_2 . According to micro-Raman spectroscopy, monolayer MoS_2 domains on GaN exhibit an average *n*-type doping of $(0.11 \pm 0.12) \times 10^{13} \text{ cm}^{-2}$ and a small tensile strain $\varepsilon \approx 0.25\%$, whereas an intense light emission at 1.87 eV was revealed by PL analyses. Furthermore, a gap at the interface was shown by cross-sectional TEM analysis, confirming the vdW bond between MoS_2 and GaN . Finally, DFT calculations of the heterostructure were carried out, considering three different configurations of the interface, i.e., (i) an ideal Ga-terminated $\text{GaN}(0001)$ surface, (ii) the

passivation of the Ga surface by a monolayer of oxygen, and (iii) the presence of an ultrathin Ga₂O₃ layer. This latter configuration is the only one which accounts for the formation of a vdW bond at the interface and a significant *n*-type doping of MoS₂, in agreement with the experimental observations. These results provide an insight on the MoS₂/GaN interfacial properties, which rule the current injection mechanisms across these vdW heterostructures. Further studies on how to tailor the structural/chemical properties of this interface will be crucial for future applications in electronics and optoelectronics.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/nano14020133/s1>. Figure S1: AFM image of GaN-on-c-sapphire with an RMS of about 0.3 nm. Figure S2: In-plane TEM image of MoS₂ triangular flakes on a carbon grid. Figure S3: Interface models used for the DFT calculations of the MoS₂/GaN heterostructure, considering three different configurations of the GaN surface. Figure S4: Band structure of freestanding MoS₂ based on DFT calculations.

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References

1. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS₂ transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150.
2. Geim, A.K.; Grigorieva, I.V. Van der Waals heterostructures. *Nature* **2013**, *499*, 419–425.
3. Kolobov, A.V.; Tominaga, J. *Two-Dimensional Transition-Metal Dichalcogenides*; Springer: Berlin/Heidelberg, Germany, 2016; Volume 239.
4. Jariwala, D.; Sangwan, V.K.; Lauhon, L.J.; Marks, T.J.; Hersam, M.C. Emerging device applications for semiconducting two-dimensional transition metal dichalcogenides. *ACS Nano* **2014**, *8*, 1102–1120.
5. Nawz, T.; Safdar, A.; Hussain, M.; Lee, S.D.; Siyar, M. Graphene to advanced MoS₂: A review of structure, synthesis, and optoelectronic device application. *Crystals* **2020**, *10*, 902.
6. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.Y.; Galli, G.; Wang, F. Emerging photoluminescence in monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275.
7. Mak, K.F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T.F. Atomically thin MoS₂: A new direct-gap semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.
8. Zeng, S.; Tang, Z.; Liu, C.; Zhou, P. Electronics based on two-dimensional materials: Status and outlook. *Nano Res.* **2021**, *14*, 1752–1767.
9. Radisavljevic, B.; Whitwick, M.B.; Kis, A. Integrated circuits and logic operations based on single-layer MoS₂. *ACS Nano* **2011**, *5*, 9934–9938.
10. Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive photodetectors based on monolayer MoS₂. *Nat. Nanotechnol.* **2013**, *8*, 497–501.
11. Wang, Q.H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J.N.; Strano, M.S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* **2012**, *7*, 699–712.
12. Singh, E.; Singh, P.; Kim, K.S.; Yeom, G.Y.; Nalwa, H.S. Flexible molybdenum disulfide (MoS₂) atomic layers for wearable electronics and optoelectronics. *ACS Appl. Mater. Interf.* **2019**, *11*, 11061–11105.

13. Late, D.J.; Huang, Y.K.; Liu, B.; Acharya, J.; Shirodkar, S.N.; Luo, J.; Yan, A.; Charles, D.; Waghmare, U.V.; Dravid, V.P.; et al. Sensing behavior of atomically thin-layered MoS₂ transistors. *ACS Nano* **2013**, *7*, 4879–4891.
14. Perkins, F.K.; Friedman, A.L.; Cobas, E.; Campbell, P.M.; Jernigan, G.G.; Jonker, B.T. Chemical vapor sensing with monolayer MoS₂. *Nano Lett.* **2013**, *13*, 668–673.
15. Chang, K.; Mei, Z.; Wang, T.; Kang, Q.; Ouyang, S.; Ye, J. MoS₂/graphene cocatalyst for efficient photocatalytic H₂ evolution under visible light irradiation. *ACS Nano* **2014**, *8*, 7078–7087.
16. Parzinger, E.; Miller, B.; Blaschke, B.; Garrido, J.A.; Ager, J.W.; Holleitner, A.; Wurstbauer, U. Photocatalytic stability of single- and few-layer MoS₂. *ACS Nano* **2015**, *9*, 11302–11309.
17. Wi, S.; Kim, H.; Chen, M.; Nam, H.; Guo, L.J.; Meyhofer, E.; Liang, X. Enhancement of photovoltaic response in multilayer MoS₂ induced by plasma doping. *ACS Nano* **2014**, *8*, 5270–5281.
18. Lopez-Sanchez, O.; Llado, A.E.; Koman, V.; Fontcuberta i Morral, A.; Radenovic, A.; Kis, A. Light generation and harvesting in a van der Waals heterostructure. *ACS Nano* **2014**, *8*, 3042–3048.
19. Xia, F.; Wang, H.; Xiao, D.; Dubey, M.; Ramasubramaniam, A. Two-dimensional material nanophotonics. *Nat. Phot.* **2014**, *8*, 899–907.
20. Low, T.; Chaves, A.; Caldwell, J.D.; Kumar, A.; Fang, N.X.; Avouris, P.; Heinz, T.Y.; Guinea, F.; Martin-Moreno, L.; Koppens, F. Polaritons in layered two-dimensional materials. *Nat. Mater.* **2017**, *16*, 182–194.
21. Xu, X.; Yao, W.; Xiao, D.; Heinz, T.F. Spin and pseudospins in layered transition metal dichalcogenides. *Nat. Phys.* **2014**, *10*, 343–350.
22. Mak, K.F.; He, K.; Shan, J.; Heinz, T.F. Control of valley polarization in monolayer MoS₂ by optical helicity. *Nat. Nanotechnol.* **2012**, *7*, 494–498.
23. Mak, K.F.; Xiao, D.; Shan, J. Light–valley interactions in 2D semiconductors. *Nat. Photonics* **2018**, *12*, 451–460.
24. Kim, J.; Jin, C.; Chen, B.; Cai, H.; Zhao, T.; Lee, P.; Khan, S.; Watanabe, K.; Taniguchi, T.; Tongay, S.; et al. Observation of ultralong valley lifetime in WSe₂/MoS₂ heterostructures. *Sci. Adv.* **2017**, *3*, e1700518.
25. Yu, L.; Lee, Y.H.; Ling, X.; Santos, E.J.; Shin, Y.C.; Lin, Y.; Dubey, M.; Kaxiras, E.; Kong, J.; Wang, H.; et al. Graphene/MoS₂ hybrid technology for large-scale two-dimensional electronics. *Nano Lett.* **2014**, *14*, 3055–3063.
26. Cho, B.; Yoon, J.; Lim, S.K.; Kim, A.R.; Kim, D.H.; Park, S.G.; Kwon, J.D.; Lee, Y.J.; Lee, K.H.; Lee, B.H.; et al. Chemical sensing of 2D graphene/MoS₂ heterostructure device. *ACS Appl. Mater. Interf.* **2015**, *7*, 16775–16780.
27. Kistanov, A.A.; Shcherbinin, S.A.; Ustiuzhanina, S.V.; Huttula, M.; Cao, W.; Nikitenko, V.R.; Prezhdo, O.V. First-principles prediction of two-dimensional B₃C₂P₃ and B₂C₄P₂: Structural stability, fundamental properties, and renewable energy applications. *J. Phys. Chem. Lett.* **2021**, *12*, 3436–3442.
28. Liu, Y.; Weiss, N.O.; Duan, X.; Cheng, H.C.; Huang, Y.; Duan, X. Van der Waals heterostructures and devices. *Nat. Rev. Mater.* **2016**, *1*, 16042.
29. Jariwala, D.; Marks, T.J.; Hersam, M.C. Mixed-dimensional van der Waals heterostructures. *Nat. Mater.* **2017**, *16*, 170–181.
30. Wang, P.; Jia, C.; Huang, Y.; Duan, X. Van der Waals heterostructures by design: From 1D and 2D to 3D. *Matter* **2021**, *4*, 552–581.
31. Butanovs, E.; Kadiwala, K.; Gopejenko, A.; Bocharov, D.; Piskunov, S.; Polyakov, B. Different strategies for GaN–MoS₂ and GaN–WS₂ core–shell nanowire growth. *Appl. Surf. Sci.* **2022**, *590*, 153106.
32. Dezfuli, F.M.; Boochani, A.; Parhizgar, S.S.; Darabi, E. Electronic, optical and thermoelectric properties of MoS₂–GaN interface, *International. J. Mod. Phys. B* **2022**, *36*, 2250096.
33. Kimoto, T.; Cooper, J.A. *Fundamentals of Silicon Carbide Technology: Growth, Characterization, Devices and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2014.
34. Roccaforte, F.; Fiorenza, P.; Greco, G.; Lo Nigro, R.; Giannazzo, F.; Iucolano, F.; Saggio, M. Emerging trends in wide band gap semiconductors (SiC and GaN) technology for power devices. *Microelectron. Eng.* **2018**, *187*, 66–77.
35. Giannazzo, F.; Panasci, S.E.; Schilirò, E.; Roccaforte, F.; Koos, A.; Nemeth, M.; Pécz, B. Esaki diode behavior in highly uniform MoS₂/silicon carbide heterojunctions. *Adv. Mater. Interf.* **2022**, *9*, 2200915.
36. Giannazzo, F.; Panasci, S.E.; Schilirò, E.; Greco, G.; Roccaforte, F.; Sfunzia, G.; Nicotra, G.; Cannas, M.; Agnello, S.; Frayssinet, E.; et al. Atomic resolution interface structure and vertical current injection in highly uniform MoS₂ heterojunctions with bulk GaN. *Appl. Surf. Sci.* **2023**, *631*, 157513.
37. O'Regan, T.P.; Ruzmetov, D.; Neupane, M.R.; Burke, R.A.; Herzog, A.A.; Zhang, K.; Birdwell, A.G.; Taylor, D.E.; Byrd, E.F.C.; Walck, S.D.; et al. Structural and electrical analysis of epitaxial 2D/3D vertical heterojunctions of monolayer MoS₂ on GaN. *Appl. Phys. Lett.* **2017**, *111*, 051602.
38. Liu, Y.; Fang, Y.; Yang, D.; Pi, X.; Wang, P. Recent progress of heterostructures based on two dimensional materials and wide bandgap semiconductors. *J. Phys. Condens. Matter* **2022**, *34*, 183001.
39. Singh, D.K.; Pant, R.K.; Nanda, K.K.; Krupanidhi, S.B. Differentiation of ultraviolet/visible photons from near infrared photons by MoS₂/GaN/Si-based photodetector. *Appl. Phys. Lett.* **2021**, *119*, 121102.
40. Jain, S.K.; Low, M.X.; Taylor, P.D.; Tawfik, S.A.; Spencer, M.J.; Kuriakose, S.; Arash, A.; Xu, C.; Sriram, S.; Gupta, G.; et al. 2D/3D hybrid of MoS₂/GaN for a high-performance broadband photodetector. *ACS Appl. Elect. Mater.* **2021**, *3*, 2407–2414.
41. Stockmeier, M.; Müller, R.; Sakwe, S.A.; Wellmann, P.J.; Magerl, A. On the lattice parameters of silicon carbide. *J. Appl. Phys.* **2009**, *105*, 033511.

42. Ruzmetov, D.; Zhang, K.; Stan, G.; Kalanyan, B.; Bhimanapati, G.R.; Eichfeld, S.M.; Burke, R.A.; Shah, P.B.; O'Regan, T.P.; Crowne, F.J.; et al. Vertical 2D/3D semiconductor heterostructures based on epitaxial molybdenum disulfide and gallium nitride. *ACS Nano* **2016**, *10*, 3580–3588.
43. Wan, Y.; Xiao, J.; Li, J.; Fang, X.; Zhang, K.; Fu, L.; Li, P.; Song, Z.; Zhang, H.; Wang, Y.; et al. Epitaxial Single-Layer MoS₂ on GaN with Enhanced Valley Helicity. *Adv. Mater.* **2018**, *30*, 1703888.
44. Murray, R.; Evans, B. The thermal expansion of 2H-MoS₂ and 2H-WSe₂ between 10 and 320 K. *J. Appl. Crystallogr.* **1979**, *12*, 312.
45. Reeber, R.R.; Wang, K. Lattice parameters and thermal expansion of GaN. *J. Mater. Res.* **2000**, *15*, 40–44.
46. Moun, M.; Kumar, M.; Garg, M.; Pathak, R.; Singh, R. Understanding of MoS₂/GaN heterojunction diode and its photodetection properties. *Sci. Rep.* **2018**, *8*, 11799.
47. Ruzmetov, D.; Neupane, M.R.; Herzing, A.; O'Regan, T.P.; Mazzoni, A.; Chin, M.L.; Burke, R.A.; Crowne, F.J.; Birdwell, A.G.; Taylor, D.E.; et al. Van der Waals interfaces in epitaxial vertical metal/2D/3D semiconductor heterojunctions of monolayer MoS₂ and GaN. *2D Mater.* **2018**, *5*, 045016.
48. Desai, P.; Ranade, A.K.; Shinde, M.; Todankar, B.; Mahyavanshi, R.D.; Tanemura, M.; Kalita, G. Growth of uniform MoS₂ layers on free-standing GaN semiconductor for vertical heterojunction device application. *J. Mater. Sci. Mater. Electron.* **2020**, *31*, 2040–2048.
49. Krishnamoorthy, S.; Lee, E.W.; Lee, C.H.; Zhang, Y.; McCulloch, W.D.; Johnson, J.M.; Hwang, J.; Wu, Y.; Rajan, S. High current density 2D/3D MoS₂/GaN Esaki tunnel diodes. *Appl. Phys. Lett.* **2016**, *109*, 183505.
50. Zhuo, R.; Wang, Y.; Wu, D.; Lou, Z.; Shi, Z.; Xu, T.; Xu, J.; Tian, Y.; Li, X. High-performance self-powered deep ultraviolet photodetector based on MoS₂/GaN p–n heterojunction. *J. Mater. Chem. C* **2018**, *6*, 299–303.
51. Janardhanam, V.; Zummukhozol, M.; Jyothi, I.; Shim, K.H.; Choi, C.J. Self-powered MoS₂/n-type GaN heterojunction photodetector with broad spectral response in ultraviolet–visible–near-infrared range. *Sens. Actuators A Phys.* **2023**, *360*, 114534.
52. Xue, F.; Yang, L.; Chen, M.; Chen, J.; Yang, X.; Wang, L.; Chen, L.; Pan, C.; Wang, Z.L. Enhanced photoresponsivity of the MoS₂-GaN heterojunction diode via the piezo-phototronic effect. *NPG Asia Mater.* **2017**, *9*, e418.
53. Zahir, N.H.; Ripain, A.H.A.; Said, S.M.; Zakaria, R. Sulfurization engineering of single-zone CVD vertical and horizontal MoS₂ on p-GaN heterostructures for self-powered UV photodetectors. *Nanoscale Adv.* **2023**, *5*, 879–892.
54. Vashishtha, P.; Prajapat, P.; Sharma, A.; Singh, P.; Walia, S.; Gupta, G. Self-Driven UVC–NIR Broadband Photodetector with High-Temperature Reliability Based on a Coco Palm-Like MoS₂/GaN Heterostructure. *ACS Appl. Electr. Mater.* **2023**, *5*, 1891–1902.
55. Yang, P.; Yang, H.; Wu, Z.; Liao, F.; Guo, X.; Deng, J.; Xu, Q.; Wang, H.; Sun, J.; Chen, F.; et al. Large-Area Monolayer MoS₂ Nanosheets on GaN Substrates for Light-Emitting Diodes and Valley-Spin Electronic Devices. *ACS Appl. Nano Mater.* **2021**, *4*, 12127–12136.
56. Gao, R.; Liu, H.; Liu, H.; Yang, J.; Yang, F.; Wang, T. Two-dimensional MoS₂/GaN van der Waals heterostructures: Tunable direct band alignments and excitonic optical properties for photovoltaic applications. *J. Phys. D Appl. Phys.* **2020**, *53*, 095107.
57. Poudel, Y.; Sławińska, J.; Gopal, P.; Seetharaman, S.; Hennighausen, Z.; Kar, S.; D'souza, F.; Nardelli, M.B.; Neogi, A. Absorption and emission modulation in a MoS₂-GaN (0001) heterostructure by interface phonon–exciton coupling. *Photonics Res.* **2019**, *7*, 1511–1520.
58. Henck, H.; Aziza, Z.B.; Zill, O.; Pierucci, D.; Naylor, C.H.; Silly, M.G.; Gogneau, N.; Oehler, F.; Collin, S.; Brault, J.; et al. Interface dipole and band bending in the hybrid p–n heterojunction MoS₂/GaN (0001). *Phys. Rev. B* **2017**, *96*, 115312.
59. Zhang, Z.; Qian, Q.; Li, B.; Chen, K.J. Interface Engineering of Monolayer MoS₂/GaN Hybrid Heterostructure: Modified Band Alignment for Photocatalytic Water Splitting Application by Nitridation Treatment. *ACS Appl. Mater. Interf.* **2018**, *10*, 17419–17426.
60. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Guido, L.C.; Cococcioni, M.; Dabo, I. et al. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* **2009**, *21*, 395502.
61. Hamada, I. van der Waals density functional made accurate. *Phys. Rev. B* **2014**, *89*, 121103.
62. Prandini, G.; Marrazzo, A.; Castelli, I.E.; Mounet, N.; Marzari, N. Precision and efficiency in solid-state pseudopotential calculations. *Npj Comput. Mater.* **2018**, *4*, 72.
63. Lejaeghere, K.; Bihlmayer, G.; Björkman, T.; Blaha, P.; Blügel, S.; Blum, V.; Caliste, D.; Castelli, I.E.; Clark, S.J.; Corso, A.D.; et al. Reproducibility in density functional theory calculations of solids. *Science* **2016**, *351*, aad3000.
64. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
65. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.
66. Sarma, S.; Ray, S.C. Trigonal (1T) and hexagonal (2H) mixed phases MoS₂ thin films. *Appl. Surf. Sci.* **2019**, *474*, 227–231.
67. Baker, M.A.; Gilmore, R.; Lenardi, C.; Gissler, W. XPS investigation of preferential sputtering of S from MoS₂ and determination of MoS_x stoichiometry from Mo and S peak positions. *Appl. Surf. Sci.* **1999**, *150*, 255–262.
68. Mignuzzi, S.; Pollard, A.J.; Bonini, N.; Brennan, B.; Gilmore, I.S.; Pimenta, M.A.; Richards, D.; Roy, D. Effect of disorder on Raman scattering of single-layer MoS₂. *Phys. Rev. B* **2015**, *91*, 195411.
69. Lee, C.; Yan, H.; Brus, L.E.; Heinz, T.F.; Hone, J.; Ryu, S. Anomalous lattice vibrations of single- and few-layer MoS₂. *ACS Nano* **2010**, *4*, 2695–2700.

70. Panasci, S.E.; Schilirò, E.; Greco, G.; Cannas, M.; Gelardi, F.M.; Agnello, S.; Roccaforte, F.; Giannazzo, F. Strain, Doping, and Electronic Transport of Large Area Monolayer MoS₂ Exfoliated on Gold and Transferred to an Insulating Substrate. *ACS Appl. Mater. Interf.* **2021**, *13*, 31248–31259.
71. Schilirò, E.; Panasci, S.E.; Mio, A.M.; Nicotra, G.; Agnello, S.; Pécz, B.; Radnoczi, G.Z.; Deretzis, I.; La Magna, A.; Roccaforte, F.; et al. Direct atomic layer deposition of ultra-thin Al₂O₃ and HfO₂ films on gold-supported monolayer MoS₂. *Appl. Surf. Sci.* **2023**, *630*, 157476.
72. Lloyd, D.; Liu, X.; Christopher, J.W.; Cantley, L.; Wadehra, A.; Kim, B.L.; Goldberg, B.B.; Swan, A.K.; Bunch, J.S. Band gap engineering with ultralarge biaxial strains in suspended monolayer MoS₂. *Nano Lett.* **2016**, *16*, 5836–5841.
73. Mak, K.F.; He, K.; Lee, C.; Lee, G.H.; Hone, J.; Heinz, T.F.; Shan, J. Tightly bound trions in monolayer MoS₂. *Nat. Mater.* **2013**, *12*, 207–211.
74. Mouri, S.; Miyauchi, Y.; Matsuda, K. Tunable photoluminescence of monolayer MoS₂ via chemical doping. *Nano Lett.* **2013**, *13*, 5944–5948.
75. Lee, J.Y.; Kim, J.H.; Jung, Y.; Shin, J.C.; Lee, Y.; Kim, K.; Kim, N.; van der Zende, A.M.; Son, J.; Lee, G.H. Evolution of defect formation during atomically precise desulfurization of monolayer MoS₂. *Commun. Mater.* **2021**, *2*, 80.
76. Panasci, S.E.; Koos, A.; Schilirò, E.; Di Franco, S.; Greco, G.; Fiorenza, P.; Roccaforte, F.; Agnello, S.; Cannas, M.; Gelardi, F.M.; et al. Multiscale Investigation of the Structural, Electrical and Photoluminescence Properties of MoS₂ Obtained by MoO₃ Sulfurization. *Nanomaterials* **2022**, *12*, 182.
77. Zhu, Z.Y.; Cheng, Y.C.; Schwingenschlögl, U. Giant spin-orbit-induced spin splitting in two-dimensional transition metal dichalcogenide semiconductors. *Phys. Rev. B* **2011**, *84*, 153402.
78. Scheuschner, N.; Ochedowski, O.; Kaulitz, A.M.; Gillen, R.; Schleberger, M.; Maultzsch, J. Photoluminescence of freestanding single- and few-layer MoS₂. *Phys. Rev. B* **2014**, *89*, 125406.
79. Panasci, S.E.; Schilirò, E.; Migliore, F.; Cannas, M.; Gelardi, F.M.; Roccaforte, F.; Giannazzo, F.; Agnello, S. Substrate impact on the thickness dependence of vibrational and optical properties of large area MoS₂ produced by gold-assisted exfoliation. *Appl. Phys. Lett.* **2021**, *119*, 093103.
80. Panasci, S.E.; Schilirò, E.; Koos, A.; Nemeth, M.; Cannas, M.; Agnello, S.; Roccaforte, F.; Pécz, B.; Giannazzo, F. Micrometer-size crystalline monolayer MoS₂ domains obtained by sulfurization of molybdenum oxide ultrathin films. *Microelectr. Eng.* **2023**, *274*, 111967.
81. Panasci, S.E.; Deretzis, I.; Schilirò, E.; La Magna, A.; Roccaforte, F.; Koos, A.; Pécz, B.; Agnello, S.; Cannas, M.; Giannazzo, F. Interface structure and doping of CVD grown MoS₂ on 4H-SiC by microscopic analyses and ab initio calculations. *Phys. Status Solidi Rapid Res. Lett.* **2023**, *17*, 2300218.
82. Dycus, J.H.; Mirrieles, K.J.; Grimley, E.D.; Kirste, R.; Mita, S.; Sitar, Z.; Collazo, R.; Irving, D.L.; LeBeau, J.M. Structure of ultrathin native oxides on III–nitride surfaces. *ACS Appl. Mater. Interf.* **2018**, *10*, 10607–10611.

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