



Communication The Role of Carbon in Metal–Organic Chemical Vapor Deposition-Grown MoS₂ Films

Tianyu Hou¹, Di Li^{2,*}, Yan Qu³, Yufeng Hao¹ and Yun Lai¹

- ¹ National Laboratory of Solid State Microstructures, School of Physics, College of Engineering and Applied Sciences, Jiangsu Key Laboratory of Artificial Functional Materials and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, China
- ² Key Laboratory of Photovoltaic and Energy Conservation Materials, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China
- ³ The Sixth Element (Changzhou) Materials Technology Co., Ltd. and Jiangsu Jiangnan Xiyuan Graphene Technology Co., Ltd., Changzhou 213161, China
- Correspondence: lidi@issp.ac.cn

Abstract: Acquiring homogeneous and reproducible wafer-scale transition metal dichalcogenide (TMDC) films is crucial for modern electronics. Metal–organic chemical vapor deposition (MOCVD) offers a promising approach for scalable production and large-area integration. However, during MOCVD synthesis, extraneous carbon incorporation due to organosulfur precursor pyrolysis is a persistent concern, and the role of unintentional carbon incorporation remains elusive. Here, we report the large-scale synthesis of molybdenum disulfide (MoS₂) thin films, accompanied by the formation of amorphous carbon layers. Using Raman, photoluminescence (PL) spectroscopy, and transmission electron microscopy (TEM), we confirm how polycrystalline MoS₂ combines with extraneous amorphous carbon layers. Furthermore, by fabricating field-effect transistors (FETs) using the carbon-incorporated MoS₂ films, we find that traditional n-type MoS₂ can transform into p-type semiconductors owing to the incorporation of carbon, a rare occurrence among TMDC materials. This unexpected behavior expands our understanding of TMDC properties and opens up new avenues for exploring novel device applications.

Keywords: MOCVD; transition metal dichalcogenide; amorphous carbon; field-effect transistors

1. Introduction

Transition metal dichalcogenides (TMDCs) have attracted significant attention as promising materials for next-generation electronic and optoelectronic devices [1–11]. These applications heavily rely on the merits of TMDCs, including high carrier mobility [12,13], mechanical bandgap modulation [14-16], and spin valley coupling [17,18]. To meet the needs of modern electronics and optoelectronics, the scalable and atomically thin growth of TMDCs is a prominent challenge for the deposition of two-dimensional materials. To overcome the challenge, various synthesis methods have been explored, including chemical vapor deposition (CVD) [19-22], molecular beam epitaxy [23,24], and metal-organic chemical vapor deposition (MOCVD) [25–30]. In particular, MOCVD has shown potential in synthesizing wafer-scale TMDC films on insulating substrates, providing better control over film thickness and eliminating the need for transfer. During the MOCVD growth for large-scale TMDCs, particularly in situations where organic chalcogen precursors are desired as a less hazardous substitute for more toxic chalcogen hydrides, carbon will be inevitably introduced as an unintentional film impurity owing to pyrolysis side products from organic ligands [31]. However, the role of unintentional carbon incorporation is still a topic of ongoing debate. Some research teams reported that carbon can be incorporated through CH functionalization [32,33] or substitutional carbon doping [34], which are generally at the chalcogen sides of TMDC basal planes, or carbide transformation of



Citation: Hou, T.; Li, D.; Qu, Y.; Hao, Y.; Lai, Y. The Role of Carbon in Metal–Organic Chemical Vapor Deposition-Grown MoS₂ Films. *Materials* **2023**, *16*, 7030. https:// doi.org/10.3390/ma16217030

Academic Editor: Giovanni Sotgiu

Received: 25 September 2023 Revised: 20 October 2023 Accepted: 1 November 2023 Published: 3 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). TMDC edges [35]. Zhang et al. noted that "defective graphene" can be formed along with the formation of the TMDC layer, which hinders the lateral growth and the quality of TMDC films (e.g., continuity, stoichiometry, grain size, and phase purity) [31,36]. In this work, we investigate the growth of wafer-scale MoS₂ films on sapphire substrates with metal–organic precursors of molybdenum hexacarbonyl (Mo(CO)₆) and di-tert-butyl sulfide (DTBS, (CH₃)₃C)₂S). Through analyses of Raman and PL spectra, we confirm the existence of co-deposited "amorphous carbon" during the growth of MoS₂. In addition, atomic force microscopy (AFM) and transmission electron microscopy (TEM) reveal how polycrystalline MoS₂ combines with extraneous amorphous carbon layers. Furthermore, by the fabrication of FETs, we find that even small amounts of unintentional carbon incorporated in the coalesced ultrathin MoS₂ films, n-type MoS₂, are transformed into p-type semiconductors, which is uncommon among TMDC materials. These findings show a new approach for the growth and integration of atomically thin TMDC films with process-induced carbon impurity doping, offering valuable insights into the promising prospects of utilizing this composite material for advanced electronic applications.

2. Materials and Methods

Sample preparation. MoS_2 thin films were synthesized using a custom-made hotwall reactor through the MOCVD technique. Sapphire substrates were positioned facing downwards on a quartz sample holder bar that was within a vertical quartz tube reactor chamber. The growth temperature was carefully controlled using a thermocouple and temperature controller. The reactor was then gradually heated at a rate of approximately 40 °C/min, while a 100 sccm flow of high-purity Ar (Air Liquide, Shanghai, China, Alphagaz 1, 99.999%) was maintained to create an inert environment. Once the desired growth temperature was reached, Ar was ceased, and the growth of MoS_2 was initiated by vapor draw of molybdenum hexacarbonyl Mo(CO)₆ (Sigma-Aldrich 577766, Beijing, China, >99.9% trace metal basis) and (CH3)₃C)₂S from separate containers, without the need for an additional carrier gas. Mo(CO)₆ powder was placed on glass beads to increase surface area, and DES precursors were maintained at 30 and 12 °C, respectively. The flow rates of these precursors were precisely controlled using needle metering valves (SS-SS4-VH, Swagelok, Nanjing, China) and were determined based on their equilibrium vapor pressures. The nominal Mo(CO)₆ flow rate was set at 0.02 sccm, and DES flow rates varied between 0.3 and 13.2 sccm. Furthermore, controlled amounts of high-purity H₂ gas (Air Liquide, Alphagaz 1, 99.999%) with flows between 0 and 30 sccm were introduced into the system via a separate line, regulated by a mass flow controller. The entire process was conducted at working pressures ranging from 10^{-2} to 10^{-1} Torr. The growth temperature is 750 °C. Growth was stopped by cutting the Mo(CO)₆, DES, and H₂ flows off. The reactor was then cooled down to room temperature under 100 sccm Ar flow before the sample was removed. After each growth run, the reactor was annealed at 800 $^{\circ}$ C in Ar/H₂ flow to eliminate the remaining reaction byproducts. Between runs, the reactor was maintained under a vacuum at a base pressure of around 1×10^{-3} Torr. During the loading and unloading of samples, an Ar flow of 150 sccm was employed to minimize exposure to ambient conditions.

Optical characterizations. An optical microscope (Nikon, Shanghai, China, Eclipse LV100ND) was utilized to take optical microscope images. A white balance was calibrated before taking the images. Raman and PL spectra were acquired using a WITEC optical microscopy (alpha 300R, Beijing, China) with a laser wavelength of 532 nm. The films were characterized under ambient conditions at $50 \times$ or $100 \times$ magnification with a spot size of approximately 1 μ m. A low laser power of 0.1 mW was used to minimize heating effects and prevent optical doping and multiexciton dynamics in PL measurements. A 600 or 1200 grooves/mm grating was employed. Raman and PL measurements were conducted using integration times of 10 s and five accumulations. For each sample, five spots were measured along the sample diagonal in order to obtain the average data.

Structure characterizations. TEM (FEI Tecnai-G2 F20 operating at 200 kV, Beijing, China) was utilized to probe the atomic structure of the films. AFM was measured by NT-

MDT NTEGRA Prima AFM, Shanghai, China. The chemical composition and stoichiometry of the films were investigated by XPS in an ultrahigh vacuum of 5×10^{-10} mbar using monochromatic Al K α radiation with an energy of 1486.6 eV.

Film transfer. First, the as-grown films grown on sapphire substrates were coated with poly(methyl methacrylate) (PMMA, A4) by a spin coater, followed by a two-step process: 800 rpm for 15 s and 2000 rmp for 45 s. Then, the sample was baked at 180 °C for 2 min. Next, the samples were immersed in a diluted HF solution, and the PMMA/TMDCs assemblies were peeled off the substrate and floated on the HF solution. Then, the films were cleaned in deionized water for 20 min five times to guarantee the thorough elimination of the residual HF and transferred onto the desired substrate, such as the SiO₂/Si substrate or patterned Au electrode. The sample was then put into a vacuum tank and dried at room temperature. Finally, the assembly was moved into the acetone and then isopropyl alcohol to dissolve the PMMA film.

3. Results and Discussion

Figure 1 displays a continuous and atomically thin film for wafer-scale MoS₂ and exhibits intrinsic optical properties. As shown in Figure 1a, one can see a wafer-scale MoS_2 film grown on a semi-polished 2-inch sapphire substrate. To enable measurements and applications of large-area uniform MoS₂ and accurately determine the thickness of the MoS_2 film, we use an etching-free, easy-processing, and large-area polymethyl methacrylate (PMMA)-assisted high-quality transfer strategy, which involves transferring the as-grown MoS_2 film onto a SiO₂/Si substrate, leveraging the hydrophilic behavior of the sapphire substrate and the accompanying capillary force [37]. In Figure 1b, we can observe the segments of MoS_2 films after their wet transfer onto the SiO_2/Si substrates. When examined under an enlarged optical microscope, the highly uniform color contrast showcases a homogenous thickness and in-plane continuity of the MoS₂ film. The Raman spectroscopy shows a clear separation in the spectral domain, with peaks observed in the range of 360 cm⁻¹ $\leq \omega \leq 420$ cm⁻¹ and 1300 cm⁻¹ $\leq \omega \leq 3000$ cm⁻¹, as indicated in Figure 1c. Two characteristic peaks, E_{2g}^1 (~385 cm⁻¹) and A_{1g} (~405 cm⁻¹), confirm the presence of MoS₂. These two phonon modes can be attributed to the in-plane displacement of both molybdenum and sulfur atoms (E_{2g}^1) and the out-of-plane displacement of the sulfur atoms (A_{1g}), respectively [38]. The specific frequency difference of 20 cm⁻¹ between E_{2g}^1 and A1g peaks, commonly used as a layer thickness indicator, confirms the ultrathin nature of the obtained film compared to bulk MoS₂ [39]. Additionally, the spectra in the range of 1300 cm⁻¹ $\leq \omega \leq$ 3000 cm⁻¹ suggest that the amorphous carbon co-deposits simultaneously with the MoS₂ thin film, which originates from the pyrolysis of organic ligands of metal–organic precursors. The features of the G peak (\sim 1595 cm⁻¹) arising from the normal first-order Raman scattering process in graphene and the G' band ($\sim 2680 \text{ cm}^{-1}$) resulting from a second-order process indicate a graphene-like structure [40–43]. The high intensity of the disorder-induced D-band (~1345 cm⁻¹) indicates that the carbon incorporated in the film is highly defective. The additional weak disorder-induced shoulder peak (D' band) at ~1620 cm⁻¹ and the D + D' peak (~2940 cm⁻¹) are also observed by Raman spectroscopy. Based on the D and G peak positions and an integrated I_D/I_G intensity ratio (\approx 1.71), we assign this Raman feature to sp^2 carbon, such as pyrolytic graphite [43,44], indicating that the MOCVD-grown sample is a MoS_2 /amorphous carbon composite film. In comparison, the characteristic peaks associated with amorphous carbon disappear in the exfoliated and CVD-grown MoS₂. Figure 1d displays the PL spectroscopy, where two characteristic peaks of MoS_2 (~660 nm and ~640 nm) are observed, which can be attributed to the A and B direct bandgap optical transitions [45]. However, in addition to these intrinsic characteristic peaks of MoS₂, two other distinctive and non-negligible peaks at ~620 nm and ~630 nm are observed in comparison with the exfoliated MoS₂ and CVD-grown MoS₂, which may be induced by the Raman shift of the G' and D + D' bands in the amorphous carbon.



Figure 1. Optical characterizations of wafer-scale MOCVD-grown MoS₂ films. (**a**) The photograph of MoS₂ film grown on a sapphire substrate. (**b**) White-light microscope image of the as-grown large-area MoS₂ film transferred onto the SiO₂/Si substrate. (**c**) Raman spectra of transferred MOCVD-grown MoS₂ films, exfoliated MoS₂, and CVD-grown MoS₂. (**d**) Photoluminescence spectra of the transferred MOCVD-grown MoS₂ films, exfoliated MoS₂, and CVD-grown MoS₂.

In order to examine the atomic structure and morphology of the MoS_2 /amorphous carbon composite film, high-resolution TEM imaging and AFM provide a distinctive atomiclevel perspective of the MoS_2 and carbon combination (shown in Figure 2). As depicted in Figure 2a, the atomic structure of the MoS_2 /carbon composite film is characterized by aberration-corrected high-resolution TEM. The image reveals a well-organized honeycomb lattice with an interatomic distance of approximately 0.316 nm, which is consistent with previous observations for MoS₂ [46,47]. The lattice consists of hexagonal rings formed by alternating molybdenum and sulfur atoms. Owing to the contrast of bright-field TEM image scales that are roughly at the square of atomic number Z [48], the brighter atomic spots are molybdenum sites, and the dimmer ones are the two stacked sulfur atoms, as indicated by the top-view schematic. The fast Fourier transform (FFT) pattern in the inset of Figure 2a reveals only one set of six-fold symmetry diffraction spots, suggesting a hexagonal arrangement. And the lattice spacing of 0.27 nm can be assigned to (1 0 0) planes. In Figure 2b, a grain boundary is highlighted within the white dashed box. The FFT pattern reveals two sets of six-fold symmetrical diffraction spots with a rotation angle of $\sim 21^{\circ}$, indicating the presence of two grains in this region. Figure 2c demonstrates the high-angle annular dark field transmission electron microscopy (HAADF) image of the crystal structure for the corresponding composite. The composite image is obtained from overlapping false color-coded HAADF-TEM images, where the color contrast corresponds to different domains. The intersections of the grains constitute many faceted tilt and twisted boundaries, arising from disordered crystals that form randomly oriented polycrystalline aggregates. As shown in the legend, the black areas are holes of the TEM grid, the brown and grey areas correspond to carbon films, and the other colorful areas represent MoS_2

on the carbon films. Energy-dispersive X-ray spectroscopy (EDS) elemental maps also show the chemical composition and are zoomed-in in the HAADF image. The maps reveal that the carbon element uniformly distributes throughout the detection area, while Mo and S are vertically localized within their corresponding irregular domains. This indicates that carbon layers form on top of MoS₂ without forming any inter- or in-plane chemical bonds. Therefore, the interaction between these layers is primarily governed by van der Waals forces.



Figure 2. Structure characterizations of the transferred $MoS_2/carbon$ composite film. (**a**) The highresolution bright-field TEM image of a freely suspended $MoS_2/carbon$ composite film on a TEM grid. The inset shows the FFT pattern of the TEM image and the intensity profile of the corresponding white dashed box. (**b**) The grain boundary is highlighted by the white dashed box with a rotation angle of ~21°, as confirmed by the FFT pattern shown in the inset. (**c**) The false color-coded HAADF-TEM image. Corresponding EDS elemental maps display the composition and distribution of each chemical element.

To further confirm the growth process of the $MoS_2/carbon film$, the cross-sectional TEM samples are fabricated by focused ion beam (FIB) milling. A thin layer of aluminum is thermally evaporated on top of the sample to enhance the color contrast with carbon. A thin layer of gold is thermally evaporated to prevent the oxidation of aluminum and enhance conductivity. The cross-sectional TEM of the sample (Figure 3a) confirms the presence of MoS_2 with pristine interfaces and reveals the carbon layers above the MoS_2 . The thickness of the $MoS_2/carbon$ film is approximately 3 nm, which is consistent with the corresponding height profile value of ~3.16 nm shown in the AFM image of the sample edge (Figure 3b).



Figure 3. (a) The cross-sectional TEM of the $MoS_{2/}$ amorphous carbon composite film grown on sapphire. The EDS elemental maps are on the right panel. (b) The AFM image of the $MoS_2/$ amorphous carbon composite film edge transferred onto the SiO_2/Si substrate.

To assess the elemental composition of our MOCVD-grown samples, we perform X-ray photoelectron spectroscopy (XPS) measurements of the films. The XPS spectra of films grown on sapphire are displayed in Figure 3. As shown in the legend, in addition to the prominent peaks corresponding to Mo, S, and C elements (Figure 4a–c), signals related to O and Al are also observed (Figure 4d). This suggests good surface coverage of

the substrate and the formation of large-area continuous MoS₂ layers. The XPS spectrum of the Mo 3d core level (Figure 4b), which corresponds to the expected energy positions of the MoS₂ film, exhibits correct splitting spin orbitals, displaying two main peaks at approximately 229.6 eV (Mo $3d_{5/2}$) and 232.8 eV (Mo $3d_{3/2}$) for the 2H phase, respectively. These peaks are characteristic of Mo^{4+} in MoS_2 [49–56]. Additionally, the MoS_2 film on sapphire exhibits a minor but discernible peak at ~227.1 eV, which is attributed to the presence of S 2s or the molybdenum carbide (Mo-C bond) [50,56]. Another notable peak at a higher binding energy in the Mo 3d core level spectrum is related to the Mo⁶⁺, which arises from the oxidation of MoO₃ [49]. Regarding the S 2p region (Figure 4c), the binding energy peaks observed at 162.5 eV and 163.8 eV correspond to the S $2p_{3/2}$ and $2p_{1/2}$ core orbitals, respectively, further confirming the presence of MoS_2 in the 2H phase [50]. The XPS survey spectrum of the C 1s orbital exhibits two main peaks centered at 284.6 eV and 288.8 eV [49,55], where the major peak at 284.6 eV represents the hybridization of sp^2 bond (Figure 4a). It indicates the presence of graphene and further verifies that our MOCVD-grown sample is a MoS_2 /carbon composite film. However, the minor but unique peak (288.8 eV) remains dim; therefore, we cannot definitively conclude that the peak at ~227.1 eV in the Mo 3d binding energy represents the Mo-C bond.



Figure 4. XPS spectra of the MOCVD-grown MoS₂/carbon film on the sapphire substrate. The XPS spectrum of (**a**) the C 1s orbit, (**b**) the Mo 3d orbit, and (**c**) the S 2p orbit of MOCVD-grown MoS₂/carbon films. (**d**) The XPS spectrum of the sapphire substrate.

To investigate the electrical properties of the $MoS_2/carbon$ composite films, we transfer the films onto a pre-patterned gold electrode (Figure 5a). It can be found that the transfer curves show a notable decrease in behavior in the left section when the gate voltage varies from -40 to 40 V (Figure 5b), indicating an "off" process. The right section shows a gradual increase in current, which can be interpreted as an "on" process. Although the current does not drop to the -12 or even -13 power of a completely off state, the source drain current exhibits a switching behavior, with a maximum current of up to 20 nA. It is important to note that the carbon incorporation results in the conversion of the MoS₂ film from a typical ntype semiconductor to a p-type semiconductor. The pristine MoS₂ electric devices generally display unipolar n-type behavior. However, the carbon-incorporated devices exhibit a p-type current compared to pure MoS₂ devices. This can be attributed to the influence of carbon within the composite films, altering the semiconducting properties of MoS₂. As shown in Figure 5c, for pristine TMDC devices, the metal Fermi level aligns more closely with the conduction band (CB) than the valence band (VB), leading to a diminished electron Schottky barrier (Φ_{SB-n}) compared to the hole Schottky barrier (Φ_{SB-P}) [57]. After carbon incorporation, the incorporation will shift from the Fermi level to the VB. This realignment of the metal MoS₂ Fermi level pinning leads to a reduction in Φ_{SB-P} (Figure 5d). [32,58]. As theoretically calculated by A. Chanana et al. [59], the Φ_{SB-P} for the MoS₂-Au interface is 1.2 eV. When inserted by graphene, the Φ_{SB-P} for MoS₂–graphene–Au interface decreases to 1.14 eV; namely, the Fermi level shifts to VB. The smaller Schottky tunnel barrier no longer impedes hole injections [32]. Therefore, carbon impurities alter the electronic or optoelectronic properties of our composite TMDC films. The carrier concentration can be estimated by the following formula [60]:

$$n = C_{bg}(V_{bg} - V_{th})/e,$$

 $C_{bg} = \varepsilon_0 \varepsilon_r/d,$

where $C_{bg} \approx 1.2 \times 10^{-4} \text{ F/m}^2$ is the gate capacitance per unit area for 285 nm SiO₂ dielectric, V_{bg} is the back gate voltage, V_{th} is the threshold voltage for the channel to start accumulating charge and conducting, e is the elementary charge, ε_0 is the permittivity of free space, ε_r is the relative permittivity, and d is the thickness of the dielectric layer. A back gate voltage can be applied to the conducting Si substrate to modulate the MoS₂ carrier concentration. When V_{bg} is 40 V, the carrier concentration is calculated to be $1.2 \times 10^{11} \text{ cm}^{-2}$.



Figure 5. Electrical characterization of $MoS_2/carbon FETs.$ (a) The optical micrograph of the $MoS_2/carbon$ film transferred onto the patterned SiO_2/Si substrate. (b) Typical transfer characteristics (I_d - V_g) of as-fabricated $MoS_2/carbon$ FETs. Schematics of the valence band position (E_{VB}) near the source for pristine (c) and carbon-incorporated (d) FET devices. For the pristine devices, the hole conduction is prevented by a wide Φ_{SB-P} , so the device shows n-type behavior. However, after carbon incorporation, the Au Fermi level pins closer to the VB of MoS_2 , leading to a smaller Φ_{SB-P} for the hole injection.

4. Conclusions

In conclusion, we comprehensively investigate the structure, optical, and electrical properties of a large-scale and coalesced $MoS_2/carbon$ composite film. Compared to CVD-grown and exfoliated MoS_2 , MOCVD-grown MoS_2 can introduce unintentional carbon incorporation, leading to the shift of the PL characteristic peak, the emergence of carbon features in Raman properties, the alteration of the (opto)electronic properties, etc. Specifically, through Raman and PL spectra, we verify the presence of carbon incorporation. Additionally, cross-sectional TEM and XPS are employed to observe the combination of carbon and the MoS_2 material. Furthermore, by fabricating FET devices, we explore the influence of carbon on the electric performance of the composite film. We find that the general n-type MoS_2 can be converted to a p-type semiconductor owing to the incorporation of carbon in the MoS_2 film. A comparison chart is tabulated in Table 1. Our study provides a valuable understanding of process-induced C impurity doping in MOCVD-grown two-dimensional semiconductors and might have important influences on advanced electronic applications.

Table 1. Comparison chart of the properties with other methods used for MoS_2 .

	Carbon Incorporated or Not	Precursors	Raman [61,62]	PL [61,63]	Semiconducting Property
MOCVD-grown MoS ₂	yes	Mo(CO) ₆ , (CH ₃) ₃ C) ₂ S	E ¹ _{2g} (~385 cm ⁻¹), A _{1g} (~405 cm ⁻¹) and some carbon related peaks	A (~660 nm), B (~640 nm)	p-type
CVD-grown MoS ₂	no	MoO ₃ and S powders	E_{2g}^{1} (~385 cm ⁻¹), A _{1g} (~403 cm ⁻¹)	A (~660 nm)	n-type
exfoliated MoS ₂	no	bulk materials	E_{2g}^{1} (~385 cm ⁻¹), A _{1g} (~403 cm ⁻¹)	A (~660 nm), B (~610 nm)	n-type

Author Contributions: Conceptualization, Y.H., D.L. and Y.Q.; methodology, Y.H., T.H., Y.Q. and D.L.; data curation, T.H. and D.L.; validation, Y.H., T.H., D.L. and Y.L.; formal analysis, T.H.; visualization, T.H.; investigation, T.H., Y.H., D.L., Y.L. and Y.Q.; resources, Y.H., Y.L. and Y.Q.; writing—original draft preparation, T.H.; writing—review and editing, T.H., Y.H., D.L., Y.Q. and Y.L.; supervision, Y.H., D.L. and Y.L.; funding acquisition, Y.H., Y.Q. and Y.L.; project administration, D.L., Y.H. and Y.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Key R&D Program of Jiangsu Province, grant No. BE2021007-1 and BE2023009-2.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Kim, S.; Konar, A.; Hwang, W.; Lee, J.H.; Lee, J.; Yang, J.; Jung, C.; Kim, H.; Yoo, J.; Choi, J.; et al. High-mobility and low-power thin-film transistors based on multilayer MoS₂ crystals. *Nat. Commun.* **2012**, *3*, 1011. [CrossRef] [PubMed]
- Li, S.; Wakabayashi, K.; Xu, Y.; Nakaharai, S.; Komatsu, K.; Li, W.; Lin, Y.; Aparecido-Ferreira, A.; Tsukagoshi, K. Thicknessdependent interfacial coulomb scattering in atomically thin field-effect transistors. *Nano Lett.* 2013, 13, 3546–3552. [CrossRef] [PubMed]
- 3. Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive photodetectors based on monolayer MoS₂. *Nat. Nanotechnol.* **2013**, *8*, 497–501. [CrossRef] [PubMed]
- 4. Pospischil, A.; Furchi, M.; Mueller, T. Solar-energy conversion and light emission in an atomic monolayer p-n diode. *Nat. Nanotechnol.* **2014**, *9*, 257–261. [CrossRef]
- Branny, A.; Kumar, S.; Proux, R.; Gerardot, B.D. Deterministic strain-induced arrays of quantum emitters in a two-dimensional semiconductor. *Nat. Commun.* 2017, *8*, 15053. [CrossRef] [PubMed]

- Yu, W.J.; Liu, Y.; Zhou, H.; Yin, A.; Li, Z.; Huang, Y.; Duan, X. Highly efficient gate-tunable photocurrent generation in vertical heterostructures of layered materials. *Nat. Nanotechnol.* 2013, *8*, 952–958. [CrossRef]
- Withers, F.; Del Pozo-Zamudio, O.; Mishchenko, A.; Rooney, A.P.; Gholinia, A.; Watanabe, K.; Taniguchi, T.; Haigh, S.J.; Geim, A.K.; Tartakovskii, A.I.; et al. Light-Emitting Diodes by Band-Structure Engineering in van der Waals Heterostructures. *Nat. Mater.* 2015, 14, 301–306. [CrossRef]
- Cheng, R.; Li, D.; Zhou, H.; Wang, C.; Yin, A.; Jiang, S.; Liu, Y.; Chen, Y.; Huang, Y.; Duan, X. Electroluminescence and photocurrent generation from atomically sharp WSe₂/MoS₂ heterojunction p-n diodes. *Nano Lett.* 2014, 14, 5590–5597. [CrossRef]
- 9. Xiong, Y.; Wang, Y.; Zhu, R.; Xu, H.; Wu, C.; Chen, J.; Ma, Y.; Liu, Y.; Chen, Y.; Watanabe, K.; et al. Twisted black phosphorus–based van der Waals stacks for fiber-integrated polarimeters. *Sci. Adv.* **2022**, *8*, eabo0375. [CrossRef]
- 10. Zhu, Y.; Li, Y.; Arefe, G.; Burke, R.A.; Tan, C.; Hao, Y.; Liu, X.; Liu, X.; Yoo, W.J.; Dubey, M.; et al. Monolayer molybdenum disulfide transistors with single-atom-thick gates. *Nano Lett.* **2018**, *18*, 3807–3813. [CrossRef]
- Baugher, B.W.H.; Churchill, H.O.H.; Yang, Y.; Jarillo-Herrero, P. Optoelectronic Devices Based on Electrically Tunable p-n Diodes in a Monolayer Dichalcogenide. *Nat. Nanotechnol.* 2014, *9*, 262–267. [CrossRef] [PubMed]
- Kang, K.; Xie, S.; Huang, L.; Han, Y.; Huang, P.Y.; Mak, K.F.; Kim, C.; Muller, D.; Park, J. High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity. *Nature* 2015, 520, 656–660. [CrossRef] [PubMed]
- Ovchinnikov, D.; Allain, A.; Huang, Y.-S.; Dumcenco, D.; Kis, A. Electrical transport properties of single-layer WS₂. ACS Nano 2014, 8, 8174–8181. [CrossRef] [PubMed]
- 14. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.; Galli, G.; Wang, F. Emerging photoluminescence in monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275. [CrossRef]
- 15. Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from chemically exfoliated MoS₂. *Nano Lett.* **2011**, *11*, 5111–5116. [CrossRef]
- 16. 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. [CrossRef]
- 17. Xiao, D.; Liu, G.; Feng, W.; Xu, X.; Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides. *Phys. Rev. Lett.* **2012**, *108*, 196802. [CrossRef]
- 18. Zeng, H.; Liu, G.; Dai, J.; Yan, Y.; Zhu, B.; He, R.; Xie, L.; Xu, S.; Chen, X.; Yao, W.; et al. Optical Signature of symmetry variations and spin-valley coupling in atomically thin tungsten dichalcogenides. *Sci. Rep.* **2013**, *3*, 1608. [CrossRef]
- 19. Zhao, Z.; Hou, T.; Wu, N.; Jiao, S.; Zhou, K.; Yin, J.; Suk, J.W.; Cui, X.; Zhang, M.; Li, S.; et al. Polycrystalline few-layer graphene as a durable anticorrosion film for copper. *Nano Lett.* **2021**, *21*, 1161–1168. [CrossRef]
- 20. Zhou, H.; Wang, C.; Shaw, J.C.; Cheng, R.; Chen, Y.; Huang, X.; Liu, Y.; Weiss, N.O.; Lin, Z.; Huang, Y.; et al. Large area growth and electrical properties of P-type WSe₂ atomic layers. *Nano Lett.* **2015**, *15*, 709–713. [CrossRef]
- Ling, X.; Lee, Y.; Lin, Y.; Fang, W.; Yu, L.; Dresselhaus, M.S.; Kong, J. Role of the seeding promoter in MoS₂ growth by chemical vapor deposition. *Nano Lett.* 2014, 14, 464–472. [CrossRef] [PubMed]
- 22. Hao, Y.; Wang, L.; Liu, Y.; Chen, H.; Wang, X.; Tan, C.; Nie, S.; Suk, J.W.; Jiang, T.; Liang, T.; et al. Oxygen-activated growth and bandgap tunability of large single-crystal bilayer graphene. *Nat. Nanotechnol.* **2016**, *11*, 426–431. [CrossRef] [PubMed]
- Zhang, Y.; Ugeda, M.M.; Jin, C.; Shi, S.-F.; Bradley, A.J.; MartínRecio, A.; Ryu, H.; Kim, J.; Tang, S.; Kim, Y.; et al. Electronic structure, surface doping, and optical response in epitaxial WSe₂ thin films. *Nano Lett.* 2016, 16, 2485–2491. [CrossRef] [PubMed]
- Nakano, M.; Wang, Y.; Kashiwabara, Y.; Matsuoka, H.; Iwasa, Y. Layer-by-layer epitaxial growth of scalable WSe₂ on Sapphire by molecular beam epitaxy. *Nano Lett.* 2017, 17, 5595–5599. [CrossRef] [PubMed]
- Ji, R.; Liao, J.; Li, L.; Wen, R.; Liu, M.; Ren, Y.; Wu, J.; Song, Y.; Qi, M.; Qiao, Z.; et al. Step-edge controlled fast growth of wafer-scale MoSe₂ films by MOCVD. *Nano Res.* 2023, 16, 9577–9583. [CrossRef]
- 26. Liu, M.; Liao, J.; Liu, Y.; Li, L.; Wen, R.; Hou, T.; Ji, R.; Wang, K.; Xing, Z.; Zheng, D.; et al. Periodical ripening for MOCVD growth of large 2D transition metal dichalcogenide domains. *Adv. Funct. Mater.* **2023**, *33*, 2212773. [CrossRef]
- Kalanyan, B.; Kimes, W.A.; Beams, R.; Stranick, S.J.; Garratt, E.; Kalish, I.; Davydov, A.V.; Kanjolia, R.K.; Maslar, J.E. Rapid Wafer-Scale Growth of Polycrystalline 2H-MoS₂ by Pulsed MetalOrganic Chemical Vapor Deposition. *Chem. Mater.* 2017, 29, 6279–6288. [CrossRef]
- Schaefer, C.M.; Caicedo Roque, J.M.; Sauthier, G.; Bousquet, J.; Hébert, C.; Sperling, J.R.; Pérez-Tomás, A.; Santiso, J.; Corro, E.d.; Garrido., J.A. Carbon Incorporation in MOCVD of MoS₂ Thin Films Grown from an Organosulfide Precursor. *Chem. Mater.* 2021, 33, 4474–4487. [CrossRef]
- 29. Mawlong, L.P.L.; Hoang, A.T.; Chintalapalli, J.; Ji, S.; Lee, K.; Kim, K.; Ahn, J.-H. Reduced Defect Density in MOCVD-Grown MoS₂ by Manipulating the Precursor Phase. *ACS Appl. Mater. Interfaces* **2023**, *15*, 47359–47367. [CrossRef]
- 30. Yang, X.; Li, S.; Ikeda, N.; Ohtake, A.; Sakuma, Y. Scalable growth of atomically thin MoS₂ layers in a conventional MOCVD system using molybdenum dichloride dioxide as the molybdenum source. *Appl. Surf. Sci.* **2023**, *636*, 157756. [CrossRef]
- Zhang, X.; Balushi, Z.Y.A.; Zhang, F.; Choudhury, T.H.; Eichfeld, S.M.; Alem, N.; Jackson, T.N.; Robinson, J.A.; Redwing, J.M. Influence of carbon in metalorganic chemical vapor deposition of few-layer WSe₂ thin films. *J. Electron. Mater.* 2016, 45, 6273–6279. [CrossRef]
- 32. Zhang, F.; Lu, Y.F.; Schulman, D.S.; Zhang, T.Y.; Fujisawa, K.; Lin, Z.; Lei, Y.; Elias, A.L.; Das, S.; Sinnott, S.B.; et al. Carbon doping of WS₂ monolayers: Bandgap reduction and p-type doping transport. *Sci. Adv.* **2019**, *5*, eaav5003. [CrossRef]

- Cochrane, K.A.; Zhang, T.; Kozhakhmetov, A.; Lee, J.-H.; Zhang, F.; Dong, C.; Neaton, J.B.; Robinson, J.A.; Terrones, M.; Bargioni, A.W.; et al. Intentional carbon doping reveals CH as an abundant charged impurity in nominally undoped synthetic WS₂ and WSe₂. 2D Materials 2020, 7, 031003. [CrossRef]
- Liang, T.; Habib, M.R.; Xiao, H.; Xie, S.; Kong, Y.; Yu, C.; Iwai, H.; Fujita, D.; Hanagata, N.; Chen, H.; et al. Intrinsically Substitutional Carbon Doping in CVD-Grown Monolayer MoS₂ and the Band Structure Modulation. *ACS Appl. Electron. Mater.* 2020, 2, 1055–1064. [CrossRef]
- Jeon, J.; Park, Y.; Choi, S.; Lee, J.; Lim, S.S.; Lee, B.H.; Song, Y.J.; Cho, J.H.; Jang, Y.H.; Lee, S. Epitaxial Synthesis of Molybdenum Carbide and Formation of a Mo₂C/MoS₂ Hybrid Structure via Chemical Conversion of Molybdenum Disulfide. ACS Nano 2018, 12, 338–346. [CrossRef]
- 36. Choudhury, T.H.; Simchi, H.; Boichot, R.; Chubarov, M.; Mohney, S.E.; Redwing, J.M. Chalcogen Precursor Effect on ColdWall Gas-Source Chemical Vapor Deposition Growth of WS₂. *Cryst. Growth Des.* **2018**, *18*, 4357–4364. [CrossRef]
- 37. Yang, P.; Zou, X.; Zhang, Z.; Hong, M.; Shi, J.; Chen, S.; Shu, J.; Zhao, L.; Jiang, S.; Zhou, X.; et al. Batch production of 6-inch uniform monolayer molybdenum disulfide catalyzed by sodium in glass. *Nat. Commun.* **2018**, *9*, 979. [CrossRef]
- 38. Ganatra, R.; Zhang, Q. Few-layer MoS₂: A promising layered semiconductor. ACS Nano 2014, 8, 4074–4099. [CrossRef]
- 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. [CrossRef]
- 40. Malard, L.M.; Pimenta, M.A.; Dresselhaus, G.; Dresselhaus, M.S. Raman spectroscopy in graphene. *Phys. Rep.* **2009**, *473*, 51–87. [CrossRef]
- 41. Maultzsch, J.; Reich, S.; Thomsen, C. Double-resonant Raman scattering in graphite: Interference effects, selection rules, and phonon dispersion. *Phys. Rev. B* 2004, *70*, 155403. [CrossRef]
- 42. Ferrari, A.C.; Meyer, J.C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K.S.; Roth, S.; et al. Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **2006**, *97*, 187401. [CrossRef] [PubMed]
- 43. Ferrari, A.; Basko, D. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat. Nanotechnol.* **2013**, *8*, 235–246. [CrossRef] [PubMed]
- López-Díaz, D.; López Holgado, M.; García-Fierro, J.L.; Velázquez, M.M. Evolution of the Raman spectrum with the chemical composition of graphene oxide. J. Phys. Chem. C 2017, 121, 20489–20497. [CrossRef]
- Tonndorf, P.; Schmidt, R.; Böttger, P.; Zhang, X.; Börner, J.; Liebig, A.; Albrecht, M.; Kloc, C.; Gordan, O.; Zahn, D.R.T.; et al. Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂. *Opt. Express* 2013, 21, 4908–4916. [CrossRef]
- 46. Najmaei, S.; Liu, Z.; Zhou, W.; Zou, X.; Shi, G.; Lei, S.; Yakobson, B.I.; Idrobo, J.-C.; Ajayan, P.M.; Lou, J. Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nat. Mater.* **2013**, *12*, 754–759. [CrossRef]
- van der Zande, A.M.; Huang, P.Y.; Chenet, D.A.; Berkelbach, T.C.; You, Y.; Lee, G.; Heinz, T.F.; Reichman, D.R.; Muller, D.A.; Hone, J.C. Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide. *Nat. Mater.* 2013, 12, 554–561. [CrossRef]
- Krivanek, O.L.; Chisholm, M.F.; Nicolosi, V.; Pennycook, T.J.; Corbin, G.J.; Dellby, N.; Murfitt, M.F.; Own, C.S.; Szilagyi, Z.S.; Oxley, M.P.; et al. Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy. *Nature* 2010, 464, 571–574. [CrossRef]
- 49. Yoon, S.F.; Huang, Q.F.; Rusli; Yang, H.; Ahn, J.; Zhang, Q.; Blomfield, C.; Tielsch, B.; Tan, L.Y.C. X-ray photoelectron spectroscopy of molybdenum-containing carbon films. *J. Appl. Phys.* **1999**, *86*, 4871–4875. [CrossRef]
- Xiang, Z.C.; Zhang, Z.; Xu, X.; Zhang, Q.; Yuan, C. MoS₂ nanosheets array on carbon cloth as a 3D electrode for highly efficient electrochemical hydrogen evolution. *Carbon* 2016, *98*, 84–89. [CrossRef]
- 51. Varga, M.; Izak, T.; Vretenar, V.; Kozak, H.; Holovsky, J.; Artemenko, A.; Hulman, M.; Skakalova, V.; Lee, D.S.; Kromka, A. Diamond/carbon nanotube composites: Raman, FTIR and XPS spectroscopic studies. *Carbon* **2017**, *111*, 54–61. [CrossRef]
- 52. Pimentel, J.V.; Polcar, T.; Cavaleiro, A. Structural, mechanical and tribological properties of Mo-S-C solid lubricant coating. *Surf. Coat. Technol.* **2011**, 205, 3274–3279. [CrossRef]
- 53. Wu, Y.P.; Fang, S.; Jiang, Y.; Holze, R. Effects of doped sulfur on electrochemical performance of carbon anode. *J. Power Sources* **2002**, *108*, 245–249. [CrossRef]
- 54. Yang, C.; Yin, Y.; Ye, H.; Jiang, K.; Zhang, J.; Guo, Y. Insight into the effect of boron doping on sulfur/carbon cathode in lithium-sulfur batteries. *ACS Appl. Mater. Interfaces* **2014**, *6*, 8789–8795. [CrossRef] [PubMed]
- Hu, Q.; Paau, M.C.; Zhang, Y.; Gong, X.; Zhang, L.; Lu, D.; Liu, Y.; Liu, Q.; Yao, J.; Choi, M.M.F. Green synthesis of fluorescent nitrogen/sulfur doped carbon dots and investigation of their properties by HPLC coupled with mass spectrometry. *RSC Adv.* 2014, 4, 18065. [CrossRef]
- 56. Wan, C.; Regmi, Y.N.; Leonard, B.M. Multiple phases of molybdenum carbide as electrocatalysts for the hydrogen evolution reaction. *Angew. Chem. Int. Ed.* **2014**, *53*, 6407–6410. [CrossRef]
- Schulman, D.S.; Arnold, A.J.; Das, S. Contact engineering for 2D materials and devices. *Chem. Soc. Rev.* 2018, 47, 3037–3058. [CrossRef]
- Chee, S.-S.; Seo, D.; Kim, H.; Jang, H.; Lee, S.; Moon, S.P.; Lee, K.H.; Kim, S.W.; Choi, H.; Ham, M.-H. Lowering the Schottky barrier height by graphene/Ag electrodes for high-mobility MoS₂ field-effect transistors. *Adv. Mater.* 2019, *31*, 1804422. [CrossRef]

- 59. Chanana, A.; Mahapatra, S. Prospects of zero Schottky barrier height in a graphene-inserted MoS₂-metal interface. *J. Appl. Phys.* **2016**, *119*, 014303. [CrossRef]
- Wang, J.-W.; Liu, Y.-P.; Chen, P.-H.; Chuang, M.-H.; Pezeshki, A.; Ling, D.-C.; Chen, J.-C.; Chen, Y.-F.; Lee, Y.-H. Controlled low-frequency electrical noise of monolayer MoS₂ with Ohmic contact and tunable carrier concentration. *Adv. Electron. Mater.* 2018, 4, 1700340. [CrossRef]
- Wang, Q.; 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. [CrossRef] [PubMed]
- O'Brien, M.; McEvoy, N.; Hanlon, D.; Hallam, T.; Coleman, J.N.; Duesberg, G.S. Mapping of low-frequency Raman modes in CVD-grown transition metal dichalcogenides: Layer number, stacking orientation and resonant effects. *Sci. Rep.* 2016, *6*, 19476. [CrossRef] [PubMed]
- 63. Ponomarev, E.; Gutiérrez-Lezama, I.; Ubrig, N.; Morpurgo, A.F. Ambipolar light-emitting transistors on chemical vapor deposited monolayer MoS₂. *Nano Lett.* **2015**, *15*, 8289–8294. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.