Nonthermal Plasma-Enhanced Chemical Vapor Deposition of Two-Dimensional Molybdenum Disulfide

Chad A. Beaudette,* Jacob T. Held, K. Andre Mkhoyan, and Uwe R. Kortshagen*

ABSTRACT: Molybdenum disulfide (MoS2) is being studied for a wide range of applications including lithium-ion batteries and hydrogen evolution reaction catalysts. In this paper, we present a single-step nonthermal plasma-enhanced chemical vapor deposition (PECVD) process for the production of two-dimensional MoS2. This method provides an alternative route to established CVD and plasma synthesis routes. The approach presented here synthesizes films in only a few minutes using elemental sulfur (S8) and molybdenum pentachloride (MoCl5) as precursors. Deposition utilizes a nonthermal inductively coupled plasma reactor and temperatures around 500 °C. Film growth characteristics and nucleation are studied as a function of precursor concentrations, argon flow rate, plasma power, and deposition time. Few-layer two-dimensional (MoS2) films were formed at low precursor concentrations. Films with nanoparticle-like features were formed when the precursor concentration was high. Noncontinuous nonstoichiometric films were found at low plasma power, while high plasma power led to continuous films with good stoichiometry. The vacancies and defects in these films may provide active sites for hydrogen evolution.

1. INTRODUCTION

MoS2 has found a wide range of uses in applications including transistors,1−3 flexible electronics,4−6 optoelectronics,7−9 biological applications,10 lithium-ion batteries,11 and hydrogen evolution reaction (HER) catalysts.9,10 However, the optimal morphology of an MoS2 film is heavily dependent on the application: for HER catalysts, sulfur vacancies, surface defects, and high surface area structures are desired,10 whereas for transistors, single-crystal defect-free monolayer MoS2 is required.11 Chemical vapor deposition (CVD) has been used to produce large single-crystal grains of MoS2.12 However, many authors have reported different grain sizes, layer thicknesses, and crystal shapes with few changes to synthesis conditions.13−18 Furthermore, the high temperatures required make this process poorly suited for producing films on thermally budgeted substrates and the long reaction times are also undesirable. This has led to the development of alternative synthesis routes for MoS2, many of which are low-temperature routes.

Low-temperature syntheses of MoS2 often involve long reaction times, postannealing, the use of hazardous hydrogen disulfide (H2S), and often produce multilayered films. Atomic layer deposition (ALD) methods can deposit MoS2 at low temperatures but either requires some form of postannealing to improve the crystallinity of the samples19−21 or produces rough films at low temperatures.22 Exfoliation methods are not suitable for the production of large-area films that are required for many industrial applications.23−25 Low-temperature metal−organic CVD has been the most successful technique for producing ultrathin two-dimensional films at low temperatures with short reaction times on the order of minutes.25
nonthermal plasma process for two-dimensional MoS2 films to date has not been reported.

In this paper, we address some of the issues of long process times and hazardous H2S by demonstrating a fast single-step nonthermal plasma synthesis of MoS2. The process utilizes two solid precursors, molybdenum pentachloride (MoCl5) and elemental sulfur (S8), with process times on the order of a few minutes. By tuning precursor concentrations in the gas phase, the process can be controlled to deposit few-layer two-dimensional MoS2 films or MoS2 films with nanoparticle-like features. We examine the correlation between film morphologies and process parameters such as the precursor flow rates, plasma power, and process duration. Films are characterized with standard techniques including Raman spectroscopy, UV–visible spectroscopy (UV–vis), X-ray photoelectron spectroscopy (XPS), scanning transition electron microscopy (STEM), and atomic force microscopy (AFM).

2. RESULTS AND DISCUSSION

2.1. Film Properties and Influence of Precursor Flow.

Figures 1–3 demonstrate the ability of our plasma process to deposit MoS2 both in the form of a two-dimensional material and in the form of films containing nanoparticle-like features. The flow rate of the precursors was found to play a significant role in controlling the morphology of the films.

Figure 1 shows the film morphology determined by AFM for different Ar flow rates through the sulfur sublimator (Arprecursors) while holding all other parameters constant. The
evolution from rough nanoparticle-like films, Figure 1a, to few-layer MoS\textsubscript{2} films, Figure 1c, is shown. These images demonstrate that nucleation of both high surface area and smooth two-dimensional films is possible in a single reactor. This transition, from nanoparticle-like films to smooth two-dimensional films, occurs when the flow rate of Ar\textsubscript{precursors} through the sulfur bubbler is increased, which decreases the gas-phase concentration of sulfur and molybdenum chloride species relative to the total amount of Ar. The vapor pressure of these precursors is limited by their rate of evaporation, and as the Ar\textsubscript{precursors} flow rate is increased, these sublimating precursors cannot increase their vapor pressure in the gas phase quickly enough to maintain the previous concentration. The result is a reduction in the vapor pressure of these precursors because of the increased Ar\textsubscript{precursors} flow rate, which dilutes the precursor vapor in Ar. Temperature differences cannot account for this change because they are negligible over this range as the Ar\textsubscript{precursors} flow is increased (Figure 7). The impact of the precursor concentration on the film morphology will be discussed further in the text.

To verify the identity and two-dimensional characteristics of the films, XPS, Raman spectroscopy, and UV–vis spectroscopy were used. Figure 2a depicts Raman scattering with a 532 nm laser from the films produced at various Ar\textsubscript{precursors} flow rates. The films produced at flow rates of 30 and 40 standard cubic centimeter per minute (sccm) exhibit A\textsubscript{1g} modes at 405.7 cm\textsuperscript{-1}, which correspond to a film of three monolayers,\textsuperscript{40} while the frequency difference of 20.63 cm\textsuperscript{-1} between the A\textsubscript{1g} and E\textsubscript{2g} modes is also consistent with a two-dimensional MoS\textsubscript{2} thin film.\textsuperscript{41} The films produced at 10 and 20 sccm show A\textsubscript{1g} modes, 405.7 and 406.9 cm\textsuperscript{-1}, that are consistent with a film that consists of three and four monolayers, respectively.\textsuperscript{40} The 10 and 20 sccm samples exhibit frequency shifts of 24.3 and 21.8 cm\textsuperscript{-1}, which correspond to quad- and bilayer films, respectively.\textsuperscript{41} Peaks located at 378 and 418 cm\textsuperscript{-1} are consistent with those of the underlying sapphire substrate.\textsuperscript{42}

A 532 nm Raman laser was used to excite photoluminescence (PL) of the 30 and 40 scm Ar\textsubscript{precursors} films (Figure 2b).\textsuperscript{40,43} The two PL peaks are located at roughly 670 and 630 nm and correspond to the A and B direct excitonic transitions.\textsuperscript{44} The strongest PL is associated with the film that has 1.5 nm thickness (30 sccm) rather than the thinnest 1 nm (40 sccm) film, likely because of the defects in the thinner film whose surface is much rougher than that of the 1.5 nm film, Figure 1c,d.

UV–vis absorption peaks were consistent with a monolayer film, as indicated in Figure 2c. The background (BG) peak is located at roughly 2.9 eV (420 nm), which is consistent with that reported for two-dimensional MoS\textsubscript{2}.\textsuperscript{44} The A and B excitons indicate direct transitions at the K point of the Brillouin zone. The A exciton is located at 1.89 eV and the B exciton is located at 2.08 eV for both samples, consistent with two-dimensional film absorption.\textsuperscript{44}

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used to examine the...
structure of an MoS$_2$ film produced at 5 sccm of Ar$_{\text{precursors}}$, 137 W of power, and 2 min of deposition. The HAADF-STEM images in Figure 3 show that the film contains between 1 and 2 monolayers of MoS$_2$ with lateral grain sizes of approximately 10–30 nm. The films include a high concentration of defects, as shown by the irregular structure in Figure 3b. Furthermore, amorphous nanoparticle-like structures are found in a few locations across the surface of the sample shown in Figures 3b and S1. From these images, it appears that Raman peaks are from the underlying MoS$_2$ films because of the amorphous nature of the nanoparticle-like features. A damaged portion of the underlying sapphire substrate is also shown in Figure 3a. This phenomenon could be due to chemical or physical etching within the plasma during material synthesis or from the focused ion beam (FIB) used during sample preparation for STEM. Most of the analysis utilized AFM because of the difficulties in sample preparation for STEM.

Figure 2d–f shows the results of the XPS analysis of a film produced at a flow of 30 sccm of Ar$_{\text{precursors}}$. These data contain information about the molybdenum (Mo) and sulfur (S) binding energies, which allowed for the determination of the chemical composition of the films. Peak locations at 229.8 and 232.9 eV are consistent with those of MoS$_2$ bonding. Peak locations for MoO$_3$ are found at 233.1 eV. Features at 162.7 and 163.8 eV of S binding to Mo further confirm the presence of MoS$_2$. To confirm the overall film composition and measure any possible contaminants, XPS survey scans at 280 eV were performed (Figure 2f). Contaminants of nickel (Ni) and chlorine (Cl) were on the order of 1% or lower, and carbon (C) content was consistent with films exposed to open air for extended periods of time. Aluminum and oxygen peaks are attributed to the underlying sapphire (Al$_2$O$_3$) substrate, unless specified elsewhere. The Ni 201 alloy substrate holder is the source of Ni contamination. We point out that thicker films did contain a few NiS particles and contaminants, although their total percentage of the film was small as indicated by the XPS data.

### 2.2. Effect of Plasma Power

Plasma power was varied in order to understand its relation to film growth and stoichiometry at 5 sccm Ar$_{\text{precursors}}$ flow rate. Film morphology, chemical composition, and density of surface grains change with increasing power, as shown in Figure 4a,c. At 100 W, the substrate surface is poorly covered and contains few nanoparticle-like features (Figure 4a). Although MoS$_2$ peaks are evident, the largest peak is that from the underlying sapphire substrate at 417 cm$^{-1}$ (Figure 4b). Although, at 125 W, nanoparticle structures are present, the Raman mode at 417 cm$^{-1}$ indicates that the substrate is not completely covered. Increasing the power further causes a reduction in the average surface height and a more consistent coverage of the substrate, as indicated by the disappearance of the sapphire-related peak.

The films produced at low power had an S/Mo ratio of roughly 1:1, as shown in Figure 4c. As the power is increased, the Raman modes for sapphire at 417 cm$^{-1}$ start to disappear until the power reaches 137 W (Figure 4b), and the S/Mo ratio increases to 1.93:1 at 137 W (Figure 4c). These results indicate that a minimum power level is essential for dissociating S. Nonetheless, increasing the power to 150 W reduces the S/Mo ratio slight. Ni and Cl contaminants remained around 1% for all films produced and Cl became undetectable at 150 W (Figure 4c).

Chlorine contamination in all of the produced samples is at or below 1% (Figures 2 and 4c). This is likely due to a combination of Ar bombardment and Cl etching. Cl radicals that attach to an MoS$_2$ molecule at the surface reduce the molecule’s adsorption to the surface and make it easier for incoming Ar ions to sputter it into the gas phase while pure MoS$_2$ is harder to sputter. Substrate holder contaminants are also reduced to a minimum (below 1%) by using a Cl-resistant Ni 201 alloy substrate holder (Figure 4). The samples produced at 5 sccm Ar$_{\text{precursors}}$ flow had the highest
contamination from the Ni substrate holder, although it remained on the order of 1% or less.

2.3. Nanoparticle-like Films and Surface Nucleation.

From the previous studies, it remains unclear whether or not the roughness observed in Figure 1a is due to the deposition of nanoparticles formed in the gas phase or from the nucleation of particles on the substrate surface. Therefore, a high precursor concentration in the gas phase, associated with a low \( \text{Ar}_{\text{precursors}} \) flow, of 5 sccm, was used as such conditions are typically associated with particle growth in the plasma.\(^{49,50}\)

Figure 5 demonstrates that nanoparticle-like MoS\(_2\) films are observed under the chosen precursor flow rate conditions. These nanoparticle features are better observed under higher-resolution AFM, as shown in Figure S2. After a 1 min deposition, only a few nanoparticle-like features are observed on the substrate, which are rich in Mo (Figures S1 and S3). This suggests that particles are not formed in the gas phase, as nucleation events in the plasma are typically associated with high particle concentrations, on the order of \(10^{11}\) to \(10^{12}\) cm\(^{-2}\).\(^{49,50}\) Because a significant fraction of the few nanometer-sized particles created during a nucleation event is neutral, and thus not trapped by the electric fields in the plasma, a larger concentration of particles should be expected on the substrate after 1 min of deposition.

Depositions for longer times show that the number and size of the nanoparticle-like features on the substrate continue to increase. Figure Sb shows the increase in the average particle size with deposition time. Higher-resolution AFM is shown in Figure S2 for three different times, detailing the profiles of the particle-like features on the surface. The few areas with spikes located on the surface of the nanoparticles are acoustic artifacts and not representative of actual surface morphology.\(^{52}\) It should be noted that the regions between the particle-like features are devoid of smaller particles, which also suggests that there are no nanoparticles formed through gas-phase nucleation.

Raman scattering indicates that the \( A_{1g} \) and \( E_{2g} \) modes associated with two-dimensional MoS\(_2\) are present in all films, regardless of the size of the nanoparticle-like features (Figure S5). The \( A_{1g} \) and \( E_{2g} \) modes are located at 406.9 and 382.6 cm\(^{-1}\) for 1 and 2 min deposition films, consistent with four monolayers.\(^{46}\) The modes shift to 405.7 and 382.6 cm\(^{-1}\) for the 4 and 6 min deposition films, consistent with three monolayers.\(^{46}\) The lack of the sapphire-related peak at deposition times longer than 1 min suggests that the substrate is largely covered with two-dimensional MoS\(_2\) between the particle-like features. The XPS results of these films are provided in Figure S3. All of the above observations suggest a surface nucleation mechanism of the particle-like features, rather than a gas-phase nucleation mechanism.

The transition to smooth films can be interpreted in terms of changes in the surface nuclei and the stoichiometry of the growing films. The films are initially limited by the molybdenum species attaching to, or decomposing on, the surface of the sapphire substrate as the sulfur would evaporate at these temperatures. As deposition continues, there is a distinct transition from a surface that contains several Mo-rich nanoparticle-like features at 1 min of deposition (Figures S1 and S3) to a continuous MoS\(_2\) film with larger nanoparticle-like features at 2 min (Figure 5a). These amorphous substoichiometric MoS\(_2\) particles have dangling bonds, which pervade the surface. Because of their amorphous nature, the nanoparticle-like features can undergo significant radial and vertical growth while acting as sites for lateral nucleation of crystalline MoS\(_2\) during synthesis (Figure S5a,b).

In order to prevent the formation of larger amorphous substoichiometric MoS\(_2\), nanoparticle-like features, we reduced the total concentration of the precursors in the gas phase to reduce the size and growth rate of the initial Mo-rich nanoparticle-like nuclei. This delays the rapid growth of the amorphous structures by allowing more time for these smaller nanoparticle-like nuclei to crystallize and form stoichiometric MoS\(_2\). These crystalline surface MoS\(_2\) nuclei then become the seeds for growth, rather than the larger amorphous features. Because of the lattice match and growth direction, the basal plane of the crystalline MoS\(_2\) is perpendicular to the sapphire substrate which forces growth in the lateral rather than the vertical direction, resulting in ultrathin films, which explains the transition found in Figure 1a–d.

3. CONCLUSIONS

Both smooth few-layer two-dimensional MoS\(_2\) thin films and films with nanoparticle-like features were produced using PECVD with a total process time of 5 min for most films, which is faster than most conventional processes. Furthermore, this process realized Cl-free films without the use of H\(_2\) while utilizing nontoxic elemental sulfur, rather than H\(_2\)S, as the sulfur precursor. The morphology of the films was found to vary with the precursor concentration in the gas phase, controlled via the Ar flow rate (\( \text{Ar}_{\text{precursors}} \)) through the sulfur sublimator. Few-layer two-dimensional films with minimal particle contamination were grown by utilizing a high \( \text{Ar}_{\text{precursors}} \) flow rate. Films with large nanoparticle-like features could be grown by utilizing a low \( \text{Ar}_{\text{precursors}} \) flow rate. Studies
of different deposition times suggest that the nanoparticle-like features nucleate on the surface rather than in the gas phase.

Few-layer two-dimensional films were characterized with Raman, UV–vis, XPS, and STEM and were found to be consistent with previously reported literature on two-dimensional MoS₂. Plasma power was positively correlated with increasing sulfur incorporation, the rate of film growth, and good MoS₂ stoichiometry. Low plasma powers did not produce continuous films and contained only a few nanoparticle features.

The nonthermal plasma process demonstrated here has offered a fast process for producing MoS₂ films with characteristics that may be advantageous for HER devices as the vacancies and defects in these films may provide active sites for hydrogen evolution. Furthermore, secondary plasma processing could provide options for film modification that may further increase the films’ potential for HER catalysts. Although proper precautions, such as the use of a Ni alloy, can mitigate much of the damage and possible contamination caused by the corrosive environment, further design considerations to adjust for continuous operation under such an environment would need to be implemented for industrial applications.

4. METHODS

4.1. Plasma Synthesis Conditions and Reactor Details. MoS₂ thin films are synthesized via a nonthermal PECVD process. The reactor is shown in Figure 6. An inductively coupled plasma (ICP) is excited with a seven-turn copper coil with a length of 3.8 cm that was wrapped around a quartz reactor tube. The quartz tube has the following dimensions: 355 mm length, 25 mm outer diameter, and 21.8 mm inner diameter. The injection port is a 9.6 mm outer diameter quartz tube with a 7 mm inner diameter and is 51 mm in total length inside the reactor. It is located 127 mm from the left end of the reactor and delivers the precursor gas flow to the center of the inductive plasma region. A primary Ar flow (Armain) is held constant at 30 sccm for all experiments. Heated portions of the reactor are highlighted in red in Figure 6. The sapphire substrate is held by a nickel 201 alloy rod and clamp at a distance of 2.54 cm from the inlet (X in Figure 6) and 0.64 cm (Y in Figure 6) from the 3.8 cm long ICP coil. Reactions are carried out at rough vacuum (220–400 mTorr). The pump used was a D16B Leybold pump with Krytox PFPE oil because of the corrosive nature of Cl released from the Mo precursor.

Two solid precursors are heated to provide sufficient vapor pressure and carried into the reactor via an Ar flow (Arprecursors). Molybdenum pentachloride (MoCl₅, Sigma-Aldrich 95%) was kept at 80 °C using a BriskHeat heating tape (BWH051040L) and controller (SDC120JC-A) in a metal containment vessel with Swagelock SS-4B8 valves. Elemental sulfur (S₀, Alfa-Aesar puratronics 99.99999%) was heated to 120 °C with a BriskHeat heating tape (BWH051080L) and controller (SDC120JC-A) in a vessel with Swagelock SS-4B8 valves. The outlets of the S₀ and MoCl₅ sublimators meet in a three-way section, which connects to a quartz tube reactor via a quartz to metal weld. All heated elements were connected with SS-VCR or SS Swagelock connections. Ar (99.9993%) (Arprecursors) at 5–30 sccm was flown through the sulfur (Alfa Aesar 99.9995% puratronics sulfur) sublimator to carry its vapor into the system. The mass flow of MoCl₅ was adjusted through the sublimator temperature; no independent mass flow controller was used. Armain was maintained at 30 sccm for all experiments.

Although not well known, carbon contamination from elemental sulfur sources can be a very detrimental and a significant contributor to contamination in plasma-produced films.⁵³ Though a high-purity sulfur precursor was used, this precursor still contains contaminants from hydrocarbons and sulfur oxide compounds at mass fractions on the order of μg/g. Because we are growing atomically thin materials, we have found these contaminants to be significant. Hence, sulfur was purified by first grinding it into a powder and removing all visible black chunks, ostensibly carbon. The sulfur powder was then placed in a glass container and heated to 80 °C for 4 days under air to remove as many remaining hydrocarbons as possible. Prior to running experiments, an initial sacrificial sample was produced under normal running conditions before actually running the rest of the experiments.

To run experiments, sapphire substrates were cleaned with methanol and dried under vacuum. They were then placed on the substrate holder. After the substrate was placed into the reactor, the reactor was allowed to achieve vacuum for 1 min. Then, an ICP was initiated by applying high-frequency power to the induction coil using an ENI A150-1210 power amplifier fed by a Tektronix AFG 3251 arbitrary function generator running between 300 and 700 mVpp, and a Vectronics HFT-1500 matching network.

To produce thin films, power is set to 137 W (nominal power) and the pressure is set to 200 mTorr using 30 sccm Armain and 30 sccm Arprecursors. First, a sapphire substrate is loaded into the vacuum chamber and allowed to rest for 1 min with Armain flowing at 30 sccm and Arprecursors at 30 sccm. Second, a 137 W ICP in pure Ar is ignited for 1 min. The purpose of this step is to clean the reactor tube and heat up the substrate, as shown in Figure 7, the region with light blue background. Third, the plasma is turned off and the precursor valves are opened. Fourth, the ICP is reignited and is sustained for 2 min. Finally, the plasma is turned off and both precursor flows are stopped by closing the valves. The substrate remains in the chamber for 1 min before being removed.

Run conditions for films exhibiting nanoparticle-like features are identical to the thin-film process with the exception of the change in Arprecursors to 5 sccm and deposition time to 2–8 min.

![Figure 7. Transient temperature profile of the substrate holder measured with (red circle/black diamond) and without (green down triangle/blue triangle) a substrate in the holder. Temperature measurements were taken at 15 s time intervals using the standard operating procedure for all films at 137 W for two different flow rates of 5 sccm (black diamond/blue triangle) and 30 sccm (red circle/green down triangle) of Arprecursors.](https://doi.org/10.1021/acsomega.0c02947)
The temperature of the substrate is obviously expected to be an important parameter in the deposition of MoS2. Unfortunately, because of the heat fluxes associated with the ICP and the thermal mass of the metallic sample holder, it is difficult to achieve a steady substrate temperature or to actively control the temperature. Hence, we adopted the 1 min cleaning/preheating step to raise the substrate temperature before introducing precursors. In Figure 7, the time from −1 to 0 min refers to this clean/preheat stage, followed by actual deposition at times after 0 min that contained an Ar plasma with S8, MoCl5, and Ar precursors flowing. The figure demonstrates that there is an about 50 °C difference in the temperature measured with and without the substrate in place, likely because of the thermal interface resistance between the substrate and the holder. It should thus be assumed that the substrate temperature is closer to the higher temperatures, that is, the green and blue curves in this figure. The figure also demonstrates that the influence of the flow rate of Ar precursors is small.

4.2. Material Characterization. XPS was conducted on a PHI Versa Probe III XPS and UPS (UV photoelectron spectroscopy) system. High-resolution scans were performed at 55 eV band-pass energy for 10 scans. An Al Kα source was used. A 100 μm spot was used for collection. Data collection was performed under neutralizing ion and electron irradiation (dual-beam charge neutralization). Peaks were adjusted according to the adventitious carbon peak located at 248.8 eV. Subsequent analyses of the peaks were performed using PHI’s “Multipak” software. To collect atomic percentages, XPS survey scans were taken at a band-pass energy of 280 eV for five scans. The atomic percentages were then calculated using PHI’s “Multipak” software. The analysis procedure for these films can be found in the Supporting Information (Figure S4).

Raman spectroscopy analysis was completed on a Witec Alpha 300R confocal Raman microscope with a 532 nm laser. Spectra were collected with a grating of 1800 grooves/mm with five accumulations of 10 s.

AFM was performed on a Bruker Nanoscope V Multimode 8 with QNM. Images were taken using a n-type silicon tip coated in aluminum (HQ:NSC36/AL BS-15) with a force constant of 0.6 N/m and a resonant frequency of 65 kHz. The coated in aluminum (HQ:NSC36/AL BS-15) with a force constant between 8 and 20 nN. peak force tapping mode was used with a frequency of 1 Hz and a force constant between 8 and 20 nN.

Ultraviolet–visible (UV–vis) absorbance measurements were carried out on a Cary 700 UV–vis spectrometer. Corrections were made to the spectrum based on a sapphire background taken prior to data collection.

STEM was performed on an aberration-corrected FEI Titan G2 60–300 STEM operated at 200 kV with a convergence angle of 25 mrad and a beam current of 125 pA. Cross-sectional lamellae of the films were prepared using a Helios NanoLab G4 dual-beam FIB.

Associated Content

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02947.

Additional XPS and AFM data (PDF)
Films Directly on a Plastic Substrate Using Plasma-Enhanced Chemical Vapor Deposition. *Adv. Mater.* 2015, 27, 5223–5229.

(28) Jang, Y.; Yeo, S.; Lee, H.-B.-R.; Kim, H.; Kim, S.-H. Wafer-scale, conformal and direct growth of MoS2 thin films by atomic layer deposition. *Appl. Surf. Sci.* 2016, 365, 160–165.

(29) Kim, Y.; Kwon, S.; Seo, E.-J.; Nam, J. H.; Jang, H. Y.; Kwon, S.-H.; Kwon, J.-D.; Kim, D.-W.; Cho, B. Facile Fabrication of a Two-Dimensional TMD/Si Heterojunction Photodiode by Atmospheric-Pressure Plasma-Enhanced Chemical Vapor Deposition. *ACS Appl. Mater. Interfaces* 2018, 10, 36136–36143.

(30) Hussain, S.; Singh, J.; Vikraman, D.; Singh, A. K.; Iqbal, M. Z.; Khan, M. F.; Kumar, P.; Choi, D. C.; Song, W.; An, K. S.; Eom, J.; Lee, W. G.; Jung, J. Large-area, continuous and high electrical performances of bilayer to few layers MoS2 fabricated by RF sputtering via post-deposition annealing method. *Sci. Rep.* 2016, 6, 30791.

(31) Sharma, A.; Verheijen, M. A.; Wu, L.; Karwal, S.; Vandalon, V.; Knoops, H. C. M.; Sundaram, R. S.; Hofmann, J. P.; Kessels, W. M. M.; Bol, A. A. Low-temperature plasma-enhanced atomic layer deposition of 2-D MoS2: Large area, thickness control and tuneable morphology. *Nanoscale* 2018, 10, 8615–8627.

(32) Bertolazzi, S.; Bonato, V.; Nan, G.; Pershin, A.; Beljonne, D.; Samori, P. Engineering Chemically Active Defects in Monolayer MoS2 Transistors via Ion-Beam Irradiation and Their Healing via Vapor Deposition of Alkanethiols. *Adv. Mater.* 2017, 29, 1606760.

(33) Lei, Y.; Zhou, X.; Zong, W.; Li, N.; Wang, J.; Meng, J.; Liao, M.; Zhao, J.; Li, X.; Xu, L.; Zhang, Y.; Zang, X.; Zhan, G. Argon Plasma Induced Phase Transition in Monolayer MoS2. *J. Am. Chem. Soc.* 2017, 139, 10216–10219.

(34) Liu, Y.; Nan, H.; Wu, X.; Pan, W.; Wang, W.; Bai, J.; Zhao, W.; Sun, L.; Wang, X.; Ni, Z. Layer-by-layer thinning of MoS2 by plasma. *ACS Nano* 2013, 7, 4202–4209.

(35) Xiao, S.; Xiao, P.; Zhang, X.; Yan, D.; Gu, X.; Qin, F.; Ni, Z.; Han, Z. J.; Ostrrikov, K. Atomic-layer soft plasma etching of MoS2. *Sci. Rep.* 2016, 6, 19945.

(36) Lin, T.; Kang, B.; Jeon, M.; Huffman, C.; Jeon, J.; Lee, S.; Han, W.; Lee, J.; Lee, S.; Yeom, G.; Kim, K. Controlled Layer-by-Layer Etching of MoS2. *ACS Appl. Mater. Interfaces* 2015, 7, 15892–15897.

(37) Jeon, M. H.; Ahn, C.; Kim, H.; Kim, K. N.; LiN, T. Z.; Qin, H.; Kim, Y.; Lee, S.; Kim, T.; Yeom, G. Y. Controlled MoS2 layer etching using CF6 plasma. *Nanotechnology* 2015, 26, 355076.

(38) Chen, X.; Park, Y. J.; Das, T.; Jang, H.; Lee, J.-B.; Ahn, J.-H. Lithography-free plasma-induced patterned growth of MoS2, and its heterojunction with graphene. *Nanoscale* 2016, 8, 15181–15188.

(39) Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From bulk to monolayer MoS2 Evolution of Raman scattering. *Adv. Funct. Mater.* 2012, 22, 1385–1390.

(40) Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S.; Ryu, S. Anomalous Lattice Vibrations of Single- and few-layer MoS2. *ACS Nano* 2010, 4, 2695–2700.

(41) Porto, S. P. S.; Krishnan, R. S. Raman effect of corundum. *J. Chem. Phys.* 1967, 47, 1009–1012.

(42) 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.

(43) Dhakal, K. P.; Duong, D. L.; Lee, J.; Nam, H.; Kim, M.; Kan, M.; Lee, Y.; Kim, J. Confocal absorption spectral imaging of MoS2: Optical transitions depending on the atomic thickness of intrinsic and chemically doped MoS2. *Nano Letters* 2014, 6, 13028–13035.

(44) Wu, R. J.; Udyavara, S.; Ma, R.; Wang, Y.; Chhowalla, M.; Birol, T.; Koester, S. J.; Neurock, M.; Mikhoyan, K. A. Visualizing the metal-MoS2 contacts in two-dimensional field-effect transistors with atomic resolution. *Phys. Rev. Mater.* 2019, 3, 111001.
(46) Ganta, D.; Sinha, S.; Haasch, R. T. 2-D Material Molybdenum Disulfide Analyzed by XPS. Surf. Sci. Spectra 2014, 21, 19–27.
(47) Scanlon, D. O.; Watson, G. W.; Payne, D. J.; Atkinson, G. R.; Egdell, R. G.; Law, D. S. L. Theoretical and experimental study of the electronic structures of MoO₃ and MoO₂. J. Phys. Chem. C 2010, 114, 4636–4645.
(48) Klapper, H. S.; Zadorozne, N. S.; Rebak, R. B. Localized Corrosion Characteristics of Nickel Alloys: A Review. Acta Metall. Sin. 2017, 30, 296–305.
(49) Bouchoule, A.; Boufendi, L. Particulate formation and dusty plasma behaviour in argon-silane RF discharge. Plasma Sources Sci. Technol. 1993, 2, 204–213.
(50) Hwang, H. H.; Kushner, M. J. Regimes of particle trapping in inductively coupled plasma processing reactors. Appl. Phys. Lett. 1996, 68, 3716–3718.
(51) Schweigert, V. A.; Schweigert, I. V. Coagulation in a low-temperature plasma. J. Phys. D: Appl. Phys. 1996, 29, 655–659.
(52) Ricci, D.; Braga, P. C. Atomic Force Microscopy; Humana Press: New Jersey, 2004; Vol. 242, pp 25–38.
(53) Susman, S.; Clark Rowland, S.; Volin, K. J. The purification of elemental sulfur. J. Mater. Res. 1992, 7, 1526–1533.