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Atomic Layer Deposition of Al-Doped MoS₂: Synthesizing a p-type 2D Semiconductor with Tunable Carrier Density

Vincent Vandalon,* Marcel A. Verheijen, Wilhelmus M. M. Kessels, and Ageeth A. Bol*

ABSTRACT: Extrinsic doping of two-dimensional (2D) semiconductors is essential for the fabrication of high-performance nanoelectronics among many other applications. Herein, we present a facile synthesis method for Al-doped MoS₂ via plasma-enhanced atomic layer deposition (ALD), resulting in a particularly sought-after (virtually) Ohmic contacts needed for high-performance doping is also a promising route toward realizing high-quality not intentionally doped) TMDs. The ALD-based approach also offers excellent control over the doping profile, as demonstrated by a combined transmission electron microscopy and energy-dispersive X-ray spectroscopy study. Sharp transitions in the Al concentration were realized and both doped and undoped materials had the characteristic 2D-layered nature. The fine control over the doping concentration, combined with the conformality and uniformity, and subnanometer thickness control inherent to ALD should ensure compatibility with large-scale fabrication. This makes Al:MoS₂ ALD of interest not only for nanoelectronics but also for photovoltaics and transition-metal dichalcogenide-based catalysts.

KEYWORDS: ALD, transition-metal dichalcogenide, 2D TMD, MoS₂, doped semiconductor, thin film

INTRODUCTION

Two-dimensional (2D) layered transition-metal dichalcogenides (TMDs) are of interest for the fabrication of future nanoelectronics because of their promising (electronic) properties that remain predictable in the mono- and few-layer thickness regime. As a result, a significant effort has already been made to fabricate and characterize intrinsic (i.e., not intentionally doped) TMD films and devices. Most of the intrinsic TMDs, despite not being intentionally doped, show a slight n-type behavior. However, for the fabrication of future TMD-based nanoelectronics, not only an intrinsic material with good electronic properties is needed but also p-type semiconducting TMDs with extrinsic (i.e., intentional) doping are essential. TMD-based field-effect transistors (FETs) have already been realized with intrinsic materials. However, to fabricate truly high-performance FETs, locally doped regions and control over the carrier density are essential. Extrinsic doping of TMDs will also play a role in other transistor designs. For example, the operating principle of bipolar junction transistors is based on junctions between p- and n-type materials and cannot be realized until TMDs with both carrier types can be synthesized. Control over doping is also a promising route toward realizing high-quality (virtually) Ohmic contacts needed for high-performance TMD-based devices. In other fields such as photovoltaics, energy storage, and catalysis, controlled doping can also be beneficial. Hence, it is clear that synthesis processes that offer precise control over the charge carrier type, concentration, and doping profile in these TMDs are highly sought-after.

Both the synthesis process and the doping strategy have to be compatible with semiconductor fabrication for successful adoption in future nanoelectronic fabrication. Therefore, both the synthesis and doping need to exhibit conformity over complex 3D features and show wafer-scale uniformity. The synthesis process should exhibit atomic thickness control, the dopant strategy should result in good control over the doping fraction, and the resulting doping should be stable under semiconductor processing conditions. For broad adoption, the synthesis temperature should be below 450 °C to be compatible with back-end-of-line processing although even lower temperatures will be required for demanding substrates such as in flexible electronics. Taking extrinsic doping a step further, control over the doping profile (stepped, graded, linear, and so forth) is also desirable for many nanoelectronic applications.

Several promising synthesis routes for intrinsic TMDs such as MoS₂ and WS₂ have already been identified that are scalable. TMDs synthesized by chemical vapor deposition (CVD) have shown excellent material properties, although their fabrication...
requires relatively high temperatures. With enough care and sufficient optimization, uniform films with good thickness control can be deposited by CVD. Synthesis of TMDs by atomic layer deposition (ALD) yields good quality material at relatively low-growth temperatures (<450 °C), as has been demonstrated by us and others. Furthermore, ALD is known for its excellent thickness control, uniformity, and it is inherently capable of conformally coating complex 3D structures.

Doped variants of semiconducting TMDs such as MoS2 are of interest because of their distinct and tunable (electronic) properties. Naturally occurring MoS2 and most of the synthesized intrinsic MoS2 exhibit weak n-type behavior linked to sulfur vacancies (Sv). These sulfur vacancies are the most common type of defect and act as electron donors. On the other hand, extrinsically (i.e., intentionally) doped materials should allow the synthesis of both p- and n-type doped materials with—in the ideal case—widely tunable and precisely controlled electronic properties. Various extrinsic doping strategies for TMDs have already been explored mainly focusing on the archetype MoS2. Surface-induced doping, such as applying surface treatments (supercacids, functionalization, or plasma exposure) or capping (dielectric films), can effectively induce doping in the TMD but so far leaves a lot to be desired with respect to stability and/or tunability. This is, for example, illustrated by the effect of pressure on surface doping, impacting the carrier density and carrier type such that in specific cases the material changes from p-type to n-type when going from ambient pressure to high vacuum as shown by Di Bartolomeo et al. A more established strategy is substitutional doping; it is the main strategy used to dope bulk materials such as c-Si and this approach is actively being explored for TMDs. In most cases, substitutionally doped MoS2 is synthesized by high-temperature sulfurization (900 °C is not uncommon) of an alloy or a nanolaminate of metallic Mo and the pure dopant. Substitutional doping of TMDs with, for example, Nb, Er, C, Ti, Zn, and Cl, has already been reported using this strategy, resulting in mainly n-type doping, in a few instances, p-type doping, and in most cases this approach exhibited limited control over the dopant level.

With respect to Al as a dopant for TMDs, spontaneous Al doping of MoS2 from an Al2O3 capping layer was shown by Kim et al., indicating that Al could be a promising dopant. For the related WS2, Al doping was obtained by sulfurizing WO3 doped with Al. This resulted in a p-type material with a tunable carrier density ranging between 3 × 10^{15} cm^{-3} and 12 × 10^{15} cm^{-3} for doping up to 8 at. % Al. So far, a doping strategy or synthesis process for p-type doped MoS2 with good control over the dopant level is lacking. Moreover, good control over the doping profile (i.e., spatial distribution) has not been demonstrated for any TMD. In the context of TMD doping, ALD is of particular interest because of the following: ALD has been shown to allow introduction of dopants in an extremely controlled fashion for metal oxides and it is nearly trivial to realize fine-grained control over the doping profile.

In this work, we will demonstrate the synthesis of p-type MoS2 doped with Al by plasma-enhanced ALD at ~350 °C, resulting in a tunable carrier density ranging from ~10^{17} cm^{-3} up to ~10^{20} cm^{-3} while also demonstrating excellent control over the doping profile. Al-doped MoS2 was synthesized by ALD using a supercycle scheme, as illustrated in Figure 1, a strategy well established in the field of ALD. In brief, the ALD supercycle used in this work consisted of N conventional ALD cycles of MoS2 followed by one conventional ALD cycle of AlS3 (see the Supporting Information). In both cases, the ALD cycle started with a precursor dose—using (NtBu)2(N(CH3)2)2Mo for MoS2 and Al(CH3)3 for AlS3—followed by a purging step, a H2S plasma exposure step, and a purging step. This supercycle of 1-AlS3 + N-MoS2 cycle—denoted 1:N for brevity—is repeated until the desired thickness is reached. This Mo precursor was chosen because of its favorable properties for use in ALD (adequate vapor pressure, good temperature stability, and so on), commercial availability, and good film properties demonstrated for the undoped MoS2 ALD processes using this precursor. The control over the dopant concentration by varying N was demonstrated by synthesizing and characterizing films with different dopant cycle ratios. The electronic properties of the Al-doped MoS2 films, their composition, and their crystallinity were studied for various doping cycle ratios. Special attention was paid to the doping profile of Al in the Al:MoS2 films, which was studied by cross-sectional transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) mapping. Finally, our initial insights into the most likely mechanisms describing how Al is doping the MoS2 are discussed.

RESULTS AND DISCUSSION

Influence of Al Doping on the Electronic Properties of ALD MoS2

Aluminum-doped and intrinsic MoS2 films were prepared by ALD to study the impact of Al doping on film properties such as composition, crystallinity, resistivity, and carrier density. Not only the doping cycle ratio was systematically varied to demonstrate the tunability of doping introduced by ALD but also other factors influencing the film properties such as film thickness and annealing were investigated.

Given the central role of the electrical properties of the Al-doped MoS2 films, the resistivity, mobility, and carrier density will be discussed first. A series of samples was fabricated with a doping cycle ratio ranging from 1:1 up to 1:19. An intrinsic MoS2 film, that is, without Al doping, was also fabricated and served as a reference point. For straightforward comparison, all films were grown by 100 total ALD cycles, resulting in ~10 nm thickness, unless stated otherwise. Figure 2 shows the sheet resistance as a function of doping cycle ratio measured by a linear four-point probe (4PP) setup. The figure also shows the
resistivity calculated from the sheet resistance using film thickness measured by spectroscopic ellipsometry (SE), see also the Supporting Information. The intrinsic MoS2 film had a resistivity of 400 Ω·cm (2.5 mS/cm), which decreased with increasing Al doping cycle fraction. The resistivity of the intrinsic film falls within the (wide) range of resistivities reported for synthesized MoS2 ranging from 5 up to 104 Ω·cm.46–49 A minimum resistivity of 0.2 Ω·cm (5 S/cm) was found for a doping cycle ratio of 1:4 after which the resistivity increased with increasing Al:MoS2 doping cycle ratio. To gain additional information about the nature of doping, the electronic properties of the 1:4-doped sample were also measured at 77 K.46 The resistivity was found to increase from 0.2 Ω·cm at room temperature to 72 Ω·cm at 77 K in line with what is typically reported for common dopants with activation energies of typically tens of meV.50,51

The carrier density and carrier mobility were determined using Hall measurements in order to identify the underlying cause for the decrease of resistivity by 3 orders of magnitude. Figure 3 shows the carrier density and the Hall mobility of the same samples as in Figure 2 measured using van der Pauw geometry in air, on a thermally grown SiO2/Si(100) substrate, and at room temperature. All doped samples showed a Hall voltage indicative of p-type charge carriers. The carrier density increased with the doping cycle ratio from 1019 cm−3 for the 1:19 sample up to 1021 cm−3 for the 1:4 sample and then decreased to 1020 cm−3 for the 1:1 sample. The Hall mobility decreased with increasing doping from 0.08 cm2 V−1 s−1 for the sample prepared using the 1:19 doping to 0.01 cm2 V−1 s−1 for the 1:4 doping. Typical values for the mobility of (intrinsic) ALD-grown MoS2 in the literature range from 0.001 up to ~10 cm2 V−1 s−1.20,32 In these synthesized films, the mobility is limited, in most cases, by grain boundary scattering because of the grain size which is typically tens of nanometers. The Hall voltage of the intrinsic sample was below the detection limit of the AC Hall setup; the carrier density was estimated from the resistivity assuming a mobility similar to that of the lowest doped film. The error was calculated using the standard deviation of multiple measurements.

Figure 2. Sheet resistance of intrinsic (0,∞) and Al-doped MoS2 films grown at ~350 °C determined by 4FP measurements plotted as a function of doping cycle ratio. The resistivity was calculated from the sheet resistance using film thickness determined by SE. The error in the resistivity was calculated using the error in the film thickness.

Figure 3. Charge carrier density and mobility of the same Al-doped MoS2 films shown in Figure 2 as a function of doping cycle ratio, as determined from AC Hall measurements. The Hall voltage generated in the intrinsic sample (0,∞) was below the detection limit of the measurement system, and the carrier density was estimated from the resistivity assuming a mobility similar to that of the lowest doped film. The error was calculated using the standard deviation of multiple measurements.

often observed at high or nearly degenerate charge carrier density is largely masked by the limited mobility because of the aforementioned grain-boundary scattering. The one-to-one relation between the doping cycle ratio and the carrier concentration results in precise control over both the carrier density and the resistivity of Al-doped MoS2. Increasing the doping level further from 1:4 to 1:1 shows an increase in resistivity caused by a decrease in carrier concentration. This suggests that ionized impurity scattering or defect scattering is not the main factor contributing to the resistivity; either effect would mainly impact mobility and not carrier density. At a high 1:1 doping cycle ratio, perhaps changes in the crystal structure or formation of (inclusions of), for example, highly resistive Al2S3 could cause the increase in resistivity.

The influence of annealing was studied as this commonly impacts the (electronic) properties of doped thin films.34–36 Both mild annealing—that is, dwelling the sample in the reactor at the deposition temperature of ~350 °C—and high-temperature annealing at 900 °C were studied. To study the impact of mild annealing, two films were grown by performing 100 ALD cycles using the normal process workflow for 1:4 doping. One of the samples was retrieved from the reactor immediately after deposition (normal workflow, duration ~1 h 30 min) and the other sample was kept in the reactor for a duration equivalent to a deposition with 200 cycles before it was retrieved (~3 h). During the extra dwell step, the gas background during a typical deposition was mimicked by flowing H2S, H2, and Ar. No plasma was struck to ascertain the influence of the elevated temperature on the film properties. The sample which was kept longer in the reactor showed a reduction of a factor of ~2 of resistivity (σ = 0.162 Ω·cm, μ = 0.03 cm2 V−1 s−1, and Nh = 1.5 × 1021 cm−3) compared to the standard sample (σ = 0.282 Ω·cm, μ = 0.02 cm2 V−1 s−1, and Nh = 1.4 × 1021 cm−3). The Raman response of the samples was measured, and both samples showed the A1g and E2g peaks indicative of crystalline MoS2. The Raman response of the two samples was of similar strength, indicating that the sample that...
The impact of high-temperature annealing was studied on as-deposited 1:4 and 1:9 samples using a separate furnace setup operated at 900 °C for 45 min flowing Ar + H2S at ambient pressure. The high-temperature annealing did show a significant improvement in crystallinity, as reflected in the Raman response showing stronger and more narrow \( A_{2g} \) and \( E_{2g} \) peaks after annealing (see the Supporting Information). This improved crystallinity is also typically observed for the intrinsic films after high-temperature annealing.\(^{21,57}\) However, the resistivity of both samples increased by more than an order of magnitude to 40 and 70 \( \Omega \cdot \text{cm} \), respectively. This high-temperature annealing was not investigated further because adding a high-temperature annealing rules out compatibility with back-end-of-line processing and deposition on temperature-sensitive substrates, which is one of the benefits of this approach. In contrast to mild annealing, in this case, the temperature is high enough to trigger a rigorous restructuring (approaching the melting point of MoS2) and subsequent recrystallization of the film. It is also possible that at 900 °C—in contrast to the lower deposition temperatures—inclusions of Al2S3 could be formed or Al becomes mobile and is expelled, increasing the resistivity of the films. At the same time, the restructuring would allow the crystallinity of MoS2 to improve, explaining the opposite behavior seen in this case compared to mild annealing.

To gain insight into the influence of deposition temperature on the material properties, doped and intrinsic films were grown at 200 °C. All the films grown at 200 °C were amorphous and had a high resistivity compared to materials deposited at 350 °C for all investigated doping cycle ratios (e.g., 4 \( \times 10^3 \) \( \Omega \cdot \text{cm} \) for a 1:4 doping). Subsequent annealing of these films at 350 °C for 1 h in an H2S environment—similar to the typical deposition conditions at 350 °C—showed a large degree of crystallization but a relatively small reduction of resistivity for all doping cycle ratios (e.g., 20 \( \Omega \cdot \text{cm} \) for the 1:4 sample) compared to the samples grown at 350 °C (0.282 \( \Omega \cdot \text{cm} \) for the 1:4 sample). This higher resistivity for films grown at lower temperatures even after annealing at 350 °C suggests a different doping mechanism for films grown at 350 °C, which is more effective than the doping mechanism for films grown at lower temperatures with or without subsequent annealing at 350 °C. This difference between the Al:MoS2 film grown at 350 °C and the films annealed at 350 °C but grown at 200 °C might also explain why most two-step approaches such as sulfurization of metals and metal oxides have so far been less successful in achieving a widely tunable carrier concentration.

The influence of film thickness on the electrical properties was explored for the optimal 1:4 doping at 350 °C varying between 5 nm up to 30 nm (50 up to 300 cycles). The Hall mobility showed a subtle increase from \( \mu = 0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \) to \( \mu = 0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \) with increasing film thickness, and the carrier density increased from \( N_h = 5 \times 10^{20} \text{cm}^{-3} \) up to \( N_h = 1.2 \times 10^{21} \text{ cm}^{-3} \) for the thickest film (see the Supporting Information). The cause of the increase in mobility and carrier density with film thickness could be related to subtle changes in grain structure, as regularly seen for other materials.\(^{56,59}\) On the other hand, the thicker films are also simply subjected to the deposition temperature (~350 °C substrate temperature) for longer. Effectively, thicker films are annealed longer in a H2S environment than thinner films. Considering the impact of annealing studied earlier, both effects will contribute to the lower resistivity to some extent. Overall, the impact of film thickness on the carrier density is small compared to the tunability range accessible by varying the doping cycle ratio.

To summarize, these results demonstrate control over doping using the ALD supercycle approach. By changing the doping cycle ratio, the carrier density could be tuned over a wide range and showed a 1-to-1 correspondence with the Al doping cycle ratio. This 1-to-1 relation allows for fine control over the carrier density and resistivity by changing the Al:Mo cycle ratio.

**Dopant Profile and Film Characterization.** ALD allows for fine control over the introduction of the Al dopant in the MoS2 films with respect to both the doping concentration and the doping profile. The dopant concentration is determined by the doping cycle ratio. The doping profile is the result of the sequence of supercycles where each consecutive supercycle can have a different doping concentration if desired. In this section, the control that ALD affords over the doping profile will be demonstrated. The local structure and especially the doping profile were studied in dedicated TEM and EDX experiments. The impact of doping on macroscopic aspects such as the chemical composition, crystal structure, and the crystallinity of the doped films will also be investigated.

**Figure 4** shows a high-angle annular dark-field (HAADF)-scanning TEM (STEM) image of a cross-section of a stack consisting of three doped MoS2 regions with intrinsic regions in between. The full stack structure is illustrated in **Figure 4** as well. A Si wafer with 450 nm SiO2 on top was used as a substrate and the MoS2 stack was capped by SiO2 which was needed for focused ion beam (FIB) processing. Each of the MoS2 regions was grown by 100 cycles of ALD, resulting in a thickness of ~10 nm each. The 1:9-doped MoS2 region...
adjacent to the bottom SiO₂ layer in Figure 4 clearly shows the 2D layered structure of MoS₂ in the TEM image, indicating that the doped material is crystalline and layered in nature. Furthermore, the layered structure of the doped region cannot be differentiated from the layered structure of the intrinsic MoS₂ region deposited directly on top of it. A fast Fourier-transform (FFT) analysis of the lattice spacing using HAADF-STEM imaging (see the Supporting Information) of the stack revealed a c axis of 0.65 ± 0.1 nm for both the doped and intrinsic regions. Therefore, these results show that the impact of the Al dopant on the crystal structure and crystallinity is minimal. The minimal changes to the crystal structure are also in line with the observation that doping impacts the carrier density but does not significantly impact the mobility. If the film texture (grain size and orientation) would be strongly impacted by doping, this would influence the mobility which is not observed in the electrical measurements. Also, it should be noted that the unchanged crystal structure is a strong argument to label this material as doped MoS₂.

An open question is how the Al atoms are incorporated in the MoS₂ lattice. Apart from true substitutional doping (i.e., Al on a Mo or S site), these materials are known to allow intercalation of small atoms between the 2D layers, perturbing the distance between the layers. For MoS₂ intercalated with Al, Miremadi and Morrison reported a 0(02) spacing based on X-ray diffraction of 0.550 nm to 0.575 nm for an Al:Mo atomic ratio ranging from 0 to 0.5. In our case, such a change in (002) spacing was below the accuracy of the HAADF imaging combined with FFT analysis (accuracy ~0.1 nm) and therefore could not be observed. It should be noted that even for bulk semiconductors such as Si, it is not trivial to determine the exact site of the dopants, and further dedicated studies will be needed to resolve this.

The doping profile was probed directly by acquiring an EDX mapping from a region across the entire stack. The elemental distributions of Mo, Si, and Al were extracted from the EDX dataset upon pixel-by-pixel quantification of the EDX spectra. Figure 4b shows a combined EDX mapping. Figure 4c the individual mapping of Mo and Figure 4d the mapping of Al. See the Supporting Information for additional Si, O, and S mappings. The Mo mapping shows a uniform distribution throughout the whole stack. The Al mapping shows the three doped and two undoped regions of the same sample, with the sparse 1:19 doping region being faint but still discernible. The spatial distribution of Al inside the doped regions (e.g., homogeneous or layered) could not be revealed because of the low Al concentration combined with the limited spatial resolution of the EDX measurement caused by sample drift. The Al profile, calculated by horizontally integrating the Al signal in the mapping, is shown in Figure 5. This line profile shows the three doped regions, each separated by an intrinsic region. The out-of-plane oriented fin structures, as indicated in Figure 4, are commonly observed in synthesized MoS₂ thicker than ~20 nm, and their formation is not fully understood. For thick films, the fin structure will negatively impact the mobility in conjunction with the limited grain size. These fins lead to an open structure that effectively decreases the density of the film and causes the concurrent decrease seen in the Mo, S, and Al signals in Figure 5. Because of the chosen sequence of doped and intrinsic layers, the fins mainly consist of a "core" of intrinsic MoS₂ which is uniformly coated with Al:MoS₂ reflecting the conformal nature of the ALD growth. Complementary to the TEM and EDX analyses, an X-ray photoemission spectroscopy (XPS) depth profile by Ar sputtering was also obtained on the same sample. This method has a rather coarse depth resolution limited by factors such as preferential sputtering, the probing depth of XPS, and the flat morphology of the sample. Nevertheless, the Al concentration profile did show the expected trend as a function of depth (see also the Supporting Information).

The sharp transition from the 1:9-doped region to the intrinsic MoS₂ seen in Figure 5 demonstrates the capability of ALD to control the doping profile with a resolution better than 1 nm. The interpretation of the subsequent transitions is less clear as they are affected by fin-like features roughening the interface, which is also reflected in the decrease in the Al, Mo, and S signals starting at ~40 nm from the interface. Effectively, the material is becoming less dense from this point onward due to the fin formation. The EDX mapping clearly shows that the bottom layer contains Al, while at the same time the HAADF-STEM imaging did not show any change in the crystal structure between the doped and intrinsic regions, nor is there a visible disruption of the 2D layered nature or crystal structure at the transition point. Large-scale migration or clustering of Al can be ruled out based on the combined EXD and HAADF-STEM analysis of the unannealed material prepared at 350 °C.

The impact of dopant incorporation on the crystallinity of the films was also studied by Raman spectroscopy. All films exhibited the characteristic A₁g and E₂g peaks of crystalline MoS₂, in line with the crystallinity seen in the cross-sectional TEM results. The Raman response of the doped MoS₂ films showed only minimal changes compared to the intrinsic film (see the Supporting Information), with the 1:4 doping showing a slight decrease in intensity and broadening of the characteristic A₁g and E₂g peaks. This suggests a slightly more disordered, yet crystalline structure. The dopant concentration in TMDs has been shown to affect the spectral position of the Raman peaks, however, this effect is difficult to isolate from other effects such as texture, strain, and grain size, which also likely play a role in these films.

The chemical composition of the Al:MoS₂ films was determined by XPS surface scans. Figure 6 shows the typical XPS response in the Mo 3d and S 1s, S 2p, Al 2p, and C 1s regions (in this case, the 1:4 sample). The elemental composition of the films was quantified from the XPS spectra using appropriate sensitivity factors resulting in Table 1. Both the doped and intrinsic films are stoichiometric in their Mo to S content. The concentration of C and O in the bulk of the
Extended X-ray absorption fine structure combined with \textit{ab initio} simulation will most likely be necessary to directly address these questions. While there is insufficient evidence to conclusively answer these questions, several possibilities can already be ruled out at this stage. The XPS results indicate that Al is not bound to Mo or Al, ruling out (i) the formation of large metallic clusters and (ii) Al occupying a S site. This is also in line with the EDX mapping not showing Al clusters. The position of the Al 2p peak suggests that Al is bonded to S. Another possibility that can be ruled out is the formation of Al$_2$S$_3$ clusters. Although Al$_2$S$_3$ exists and can be synthesized by ALD,\textsuperscript{53,69,69} this material is a wide band gap insulator.\textsuperscript{33,70} Therefore, formation of Al$_2$S$_3$ inclusions on a large scale would almost certainly lead to an increase in resistivity with increasing Al concentration rather than the decrease observed in this work. The Al atoms could occupy a Mo site, but other possibilities including interstitial positions and intercalation (as discussed earlier) cannot be ruled out based on our current data. \textit{Ab initio} density-functional theory (DFT) simulations by Zhang \textit{et al.} and Luo \textit{et al.} have shown that it is energetically favorable for Al to occupy a Mo site.\textsuperscript{71,72} On the other hand, extrapolating the DFT simulations by Zhao \textit{et al.} for Sc through Zn doping of the related MoSe$_2$ would suggest that Al could occupy an interstitial site.\textsuperscript{73} It is not straightforward to determine the doping efficiency as it is not yet known how Al dopes with MoS$_2$ combined with the fact that Al can assume different dopant multiplicities (from Al$^+$ up to the Al$^{3+}$ state).\textsuperscript{68,74–78} However, the simplest scenario of Al acting as a 1-fold acceptor seems unlikely based on a carrier density of $10^{21}$ cm$^{-3}$ and an Al density of $5 \times 10^{20}$ cm$^{-3}$ (estimated using the known Mo density of MoS$_2$ and the atomic percentage of Al, as measured by XPS). Al could act as a dopant with higher multiplicity or more indirectly dope the material by, for example, impacting other impurities in the material.\textsuperscript{51}

Taking a step back, at this stage, several scenarios have been ruled out: there is no evidence for the formation of clusters of metallic Al or insulating Al$_2$S$_3$ which could impact the electronic properties. It is also not likely that Al acts as a simple one-fold substitutional donor. As stated before, further work most likely in the form of dedicated mechanistic studies is necessary to fully understand how Al dopes MoS$_2$, but this does not diminish the practical application of this material.

### CONCLUSIONS

Aluminum doped MoS$_2$ films were synthesized by ALD, resulting in a p-type doped material with excellent control over the carrier concentration ranging from $10^{17}$ to $10^{22}$ cm$^{-3}$ without a significant impact on the charge carrier mobility by varying the dopant cycle ratio. This precise control is also reflected in the 1-to-1 relation between the Al-to-MoS$_2$ cycle ratio and the carrier density. Our supercycle ALD approach also afforded excellent control over the doping profile: a TEM and EDX study mapping a cross-section of a stack of doped and undoped layers demonstrated control over the doping concentration on the nanometer scale. The Al:MoS$_2$ grown by ALD at 350 °C was found to be crystalline and the introduction of the dopant did not disturb the 2D layered nature of the material or the crystal growth. Furthermore, the well-behaved nature of the ALD supercycle scheme implies that the key merits of ALD such as excellent thickness control, uniformity, and conformality are retained. The ALD supercycle scheme used here to synthesize the Al-doped MoS$_2$ film has already been shown to be compatible with large-scale material
synthesis for more conventional materials such as doped metal oxides. Therefore, the workflow presented here is expected to be compatible with the fabrication of nanoelectronics. To conclude, the realization of the desirable \( p \)-type 2D material doping, the widely tunable carrier concentration, and the control over the doping profile combined with the compatibility of the approach with semiconductor fabrication make the Al:MoS\(_2\) process a promising step toward the fabrication of high-performance (doping-based) nanoelectronics.

**EXPERIMENTAL DETAILS**

The Al-doped MoS\(_2\) films were synthesized using an Oxford Instruments FlexAL2 using a supercycle scheme. The films were grown using a table temperature of 450 °C, resulting in a sample temperature estimated to be 350 °C.\(^{7,8}\) The Al part of the supercycle recipe was based on the approach of Kuhs \textit{et al.}\(^{23}\) for the synthesis of Al\(_2\)S\(_3\) and consisted of a trimethylaluminum (Al(CH\(_3\))\(_3\)) dose of 40 ms followed by a purge and a H\(_2\)-H\(_2\)S-\( \text{Ar} \) plasma exposure (low: 2, 9, and 50 sccm, respectively) for a duration of 20 s again followed by a purge. The residual gases from the ALD reactor are routed through a mechanical filter and a carbon filter, diluted, and then go through a water-scrubber before being fed into the exhaust lines of the cleanroom in which the setup is situated. The MoS\(_2\) part of the supercycle is a replicate of the work of Sharma \textit{et al.}\(^{21}\) performed in the same ALD system. In brief, during the MoS\(_2\) cycle, (\( \text{NBTi} \), (\( \text{NCH}_3 \)), \( \text{Mo} \)) was dosed for 6 s as the Mo precursor, followed by a purge, then the aforementioned H\(_2\)-H\(_2\)S-\( \text{Ar} \) plasma exposure for a duration of 20 s, and a purge. All films were grown on a Si(100) substrate with a thermally grown 450 nm SiO\(_2\) film on top.

The thickness of the films grown by the supercycle-based ALD process was monitored during growth by \textit{in situ} SE using a Woollam M2000F. The optical properties of the Al:MoS\(_2\) film were described using a B-spline model, which showed a complex refractive index.

To summarize, the characteristics are indicative of a well-behaved ALD process.

The electrical characterization of the films was performed with a four-point probe (4PP) setup based on a Keithley 2400 source using a Signatone SP4-4004TRS as a probe head. The resistivity was calculated from the sheet resistance measured by the 4PP using the film thickness determined by SE using a Woollam M2000D. The mobility and carrier density were measured in a van der Pauw configuration using a Lakeshore 8404 Series HMS. To detect the relatively weak Hall voltages, an AC measurement scheme with lock-in on the oscillating magnetic field was used on all samples. The chemical composition of the samples was studied by XPS using a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic Al \( K \alpha \) X-ray source (\( h\nu = 1486.6 \text{ eV} \)). The charge on the samples was neutralized during the XPS analysis using a flood gun in order to correct for differential or nonuniform charging. The Raman response was measured using a Renishaw invia confocal Raman microscope with a 415 nm laser and a 50× NA = 0.75 objective. For each measurement, 10 spectra were acquired with an integration time of 10 s each and a laser power of \( \sim 0.2 \text{ mW} \) focused on a \( \sim 1 \mu \text{m} \) diameter spot. The TEM and STEM imaging was performed using a probe-corrected JEOL ARM 200F operated at 200 kV, equipped with a 100 mm\(^2\) Centurio SDD EDS detector. The cross-sectional TEM sample was obtained using FIB preparation following a standard lift-out procedure.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c02167.

**REFERENCES**

1. Rai, A.; Movva, H.; Roy, A.; Taneja, D.; Chowdhury, S.; Banerjee, S. Progress in Contact, Doping and Mobility Engineering of MoS\(_2\): An Atomically Thin 2D Semiconductor. \textit{Crystals} 2018, 8, 316.
2. McDonnell, S. J.; Wallace, R. M. Atomically-Thin Layeredfilms for Device Applications Based upon 2DTMDM Materials. \textit{Thin Solid Films} 2016, 616, 482–501.
3. Davies, J. H. \textit{The Physics of Low-Dimensional Semiconductors: An Introduction}; Cambridge University Press, 1998.
4. Yu, Z.; Ong, Z. Y.; Li, S.; Xu, J. B.; Zhang, G.; Zhang, Y. W.; Shi, Y.; Wang, X. Analyzing the Carrier Mobility in Transition-Metal Dichalcogenide MoS\(_2\) Field-Effect Transistors. \textit{Adv. Funct. Mater.} 2017, 27, 1604093 DOI: 10.1002/adfm.201604093.
5. Zhou, W.; Zou, X.; Najaime, S.; Liu, Z.; Shi, Y.; Kong, J.; Lou, J.; Ayajan, P. M.; Yakobson, B. I.; Idrobo, J.-C. Intrinsic Structural Defects in Monolayer Molybdenum Disulfide. \textit{Nano Lett.} 2013, 13, 2615–2622.
6. Pierucci, D.; Henck, H.; Ben Aziza, Z.; Naylor, C. H.; Balan, A.; Rault, J. E.; Silly, M. G.; Dappe, Y. J.; Bertran, F.; Le Fèvre, P.; Sirotti, F.; Johnson, A. T. C.; Ouerghi, A. Tunable Doping in Hydrogenated....

**AUTHOR INFORMATION**

**Corresponding Authors**

Vincent Vandalon — Applied Physics, Eindhoven University of Technology, 5600MB Eindhoven, The Netherlands; Email: v.vandalon@tue.nl

Ageeth A. Bol — Applied Physics, Eindhoven University of Technology, 5600MB Eindhoven, The Netherlands; Email: a.a.bol@tue.nl

**Authors**

Marcel A. Verheijen — Applied Physics, Eindhoven University of Technology, 5600MB Eindhoven, The Netherlands; Eurofins Material Science Netherlands BV, 5656AE Eindhoven, The Netherlands; Email: a.a.bol@tue.nl

Willem M. M. Kessels — Applied Physics, Eindhoven University of Technology, 5600MB Eindhoven, The Netherlands; Email: a.a.bol@tue.nl

Complete contact information is available at: https://pubs.acs.org/10.1021/acsanm.0c02167

**Notes**

The authors declare no competing financial interest.

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Single Layered Molybdenum Disulfide. *ACS Nano* **2017**, *11*, 1755–1761.

(12) Sharma, A.; Verheijen, M. A.; Knoch, H. C. M.; Potts, S. E.; Bol, A. A.; Kessels, W. M. M. Atomic Layer Deposition. Handbook of Crystal Growth; Elsevier, 2015; Vol. 39, pp 1101–1134.

(13) Kim, H.-J.; Yang, S.; Kim, H.; Moon, J. Y.; Park, K.; Park, Y.-J.; Kwong, Y. J. Enhanced Electrical and Optical Properties of Single-Layered MoS2 by Incorporation of Aluminum. *Adv. Funct. Mater.* **2018**, *28*, 11907–11913.

(14) Mattinen, M.; Hatanpää, T.; Sarnet, T.; Mizohata, K.; Meinander, K.; King, P. J.; Khiatichuev, L.; Rääsiäinen, J.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of Crystalline MoS2 Thin Films: New Molybdenum Precursor for Low-Temperature Film Growth. *Adv. Mater. Interfaces* **2017**, *4*, 1700132.

(15) Knoch, H. C. M.; Potts, S. E.; Bol, A. A.; Kessels, W. M. M. Atomic Layer Deposition. Handbook of Crystal Growth; Elsevier, 2015; Vol. 39, pp 1101–1134.

(16) Knoch, H. C. M.; Potts, S. E.; Bol, A. A.; Kessels, W. M. M. Atomic Layer Deposition. Handbook of Crystal Growth; Elsevier, 2015; Vol. 39, pp 1101–1134.

(17) Knoch, H. C. M.; Potts, S. E.; Bol, A. A.; Kessels, W. M. M. Atomic Layer Deposition. Handbook of Crystal Growth; Elsevier, 2015; Vol. 39, pp 1101–1134.

(18) Liao, Z.; Liu, S.; Zhang, G.; Zeng, W.; Wang, Z.; Zhao, Y.; Yang, Z.; Hu, Y.; Yang, F.; Zeng, W.; Zeng, H.; Yang, Z. Modulating Electronic, Magnetic and Chemical Properties of MoS2 Monolayer Sheets by Substitutional Doping with Transition Metals. *Adv. Sci.* **2016**, *3*, 1600204.

(19) Delabie, A.; Vandervorst, W.; De Gendt, S.; Heyns, M.; Radu, I.; Caymax, M.; Ceyssens, P.; Verdonck, P.; Van Elshocht, S.; Heuvel, L.; Knoops, H. C. M.; Sundaram, R. S.; Hofmann, J. P.; Kessels, W. M. M.; Bol, A. A.; Large Area, Patterned Growth of 2D MoS2 and Later MoS2-WSe2 Heterostructures for Nano- and Opto-Electronic Applications. *Nano Letters* **2020**, *20*, 355603.

(20) Eranna, G.; Chaudhary, N.; Park, J.; Hwang, J. Y.; Choi, W.; Bloodgood, M. A.; Godiksen, R. H.; Zeng, Y.; Ager, J. W.; Wallace, R. M.; Javey, A. Recombination Kinetics and Effects of Superacid Treatment in Sulfur and Selenium Based Transition Metal Dichalcogenides. *Nano Lett.* **2016**, *16*, 2786.

(21) Balasubramanyam, S.; Shirazi, M.; Bloodgood, M. A.; Wu, L.; Li, T.; Zeng, X.; He, C.; Ma, B.; Tang, Y.; Lu, Z.; Yang, Z. Modulating Electronic, Magnetic and Chemical Properties of MoS2 Monolayer Sheets by Substitutional Doping with Transition Metals. *Adv. Sci.* **2018**, *5*, 1700416.

(22) Balasubramanyam, S.; Shirazi, M.; Bloodgood, M. A.; Wu, L.; Li, T.; Zeng, X.; He, C.; Ma, B.; Tang, Y.; Lu, Z.; Yang, Z. Modulating Electronic, Magnetic and Chemical Properties of MoS2 Monolayer Sheets by Substitutional Doping with Transition Metals. *Adv. Sci.* **2018**, *5*, 1700416.
(42) Nipane, A.; Karmakar, D.; Kaushik, N.; Karande, S.; Lodha, S. Few-Layer MoS2 P-Type Devices Enabled by Selective Doping Using Low Energy Phosphorus Implantation. ACS Nano 2016, 10, 2128–2137.

(43) Na, J.-S.; Peng, Q.; Scarel, G.; Parsons, G. N. Role of Gas Doping Sequence in Surface Reactions and Dopant Incorporation during Atomic Layer Deposition of Al-Doped ZnO. Chem. Mater. 2009, 21, 5855–5893.

(44) Wu, Y.; Giddings, A. D.; Verheijen, M. A.; Macco, B.; Prosa, T. J.; Larson, D. J.; Roozeboom, F.; Kessels, W. M. M. Dopant Distribution in Atomic Layer Deposited ZnO:Al Films Visualized by Transmission Electron Microscopy and Atom Probe Tomography. Chem. Mater. 2018, 30, 1209–1217.

(45) Wu, Y.; Potts, S. E.; Hermkens, P. M.; Knoops, H. C. M.; Roozeboom, F.; Kessels, W. M. M. Enhanced Doping Efficiency of Al-Doped ZnO by Atomic Layer Deposition Using Dimethylaluminum Isopropoxide as an Alternative Aluminum Precursor. Chem. Mater. 2013, 25, 4619–4622.

(46) Shin, S.; Jin, Z.; Kwon, D. H.; Bose, R.; Min, Y.-S. High Turnover Frequency of Hydrogen Evolution Reaction on Amorphous MoS2 Thin Film Directly Grown by Atomic Layer Deposition. Langmuir 2015, 31, 1196–1202.

(47) Tong, K. C.; Liao, P. C.; Ho, C. H.; Huang, Y. S. Growth and Characterization of Rhenum-Doped MoS2 Single Crystals. J. Cryst. Growth 1999, 205, 543–547.

(48) Tang, H.; Roy Morrison, S. Optimization of the Anisotropy of Composite MoS2 Films. Thin Solid Films 1993, 227, 90–94.

(49) Serna, M. I.; Yoo, S. H.; Moreno, S.; Xi, Y.; Orvedo, J. P.; Choi, H.; Alshareef, H. N.; Kim, M. J.; Minery-Jolandan, M.; Quevedo-Lopez, M. A. Large-Area Deposition of MoS2 by Pulsed Laser Deposition with In Situ Thickness Control. ACS Nano 2016, 10, 6054–6061.

(50) McCluskey, M. D.; Haller, E. E. Dopants and Defects in Semiconductors; CRC Press, 2018.

(51) Ellmer, K.; Bikowski, A. Intrinsic and Extrinsic Doping of ZnO and ZnO Alloys. J. Phys. D: Appl. Phys. 2006, 49, 413002.

(52) Tian, Z.-L.; Zhao, D.-H.; Liu, H.; Zhu, H.; Chen, L.; Sun, Q.-Q.; Zhang, D. W. Optimization of Defects in Large-Area Synthetic MoS2 Thin Films by CS2 Treatment for Switching and Sensing Devices. ACS Appl. Nano Mater. 2019, 2, 7810–7818.

(53) Kuh, J.; Hens, Z.; Detavernier, C. Plasma Enhanced Atomic Layer Deposition of Atomic Sulphide Thin Films. J. Vac. Sci. Technol., A 2018, 36, 01A113.

(54) Macco, B.; Knoops, H.C.; Kessels, WM Electron Scattering and Doping Mechanisms in Solid Phase Crystalized In 2 O 3 :H Prepared Films. Deduct, R.-J.; Rud, I.; Neyts, E. C.; De Gendt, S. Thermal Recrystallization of Short-Range Ordered WS2 Films. J. Vac. Sci. Technol., A 2018, 36, 05G501.

(56) Chiappe, D.; Asselberghs, I.; Sutar, S.; Iacovo, S.; Afanas’ev, V.; Stesmans, A.; Balaji, Y.; Peters, L.; Heyne, M.; Mannarino, M.; Vandervorst, W.; Sayan, S.; Hughebaert, C.; Caymaz, M.; Heyns, M.; De Gendt, S.; Rudu, I.; Thean, A. Controlled Sulphurization Process for the Synthesis of Large Area MoS2 Films and MoS2 /WS2 Heterostructures. Adv. Mater. Interfaces 2016, 3, 1500635.

(57) Vandalon, V.; Sharma, A.; Ferrotta, A.; Schrode, B.; Verheijen, M. A.; Bol, A. A. Polarized Raman Spectroscopy to Elucidate the Texture of Synthesized MoS2. Nanoscale 2019, 11, 22860.

(58) Knoops, H. C. M.; van de Loo, B. W. H.; Smit, S.; Ponomarev, M. V.; Weber, J.-W.; Sharma, A.; Kessels, W. M. M.; Creatore, M. Optical Modelling of Plasma-Deposited ZnO Films: Electron Scattering at Different Length Scales. J. Vac. Sci. Technol., A 2015, 33, 021509.

(59) Ponomarev, M. V.; Verheijen, M. A.; Keuning, W.; van de Sanden, M. C. M.; Creatore, M. Controlling the Resistivity Gradient in Aluminum-Doped Zinc Oxide Grown by Plasma-Enhanced Chemical Vapor Deposition. J. Appl. Phys. 2012, 112, 043708.