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Large Area Deposition of MoS₂ by Pulsed Laser Deposition with *In-Situ* Thickness Control

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ABSTRACT: A scalable and catalyst-free method to deposit stoichiometric Molybdenum Disulfide (MoS₂) films over large areas is reported with the maximum area limited by the size of the substrate holder. The method allows deposition of MoS₂ layers on a wide range of substrates without any additional surface preparation including single crystals (sapphire and quartz), polycrystalline (HfO₂), and amorphous (SiO₂). The films are deposited using carefully designed MoS₂ targets fabricated with excess of sulfur (S) and variable MoS₂ and S particle size. Uniform and layered MoS₂ films as thin as two monolayers, with an electrical resistivity of $1.54 \times 10^4 \Omega \text{ cm}^{-1}$ were achieved. The MoS₂ stoichiometry was as confirmed by High Resolution Rutherford Backscattering Spectrometry (HRRBS). With the method reported here, *in situ* graded MoS₂ films ranging from ~1 to 10 monolayers can also be deposited.

Recent advancements in 2D materials have created great opportunities for devices based on single semiconductor, dielectric and conductive layers.¹ Some of these opportunities include the development of new generation of sensors, transistors and high performance devices with superior performance compared to those fabricated with bulk materials due to the high quantum efficiency in 2D materials.^{2,3,4} Some of the most common 2D materials include graphene, molybdenum disulfide (MoS₂), Tungsten disulfide (WS₂), among others. Unlike graphene, the band gap of transition metal di-chalcogenides (TMDs) can be tuned from direct to indirect by simply varying the number of layers.⁵ Among 2D-TMD materials, layered MoS₂ films are the most extensively studied.⁶⁻⁹ Some of the MoS₂ applications reported include gas sensors,¹⁰ phototransistors,² flexible thin film transistors,¹¹ electrodes for lithium ion batteries,¹² and heterojunctions diodes with black phosphorous.¹³ Recently, the piezoelectric effect in monolayer MoS₂ was also reported.¹⁴ 2D MoS₂ films incorporated as the active layer in thin film transistors have shown mobilities of $\sim 200 \text{ cm}^2 / \text{V-s}$ and on/off current ratio of $\sim 1 \times 10^8$ with HfO₂ as the gate insulator.¹⁵ More recently, mobilities of $\sim 480 \text{ cm}^2 / \text{V s}$ (holes) and $\sim 470 \text{ cm}^2 / \text{V s}$ (electrons) for MoS₂ on PMMA substrates was reported.¹⁶ These materials are also theoretically ideal for Field Effect transistors (FET) with dimensions of less than 10 nm since the use of these materials greatly reduce short channel effects without affecting the Drain-Induced Barrier Lowering (DIBL, $\sim 10 \text{ mV} / \text{V}$).¹⁷ Besides the exciting applications mentioned above new applications for 2D MoS₂ are continuously reported. However, any practical applications of 2D-

MoS₂ require the growth of high quality and large area compatible films to enable reliable and reproducible devices at a reasonable cost.

Some of the fabrication methods reported for 2D MoS₂ include mechanical exfoliation,¹⁸ laser thinning,¹⁹ chemical vapor deposition (CVD),²⁰⁻²² chemical bath deposition,²³ liquid exfoliation,^{24, 25} and Lithium intercalation.²⁶ Mechanical exfoliation produces monolayers and multilayers with excellent quality; however, this method lacks precise control of the exfoliated area, geometry, size, and consistency among number of layers. Laser thinning, although relatively new, often results in increased roughness of up to three orders of magnitudes of the MoS₂ films after thinning.²⁷

In this article, we report PLD methods for the fabrication of MoS₂ films. Using PLD for layered MoS₂ films offers several advantages. For example, during laser deposition the ablated species from the target are often activated. This results in enhanced associative chemistry on the growing film surface that reduces the need for surface activation.²⁸ Also, thickness control is achieved by controlling the growth kinetics by simply manipulating the repetition rate (frequency) and energy of the laser as well as the deposition pressure. One additional advantage of PLD is the stoichiometric transfer of the ablated material from the target to the substrate. This characteristic is a consequence of ablation produced by the absorption of the laser energy on a very small volume of the target. The absorption of the laser energy by this small volume consequently forms a plasma, or plume, at the surface of the target and the species get transferred to the substrate. This process is not dependent on the partial pressures of the constituent cations.²⁹ However, the deposition pressure can be used to modify the mean free path of the ablated species to either minimize or maximize the energy of the species reaching the surface of the substrate. In PLD processes, only the stoichiometry is transferred from the target to the substrate and the crystalline phase of the resulting film is not necessarily the same as that of the target.²⁹ Avoiding expensive and potentially dangerous precursors (See the Supplementary Information for approximate costs) is additional advantage of this technique over other methods such as CVD.

Earlier reports of MoS₂ deposited by PLD focused on films deposited on stainless steel for tribological applications and the process resulted in films with increased sulfur vacancies as the

substrate temperature increased.^{30,31} Although this might not be an issue for tribological applications, Sulfur deficiency or Oxygen contamination can have a negative effect on the electrical properties of 2D MoS₂ films. MoS₃ conversion to MoS₂ using laser annealing has also been reported.³² The annealing process generated heterogeneous MoS₂ films with amorphous Sulfur incorporated in the bulk of the MoS₂, producing inadequate films for device applications. However, through fine-tuning of the PLD deposition parameters and proper target preparation, such defects may be avoided. The selection of the deposition parameters must allow the Mo and S species to properly arrange on the substrate during the deposition and substrate cooling process. Special considerations for MoS₂ deposition by PLD on metallic substrates must be considered. For example, MoS₂ deposited on Ni and Ag substrates form NiS₂ and AgS₂.³³ Multilayered MoS₂ by PLD was also demonstrated on Al₂O₃, GaN, and SiC-6h substrates.³⁴⁻³⁷

In those studies, although layered MoS₂ films were obtained, the HRBS stoichiometric analysis of the resulting MoS₂ films were not reported.

RESULTS AND DISCUSSION

In this work, a large-area compatible process to deposit stoichiometric MoS₂ with layers ranging from 1-10 is reported. This is achieved by properly controlling target composition, MoS₂ to Sulfur particle size in the target, and PLD deposition conditions. 1.33 nm thick MoS₂ films and Mo/S ratio of ~0.5 can be achieved with the method reported here. Furthermore, this process can be used to deposit layered MoS₂ on amorphous, polycrystalline and single crystal substrates. PLD deposition conditions evaluated to enable layered MoS₂ include cooling rate of the substrate, laser fluency and deposition pressure. These parameters were optimized to allow the nucleation and arrangement of the MoS₂ layers on the substrate. Three different targets with excess of Sulfur were used to compensate the potential loss of this element during the laser ablation. The combination of target composition and proper PLD conditions results in deposition of MoS₂ films on ~50.8 mm diameter substrates. In addition, the influence of the target characteristics on the chemistry, crystallinity, and electronic properties of the layered MoS₂ films was studied. An additional advantage of the method reported here is the capability of tuning the MoS₂ thickness across the entire substrate by simply modifying the PLD deposition conditions.

This enables *in situ* thickness gradient control on a whole substrate and under the same deposition conditions.

Figure 1. MoS₂: S targets, Transmission Electron Microscopy (TEM) for the MoS₂ films deposited from the different targets, and Raman spectra of the thin films. (a) to (d) show PLD targets, TEM cross-sections and interlayer spacing for films deposited using targets fabricated at 100°C / 2 μm, 75°C / 2 μm, 75°C / 43 μm, and the commercially available target. The thinnest MoS₂ film (c) was deposited from the target with the highest density and larger MoS₂ particles (43 μm). Raman spectra (e) acquired for the MoS₂ shown in Figures a-d. For reference, the dashed lines in Figure 1e show the Raman shift values for a monolayer of MoS₂.

Targets fabrication for the stoichiometric MoS₂ synthesis by PLD

Conventional powder metallurgy methods were used to fabricate the PLD targets with MoS₂ to S ratio of 1:1. Particle size for the target preparation was 20 μm (Sulfur) and 43 and 2 μm (MoS₂). Two different hot press conditions for the target fabrication were evaluated: a) 100°C and compression of 25 tons per one hour, and b) 75°C with compression of 18 tons for 3 hours (**Figure S1**). For comparison, a commercial MoS₂ target with no excess of Sulfur (MoS₂ to S ratio of 1:0) from Testbourne Ltd was used. This is referred as target “T” in this article. The 3 targets fabricated for this work are identified as follows: 100°C / 2 μm, 75°C / 2 μm, and 75°C / 43 μm. A detailed outline of the target preparation conditions is shown in Table 1 in the Supporting Information section. The relative density of each target was measured by Archimedes

principle and defined as the ratio of the experimental and theoretical density values. Relative densities of 88.1%, 88.7% and 99.9% were obtained for targets 100°C / 2 μm , 75°C / 2 μm , and 75°C / 43 μm , respectively. It is important to note that the 100°C / 2 μm and 75°C / 2 μm have the same S particle size (**Figure S2**). The difference in the density with respect to the 75°C / 43 μm target is due to the MoS₂ particle size and target fabrication conditions.

Thin film Thicknesses and cross section - layered structure

All the targets described before were used to initially deposit MoS₂ films by PLD on sapphire (single crystal). The cross-section for each MoS₂ film was obtained using Transmission Electron Microscopy (TEM) (**Figure 1a to 1d**). MoS₂ films with thicknesses of 8.87 nm, 4.79 nm, 1.33 nm and 6.67 nm were obtained for films deposited from targets 100°C / 2 μm , 75°C / 2 μm , 75°C / 43 μm and T, respectively. The TEM results showed that MoS₂ films obtained from targets 100°C / 2 μm , 75°C / 2 μm , and T have a well-defined layered structure with some areas showing a wavy-like structure. Nevertheless, layered films were observed for all these films. Films obtained from the target with the largest MoS₂ particle size (75°C / 43 μm) showed the thinnest and most ordered layered structure (**Figure 1d**). The interlayer spacing evaluated from the TEM images were 6.27, 6.19, 6.70, and 6.41 Å for 100°C / 2 μm , 75°C / 2 μm , 75°C / 43 μm , and T, respectively. These values are very close to the theoretically expected value for monolayers of MoS₂ which is ~ 6.5 Å.⁸ The small variations observed are likely due to the resolution of the TEM measurement and/or to small local stoichiometry variation in the films due to Sulfur depleted areas, which will be further discussed in the following sections.

Thin films chemical characterization

The Raman spectroscopy analyses of the films showed the typical E_{2g}¹ and A_{1g} vibration modes for MoS₂ (**Figure 1e**). The red dashed lines in the **Figure 1e** indicate the expected vibration modes values for a monolayer of MoS₂.³⁸ The additional vibration bands observed for this films are from the sapphire (Al₂O₃) substrate.³⁷ The difference in frequency in the MoS₂ vibration modes, defined as $\Delta\beta$, is proportional to the separation of the Raman peaks and can be used to estimate the thickness of the films.³⁸ The difference in the $\Delta\beta$ values with thickness is due to the dipolar interaction of the substrate with the MoS₂ thin film due to variations in the electrostatic surroundings and interaction between the substrate and the Sulfur atoms. This affects the MoS₂

vibration modes.⁴⁰ The $\Delta\beta$ values calculated from **Figure 1e** were 24 cm^{-1} , 23 cm^{-1} , 20 cm^{-1} , and 24 cm^{-1} for thin films $100^\circ\text{C} / 2\text{ }\mu\text{m}$, $75^\circ\text{C} / 2\text{ }\mu\text{m}$, $75^\circ\text{C} / 43\text{ }\mu\text{m}$ and T, respectively. The expected $\Delta\beta$ values as function of number of layers are: 18 cm^{-1} (one layer), 22.4 cm^{-1} (two layers), 23 cm^{-1} (3 monolayers), and 25 cm^{-1} for bulk MoS_2 .³⁸ From the TEM data, it is clear that films $100^\circ\text{C} / 2\text{ }\mu\text{m}$, $75^\circ\text{C} / 2\text{ }\mu\text{m}$, and T are relatively thick and, therefore, show $\Delta\beta$ values closer to bulk MoS_2 . However, thin film $75^\circ\text{C} / 43\text{ }\mu\text{m}$ showed the lowest value for $\Delta\beta$ ($\sim 20\text{ cm}^{-1}$) indicating that this is the thinnest film and in the order of 1-2 monolayers. This is in agreement with the TEM results shown in **Figure 1c**.

In general, the thickness of the MoS_2 films are inversely proportional to the density of the target. Therefore, the target with the highest density ($75^\circ\text{C} / 43\text{ }\mu\text{m}$) yielded the thinnest MoS_2 films. The thinner MoS_2 films resulting from targets with higher density is likely due to lower ablation rates from denser targets. Additionally, besides producing thicker MoS_2 films, low-density targets also produced more particles on the MoS_2 surface (**Figure S2**).⁴¹ Excess of Sulfur was used to saturate the deposition ambient and minimize vacancies in the MoS_2 films. During the ablation, the excess of Sulfur from the target evaporates more readily than the MoS_2 producing and *in-situ* sulfurization environment allowing more stoichiometric MoS_2 to be deposited on the substrate. We used an RGA system (Residual Gas Analyzer) during the deposition to monitor the increase in Sulfur partial pressure during the ablation.

Figure 2. (a) 1.33 nm thick (2 monolayers) MoS₂ thin film deposited by PLD on a 50.8 mm diameter sapphire wafer. (b) Sapphire wafer without MoS₂ thin film (c) Raman spectroscopy from the MoS₂ films. (a) Shows that the characteristic E'_{2g} and A_{1g} vibration modes for MoS₂ are present across the entire surface of the substrate. The (*) shows the vibration modes for sapphire

Large area depositions were performed on 50.8 mm sapphire substrates using the target with the highest density (75°C / 43 μm). This target was selected because it yielded the thinnest MoS₂ film (**Figure 2a**). For large area PLD deposition of thin films on large substrates, a laser deposition power of less than 6W is recommended.⁴² Therefore, the power used in the deposition reported in this paper was set to 3W. This PLD deposition power yields MoS₂ films, as shown in the optical image shown in **Figure 1a**, the whole sapphire wafer (**Figure 2b**) was covered with exception on the small wafer edges that were suspended on the substrate holder during the deposition (**Figure S3**). The Raman spectroscopy obtained in different areas of the same substrate: top, bottom, left side, right side and center of the wafer (**Figure 2b**). All areas showed the E'_{2g} and A_{1g} MoS₂ vibration modes indicating presence of the MoS₂ thin film on the wafer area. The overall thickness of the films, as measured by TEM was 1.33 nm, or close to 2 monolayers. The (*) represents the vibration modes E'_{1g} (~379 cm⁻¹) and A_{1g} (~416 cm⁻¹) for the

sapphire substrate.⁴³ The variation of the intensity of these peaks can be evidence of little defects or our thin films.

X-ray photoelectron spectroscopy (XPS) studies were further used to analyze the films after a subtle sputter-clean with Ar⁺ ions. The Mo 3d region shown in **Figure S4a** showed typical binding for MoS₂ (red dashed lines) for thin films deposited from targets 100 °C / 2 μm and T. The small variation in the S2p region observed in **Figure S4b** for films deposited from targets 75 °C / 2 μm and T can be attributed to Fermi level pinning due to sulfur vacancies.⁴⁴ Nevertheless, all the thin films showed bands typical for MoS₂ (**Figure S5**). The data fitting shows some low intensity oxides peaks (MoO₂ and MoO₃) for all the films, with the highest concentration for the films deposited from the commercial target, T. Thin film 75 °C / 43 μm was not subjected to sputter cleaning due to its thickness, but showed the closest binding energies to bulk MoS₂.

Figure 3. Rutherford Backscattering Spectra for the MoS₂ films. (a) Experimental spectra. The inset shows the experimental spectra (continuous dark line) and simulation spectra (red line) for thin film 75 °C / 43 μm. (See Figure S6 for simulations details for all the films). The Mo/S ratio depth profiling for all the MoS₂ thin films on sapphire was measured (b). The inset shows the zoomed-in view for 75 °C / 43 μm (green) and the commercial target (T).

High-Resolution Rutherford Backscattering (HRRBS) analyses were performed to better evaluate the composition of the MoS₂ films (**Figure 3a**). Peaks for S, Mo and the substrate are clearly observed in the experimental data. The difference in peak width and intensity observed in the HRRBS spectra is related to the thickness of the MoS₂. The thinnest film was obtained from 75 °C / 43 μm target, in agreement with Raman and TEM. The HRRBS experimental data was fitted to obtain the depth profile for each film. The inset in **Figure 3a** shows typical fits (red line) and experimental data (black line). The depth profile extracted from the fitting is shown in **Figure 3b**. Thin film 100 °C / 2 μm shows a large depletion of S at the surface with composition variation throughout the entire thickness of the thin film. Thin film 75 °C / 2 μm showed higher Mo/S ratios close to the surface, but from 1.0 to 2.2 nm the Mo/S ratio approached the theoretical ratio of 0.5. The film from the commercial target (T) also showed variations in the Mo/S ratio. On the other hand, thin film 75 °C / 43 μm showed ratios close to 0.5 throughout the entire thickness of about 2 monolayers. The inset in **Figure 3b** shows the stoichiometricity of these films over the entire thickness. The complete HRRBS spectra and simulations are shown in **Supporting Information Figure S6**.

Thin film resistivity and Mo / S ratio

Figure 4. Resistivity and Mo/S atomic ratio for thin films 100°C / 2μm, 75°C / 2μm, 75°C / 43 μm and T is shown. The Mo/S ratio is closer to the ideal value of 1:2 (0.5) for thinner films and the contact resistivity increases as the thickness is reduced. This shows a relationship between the content of Sulfur and the contact resistivity of the films. The 75°C / 43 μm film, which is the thinnest, has an approximate ratio of 0.5 and highest resistivity (~10⁴ Ω-cm).

The mechanisms for electronic transport in 2D materials are not entirely clear yet since the carrier transport in layered MoS₂ films as well as in the contact interface is very complex.^{8, 45-48} In this paper, we used a well-accepted method (Circular Transfer Method, CTLM) to measure sheet resistance and resistivity that eliminates potential contact resistance issues while performing the measurement. Gold contacts were used for the analyses (**Figure S7**). The results were then correlated to the Mo/S ratio in each film. For the CTLM method, the I-V responses of the structured were measured at room temperature and in air. From these data, electrical resistivity values of 8.0, 7.0, 1.3, and $1.54 \times 10^4 \Omega \text{ cm}^{-1}$ were obtained for 100 °C / 2 μm, 75 °C / 2 μm, T, and 75 °C / 43 μm films, respectively (**Figure 4**).

Clearly, as Mo/S ratio increases the electrical resistivity of the films is reduced. This can be produced by presence of defects on the thin film metal interface too. The area analyzed by both Raman ($\sim 2 \times 10^9 \mu\text{m}^2$) and HRRBS ($9 \times 10^6 \mu\text{m}^2$) is much larger than the size of the CTLM structure used for the measurements, which is $1.2 \times 10^6 \mu\text{m}^2$ (**Figure S8**) which is considerably larger than commonly exfoliated MoS_2 flakes.⁴⁹ In addition, The sheet resistance (R_{sh}) values reported in this paper are $1.15 \times 10^{11} \Omega/\text{sq.}$, $1.4 \times 10^7 \Omega/\text{sq.}$, $9.4 \times 10^4 \Omega/\text{sq.}$, and $1.9 \times 10^6 \Omega/\text{sq.}$, for films $75^\circ\text{C} / 43\mu\text{m}$, $75^\circ\text{C} / 2\mu\text{m}$, $100^\circ\text{C} / 2\mu\text{m}$, and T, respectively. These large values for sheet resistance might indicate uniform MoS_2 films on the analyzed areas. For reference, the largest sheet resistance for large area deposition of MoS_2 by Chemical Vapor Deposition reported range from $1.46 - 2.84 \times 10^7 \Omega/\text{sq.}$ ⁵⁰ Furthermore, the values of R_{sh} and ρ are much larger for bilayers than for films with several layers of MoS_2 , which has been reported in previous works.⁵¹ The thinnest thin film showed a Mo/S ratio of 0.5, but the material still needs improvement for electronic applications. The changes in resistivity could also be affected by defects and impurities at the interface metal – semiconductor as well.⁵¹

Thin film deposition on different substrates

Figure 5. MoS₂ thin films deposited on different substrates. MoS₂ films are achieved on SiO₂ (amorphous) (a), Quartz (single crystal) (b), and HfO₂ (polycrystalline) (c) substrates. The thicknesses of the films were 2.5 nm, 2.8 nm and 2.1 nm for SiO₂, quartz, and HfO₂, respectively.

The PLD method reported here was also used to deposit MoS₂ on various substrates including SiO₂, quartz, and polycrystalline HfO₂ (**Figure 5a-c**). The films were deposited from the target that produced the most stoichiometric film (75°C / 43 μm). The quartz substrate had some amorphization during the TEM sample preparation due to the use of Focus Ion Beam (FIB) during sample preparation. The MoS₂ thin films deposited on HfO₂ (**Figure 5c**) seems to have better quality than films deposited on amorphous SiO₂ substrates. These initial outcomes indicate that further improvements in the PLD process for amorphous substrates are required. The thicknesses for the films deposited on SiO₂, quartz, and HfO₂ were 2.5 nm, 2.83 nm, and 2.08 nm, respectively. The films were evaluated by Raman spectroscopy and the vibration modes for MoS₂ were present on all the substrates. However, the Raman bands for MoS₂ on SiO₂ and quartz were broader than those on crystalline HfO₂, indicating better quality of the MoS₂ films deposited on this dielectric (**Figure 5d**).

In-Situ Thickness Control

The process demonstrated here is also a great method to achieve different MoS₂ thicknesses on the same substrate. Such thickness control can be used to fabricate devices on the same substrate with variable number of MoS₂ layers. The analyses of these films are shown in **Figure 6** with area-1 corresponding to the thickest and area-5 the thinnest MoS₂ films, respectively. Raman spectroscopy (**Figure 6b**) and Raman mapping (**Figure 6c**) was carried on the entire area of the wafer to evaluate the uniformity of the MoS₂ films. The typical modes for MoS₂ (E_{2g}¹ and A_{1g}) monotonically decrease with thickness, as expected. In addition, the separation of the peaks (Δβ) was also proportional to the thickness of the thin films indicating a thickness gradient across the substrate.³⁸ For the gradient generation the substrate speed rotation was reduced and it was moved off-axis from the target, followed by a normal process of deposition.

Figure 6. MoS₂ thin film with graded thickness and the corresponding Raman mapping. (a) The optical image shows a MoS₂ thin film thicknesses gradient on half sapphire wafer deposited by PLD thicknesses gradient. Raman spectra and Raman mapping are shown (b-c). Areas of high and low intensity are represented by red and blue colors in the Raman mapping. (d) TEM cross-section results for areas 1 through 5 showing the thickness gradient for the MoS₂ films along the entire substrate. The scale in every Raman mapping picture is 5 μm.

The thickness of each area was approximately: 10 layers, 8 layers, 3, layers, 2 layers and 1 layer for areas 1, 2, 3, 4, and 5, respectively (**Figure 6d**). These results shows that PLD process is potentially capable of producing a surface on which different electronic structures with several MoS₂ thicknesses can be created and studied.

High Resolution Transmission Electron Microscopy Analyses

Figure 7. (a) Top view of a 75 °C / 43 μm MoS₂ deposited on h-BN/Graphene. (b) Inversed Fast Fourier Transform (FFT) results. Zoomed FFT images for MoS₂ (c) and MoS₂/h-BN/Gr (d).

In order to evaluate the crystallinity of PLD MoS₂, the thinnest and stoichiometric MoS₂ film (75 °C / 43 μm) sample was deposited on exfoliated Hexagonal Boron Nitride (h-BN) / Graphene (Gr) stack and subjected to TEM analysis. The top view TEM results for the MoS₂ on h-BN/Gr and the corresponding Fast Fourier Transform (FFT) patterns are shown in **Figure 7a-b**, respectively. The inversed FFT patterns in **Figure 7b** reveals the presence of lattices for the MoS₂/h-BN/Gr stack demonstrating the crystalline nature of the films. For reference, the corresponding lattice points for MoS₂ and h-BN/Graphene are shown in **Figure 7b**. Detailed FFT analyses were carried out to separate the signals from MoS₂ and h-BN/Gr (**Figure 7c-d**). The filtered FFT analyses reveal a crystalline MoS₂ lattice on these substrate (**Figure 7c**). **Figure 7d** shows the filtered FFT for the entire MoS₂/h-BN/Gr stack. From these results it become clear that it is possible to deposit MoS₂ by PLD in other substrates, especially on other 2D materials such as graphene and h-BN. Furthermore, The Phase contrast imaging of each thin film in this

work deposited on sapphire was checked as well. This imaging showed an atomic arrangement for the thin films (**Figure S9**).

Furthermore, a 75 °C / 43 μm film was deposited on Graphene and its top view image showed defined grain boundaries (**Figure S10**). The average grain size was measured resulting in 16.80 nm (**Figure S11 and S12**). The grain size of the stoichiometric thin film synthesized in this work is still smaller than those reported by CVD techniques⁵². However, the continuity of the thin film 75 °C / 43 μm is found all over the sapphire substrate as demonstrated before.

CONCLUSIONS

A potential process for large-area growth of stoichiometric layered Molybdenum Disulfide (MoS₂) by PLD has been developed. The process uses laser ablation from carefully-designed targets with controlled particle size and Sulfur content—Two One to ten Layers of MoS₂ without any surface preparation can be grown using this process. The high MoS₂ electrical resistivity seems to be related with the stoichiometry of the material, showing that not just density of defects between MoS₂-metal interfaces can have effect on performance of the thin films. Furthermore, MoS₂ growth on amorphous, polycrystalline and single crystal substrates was also demonstrated. With further work, the method reported here can lead to future large-scale deposition of MoS₂ for various applications.

METHODS

Target fabrication: Powder metallurgy was used to fabricate three target types (labeled 100°C / 2 μm, 75°C / 2 μm, 75°C / 43 μm, in this article). Each target has an atomic ratio of MoS₂ to S of 1:1. MoS₂ and S precursors were acquired from Sigma-Aldrich Korea and include MoS₂ with particle size of 43 mm and 2 μm, and S powder with a particle size of 20 μm. To ensure good homogeneity, the MoS₂ and S powders were mixed for one hour before target fabrication on a SPEX mill, SPEX Sample Prep, Inc. model 8000D Dual. The resulting mixed powder was hot-pressed at 75°C for 3 h at 18 ton-force or 100°C for 1 h at 25 ton-force. More detailed information regarding this process is discussed in the supporting information.

Thin film deposition: MoS₂ films from each target used in this work were deposited using a KrF laser ($\lambda=248\text{nm}$) laser. The laser frequency was 10 Hz, with an energy of 30mJ and the substrate temperature was kept at 700°C. The MoS₂ films were deposited on Al₂O₃ (0001) double – side polished substrates (sapphire), HfO₂, Quartz, and SiO₂. Before deposition, the PLD chamber was evacuated to a pressure of $<10^{-6}$ Torr. The process was carried out at 0.1 mTorr without any background gas. After the deposition, the substrate was cooled down at a rate of 2 °C/min.

Thin film characterization: The first thin films characterization studies were evaluated by Raman spectroscopy Thermo Scientific™ DXR™ Raman microscope with 532 nm excitation and 50X objective. The laser power was kept at 0.3 mW during the experiment. The XPS measurements were executed using a PHI 5000 Versa Probe II. All the evaluations were taken at a 45 take-off angle with respect to the sample surface. A monochromatic Al K α radiation ($h\nu=1486.6$ eV) was used with a 0.1 eV step size and a pass energy of 23.50 eV. The base pressure in the analysis was 1.6×10^{-8} Torr. All binding energies reported in this work are relative to the C 2S peak at a binding energy of 284.8 eV. The cross section of each film was used to examine crystalline structures and thicknesses of the film by high-resolution transmission electron microscope (HRTEM, Tecnai F20 G2, FEI, USA) with an energy dispersive spectroscope (EDS, PV9761/55, Ametek, USA). The TEM samples were prepared using a focused ion-beam system (FIB) system (Nova nanolab 600, FEI Ltd., USA). The electrical properties of the thin films were studied by Circular Transfer Method (CTLM). Au contacts were defined by lift off lithography. A resin 1813 available commercially was applied by spin coating on the films. Afterwards, the samples were exposed to UV light and the areas for conversion were under covered. All samples were developed with MF311. After this step, gold contacts 400 nm were deposited on the samples by Thermal Evaporation at 10^{-6} Torr. Subsequently, the excess of gold Au was detached from the CTLM structures with acetone. Then, the remaining organic components were removed by washing the samples with Isopropanol and deionized water. Several circles and gaps were measured and averaged during this study with a probe station Cascade Model SUMMIT 11741B-HT. The RBS composition vs depth profile was obtained with 400 keV He⁺ ions with a beam size about 1 mm. The experimental data was fitted using Analysis IB RBS software 2007 Kobelco. **Figure S6** shows the RBS fitting for each thin film fabricated in this work on sapphire.

ASSOCIATED CONTENT

Supporting Information This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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AUTHOR CONTRIBUTIONS

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NOTES

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