DIRECT SYNTHESIS OF CRYSTALLINE MoS₂ THIN FILMS ON LARGE AREA, STRETCHABLE POLYMER SURFACES (PREPRINT)

Michael E. McConney, Christopher Muratore, Travis Shelton, Randall E. Stevenson, John E. Bultman, Jianjun Hu, Michael L. Jespersen, Nicholas R. Glavin, Abigail T. Juhl, Michael F. Durstock, Michael H. Check, Aman Haque, Rachel D. Naguy, and Andrey A. Voevodin

AFRL/RX

15 MAY 2015
Interim Report

Distribution Statement A.
Approved for public release: distribution unlimited.
**REPORT DOCUMENTATION PAGE**

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

<table>
<thead>
<tr>
<th>1. REPORT DATE (DD-MM-YY)</th>
<th>15 May 2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. REPORT TYPE</td>
<td>Interim</td>
</tr>
<tr>
<td>3. DATES COVERED (From - To)</td>
<td>19 April 2013 – 15 April 2015</td>
</tr>
<tr>
<td>4. TITLE AND SUBTITLE</td>
<td>DIRECT SYNTHESIS OF CRYSTALLINE MoS2 THIN FILMS ON LARGE AREA, STRETCHABLE POLYMERIC SURFACES (PREPRINT)</td>
</tr>
<tr>
<td>5a. CONTRACT NUMBER</td>
<td>FA8650-11-D-5800-0005</td>
</tr>
<tr>
<td>5b. GRANT NUMBER</td>
<td></td>
</tr>
<tr>
<td>5c. PROGRAM ELEMENT NUMBER</td>
<td>62102F</td>
</tr>
<tr>
<td>5d. PROJECT NUMBER</td>
<td>4348</td>
</tr>
<tr>
<td>5e. TASK NUMBER 0005</td>
<td></td>
</tr>
<tr>
<td>5f. WORK UNIT NUMBER</td>
<td>X0K5</td>
</tr>
<tr>
<td>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</td>
<td>AFRL/RX Wright-Patterson Air Force Base, OH 45433-7750</td>
</tr>
<tr>
<td>8. PERFORMING ORGANIZATION REPORT NUMBER</td>
<td>AFRL-RX-WP-JA-2016-0239</td>
</tr>
<tr>
<td>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</td>
<td>Air Force Research Laboratory Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force</td>
</tr>
<tr>
<td>10. SPONSORING/MONITORING AGENCY ACRONYM(S)</td>
<td>AFRL/RXAN</td>
</tr>
<tr>
<td>11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)</td>
<td>AFRL-RX-WP-JA-2016-0239</td>
</tr>
<tr>
<td>12. DISTRIBUTION/AVAILABILITY STATEMENT</td>
<td>Distribution Statement A. Approved for public release: distribution unlimited.</td>
</tr>
<tr>
<td>13. SUPPLEMENTARY NOTES</td>
<td>PA Case Number: 88ABW-2015-0239; Clearance Date: 15 May 2015. This document contains color. The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.</td>
</tr>
<tr>
<td>14. ABSTRACT (Maximum 200 words)</td>
<td>Here, we present a scalable, low-temperature approach to directly synthesizing thin MoS2 films on flexible and stretchable polymeric materials. Specifically, magnetron sputtering from a MoS2 target is used to apply amorphous MoS2 films at room temperature on large area PDMS substrates. Films of thicknesses from 5-20 nm were continuous and uniform over areas greater than 4 cm². The films were subsequently laser annealed to form well-ordered, few layer hexagonal MoS2 semiconducting films. A kinetically controlled photothermal process was identified as the driving force for crystallization, and a laser power density of 5.5 mW/μm² was used to direct laser write semiconducting 2D MoS2 regions bounded by electrically insulating amorphous material on PDMS surfaces. This combination of sputtering and laser annealing is well-suited for large-scale fabrication of 2D MoS2 devices on flexible polymer substrates.</td>
</tr>
<tr>
<td>15. SUBJECT TERMS</td>
<td>MoS2 films, PDMS substrates, photothermal, amorphous material, polymer substrate</td>
</tr>
<tr>
<td>16. SECURITY CLASSIFICATION OF:</td>
<td>Unclassified</td>
</tr>
<tr>
<td>17. LIMITATION OF ABSTRACT: SAR</td>
<td></td>
</tr>
<tr>
<td>18. NUMBER OF PAGES</td>
<td>13</td>
</tr>
<tr>
<td>19a. NAME OF RESPONSIBLE PERSON (Monitor)</td>
<td>Nicholas Glavin</td>
</tr>
<tr>
<td>19b. TELEPHONE NUMBER (Include Area Code)</td>
<td>(937) 255-6977</td>
</tr>
</tbody>
</table>

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18
Direct synthesis of crystalline MoS$_2$ thin films on large area, stretchable polymer surfaces

Michael E. McConney, Christopher Muratore, Travis Shelton, Randall E. Stevenson, John E. Bultman, Jianjun Hu, Michael L. Jespersen, Nicholas R. Glavin, Abigail T. Juhl, Michael F. Durstock, Michael H. Check, Aman Haque, Rachel D. Naguy, and Andrey A. Voevodin

Abstract
Here, we present a scalable, low-temperature approach to directly synthesizing thin MoS$_2$ films on flexible and stretchable polymeric materials. Specifically, magnetron sputtering from a MoS$_2$ target is used to apply amorphous MoS$_2$ films at room temperature on large area PDMS substrates. Films of thicknesses from 5-20 nm were continuous and uniform over areas greater than 4 cm$^2$. The films were subsequently laser annealed to form well-ordered, few layer hexagonal MoS$_2$ semiconducting films. A kinetically controlled photo-thermal process was identified as the driving force for crystallization, and a laser power density of 5.5 mW/$\mu$m$^2$ was used to direct laser write semiconducting 2D MoS$_2$ regions bounded by electrically insulating amorphous material on PDMS surfaces. This combination of sputtering and laser annealing is well-suited for large-scale fabrication of 2D MoS$_2$ devices on flexible polymer substrates.

Two dimensional materials possess a unique combination of electronic and mechanical properties enabling the next generation of electronic devices such as wearable sensors and electronics.$^1$ For example, molecularly thin molybdenum disulfide demonstrates high charge mobility$^2$ and a direct band gap of 1.8eV$^{3,4}$ coupled with extreme mechanical flexibility.$^5$ Unfortunately, synthesis of continuous MoS$_2$ over larger areas without severe surface or interfacial contamination or high concentrations of structural defects has proven quite challenging.$^6$ The majority of electronic device studies involving high quality MoS$_2$ crystals use chemically or mechanically exfoliated films.$^7,8$ At present, only relatively small samples (~100 $\mu$m$^2$) of these 2D device-quality materials can be synthesized on a routine basis. Chemical vapor deposition (CVD) is now a commonly employed method to generate high quality, large area 2D thin films.$^9$–$^{11}$ Unfortunately CVD is not amenable to stretchable polymeric substrates due to high deposition temperatures (~700-900$^\circ$C) required for decomposition of most TMD precursor
gases. Film lift off methods\textsuperscript{9,12–14} can be used to transfer either exfoliated or CVD grown materials to soft substrates at low temperatures, but these methods are far from ideal, as they can introduce interfacial contamination or wrinkle defects, and are difficult to scale for continuous manufacturing.

Most recently magnetron sputtering from TMD targets has been demonstrated to directly grow large area uniform films on amorphous SiO\(_2\) and other substrate surfaces at temperatures \(<350^\circ\text{C}\).\textsuperscript{15,16} The sputtering approach is scalable to very large areas (> 1m) and is easily integrated into wafer scale manufacturing processes and roll to roll processing of large polymer sheets. Unfortunately processes employing temperatures no higher than 250\(^{\circ}\text{C}\) are required to generate films on most flexible and stretchable substrates for wearable electronic applications. Very thin sputtered MoS\(_2\) films generally do not show desirable 2D characteristics when processes at such low temperatures. While these MoS\(_2\) films grown at room temperature do exhibit compositional and thickness uniformity, as well as hole-free morphology, the films lack hexagonal crystallinity required for the semiconductor electronic characteristics. Here, we present a laser annealing process that converts amorphous MoS\(_2\) prepared by magnetron sputtering at room temperature on elastomeric substrates into crystalline hexagonal MoS\(_2\) films of few monolayer thicknesses over large areas. The processing steps for direct synthesis of the crystalline 2D MoS\(_2\) films on flexible substrates are presented schematically in Figure 1(a). The PDMS is loaded into the ultra-high vacuum chamber. With a very low elastic modulus of 1.5-2 MPa, the transition to a vacuum environment isotropically stretches the PDMS by several percent from its initial dimensions established under ambient atmospheric conditions. Then the MoS\(_2\) precursor film is deposited via magnetron sputtering from a polycrystalline MoS\(_2\) target. These films are prepared with mid-frequency pulsed magnetron sputtering\textsuperscript{15,17} at room temperature to produce an amorphous MoS\(_2\) coating at a growth rate of 0.5 nm s\(^{-1}\). The sample is then removed from the vacuum processing chamber. The transition back to atmospheric pressure induces shrinking of the PDMS substrates, which results in a residual compressive strain on the MoS\(_2\) film and is accompanied by isotropic surface buckling. An atomic force microscopy (AFM) image of the amorphous MoS\(_2\) as deposited onto the elastomer with magnetron sputtering is shown in Figure 1(b) to illustrate the typical buckled morphology. This morphology is a common feature of thin stiff films that are intimately bound to elastomers with isotropic compressive residual stress and is a result of strain accommodation through out-of-plane
deformations.\textsuperscript{18–21} This morphology is distinctly different from delaminated buckling common in thicker films with residual stress and poor substrate adhesion.\textsuperscript{22} This isotropic buckled morphology enhances the maximum strain without fracture, breaking, or delamination, enabling stretchable and wearable electronics even beyond the inherent flexibility of 2D TMDs.\textsuperscript{21,23} Referring back to Figure 1(a), the as-deposited amorphous MoS\textsubscript{2} precursor films are exposed to 514 nm laser radiation for up to 1 second with an intensity of 5.5 mW/\( \mu \)m\textsuperscript{2}. Upon laser annealing the continuous thin amorphous precursor film is converted to hexagonal 2D MoS\textsubscript{2}.

An AFM micrograph of a sample with two laser annealed lines is shown in figure 1(c). The laser spot diameter is \(~1.5\ \mu\text{m}\) and the writing speed is typically \(~25\ \mu\text{m/s}\). There is a significant change in the buckled morphology upon laser annealing, which is apparent when comparing figure 1(b) and 1(c). There is a pronounced depression in the regions that were directly laser annealed. The depth of the depression is roughly 10x the film thickness and thus likely results from residual stress relaxation rather than surface ablation by the laser. In the area surrounding the laser annealed regions there is a significant decrease in the amplitude of the buckled morphology (notice the z-range difference between the images), thereby indicating a decrease in the residual compressive stress of the localized surrounding areas. It is also notable that the orientation of alignment of the buckled morphology after treatment in contrast to the initial random and isotropic morphology. In the laser annealed regions the buckles are parallel to the direction of the laser movement, whereas, in the regions without laser annealing, the long axis of the buckled morphology is perpendicular to the laser drawn lines. Laser annealing is amenable to many different ways of exposure and we have found that the history of the exposure process can significantly change the morphology. Thus the laser annealing exposure procedure sequence may provide an additional surface morphology control mechanism that can be used in the design optimization for mechanics and surface energy of flexible devices.

The transition from the amorphous to crystalline MoS\textsubscript{2} associated with laser annealing is confirmed with Raman spectroscopy. The Raman spectrograph of the amorphous MoS\textsubscript{2} precursor film, as shown in Figure 2(a), shows neither the characteristic \( E_{2}^{1g} \) peak associated with in-plane stretching around 383 cm\textsuperscript{-1} nor the characteristic \( A_{1g} \) peak expected for out-of-plane stretching around 407 cm\textsuperscript{-1}. After laser annealing by illuminating the surface with 5.5 mW/\( \mu \)m\textsuperscript{2} of green radiation, both peaks clearly appear in the Raman spectra as shown in Figure 2(a).
Based on analysis of the central peak positions the film thickness is several layers thick. It should be noted that the peak at 488 cm\(^{-1}\) is associated with the PDMS substrate.

Figure 2(b) presents Raman spectra of amorphous sputtered MoS\(_2\) samples exposed to the same total dosage (50 mW-sec in a 1.5 \(\mu\)m diameter spot) but with different combinations of laser powers and exposure times. The Figure 2b inset is a plot of the \(A_{1g}\) peak intensity versus the laser power for the identical dosage exposures plotted in Figure 2(b). A dosage dependent photo-chemical process would result in the exact same structural change for the same dosage of laser exposure, and thus a horizontal line in the figure 2(b) inset would be expected for such. From Figure 2(b), it is quite evident that the laser annealing mechanisms of hexagonal structure formation in MoS\(_2\) is not a dosage dependent process, but instead is highly dependent on the incident radiation. The amorphous sample appears undisturbed at or below a radiation density of 1mW/\(\mu\)m\(^2\), whereas when the power density is too high, e.g. above 20 mW/\(\mu\)m\(^2\), the films become damaged. At these higher radiation power densities there is enough photo-thermal energy coupled to the surface to cause localized ablation and damage to both the amorphous Mo-S film and the underlying PDMS. It is not surprising that this intense 514 nm radiation can ablate the MoS\(_2\) film; such behavior has been reported by G.A. Steele and co-workers as a method to pattern MoS\(_2\) and generate single-layer MoS\(_2\) from multi-layer exfoliated sheets. It is worth noting that PDMS is transparent to the optical laser radiation (\(\lambda = 514\) nm) employed here, thus the sample surface is unaffected by the radiation when the PDMS substrate is uncoated.

Samples were also prepared by depositing amorphous MoS\(_2\) precursor films on silicon TEM grids covered by a thin freely suspended amorphous carbon layer. These were laser annealed in an identical manner to the MoS\(_2\) samples on the PDMS. Plan-view TEM images of the as-grown precursor film (Fig. 3a) is indicative the entire sample, which was of uniform thickness over the entire TEM grid. The laser annealed regions on the grid showed strongly oriented MoS\(_2\) material with variability in the orientation of the crystallized hexagonal MoS\(_2\) grains. Figure 3(b) is taken from a region where the MoS\(_2\) crystallized with basal planes are parallel to the substrate and the hexagonal crystal structure is clearly seen. A cross-sectional view of the laser annealed MoS\(_2\) on PDMS (Fig. 3c) shows the orientation of the MoS\(_2\) basal planes parallel to the PDMS surface, however the substrate is rather wavy as expected from AFM imaging shown in Fig. 1. The inset shows a zoomed in region of 9 stacked MoS\(_2\) layers,
where a single layer thickness was directly measured as 0.65 nm, in good agreement with the accepted basal plane spacing.\textsuperscript{26}

X-ray photon spectroscopy (XPS) was performed to investigate the chemical aspects of the laser annealing process. High resolution spectra of the Mo 3d region from MoS\textsubscript{2} films with and without laser treatment are presented in Figure 3(d). The S 2s photoelectron peak is observed at 226.4 eV, which is typical for MoS\textsubscript{2}. The Mo 3d region consists of three distinct sets of doublet peaks (Mo 3d\textsubscript{5/2} and Mo 3d\textsubscript{3/2}). The doublet component with Mo 3d\textsubscript{5/2} at 229.3 eV (FWHM = 1.3 eV) indicates the presence of amorphous MoS\textsubscript{2}, while the \textit{1T} (octahedral) phase of MoS\textsubscript{2} is characterized by a doublet with Mo 3d\textsubscript{5/2} at 228.5 eV (FWHM=0.8 eV).\textsuperscript{27,28} Oxidized MoS\textsubscript{2} and other Mo(6+) species (e.g., MoO\textsubscript{3}) exhibit a doublet at higher binding energy, with Mo 3d\textsubscript{5/2} and Mo 3d\textsubscript{3/2} at 232.1 eV and 235.5 eV, respectively. The relative intensities of the Mo 3d component peaks give useful information about film composition and crystallinity. The as-deposited film shows the presence of both amorphous and \textit{1T} MoS\textsubscript{2}, and the Mo(6+) concentration is relatively low. Following laser annealing, the Mo(6+) component peak becomes more prominent, suggesting some oxidation of the MoS\textsubscript{2} film. Furthermore, whereas the majority of the MoS\textsubscript{2} appears to exist in the \textit{1T} phase in the as-deposited film, the Mo 3d\textsubscript{5/2} peak at 229.3 eV becomes narrower (FWHM = 1.0) and more intense relative to the \textit{1T}-MoS\textsubscript{2} Mo 3d\textsubscript{5/2} peak at 228.5 eV, following annealing. This suggests that both the \textit{1T}-MoS\textsubscript{2} and the amorphous MoS\textsubscript{2} undergo crystallization to the thermodynamically stable \textit{2H} phase following laser annealing. Referring back to Raman spectrum of the precursor film in Figure 2(a) there does appears to be a small residual feature at around 408 cm\textsuperscript{-1} and no feature in the 380 cm\textsuperscript{-1} region, which indicates a small presence of \textit{1T}-MoS\textsubscript{2}.\textsuperscript{29}

To probe the electrical properties of the material, multiple localized IV-curves were acquired from regions with and without laser annealing, using conductive force microscopy. Figure 4(a) indicates that the laser treatment converts the MoS\textsubscript{2} precursor film from insulating to semi-conductive. Unlike, crystalline area \textit{1T}-MoS\textsubscript{2}, the macroscopic properties of the precursor film are insulating despite the presence of some \textit{1T}-MoS\textsubscript{2} in the precursor film (as indicating from the XPS). This indicates that the amorphous nature of the precursor film is a major contributor to the electronic properties. To further investigate the semi-conducting nature of the MoS\textsubscript{2}, large area samples were made (see figure 4(b)) by exposing the sample to 830 nm light and subsequently aerosol jet printing (Optomec) electrodes. I-V curves were then acquired from
this sample at various temperatures. Figure 4(c) shows a representative IV curve. The resistance decreases with increasing temperature indicating semi-conducting behavior. It is worth noting that at 75°C the resistance shifted up, this shift is due to cracking of the electrodes due to the poor thermal expansion mismatch with the PDMS. Such behavior was commonly observed on the heating cycles of our tests.

The mechanistic details of the observed laser-induced phase transition are the subject of ongoing investigations, but the main underlying process appears to be a thermally driven kinetic controlled transformation. Essentially the thin films under laser irradiation are quickly heated sufficiently to induce the transition from amorphous films to crystalline MoS$_2$. The photo-thermal nature of the mechanism is supported by several critical observations. Firstly, the laser induced phase transformation is not directly dependent on the dosage (i.e, fluence or time-integrated irradiance), but instead is highly dependent on the laser intensity (i.e. the irradiance in W/m$^2$). Secondly, the assertion that the mechanism is a kinetically controlled photo-thermal effect is supported by the fact that we were able to achieve the same results with different laser wavelengths, including 830 nm at similar intensities as the 514nm laser used throughout these studies, except when noted. The absorption spectra of the precursor film shows a broad absorption from UV to NIR, which also tends to support a photo-thermal mechanism. These results refute a photo-electronic process, but support a photo-thermal process. Presumably, the PDMS is protected from thermal damage by the combination of the transient nature of the heating by the laser rastered on the surface and the strong thermal anisotropy in crystalline transition metal dichalcogenides where ultra-low inter-layer thermal conduction is coupled moderate in plane conduction of the rapidly formed MoS$_2$. In addition, the results from XPS and TEM provide a combined support for a mechanism of chemical rearrangement as opposed to a chemical reaction.

In summary, we have presented a method of preparing large scale semiconducting 2D MoS$_2$ films on flexible PDMS through laser annealing of PVD films grown at room temperature. The composition and crystalline nature of the few monolayer thick hexagonal laser annealed MoS$_2$ films was confirmed with Raman spectroscopy, XPS and both plan-view and cross-sectional TEM. The electrical properties of the MoS$_2$ annealed regions were characterized with C-AFM and variable temperature conductivity measurements, which confirm their semiconducting behavior, while surrounding amorphous MoS$_2$ film remains an insulator. Laser
annealing of amorphous films on polymer substrates is a simple and scalable approach to complexly pattern semiconducting MoS$_2$ film in an insulating matrix or generating large areas of semiconducting material for fabrication of 2D based flexible/stretchable electronics.

**Acknowledgments**

Financial support from Air Force Office of Scientific Research, Complex Materials and Devices program (15RXCOR184) is gratefully acknowledged. CM gratefully acknowledges support from Air Force Research Laboratory funded DAGSI program and AFRL Materials and Manufacturing Directorate Laboratory Director’s Funds to sponsor this work. CM would also like to acknowledge Advanced Energy Industries Incorporated for use of a Pinnacle Plus pulsed power supply for thin film growth.

**FIGURES:**

**Figure 1:** (a) Simple schematic of the laser annealing process (b) An AFM micrograph of amorphous MoS2 as deposited on PDMS, Z-scale: 290 nm (c) An AFM micrograph of a sample after laser annealing 2 lines from amorphous to crystalline MoS2, Z-scale: 52 nm.
**Figure 2:** (a) Raman spectra of the MoS2 with and without laser annealing (b) Raman intensity of spectra at identical dosages (50mW-sec) but different laser powers and the corresponding exposures times. Inset: Raman intensity from the $A_{1g}$ peak for the various exposures shown in (b). (c) Optical microscopy image of a sample with laser annealed lines of crystalline MoS2 (d) A Raman map of the sample shown in (c) where the intensity corresponds to the intensity of the $A_{1g}$ peak.
Figure 3: (a) & (b) A transmission electron microscopy image of a film prepared on a TEM grid without (a) and with (b) laser annealing. Cross-sectional TEM of the laser annealed MoS₂ film on PDMS. Inset: zoomed in region showing a stack of MoS₂ layers. (d) XPS spectra of the as deposited film and the laser annealed film.

Figure 4: (a) I-V curve from a region before and after laser annealing. (b) A large area (3x5 mm) of laser annealed MoS₂ on a piece of PDMS. (c) Temperature versus resistance, indicating semi-conductive behavior. The kink at 75°C is due to cracking of the electrode due to the large thermal expansion mismatch between the PDMS and the silver electrode.
Citations


