SYNTHESIS AND CHARACTERIZATION OF CRYSTALLINE TRANSITION METAL DICHALCOGENIDES ONTO STRETCHABLE SUBSTRATES BY LASER PROCESSING

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ABSTRACT

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Transition metal dichalcogenides (TMDs) are an emerging class of materials for thin film transistors (TFTs). The inherent transparent properties, functionality and large lateral dimensions offer material selection for sensor technologies and transparent flexible displays. Low temperature processing of large crystallographic ordered films is needed to prevent thermal degradation of modern flexible electronic substrates. In this study, polycrystalline TMD growth mechanisms and, for the first time, a scalable processing technique used at room temperature will be demonstrated for application of semiconducting TMDs directly onto substrates by laser processing. A means of controlling the material structure by photon-phonon excitation provides a low temperature approach to controlling structural changes in materials; in particular, these studies are conducted on thin-film molybdenum disulfide and tungsten disulfide. A
significant variance in both structure and electronic properties upon laser processing are observed in all samples. The direct deposition of molybdenum disulfide and tungsten disulfide on cross-linked polymers followed by localized laser annealing results in few atomic layer hexagonal sheets confirmed by Raman analysis, x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The strong enhanced $A^{1g}$ and $E^{2g}$ bands in Raman and bonding characteristic in XPS suggests the layered S-Mo-S and S-W-S bonding. Conductive atomic force microscopy (C-AFM) on laser-exposed samples showed a change in topography and electrical properties from insulating material to semiconducting after laser annealed. Laser annealing of amorphous films on polymer substrates is a simple and scalable approach to patterning complex patterns of semiconducting MoS$_2$ film in an insulating matrix or generating large areas of semiconducting material for fabrication of 2D based flexible/stretchable electronics.
Dedicated to my friends and family.
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# TABLE OF CONTENTS

ABSTRACT .................................................................................................................................................. iii
DEDICATION.................................................................................................................................................. v
ACKNOWLEDGEMENTS................................................................................................................................. vi
LIST OF FIGURES......................................................................................................................................... ix
LIST OF TABLES........................................................................................................................................... xii
LIST OF ABBREVIATIONS AND SYMBOLS ............................................................................................... xiii

CHAPTER I: INTRODUCTION .................................................................................................................. 1
  1.1 Motivation for Inhibiting Substrate Thermal Degradation ................................................................. 1
    1.1.1 Air Force Applications .................................................................................................................. 2

CHAPTER II: BACKGROUND .................................................................................................................. 5
  2.1 Thin Film Transition Metal Dichalcogenides ....................................................................................... 5
    2.1.1 Molybdenum Disulfide ................................................................................................................ 5
    2.1.2 Tungsten Disulfide ..................................................................................................................... 7
  2.2 Thin-Film Synthesis Techniques ......................................................................................................... 9
    2.2.1 Physical Vapor Deposition ......................................................................................................... 11
  2.3 Background on Laser Processing .......................................................................................................... 12
    2.3.1 Fundamentals of Laser Processing ............................................................................................. 12
    2.3.2 Energy Absorption Mechanism .................................................................................................. 18
    2.3.3 The Heat Equation ...................................................................................................................... 18
    2.3.4 Material Response ...................................................................................................................... 19
LIST OF FIGURES

Figure 1: Output power and frequency experienced in various commercial and military essential technologies........................................................................................................................................... 3

Figure 2: Range of power and frequency attainable with nanomaterials............................................. 4

Figure 3: (a) AFM analysis shows the thickness of a MoS2 flake, which is around 15 nm. (b) The Raman spectrum of the MoS2 flake (c) Schematic of the flexible bottom gate device structure. (d) The optical microscope picture for the MoS2 device. (e) The photograph of the flexible sample made on industrial polyimide sheet .................................................................................................................................................. 7

Figure 4: (a) Schematic stacking of thin films (b) optical image of single layer WS2 (c) optical image of single layer stacked between dielectric...................................................... 8

Figure 5: Common thin-film deposition techniques ................................................................. 9

Figure 6: (a) Photograph of 4 layers of MoS2 on a 2cm x 2cm wafer seen in (b). Raman from numbered locations determine thickness difference (c) Raman analysis of uniform thickness.................................................................................................................................................. 10

Figure 7: Schematic of film nucleation and growth processes .............................................. 11

Figure 8: Growth mechanisms according to deposition rate and diffusion rate ........... 12

Figure 9: Wavelength and energy of light ....................................................................................... 13

Figure 10: Conventional laser processing techniques................................................................. 15
Figure 11: Laser surface heat treatment ................................................................. 16
Figure 12: Schematic of the cladding process ......................................................... 17
Figure 13: Processing steps ...................................................................................... 21
Figure 14: a) The deposition system b) Schematic of main UHV magnetron sputtering system c) optical image of TMD plasma directed at PDMS substrate ............... 24
Figure 15: Amorphous film conversion to crystalline ................................................. 25
Figure 16: Laser processing schematic ....................................................................... 26
Figure 17: AFM of pristine PDMS substrate ............................................................ 28
Figure 18: a) Raman spectrum of sample b) optical image of lines annealed into material c) Raman map of area .................................................................................. 32
Figure 19: (a) Raman spectra of regions with varying laser powers and the corresponding exposures times. (b) Raman intensity from the $A_{1g}$ peak for the various exposures shown in (a). (c) Raman spectra from different exposure intensities for 1 second .................................................................................. 33
Figure 20: High-energy resolution XPS of annealed and non-annealed area ............ 35
Figure 21: (a) AFM of thin film on PDMS (b) AFM of subsequent laser annealing (c) localized laser heating to architecture .................................................................. 36
Figure 22: TEM top view (a) non-laser treated film that has amorphous structure (b) laser treated area that has structure with long range order ........................................ 36
Figure 23: Cross sectional TEM (a) electron energy loss spectroscopy for elemental analysis (b) high magnification that displays layered structure ................................ 37
Figure 24: I-V curve of sample produced by C-AFM ................................................. 38
Figure 25: Resistance of annealed area with respect to temperature ....................... 39
Figure 26: (a) Raman spectrum of WS$_2$ (b) optical image of lines annealed into material (c) Raman map of E$_{2g}$ vibration mode ......................................................... 41

Figure 27: UV-VIS of WS$_2$ ........................................................................................................ 42

Figure 28: (a) TEM top view of WS$_2$ processed area (b) high resolution amorphous region (c) high resolution crystalline area ................................................................. 43

Figure 29: High-energy resolution XPS of annealed area laid on top of non-annealed area ................................................................................................................................................. 44

Figure 30: (a) morphology of processed sample with the (b) electrical conductivity of the processed sample ................................................................................................................... 45

Figure 31: Raman analysis of laser annealed heterostructures (a) alternating layers MoS$_2$ – WS$_2$ (b) MoS$_2$ passivated by boron nitride .................................................. 46

Figure 32: (a) Optical image of device architecture (b) STEM image of nanoparticle on dielectric (c) electrical characterization of device architecture ........................................ 47

Figure 33: UV-VIS absorption of pristine PDMS substrate................................................... 59

Figure 34: Raman shift of Pristine PDMS substrate ...................................................................... 60

Figure 35: Figure 35: (a) 3 x 5 mm macroscopic view of laser annealed area (b) Optical image of annealed pattern .......................................................................................................................... 60
LIST OF TABLES

Table 1: Substrate properties ................................................................................. 59
Table 2: Laser calibration ......................................................................................... 60
## LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom ($10^{-10}$ meters)</td>
</tr>
<tr>
<td>°</td>
<td>Degrees</td>
</tr>
<tr>
<td>α</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>ρ</td>
<td>Mass density</td>
</tr>
<tr>
<td>2D</td>
<td>Two-Dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>C-AFM</td>
<td>Conductive Atomic Force Microscopy</td>
</tr>
<tr>
<td>c</td>
<td>Speed of light</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Specific heat at constant pressure</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>GPa</td>
<td>Gigapascal</td>
</tr>
<tr>
<td>$h$</td>
<td>Plank’s constant</td>
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<tr>
<td>HAZ</td>
<td>Heat-affected zone</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$I$</td>
<td>Power density</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Molybdenum disulfide</td>
</tr>
<tr>
<td>MX$_2$</td>
<td>Metal atoms (M) and chalcogen atoms (X)</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>$q$</td>
<td>Laser power</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin Film Transistor</td>
</tr>
<tr>
<td>TMD</td>
<td>Transition Metal Dichalcogenide</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum ($&lt; 10^{-7}$ Torr)</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Laser beam radius</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>Tungsten disulfide</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
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CHAPTER I

INTRODUCTION

Transition metal dichalcogenides (TMDs) have been integral materials for solid lubrication\textsuperscript{1,2} for many years, commonly referred to as “grease”. In the past decade, they have been the focus of many nanoscale electronic\textsuperscript{3,4,5} applications. Depending on whether the material structure is metallic or semiconducting, the film can be used for sensors or field effect transistors. A focused effort of deposition and isolation of few layers of material is required for such applications.\textsuperscript{6} The atomically thin dimensions and inherent wide bandgap provides potential for transparent electronics. Another benefit of TMDs is their tendency to have high breakdown voltages and high dissociation temperatures making them robust materials for devices. Consequently, the high thermal stability of these materials creates low temperature processing challenges. This study demonstrates the use of magnetron sputtering followed by laser processing as a scalable low-temperature process for nanoelectronics, specifically TMDs for thin film transistor (TFT) channels.

1.1 Motivation for Inhibiting Substrate Thermal Degradation

Numerous applications demand the development of large-area, flexible, stretchable and conformal electronics; including computing devices, health monitoring sensors, military avionic systems, and other electronic systems.\textsuperscript{7,8,9} TMDs tolerate large strain
deformations required by such dynamic applications and environments. The foundation (substrate) that the semiconductor adheres to must also be flexible and in most cases are polymers. The thermal degradation of flexible polymers limits processing techniques for TMD films. Magnetron sputtering is a physical vapor deposition (PVD) technique that possesses many benefits for deposition including uniform large area thin films at low temperatures. As a result, phase transformations based on photon-phonon coupling are under consideration to maintain room temperature ambient conditions post magnetron deposition for enhancement of material properties.

1.1.1 Air Force Applications

A representation of output powers and frequency experienced in typical military and commercial electronic applications are displayed in Figure 1. The tailoring of various range of frequencies and output powers are apparent for specific sensors and radars. Silicon is the most widely used and understood electronic material; this is a major issue with current performance because it is intrinsically limited. Silicon only provides an output power up to 1 watt with a frequency up to 3 gigahertz. This performance only covers a minute operation range for essential radio frequency applications. The use of thin film TMDs covers a higher output power and frequency range. The optimal material would include the ability to tune these properties over a greater range for tailoring the application. It has been reported that TMDs, in particular MoS$_2$ has shown a cut-off frequency up to 42GHz.$^3$
Graphene, an allotrope of graphite opened the door to 2D materials for electronic applications with its high power and high frequency capabilities.\textsuperscript{10,11,12} The lack of a bandgap limits the applications for graphene and its implementation into TFTs. Figure 2 depicts breakthrough nanomaterials in the past decade and the range of output powers and frequencies associated with them. The movement from rigid RF transmit-receive to flexible provides better design adaptability for user.
The proceeding section will provide a brief background on TMDs, their processing, and incorporation onto low thermal budget flexible substrates. To facilitate later discussion of bottom-up processing for TMDs, a review of low temperature film nucleation and growth will be discussed. This will be followed by a review of literature on localized laser processing.

Figure 2: Range of power and frequency attainable with nanomaterials
CHAPTER II

BACKGROUND

2.1 Thin Film Transition Metal Dichalcogenides

Transition metal dichalcogenides are inorganic semiconductors that have been the focus of significant research\textsuperscript{5,13} for use in electronic applications due to its combination of high mobility and bandgap. TMDs are atomically thin-layered materials with an MX\textsubscript{2} stiochiometry\textsuperscript{14} that form stacks of covalently bonded layers in the form of X-M-X with adjacent layers held together by van der Waals forces.\textsuperscript{6} Depending on the coordination and oxidation states of the transition metal atoms, TMDs can be either semiconducting or metallic in nature,\textsuperscript{15} according to the arrangement of the chalcogen atom.\textsuperscript{16} Two different arrangements of the atom symmetries include: 2H (trigonal prismatic D\textsubscript{3h}) and 1T (octahedral O\textsubscript{h}) phases, exhibiting different electronic structures as semiconducting and metallic\textsuperscript{7-16} respectively. The 1T allotrope is metastable and undergoes transition to the stable 2H phase when subjected to 95°C temperatures and higher,\textsuperscript{17} hence the 1T phase is not typically found in nature.

2.1.1 Molybdenum Disulfide

An important factor in the selection of a semiconductor is its bandgap;\textsuperscript{18,19} correlated to the structure of energy bands occupied by electrons. In bulk form, molybdenum disulfide (MoS\textsubscript{2}) has an indirect bandgap 1.29eV (961 nm), whereas monolayer MoS\textsubscript{2} is a
noncentrosymmetric material with a direct energy gap of 1.80 eV (689nm).\(^2\) The relatively wide bandgap attributes to higher breakdown voltages, lower noise generation, and ability to sustain larger electric fields.

Unlike traditional semiconducting materials such as silicon, the layered structure provides large elastic deformations for potential exploitation in stretchable electronics. TMDs such as MoS\(_2\), with Mo atoms sandwiched between S atoms forming S-Mo-S structure can accommodate up to 10% strain when its thickness is reduced to 5 nm or less.\(^20\) Monolayer MoS\(_2\) has superior strength with a reported stiffness of 180 ± 60 Nm\(^{-1}\), corresponding to a Young’s modulus of 270±100 GPa. The material typically breaks at 15±3Nm\(^{-1}\) (23 GPa).\(^11\)

In TFT devices, the semiconductor selection for the channel can affect device performance by controlling the ON/OFF switching ratio, mobility, and the gate control. The incorporation of MoS\(_2\) channels onto a flexible substrate has been demonstrated by Chang et al\(^{21}\) using mechanical transfer method. The architecture is shown in Figure 3 (a), (c), (d) as well as Raman analysis in Figure 3 (b) of the channel. Chang et al. reported ON/OFF ratios greater than \(10^7\) with field effect mobilities of 30 cm\(^2\)/V-s. The samples studied were from 7.9 nm to 21 nm in thickness, an indirect correlation was seen between thickness and mobility.
Figure 3: (a) AFM analysis shows the thickness of a MoS$_2$ flake, which is around 15 nm. (b) The Raman spectrum of the MoS$_2$ flake (c) Schematic of the flexible bottom gate device structure. (d) The optical microscope picture for the MoS$_2$ device. (e) The photograph of the flexible sample made on industrial polyimide sheet$^{12}$

2.1.2 Tungsten Disulfide

Another TMD with similar properties to MoS$_2$ and the same atomic structure is WS$_2$. WS$_2$ exhibits a bulk indirect bandgap of 1.3eV that transitions to a direct bandgap$^{22,23}$ of 2.1 eV when thinned to a monolayer. WS$_2$ contains a high mobility$^{24}$ reported at 214 cm$^2$/Vs (which compares to the mobility of 200 cm$^2$/Vs reported for single-crystalline silicon$^{25}$). Figure 4 shows the architecture of the device with the 214 cm$^2$/Vs mobility reported, again fabricated by mechanical exfoliation of a crystal.
The on/off ratios and high mobilities in Chang et al.’s MoS$_2$ films are attributed to the large crystal structure in the film. The sample was prepared by mechanical exfoliation from a commercial bulk crystal. Since the out-of-plane atoms along the c-axis interact by weak Van der Waal forces, compared to the strong in-plane covalent bonding along basal plane, exfoliation of near single crystals has been proven not only possible but also the material’s fundamental method for research. The intrinsic challenges to the scalability of exfoliation to coat large areas and complex shapes motivates the investigation of other techniques for low temperature and scalable deposition of TMD films that will yield morphology and structure optimization.
2.2 Thin-Film Synthesis Techniques

In addition to mechanical exfoliation, TMD thin films have been synthesized using chemical vapor deposition (CVD) and physical vapor deposition (PVD). The degree of continuousness, crystallographic orientations, grain size and surface roughness are dependent on the energy of material arriving at the substrate. During CVD the film is formed by a chemical reaction on the substrate surface in which the energy is typically governed by the substrate temperature; a higher temperature results in higher mobility at the surface for nucleation. During PVD, depositing at higher powers or techniques with inherently higher energy fluxes may also increase the energy.

A reference for such deposition techniques, Figure 5 displays the subdivisions of both PVD and CVD methods readily available in the scientific community. For flexible electronic research with such growth techniques are processed by growing materials onto freestanding foil followed by mechanical or chemical exfoliation of the materials onto polymer substrates. Very thin films can be prepared on flexible substrates through the exfoliation processes, but the surfaces are typically contaminated during the transfer process and exfoliation processes generally limit application to small areas (<100um²) hence not being commercially viable.

![Figure 5: Common thin-film deposition techniques](image)

Figure 5: Common thin-film deposition techniques
Recent work has shown that magnetron sputtering, a PVD technique, can facilitate the formation of continuous TMD films of 3-6 molecular layers over 4cm$^2$ areas on SiO$_2$.$^{27}$ Seen in Figure 6, his work was accomplished by Muratore et al. The growth of islands is not present in the film with surface roughness RMS of 0.58 nm compared to the 0.26 nm of the substrate. The kinetic energies within the plasma species are optimized to form the maximum atomic mobility during growth with energy just below defect formation. This PVD technique shows formation at a low temperature of 350 °C while being easily scalable for large area growth (> 1 m$^2$).

Figure 6: (a) Photograph of 4 layers of MoS$_2$ on a 2cm x 2cm wafer seen in (b). Raman from numbered locations determine thickness difference (c) Raman analysis of uniform thickness$^{17}$
2.2.1 Physical Vapor Deposition

During PVD of films, the film species arrive in a vapor phase at the substrate surface, followed by film nucleation and growth as illustrated in Figure 7. The rate at which deposited species are accommodated and add to film growth is the deposition rate.\textsuperscript{28} Full-layer nucleation and growth is promoted by strong film-substrate bonding, low film surface energy, and high substrate surface energy. Full-monolayer growth involves the nucleation and growth of islands, but these islands grow towards each other reaching essentially complete coalescence before significant clusters are developed on the next layer.\textsuperscript{29} Low substrate temperatures result in less surface mobility for the growing film, which promotes the formation of small grains and defects.

![Figure 7: Schematic of film nucleation and growth processes\textsuperscript{30}](image)

Figure 8 represents the thermodynamic and kinetic material growth behavior. The diffusion rate of the film species at the substrate may be higher than the deposition rate; under these conditions the nucleation and growth is driven by thermodynamics rather than kinetics. This is an ideal process; the mechanism is near equilibrium conditions allowing the absorbed species to have significant time to reach a minimal energy configuration. A kinetic based process, the deposition rate is higher than the diffusion rate, which results in metastable material structures. The metastable structures still have
some potential energy, however, requires some outside help to overcome the barriers to become thermodynamically stable.

![Figure 8: Growth mechanisms according to deposition rate and diffusion rate](image)

2.3. Background on Laser Processing

This next section will focus on laser processing of materials, including the background, engineering and mechanisms behind the process. The laser has unique properties for material surface engineering. It uses electromagnetic radiation in which may be absorbed by just the first few molecular layers of a material\(^7\), inducing surface heating. The major advantage for the laser as a processing tool is the ability to control large amounts of energy to confined regions for achievement of desired reactions.

2.3.1 Fundamentals of Laser Processing

Laser processing applications involve energy transfer from the incident laser source to matter it is directed upon. Lasers, a form of light, has a dual particle/wavelike property,\(^32\) interfering with matter like a particle and diffracting like a wave. Max Plank was the first to hypothesize that light consists of particles called photons. The emission
and absorption of photons occur in quanta of energy with the energy of a photon expressed as:

\[ E = \frac{hc}{\lambda} \]

where \( h \) is Planck’s constant, \( c \) is the speed of light, and \( \lambda \) is the wavelength of the photon. This is an inverse relationship between the energy and the particular wavelength. Absorption is the most important influence on the photon-phonon energy transfer, primarily because the higher absorption leads to higher energy absorbed by the material.\(^{21}\) Playing a large role in laser selection process, the wavelength is critical in acquiring enough energy for absorption by the desired material. Figure 9 presents the wavelength of electromagnetic radiation from near infrared (NIR) to ultraviolet (UV). Note, the quanta of energy associated with the wavelength is not seen; however, the visible wavelengths contain quanta of energy between 1.8 and 3.1 electron volts (eV). The longer waves of infrared radiation contain less energy while the shorter UV contain more energy relative to visible.

Figure 9: Wavelength and energy of light\(^{33}\)
The heating and quench rates, which essentially control the resultant material properties, can be controlled by the power density and interaction time. The power density for a laser is the incident power of the beam with respect to its spatial dimensions of the focused beam spot-size. Power density, easily controlled in lasers by adjusting the current source to the system and laser beam spot size. For a laser beam with a Gaussian distribution, the beam size is characterized as the radial distance at which the intensity of the beam reduces to $1/e^2$ or 13.5% of the beam energy. The power density can be calculated from the following expression:

$$I = \frac{q}{\pi w^2}$$

where $q$ is the power of the laser beam (W) and $\omega$ is the beam radius (mm). Increasing the heat input ($q$) increases the heating while reducing the cooling rate. The Gaussian beam of wavelength $\lambda$ has a beam radius as:

$$w_f = \frac{1}{\pi} \left( \frac{f \lambda}{w_0} \right)$$

The constant frequency of a CW laser provides an infinite duration output beam. The interaction time for such a laser is controlled by the scan speed of the sample in relation of the beam. Increasing the speed of the sample, decreases interaction time, as a result increases the material-cooling rate. The exposure time is independently related to the transverse velocity of the stage as seen in the equation.

$$v = \lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} = \frac{dx}{dt}$$

An absorbed energy characterization curve for a laser is displayed in Figure 10. This curve interprets laser manufacturing and processing techniques that compare power densities with respect to interaction times. The curve maps these two variables to
decipher the absorbed energy, which produces a thermal effect on the material surface. This thermal effect results in modification of properties in the material. There are five major forms of laser surface modification. These modifications are the following:  

1. Laser surface heat treatment  
2. Laser surface melting (glazing or skin melting)  
3. Laser direct metal deposition (alloying, cladding, and hard coating)  
4. Laser physical vapor deposition  
5. Laser shock peening

Figure 10: Conventional laser processing techniques

In laser surface heat treatment, no melting takes place in the material. Heat treatment is commonly used in materials of all types to improve their properties. An example of heat treatment is the enhanced mechanical properties of steel gears that have been case
hardened for vehicle transmissions. The material is exposed to a thermal cycle of rapid heating and cooling that induces a transformation while in the solid state, commonly taking place by diffusion. Diffusion is the phenomenon of material transport by atomic motion. This process is the stepwise migration of atoms from lattice site to lattice site. Vibrational in nature, for the atom to move; their must be sufficient energy to break bonds with neighboring atoms and their must be empty adjacent sites for the atom to accommodate.

Heat treatment to restore material structure to its equilibrium state is often termed an annealing treatment. This restoration at elevated temperatures results from recovery, recrystallization and may be followed by grain growth. Recovery begins to relieve internal strain energy as a result of a reduction in dislocations by diffusion at the elevated temperatures. Also, this process recovers some of the physical properties such as thermal and electrical conductivities to the original states. The next step is recrystallization, a process that drives grains to be strain free by forming equiaxed grains with relatively low dislocation densities. The new grains are produced by the difference in internal energy between the strained and unstrained material. Sometimes grain growth follows this process when left at elevated temperatures, as a result of reducing energy associated with the grain boundaries.

![Figure 11: Laser surface heat treatment](image)
Laser surface melting, on the other hand, provides high enough temperatures to thermally transform the material to liquid, which then solidifies by self-quenching. The material becomes homogenous during the liquid phase. In addition to laser surface melting, direct metal deposition may be incorporated for the laser to melt into the bulk melt zone. This is typically known as a form of hardfacing, cladding, or coating technique to enhance corrosion and wear resistance. Figure 12 shows the typical processing technique for cladding. The clad layer and bulk material form a melt zone that fuses together to alter the material properties. The interaction time of laser and workpiece is very short (<10^{-4} s) to increase the cooling rate and increase defects for mechanical strength.

![Figure 12: Schematic of the cladding process](image)

This unconventional method of processing TMDs is similar to laser hardening by utilizing morphological, structural and compositional transformations with laser-light intensities below vaporization intensity. The physical structure of TMD’s tend to dissociate before melting is capable of taking place in the material. Melting is not involved with the process, however the heat enhances atomic mobility to reorganize the crystal structure.
2.3.2 Energy Absorption Mechanism

The specific mechanism by which light absorption occurs depends on the type of material. In general, photons couple to the available vibrational or electronic states depending on the incident energy. In semiconductors and insulators, the absorption of photons is governed through transitions of valence band electrons to conduction band (interband transitions) or within bands (intersubband transitions). Energy above this transition will cause lattice phonons while energy below this threshold (unless impurities are present) will not cause such vibrations. The time it takes for this electron transfer of energy to phonons and subsequent thermalization in large band gap materials is relatively long compared to metals.

2.3.3 The Heat Equation

Laser processing of metals or semiconductors with laser pulse times that are long (> ns) is typically characterized by photothermal mechanisms. For photothermal processing, the laser beam is the heat source and the material response can be explained as a result of elevated temperatures. The heat equation, derived from Fourier’s law of heat conduction and the conservation of energy governs the temperature field in the material

\[ \rho c_p \frac{dT}{dt} - \nabla \cdot (k \nabla T) + \rho c_p q_s v_s \nabla T = Q \]

where \( \rho \) is the mass density, \( c_p \) is specific heat at constant pressure, \( k \) is the thermal conductivity, \( v_s \) is the transverse velocity of substrate relative to heat source, and \( Q \) is the internal heat. The equation describes the evolution of temperature owed to conduction and convection. In general, this equation becomes a non-linear partial differential
equation, which makes it difficult in finding a solution. In certain cases, assumptions can be applied to simplify variables into constants for analysis. This also requires the laser (heat source) to be modeled as a boundary condition at the surface.

An important quantity, the thermal diffusion length, comes out of the simplified treatment parameters. The thermal diffusion length, \( l_T = \frac{\xi}{\sqrt{D\tau}} \), characterizes the distance of temperature propagation in a characteristic time. Following the interaction between the material and laser beam, further propagation of elevated temperatures diffuse out past the actual interaction site. Material properties may change in this area beyond the interaction site and is denoted as the heat affected zone (HAZ).

### 2.3.4 Material Response

As mentioned earlier, if the laser induced excitation rates are relatively slow when compared to thermalization time, the process is known as photothermal and can result in the laser energy modeled as heat. In this situation, the material response will be a function of the local heating and cooling rates, temperature gradients, and maximum temperatures reached.

When the excitation time is shorter than the thermalization time in the materials, non-thermal, photochemical ablation mechanisms can occur.\(^{25}\) This is common in ultrafast laser pulses, ionization and electron-hole plasmas can lead to athermal phase transformations known as ablation. Ablation results in removal of material in the form of a plasma plume. The shorter the pulse length, the less time the localized area has time to transfer energy to the surrounding material.
2.4 Summary

Substrate degradation is, and will continue to be, a major concern during manufacturing of new flexible electronic materials. Current knowledge of processing TMD materials in low temperature environments is constraining the leap forward toward large-scale processing onto flexible material surfaces. Laser exposure studies are necessary in evaluating new manufacturing techniques for thin film TMDs. These studies provide means of characterizing both chemical and physical properties of processed thin film MoS$_2$ and WS$_2$. Optical excitement of surfaces can chemically and physically alter the surface to increase crystallinity. By choosing the appropriate laser parameters, control of the material properties can be achieved.
CHAPTER III

RESEARCH OBJECTIVES

Analysis of literature on TMDs has shown the need for few layer films with crystalline hexagonal structure. For incorporation of TMDs into flexible electronics, low temperature scalable processing of films is needed. The proposed method of this study utilizes room temperature amorphous material grown by magnetron sputtering. A laser treatment process is then employed to convert the amorphous TMD film prepared on the elastomeric substrates into crystalline hexagonal TMD films with semiconducting electronic characteristics. These bottom-up processing steps, seen in Figure 13, provide additional dimensional control to the device engineer. The highly localized energy density of laser processing combined with the ultra-low inter-layer thermal conduction makes it a promising technique for control of TMD microstructures.

Figure 13: Processing steps

The overall goal of this study was to demonstrate the applicability of TMD laser processing for scalable low-temperature film growth for TFT applications. This study focused on synthesis and processing in a room temperature environment for temperature
sensitive flexible substrates and identified deposition conditions that produced TMD films with hexagonal structure. The objectives of the research are as follows:

1. To investigate changes in material structure upon light irradiation.
2. Build an electronic 2D material structure on a soft flexible/stretchable substrate.
3. Characterize the 2D material’s structure and chemical composition.

To accomplish the objectives, a laser processing system was built to manufacture the samples.
CHAPTER IV

EXPERIMENTAL METHODS

4.1 The Deposition System

In this study, all material synthesis was performed under ultra-high vacuum in the custom system shown in Figure 14. The system contained three separate zones. The zone on the right in Figure 14 (a) was the load-lock chamber. The load-lock was equipped with a sample rack that allowed for up to five samples to be loaded at one time to increase throughput of samples. The chamber’s small volume allowed the chamber to evacuated quickly to pressures < 10^{-6} Torr without sacrificing pressure increase in the main chamber. Transfer forks allowed samples to be moved from this chamber to the main sphere chamber as seen on the left of in Figure 14 (a). A turbo molecular pump backed by a mechanical roughing pump was used to reduce base pressures to 10^{-8} Torr or below. This pressure in the chamber was controlled by a butterfly valve and mass flow controllers plumbed to argon, nitrogen, and oxygen. The third chamber, connected to the load-lock by a 90° port valve was used for XPS measurements post-synthesis of material.

The stainless steel substrate holder in the deposition chamber rotated the samples to induce uniformity. The substrate holder was biased that was dependent on the sputtering conditions during deposition. A tungsten resistive heater filament was built into the substrate holder, however for these experiments was not used.
The main vacuum chamber was equipped with magnetron gun faces positioned at a 45° to the substrate normal. The target on the gun face was 1 1/3” in diameter. The amorphous MoS$_2$ and WS$_2$ films were synthesized in an ultra-high vacuum chamber by magnetron sputtering from pure (>99.9%) compound target materials.

A decrease in pressure of the system (10$^{-9}$torr), the Ultra High Vacuum (UHV) Chamber removes unwanted particles from the system. The decrease in pressure puts the polymer substrate into tension during synthesis. The substrate put into atmospheric pressure relaxes, applying compression stresses onto the thin film. This mechanical force
applied may result in buckling of material. No thermal stresses are accredited during PVD of the material.

4.2 Laser Processing System

Unlike conventional thermal annealing, which raises the temperature for the entire architecture from the substrate up to the top surface, the irradiation of a localized CW laser with high energy density leads to the thermal annealing effect in a confined area. The laser enables coupling with the thin film material without interaction to an optically transparent substrate. Figure 15 shows the laser coupling with the amorphous material, resulting in a hexagonal layered structure.

![Graphical representation of amorphous film conversion to crystalline](image)

Figure 15: Graphical representation of amorphous film conversion to crystalline
4.2.1 Apparatus

The laser processing apparatus featured an optical setup along with a high-resolution Newport stage in which experimental substrates were placed during laser exposure. The optical setup consisted of an air table to dampen vibrations from the environment, with a laser and series of optics for reproducible results. The high-resolution stage moved in relative motion to the stationary laser. The laser, projected parallel to the table as well as mounted to the table for stability was elevated through two 45° mirrors. The elevated beam accommodated the design for reflecting the beam downward with a 45° mirror through an objective to provide a horizontal workpiece for experiments.

The samples subjected to processing were mounted to the high-resolution stage by a glass slide. The super hydrophobic nature of PDMS anchored the sample to the stage to maximize spatial resolution. The stage, controlled by the computer enabled spatial resolution of 1µm with velocity control between 1µm/s and 5mm/s. The laser for processing has a Gaussian TEM$_{00}$ (low order mode) profile, which allows the laser to be focused to its theoretical minimum beam radius.

![Figure 16: Laser processing schematic](image-url)
4.3 Substrate Selection and Preparation

For all depositions except for the samples subjected to TEM top views, the TMDs were deposited onto polydimethylsiloxane (PDMS). Structurally, PDMS is comprised of an inorganic siloxane backbone with side methyl groups. The use of PDMS for a stretchable substrate was due to the low modulus of elasticity, highly transparent properties, and ease of synthesis. The PDMS substrates were prepared from a Sylgard 184 kit following the procedure below:

6. Hardener mixed into prepolymer in 1:10 ratio (5 minutes)
7. Cast onto clean silicon wafer
8. Pulled under vacuum (~10⁻³ Torr)
9. Cured at 80 °C (60 minutes)
10. Peeled off from silicon wafer
11. Cut into smaller pieces (~2 x 2 cm)

The surface of PDMS that was cast onto the silicon was the surface that was used for all subsequent depositions. The substrates were individually mounted to a 1” silicon wafer.

The substrates were then placed in the load-lock shown in Figure 17. An example of PDMS substrate roughness after curing is seen in Figure 17.

For the studies investigating the top-view structure by TEM, the TMD was deposited onto a copper TEM grid with a thin membrane of carbon.
4.4 Surface Analysis

Surface analysis was performed before and after laser processing experiments to determine critical information regarding surface structuring, chemical composition, and crystal structure.

4.4.1 Raman Microscopy

Renishaw inVia Raman Microscope was equipped with a Modulaser Argon laser with a wavelength of 514.5 nm and a maximum power output of 50 mW. The Raman microscope had a Prior Scientific Proscan II programmable motorized stage. All exposures were performed with a 50x objective in the Raman microscope. The incident laser intensity for Raman analysis was less than 10% of the minimum threshold power for TMD structure transformation. There was no evidence of TMD annealing at these powers.
even after more than an hour of exposure. The vibrational wavenumbers correspond to the induced shift of the inelastically scattered photons with respect to the laser excitation.

4.4.2 X-Ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) analysis was performed with a Kratos Ultra DLD spectrometer using monochromatic Al Ka radiation (1486.6 eV) operated at 1.3 \cdot 10^{-7} \text{ Pa} \ (1 \cdot 10^{-9} \text{ Torr}) base pressure. The obtained spectra were analyzed with commercially available CasaXPS software with individual peaks fitted with a Gaussian-Lorentzian function and a Shirley background subtraction. The XPS analysis typically only penetrates several nanometers into the film itself, and so this technique was very advantageous for studies of laser annealed films.

4.4.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) imaging was vital to structure studies in order to visually inspect the material. A FEI Nova focused ion beam (FIB) microscope associated with an Omniprobe manipulator was employed to prepare lift-out TEM specimens for obtaining the cross-sectional microstructure of the film. TEM was operated using 5 keV electron beams and 30 keV Ga+ ion beams. High-resolution microstructure and chemistries of the films were measured using a FEI Talos scanning/transmission electron microscope (S/TEM), equipped with an X-ray energy dispersive spectrometer (EDS) for elemental mapping and a high-angle annular dark-field (HAADF) detector for Z-contrast imaging.
4.4.4 Conductive Atomic Force Microscopy

Conductive-AFM IV curve measurements were obtained with an Asylum MFP-3D. A silicon nitride nanometer tip is mounted to a cantilever that is brought into contact with the surface of the material with a fixed voltage and scanned across a several micron area to distinguish both non-processed and laser processed features. A laser is directed toward the cantilever and reflected toward a photodiode to measure the displacement. During the IV curve, a bias of 1V was applied from the tip to the material surface in a fixed location. The sample was grounded to create a closed circuit.
CHAPTER V

RESULTS AND DISCUSSION

5.1 Laser Processing Results

5.1.1 MoS$_2$ Results

MoS$_2$ samples were prepared using magnetron sputtering techniques as discussed previously in Section 4.1 followed by laser annealing as discussed in Section 4.2. Raman analysis followed the sputtering deposition and determined that the film growth yielded no hexagonal crystal structure to the material. The Raman spectrum in Figure 18(a) shows neither the E$_{2g}^1$ peak at 383 cm$^{-1}$ associated with the in-plane stretching$^{38}$ nor the A$_{1g}$ peak at 407 cm$^{-1}$ for out-of-plane stretching. This confirms that the initial room-temperature deposition was amorphous in structure due to the absence of phonon vibrations. Figure 18(b) presents an optical microscopy image of a sample that has crystalline MoS$_2$ lines running parallel to one another by moving the sample in this configuration to the laser. Figure 18(c) relates the Raman map of the intensity of the A$_{1g}$ peak of the sample shown in Figure 18(b). The lighter color pixels relate to an increased A$_{1g}$ intensity relative to the black pixels.
Figure 18: (a) Raman spectrum of sample (b) optical image of lines annealed into material (c) Raman map of area

Figure 19(a) presents Raman spectra of amorphous sputtered MoS$_2$ samples exposed to the same radiant fluence (50 mJ in a 1.5 mm diameter spot) but with different combinations of laser irradiance and exposure times. Figure 19(b) is a plot of the $A_{1g}$ peak intensity versus the laser power for the fluence equivalent exposures plotted in Figure 19(a). A fluence dependent photo-chemical process would result in the exact same structural change at different irradiance levels and interaction time combinations that are fluence equivalent, and thus a horizontal line in Figure 19(b) would be expected for such. This is expected because a monochromatic laser uses one wavelength, corresponding to a defined quantum of energy (see Section 2.3.1) independent of the irradiance and exposure
time. The rate of the chemical reaction would depend on the absorbed energy with respect to exposure time. The absorbed energy is equivalent for the variations in irradiance and time; which would result in the same degree of recrystallization for the variations under a photochemical reaction.

Figure 19(c) presents Raman spectra from spots exposed to different laser irradiance. The threshold laser irradiance as indicated by Figure 19(c) is 3.5 mW over a 1.5 µm diameter spot size, or a threshold irradiance of 2 mW/mm². Figure 19 promotes that the laser annealing mechanisms of hexagonal structure formation in MoS₂ is not a fluence dependent process, but instead is highly dependent on the irradiance. The amorphous sample appears undisturbed at or below an irradiance of 1.7 mW/mm² over a 1 second exposure, whereas when the irradiance is too high, e.g. above 20 mW/mm², the films become damaged. At these higher radiation power densities there is enough photothermal energy coupled to the surface to cause localized ablation and damage to both the amorphous Mo-S film and the underlying PDMS.

Figure 19: (a) Raman spectra of regions with varying laser powers and the corresponding exposures times. (b) Raman intensity from the A₁g peak for the various exposures shown in (a). (c) Raman spectra from different exposure intensities for 1 second
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$_2$ films with and without laser treatment are presented in Figure 20. The S 2s photoelectron peak is observed at 226.4 eV, which is typical for MoS$_2$. The Mo 3d region consists of three distinct sets of doublet peaks (Mo 3d5/2 and Mo 3d3/2). The doublet component with Mo 3d5/2 at 229.3 eV (FWHM = 1.3 eV) indicates the presence of amorphous MoS$_2$, while Mo-Mo bonding and the $IT$ (octahedral) phase of MoS$_2$ is characterized by a doublet with Mo 3d5/2 at 228.5 eV (FWHM = 0.8 eV).$^{39,40}$ Oxidized MoS$_2$ and other Mo(6+) species (e.g., MoO$_3$) exhibit a doublet at higher binding energy, with Mo 3d5/2 and Mo 3d3/2 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 $IT$ MoS$_2$, and the Mo(6+) concentration is relatively low. Following laser annealing, the Mo(6+) component peak becomes more prominent, suggesting oxidation of the MoS$_2$ film. Oxidation has been reported as common$^{41}$ at the surface of MoS$_2$ when in an environment above 85°C. Furthermore, whereas the majority of the MoS$_2$ appears to exist in the $IT$ phase in the as-deposited film, the Mo 3d5/2 peak at 229.3 eV becomes narrower (FWHM = 1.0) and more intense relative to the $IT$-MoS$_2$ Mo 3d5/2 peak at 228.5 eV, following annealing. This suggests that both the $IT$-MoS$_2$ and the amorphous MoS$_2$ undergo crystallization to the thermodynamically stable $2H$ phase following laser annealing. Referring back to Raman spectrum of the precursor film in Figure 10(a) there is a small residual band near 408 cm$^{-1}$ and no band in the 380 cm$^{-1}$ region, which indicates a small presence of $IT$-MoS$_2$.$^{42}$
The topography of the as deposited and laser annealed is shown in Figure 21(a),(b) respectively. The coefficient of linear thermal expansion (CTE, $\alpha$) of PDMS is $\sim$ 50 times greater than MoS$_2$ or WS$_2$ ($\alpha_{\text{PDMS}} = 325 \times 10^{-6} /{^\circ}\text{C}$; $\alpha_{\text{MoS}_2, \text{WS}_2} = 6.5 \times 10^{-6} /{^\circ}\text{C}$). The strong adhesion at the PDMS-TMD interface confines PDMS from lateral thermal expansion. The PDMS likely undergoes directional expansion in the laser zone and contracts back while cooling (depicted in Figure 21(c)), consequently setting up a single cycle of oscillatory shear in the thin film TMD.
The top view of the atomic arrangement of the material is shown in TEM micrographs in Figure 22. Figure 22(a) is a micrograph of the non-annealed region and as expected shows no order in the material; the non-annealed area appears visually to have an amorphous structure. Figure 22(b) shows the site of an annealed area from the laser. The S-Mo-S atoms have formed a long-range order.
TEM micrographs of the cross-section of a film synthesized for 20 seconds followed by laser processing are shown in Figure 23. Figure 23(a) is the energy dispersive x-ray analysis (EDX) of the sample, it shows the transition metal and chalcogenide elements clearly stacked as a thin film on the substrate interface without interaction or fusion with the bulk substrate. The clear transition between substrate and thin film supports the process being similar to surface laser heat treatment without melting. The thickness of the material is approximately 10 nm; with a 20 second magnetron sputtered sample denotes a deposition rate of 0.5 nm/s. The layer stacks are apparent in Figure 23(b), with approximately 6.5 Å spacing between Van Der Waal layers, in agreement with accepted basal plane spacing. Additional TEM micrographs can be found in the Appendix. The TEM micrograph shows stacking faults within the layers of material, a likely correlation to the substrate and material mismatch in thermal expansion coefficients, which induces compressive strain to the material after processing.

Figure 23: Cross sectional TEM (a) electron energy loss spectroscopy for elemental analysis (b) high magnification that displays layered structure
To probe the electrical properties, multiple localized IV-curves were acquired from regions with and without laser annealing by CAFM. Figure 24 indicates the laser treatment converted the MoS$_2$ film from insulating to semi-conductive. Unlike crystalline 1T-MoS$_2$, the macroscopic properties of the film are insulating despite the presence of minute 1T-MoS$_2$ phase (as indicated from XPS). The lack of an ordered lattice of the amorphous structure contains unfulfilled (“dangling”) bonds that create trap states for electrons and causes scattering that inhibits free electron migration.\textsuperscript{46}

![Image of I-V curve](image.png)

**Figure 24: I-V curve of sample produced by C-AFM**

The semi-conductive property of the processed MoS$_2$ was further investigated. A large area (> 2mm x 2mm) was processed on the sample by rastering the beam. This sample was further processed with silver conductive contacts, which were probed by a Kiethley 4200 for resistance measurements. The sample was placed in an oven to control the ambient temperature during measurements. The temperature was controlled from 30°C to 110 °C while resistance was measured in intervals of 5 °C. Three measurements were taken at each interval to understand error associated with the experiment. Figure 16
shows the material’s inverse trend of resistance with rise in temperature. This relationship solidifies semiconducting behavior from the processed material.

\[ V = IR \]

The flow of current through the material is the movement of electrons from one atom to the next under an applied electric field. The electrons are very small negatively charged particles that flow toward the positive terminal. If semiconducting, the electrons are tightly bound to the atoms, with the outer most electrons in the valence band; a discrete amount of energy is required to promote these electrons across the bandgap into the conduction band to freely migrate throughout the material. As the energy (temperature) is increased, the amount of electrons are increased into the conduction band; hence a reduction in the material’s resistance. A metal, however, has a large “sea” of electrons free to flow about the material. As the energy is increased and the atoms vibrations increase the collisions between electrons also increase.

Figure 25: Resistance of annealed area with respect to temperature
5.1.2 WS\textsubscript{2} Results

WS\textsubscript{2} samples were made using magnetron sputtering techniques as discussed previously in Section 4.1 followed by laser processing as discussed in Section 4.2. Raman analysis was performed post deposition and confirmed that the film yielded no crystal structure to the material. The Raman spectra seen in Figure 26(a) before laser exposure is similar to the MoS\textsubscript{2} spectrum in Figure 18(a), no E\textsubscript{2g} or A\textsubscript{1g} modes are present to reassure an amorphous structure. The peak 490cm\textsuperscript{-1} is present from the Si-O-Si stretching\textsuperscript{47} within the PDMS substrate. After laser irradiance, the E\textsubscript{2g} and A\textsubscript{1g} phonon modes become apparent. The intensity ratio I\textsubscript{E2g} / I\textsubscript{A1g} is greater than 1, this correlates to just a few layers\textsuperscript{48} of S-W-S bonding. The weak A\textsubscript{1g} peak intensity, with less energy dissipated out-of-plane, correlates to few layers of material. A few layers in thickness, the A\textsubscript{1g} peak position of the film will display softening compared to bulk material. The softening corresponds to less interlayer contributions to phonon restoring forces perpendicular to the basal plane. However, the spectrum bands show slight asymmetry, this correlates to defects or grain boundaries present in the probed region.

Raman mapping of the laser rastering as seen in Figure 26(b) was conducted. The map was taken over a 40 µm × 40 µm area with 0.7 µm steps. The colors of the map in Figure 26(c) correlate to the intensity of the E\textsubscript{2g} for depiction of in-plane phonons relative to location of laser irradiance. The black pixels relate to the lowest intensity while the white pixels have the most intense phonon mode. The map shows crystallinity conversion has uniformity along the laser-processed area. The most intense region is in the center of the processed direction of the laser. This region is dominant due to the Gaussian laser beam profile.
Figure 26: (a) Raman spectrum of WS$_2$ (b) optical image of lines annealed into material (c) Raman map of $E_{2g}$ vibration mode

UV-VIS experimentation can be seen in Figure 27 and shows the optical absorption through the visible wavelength range. Initially, the material displays nearly 40% more absorption at shorter wavelengths near UV compared to the longer visible region toward near infrared. The shorter visible wavelengths, violet region through green shows an increase in absorption after laser exposure of approximately 12.5% while longer wavelengths from green to red show a 6% increase. The increase in absorption at shorter wavelengths may also be related to a scattering phenomenon. The shorter wavelengths of light are more prone to being redirected from atoms of the material.
The response a material has to the application of heat is its thermal properties. The principal mode for thermal absorption is linked to the increase in vibrational energy of atoms. As atoms in a solid vibrate; neighboring atoms become involved to create traveling lattice waves. This is simply an elastic wave that has short wavelengths with high frequencies and move at the speed of sound. These vibrations occur at quantized values according to the material and a single quantum of this vibrational energy is a phonon.

TEM characterization was performed on the samples to determine any crystallographic changes that occurred during the exposure to light. This specific sample was conducted on a copper TEM grid that had a thin layer of carbon to suspend the thin film WS$_2$. The structure can be seen in Figure 28 with nano-crystalline grain formations. These grains were observed in different areas of the sample and tend to have high-angle grain boundaries. The thin film has very high surface area to volume ratio; this leads to

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**Figure 27: UV-VIS of WS$_2$**

![UV-VIS of WS$_2$](image)
dissipation by convection to atmosphere and conduction in-plane of the TMD rapidly from the localized area. Dislocations were most likely the result of thermal stresses from rapid cooling.

Figure 28: (a) TEM top view of WS\textsubscript{2} processed area (b) high resolution amorphous region (c) high resolution crystalline area

In addition to TEM, the sample was characterized using XPS for chemical composition. Survey spectra indicate that the dominant species present were tungsten and sulfur. High-energy resolution scans were then implemented for the W 4f region to provide detailed investigations of the chemical states. The analysis determined that the material absorbed oxygen during processing. This is seen in Figure 29, a higher energy shoulder is formed representing more WO\textsubscript{3} species. This oxygen contribution is most likely accountable at the grain boundary sites. These sites are not satisfied by the
maximum amount of bonds possible and become more chemically reactive than the actual grains on account of higher surface energy. To reduce this energy, materials tend to minimize, if at all possible, the total surface area with bonding.\textsuperscript{24}

![W 4f Region](image)

**Figure 29:** High-energy resolution XPS of annealed area laid on top of non-annealed area

Once the material is exposed to laser irradiance, a significant change in electrical performance is observed. These properties were probed in multiple localized areas with C-AFM. Figure 30(a) shows the morphology associated with the material surface. The height of the material is dramatically increased from the laser processing when compared to the as deposited film. The polymer and WS\textsubscript{2} contain a mismatch in CTE, however, the athermal-processing environment subdues crack formation in the film. The non-annealed area shows wrinkling of the thin film. There is a depression in the regions that were
directly exposed to the laser. The samples were biased with 1V by an AFM tip in regions with and without laser exposure. Conductive channels of 1µm widths as seen in Figure 30(b) become dominant in electrical conductance maps. This morphology decompression width is larger than the electrical width; this is due to the heat-affected zone from the laser.

Figure 30(a) shows a clear distinction of topography of the sample rastered by the laser. At first glance, humps in the processed film are seen running perpendicular to the direction of laser scan down the length of the annealed line. This is likely a result of the small beam diameter relative to the material, crystallizing material, resulting in decompression from the ordered material compared to the amorphous and driving material through the narrow channel. Looking closer at Figure 30(a), underneath the humps in the film of the laser-exposed area is a narrow region of film depression along the annealed channel.

Figure 30: (a) morphology of processed sample with the (b) electrical conductivity of the processed sample
5.1.3 Heterostructure Results

The deposition system allows for multiple magnetron targets to be present in the system at one time, this feature allows for alternating stacks thin ultra thin film material before breaking vacuum. Figure 31 (a) shows the Raman spectra of alternate stacks of both MoS$_2$ and WS$_2$ subsequent to laser annealing. The E$_{2g}$ and A$_{1g}$ phonon modes for both materials are apparent; this implies that sulfur has formed layered stacks to both molybdenum and tungsten. Figure 31 (b) is the Raman spectrum of MoS$_2$ phonon modes with a thin layer of insulating amorphous boron nitride on the top interface. The MoS$_2$ was laser processed through the thin boron nitride layer.

Figure 31: Raman analysis of laser annealed heterostructures (a) alternating layers MoS$_2$ – WS$_2$ (b) MoS$_2$ passivated by boron nitride

Figure 32(a) shows an optical image of a device architecture built. Starting from the bottom-up; bulk PDMS substrate, thin film of MoS$_2$, boron nitride islands and silver nano-particle contacts. The extremely large band gap of boron nitride results in very little
optical absorption. This allows for laser processing to be conducted through the material to the MoS$_2$ surface. The sample was rastered across the laser before the silver nanoparticles were deposited by aerosol printing. Figure 32(b) is a STEM image of the nanoparticle and boron nitride interface, which show the particles impinging into the material. Figure 32(c) shows the electrical results of the thin film device. A potential applied across the source and drain; as a bias was swept through the top gate. The graph shows mirroring of the drain and gate current, depicting leakage from the gate to the drain.

![Figure 32: (a) Optical image of device architecture (b) STEM image of nanoparticle on dielectric (c) electrical characterization of device architecture](image)

Figure 32: (a) Optical image of device architecture (b) STEM image of nanoparticle on dielectric (c) electrical characterization of device architecture
CHAPTER VI

CONCLUSIONS

In summary, a study was completed to develop a method of preparing ultra-thin (<10 nm) films on large area flexible polymer substrates through laser annealing of PVD films grown at room temperature. The composition and crystalline nature of the laser annealed MoS$_2$ and WS$_2$ films were confirmed with Raman spectroscopy, XPS and both plan-view and cross-sectional TEM. The electrical properties of the TMD annealed regions were characterized with C-AFM and variable temperature conductivity measurements, which confirm their semiconducting behavior, while surrounding amorphous film remains an insulator.

Extensive laser processing studies have been conducted to engineer changes in the physical structure of TMDs and develop theories on fundamental mechanisms behind them. Firstly, the laser induced phase transformation is not directly dependent on the radiant fluence, but instead is highly dependent on the laser irradiance. These results refute a photo-electronic process, but support a photo-thermal process. 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 405nm, 440nm, 660 nm, 785 nm, and 830 nm. The absorption spectrum of the precursor film shows an absorption peak in the UV with a long tail into the NIR. When
exposing the precursor films to other wavelengths we observed that a larger irradiance was needed to convert the precursor films at longer wavelengths, a trend also supporting a photo-thermal mechanism because the absorption of the precursor film decreases with increasing wavelength.

Laser annealing of amorphous films on polymer substrates is a simple and scalable approach to patterning complex patterns of semiconducting MoS$_2$ film in an insulating matrix or generating large areas of semiconducting material for fabrication of 2D based flexible/stretchable electronics.
CHAPTER VII

FUTURE WORK

Results on thin film MoS$_2$ and WS$_2$ substrates reveal both physical and chemical changes to the material. Laser processing the amorphous structured material transformed it to a hexagonal structure. Chemically, oxygen was introduced into the material structure. The oxygen was introduced to the system by oxidation of the material from the highly localized temperatures of the film.

Although this study contained a detailed investigation of the phase change of TMDs during laser processing, important questions about the photon-phonon interaction remain. The next steps in the characterization would be processing the samples while under vacuum; such a process would negate oxygen in the thin film from ambient atmosphere.

Additionally, incorporation of the MoS$_2$ and WS$_2$ channels into TFT devices will require detailed interface studies of the dielectric and channel, more in depth characterization of the TMD and detailed contact studies. In this study the growth kinetics of the dielectric on the amorphous TMD were not understood, resulting in an unknown thickness.
REFERENCES


49. 6.777J/2.751J Material Properties Database.
APPENDIX

SUPPLEMENTAL SUBSTRATE PROPERTIES

Table 1: Substrate properties\textsuperscript{49}

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<td>Dielectric strength</td>
<td>120-160 kv/cm</td>
</tr>
</tbody>
</table>

Figure 33: UV-VIS absorption of pristine PDMS substrate
Figure 34: Raman shift of Pristine PDMS substrate

Table 2: Laser calibration

| 405 nm Laser |  
|:-------------:|:-------------:|
| Input Current (mA) | Output Power (mW) |
| 60 | 16 |
| 80 | 27 |
| 100 | 50 |
| 120 | 55 |
| 140 | 65 |
| 150 | 67 |

Figure 35: (a) 3 x 5 mm macroscopic view of laser annealed area (b) Optical image of annealed pattern