PULSED LASER DEPOSITION OF NIOBIUM DISELENIDE

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PULSED LASER DEPOSITION OF NIOBIUM DISELENIDE

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ABSTRACT

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Niobium diselenide has potential for use as a solid lubricant in high temperature and space environments. It also has a low resistivity which permits its use in specialty applications where a conductive lubricant is necessary.

To achieve the optimal properties of low friction coefficient, high conductivity and oxidation resistance, the Se/Nb ratio and crystallinity must be carefully controlled. Pulsed Laser Deposition (PLD) permits the required degree of control, even over films with complex stoichiometries. In this study, a designed experimental approach was chosen to look at the process limits of pulsed laser deposition for niobium diselenide. This study has shown that film chemistry could be changed from substoichiometric to superstoichiometric and crystallinity varied between amorphous and crystalline by appropriate choice of PLD parameters. The experimental configuration for PLD, the data acquisition system and the resulting film property correlations will be described.
ACKNOWLEDGMENTS

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Finally, I would like to thank those closest to me: my wife, Barbara, without whose many hours of tireless dedication and support I would not have completed this thesis; my daughter, Chrystianna, for providing the reality in my life, my parents for giving me a strong foundation; and most importantly, God, for making everything possible.
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CHAPTER 1
INTRODUCTION

The research contained in this thesis deals with the pulsed laser deposition of niobium diselenide (NbSe$_2$). The experiments were designed using a statistical approach to allow the maximum amount of information to be gained from the minimum number of experiments. This first section provides the introduction and literature review as it pertains to solid lubrication. The next section will address the background and pertinence of pulsed laser deposition (PLD) based primarily on previous work with MoS$_2$ [1-5]. The introduction will clarify the following: why a study of solid lubricants, in particular NbSe$_2$, is relevant, why PLD was chosen to deposit these materials, and finally why a statistical design of experiments approach was used to set up the deposition runs and the analysis.

Solid Lubricants

When one thinks of lubricants, the tendency is to think of oils and greases, liquid lubricants. However, another whole class of lubricating compounds, solid lubricants, exists and is of great importance. According to Buckley and Johnson, "a solid lubricant is any solid which, when interposed between two
surfaces that are in contact, will reduce adhesion, friction, and wear between those surfaces" [6]. Hard fats such as tallow and lard, were probably the first solid lubricants because of their availability since the beginning of recorded history [6].

In all likelihood the next solid lubricants to come into use were graphite and/or molybdenum disulfide since they both occur naturally and can be mined. Some of the first major uses of graphite and molybdenum disulfide were for the lubrication of the wheels of wagons; these solid materials worked better than the fluid lubricants since fluids could not be retained between the axle and wheel journal [7]. As time went on more and more uses were found for these slippery black substances, but consequently people also began to wonder what caused these materials to be so slick. Because of the many questions that needed to be answered about these solid materials, a great research effort has been building in this area.

Before 1947, there were only about ten references in the literature concerning solids used as lubricants [8]. From 1947 to the early 1970's, the number increased to over 500 [6]. Today the effort to understand and produce better solid lubricants continues on with several thousand references in the literature. The market for solid lubricants extends throughout the civilian and military sectors. The aerospace industry is one area in which some of the most extreme environments are experienced (ie. vacuum, cryogenic, high temperature, oxidative, etc.). On account of this, there are extensive solid lubricant programs
located at many manufacturers of aircraft engines and space systems.

The U.S. Air Force has been directing a large effort towards improving the performance of its aircraft, driven by an eventual goal of increasing the thrust to weight ratio to twice its current capability. To accomplish this task, either the thrust of the engines has to be increased or the weight of the aircraft needs to be decreased. The use of solid lubricants can have an effect in both of these areas.

Increasing engine operating temperature permits an increase in thrust. To date, the most serious impediments to achieving this goal are the lack of structural materials and lubricants that can withstand the extremely high temperatures. The current short-term goal is for a liquid lubricant to achieve operating temperatures of 350°C. The present long-term goal is to find a lubricant that can withstand temperatures well above 350°C, therefore way beyond the capabilities of current state of the art liquid lubricants. Solid lubricants, on the other hand, have the unique ability to operate in the temperature range from cryogenic temperatures to well over 1000°C. However, since no single material can span this entire range, research is being directed towards the combination of solid materials to utilize the optimal properties of each.

Besides lubricating moving parts, liquid lubricants provide a cooling function to the turbine engine. The extensive distribution and cooling system required by liquid lubricants adds a substantial amount of weight to the engine. The use of solid lubricants could reduce the need for these types of systems and, thereby, effect a large decrease in weight for the aircraft.
Another area where solid lubricants have a major impact is in the lubrication of bearings for use in high vacuum environments including space. Materials chosen for use in these environments must not outgas and cause contamination of UHV systems or spacecraft. In a space environment there can be substantial temperature and radiation fluctuations that can turn a liquid lubricant into an ineffective glue-like substance [9]. Solid lubricants offer significant advantages under these conditions. Solid lubricants are available which undergo negligible outgassing, are not significantly affected by radiation and remain stable even at temperatures above 1200°C [10] in vacuum or inert atmospheres. There are many types of solid lubricants to choose from each having different characteristics. The following section will provide a brief discussion of the different types of solid lubricants.

Types of Solid Lubricants

It is convenient to divide the tribological coatings into two main groups based on their chemical, physical and mechanical properties: (1) the hard wear-resistant coatings (carbides, nitrides, silicides, etc.) and (2) the soft lubricating coatings with characteristic low shear strength (graphite, MoS$_2$, CaF$_2$, PbO, Au, etc.)[11].

The hard wear-resistant coatings are mainly used to protect surfaces from abrasive, corrosive and erosive wear. The hard coatings have found extensive use in highly loaded and/or high-temperature (> 1000°C) applications to reduce
wear due to their ability to keep their tribological properties under these extreme conditions. Although hard coatings are effective in reducing wear, they may not exhibit low friction coefficients [10].

The soft lubricating coatings, on the other hand, can reduce wear and reduce the friction generated between two materials in contact. Their main drawback being that they do not have as high a temperature capability as the hard coatings. There are two main types of lubrious soft coatings. They are the layered coatings (graphite, MoS$_2$, NbSe$_2$ etc.) and the nonlayered coatings (CaF$_2$, PbO, gold etc.).

Graphite, a layered lubricant, consists of hexagonal layers of covalently bonded carbon atoms that are stacked up parallel to each other. The interlayer bonding is weak compared to these covalent C-C bonds which results in its having highly anisotropic properties. A graphite crystal tested parallel to the planes will be soft, but tested perpendicular to the planes, the crystal will be almost as hard as diamond [10]. The lubricating mechanism of graphite is due to its layered structure and its ability to form strong chemical bonds with gases such as water vapor [10]. The adsorption of water vapor and other gases onto the crystalline edges causes the interlayer shear strength to decrease, thus permitting the planes to slide over each other easily and provide lubrication.

Another group of layered lubricants is the layered transition metal dichalcogenide (LTMD) compounds. MoS$_2$ is the most common example of an LTMD. MoS$_2$ is similar to graphite in that it has a layered hexagonal crystal
structure. However, it differs since the LTMD compounds form tri-layer stacks with the transition metal (i.e. Mo, W, Nb, Ta) atom layer sandwiched between two chalcogen atom (i.e. S, Se, Te) layers. The bonding between the transition metal atoms and the chalcogen atoms is strongly covalent while the bonding between the tri-layer stacks is comprised of weak van der Waals forces, thus providing an easy slip plane. Since the easy slip plane is inherent in the structure of the LTMD compounds, there is no need for adsorption of gases. This factor allows these materials to be effective in vacuum environments. The useful upper temperature limits for the layered materials is between 300 to 400°C for the reason that at temperatures above 400°C they begin to oxidize significantly.

The nonlayered solid lubricants such as gold, CaF₂ or PbO can be used at much higher temperatures. These materials have relatively low shear strengths and in the case of CaF₂ and PbO, exhibit flow characteristics above their softening point. Thus, they can provide effective solid lubrication at high temperatures (>700°C) in air [12]. Soft metals such as gold and silver are also effective high temperature lubricants and have been used in space capsules, high-performance jet engines, and high-speed machines operating under low load conditions [10].

No single type of material can perform adequately in all applications; therefore, combinations of these different types of lubricants are probably necessary to achieve the type of lubrication desired. For example, a hard coating combined with an LTMD compound, such as MoS₂, has both the capability of
reducing wear under extreme loading conditions and reducing the friction coefficient. Other combinations can be formulated to take advantage of the best characteristics of each type of lubricant.

Zabinski et. al. have developed a concept called the “adaptive” lubricant [13] in which pulsed laser deposition is used to grow composite films of different combinations of solid lubricants. The central idea of the adaptive lubricant concept is that the lubricant adapts to changing environmental conditions through designed chemical reactions to produce lubrication over a large temperature range. Zabinski et. al. produced results showing that this effect occurs when MoS$_2$ and PbO are combined: MoS$_2$ provides the lubrication at room temperature, then when the films are exposed to oxidizing environments at elevated temperatures, they adapt by forming PbMoO$_4$, a high temperature lubricant.

In addition to the “adaptive” lubricant concept, Zabinski et. al. showed a synergistic effect in using these two compounds. Their results showed a ten fold increase in wear life over a similarly tested, pure MoS$_2$ or PbO film at room temperature. This type of synergistic effect of combining two lubricants with different characteristics which results in large increases in the tribological properties has also been demonstrated by Jamison, whose work has formed some of the basis for the work described in this thesis.

Jamison [14-17] carried out an extensive characterization of the Group IV, V, and VI transition metal dichalcogenides. Through his study he determined
that the Group V materials were inherently tailorable since their coordination and structure were easily adjusted [14]. The following section contains a detailed discussion of the structure and properties of the Group IV, V, and VI transition metal dichalcogenides. The section will attempt to explain why some LTMD's are inherently good lubricants and others are not, and why some of these compounds are considered to be more tailorable than others.

Structure of the LTMD Compounds

The LTMD compounds, as mentioned previously, form tri-layered stacks. An illustration of the predominant configuration is shown in Figure 1, part (a). This stacking sequence produces the densest packing because the chalcogen atoms above settle into the pocket formed by three chalcogens in the lower layer. The metal atoms do not line up from one tri-layer to another. This is characteristic of the trigonal prismatic (TP) compounds such as MoS$_2$. Figure 1, part (b) illustrates an expanded van der Waal's gap. One would expect that the wider this van der Waal's gap, the lower the friction coefficient would be due to the shear planes being more separated resulting in less attraction between them. However, Jamison and Cosgrove showed that this is not totally correct [14]. While lubrication performance is related to gap distance, it is more dependent on the coordination of the atoms and the resulting crystal structure. Brixner [18] and Selte et. al. [19] did some of the pioneering structural characterization of these LTMD compounds. They determined that there are
Figure 1. Typical stacking sequences for the X-M-X layers of LTMD's. Part (a) shows the stacked layers settled together and part (b) shows an expanded van der Waals gap [14].
basically two types of structures associated with Groups IV-VI: the trigonal prismatic and the trigonal anti-prismatic (TAP).

An illustration, from Jamison's work, of the difference between these two structures is shown in Figure 2 [14]. The TP structure has the six chalcogen atoms directly over each other forming a regular trigonal prism, whereas in the TAP structure, the six chalcogens are directly opposite each other through the metal atom in the center. Jamison explained the differences in these two structures by showing the differences between their electronic structures. The main difference lies in the d orbitals as is illustrated in Figure 3. These are either empty (Group IV compounds), half-filled (Group V compounds) or completely filled (Group VI compounds). Based on these differences, there is either no effect, an attraction across the gap, or a repulsion across the gap.

In the case of MoS$_2$, a TP Group VI compound, the d orbitals are filled (represented by d$^2$), meaning that the two electrons are spin-paired and protrude through the hole between three chalcogen atoms [14, 16]. Because the orbitals are filled, there is no attraction across the gap. In fact, there will actually be a repulsion of the electrons on metal atoms in adjacent layers [14]. This is the reason that the Group VI metals, Mo and W, form TP structures and adopt the characteristic “MoS$_2$” type structure in which the metal atoms are not aligned vertically because of repulsion from the filled d$^2$ orbitals.

The Group V LTMD compounds have half filled d orbitals, d$^1$[14]. The result of this is that the electrons are delocalized, and therefore, electronically
Figure 2. Trigonal prismatic (TP) coordination compared to Trigonal antiprismatic (TAP) coordination. Part (a) shows a metal atom (shaded) surrounded by six chalcogen atoms in TP structure and part (b) shows the same atoms arranged in TAP structure [16].
Figure 3. The electronic structure of MoS$_2$ vs. NbSe$_2$. Part (a) shows the filled d$^2$ orbitals for MoS$_2$ and part (b) shows the half-filled d$^1$ orbitals for the NbSe$_2$. 
unsatisfied. The electrons from one metal atom will be attracted to an adjacent metal atom across the gap. This in turn causes the metal atoms to align from one tri-layer to another and also causes the interlayer separation to decrease, thus forming the typical "NbS$_2$" TAP structure (see Figure 4) [16].

The Group IV compounds form the TAP structure exclusively even though their d orbitals are completely empty, d$^0$. Huisman, et. al. used molecular orbital calculations to explain Group IV's behavior. In their model, the transition metals with a d$^0$ configuration have only their non-bonding energy levels filled. Since there are no d electrons for covalent bonding, the contribution from strong electrostatic interactions favors the octahedral (TAP) coordination [20]. The consequences of this electronic configuration are that the Group IV materials have low interlayer spacing and form very poor lubricants [16].

From the previous discussion it is clear that the electronic structure of the LTMD compounds directly affects their crystal structure. Jamison showed that the tribological properties could be substantially changed by altering the crystal structure. The next section contains a general discussion of the physical and mechanical properties of the Group IV-VI LTMD compounds, focussing primarily on the NbSe$_2$ compound, the main subject of this research.

Properties of the LTMD Compounds

Magie completed an extensive review of the physical and mechanical properties of the Groups IV-VI LTMD compounds [21]. Some of the results of
Figure 4. The NbS$_2$ structure showing the location of metal atoms in one X-M-X layer over metal atoms in adjacent layers [14].
this study are shown in Table 1. Magie presented results from Bowen [22] showing that the transition metal sulfides (such as MoS$_2$ and WS$_2$) tended to outgas more readily in vacuum at elevated temperatures than did the selenides (WSe$_2$ and NbSe$_2$) (see Figure 5). Magie also completed his own qualitative inspections of WSe$_2$ and NbSe$_2$ in ultra high vacuum environments, between 25°C and 500°C which resulted in very little outgassing [21].

A comparison of the friction coefficients, vacuum stability and stability in air from Table 1 illustrates that the sulfides and selenides of Nb, W and Ta compare very favorably to MoS$_2$. Further, among these compounds the Nb based compounds have the lowest resistivity by an order of magnitude. Jamison's work on these compounds, some of which has been previously discussed, can explain some of the differences in the tribological properties.

According to Jamison's work, the MoS$_2$ structure (TP) is the optimal electronic structure for achieving good tribological performance, i.e. low friction coefficients and long wear lives [14, 16, 17]. As discussed earlier, the TP structure is formed because of the repulsion of the filled d$_2^2$ orbitals. Jamison showed that because of this repulsion, the Group VI compounds have the largest interlayer spacing. The Group IV compounds, d$^0$, have the smallest spacing and the Group V, d$^1$, compounds are intermediate.

Jamison studied the effects of changing this interlayer spacing by intercalation with the coinage metals (Cu, Ag, Au). He found that by adding these metals to the crystalline lattice of the Group V compounds, such as NbS$_2$
Table 1. -- Properties of Heavy Metal Derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal Structure</th>
<th>Color</th>
<th>Molecular Weight</th>
<th>Actual Density in g/cm.</th>
<th>Lattice Parameter A, a-dir.</th>
<th>Lattice Parameter A, c-dir.</th>
<th>Vacuum Stability C</th>
<th>Air Stability C</th>
<th>Resistivity in ohm-cm.</th>
<th>Conduction Type</th>
<th>Comparative Coeff. of Friction (see text)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6S6</td>
<td>trigonal</td>
<td>brown-black</td>
<td>200.18</td>
<td>3.972</td>
<td>5.941</td>
<td>11.18</td>
<td>1350</td>
<td>400</td>
<td>8.51 x 10⁴</td>
<td>metal</td>
<td>0.18</td>
</tr>
<tr>
<td>C6Se6</td>
<td>trigonal</td>
<td>brown-black</td>
<td>253.38</td>
<td>6.9</td>
<td>3.29</td>
<td>12.80</td>
<td>1350</td>
<td>400</td>
<td>1.68 x 10⁴</td>
<td>metal</td>
<td>0.17</td>
</tr>
<tr>
<td>MoSe₂</td>
<td>hexagonal</td>
<td>gray</td>
<td>311.14</td>
<td>7.7</td>
<td>3.52</td>
<td>13.97</td>
<td>1210</td>
<td>400</td>
<td>3.49 x 10⁴</td>
<td>metal</td>
<td>0.19</td>
</tr>
<tr>
<td>WS₂</td>
<td>hexagonal</td>
<td>gray</td>
<td>247.98</td>
<td>7.50</td>
<td>3.29</td>
<td>12.97</td>
<td>1350</td>
<td>440</td>
<td>1.14 x 10⁴</td>
<td>N-semi</td>
<td>0.17</td>
</tr>
<tr>
<td>WSe₂</td>
<td>hexagonal</td>
<td>gray</td>
<td>311.78</td>
<td>9.0</td>
<td>3.29</td>
<td>12.95</td>
<td>1350</td>
<td>350</td>
<td>1.14 x 10⁴</td>
<td>P-semi</td>
<td>0.09</td>
</tr>
<tr>
<td>WTe₂</td>
<td>orthohomb.</td>
<td>gray</td>
<td>430.05</td>
<td>9.4</td>
<td>3.29</td>
<td>12.95</td>
<td>1350</td>
<td>350</td>
<td>3.10 x 10⁴</td>
<td>metal</td>
<td>0.49</td>
</tr>
<tr>
<td>VS₂</td>
<td>hexagonal</td>
<td>gray</td>
<td>145.00</td>
<td>6.80</td>
<td>3.29</td>
<td>5.66</td>
<td>450</td>
<td>500</td>
<td>see note a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VTe₂</td>
<td>hexagonal</td>
<td>gray</td>
<td>178.54</td>
<td>6.80</td>
<td>3.942</td>
<td>6.128</td>
<td>1000</td>
<td>500</td>
<td>see note a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiS₂</td>
<td>hexagonal</td>
<td>gray</td>
<td>157.03</td>
<td>4.11</td>
<td>3.1</td>
<td>11.80</td>
<td>1050</td>
<td>420</td>
<td>3.10 x 10⁴</td>
<td>metal</td>
<td>0.22</td>
</tr>
<tr>
<td>NiSe₂β</td>
<td>hexagonal</td>
<td>gray</td>
<td>254.43</td>
<td>6.25</td>
<td>3.440</td>
<td>13.03</td>
<td>1350</td>
<td>350</td>
<td>5.35 x 10⁴</td>
<td>metal</td>
<td>0.12</td>
</tr>
<tr>
<td>NiTe₂</td>
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<td>gray</td>
<td>344.11</td>
<td>7.8</td>
<td>10.04</td>
<td>19.89</td>
<td>325</td>
<td>57.1 x 10⁴</td>
<td>metal</td>
<td>0.53</td>
<td></td>
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<tr>
<td>TaS₂</td>
<td>hexagonal</td>
<td>gray</td>
<td>245.08</td>
<td>7.05</td>
<td>3.340</td>
<td>12.32</td>
<td>900</td>
<td>600</td>
<td>3.33 x 10⁴</td>
<td>metal</td>
<td>0.05</td>
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<tr>
<td>TaSe₂</td>
<td>hexagonal</td>
<td>gray</td>
<td>334.87</td>
<td>8.6</td>
<td>3.431</td>
<td>12.737</td>
<td>900</td>
<td>57.1 x 10⁴</td>
<td>metal</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>TaTe₂</td>
<td>trigonal</td>
<td>gray</td>
<td>436.15</td>
<td>9.4</td>
<td>10.94</td>
<td>20.675</td>
<td>325</td>
<td>1.17 x 10⁴</td>
<td>metal</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>TiS₂</td>
<td>hexagonal</td>
<td>bronze</td>
<td>112.0</td>
<td>3.28</td>
<td>3.408</td>
<td>5.702</td>
<td>950</td>
<td>130</td>
<td>8 x 10³</td>
<td>N-semi</td>
<td>0.22</td>
</tr>
<tr>
<td>TiSe₂</td>
<td>hexagonal</td>
<td>dark purple</td>
<td>205.8</td>
<td>5.29</td>
<td>3.535</td>
<td>6.004</td>
<td>950</td>
<td>300</td>
<td>2 x 10³</td>
<td>metal</td>
<td>0.17</td>
</tr>
<tr>
<td>TiTe₂</td>
<td>hexagonal</td>
<td>black</td>
<td>303.1</td>
<td>6.34</td>
<td>3.760</td>
<td>6.480</td>
<td>950</td>
<td>300</td>
<td>1 x 10⁴</td>
<td>metal</td>
<td>0.33</td>
</tr>
<tr>
<td>ZrS₂</td>
<td>hexagonal</td>
<td>violet brown</td>
<td>157.4</td>
<td>3.82</td>
<td>3.002</td>
<td>5.800</td>
<td>950</td>
<td>100</td>
<td>1 x 10⁴</td>
<td>N-semi</td>
<td>0.22</td>
</tr>
<tr>
<td>ZrSe₂</td>
<td>hexagonal</td>
<td>purple brown</td>
<td>249.1</td>
<td>5.48</td>
<td>3.770</td>
<td>6.137</td>
<td>950</td>
<td>130</td>
<td>1 x 10⁴</td>
<td>N-semi</td>
<td>0.18</td>
</tr>
<tr>
<td>ZrTe₂</td>
<td>hexagonal</td>
<td>purple brown</td>
<td>316.4</td>
<td>6.30</td>
<td>3.952</td>
<td>6.890</td>
<td>950</td>
<td>250</td>
<td>1 x 10⁴</td>
<td>metal</td>
<td>0.23</td>
</tr>
<tr>
<td>HfS₂</td>
<td>hexagonal</td>
<td>purple brown</td>
<td>242.0</td>
<td>6.03</td>
<td>3.635</td>
<td>5.837</td>
<td>940</td>
<td>100</td>
<td>1 x 10⁴</td>
<td>non-conduc.</td>
<td></td>
</tr>
<tr>
<td>HfSe₂</td>
<td>hexagonal</td>
<td>dark brown</td>
<td>336.4</td>
<td>7.48</td>
<td>3.748</td>
<td>6.159</td>
<td>940</td>
<td>2 x 10⁴</td>
<td>N-semi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfTe₂</td>
<td>hexagonal</td>
<td>black</td>
<td>493.21</td>
<td>8.9</td>
<td>3.098</td>
<td>7.158</td>
<td>1200</td>
<td>2 x 10⁴</td>
<td>metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ThS₂</td>
<td>orthohomb.</td>
<td>purple brown</td>
<td>200.2</td>
<td>7.36</td>
<td>3.344</td>
<td>12.20</td>
<td>1000</td>
<td>250</td>
<td>3.34 x 10⁴</td>
<td>non-conduc.</td>
<td></td>
</tr>
<tr>
<td>ThSe₂</td>
<td>orthohomb.</td>
<td>dark gray</td>
<td>389.0</td>
<td>7.35</td>
<td>3.344</td>
<td>12.20</td>
<td>1000</td>
<td>250</td>
<td>3.34 x 10⁴</td>
<td>non-conduc.</td>
<td></td>
</tr>
<tr>
<td>ThTe₂</td>
<td>hexagonal</td>
<td>black</td>
<td>417.2</td>
<td>8.49</td>
<td>9.01</td>
<td>19000</td>
<td>1500</td>
<td>1.5 x 10⁴</td>
<td>P-semi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U₂S₈</td>
<td>hexagonal</td>
<td>black</td>
<td>302.16</td>
<td>8.175</td>
<td>7.338</td>
<td>4.099</td>
<td>1200</td>
<td>19000</td>
<td>2 x 10⁴</td>
<td>metal</td>
<td></td>
</tr>
<tr>
<td>U₂Se₈</td>
<td>orthohomb.</td>
<td>black</td>
<td>302.95</td>
<td>8.175</td>
<td>7.338</td>
<td>4.099</td>
<td>1200</td>
<td>19000</td>
<td>2 x 10⁴</td>
<td>metal</td>
<td></td>
</tr>
<tr>
<td>U₂Te₈</td>
<td>hexagonal</td>
<td>black</td>
<td>493.21</td>
<td>8.9</td>
<td>3.098</td>
<td>7.158</td>
<td>1200</td>
<td>2 x 10⁴</td>
<td>metal</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: a: chromium and vanadium derivatives vary in resistivity under heat and magnetic force
Note b: unconfirmed results
Figure 5. Outgassing characteristics of some lubricants in vacuum of $10^{-6}$ Torr [21].
and NbSe₂, he could get a very large increase in the wear lives with a corresponding decrease in the friction coefficients (see Figures 6, 7, and 8) [16]. He attributed this dramatic increase in tribological performance to a change in the crystal structure from “NbS₂” type to “MoS₂” type after the addition of the intercalate atoms. This change in crystal structure is a direct result of a change in electronic structure caused by the addition of electron density by the intercalate metal atoms. The added electron density causes the d¹ orbitals to become satisfied and more like the d² orbitals, resulting in a change from attractive forces across the interlayer spacing to repulsive forces. An added benefit of the addition of Ag to NbSe₂ is a corresponding increase in the high temperature capability as shown in Figure 8 [16]. This figure shows a comparison of friction coefficient versus temperature for MoS₂, WSe₂ and various combinations of Nb, Se, S, and Ag. The intercalated compound Ag₀.₃₃ NbS₁.₅ Se₀.₅ shows a sharp decrease in friction coefficient at the upper temperature limit of the tests (~316°C) suggesting the potential for further decrease, while the rest of the compounds showed sharp increases in friction coefficients. This type of performance illustrates the potential for a great increase in friction and wear capabilities from these Nb LTMD compounds by the proper addition of intercalate atoms.
Figure 6. Friction coefficient versus temperature for several solid lubricants [16].
Figure 7. Friction coefficient versus silver concentration in $A_x\text{NbSe}_2$ [16].
Figure 8. Room temperature friction coefficients for $\text{Ag}_x\text{NbS}_y\text{Se}_{2-y}$ and related materials [16].
Methods of Application

There are several methods for applying solid lubricant materials. Among these techniques are dry powder/dispersion processes, bonded films, sputter deposition and, more recently, pulsed laser deposition. This section will briefly describe each of these methods using MoS\textsubscript{2} as an example. More discussion will be spent on the pulsed laser deposition technique since it was the deposition procedure selected and used for this research.

Dry Powder/Dispersion Processes

Solid lubricant materials, such as MoS\textsubscript{2}, are often used in the form of a dry powder or a powder dispersed in a volatile or other suitable transfer medium. Dry powders are mainly used to facilitate the assembly of parts, but could be used for lubrication in applications with short wear life requirements. To achieve effective lubrication using dry powders, the particle size must be suited to the application [23]. The choice of particle size depends primarily on the surface roughness. If the particles are too large, they can not enter all of the crevices in the surface to be lubricated which results in inadequate coverage. In contrast, particles that are too small are not effective as lubricants. Dry powders are generally applied by burnishing, tumbling or dispersions.

Burnishing involves rubbing the powder onto the surface to be lubricated to obtain a thin, uniform coating of material. There are many uses for burnished films since it is a quick and easy method of applying lubricants. However, the
wear lives for burnished films are not as long as those for the bonded films because of the lack of adherence to the substrate. Also, the thickness of these films cannot be precisely controlled.

Tumbling involves using a rotating drum containing a lubricating powder, such as MoS$_2$, plus cork, pine cones, and/or asbestos. The part is placed in the drum and tumbled to produce a roughly uniform covering [9].

A dispersion consists of a combination of a dry powder and a carrier such as petroleum oil, isopropanol, or mineral spirits. The dispersion is used to allow the dry powders to be transported to difficult to reach areas and also to facilitate resupply of a powder lubricant. Some examples of the many applications of these dispersed solid lubricants are automobile wheel bearings, high temperature thread coatings, and conveyor chains [9]. Generally, the applications using dry powders are low life applications since the powders are not physically bonded to the surface needing to be lubricated.

**Bonded Films**

In order to increase the wear life of a part, the solid lubricant should be bonded to the surface. Table 2 illustrates this point by showing the superior wear life obtained by bonding MoS$_2$ powder with an organic resin binder, as compared to the plain dry powder or dispersed MoS$_2$ [24].

As a result of their excellent combination of long wear life and low friction coefficient, bonded films of MoS$_2$ are used in many industrial and
Table 2. -- Endurance Life of MoS₂ Used in Various Forms [24]

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Endurance at 35,000 PST (cycles to failure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin-bonded MoS₂ film</td>
<td>9,860,000</td>
</tr>
<tr>
<td>Grease containing MoS₂</td>
<td>1,590,000</td>
</tr>
<tr>
<td>MoS₂ powder</td>
<td>130,000</td>
</tr>
</tbody>
</table>
automotive applications, as well as in aircraft, rockets, missiles, satellites and nuclear power plants where extreme environments and weight limitations are encountered [9]. Next to oil and grease dispersions of MoS₂, bonded films are the most common manner of using MoS₂ as a lubricant [9].

Sputter Deposition

Sputter deposition is one method that allows a much greater degree of control over many film properties such as adhesion, thickness and stoichiometry. Because of this enhanced control, sputter deposition is a very popular technique for growing tribological thin films. To explain in detail all of the aspects of sputter deposition is beyond the scope of this thesis. However, a short discussion is warranted as sputter deposition is an important technique for depositing solid lubricant films.

Sputter deposition, in general, is a technique in which energetic particles are used to dislodge and eject coating material from a target which then condenses on the substrate as a film. There are several methods of accomplishing this, but only the two main configurations used for deposition of solid lubricants, ion beam sputtering and glow discharge, will be covered here.

In ion beam sputtering, an inert gas, usually Ar, is used to generate a beam of positively charged ions. These ions have energies from a 100 eV to 10 keV depending on the type of sputtering required. When the ion beam hits the target, it removes material by a transfer of momentum [10]. The sputtered material is
ejected primarily in the form of atoms which can grow a film of target material if a substrate is then placed in their path.

Glow discharge sputtering involves the generation of a plasma consisting of target material and inert gas ions and neutrals. A target is placed in a vacuum chamber evacuated to approximately $10^{-7}$ Torr. The chamber is then backfilled with an inert gas such as argon to a pressure of about $10^{-1}$ Torr which is usually adequate to sustain a plasma. To achieve the plasma, a large voltage difference is produced between the target (cathode) and the substrate (anode). A negative bias from 0.5 to 5 kV, is applied to the target so that it will be bombarded by the positive ions from the plasma and eject atomic target species. The substrate is then positioned so as to intercept the flux of sputtered atoms, which will condense to form a film of target material. The energy of the sputtered species for glow discharge is in the range of 10 to 40 eV[10].

Although sputter deposited films are technologically important and recent processes permit adequate control over the film microstructure, thickness and stoichiometry, they possess several characteristics that limit their effectiveness [4, 25]. Because the sputter process takes place at relatively low vacuum, there has been a contamination problem because of background gases in the deposition chamber (i.e. $\text{H}_2\text{O}, \text{CO}, \text{CO}_2, \text{O}_2$, etc.) [26]. These background gases cause incorporation of oxygen impurities into the sputtered films which may accelerate lubricant decomposition at elevated temperatures [27]. Sputtered films of $\text{MoS}_2$ have a platelike, porous morphology with the basal planes
oriented perpendicular to the substrate surface. This orientation has been shown to expose the reactive edge planes to the environment and increase their reactivity toward oxidants [27-31]. In addition, there are a large number of sputtering parameters such as the nature of the sputtering gas, substrate bias, beam voltage, sputtering angle, etc. that have a significant influence on film stoichiometry, morphology and orientation [11, 25, 32, 33]. Some of these parameters are difficult to control precisely. Thus there is a need for improved deposition processes which can reduce the multidimensional parameter space characteristic of sputter deposition [2]. There is also a need for deposition processes which can produce films with minimum contamination, especially reduced oxygen content. Finally, we need a process that can permit precise control over the film orientation.

From previous work by Spalvins [34] and Buck [35] it has been shown that films having a basal orientation (c-axis perpendicular to the substrate) result in a reduced friction coefficient and increased wear life. Sputtered films tend to have columnar growth morphology which leads to exposure of the contamination sensitive edge planes to the environment, and increased porosity [34]. Basally oriented films are more oxidation resistant and can produce a longer wear life in atmospheric conditions. The next method, pulsed laser deposition (PLD), has been shown to solve many of the above sputter system deficiencies.
Pulsed Laser Deposition

PLD is an attractive alternate technique for the deposition of lubricant materials that does not rely on sputtering processes. The laser technique permits the deposition of dense, near stoichiometric lubricant coatings that have a significant degree of basal orientation [2, 4, 36]. Deposition of lubricants by PLD offers several other potential advantages for forming lubricious coatings: (1) films may be deposited in less than $10^{-9}$ Torr of background gases at greater than 4.0 nm/s producing high purity films and permitting precise control of dopant concentrations, (2) complex targets may be used to create complex films since photo ablation appears to be a congruent process and (3) film properties may be adjusted/controlled by proper selection of laser parameters, dopant gas, substrate temperature, and post laser anneals.

The initial studies of the PLD technique for growth of tribological materials relied on 532 nm laser radiation from the frequency doubled output of a Nd:YAG laser to ablate an MoS$_2$ target onto 440C stainless steel [4, 36]. Films were grown at both room temperature and high temperatures of 200, 300 and 450°C. All the films were reported to have good adhesion, based on the wear life of the film, and a low coefficient of friction (0.15). Films deposited at 200 to 300°C had a S/Mo ratio of 1.8 and exhibited the best and most consistent friction and wear properties. However, the films contained large (1 to 3 μm diameter) spherical surface features due to a phenomenon called “splashing.” The splashing phenomena was explained by Donley et. al. as follows: “light
energy impinging on the target produces subsurface heating of the target, and eventual melting. This molten material is ejected from the target and ‘splashes’ onto the substrate” [36]. Later efforts reduced the splashing problem by using the shorter, more energetic 193 and 248 nm radiation available from an excimer laser operating with ArF and KrF gas, respectively. Because of the excimer laser's inherent advantages, recent work has focussed on investigating the properties of tribological films deposited primarily by the excimer laser [4, 5].

As explained by Murray et. al. [3], there are three proposed mechanisms of laser-induced material removal. These mechanisms depend mostly on photon energy. The first and lowest energy mechanism is laser desorption, in which the photons provide only enough energy to desorb weakly bound species from the solid surface. The second mechanism is laser evaporation, where the photons have enough energy to remove chemically bonded species from the surface. In this mode, the laser acts as a thermal source and the irradiated area is in approximate thermodynamic equilibrium. The third and most energetic mechanism is laser ablation. In this mechanism, photons have enough energy to break chemical bonds.

Garrison and Srinivasan have performed molecular dynamics calculations on the two latter mechanisms, evaporation and ablation [37]. Their calculations describe evaporation as local melting of the target, where material is ejected in a broad angular distribution. Ablation is described as a more energetic process where material is removed layer by layer, forming well-defined pits in the target.
Material is ejected in a narrow angular distribution, similar to a supersonic expansion. The average perpendicular velocity of the ablated species was predicted to be on the order of 1-2 km/s [37].

**Design of Experiments**

This section will explain the design of experiments (DOX) approach. There are several leaders in this field of statistical design of experiments of which the two most famous are G.E.P. Box and Genichi Taguchi. The bulk of the design methodology for the experiments in this thesis were taken from the Box approach and the analysis of the data was a mixture of both the Taguchi method and the Box method. None of the statistical concepts used are extremely difficult to grasp, yet are very important.

Since the DOX concepts are a significant part of the setup and analysis of the data, it is necessary to explain the basic theory associated with DOX. The major topics to be covered are the learning process, hypothesis testing, and factorial designs at two levels. The section will then cover analysis of the data and the advantages of the DOX method over the one-factor-at-a-time approach. The primary reference for this section is Box's book, "Statistics for Experimenters" chapters one and ten [38]. These chapters give an excellent explanation of the necessary concepts for understanding the latter portions of this thesis and were therefore used liberally in writing this section.
The Learning Process

"Scientific research is a process of guided learning. The object of statistical methods is to make that process as efficient as possible" [38].

Learning can be illustrated by an iterative type process as illustrated in Figure 9. An initial hypothesis leads, by a process of deduction, to certain necessary consequences that may be compared with data. When these consequences and data fail to agree, the discrepancy can lead, by a process called induction, to a modified hypothesis. The consequences of the modified hypothesis are worked out and again compared with data (old or newly acquired) which can lead to further modification. In each iteration of this process there is an increase in knowledge. A feedback loop, as shown in Figure 10, is another way to illustrate the concept of the learning process. Similar to the first illustration, a discrepancy between the data and the consequences of hypothesis H\textsubscript{1} leads to the modified hypothesis H\textsubscript{2}, H\textsubscript{2} leads to H\textsubscript{3}, and so on.

Hypothesis Testing

In any learning cycle, there will be variables that need to be tested against a hypothesis in order to verify or disprove it. Usually it is most efficient to estimate the effects of several variables simultaneously. In order to do this efficiently, one needs to use experimental design. Each experimental design will then contain a group of experimental runs. A new design is not necessarily employed for each iterative cycle because sometimes a sequence of cycles will
Figure 9. The iterative learning process [38].
Figure 10. The learning process as a feedback loop [38].
occur in which the same data are confronted by several hypotheses successively. However, when it is not clear what modification should be made to an unsatisfactory hypothesis, or, possibly, when further confirmation of an apparently satisfactory hypothesis is needed, additional data will be required. When more data needs to be generated by further experimental runs, a new experimental design should be employed.

One important point that bears mentioning in reference to any scientific investigation, is that there is not just one unique route to a problem solution. Two equally competent investigators presented with the same problem would typically begin from different starting points, proceed by different routes, and yet could reach the same answer. What is sought is not uniformity, but convergence.

Convergence will occur most quickly and surely if the following are available: (1) efficient methods of experimental design, which enables one to obtain answers to his questions that are as unequivocal and as little affected by experimental error as possible, and (2) sensitive data analysis, which can indicate what can legitimately be concluded about current hypotheses and can suggest new ideas that should be considered.

Of these two resources, design is more important. If the experimental design is poorly chosen, so that the resultant data do not contain much information, not much can be extracted, no matter how thorough or sophisticated the analysis. On the other hand, if the experimental design is wisely chosen, a
great deal of information in a readily extractable form is usually available, and no elaborate analysis may be necessary.

Factorial Designs at Two Levels

Two level designs are very useful and important for several reasons: (1) they require relatively few runs per factor studied; and although they are unable to explore fully a wide region in the factor space, they can indicate major trends and thereby determine a promising direction for further experimentation; (2) the designs may be used as building blocks so that the degree of complexity of the finally constructed design matches that of the problem; (3) the interpretation of the observations produced by these designs is relatively simple and can proceed largely by common sense and simple arithmetic.

To perform a general factorial design, an investigator selects a fixed number of “levels” for each of the variables then runs experiments with all possible combinations. If there are $l_1$ levels for the first variable, $l_2$ for the second, $\ldots$, and $l_k$ for the $k$th, the total number of experimental runs equals $l_1 \times l_2 \times \ldots \times l_k$. For example, a $2 \times 3 \times 5$ factorial design requires 30 runs, and a $2 \times 2 \times 2 = 2^3$ factorial design requires 8 runs.

For factorial designs at two levels, the number of experiments is determined by simply raising the number two to the power of the number of factors as was done in the last example. A $2^3$ factorial, means three factors each at two levels. The next step is to set up your design into a design matrix. Box [38] has
established what is called the standard order for design matrices and it is shown in Table 3 for a $2^3$ design matrix.

The "+" and "-" signs correspond to the high and low settings for each factor. A, B, and C are the main factors and AB, BC, and AC correspond to the two factor interactions. ABC is the only 3 factor interaction in this design.

The choice of the high and low settings for each factor need to be determined by the investigator. These levels will be based on past experience, limitations of equipment, related data or other foreknowledge of the process. In the initial set of experiments these settings are chosen to be boundary conditions based on the above criteria. By operating each factor at its respective boundary condition, one can determine the overall trends for a process and also determine whether or not there are any significant interactions that must be considered in future experiments.

**Calculation of Main Effects**

Given that the design is a $2^3$ factorial design, Table 3 is the correct design matrix and will be referred to for this example.

To calculate the main effects, one simply takes the difference between two averages:

$$\text{main effect}_A = \overline{Y}_A^+ - \overline{Y}_A^-$$
Table 3. -- Standard Order for Design Matrices [38].

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>AB</th>
<th>AC</th>
<th>BC</th>
<th>ABC</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>
where  is the average response for the main factor A at the plus level and  is the average response for A at the minus level.

Notice that by using this method, all the observations are being used to supply information on each of the main effects. The two factor interaction effects are calculated in a similar fashion. To calculate the AB interaction, move to that column and again take the differences in the averages of the plus values and minus values.

This procedure will generate a response table of the effects as shown in Table 4, part (a) [39]. Once this table has been generated, the absolute value of the differences is ranked from highest to lowest. The purpose for this is to illustrate which factors and/or interactions are causing the largest changes.

The next step is to generate interaction response blocks. These are going to be used to generate the interaction plots. An example of an interaction response block is shown in part (b) of Table 4. The procedure for filling out this block is slightly different than for the main effects. The upper left square is filled in from the average of  and  ( ). The upper right block is filled in by  and so on. Once the blocks are generated, interaction plots can be generated to graphically illustrate the trends in the data. The plots should contain one line for the main effects and two lines for the interaction effects. An important note about the interaction plots: if the lines are parallel, there is no significant interaction, but if the slopes are different or the lines cross, there could be a significant interaction. When this happens, the main effects for those
Table 4. -- Response tables

(a) Calculation of interaction effects

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>AB</th>
<th>AC</th>
<th>BC</th>
<th>ABC</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Difference $(\Delta)$

Ranking

(b) Interaction Response Blocks:

```
  B-  B+
A-   A+

  C-  C+
A-   A+

  C-  C+
B-   B+
```
factors can not be looked at independently. For instance, if factor A and B interact significantly, the fact that A increases from its low setting to its high setting is invalid, unless factor B is considered also.

Advantages over the “One-Factor-at-a-Time” Method

Suppose that in the above investigation, instead of a factorial arrangement, the “one-factor-at-a-time” method had been used. This method involves the experimental factors being varied one at a time, with the remaining factors held constant. Previously, this method was regarded as the only correct way to conduct research. The method provides an estimate of the effect of a single variable at selected fixed conditions of other variables. However, for this estimate to have general relevance one must assume that the effect would be the same at other settings of the other variables—that the variables act on the response additively over the ranges of interest. However, (1) if the variables do act additively, the factorial design does the job with more precision; and (2) if the variables do not act additively, the factorial, unlike the one-factor-at-a-time design, can detect and estimate interactions that measure the nonadditivity.

For example, using the three variables A, B, and C, each at two different settings, a one-factor-at-a-time approach would require eight runs to estimate the effect of each variable, four at each level, resulting in a total of 24 runs. To gain the same precision, the factorial approach would only require eight runs for all three variables combined. In general, for \( k \) factors, a \( k \)-fold increase would
be required for factors taken one at a time to attain the same precision as a factorial design. A modified one-factor-at-a-time approach might be to use a single experimental condition from which to make all changes; even with this arrangement, however, the one-factor-at-a-time design requires \((k + 1)/2\) times as many runs as the factorial.

It was for the many above stated benefits that the \(2^3\) factorial design was chosen in structuring the system of data acquisition and analysis employed in the research brought forth in this paper.
CHAPTER 2
EXPERIMENTAL

Crystal structure and stoichiometry clearly play a significant role in the lubrication performance of the Nb based lubricants as the results of several researchers would indicate [17, 40, 41]. In order to obtain the optimal tribological properties, the crystal structure and stoichiometry must be controlled. To ensure this research would be beneficial, the author identified and considered four basic requirements for selecting a lubricating film and system for carrying out analysis of the film's properties. They are:

(1) The material must be useful. Niobium based LTMD compounds have potential to be used at temperatures exceeding those of MoS₂, the current "benchmark" solid lubricant. Also they are conductive lubricants that could be effective in applications where good electrical contact and low noise are critical, such as in electrical slip rings and brushes.

(2) The deposition process must allow control over the important parameters. PLD has been shown to be an excellent technique for growing LTMD compounds, such as MoS₂, with excellent control over the film's chemical, physical, and mechanical properties.
(3) The experiments must be planned in advance to produce the maximum amount of information from a minimum of experimental runs. The DOX approach using a two level factorial design is an excellent way to explore the boundary conditions of a new process. This approach will allow the major trends of a process to be seen directly and easily.

(4) One must have some prior knowledge or experience of similar systems that have been studied. Before deciding on a particular material to study, the whole class of NbX₂ (X = S, Se, Te) was investigated to determine the particular compound that had the most potential for use as a solid lubricant. Based on the preliminary data and literature support, NbSe₂ was chosen for further consideration.

The goal of this research was to use a statistical design of experiments approach to investigate the influence of substrate temperature, laser fluence and pulse rate on film chemistry, crystallinity and tribological properties.

The remainder of the experimental section will cover the apparatus, sample preparation, factor selection, and analysis methods used for these experiments.

**Apparatus**

The basic requirements for a PLD system are a laser, a vacuum chamber, and beam handling optics. The laser chosen for this research was a Lambda
Physik 110i excimer laser operating at 248 nm using KrF gas. The excimer was chosen over a Nd:YAG because the excimer operates at a higher energy per photon. This causes more of a photo ablation process than the thermal process of the Nd:YAG. As a result, there is less splashing of particles from target to film. There were two types of excimer wavelengths available for use (ArF at 193 nm and KrF at 248 nm). These wavelengths both produce a very energetic beam. However, the 193 nm radiation interacts with the O₂ in the air causing a significant decrease of power on target, whereas 248 nm light does not.

The PLD system, showing the path of the laser beam, can be seen in Figure 11. The laser beam travels through the air to a focussing lens (1 meter focal length) which it passes through before being reflected off a rastering mirror. This mirror is controlled using stepper motors connected to an Oriel control interface. The beam then immediately enters the vacuum chamber through a MgF₂ window fitted in a knife edge flange. The beam impinges on the target with a spot size of ~2 mm x 4 mm, causing an explosive release of a plume of material (see Figure 12). This plume is generated perpendicular to the surface of the target and impacts the substrate located approximately 5 inches away. Both the target and substrate were rotated to provide full usage of the target and to produce uniform films.

The growth chamber had a base pressure of 5 \times 10^{-9} \text{Torr}. The pressure rose to approximately 5 \times 10^{-6} \text{Torr} during depositions. The deposition chamber was fitted with a quartz crystal thickness monitor, used to measure film
Figure 11. Chamber setup. Shows Lambda Physik 110i excimer laser, deposition chamber, and mobile transfer shuttle.
PULSED LASER DEPOSITION PROCESS

Figure 12. Details of the plume, substrate and heater configuration.
thickness and growth rates, and a vacuum gauge to monitor the background partial pressures during growth. These two sensors were controlled by a 488 controller interface connected to a Macintosh IIfx computer which allowed real time data acquisition.

A problem with surface contamination from surface oxides led to the development of the next apparatus. During initial x-ray photoelectron spectroscopy (XPS) analysis of the calibration films, this surface contamination made evident a real need for the ability to transfer films from the growth chamber to the XPS spectrometer without exposing them to air. In response to this need, a mobile high vacuum transfer shuttle was designed and constructed to permit the transfer of films under continuous high vacuum. Through a system of pressure interlocks and transfer forks, the films could be transferred from the growth chamber to the XPS chamber under 10⁻⁷ Torr vacuum. This apparatus significantly reduced the contamination problem.

The surface chemistry was investigated using a Surface Science M-Probe XPS spectrometer. This instrument was operated at 3x10⁻⁹ Torr using a 300μm line spot and a 25 eV pass energy to provide a full width at half maximum (FWHM) of 0.70 eV for the Au 4f\textsubscript{7/2} peak. Binding energy positions were calibrated using the Au 4f\textsubscript{7/2} peak at 83.00 eV, the Cu 3s peak at 122.39 eV and the Cu 2p\textsubscript{3/2} peak at 932.47 eV.

The surface sensitive XPS technique was also used to obtain a bulk stoichiometry measurement. This was accomplished by using a short argon
sputter to remove the surface layers. It was determined from several depth profiles, that the majority of the surface oxides and excess selenium was removed after twelve minutes of sputtering. After 12 minutes, the film stoichiometry was constant until the substrate interface was reached.

Further confirmation of the validity of the sputtered XPS (XPS\textsubscript{sp}) technique was obtained from Rutherford backscattering spectroscopy (RBS) measurements. RBS provided nondestructive elemental depth profiles of niobium, selenium and oxygen using a 2 MeV He\textsuperscript{+} ion beam with a detector located at a backscattering angle of 170°.

The bulk crystallinity was measured using glancing angle x-ray diffraction (GAXRD) on a Rigaku D/max -1B diffractometer equipped with a thin film attachment and a monochrometer.

The morphology of the films was studied in both cross-sectional and planar views using two different scanning electron microscopes. The cross-sectional SEM samples were analyzed using a Hitachi S-900 field emission microscope and the planar views were obtained using a JEOL 840 SEM.

A ball-on-flat tribometer was used to determine friction coefficients and wear lives. A 1/8” diameter ball was loaded with a 30 gram weight that rested on the sample. The sample was attached to a platent which rotated at approximately 200 rpm. The ball sliding on the substrate generated a frictional force which was measured using a strain gauge. The output from the strain gauge was translated into a friction coefficient and the cycles to film failure were
translated into wear life. The tribometer is enclosed in a bell jar which allowed tests to be carried out in both dry nitrogen and laboratory air environments.

**Sample Preparation**

The target powder materials were obtained from Aesar and were 99.9% pure crystalline NbSe$_2$ which was verified using powder x-ray diffraction. These powders were then pressed into 1" diameter x 1/4" thick pellets in an inert atmosphere at 400°C.

There were three different types of substrates: 440C stainless steel, silicon and graphoil. The 440C stainless steel substrates were analyzed using x-ray photoelectron spectroscopy (XPS), glancing angle X-ray diffraction (GAXRD), and a ball-on-flat tribometer. The silicon samples were used for the Rutherford Backscattering (RBS) and scanning electron microscopy (SEM) analysis; the graphoil samples were used solely for RBS.

All of the substrates were rinsed using acetone and ethanol, but the 440C stainless steel substrates were subjected to an initial wash with soap and deionized water. The substrates were placed in the vacuum chamber prior to deposition and were flash heated to 600 K for fifteen minutes and allowed to cool for at least 45 minutes. These temperatures were monitored using a calibrated infrared pyrometer.

The SEM cross-section samples were prepared by placing 4 x 8 mm strips of silicon adjacent to the 440C stainless steel substrates during growth runs. The
silicon strips were removed after growth and cleaved carefully to produce a cross-section view of the film. The SEM planar views were obtained using the films on stainless steel substrates.

Factor Selection

In this study, there were three main variables or factors. They were repetition rate, pulse energy and substrate temperature. These variables have been shown in past work on MoS$_2$ to be the main factors that affect the adhesion, nucleation and growth of tribological films [4, 5, 36]. For each of these factors, two levels were chosen that represented the process boundaries.

Process boundaries for repetition rate were chosen to be 10 Hz and 100 Hz. The laser's minimum repetition rate is 1 Hz. However, since a growth run at this repetition rate would take an inordinate amount of time to obtain an adequate thickness of 3-4 kÅ, a more reasonable rate of 10 Hz was chosen. Also, based on previous experiments with MoS$_2$, this was the minimum repetition rate reported for growth. The 100 Hz setting was a limit of the laser itself.

A similar process was adopted in selecting the pulse energies and substrate temperatures. The lower pulse energy, 100 mJ (corresponding to 1.3 J/cm$^2$ at the target), was the minimum reported value for MoS$_2$. Below this value the deposition rates are too low. The high pulse energy, 220 mJ (corresponding to 2.8 J/cm$^2$ at the target), was the maximum value that the laser could sustain at 100 Hz.
The temperature limits were set based on the prior work with PLD MoS\textsubscript{2} films \cite{4, 5, 36}, which showed that temperatures above 600K caused excessive losses in chalcogen content. There was no substrate cooling capability. Therefore, the lowest growth temperature possible was room temperature, which is also the desired temperature since it simplifies the process.

Sample Analysis

Several analysis techniques have been used to characterize these films to determine their chemical, physical and mechanical properties. A schematic representation is shown in Figure 13.

First of all, the initial films from this study (grown on the quartz crystal thickness monitor) were used to obtain thickness versus time calibration curves. These curves were then plotted to determine the relative growth rates of the materials (see Figure 14). These films were then removed from the chamber and transferred in air to the x-ray photoelectron spectrometer (XPS) to study the surface chemistry.

As discussed previously, the problem with surface oxide contamination on the samples at this point led to the development of the mobile high vacuum transfer shuttle system that would be used for the rest of the samples.

With the development of the new transfer system, the rest of the samples could now undergo surface analysis in the XPS, the first analysis technique, without exposing the films to air.
Figure 13. Analysis Techniques
Figure 14. Family of growth rate curves determined for Niobium diselenide illustrating the boundary conditions, data from quartz crystal thickness monitor.
The XPS analysis involves taking broad survey scans to determine the elements present in the film and also to see if any contaminants are present. A representative set of survey scans is shown in Figure 15. At the same time several high resolution scans are taken of important regions to get a better view of changes in chemistry. In this study, the high resolution scans for niobium, selenium, carbon and oxygen were monitored.

After the initial spectra were taken on the “as deposited” surface, the films were then subjected to a 12 minute ion sputter etch to remove the surface oxide and excess surface selenium (discussed later). The same types of spectra were again taken after sputtering. The data from these spectra are referred to as the XPS\textsubscript{sp} data.

The high resolution XPS spectra were fit using a Voight function which is a combination of Lorentzian and Gaussian peak shapes using a least squares procedure. (The XPS spectra for each of the samples are displayed in Appendix A.) A more detailed discussion of the actual peak fitting methodology follows.

The same systematic method was used to fit all of the peaks for both the XPS and XPS\textsubscript{sp} data. First the Nb 3d\textsubscript{5/2}, 3d\textsubscript{3/2} doublet for NbSe\textsubscript{2} was fit. This set of peaks was easy to distinguish because they were at the lowest binding energy (see Figure 16). A 3d\textsubscript{5/2}/3d\textsubscript{3/2} area ratio of 1.5 and a peak separation of 2.75 were used as fitting factors.

The next set of peaks fitted were those corresponding to the Nb\textsubscript{2}O\textsubscript{5} surface oxide. This oxide was prevalent in many of the films in various amounts
Figure 15. Representative XPS Survey Scans
Figure 16. Example of XPS Peak Fitting Procedure
and was easy to fit because the 3d\textsubscript{3/2} peak was always the highest binding energy in the spectra. All of the oxides of Nb were fit using a 3d\textsubscript{5/2} /3d\textsubscript{3/2} ratio of 1.5 and a peak separation of 2.8 eV.

The final set of peaks to fit were the NbO\textsubscript{x} compounds. Since the exact species of oxide was not a concern in this study, the exact identity of “x” was not determined. The NbO\textsubscript{x} compounds had an average full width at half max (FWHM) of 1.55 eV. The average FWHM of Nb due to NbSe\textsubscript{2} bonding was 1.21 eV and the average FWHM of the Nb due to Nb\textsubscript{2}O\textsubscript{5} bonding was quite broad at 2.66 eV.

The sputtered XPS data were fit using the same methods as above; the main difference being that the Nb\textsubscript{2}O\textsubscript{5} peaks were no longer easily fit. The sputtering process tends to reduce the native oxide (Nb\textsubscript{2}O\textsubscript{5}) to a mixture of various sub-oxides (NbO\textsubscript{2}, NbO, Nb\textsubscript{2}O etc.). This type of effect has been seen and investigated by several researchers [42-47] whose results agree with the results of this study. Also, there was a significant broadening and a shift to lower binding energy that takes place in the higher binding energy oxide doublet (increasing to an average FWHM of 3.10). The NbO\textsubscript{x} peaks also shift to lower binding energy, but do not show a definite trend toward broadening. Sputtering shifts all of the Nb 3d peaks toward lower binding energy but has little effect on the FWHM for the NbSe\textsubscript{2} doublet, whose FWHM decreases slightly to an average of approximately 1.15 eV. The binding energy data is tabulated in Table 5 for ease of reference.
Table 5. -- XPS binding energy data from PLD NbSe$_2$ films on stainless steel before and after ion gun sputter cleaning.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RR/Energy/Temp</th>
<th>Nb</th>
<th>NbOx</th>
<th>Nb2O5</th>
<th>Se</th>
<th>O 1s (surf)</th>
<th>O 1s (ox)</th>
<th>C 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>a NbSeRR10a</td>
<td>10/100/293K</td>
<td>203.64</td>
<td>204.39</td>
<td>205.65</td>
<td>54.92</td>
<td>533.16</td>
<td>531.24</td>
<td>284.75</td>
</tr>
<tr>
<td>b NbSeRR10</td>
<td>10/100/293K</td>
<td>204.35</td>
<td>205.35</td>
<td>207.02</td>
<td>54.80</td>
<td>532.98</td>
<td>530.95</td>
<td>284.83</td>
</tr>
<tr>
<td>c NbSeRR05a</td>
<td>10/100/600K</td>
<td>203.86</td>
<td>204.72</td>
<td>206.81</td>
<td>54.77</td>
<td>N/A</td>
<td>531.13</td>
<td>284.77</td>
</tr>
<tr>
<td>d NbSeRR05</td>
<td>10/100/600K</td>
<td>204.36</td>
<td>206.55</td>
<td>N/A</td>
<td>54.42</td>
<td>532.78</td>
<td>530.91</td>
<td>285.45</td>
</tr>
<tr>
<td>e NbSeRR07a</td>
<td>10/220/293K</td>
<td>203.73</td>
<td>204.57</td>
<td>206.20</td>
<td>54.84</td>
<td>533.17</td>
<td>531.24</td>
<td>284.56</td>
</tr>
<tr>
<td>f NbSeRR07</td>
<td>10/220/293K</td>
<td>204.37</td>
<td>205.44</td>
<td>207.01</td>
<td>54.92</td>
<td>533.10</td>
<td>530.93</td>
<td>284.79</td>
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<tr>
<td>g NbSeRR06a</td>
<td>10/220/600K</td>
<td>203.48</td>
<td>204.24</td>
<td>N/A</td>
<td>54.92</td>
<td>533.20</td>
<td>531.31</td>
<td>284.69</td>
</tr>
<tr>
<td>h NbSeRR06</td>
<td>10/220/600K</td>
<td>203.95</td>
<td>204.92</td>
<td>206.27</td>
<td>54.67</td>
<td>532.69</td>
<td>531.02</td>
<td>284.57</td>
</tr>
<tr>
<td>i NbSeRR13a</td>
<td>100/100/293K</td>
<td>203.98</td>
<td>204.74</td>
<td>206.35</td>
<td>54.54</td>
<td>532.65</td>
<td>530.95</td>
<td>284.69</td>
</tr>
<tr>
<td>j NbSeRR13</td>
<td>100/100/293K</td>
<td>204.4</td>
<td>205.22</td>
<td>206.28</td>
<td>54.98</td>
<td>532.26</td>
<td>530.67</td>
<td>284.75</td>
</tr>
<tr>
<td>k NbSeRR08a</td>
<td>100/100/600K</td>
<td>203.95</td>
<td>204.78</td>
<td>206.39</td>
<td>54.92</td>
<td>532.56</td>
<td>531.19</td>
<td>284.97</td>
</tr>
<tr>
<td>l NbSeRR08</td>
<td>100/100/600K</td>
<td>203.79</td>
<td>204.77</td>
<td>207.34</td>
<td>54.44</td>
<td>533.00</td>
<td>530.90</td>
<td>284.80</td>
</tr>
<tr>
<td>m NbSeRR03a</td>
<td>100/220/293K</td>
<td>203.99</td>
<td>204.81</td>
<td>206.14</td>
<td>54.51</td>
<td>N/A</td>
<td>530.77</td>
<td>284.40</td>
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<tr>
<td>n NbSeRR03</td>
<td>100/220/293K</td>
<td>204.4</td>
<td>205.50</td>
<td>N/A</td>
<td>54.90</td>
<td>532.68</td>
<td>530.63</td>
<td>285.09</td>
</tr>
<tr>
<td>o NbSeRR04a</td>
<td>100/220/600K</td>
<td>203.85</td>
<td>204.70</td>
<td>206.58</td>
<td>54.58</td>
<td>532.76</td>
<td>531.02</td>
<td>284.86</td>
</tr>
<tr>
<td>p NbSeRR04</td>
<td>100/220/600K</td>
<td>203.75</td>
<td>204.65</td>
<td>207.22</td>
<td>54.34</td>
<td>532.21</td>
<td>530.73</td>
<td>284.90</td>
</tr>
</tbody>
</table>

NOTE: Shaded lines contain sputtered data. (See Appendix A for raw data.)
Following the XPS analysis, the samples were brought up to air for the first time to run glancing angle x-ray diffraction (GAXRD) spectra. After performing these fairly nondestructive testing techniques (XPS and GAXRD), the samples were then subjected to the more destructive testing techniques of SEM and ball-on-flat tribometry.

Finally, some selected samples were also taken to Boston, MA to the Army Materials Technology Laboratory to take RBS measurements. The RBS measurements provided a nondestructive depth profile of the films which was very different than what was observed at the surface level.
CHAPTER 3
RESULTS

The results of the various analysis techniques discussed in chapter two will be presented in this section.

To begin this examination, the XPS and RBS data will be presented in relation to the deposition parameters. This will provide a preview of the effects that substrate temperature, laser fluence and pulse rate had on the film chemistry. This information, together with XRD, SEM, and wear test results form the basis for establishing the synthesis-structure-property relationships for pulsed laser deposited NbSe$_2$. For ease of reference, interaction plots were produced to show the main trends of the XPS results. Some spectra will be shown in this chapter to highlight significant features. XPS and RBS spectra used in this investigation, but not shown here, are included in Appendix A and Appendix B, respectively.

The next set of results examined will be the GAXRD data. The spectra presented are those showing significant changes in crystallinity. They are included to illustrate the relationship of the parameters to the corresponding changes in the crystalline nature of the films.
To give a pictorial representation of the surface of the films, a representative selection of SEM photographs will be shown of planar and cross-sectional views of the films.

Finally, there will be a brief section stating the general results obtained from the friction and wear studies.

**XPS and RBS**

The results for unsputtered-XPS (XPS), sputtered-XPS (XPS$_{sp}$) and RBS are presented in Table 6. From the use of these three chemical analysis probes, the film's surfaces and bulk chemistries were well characterized.

Film stoichiometries (Se/Nb ratios) were calculated using the Se 3d and the Nb 3d peaks and a normalization factor (derived from the starting target materials) before and after sputtering (also shown in Table 6). Even though films were transferred between the deposition and analysis chamber under high vacuum, some surface oxide and elemental selenium were present after transfer and were removed by a short Ar$^+$ ion sputter etch.

The response variable shown for each technique is the Se/Nb ratio, which is the stoichiometry of the compound. A comparison of these values shows a large difference in the results for the unsputtered XPS data compared to XPS$_{sp}$ and RBS data which were in agreement. In contrast, the unsputtered XPS data consistently had higher Se/Nb ratios and a small amount of the native surface oxide, Nb$_2$O$_5$. 
Table 6. -- Deposition Parameter Matrix (values shown are for Se/Nb ratio)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>AB</th>
<th>AC</th>
<th>BC</th>
<th>ABC</th>
<th>XPS</th>
<th>XPSsp</th>
<th>RBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.90</td>
<td>0.753</td>
<td>0.892</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>2.54</td>
<td>0.853</td>
<td>------</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>1.89</td>
<td>0.716</td>
<td>0.818</td>
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<td>+</td>
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<td>+</td>
<td>5.37</td>
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<td>7</td>
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<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
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<td>2.387</td>
<td>------</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>2.19</td>
<td>1.0</td>
<td>1.326</td>
</tr>
</tbody>
</table>

A = Repetition Rate ("-" represents 10 Hz, "+" represents 100 Hz)
B = Pulse Energy ("-" represents 100 mJ, "+" represents 220 mJ)
C = Substrate Temperature ("-" represents 293 K, "+" represents 600 K)
The results of the interaction effect calculations described in the Design of Experiments Section of this thesis are shown in Tables 7 and 8. The first three columns (i.e. A, B, C) are the experimental settings used to determine the main effects. The next four columns (i.e. AB, AC, BC, ABC) were used to determine the two and three factor interaction effects.

From Table 7, parts (a) and (b), we can generate interaction plots of the main and two factor interactions for the XPS data (see Figure 17). Table 8, parts (a) and (b), were used to generate the interaction plots seen in Figure 18 for the XPS_{sp} data. These interaction plots illustrate the mean change in the response from the "-" condition to "+" condition for a given variable or set of variables.

The main factor effects are shown in the top three plots on Figures 17 and 18 and the effects of the 2 factor interactions can be seen in the bottom three plots.

These plots illustrate that each of the corresponding main factor and two factor interaction plots from the XPS and XPS_{sp} data correlate to show the same trends. However, the absolute Se/Nb ratios are lower for the sputtered results as will be discussed in the next section. The largest interaction effect for both sets of data, is seen on the repetition rate versus substrate temperature plot; here the two lines have very different slopes, causing an intersection.

The RBS data was not complete because some of the films were not analyzed. Nevertheless, because of the strong correlation between RBS and XPS_{sp}, it is likely that the trends would have been similar.
Table 7: -- Response tables for unsputtered XPS data after normalization to target stoichiometry:

(a) Calculation of interaction effects

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>AB</th>
<th>AC</th>
<th>BC</th>
<th>ABC</th>
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<tr>
<td>-</td>
<td>1.89</td>
<td>2.92</td>
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<td>1.97</td>
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<td>3.16</td>
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<td>3.07</td>
<td>2.37</td>
<td>3.00</td>
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</table>

| Difference (Δ) | 1.28 | -0.81 | -1.14 | 0.14 | 1.10 | -0.58 | 0.96 |

| Ranking | 1 | 5 | 2 | 7 | 3 | 6 | 4 |

(b) Interaction Response Blocks:

<table>
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<th>B+</th>
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</thead>
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<td>3.64</td>
</tr>
<tr>
<td>B+</td>
<td>2.54</td>
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</tbody>
</table>
Table 8. -- Response tables for sputtered XPS data:

(a) Calculation of interaction effects

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<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>AB</th>
<th>AC</th>
<th>BC</th>
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<tr>
<td>-</td>
<td>0.70</td>
<td>1.33</td>
<td>1.57</td>
<td>1.25</td>
<td>0.94</td>
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<td>1.23</td>
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<tr>
<td>+</td>
<td>1.78</td>
<td>1.15</td>
<td>0.91</td>
<td>1.23</td>
<td>1.53</td>
<td>1.31</td>
<td>1.26</td>
</tr>
<tr>
<td>Δ</td>
<td>1.08</td>
<td>-0.18</td>
<td>-0.66</td>
<td>-0.02</td>
<td>0.60</td>
<td>0.14</td>
<td>0.02</td>
</tr>
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</table>

Ranking 1  5  2  7  3  6  4

(b) Interaction Response Blocks:

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<td>A+</td>
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<table>
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<td>B+</td>
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Figure 17. Interaction Plots for the unsputtered XPS results.
Figure 18. Interaction Plots for the sputtered XPS results.
For representative purposes, the XPS, GAXRD and RBS data corresponding to the four end points from the repetition rate versus substrate temperature plots are shown in Figures 19, 20 and 21.

Since both the sputtered and unsputtered XPS correlate very well, only the unsputtered spectra will be shown to represent the changes that took place. Figure 19a shows the Nb 3d_{5/2,3/2} doublets for the four spectra and Figure 19b shows the corresponding Se 3d peaks. These peaks are stacked up to illustrate the changes in peak position that took place due to the change in deposition conditions. The repetition rates, substrate temperatures, and pulse energies are included on the right for each of the spectra. The peak fitting carried out on each of the spectra is not shown. Notice that there is a small peak at higher binding energy in part (a) of Figure 19 which corresponds to the Nb 3d_{3/2} for niobium bonded to oxygen in Nb₂O₅. This peak was not evident in the films deposited with the lower repetition rate at either 293 K or 600 K. There is also a 0.4-0.6 eV shift to lower binding energy with the increase in repetition rate seen in both the Nb 3d and Se 3d peaks.

**GAXRD**

The glancing angle diffraction spectra obtained from this set of samples shows that the degree of crystallinity is also highly dependent upon the temperature and the repetition rate (see Figure 20).
Figure 19. (a) XPS Spectra of the Nb 3d$_{5/2}$ - 3/2 peaks
(b) XPS Spectra of the Se 3d peaks
Figure 20. GAXRD spectra for four NbSe$_2$ films corresponding to the endpoints of the significant two factor interaction plot.
Figure 21. RBS Data

Conditions: 10 Hz, 100 mJ, 293 K
Composition: Nb 37.000 Se 33.000 O 30.000

Conditions: 100 Hz, 100 mJ, 600 K
Composition: Nb 30.000 Se 40.000 O 30.000

Conditions: 10 Hz, 220 mJ, 293 K
Composition: Nb 38.500 Se 31.500 O 30.000

Conditions: 100 Hz, 220 mJ, 600 K
Composition: Nb 32.250 Se 42.750 O 25.000
The degree of crystallinity was obtained from the intensity of the peak at $2\theta = 14.10 - 13.69$ degrees corresponding to the NbSe$_{2-x}$ phase where $x = 0$ to 1.5. At room temperature and 10 Hz, the films tended to be completely amorphous as evidenced by the lack of any sharp peaks in the spectrum.

The high settings (600 K and 100 Hz), in contrast, exhibited a significant increase in crystallinity. The crystalline phase for these peaks shown in Figure 20 was a substoichiometric NbSe$_{2-x}$ phase (where $x = 0.5 - 1.5$). This phase was shifted down in the spectrum to $2\theta = 13.69 - 13.89$ degrees. The actual phase could not be determined exactly because there were no other x-ray peaks to verify the identification. The pulse energy did not have a significant effect on the degree of crystallinity. The only other growth condition that produced crystallinity was seen in the films grown at 100 Hz, 100 mJ, 293 K (see Figure 22) These films had a peak at $2\theta = 14.10$ degrees and was identified as the (002) plane in crystalline NbSe$_2$.

The effect of simply raising the temperature (i.e. 100 Hz, 100 mJ, 600 K) is also shown in Figure 22. This GAXRD spectrum shows a broad hump with a shoulder at $2\theta = 14.10^\circ$. This broad peak is similar to the spectral feature seen in some of the early MoS$_2$ PLD films grown by Donley et al. [36] under similar conditions. In their research the broad peak was described as “being composed of at least three sub-peaks which were apparently produced by basal plane reflection”[36]. Donley points out that there was also no evidence of an edge plane reflection in the MoS$_2$ films. This also corresponds well as there was no
Figure 22. GAXRD spectra for NbSe$_2$ films. Top spectra of film grown at 100 Hz, 100 mJ, 293 K; bottom spectra of film grown at 10 Hz, 100 mJ, 600 K.
evidence of edge orientation in any of the NbSe$_2$ films grown at any condition. The films were either amorphous or crystalline with a basal texture.

**SEM**

Scanning electron microscopy was completed on most of the films in both planar and cross-sectional views. Representative photos were chosen to illustrate the main features of the films grown at 10 Hz, 293 K and 100 Hz, 600 K in both views (see Figures 23-26).

From the planar SEM photos in Figures 23 and 25, a uniform density of spherical particles is present. The size distribution ranges from 0.25 $\mu$m to 0.75 $\mu$m and does not appear to be dramatically changed by deposition conditions. However, there does appear to be fewer particles on the surface of the high temperature film which is consistent with MoS$_2$ results at similar conditions [48]. There was very little difference seen in the morphology of the films due to changes in the pulse energy.

The cross-sectional views of the samples (Figures 24 and 26) depict uniform film thickness and dense, non-porous films. Figure 24 shows a spherical particle that hit the film during the initial growth and was incorporated into the morphology. The aberrations in the film, observed in Figure 26, are actually just artifacts caused by the cleaving process.
Figure 23. Planar view of a PLD NbSe$_2$ film (Grown at 10 Hz, 220 mJ, and 293 K).

Figure 24. Cross-sectional view of PLD NbSe$_2$ film (Grown at 10 Hz, 220 mJ, and 293 K) showing flat, fully dense film.
Figure 25. Planar view of a PLD NbSe$_2$ film (Grown at 100 Hz, 100 mJ, and 600 K).

Figure 26. Cross-sectional view of PLD NbSe$_2$ film (Grown at 100 Hz, 100 mJ, and 600 K) showing flat, fully dense film.
Friction and Wear

The friction and wear data obtained for these films was poor compared to the results obtained for MoS$_2$ films whose typical friction coefficient is 0.15 for over 100 k cycles in dry nitrogen. For these NbSe$_2$ films, the initial friction coefficients varied from 0.14 to 0.85 and the wear lives for all of the films were less than 4500 cycles. There were two basic types of wear patterns. Some of the films broke through immediately which resulted in a friction coefficient greater than 0.60. Other films showed an initial friction coefficient of $\mu = 0.14$ - 0.45, for the first 50 - 250 cycles, then the friction coefficient rapidly increased to above 0.60 which was the value chosen as the failure criteria. There was a nominal increase in wear life for a couple of films when tested in laboratory air compared to those run under dry nitrogen, but most films failed almost immediately.
CHAPTER 4
DISCUSSION

The synthesis-structure-property relationships reported in this thesis can be understood in terms of three competing processes which seem to play a role in the evolution and formation of NbSe$_2$. The first process involves whether or not the species generated in the laser plume actually stick to the substrate or not. The second is reaction kinetics, meaning that all of the selenium atoms arriving at the surface of the substrate do not necessarily react with niobium to form NbSe$_2$. The final process considered is the desorption of selenium due to an increase in vapor pressure caused by heating the substrate or target. The interaction plots will be used to discuss the results in an organized manner.

The interaction plots in Figure 17 are from the unsputtered XPS values. By comparing these plots and those generated from the sputtered XPS data, one can see that the trends are the same, but that the unsputtered plots show much higher Se/Nb ratios. This is because the surface of the films is selenium rich. This excess selenium could come from the fact that the vapor pressure of selenium is so much higher than that of niobium (vapor pressure of Se and Nb at 600 K is approx. $10^1$ Torr and $<10^{-11}$ Torr respectively). This causes more
selenium to be in the vapor phase during a deposition than niobium. When the deposition is complete, there is still selenium in the vapor phase surrounding the substrate which can then condense on the substrate surface causing the surface to be selenium rich. XPS analysis further shows that this surface Se is not bonded, but in fact is more metallic in nature based on peak position and peak shape (see Figure 19 b). This same type of effect was evident in the PLD films of MoS$_2$ where the excess sulfur in the vapor phase condensed causing the surface of the films to be sulfur rich [4, 5, 13]. Since this excess Se is confined mainly to the surface region which represents less than one percent of the total film thickness, the data contained in Figure 18, representing the bulk of the films, will be used to discuss the effects of the competing processes.

The pulse energy main effect plot shows a slight downward trend in the Se/Nb ratio for a change from 100 mJ to 220 mJ. A possible explanation is that the lower energy per pulse will preferentially remove the Se from the target causing the plume to be Se rich, but when these atomic species reach the surface of the substrate, they do not all stick. In fact, if the Nb atoms were considered to have a sticking coefficient of one, meaning each Nb atom arriving at the surface stuck, then, from the data, the Se atoms would have a sticking coefficient less than 0.5, meaning less than half of the Se atoms arriving actually stick to the substrate. In the 220 mJ case, the target evaporation is more congruent which would mean that the plume has less Se which results in a slightly lower average value for the Se/Nb ratio at this higher setting. The reaction kinetics and vapor pressure are going to be similar for both settings of pulse
energy. Therefore, they do not play a major role in this case.

The next main effect plot from Figure 18 is for substrate temperature. In this case there is also a decrease in the Se/Nb ratio for a change from 293 K to 600 K. This decrease in Se content in the higher temperature films could be from the increased vapor pressure of Se at these high temperatures. One would expect the Se to be preferentially desorbed from the surface of the growing films at the higher temperatures. A competing process would be the reaction of the Se with the Nb to form NbSe$_2$. One would expect the reaction rate to increase with an increase in temperature. However, from the data it is evident that the increase in reaction rate is less than the increase in thermal desorption of the Se.

The final main effect plot from Figure 18 shows an increase in the Se/Nb ratio for an increase in repetition rate from 10 Hz to 100 Hz. This effect is most likely due to target heating. At 100 Hz the pulses overlap causing the target to heat up significantly. The heated target could cause a preferential thermal desorption of Se which results in increased Se in the film. The actual temperature of the target is unknown, but from qualitative assessments of the target, the temperature during depositions was considerably higher than at 10 Hz. The targets were too hot to handle if taken out immediately after deposition at 100 Hz. Because of this, the targets were allowed to cool for at least an hour before removal from the system.

The bottom three two factor interaction plots follow a similar explanation. The pulse energy versus repetition rate plot shows an increase in the Se/Nb ratio for an increase in repetition rate. Also the 100 mJ line is higher than the 220 mJ line which
is consistent with more Se being generated at 100 mJ than at 220 mJ. Since the lines are nearly parallel there is not a significant interaction between these factors.

For the substrate temperature versus repetition rate plot, there is a significant interaction between the two factors as evidenced by the diverging lines. An interaction signifies that these two factors are inter-related and can not be considered independently. At 10 Hz, the Se/Nb ratios are very similar for both a substrate temperature of 293 K and 600 K. However, at 100 Hz there is a drastic difference in the Se/Nb ratios between the two substrate temperatures. This can be explained in terms of the competition between the thermal desorption taking place at the target for a repetition rate of 100 Hz and the thermal desorption taking place at the substrate at 600 K. The upper line corresponds to films grown at 293 K where there are no thermal effects expected at the substrate. When the repetition rate is 100 Hz, however, there is a significant increase in the Se flux at the substrate causing the films to have a dramatically increased Se content. For the conditions of 100 Hz and 600 K, the excess Se generated from the target is counteracted by the desorption of Se from the heated substrate. This causes somewhat of a balance in the processes, even though the effect of target heating seems to be slightly more significant.

The interaction plots (Figures 17 and 18) are not only an effective way of displaying and analyzing the data, but can also be used to determine how the experimental parameters should be set to achieve a desired outcome and to predict a value for the Se/Nb ratio based on the inputs of the optimal levels for the three factors.
From the calculated data in Table 7, parts (a) and (b), and the interaction plots in Figure 18, we can obtain a relative ranking of the effects for the sputtered films. This ranking shows that the top three effects are repetition rate (A), substrate temperature (C), and the interaction between repetition rate and substrate temperature (AC). Since these factors have the most effect on the process, they should be set first, with the less significant factor, pulse energy (B), to follow. In this case, there is a strong interaction between the main effects A and C. As a result of this, even though they also show strong individual effects, the two factor interaction takes precedence. This is because the effect that the individual factor A, for example, may have on the process is directly affected by the interacting factor, C. These two factors must be considered jointly from this point forward.

The bulk Se/Nb ratios will be considered as the primary response variable, meaning that the significant factors will be set to optimize this variable. Final selection of the factor settings will also consider the crystallinity, deposition rate and process variability.

In order to obtain the bulk Se/Nb ratio closest to the optimal value, in this case, 2.00, one must choose and predict the response for the optimal settings of the main factors then continue experimentation around these optimal settings. From the data contained in Figure 18, the settings for repetition rate (A) and substrate temperature (C) to achieve a stoichiometry of 2.40 are 100 Hz (A+) and 293 K (C-). Even though the Se/Nb ratio is over 2.00, the predominant phase from the GAXRD data for this sample, was stoichiometric, basally textured, crystalline NbSe$_2$. This means that the
extra Se must have been either incorporated into the bulk of the film but was not bonded to Nb or was taken up in an amorphous, superstoichiometric phase. Once the two significant factors have been set, pulse energy (B) can be set to a value that would help achieve the optimal Se/Nb ratio. A 220 mJ (B+) setting for pulse energy would result in a slight decrease in the Se/Nb ratio, closer to the desired value of 2.00, without causing a detrimental effect on the crystallinity.

At this point, one needs to consider the deposition rate and process variability. At the settings of 100 Hz (A+), 220 mJ (B+), 293 K (C-), one obtains the highest deposition rate as can be seen from Figure 14. The process variability could be high because of the interaction between the repetition rate and substrate temperature. The steep slope of the 293 K line would mean that a small change in temperature or repetition rate would result in a large change in Se/Nb ratio. A setting of 600 K would result in a more robust process because there is less variability in the Se/Nb ratio at this temperature. However, the films grown at 600 K are substoichiometric, and even though the films still have a crystalline phase at 100 Hz and 600 K, the crystalline phase is that of NbSe$_{2-x}$ where $x = 0.5 - 1.5$ based on JCPDS diffraction tables [49].

Based on the above considerations of chemistry, crystallinity and process variability, the optimal settings of the factors from this set of experiments was A+, B+, C- corresponding to 100 Hz, 220 mJ, and 293 K respectively. The predicted response for these settings was calculated in Appendix C to be a Se/Nb ratio = 2.31. The next set of experiments could try the following ranges for their factor settings: repetition rate from 50 to 100 Hz, pulse energy of 180 to 220 mJ and substrate temperature
between 500 and 800 K. These settings should provide Se/Nb ratios closer to 2.00, while further defining the deposition process.

Even though the actual NbSe$_{2-x}$ phase could not be identified exactly because there was only one peak in the spectrum, the JCPDS tables do seem to illustrate a trend for the various NbSe$_{2-x}$ compounds which allows insight into the possible crystalline phases present in some of these films. The stoichiometric NbSe$_2$ compound has an (002) diffraction peak at $2\theta = 14.1$ degrees. From the JCPDS diffraction files [49], the films having a NbSe$_{2-x}$ phase, where $1.5 > x > 0.5$, show a d-spacing corresponding to $2\theta = 12.3 - 13.95$ degrees which is lower than the value for stoichiometric NbSe$_2$. This would mean that the crystalline response for a substoichiometric phase of NbSe$_{2-x}$ causes a corresponding shift toward lower theta values in the GAXRD spectrum. This shift could give some verification of the bulk stoichiometry, at least for the crystalline phases. For this research the lower theta values in the GAXRD spectra do correspond to the lower stoichiometry found from the bulk chemistry measurements.

One would have expected, based on the available literature, that the wear lives for these films would have changed significantly due to changes in crystal structure and stoichiometry. In contrast, this research indicated that none of the films demonstrated any noticeable friction and wear life trends for changes in the growth parameters.

The wear testing apparatus used for this research was the ball-on-flat technique, using a point load to generate a high Hertzian stress. Pulsed laser deposited MoS$_2$ films have been tested using this test with a load of 100 grams on an 1/8 inch stainless
steel ball to produce a Hertzian stress of 0.98 GPa [4, 5, 25]. The lowest reported wear life for these films tested in dry nitrogen was 66 k cycles, whereas the films of NbSe$_2$ from this study, tested using these conditions, failed instantly. The load was decreased by one third to 30 grams, which resulted in a nominal increase in wear life to a maximum of 4.5 k cycles. At this point in the research, the films would have to be considered poor lubricants, which is consistent with Jamison’s work [16] which indicated that the unintercalated pellets used for his wear test actually disintegrated very quickly due to the high friction coefficient.

What could some of the reasons be for such poor tribological properties? From the literature [14, 16, 34, 35], it has been shown that stoichiometry, crystal structure and purity all have a large effect on the friction and wear properties of these layered transition metal dichalcogenide compounds. Even though the surfaces of the films showed that the films were stoichiometric to superstoichiometric, the bulk measurements showed a much different story. The bulk of the films, in many cases, was substoichiometric. The poor bulk stoichiometry could have played a role in the lack of good wear properties.

The fact that they were crystalline and basally textured should have resulted in a decrease in friction coefficient and an increase in wear life, based on work by Spalvins [34] and Buck [35]. Even though several of the films grown in this study showed crystalline phases present, there were very few that actually could be identified as the stoichiometric NbSe$_2$ phase. The rest of the films were substoichiometric NbSe$_{2-x}$ phases. From the friction and wear data, it would seem
that these NbSe$_{2-x}$ phases do not possess good tribological properties.

Finally, purity must be considered. The XPS and RBS data showed that these films contained significant amounts of oxygen (10 - 30 %). Jamison et. al. [14, 16] have shown that purity plays a major role in determining the wear life of a material. An impurity, such as a coinage metal, can add electron density to the unfilled d$^1$ orbital in a group V transition metal dichalcogenide. This will tend to fill the d orbital causing a repulsion across the van der Waal’s gap and a corresponding change in coordination and structure towards that of MoS$_2$, resulting in an increase in tribological response. Whereas, an impurity, such as oxygen, would be expected to act in an opposite manner and remove electron density from the d$^1$ orbitals causing a decrease in the tribological response.

The impurity argument could also explain the seeming discrepancy between Magie’s work [21] which showed NbSe$_2$ having a smaller coefficient of friction than MoS$_2$, and Jamison [16] who theorized and demonstrated that MoS$_2$ has a lower friction coefficient. It is possible that Magie’s NbSe$_2$ sample was impure and the impurity acted to improve the tribological properties.
There are several conclusions as a result of this research. First of all, this study showed that pulsed laser deposition of stoichiometric, crystalline NbSe$_2$ is possible. Also, it demonstrated the utility of a design of experiments approach to investigate the process boundary conditions. There is a clear interaction between the repetition rate of the laser and the substrate temperature. Film chemistry was changed from substoichiometric to superstoichiometric and crystallinity was varied from amorphous to crystalline. From the design of experiments approach, a “map” of the process trends was obtained. These trends were analyzed to obtain the optimal settings of the factors for the next set of experiments. The conditions are A+, B+, C- corresponding to 100 Hz, 220 mJ and 293 K respectively. The predicted response for these settings was calculated in Appendix C to be a Se/Nb ratio = 2.31. The next set of experiments could try the following ranges for their factor settings: repetition rate from 50 to 100 Hz, pulse energy of 180 to 220 mJ and substrate temperature between 500 and 800 K. These settings should provide Se/Nb ratios closer to 2.00, while further defining the deposition process.
The tribological properties for the films grown in this study were poor, but that is consistent with previous work by Jamison on unintercalated films. Some theories to explain this lack of performance were discussed.

There are several areas where further study would be valuable. One of the problems with this study was the incorporation of oxygen in the target materials. The targets used to grow the films from this study were always stored in a dessicator when not in use. However, this normally adequate precaution was not sufficient to prevent significant oxidation in the bulk of the targets.

Target oxidation could be greatly reduced or eliminated by taking extreme precautionary measures. New NbSe$_2$ powder, packed under argon gas, was ordered from Aesar. Upon arrival, the powder was cold pressed into a pellet for use as a target and immediately stored in a 10$^{-8}$ Torr vacuum. After the results of this study were completed, some preliminary films were grown using this target. The XPS and RBS results for these films showed no significant oxidation of these films even after significant air exposure. These low oxygen films were wear tested and some showed a marked increase in wear life (up to 13 k cycles using the 30 gram load), but they still had a high friction coefficient of approximately 0.24. Even though the tribological properties do not come close to those of MoS$_2$, this friction coefficient is very similar to the friction coefficient reported by Jamison [16] and shown in Figures 7 and 8 of this thesis. Future work on NbSe$_2$ should incorporate the use of carefully handled targets to produce these types of low oxygen films.
The use of additives to try to achieve the type of synergistic effect seen by Jamison would be a logical next step. Jamison used bulk pellets to determine his friction and wear results whereas, the use of a pulsed laser to grow intercalated films should provide excellent films having the same type of superior properties as seen in the bulk tests.

Target and substrate temperatures definitely played significant roles in this study. A more accurate method of monitoring the target temperature and also monitoring the species being desorbed from the target and substrate as a function of temperature and time will be necessary to fully understand the pulsed laser deposition process.
APPENDIX A
XPS SPECTRA

Figure 27. XPS Spectra corresponding to Table 5, a through h.
Figure 28. XPS Spectra corresponding to Table 5, i through p.
APPENDIX B
RBS DATA

Layer # | Thickness | Composition
1 | 2100.00/cm² | Nb 38.500, Se 31.500, O 30.000

Figure 29. RBS data for the conditions of 10 Hz, 220 mJ, 273 K.
Layer #  Thickness      Composition
1        1525.00/cm²   Nb 38.500, Se 31.500, O 30.000

Figure 30. RBS data for the conditions of 10 Hz, 220 mJ, 600 K.
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<td>2100.00/cm²</td>
<td>Nb 30.000, Se 40.000, O 30.000</td>
</tr>
</tbody>
</table>

Figure 31. RBS data for the conditions of 100 Hz, 100 mJ, 600 K.
Layer # | Thickness | Composition
--- | --- | ---
1 | 5950.00/cm² | Nb 22.500, Se 62.500, O 15.000

Figure 32. RBS data for the conditions of 100 Hz, 100 mJ, 273 K.
Figure 33. RBS data for the conditions of 10 Hz, 100 mJ, 273 K.
Figure 34. RBS data for the conditions of 10 Hz, 220 mJ, 600 K.

Layer # | Thickness | Composition
--- | --- | ---
1 | 1420.00/cm² | Nb 32.250, Se 42.750, O 25.000
Figure 35. RBS data for the conditions of 10 Hz, 220 mJ, 600 K.
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<td>850.00/cm²</td>
<td>Nb 26.667, Se 53.333, O 20.000</td>
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<tr>
<td>2</td>
<td>1250.00/cm²</td>
<td>Nb 25.000, Se 50.000, O 25.000</td>
</tr>
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</table>

Figure 36. RBS data for the conditions of 100 Hz, 100 mJ, 273 K.
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<tbody>
<tr>
<td>1</td>
<td>2035.00/cm²</td>
<td>Nb 43.000, Se 57.000</td>
</tr>
</tbody>
</table>

Figure 37. RBS data for the conditions of 10 Hz, 100 mJ, 273 K.
Layer # | Thickness  | Composition               
--- | --- | --- 
1  | 800.00/cm² | Nb 40.000, Se 60.000 
2  | 900.00/cm² | Nb 37.200, Se 55.800, O 7.000 
3  | 500.00/cm² | Nb 40.000, Se 60.000 

Figure 38. RBS data for the conditions of 10 Hz, 220 mJ, 600 K.
APPENDIX C
PREDICTED RESPONSE CALCULATION

From discussion section, the chosen levels for the main factors are:

\[ \text{A+ B+ C-} \]

The predicted response (PR) is:

\[ \text{PR} = (\text{Overall average (} \bar{Y} \text{)}) + (\text{Influence of significant main factors}) + \]

\[ (\text{Influence of significant interactions}). \]

e.g. Influence of a main factor  \[ = \bar{A}_+ - \bar{Y} \]
e.g. Influence of an interaction  \[ = (\bar{A}_+ \bar{B}_+ - \bar{Y}) - (\bar{A}_+ - \bar{Y}) - (\bar{B}_+ - \bar{Y}) \]

\[ = \bar{A}_+ \bar{B}_+ - \bar{A}_+ - \bar{B}_+ + \bar{Y} \]

In this case:

\[ \text{PR} = \bar{Y} + (\bar{A}_+ - \bar{Y}) + (\bar{C}_- - \bar{Y}) + (\bar{B}_+ - \bar{Y}) + (\bar{A}_+ \bar{C}_- - \bar{A}_+ - \bar{C}_+ + \bar{Y}) \]

\[ \text{PR} = \bar{B}_+ + \bar{A}_+ \bar{C}_- - \bar{Y} \]

\[ \text{PR} = 1.15 + 2.40 - 1.24 \]

\[ \text{PR} = 2.31 \]
BIBLIOGRAPHY


